In The Name Of Allah

Dear participant

Welcome to 18th Iranian Seminar of Organic Chemistry (18th ISOC). the seminar will be held during March 7-9, 2012(Esfand 17-19, 1390),at the department of chemistry, faculty of science, University of Sistan and Baluchestan with the collaboration of the Iranian chemical society to expand upon the knowledge and technology in organic chemistry, dependent fields and applications in industries, nanotechnology, environment, etc.
The scientific programs cover a wide variety of topics in organic chemistry, including synthesis, methodology, physical organic chemistry, stereochemistry, spectroscopy, polymer, nano-chemistry and all subjects related to the organic chemistry.
The scientific and organizing committee would like to express their deep gratitude to all authors for their contribution in this seminar.
We hope that you will enjoy the 18th Iranian seminar of organic chemistry alongside it's scientific and relaxing social programs. Also, we hope that you will have a wonderful experience in zahedan city and beautiful University of Sistan and Baluchestan that will stay in your memories forever.
With the best regards,
We would like to heartily appreciate the Chancellor, Finance Vice Chancellor, and Research Vice Chancellor of the University Of Sistan and Baluchestan, and also the Iranian chemical society, scientific committee, department of chemistry, and organizing committee for their valuable contribution and organizing the seminar.
With the best regards,

N. Hazeri

Associate Professor In Organic Chemistry

The chairman of the 18th Iranian seminar of Organic Chemistry

تنها تنها، در بی چراغی شب ها می رفتم
دست‌هایم از یادِ مشعل‌ها تهی شده بود
همه ستاره‌هایم به تاریکی رفته بود
مُشتِ من ، ساقه خشکِ تپش‌ها را می‌فشرد
لحظه‌هایم، از طنینِ ریزش پیوندها پُر بود
تنها می‌رفتم، می‌شنوی؟ تنها
ناگهان......
قطره‌هایِ ستاره‌ای در تاریکیِ درونم درخشید
و سرانجام در آهنگ پُر تلالو زمزمه‌هایش
اِی فرهیخته، ای مرزِ بی انتهای دانش، ترا پیدا کردم
و من در پیدایش تو رفتم و می‌رفتم...........
تا با تکیه‌ی به تو و هم اندیشی‌ات در پایانِ خود فرو اُفتم.

تقدیم به همه اندیشمندان شرکت کننده در هجده مین سمینار
شیمی ایران
اسفند ماه ۹۰

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– دکتر الهه مصدق	پژوهشکده مواد مرکز بین المللی علوم و تکنولوژی پیشرفته و علوم محیطی
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– دکتر حمیدرضا شاطریان	دانشگاه سیستان و بلوچستان

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– دکتر مصطفی حبیبی	مدیر تحصیلات تکمیلی دانشگاه
– دکتر نورا... حاضری	دبیر سمینار
– دکتر ملک طاهر مقصودلو	عضو هیئت علمی
– دکتر حمیدرضا شاطریان	عضو هیئت علمی
– دکتر رضا حیدری	عضو هیئت علمی
– دکتر علیرضا مدرسی عالم	عضو هیئت علمی
– دکتر ابراهیم ملاشاهی	عضو هیئت علمی
– دکتر حمیده سراوانی	عضو هیئت علمی
– اسماعیل ناروئی	کارشناس گروه
– زهره خواجه علی	کارشناس گروه

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- امیرحسین ژاسم
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- ساراحسین زادگان
- نسرین محمود آبادی

Formation of 2H-Pyran-2-ones from 1,3-Dicarbonyl Compounds, Acetylenic Esters and Sodium O-Alkyl Carbonodithioates

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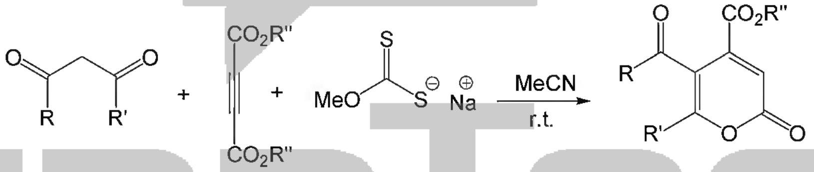
Introduction:

The pyran-2-one motif is found in a large number of naturally occurring compounds, many of which have interesting pharmacological properties [1, 2]. For this reason, pyran-2-ones have long been recognized as important synthons for organic synthesis and medicinal chemistry and their reactivity has received substantial attention. Pyran-2-ones are useful as Diels-Alder dienes, and therefore cycloadditions comprise much of the literature pertaining to these compounds. Deils-Alder reactions with pyran-2-one are facile with alkynes in addition to alkenes [3, 4].

Results and discussion:

As part of our current studies on the development of new routes in heterocyclic synthesis [5], we report an efficient synthetic route to 2H-pyran-2-ones. Thus, the reaction of 1,3-dicarbonyl compounds **1** with dialkyl acetylenedicarboxylates **2**, in the presence of sodium O-methyl carbonodithioate (**3**) at room temperature in MeCN as a solvent, produced 2H-pyran-2-ones **4** in good yields



1 **2** **3** **4**

In conclusion:

we have developed a convenient, one-pot method for the preparation of functionalized 2H-pyran-2-ones from 1,3-carbonyl compounds and dialkyl acetylenedicarboxylates in the presence of sodium O-methyl carbonodithioate. The simplicity of the present procedure makes it an interesting alternative to complex multistep approaches.

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Phenolic Compounds of Stachys Byzantina from Northwest of Iran

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The Vascular plants are able to synthesize a multitude of organic molecules as phytochemical, referred to as secondary metabolites. These molecules are involved in a varity of roles in the life span of plants ranging from structural ones to protection [1]. Phenolic compounds are regarded as one such group that are synthesized by plants during development and in response to conditions such infection, wounding and Uv radiation etc. Approximately 8000 naturally occurring compounds belong to the category of phenolics [2].

Phenolic compounds are known to act as antioxidants not only because of their ability to donate hydrogen or electrons but also because they are stable radical intermediates [3].

Phenolic acids are also well-known inhibitors of seed germination and interact synergistically to enhance the inhibitory effect [4].

Phenolics have an array of health promoting benefits, they are current interest due to their important biological and pharmacological properties, especially the anti-inflammatory, antioxidant, anticarcinogenic activities [5].

In this study, at the first step, our main aim was extraction and separation these phytochemicals with pharmacological effects. For this purpose, the aerial parts of this plant (leaf) were collected in May 2010 at Euromieh, Provience of Western Azarbaijan. The air dried leafs are extracted with ethanol. The ethanolic extracts are used for extraction of phenolic acids. Phenolic acids purified with preparative thin layer chromatography, and 5 different type of phenolic acids were analyzed by mass spectrometry (MS) and Infrared spectroscopy (IR).

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Chemical Constituents of the Essential Oil of Stachys Byzantina from Northwest of Iran

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The Vascular plant genus Stachys Byzantina considered as one of largest genera of the Lamiaceae, which grow wild in Turkey, Armenia and Iran. More than 270 Species of genera Lamiaceae is known in the world [1]. The stachys genus is one of the largest groups of this family. Plants of this genus have included more than 34 species in Iran [2]. Stachys Byzantina belongs to aromatic plants that grow in North and North-West of Iran. Plants of this genus have long been applied in folk medicine of NW Iran (Khoi, Euromieh) approved for healing wounds, treating abdominal pains, and as disinfectant. The other phytochemical that recently attracted the attention of many scientists, are essential oils [3]. Many papers on the biological activities as antimicrobial, antiviral, antifungal and antinoceptive were introduced [4, 5]. In this study the essential oils of air dried leaf evaluated by steam distillation. After extraction of essential oils with Dichloromethane, steam distilled of Stachys Byzantina oils were analyzed by a Hewelt-Packard 5973 mass selective detector connected with HP 6890 gas chromatograph, and 23 compounds were detected.

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Synthesis and Thermodynamics of Binding in the interaction of a water soluble and anti-cancer Platinum (II) complex with Calf Thymus DNA

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A new platinum (II) anticancer complex of [Pt(phen)(pyr-dtc)] (where phen is 1,10 phenanthrolin and pyr-dtc is pyrrolidindithiocarbamate) was synthesised and the interaction of this complex with Calf Thymus DNA was studied by isothermal titration method in 30mM Tris_HCl buffer solution (pH=7.0) at 300 and 310K.
There is a set of 6 binding sits(g) for the complex on the DNA with positive cooperativity in binding. n,the Hill coefficient (as a criterion of cooperativity) find out to be 3 at 300 K and 5at 310K respectively. K_{app} the apparent equilibrium constant are 42.5 mM^{-1} and 49.5 mM^{-1} at 300K and 310K respectively.
The above compound can denature the DNA and the concentration of this ligand in the midpoint of transition ($[L]_{1/2}$), is decreased by improving temperature, from 0.093 mmol/L at 300K to 0.087 mmol/L at 310K. the conformational stability of DNA in the interaction with ligand (ΔG^0_{H2O}) determined to be 23.4 kJ/mol and 25.9kJ/mol at 300K and 310K respectively.
Presence of ligand led to less stability of the DNA . values for m, (a measure of ligand strength for DNA denaturation) are 0.65 and 0.79 (kJ/mol).$(mol/L)^{-1}$ at 300K and 310K respectively.
Enthalpy of DNA denaturation by the complex ($\Delta H^0_{coformation}$ or $\Delta H^0_{denaturation}$) in the range of 300K and 310K is find out to be 6.3 kJ/mol. In addition, the calculated entropy (ΔS^0_{H2O}) of DNA denaturation by complex is -0.17 kJ/mol at 300K. the negative value of entropy change is related to the more disorder of denatured DNA with respect to the native DNA.

Keywords: Thermodynamic Studies, anti-cancer Palladium (II) complex

Investigation of plasticizing properties of ABA triblock copolymers based on PEG in cementitious systems

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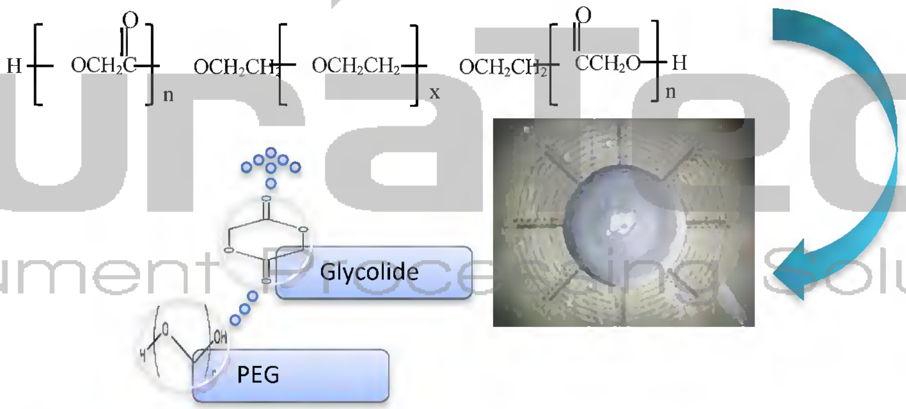
Plasticizers in cementitious systems are additives that uppon addition at a low dosage can change the workability, mechanical strength and other properties of cement paste effectively.[1] Plasticizers cause dispersion of cement particles and increase their mobility by two mechanisms: steric hindrance and electrostatic repulsion between cement particles by adsorption of negative functional groups on the plasticizer molecules.[2]

Slump retaining agents control the rate of setting of cement paste, so they can retain the workability of cement long enough for placing and finishing operation.

In this study, triblock copolymers based on poly ethylen glycol (PEG) was synthesised and their applications in the cementitious systems was investigated. The main purpose was verification of plasticizing effects of these copolymers in the cement paste. Ability of plasticizers depends on their structure, dosage and the water to cement ratio (W/C).[3]

ABA triblock copolymers with PEG (1000 and 1500 g/mol) as B block, poly caprolactone (PCL) and poly glycolide (PGA) (with different weigth ratio) as A block was synthesised via ring opening polymerization with stannous octanoate as catalyst. Their plastisizing effects and rheological properties was studied by mini-slump test and cylinder-cup rheometer. The Results show that by adding these copolymers to cement paste, the flowability increases, with PGA-PEG-PGA showing the highest performance. In this case the time of setting of hydraulic cement was also determined by Vicat Needle instrumen

Although these copolymers are not as efficient as commercial superplasticizer, they provide more insight into possibility and mechanism of plasticizing effects by non-ionic copolymers.



$$H\left[OCH_2\overset{O}{\overset{\|}{C}}\right]_n OCH_2CH_2\left[OCH_2CH_2\right]_x OCH_2CH_2\left[\overset{O}{\overset{\|}{C}}CH_2O\right]_n H$$

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Synthesis of novel pyrimido[4,5-b]quinolines using ionic liquid as catalyst

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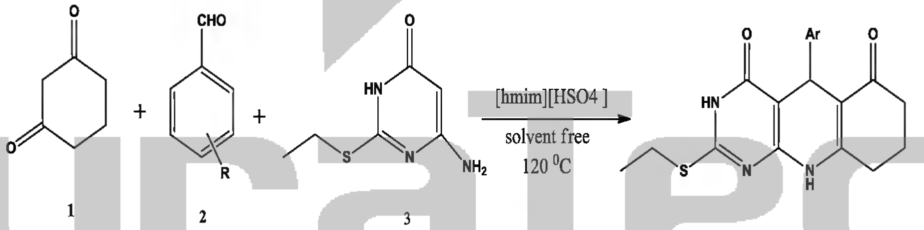
Multi-component reactions (MCRs) by virtue of their convergence, productivity, ease of execution and generally high yields of products have attracted considerable attention from the point of view of combinatorial chemistry [1]. On the other hand pyrimido[4,5-b]quinolines are important compounds because of their biological properties which are known to depend mainly on the nature and position of the substituent [2]. Quinoline derivatives display a broad range of biological activities such as anti-malarial [3], anti-tumor [4] and anti-bacterial [5]. Thus, considerable attention has been focused on the development of new methodologies to synthesize many kinds of pyridoquinoline systems.

Following our continued interests in the synthesis of biologically important heterocycles [6], in this research, we wish to report a very simple and highly efficient one-pot method for the synthesis of novel pyrimido[4,5-b]quinolines via a three-component cyclocondensation of equimolar amounts of 1,3-cyclohexadiene، aromatic aldehydes and 6-amino-2-(ethylthio)pyrimidin-4(3H)-one derivatives in the presence of ionic liquid [hmim][HSO4] (Scheme 1).



Scheme 1

4

This efficient method furnished the desired products (4) in high yields (75-95%) and short reaction times (10-30 min). High yields and ease of recovery and reusability of ionic liquid with consistent activity, makes this protocol efficient and environmentally benign.

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Theoretical study on the H-bonded complexes between 8-oxoguanine and formamide

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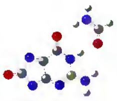
Hydrogen bonding is one of the most important concepts in chemistry because it is decisive to understand many different interactions both in the gas phase and condensed media [1]. Intramolecular and intermolecular bonds for the interaction between nucleotide bases and the folding pattern of proteins. Therefore, hydrogen bonds between biomolecules and the effects of hydrogen bonds on their properties are of great interest. 8-oxoguanine (8-OG) is one of the most abundant bases generated when DNA is attacked by reactive oxygen species, which are produced by cellular oxidant [2]. Formamide, also known as methanamide, is an amide derived from formic acid. Its formula is $HCONH_2$ or CH_3NO. The aim of this work is to find the complexes formed from interaction between 8-OG and formamide. All the structures studied in this work were optimized by using B3LYP method with 6-311++G(2d,2p) basis set by Gaussian 98 program package [3].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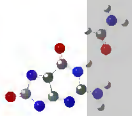
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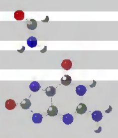
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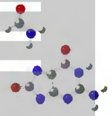
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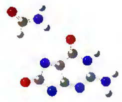
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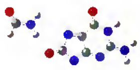
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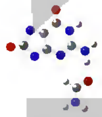
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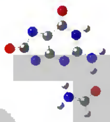
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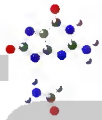
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There are six positions in 8-OG for interaction with formamide. We found nine major structures for interaction of 8-OG with formamide on the potential energy surface. All optimized complexes have cyclic structures (with the exception of 8-OG3b). In all structures (with the exception of 8-OG2a and 8-OG3b complexes) there are two H-bonds interactions. In 8-OG2a and 8-OG3b complexes there are one and three hydrogen bonds interactions respectively. The calculated binding energies (kJ/mol) for complexes at B3LYP/6-311++G(2d,2p) level of theory have been computed as a difference between the energy of the complex and the sum of energies of monomers. All complexes are more stable than the monomers. The relative stability order of the complexes is: 8-OG1a>8-OG5a>8-OG1b>8-OG5b>8-OG4>8-OG3a>8-OG3b> 8-OG2a>8-OG2b

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One-Pot synthesis of hexahydroquinoline derivatives using $AlPW_{12}O_{40}.XH_2O$ catalyst

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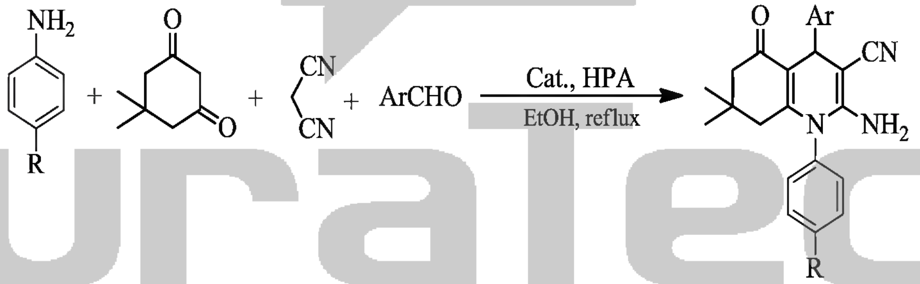
In recent years, an increasing interest has been focused on the synthesis of 1,4-dihydropyridine (DHP) compounds owing to their significant biological activities.[1] Quinolines having a 1,4-dihydropyridine nucleus are very important compounds because of their pharmacological properties such as antitumalarial, anti-inflamatory, antiasthamatic, antibacterial and antihypertensive.[2] Alternative strategies for their synthesis involving different catalysts and conditions have been developed.[3,4] However, some method suffer from drawbacks like some longer reaction times, unsatisfactory yields, harsh reaction conditions. In continuation of our investigations on the synthesis of 1,4-dihydropyridine,[5] herein we describe a novel and efficient one-pot method for the preparation of 2-amino-7,7-dimethyl-5-oxo-1,4-diaryl-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile derivatives from cyclo-condensation of aldehydes, malononitrile, anilines and dimedone in reflux of ethanol as solvent and HPA as catalyst. This new one pot method has the advantages to give high yields, to be completed in short reaction times, with simple product isolation procedure.



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Evaluation of the origin of conformational and tautomeric preference of N-formylformamide and its thio and seleno derivatives

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The amide functional group is the fundamental unit of proteins, peptides, and other biologically important molecules and has been traditionally characterized by a restricted C—N bond rotation, coplanarity of the attached atoms, short C—N bond lengths, and protonation at oxygen rather than nitrogen [1]. N-Formylforamide, as the simplest members of β-diamides, can participate in the amide↔imidic acid equilibrium (Fig.1) which interconverts by classical and quantum mechanical paths. Moreover, the imidic form of this molecule involved in O-H...O intramolecular hydrogen bonds that strongly coupled with π-electron delocalization and belong to the resonance assisted hydrogen bonds (RAHB) systems [2]. In the present study, we evaluated the origin of conformational and tautomeric preferences of N-Formylforamide with its thio (S) and seleno (Se) analogues. Moreover, the local and global minimums of potential energy surface, proton transfer process and intramolecular hydrogen bonding were also investigated.

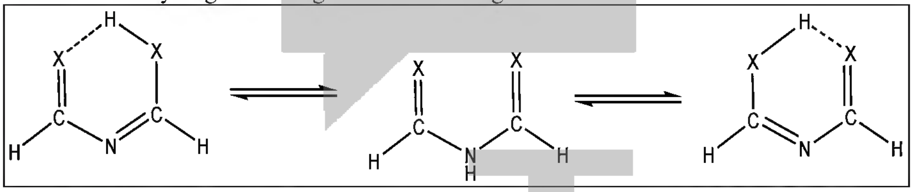

Fig.1. Amide↔imidic acid tautomeric equilibriums in title molecules (X= O, S, Se)

The geometrical optimization for all of the local minimums and transition structures were carried out by HF, B3LYP and MP2 methods with the standard 6-311++G(d, p) and 6-311++G(3df,3pd) basis sets. The optimized Structures were used to obtain the appropriate wave function files for AIM and NBO analyses. At all of theoretical levels, the amide forms and its chalgogen derivatives have more stability with respect to the imidic conformers. The NBO analysis show that the origin of tautomeric preference is mainly due to the electron delocalization in amide tautomers, especially LP(N)→π*C=X charge transfer.

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$Fe(DS)_3$-Catalyzed Synthesis of 2-Substituted Benzoxazoles

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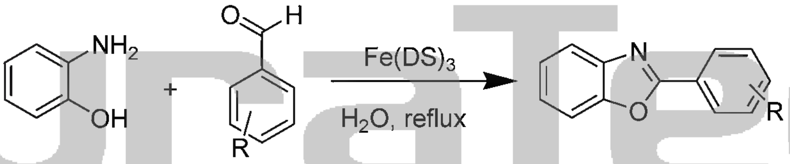
Synthesis of 2-substituted benzoxazoles has attracted interest in diverse areas of chemistry.[1] These heterocycles have shown different pharmacological activities such as antiviral, antimicrobial, anti-Parkinson, anticancer, and antibiotic properties.[2] The benzoxazole scaffold is also found in many biologically active compounds such as elastase inhibitors[3] and H_2 antagonists.[4] There are different methods for the synthesis of 2-arylbenzoxazoles based on substituted 2-aminophenols as starting materials.[5] Many of the procedures produce toxic or environmentally problematic by-products, often involve laborious workup procedures, or suffer from poor yields. Therefore, development of more convenient, environmentally friendly, and practical synthetic methods for benzoxazoles still remains an active area of research.

Therefore, we wish to report an efficient synthesis of 2-substituted benzoxazoles using of 2-aminophenol and various substituted arylaldehydes by $Fe(DS)_3$ in H_2O at reflux temperature (Scheme 1). The advantages of this method are higher reaction yields, short reaction times and use of H_2O as an environment friendly solvent(Scheme 1).



Scheme 1

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One-pot synthesis of 2,4,6,8,10,12- hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane in ionic liquids

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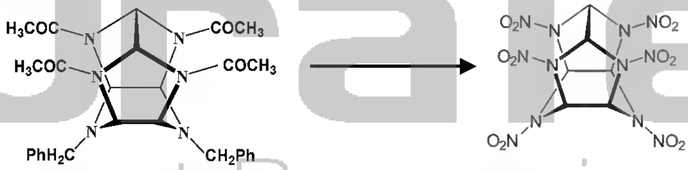
One of the most powerful explosives recently manufactured worldwide on a semi-commercial scale known as CL-20 or HNIW or 2,4,6,8,10,12- hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane. Also CL-20 is a potential candidate to replace HMX[1].

There has been much literature about the synthesis of HNIW,and several synthetic routs for the preparation of HNIW have been introduced.

Among all of the precursors, the following compounds are thought to be worthy for synthesis of HNIW:TADB(tetraacetyldibenzylhexaazaisowurtzitane),TADE(tetraacetyldiethylhexaazaiowurtzitane),TADF(tetraacetyldiformylhexaazaisowurtzitane),TAIW(tetraacetylhexaazaisowurtzitane), and HAIW (hexaacetylhexaazaisowurtzitane). All of the known methods for producing HNIW are based on the same starting material, 2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazaisowurtzitane (HBIW), which is prepared by reacting benzylamine and glyoxal in an acetonitrile solvent at 25°C. In the synthesis of HNIW, HBIW is first reductively acylated to form TADB. The remaining benzyl groups can then be removed either by reductive formylation,with formation of TADF, or by nitrosation, leading to tetraacetyldinitrosohexaazaisowurtzitane (TADNSO), which both are easily converted to HNIW by nitration with different nitrating systems[2].

The first method for synthesis of HNIW from TADBIW is the reaction that used (NOBF4) as a nitrosing agent . This reaction affords a product of high purity, which is the highest in comparison with other methods. A disadvantage of this method, however, is its moderate yield that is up to 55% and a high price of the nitrosing agent,nitrosotetrafluoroborate[3]. Debenzylation of TADB in presence of larger quantity of palladium catalysts yields another nitrolysable precursor TAIW,which can be easily nitrated to CL-20with common nitrating agent.Both these debenzilation reactions make use of expensive palladium catalysts[1]. In The other two methods dinitrogen tetroxide is used as a nitrosing agent[3,4] . N_2O_4 has a low boiling point and work with it ,is hard.



Most of these reactions carried out within two stages. In this work, we used ionic liquid media,for synthesis of HNIW from TADBIW. HNIW was synthesized by the one-pot method described in this paper. We optimize the reaction parameters affect on synthesis of HNIW for obtaining high yield.

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An efficient , simple and green method for the synthesis of N-benzylphthalimide

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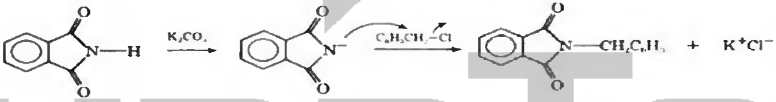
N-alkylating phthalimides are important intermediates in synthesizing the fatty primary amine and α-amino acid and are used as drugs[1- 2]. In the classical method for the synthesis of this drug, the N-alkylating phthalimides, was synthesized in N,N-dimethylformamide (DMF) by the reaction of halogenated compound with the salt, which was prepared by the reaction of phthalimide and KOH[3].

N-benzylphthalimide was firstly synthesized catalyzed by the alkaline reagent K_2CO_3-Al_2O_3 under microwave irradiation in 2002. In this reaction, a higher yield of 98% was obtained within a shorter time of 420s. However, it took about 6-7h to prepare the catalyst (alkaline reagents K_2CO_3-Al_2O_3) and 3h to purify the product after the completion of the reaction. Although the reaction time is only 420s, the work up is far from simplicity[4]. In this respect, the preparatory method was further improved.

The methods have been established for N-alkylation of phthalimide are associated with one or more of the following drawbacks: (i) long reaction time, (ii) moderate yield, (iii) the use of solvents such as DMSO and DMF that the workup of reaction is not only cumbersome, but also the green aspect of reaction is annihilated using these solvents. In addition, these reactions often are performed at high temperature[5].

The process could be expressed by the following equation:



We present here an efficient and simple method for the synthesis of N-benzylphthalimide in the presence of K_2CO_3 under microwave irradiation (MW) in good to excellent yield (99%) and short reaction times (360s). The reported method does not require the use of solvent. The experimental conditions were optimized and Several influence factors on the product yield were investigated, such as the proportion of reagents,the irradiation time, Phase transfer catalysts and the quantity of them.

All operation cycle took only about 20min. The method was very easy to operate, not only energy used was greatly saved, but also the reagents were reduced, which brought the highest economic value. In addition, pollution could be further reduced.

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Silica Sulfuric Acid/HNO$_3$ as a Novel Heterogeneous System for the Nitrolysis of DADN to HMX under Mild Conditions

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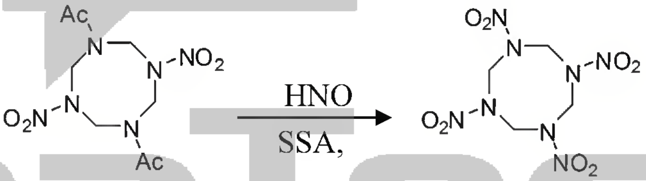
1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (HMX), also referred to as octogen or cyclotetramethylenetetramine, is a highly energetic material that is useful in variouse explosives and propellants for military and non-military applications[1–3].

Some procedures are described for preparing HMX from hexamine. The first know process for the manufacture of HMX was developed in 1940's as Bachmann process [4]. This process typically provides yields of 80-84% which only about 10-40% is HMX. There are several drawback in this process and a great amount of another explosive, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) is produced. For improving of these problems another synthetic routs involving various intermediates for making HMX have been proposed. Some intermediates that have been use to produced HMX are 3,7-dinitro-1,3,5,7-tetraazabicyclo [3,3,1] nonane (DPT), 1,3,5,7-tetraacetyl 1,3,5,7-tetraazacyclooctane (TAT) , etc. One of these intermediate involving 1,5-diacetyl-3,'7-dinitro-1,3,5,7-tetraazacyclooctane (DADN) gives a better yield of HMX than the established Bachmann process.



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4

The present investigation focuses on a new method for nitrolysis of DADN to HMX by developing a new nitrolysis process involving the use of nitric acid catalyzed by Silica Sulfuric Acid (SSA). In order to optimize the process parameters for synthesis of HMX to obtain higher yield and purity, a study was carried out with variation of some parametric conditions like time, mole ratio of SSA and nitric acid. This method gave us a green and mild conditions for nitration reaction.

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Tetramethylguanidinium triflate: An efficient catalyst solvent for henry reaction

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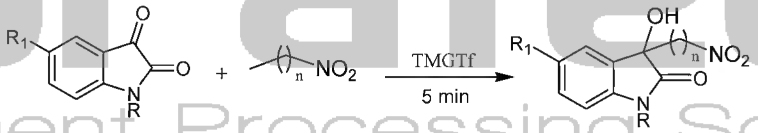
Several carbon-carbon bond forming reactions have been discovered and well reported in the literature.[1] The most prominent ones are aldol reaction, Gringnard reaction, … and Henry reaction.[2] Henry reaction is a classic-carbon-carbon bond-forming reaction and has been applied extensively in organic synthesis of β-nitroalkanols which are versatile intermediates for the preparation of nitro alkenes, 2-amino-alchohols, 2-nitro-ketones and biological compounds including fungicides, insecticides, natural prouducts and certain antibiotics.[3] Isatin is an active carbonyl compound, which like aldehydes can take part in henry reaction. Being prompted by recent interests in the synthesis of indolin-2-ones from isatin derivatives, we planned to investigate the possible improvement of henry reaction of isatin and nitro alkane for synthesis of 3-hydroxy-3-nitromethyl-oxindole. Based on our literature survey, there are only two reports on the henry reactions of isatin derivatives.[4,5] Thus, the development of simple and efficient reaction condition is an active area of research and there is a scope for further improvement towards milder reaction conditions, short reaction time and higher product yields. Ionic liquids, by virtue of their organic and ionic nature, are potent solvents, exerting nearly all kinds of interactions on reacting species, including transition states, whereupon sometimes give rise to improved yields and rate enhancements.[6] Structural variation of ionic liquids gives more flexibility to their applications, as provides fine tunning of their miscibility to merit phase-separation from products. In conclusion an efficient and convenient route to the synthesis of the title compounds was introduced here. Tetramethylguanidinium triflate ionic liquid plays as a catalyst solvent and can be recovered for reuse several times. Another advantages of the present method may be; requiring no metal catalysts or additional solvent.



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accelerated aging of epoxy nanocomposite based on response surface method: Dynamic mechanical behavior and nano-addition effect

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Epoxy resin based materials are thermosetting polymers widely used for structural applications, adhesives, organic coatings, electrical engineering and aeronautics[1]. When considering composites for long-term applications, it is necessary to know how the materials will behave during the intended service life. [2-3] almost all resins are adapted with various additives and fillers to pick up the process ability and the mechanical, thermal and electrical properties. additive are commonly mixed with the monomer in order to prevent premature reaction and increase the shelf life [7].they used not only favor the casting but also extend the storage life of the resin system. Recent studies show that nano silica has been attracting increasing attention due to its fascinating properties and potential applications. [4], as they are stable in most solvent environments.

Having known all this, in the present work, it is planned to accomplish a methodical experimental of study, to assess the performance characteristics of the epoxy nano composite, an epoxy resin containing different proportion of Fumed silica (Aerosil 200) and the results of the study were compared with epoxy resin without nano filler content. Results are presented from accelerated ageing in natural sea water.

Response surface methodology is a collection of statistical and mathematical techniques useful for the modeling and test analysis of in which a relevant response is influenced by several variables and the objective is to optimize this response. its use has been widely adopted in texts on chemometrics. [5] Experimental design and statistical analysis was performed using Design-Expert 7 computer software (trial version, Stat-Ease Inc., USA).

In this study, the effect of three identified process variables such as: different amount of nano silica(0-4%wt), aging time(1-3 month), temperature(20°-60° C)of aging were investigated and optimized with RSM. three quadratic polynomial equations were fit for loss module, Tg (from DMTA data) and mass gain(by periodic weighing with precision 0.1 mg)

also thermal aging and moisture absorption were described by Raman spectroscopy

Keywords: epoxy composite , accelerated aging, Response surface method, nano sillica, Raman

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A simple and efficient procedure for the synthesis of 1H-Pyrazolo[1,2-b]phthalazine-5,10-dione Derivatives

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After the discovery of multicomponent reactions (MCR), the concept has stimulated substantial interest in organic chemistry because it provides useful products in a single step by the creation of several new bonds in one pot. In drug discovery as well as 'green chemistry', MCR are the preferred techniques due to high throughput synthesis of compounds in a cost- and time-effective manner.[1,2]

Multicomponent reactions of malononitrile, an aldehyde and nucleophilic compounds have recently attracted the interest of the synthetic community because the formation of different condensation products can be expected on the specific conditions and structure of the building blocks.

Heterocycles containing the pyrazole ring are important targets in synthetic and medicinal chemistry because this fragment is a key moiety in numerous biologically active compounds, among them such prominent drug molecules as celecoxib, pyrazofurine, and many others. Similarly, heterocycles containing a phthalazine moiety are of interest because they show some pharmacological and biological activities.[3,4]

we report the synthesis of 1H pyrazolo[1,2-b]phthalazine- 5,10-dione derivatives via the simple, efficient, one-pot, and three-component condensation reaction of malononitrile, phthalhydrazide and aromatic aldehydes in the presence of a catalytic amount of **solid acid** in ethanol as solvent at 70 °C. The structures of all products were confirmed using physical and spectral (NMR and IR) data.

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H-bonded complexes between uracil and nitrous acid: An ab initio study

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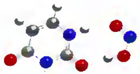
The nucleic acid bases have tremendous versatility in the formation of hydrogen bond complexes because of the presence of numerous hydrogen bond donor and acceptor groups [1]. Because of the simple structure of uracil, the theoretical analysis of its interaction with one or several water molecules has received a great deal of attention during the past years [2]. Nitrous acid, HONO, is one of the most important odd nitrogen species that plays an important role in atmospheric chemistry [3]. It is known as one of the most important sources of the OH radical in the atmosphere during the day, especially during sunrise, according to the dissociation channels. The OH radical has been known as the primary oxidant in the daytime chemistry [4]. The aim of this work is to study H-bonded complexes between uracil and nitrous acid. There are four positions in uracil for interaction with glycine. For the study of interactions between uracil and nitrous acid (UN), computations were carried out using B3LYP, B3PW91 and MP2 methods whit the 6-311++G (2d,2p) basis set.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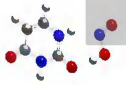
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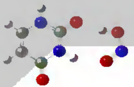
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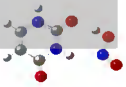
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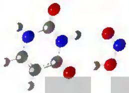
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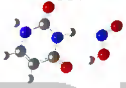
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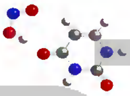
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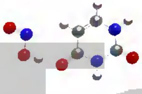
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The counterpoise procedure (CP) was used to correct for basis set superposition error (BSSE) in the calculation of binding energy. All optimized complexes have cyclic structures with two H-bond involved in the interaction. The structures UN1, UN3, UN5 and UN7 are eight-membered cyclic complexes. In eight-membered structures UN1, UN3, UN5 and NU7 the O atom of nitrous acid and one C=O group of uracil act as proton acceptors and C-H bond of nitrous acid and N-H uracil (with the exception of C-H bond in UN8) as proton donors. In seven-membered structures UN2, UN4, UN6 and U8 the N atom of NO group acts as proton acceptor. The electronic binding energies (D_e) range from -46.30 to -33.19 kJ/mol. The relative stability order of the seven complexes is UN1> UN2> UN3> UN4> UN5> UN6> UN8> UN7. The structure UN2 is the most stable and UN7 structure is the less stable.

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Tetramethylguanidinium triflate: An efficient catalyst solvent for henry reaction

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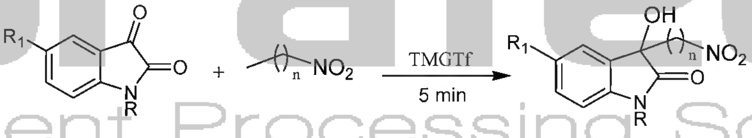
Several carbon-carbon bond forming reactions have been discovered and well reported in the literature.[1] The most prominent ones are aldol reaction, Gringnard reaction, … and Henry reaction.[2] Henry reaction is a classic-carbon-carbon bond-forming reaction and has been applied extensively in organic synthesis of β-nitroalkanols which are versatile intermediates for the preparation of nitro alkenes, 2-amino-alchohols, 2-nitro-ketones and biological compounds including fungicides, insecticides, natural prouducts and certain antibiotics.[3] Isatin is an active carbonyl compound, which like aldehydes can take part in henry reaction. Being prompted by recent interests in the synthesis of indolin-2-ones from isatin derivatives, we planned to investigate the possible improvement of henry reaction of isatin and nitro alkane for synthesis of 3-hydroxy-3-nitromethyl-oxindole. Based on our literature survey, there are only two reports on the henry reactions of isatin derivatives.[4,5] Thus, the development of simple and efficient reaction condition is an active area of research and there is a scope for further improvement towards milder reaction conditions, short reaction time and higher product yields. Ionic liquids, by virtue of their organic and ionic nature, are potent solvents, exerting nearly all kinds of interactions on reacting species, including transition states, whereupon sometimes give rise to improved yields and rate enhancements.[6] Structural variation of ionic liquids gives more flexibility to their applications, as provides fine tunning of their miscibility to merit phase-separation from products. In conclusion an efficient and convenient route to the synthesis of the title compounds was introduced here. Tetramethylguanidinium triflate ionic liquid plays as a catalyst solvent and can be recovered for reuse several times. Another advantages of the present method may be; requiring no metal catalysts or additional solvent.



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An investigation on the curing behavior of epoxy resin based on bisphenol A (DGEBA), in the presence of nano filler

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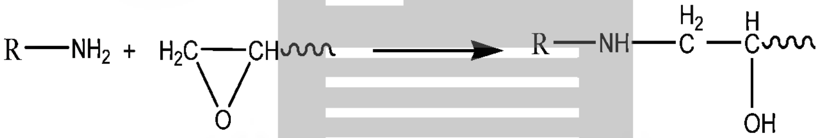
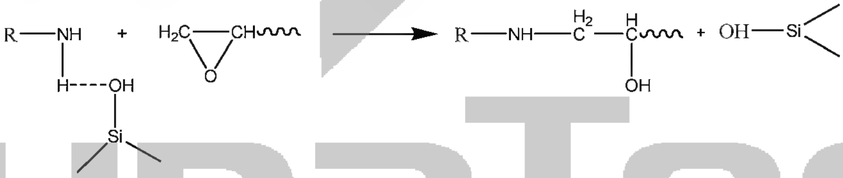
Epoxy resin has been developed rapidly since invented, and are widely used in modern life [1–3]. The most important and industrialized epoxy is bisphenol A. In this study, the cure process of epoxy resin based on bisphenolA (DGEBA) with polyamine hardener in presence of nano silica investigated through Differential Scanning Calorimetry (DSC) and Fourier Transform Infrared (FT-IR) [4]
In this study, the cure process of epoxy resin based on bisphenolA (DGEBA) with polyamine hardener (equation 1) in presence of fumed silica investigated through Differential Scanning Calorimetry (DSC) and Fourier Transform Infrared (FT-IR) [1]



(1)

The total reaction enthalpy (the maximum produced heat of reaction during curing) and glass Transition (Tg) was measured by DSC scans from 25 to 200 °C at rate of 10°C/min. All results were compared to those of bare epoxy resin. Fumed silica contains surface hydroxy groups, which can act as catalysis (equation 2) so the rate of reaction and Tg increases.



(2)

As a consequence of DSC, total reaction enthalpy decrease, Therefore, some of epoxy rings residue in the matrix as a result FT-IR spectra shows epoxy ring peak (the band at 914 cm^{-1}) after curing with the same amount of hardener . This may related to cover some amine active hydrogen with nano particles [5,6].
By preparing composites with different percent of fumed silica, nano composites with 1 wt% of SiO2 have a good dispersion of nano particles, within fully cured DGEBA matrix were easily produced through the proposed synthesis route. By increasing amount of fumed silica, cure kinetics reduces. Cure activation energy is not influenced by the silica presence.

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18th Iranian Seminar Of Organic Chemistry
7-9 March 2012

Thermal curing comparison of epoxy resin with amine and amide curing agents

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Abstract

Epoxy composites have extensive applications, for instance in adhesive, medical devices, optical component owing to their admirable resistance compared many materials [1-3]. The type of curing agent for modifications of epoxy resins can influence the curing chemistry, the curing rate, crosslink density, morphology, etc. So the choice of curing agent is very essential and requires to be considered very carefully. Epoxy resins can be cured with a wide variety of curing agents. Aliphatic and aromatic polyamines, polyamides, and their derivatives are the commonly used amine type curing agents. In this study, influence of different curing agents on thermal curing process of epoxy composite is investigated. Therefore the curing process of epoxy resin based on diglycidyl ether of bisphenol F (DGEBF) in the presence of amine and amide curing agent is determined through differential scanning microscopy (DSC) that were performed from 25 to 250 K at 10°C. Moreover, Fourier Transform Infrared Spectroscopy (FT-IR) was used to discuss the complete curing of composites. The FTIR results revealed that epoxy resin cross linked with amine curing agent more completely than amide curing agent. Because the epoxide ring is strained (unstable), polar groups (nucleophiles) can attack it. The amine groups react with matrix after completing the curing process of DGEBF and the epoxide ring peak is disappeared (figure1). The curing process with using polyamide curing agent due to presence of electron acceptor groups of oxygen which attract the nitrogen nonbonding electrons is more difficult (figure2).

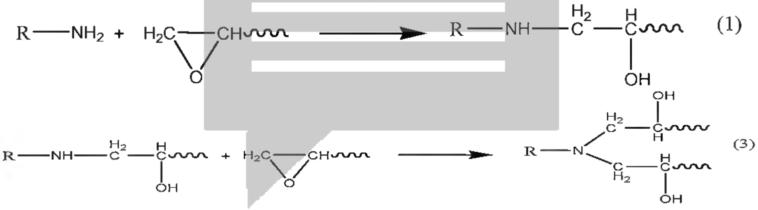

Figure 1: the curing process of amine curing agents

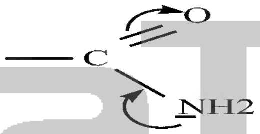

Figure 2: amide functional group

DSC results showed higher glass transition temperature (Tg) and total reaction enthalpy (the maximum produced heat of reaction during curing) of polyamine system. Therefore polyamine system has more thermal stability than polyamide system. Furthermore crosslinking decrease is due to increasing flexibility of epoxy/ polyamide that depends on lower Tg. On the basis of obtained results, the curing behavior of epoxy composite depends on the type of curing agent.

Keywords: epoxy resin, thermal curing, polyamine, polyamide

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Synthesis and Study of the Solvent Effect on Self-Assembly in a Novel Tripeptide Molecule contained unusual amino acid using Molecular Dynamics Simulations.

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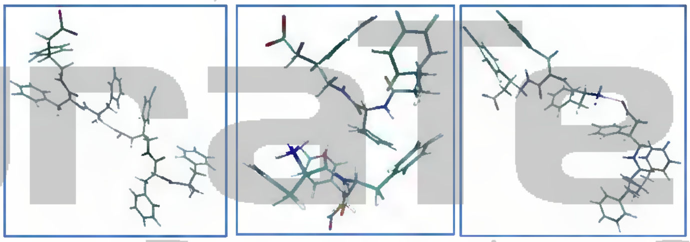
The diphenylalanine dipeptide is a suitable building block for molecular self-assembly. It is well reported that misfolding of the peptidic chain may produce unwanted processes that provoke fatal diseases. One of these problematic processes could be peptide assembly or aggregation. For instance, amyloid proteins may suffer conformational changes during folding processes leading to intermediate misfolded structures that can evolve into amyloid assemblies. These assemblies may precipitate as plaques over important parts of the body such as neural tissues and produce the so called amyloidogenic diseases[1]. We were encouraged to synthesis some novel peptides which contained γ- amino acids in their backbones. Gabapentin and baclofen were the best candidates for this approach. Baclofen is a muscle relaxer and an antispastic agent. In this article, we focused on the synthesis of some peptides. Between the synthesized peptides, H-Phe-Phe-Baclofen-OH was selected due to the existence of aromatic moiety in the structure of baclofen which is responsible for self-assembly via π-π stacking.
The realm of applications of computational chemistry is considerably expanding owing to steady advances in computer power. An ab initio quantum mechanical calculation was performed on H-Phe-Phe-Baclofen-OH tripeptide using Gaussian 03 package. The gas phase energy of the tripeptide was optimized at the HF/3-21G level. Molecular Dynamics Simulations were carried out with explicit solvent (water) using Gromacs 4.0.7 package. The details of simulations will be reported. Figure 1 shows screen captures in trajectory of the MD simulation of the tripeptide in bulk solvent. Different possible ways of self-assembly such as H-bonding, π-π stacking and T-Stacking can be seen in this Figure. The details about the self assembly of these compounds will discuss in the conference.



Keywords: Phenylalanine, Baclofen, Hydrogen bonds, Synthesis of tripeptide, Molecular Dynamics

Acknowledgment: We thank Iran Nanotechnology Initiative Council for financial support.

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Synthesis of Some New Small Molecules Towards OLED Application

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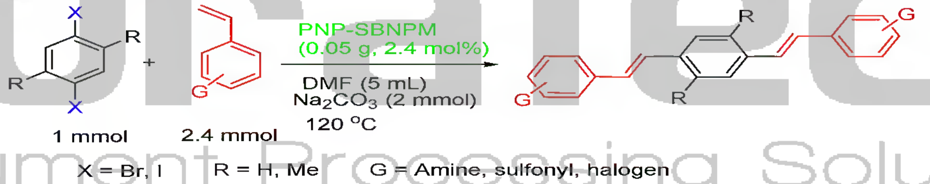
There is widespread interest in the use of conjugated organic materials in emerging optoelectronic technologies.[1] Conjugated materials such as small molecules and polymers have appeared that emission from organic-based light-emitting diodes (OLEDs) covers the entire visible spectrum.[1,2] In contrast to conjugated polymers, conjugated small molecules are desirable because their relatively simple structure enables straight forward structure-property relationships to be determined and thus regular structure films of specified thickness can be created by using evaporation techniques in a pure form.[3]

Some new 1,4-distrylbenzene derivatives were synthesized by using immobilized palladium nanoparticles on silica bonded N-propyl morpholine (PNP-SBNPM) as a heterogeneous catalyst. These one-pot reactions afforded a range of stereoselective symmetrical (E)-1,4-distyrylbenzene derivatives with high yields (78–90%). The green catalyst system is recyclable and allows facile product isolation. The recycled catalyst could be reused four times without appreciable loss in the catalytic activity. Single layer organic light emitting diodes (OLEDs) based on 1,4-distyrylbenzenes using thermal evaporation under vacuum condition has been fabricated and their optical properties such as electroluminescence (EL) and photoluminescence (PL) have been investigated. Fabricated OLEDs had EL emission in visible spectrum from 480 to 600 nm.



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Synthesis of Some Novel 4-Pyridyl-2-Aminothiophene and Related Schiff-Bases

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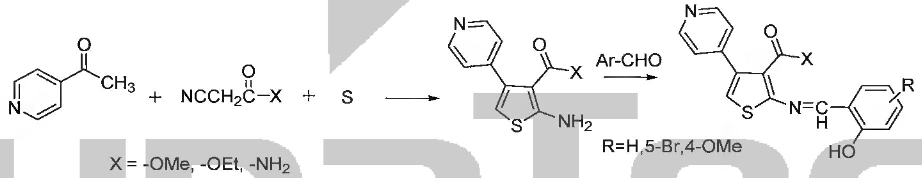
Thiophene derivatives exert broad applications such as functional materials in dyes, liquid crystals, molecular wires, organic light-emitting diodes, field-effect transistors and agrochemicals [1]· They can also be used as selective site-directed inhibitors of various biological targets [2]· On the other hand, Schiff bases derived from aromatic amines and aromatic aldehydes are very important class of organic compounds because of their applications in many fields including biological, inorganic and analytical chemistry [3].

In view of aforesaid points, we decided to extend our research [4] and have synthesized some novel 4-pyridin-2-amino thiophene by reaction of a ketone and elemental sulfur with methyl-, ethyl cyanoacetate or cyanoacetamide in the presence of morpholine, which followed by reaction with aromatic aldehydes to prepare related Schiff-bases (Scheme 1.). ^{1}H NMR and IR spectra together with UV spectroscopy data were used to identification of these compounds.



Scheme 1.

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An efficient approach to the synthesis of polyfunctionalized amino acids

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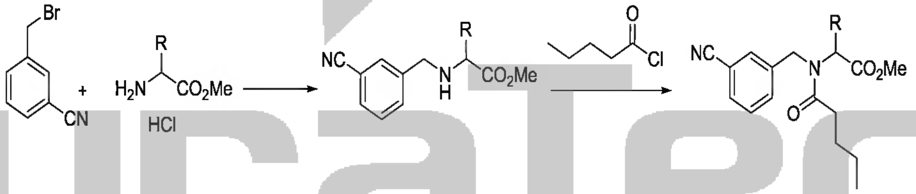
Functionalized amino acids are ubiquitous in many important biologically active molecules, synthetic drugs and drug candidates. For instance, Valsartan which is a nonpeptide, orally active, and specific angiotensin II receptor blocker acting on the AT_1 receptor subtype has been used in treatment of hypertension, heart failure and in left ventricular dysfunction post myocardial infarction (heart attack)[1,2]. The existence of the different functional groups can affect the chemical behavior of the molecule and may increase transforming potential of desired products.
In this approach we wish to report the synthesis of a series of amino acid methyl ester. The synthesized amino acid methyl esters are then carried to the next step to undergo coupling with aryl halides and carboxylic acids or acyl halides respectively. The products have different functional groups which could be used for further transformation. The general reaction is shown below.



The products could be used in different reactions, such as addition of azide, hydrolysis and reduction of nitrile groups. The details about this research project will be discussed in the conference.

Key words: Functionalized amino acids, hypertension drugs, Tertiary amides,

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New Sequential Ugi/Click Reaction for the Synthesis of Functionalized Pseudopeptides

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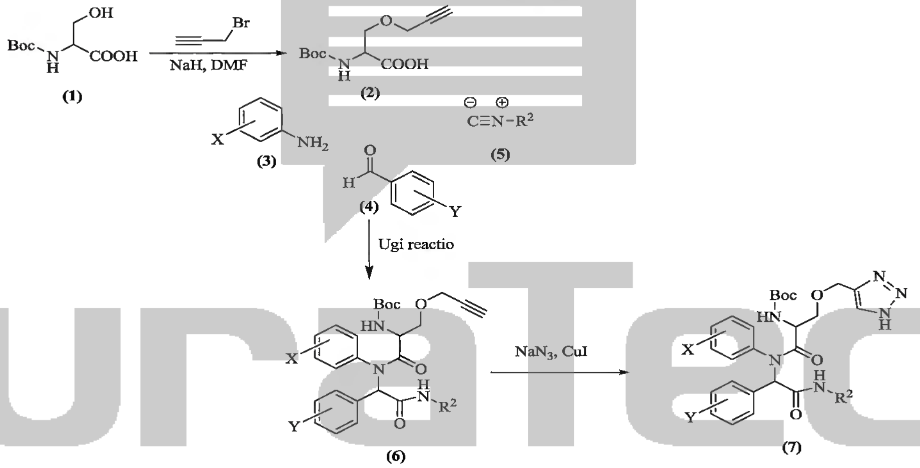
Multi-component reactions have huge potential for the rapid generation of small molecules libraries. However, there is a continuous need for designing and carrying out the reactions with novel starting materials in organic synthesis [1]. Ugi-4CR based on isocyanide is an efficient approach for the synthesis of structurally functionalized diverse complex molecules and they could supply the feedstock for advanced research in chemical biology [2].

In this approach, we would like to introduce protected N-tert-butoxy carbonyl O-propargylated -L-serine **(2)** as a starting material in Ugi-4CR.

Reaction of N-tert- butoxy carbonyl O-propargyl -L-serine **(2)**, aromatic aldehyde **(4)**, primary amines **(3)**, and isocyanides **(5)** leads to synthesis of pseudopeptide **(6)** which could be used for click reaction with Natrium azide in the presence of cuprous iodide. The existence of acetylenic moiety in the structure of product could add the huge potential for the synthesis of new small library.



Scheme1: Synthesis of functionalized pseudopeptide

Acknowledgment
We gratefully acknowledge K. N. Toosi University of Technology research council for financial support.

Key word: pseudopeptide, Ugi/click reaction, N-tert- butoxy carbonyl O-propargyl -L-serine.

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Highly efficient Suzuki Cross-Coupling Reactions catalyzed by heterogeneous palladium porphyrin

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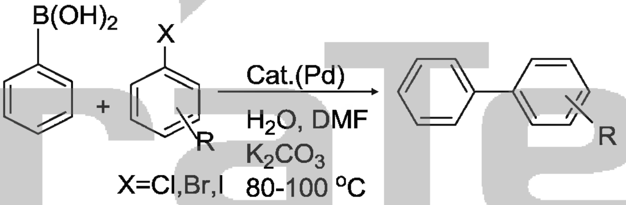
Suzuki cross-coupling reaction represents a powerful method for the C-C bond formation [1-3]. Construction of biaryl compounds via the palladium-catalyzed Suzuki reaction is an interesting area in organic synthesis. The importance of biaryl units as molecular components in pharmaceuticals, herbicides and natural products, as well as in engineering materials such as conducting polymers, molecular wires and liquid crystals, has attracted enormous interest [4-6]. The reaction represents an attractive alternative over other methods using organometallics because organoboranes are air- and moisture-stable with relatively low toxicity. With various metals being employed in coupling reactions, palladium is the most versatile metal in promoting or catalyzing reactions involving C-C formation due to its excellent catalytic efficiency in this type of reactions [7-10]. A control experiment indicated that the coupling reaction did not occur in the absence of catalyst.

In the present work, we have prepared heterogeneous tetrakis(4-aminophenyl)porphyrinatopalladium(II) and its catalytic activity was tested for the Suzuki cross-coupling reactions under various conditions. The catalyst exhibits high catalytic activities for the coupling of various aryl halides with organoboronic acid providing excellent yields of desired product [11]. The catalyst was characterized by various physicochemical and spectroscopic techniques.



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Efficient Synthesis of Polyfunctional N-Substituted 1,4-Dihydropyridines

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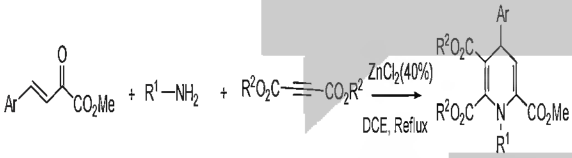
1,4-Dihydropyridine derivatives (1,4-DHPs) have interesting pharmacological and biological properties. It is clear that 1,4-DHP nucleus serves as the scaffold of important cardiovascular drugs and act as calcium channel blockers. It was shown that the activities of these compounds are related to the substituents and especially the number of ester functional groups [1].Due to the biological activity of 1,4-DHPs, we wish to report herein an efficient approach for the synthesis of polyfunctional 1,4-DHPs with three alkyl ester groups.

Aryl methylidene methylpyruvates were used as starting material which could be synthesized via reaction of pyruvic acid and aromatic aldehydes in the presence of Potassium hydroxide. Three-component reaction of arylmethylidene pyruvates, dialkylacetylene dicarboxylates and primary amines in the presence of Zinc choloride (40%) as Lewis acid, leads to form polyfunctional N-substituted 1, 4-dihydropyridines in 42-87% yields.

The synthesized novel 1,4-DHPs bearing three alkyl ester groups at C-2, C-5, and –C-6, which could be used for further transformation.



It seems that the existence of more alkyl ester functional groups could add the interaction activity of these compounds with lipase enzymes[2].The investigation of the biological activity of these compounds is in progress.Reaction could follow via these procedures:

a) Formation of enaminone via reaction of dialkyl acetylene dicarboxylate.
b) Addition of enaminone to activated aryl methylidene pyruvates.
c) Cyclization and finally dehydration.

In conclusion, this work describes a convenient and efficient process for the synthesis of functionalized 1,4-dihydropyridines via 3-MCR.The details will discuss in the conference.

Key words: N-substituted 1,4-dihydropyridines, Alkyl Aryl methylidene pyruvates, calcium channel blockers

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Effect of Synthesis Procedure on The Dynamic Properties of two Types Hydroxy Terminated Poly Butadiene (HTPB) base Polyurethane

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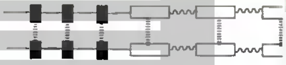
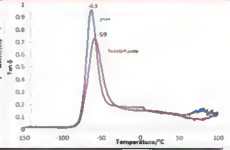
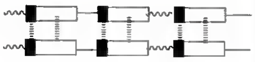
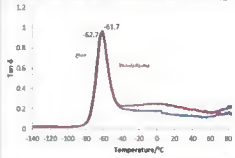
Application of polyurethane elastomers under cyclic loading (dynamic) is depend on to its structure and morphology [1]. In this study, we have prepared two types of polyurethane by using a one shot and prepolymer procedures [2]. In the first method all ingredient (HTPB, Chain extender (bis N,N (hydroxyl ethyl) cyanoactamide ,IPDI) is reacted in one stage and in the latter ,we prepared an isocyanate terminated prepolymer (reaction of bis N,N (hydroxyl ethyl)cyanoactamide and IPDI (1:2)) and react it with HTPB. In both methods the ratio of NCO/OH is equal .Our results have shown that the polyurethane is produced in one shot process have pseudo filler effect, so it show better dynamic properties (less Loss Compliance (J")) than the polyurethane elastomers are obtained by a prepolymer method [1, 3, 4].

Procedure	Structure	Morphology*	Properties
One shot	NCO/OH=1 (HTPB, Chain extender (bis N,N (hydroxyl ethyl)cyanoactamide ,IPDI)		
Prepolymer	NCO/OH=1 (bis N,N (hydroxyl ethyl)cyanoactamide and IPDI (1:2)),HTPB		

*morphology abbreviation

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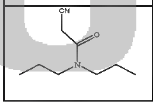	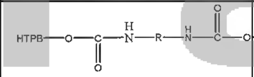	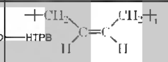	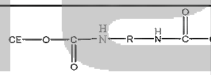	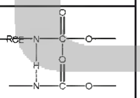

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Synthesis and Characterization of a New Chairal Composite from Polymerization of (+)-2-sec-Butylaniline-(+)-camphorsulfonate under Solvent-free Condition

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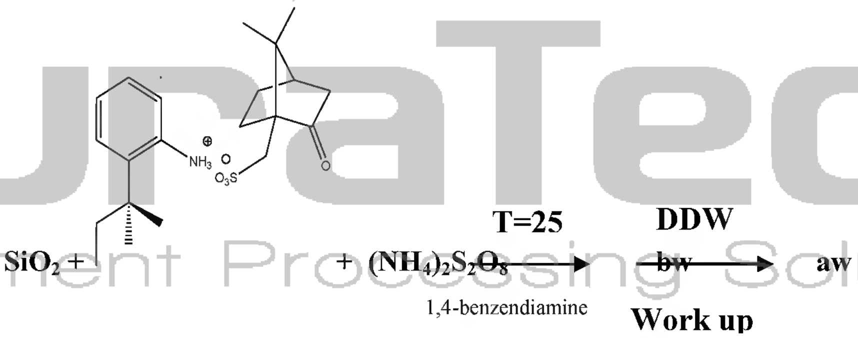
Conductive polymeric materials containing conjugated bonds have attracted much interest in scientific and technological areas in recent years.The conductivity in these polymers can be varied by doping them with different protonic acids or by using functionalized protonic acids.Among all the conducting polymers, polyaniline has received a great deal of attention owing to its simple synthesis, good environmental stability, ability to dope with protonic acids and moderately high electrical conductivity [1]. The most common method of chemical synthesis includes oxidation of the monomer with an oxidizing agent, e.g. ammonium persulfate, which is added to monomer solution. The resulting polymer is typically obtained in form of an amorphous suspension [2]. In recent years, polyanilines have received great attention due to their environmental stability, ease in preparation, exciting electrochemical, optical and electrical propertiesw [3,4]. This class of conducting polymers has also been postulated as potential candidates for numerous applications inelectrochromic displays, rechargeable batteries, microelectronics devices, biosensors, protective coatings and chemical sensorsw [5].

In this work, salt of (+)-2-sec-butylanilinum-(+)-camphorsulfonate, as monomer, was polymerized to form a new composite by in situ oxidative polymerization in the presence of ammonium peroxodisulfate as oxidant and silica under solid-state (solvent free) condition for the first time. The resulting composite was characterized using Fourier transform infrared (FT-IR)and ultraviolet-visible (UV-vis) spectroscopy.The morphology of composite was determined using scanning electron microscopy (SEM).



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Preparation of a New Chiral Nanocomposite from Polymerization of (+)-2-sec-Butylaniline-(+)-camphorsulfonate in the Presence of Nanosilica under Solid-State Condition

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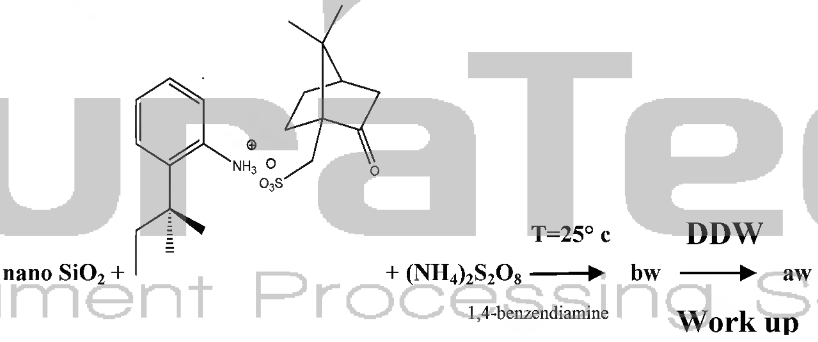
Conducting polymers and silica (SiO_2) are very important materials for a wide range of technological applications. Electrical properties of polymers are modified by adding inorganic particles within the polymer matrix. Composites containing organic polymers and inorganic particles regime provide a completely new class of materials with novel properties [1,2]. Among them, many PANI/inorganic polymer composites have been prepared recently. These composites based on polyaniline have been harvesting several intriguing properties within themselves due to the mutual influence of the individual constituents and synergism of their properties [3]. Nanocomposites are a special class of materials originating from suitable combinations of two or more such nanoparticles ornanosized objects in some suitable technique, resulting in materials having unique physical properties and wide application potential in diverse area. The development of nanocomposites is a topic of great current interest.

In this work, salt of (+)-2-sec-butylanilinum-(+)-camphorsulfonate was separated from its diastereomer (-)-2-sec-butylanilinum-(+)-camphorsulfonate by resolution method in solution. The former, as monomer, was polymerized to form a new chiral nanocomposite by in situ oxidative polymerization in the presence of ammonium peroxodisulfate as oxidant and nanosilica under solid-state (solvent free) condition for the first time. The resulting nanocomposite was characterized using Fourier transform infrared (FT-IR) and Ultraviolet-visible (UV-vis) spectroscopy. The morphology of nanocomposite was determined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM).



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Synthesis and characterization of novel thermally stable and aromatic PAI/TiO_2 nanocomposites under ultrasonic process

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In the recent years, the preparation of polymer nanocomposite materials has been extremely considered due to their comparatively remarkable properties [1]. Titanium dioxide (TiO_2) nanoparticles have unique properties such as higher stability, safe, inexpensive and shown antibacterial activity [2]. TiO_2 nanoparticles have been especially the center of attention for their photo-catalytic activities. This makes TiO_2 nanoparticles applicable in many fields such as self-cleaning, anti-bacterial agent, UV protecting agent, environmental purification [3]. In this study, the novel poly (amide-imide) (PAI) with flame retardancy property was synthesized from the polymerization reaction of a novel diacid with 4,4′-methylenebis(3-chloro-2,6-diethylaniline) using molten tetrabutylammonium bromide (TBAB) and triphenyl phosphite (TPP) as solvent and activating agent. As well TBAB/TPP was used as easy, safe and nontoxic method for the preparation of PAI. The obtained polymer and inorganic metal oxide nanoparticles were used to prepare PAI/TiO_2 nanocomposites through ultrasonic irradiation. The resulting materials were characterized by ^{1}H-NMR, fourier transform infrared spectroscopy, elemental analysis, powder X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and thermogravimetric analysis (TGA) techniques. TEM and FE-SEM images showed that the nanoparticles were uniformly dispersed in the polymer matrix. FE-SEM of pure PAI and PAI/TiO_2 nanocomposites (15 wt %) showed in Fig. 1. TGA data demonstrated that new synthesized PAI/TiO_2 nanocomposites are more thermally stable than pure PAI.

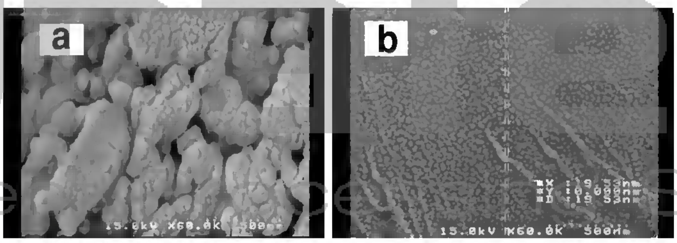

Fig. 1. Pure polymer (a), PAI/TiO_2 (15wt %) (b)

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Synthesis and Polycondensation of N-phenyl-N′-(1,2,4-triazolidine-3,5-dione-4-yl) thiourea with diisocyanates

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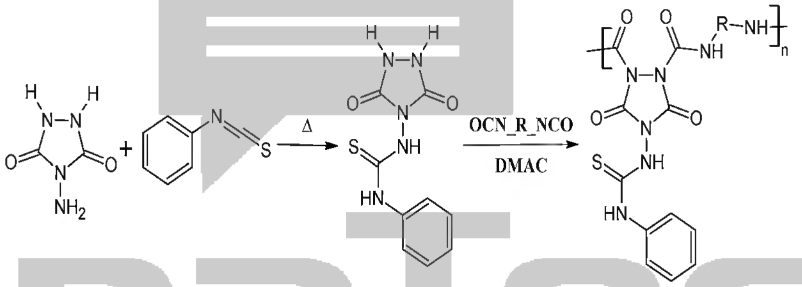
Some Urazole derivatives were found to be potent cytotoxic agents in murrain and human cancer cell lines. Other pharmaceutical properties of Urazole derivatives are hypolipidemic activity via lowering serum, cholesterol, and triglyceride levels [1], pesticides [2] and insecticides[3]. Preparations of thermoplastics, production of heat resistant coatings[4], tire rubbers with high gripability and melamine resins, are among the applications in the field of polymerization of urazole derivatives. Among a large variety of nitrogen-containing heterocyclic compounds, p-urazine (4-amino-1,2,4-triazolidine-3,5-dione) is interesting because It is used as a laboratory reagent for the synthesis of novel heterocyclic and organometallic compounds. In this work, we present synthesis of new polymers based on 1-phenyl-2-(1,2,4-triazolidine-3,5-dione-4-yl)thiourea.

p-Urazine was prepared according to a common procedure [5]. The mentioned compound was reacted with phenylisothiocyanate to its phenylurea-derivative directly. The phenylurea -derivative was introduced to various aliphatic and aromatic diisocyanates, as a DMAC solution. Some physical properties and spectroscopic data of the resulting polymers (4-7) were reported.



Diisocyanates: HMDI, IPDI, TDI,DPMDI

Polymers(4-7)

References:

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Chemical Oxidative Synthesis of a New Composite of Poly(o-methoxyaniline) under Solvent-Free Condition

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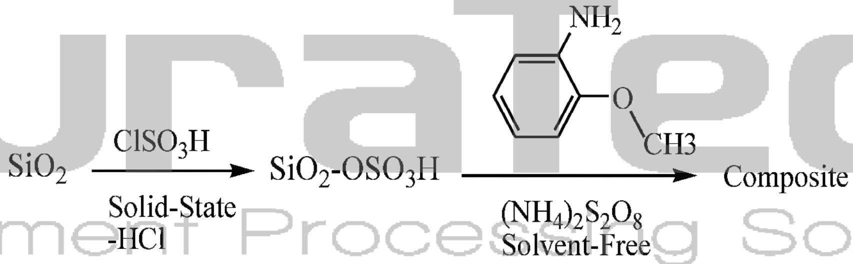
Recently, many research efforts have been made indeveloping polymer-silica hybrid composites [1–3].The combination of superior properties of polymers such as flexibility, dielectric, toughness and process ability, and that of oxides which have high thermal stability, good mechanical and optical properties, can lead to product of highly functionalized materials with desired properties to meet the demands of many industrial and high technology applications [4]. Organic/inorganic composite materials have been extensively studied for a long time. Organic/inorganic composites are generally organic polymer composites with inorganic nanoscale building blocks. They combine the advantages of the inorganic material (e.g., rigidity, thermal stability) and the organic polymer (e.g., flexibility, dielectric, ductility, and processability).

The compound ortho-methoxyaniline can be polymerized by both chemical and electrochemical methods. ortho-methoxyaniline or o-anisidine was chosen because of the potential effect of the methoxy group on chain solubility. The ortho-isomer was used instead of the meta because of the ortho-para directing nature of the methoxy group. With the ortho-isomer no one position is highly activated and a linear chain polymer is more likely [5].

In this work, we prepared a new composite from POMA by polymerization of 2-methoxy aniline in the presence of ammonium peroxydisulfate as under solvent free-condition. The UV-vis absorption spectra of composite were obtained in N-methyl-2-pyrrolidinone (NMP). The FT-IR spectra of composite were obtained from compressed KBr pellet. SEM image of composite particles has been used to determine the morphology and average size of the particles.



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Synthesis and Polycondensation of N-phenyl-N′-(1,2,4-triazolidine-3,5-dione-4-yl) thiourea with diisocyanates

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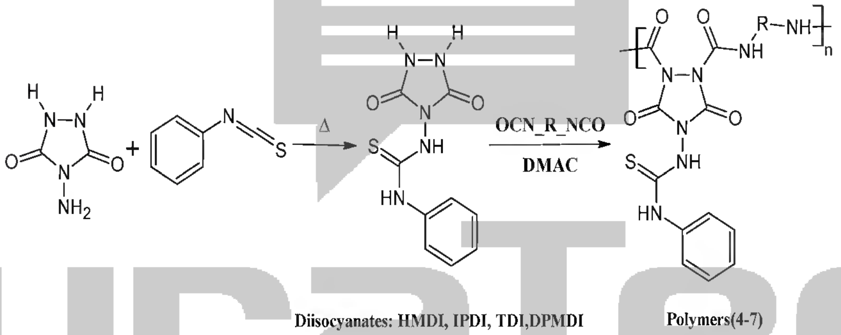

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Chemical Oxidative Synthesis of a New Composite of Poly(o-methoxyaniline) under Solvent-Free Condition

Ali Reza Modarresi-Alam[a*], Ilnaz Shariati[a]*, Tahere Akhondi[a], Sakineh Zafari[a]
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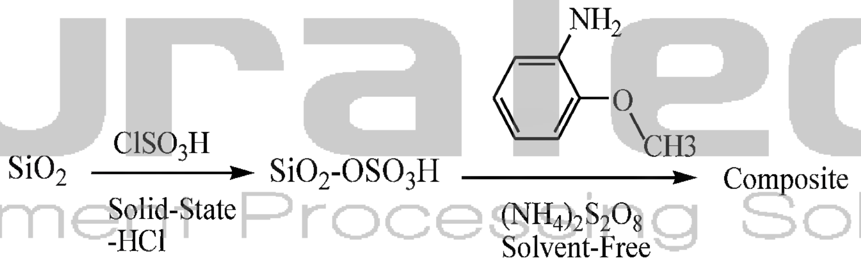

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Synthesis and Characterization of Aromatic tetra-Functional Methacrylate as Cross-linker for UV-Curable Coatings

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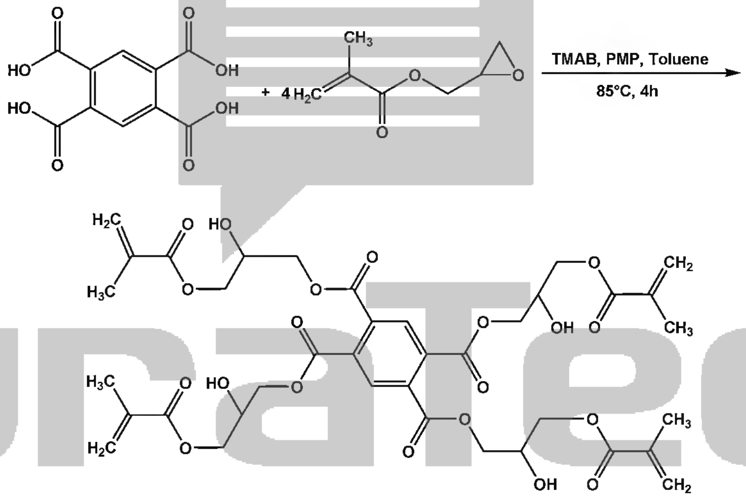
Aromatic tetra-functional methacrylate (ATM) can be used as a cross-linker in UV-curable coatings. The ATM was synthesized by 1,2,4,5 benzenetetracarboxylic acid and glycidyl methacrylate in present of tetramethylammonium bromide (TMAB) as catalyst, p-methoxy phenol (PMP) as radical inhibitor and toluene as solvent in 85°C for 4h. ATM was formulated in epoxy dimethacrylate as binder, benzophenone and N-metyl diethanol amine as photoinitiator and co-initiator, respectively. Curing time and film properties such as hardness, gloss, impact and adhesion have been evaluated after ultraviolet radiation curing.



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Synthesis of New Composite of Poly(anilinum hydrochloride)-Silica Under Solvent-Free Condition

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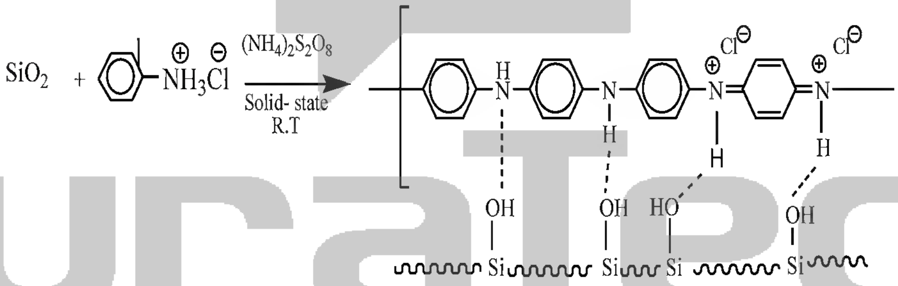
As a key material in the family of conducting polymers, polyaniline (PANI) has attracted intensive interest due to its promising electrical, electrochemical and optical properties [1]. In recent years, composites of PANI and inorganic compounds have been synthesized in order to get new materials with modified properties [2,3].

One way of making composites involves synthesizing the conductive polymer inside the matrices of conventional polymers (for example, inorganic polymers such as silica) or incorporating the inorganic component into the conducting PANI matrix using chemical or electrochemical polymerization [4]. Among those inorganic materials, silica (SiO_2) has received great attention because of its unique properties and wide applications [5].

In the present work, a new composite, poly (anilinum hydrochloride), with silica (SiO_2) was synthesized under solid-state or solvent-free condition. Ammonium peroxydisulfate was used as oxidant. The resulting composite was characterized by the UV-vis, FT-IR spectroscopy and Scanning electron microscopy (SEM) was done to study the morphology of composite.



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Synthesis and Characterization of Crosslinked CMC-Chitosan Full-Polysaccharide Biodegradable Films

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Introduction

During the past decades, researches on biopolymers have become an interesting area because of their versatile applications in various fields such as medical applications and nano-biocomposites [1,2]. Polysaccharides constitute the majority of the natural based biodegradable films because of their exceptional properties, i.e. biocompatibility, biodegradability, renewability, and non-toxicity. Carboxymethyl cellulose (CMC) is a renewable and biodegradable natural polymer that is used in a variety of commercial applications because of its capacity for gelatinization. Chitosan is a biodegradable copolymer composed of D-glucosamine and N-acetyl-D-glucosamine [3]. Chitosan is currently receiving enormous interest in medical and pharmaceutical applications since it is a safe and friendly substance for the human organism and because it has beneficial intrinsic properties [4]. The aim of the present work was to synthesize a biodegradable and biocompatible film that can be used in some applications such as tissue engineering and drug delivery systems.

Results and discussion

CMC-Chitosan full-polysaccharide hydrogels were prepared by crosslinking of chitosan with CMC polyaldehyde and subsequent reductive alkylation. CMC polyaldehyde molecule was prepared by periodate oxidation of CMC and then applied as a crosslinking agent to form a new hydrogel network. The swelling behavior of the polymer was studied at various pH values between 2.0 and 10.0 at room temperature. The swelling of the hydrogel decreased with increasing pH from 1 to 10. The dynamic swelling behavior of the hydrogel was determined with certain particles size (40–60 mesh) in water at room temperature. The equilibrium swelling was achieved after 20 min. Power law behaviors are obvious from the data and they may be well fitted with a Voigt-based equation.

Conclusion

CMC-Chitosan full-polysaccharide hydrogels were prepared by crosslinking of chitosan with CMC polyaldehyde and subsequent reductive alkylation. The structure of the hydrogel was confirmed by FTIR spectroscopy, scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). Swelling and deswelling measurements of the synthesized hydrogel in different salt solutions showed good swelling capacity. The polymer will most probably possess high biodegradability due to the presence of natural polysaccharides and low toxicity since no toxic material is used in the synthesis process. This practical approach may be preferred as a relative “green process”. The synthesize polymer has potential applications in the controlled delivery of bioactive agents and for wound dressing application in the form of sheets or film.

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Synthesis of poly(3,4-ethylenedioxythiophene)/silver nanocomposites in the presence of sodium dodecyl sulfate in aqueous medium

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Nanocomposites formed by metal nanoparticles (NPs) dispersed in electrically-conducting polymers, such as polyaniline, polypyrrole, or poly(3,4-ethylenedioxythiophene) (PEDOT), have received attention in the past few years [1]. The polymer and metal nanoparticles in these hybrid nanomaterials are expected to display several synergistic properties, making them potential candidates for application in several fields: catalysis [2], sensors and biosensors [3] and memory devices [4]. In polymeric core-shell nanohybrids, the polymer shell protects the metal core from oxidation and corrosion, allowing good performance to be maintained. In the present research, we report a novel one-step synthesis of PEDOT-coated silver nanocomposites with core-shell morphology by aqueous chemical oxidative dispersion polymerization and an electron exchange of PEDOT with silver nitrate. This discovery substantially broadens and extends the scope of core-shell particle syntheses.

Firstly, 3,4-ethylenedioxythiophene (EDOT) (0.85 mL, 8 mmol) was added to a colloidally-stable Ag NPs with sodium dodecyl sulfate (SDS) as the colloidal stabilizer. The mixture was then stirred at 25 °C FOR 1 h. Next, the solution of $FeCl_3$ oxidant (3.2442 g, 20 mmol) in distilled deionized water (DDW) (20 mL) was added dropwise to the reaction vessel. The final mixture was stirred for an additional 24 h. Secondly, to compare the results obtained; a pure sample of PEDOT in the presence of SDS was also prepared in a similar manner. Note that the SDS used in the first work plays simultaneously the role of both the dispersant of the nanosilver particles and the creator of micelles in polymerization step. The SDS used in the next work, however, acts only as an emulsifier. The resulting products were characterized by IR, UV-vis, X-ray diffraction (XRD), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). In addition, the homogeneously-dispersed silver nanoparticles in the matrix of polymeric sample were obviously observed by transmission electron microscopy (TEM).

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Synthesis and Characterization of Wholly Aromatic Poly (amide-imide), Thermally Stable and Organosolubl Based on Trimellitic acid

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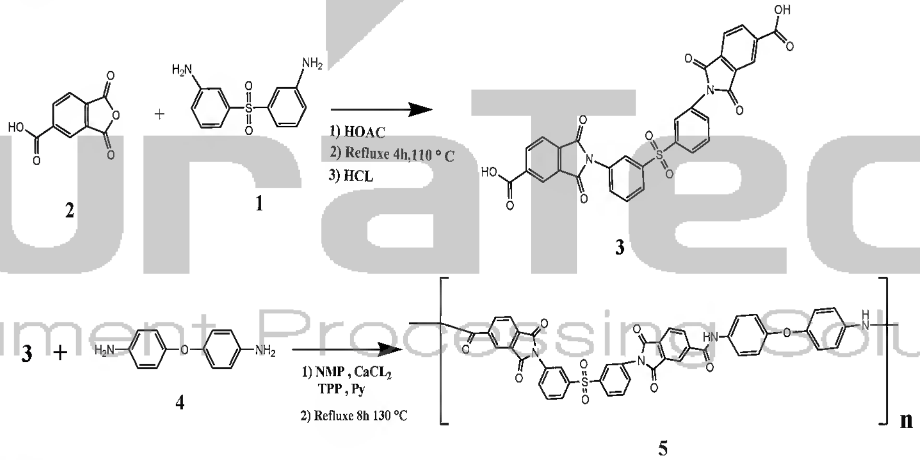
Poly (amide-imide) s (PAI) s as high performance materials (excellent thermal stability and mechanical properties) have been noted in new century [1], however, it has some defects such as low solubility and processing that cause difficulty for synthesis [2]. The use of aromatic groups in poly (amide-imide) s has been shown better resistance compared to ones containing nonaromatic groups but these groups are rigid and may decrease solubility. The use of some flexible groups (such as -O- ,$-SO_2-$, $-CH_2-$) may improve these deficiencies. In this project, new monomer (3) was synthesized with condensation reaction between 3, 3'-diamino diphenyl sulfone (1) and trimellitic acid (2), it was fully characterized by FTIR spectroscopy, elemental analysis and melting point successfully in high yield (90%). The poly (amide-imide) (5) was prepared reaction of diacid (3) and 4, 4'-diamino diphenyl ether (4) by direct polymerization at the presence of triphenyl phosphite, $CaCl_2$ and pyridine in N-methyl-2-pyrolidone (NMP), the structure of this organosolubl PAI was determined by FTIR spectroscopy, elemental analysis, thermal gravimetric analysis (TGA and DTG) and inherent viscosity of this polymer is 0.3 dLg^{-1} in high yield (97.77%). The resulting PAI was shown excellent thermal stability (T_5: 285.18 °C, T_{10}: 340.63 °C) since existence a lot of aromatics groups in it (see figure-1), and this PAI has been shown so high solubility due to there are flexible linkage groups like $-SO_2-$ and -O- in the main chain of PAI. This new soluble poly (amide-imide) could be considered as new processable high-performance polymeric material.



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Fabrication and study on morphology and properties of biodegradable poly(amide-imide)/organo-montmorillonite/modified ZnO nanoparticles

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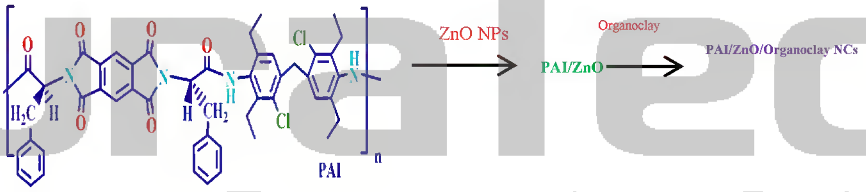
Polymer nanocomposites (NCs) are a very interesting material because of their remarkable mechanical properties like elastic stiffness, strength and thermal stability with a small amount of the nanoadditives [1-3]. Whether the nanocomposites would have high thermal stability and improved mechanical property, when two types of nanomaterials are incorporated into the polymer matrix [4]. The objective of this study was to investigate the effect of addition of organoclay on the properties of the Poly(amide-imide) (PAI)/zinc oxide (ZnO) NCs. At first optically active PAI was synthesized from the direct polycondensation reaction of N,N-(pyromellitoyl)-bis-L-phenylalanine diacid with 4,4-methylene bis(3-chloro-2,6-diethylaniline) under green media using tetrabutylammonium bromide/triphenyl phosphite. Subsequently dispersion of ZnO nanoparticle in a PAI matrix was performed using ultrasonic system. Then, PAI/organoclay/ZnO NCs with 1, 3, 5, 7 and 9% of organoclay content were prepared via a solution intercalation technique (Scheme-1). The morphostructural properties of the synthesized materials were studied by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), FT-IR spectroscopy and thermogravimetric analysis techniques. It was found that the PAI/organoclay/ZnO NCs exhibit considerably enhanced thermal properties compared with the PAI/ZnO NCs. XRD analysis showed that organoclay layers are exfoliated during the solution intercalation process in NCs with 5 wt% organoclay loading. This exploration presented a favorable method for preparation of environment-friendly biodegradable polymer NCs with two nanomaterials of organoclay and ZnO.



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Preparation and characterization of phtoluminescent polyimide/titania(TiO_2) hybrid nanocomposites by sol-gel processes

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In the past two decades, organic/inorganic nanocomposite materials obtained by sol-gel process have drawn a vast deal of consideration in material science owing to their unique properties [1]. In inorganic nanoparticles, TiO_2 is one of the most potential materials in research and application fields because of its versatile functions. Due to the expected properties of TiO_2, considerable attention has been devoted to the manufacture of well-dispersed TiO_2 in polymer matrix used as interference filter, antireflective coating, and optical waveguides [2,3]. These polymer/inorganics hybrid materials can effectively increase the mechanical and thermal properties by the microstructure of inorganics particles well-dispersing in polymer matrices. In this study, when titanium alkoxide is added into polyimide (PI) matrix, the gelation and phase separation occurred easily due to the relatively fast hydrolysis rate to create precipitates of titanium alkoxides. Thus, the use of acetylacetone (ACAC) chelating agent is necessary in order to control the reactivity of titanium alkoxides of the resulting nanocomposite materials [4,5]. PI/TiO_2 hybrid films via sol-gel process in situ preparation show higher glass transition temperature, an increase and flattening of the rubbery plateau modulus, and a decrease in crystallinity and could be dried afterwards without any post-treatment utilized in gas separation.

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Synthesis and polymerization of new anthracene -Based diamine

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The overall goal of this ongoing research is to modify the structure of aromatic polyimides to attain solubility in common organic solvents without substantially decreasing the rigidity of their backbone [1,2]. Solubility is sought to allow processing in the imide form and, thus, avoid the many problems associated with handling poly(amic acid) (PAA) precursors [3,4]. This is especially important in microelectronic and optical applications where the imidization conditions for PAAs used during processing can dramatically affect the final material properties [5,6]. The objective of this research was to investigate the effects of introducing pendent anthracene groups along the polyimide backbone. Thus, the new diamine was to be synthesized and polymerized with a series dianhydrides. The resulting polyimides were to be thoroughly characterized. In particular, the effects of the anthracene groups on the solubility of the polymers and the optical properties of their films were to be carefully determined.

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Preparation and characterization of phtoluminescent polyimide/titania(TiO_2) hybrid nanocomposites by sol-gel processes

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Synthesis and polymerization of new anthracene -Based diamine

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The overall goal of this ongoing research is to modify the structure of aromatic polyimides to attain solubility in common organic solvents without substantially decreasing the rigidity of their backbone [1,2]. Solubility is sought to allow processing in the imide form and, thus, avoid the many problems associated with handling poly(amic acid) (PAA) precursors [3,4]. This is especially important in microelectronic and optical applications where the imidization conditions for PAAs used during processing can dramatically affect the final material properties [5,6]. The objective of this research was to investigate the effects of introducing pendent anthracene groups along the polyimide backbone. Thus, the new diamine was to be synthesized and polymerized with a series dianhydrides. The resulting polyimides were to be thoroughly characterized. In particular, the effects of the anthracene groups on the solubility of the polymers and the optical properties of their films were to be carefully determined.

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Magnetic Hyperbranched Polymer Based on Carbon Nanotube

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Carbon nanotubes (CNTs), discovered by Iijima [1], have attracted more and more attention for their unique structure and excellent mechanical, electrical and thermal properties [2]. Due to their fascinating nanoscale dimensions and high surface areas, CNTs are considered as an ideal carrier to direct assembly of inorganic nanoparticles (NPs) which have special properties [3]. Among these inorganic NPs, iron oxide nanoparticles (Fe3O4 NPs) are of great importance for their good magnetic properties which endow them with potential applications in color imaging, magnetic recoding media, soft magnetic materials and for Adsorption of Dyes [4]. the modification of surface of CNTs which is based on chemical reactions on the sidewall and tips of CNTs. Different chemical reactions have been used to conjugate variety of molecules on the convex walls and tips of CNTs [5,6].

In summary, we reported a facile method to prepare magnetic MWMTs/Fe3O4 NPs/PCA composite nanotubes through a two-step process. We first in situ synthesize Fe3O4 NPs on the surface of MWNTs and then coated the nanocomposites with PCA layer via polycondensation reaction. SEM and TEM images confirmed the core-sheath nanostructure and the attachment of Fe_3O_4 NPs on the surface of MWNTs. However CNT-g-PCA is probably the biocompatible nanocomposite which is soluble in the water freely.The combination of these properties in a nanocomposite makes it promising material for nanomedicine applications.

The molecular structure and composition of MWNTs/Fe_3O_4 NPs/PCA nanotubes were characterized by Fourier transform infrared spectra (FTIR, X-ray diffraction (XRD) and Raman spectra. UV–vis spectra confirmed the existence of PCA.

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Micelle-assisted one-pot preparation of polyaniline/Ag nanohybrids in a water-based nanofluid

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It has been demonstrated that the incorporation of metal nanoparticles (NPs) could effectively improve the electrical, optical and dielectric properties of polyaniline (PANI) composites [1-3]. Composites of PANI with silver NPs have been prepared in three ways: (1) template Ag NPs were embedded into PANI during its conventional polymerization using APS oxidant (2) presynthesized PANI was used as a reductant of silver salts to metallic silver, and (3) the oxidation of aniline with silver ion as oxidant yielded a composite of PANI and metallic silver [1-3].

In the present work, we tried to apply the first approach in a new form. In the first step, a stable water-based nanofluid of metallic silver was prepared using silver nitrate, sodium iodide and sodium borohydride in the presence of sodium dodecyl sulfate (SDS) surfactant, which plays only the role of a dispersant in this step. The concentration of SDS was willfully selected upper than its critical micelle concentration (CMC), able to provide micelles for the next step. To acidify the medium (PH=1), hydrochloric acid was added. Aniline and ammonium peroxydisulfate (APS) were then added dropwise into the resulting nanofluid, respectively. The molar ratios of APS oxidant to monomer and monomer to surfactant were 1.2 and 5.0, respectively. The emulsion polymerization reaction was allowed to proceed for 48 h, while stirring at room temperature. Acetonitrile was added to the green dispersion to destroy the micelles. The suspension was filtered, and the solid was washed with the corresponding acid solution and acetone to remove residual monomer, SDS, oxidant as well as other low molecular weight oligomers. A thorough final washing with acetone also prevents the aggregation of PANI precipitate during the drying stage so that the product is obtained as a fine powder. The product was characterized by IR, UV-vis, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). In sum, it could be concluded that this novel micelle-aided one-pot strategy provides an exceptional method to prepare PANI/Ag nanocomposites with the best nanoparticle distribution, optical, morphological and thermal characteristics.

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Probing effects of employing binary organic solvents in synthesis line of poly(3-methylthiophene)/SiO_2 nanocomposite using surfactants

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Unlike polythiophene, poly(3-alkylthiophene)s are both readily soluble in many organic solvents and melt processable. This class of materials has good chemical and environmental stability with excellent electronic and optical properties suitable for various applications in advanced technology [1-3]. Chemical oxidative polymerization technique, which kindly provides a large scale of it in each batch process,has a notable limitation associated with low organosolubility of the oxidant used. The most commonly used oxidant to prepare poly(3-alkylthiophene)s is ferric chloride. It has been demonstrated that the least concentration of this oxidant that should be present in the reaction vessel is two times of mole ratio relative to the monomer. However, solubility of $FeCl_3$ in chloroform, as the usual solvent for preparing these types of polymers is too little to be ideal. Accordingly, the plan of employing binary organic solvents in synthesis line of the most important poly(3-alkylthiophene)s namelypoly(3-methylthiophene) seems to be very useful if performed well. Meanwhile, this ingenious plan for the first time was successfully exercised by Im et al. [4]. On the other hand, it is well-accepted that the embedment of nanosized particles such as nano-Ag, Au, TiO_2 and SiO_2 into the matrix of these polymers has some exceptional results that develops their applicationextensively.

Here, we report a unique chemical oxidativemethod using two kinds of miscible organic solvents including acetonitrile and chloroform for thesynthesisof poly(3-methylthiophene)/SiO_2nanocomposite.To prepare ahomogeneous nanofluid from nanoparticles of $SiO_2$by sonication in chloroform, two dispersants including sodium dodecylbenzenesulfonate (SDBS) and sodium polystyrene sulfonate (SPSS) were separately used. Firstly, a solution of $FeCl_3$ oxidant in CH_3CN was added slowlyto the stabilized $CHCl_3$-based nanofluid while stirring. In this modified technique, we could reach five for the molar ratio of $FeCl_3$ to 3-methylthiophene, which this had some positive effects on the composite optical and thermal behavior according to UV-vis, XRD, SEM, TEM and TGA results. Polymerization was carried out at room temperature with 24 h stirring. To compare the results, a sample of poly(3-methylthiophene)/SiO_2nanocomposite was also prepared in its classical form under the same conditions without the use of CH_3CN.In both cases, the composite suspensions were filtered out, washed with methanol and then dried at 50 °C under vacuum. Obviously, it should be noted that the employing binary solvents to preparepoly(3-methylthiophene)/SiO_2nanocomposite using surfactantsopensa new window toward us in the field of nanotechnology.

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Controlled drug delivery of Phenobarbital using of melamine modified poly(vinyl acetate-alt-maleic anhydride)hydrogel

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Hydrogels are hydrophilic three dimensional swellable networks that can be obtained by chemical and/or physical crosslinking of polymers. They show a wide variety of applications as medical devices and in the field of pharmaceutics.[1]

Hydrogels have been developed as stimuli-responsive materials, which can undergo abrupt volume change in response to small change in environmental parameters: temperature, pH, ionic strength, etc.[2-4]

In these work we synthesized pH sensitive hydrogels base on poly (vinyl acetate-alt-maleic anhydride). The melamine was grafted on backbone of poly (vinyl acetate-alt-maleic anhydride) in various ratios. The cloudy point of prepared polymer in aqoues solution respect to pH was measured and the pHs of sol-gel transitions were in about 7.5. The swelling index of prepared polymers was measured. Then the Phenobarbital drug was loaded on prepared hydrogel and in-vitro drug release behavior of drug-adduct hydrogel was investigated.

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Preparation of 1,2-bis-(2-hydroxy ethyl)-4-tetrabromo phthalimido-1,2,4-triazolidine-3,5-dione of p-urazine

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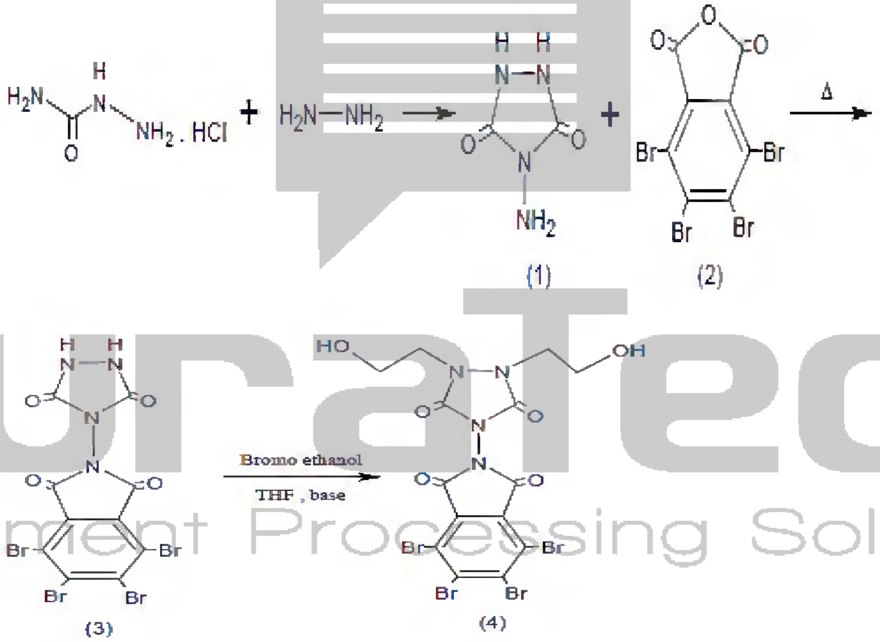
Heterocyclic nitrogen-containing molecules constitute the largest portion of chemical entities, which are part of many natural products, fine chemicals, and biologically active pharmaceutical compounds, vital for enhancing the quality of life [1]. Among a large variety of nitrogen-containing heterocyclic compounds, p-urazine (4-amino-1,2,4-triazolidine-3,5-dione) **(1)** is interesting, because it is used as a laboratory reagent for the synthesis of novel heterocyclic and organometallic compounds [2]. In this work, we present synthesis of 1,2-bis-(2-hydroxyethyl)-4-tetrabromo phthalimido-1,2,4-triazolidine-3,5-dione. p-Urazine was prepared according to a common procedure [3]. The mentioned compound was reacted with tetraboromophthalic anhydride **(2)** to its related phthalimid derivative **(3)** directly. tetraboromophthalimido-1,2,4-triazolidine-3,5-dione reacted with excess amount of 2-bromoethanol. as the result, 4-phthalimido-1,2,4triazolidine-3,5-dione was introduced to 1,2-bis-(2-hydroxyethyl)-4-tetra bromo phthalimido-1,2,4-triazolidine-3,5dione **(4)**, was produced. The resulted molecule was identified by varius spectroscopic methods. Polymerization reactions of the mentioned product is under investigation.



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Synthesis of Conductive blend based on Polyaniline/ Ciricacid grafted copolymer

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In recent years, polymer-polyaniline (PANI) conductive polymeric blends have received considerable attention because of their potential applications in electrodes, biosensors, batteries, antistatic coatings, gas sensors, membranes and light emitting diodes[1-3].
Citric acid grafted Poly(styrene-alt-maleic anhydride) was synthesized by ring opening graft reaction of citric acid on poly(styrene-alt-maleic anhydride) copolymer with various molar ratio in THF as solvent. The prepared copolymer was characterized by FT-IR and H-NMR spectroscopy. Conducting polyaniline (PANI) nano particles doped with HCl was synthesized by a sonochemical method. Polyaniline/citric acid modified Poly(styrene-alt-maleic acid) blend with different polyaniline content were developed by solution-dispersion blending method. The influence of citric acid Poly(styrene-alt-maleic acid) concentration in blend structure was also investigated. The blend dispersed solution in water/ethanol cast to fabricate conductive films with evaporation of the solvent. With only a mixing procedure and without any dispersant added, the PANI nanoparticles were well dispersed in the matrix polymer as indicated by AFM images. The conductivity of obtained blends was measured with four probe technique. The obtained blend characterized by FT-IR and UV-Vis spectroscopy.

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Synthesis and Characterization of a New Composite of Polyaniline by Doping Polymer with Silica Sulfuric Acid under Solvent-Free Condition.

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Polyaniline (PANI) is a very important polymer owing to its diversified chemistry and interesting physical properties [1]. Polyaniline can be doped and undoped on exposure to an acidic or alkaline environment without changing the number of π-electrons in the polymer [2]. This aspect of doping and undoping makes polyaniline and its analogous highly suitable for industrial applications. Various organic and inorganic acids and salts can dope polyaniline [3,4]. In this work, a new composite of polyaniline-silica sulfuric acid (PANI-SSA) was synthesized at room temperature and under solid-state or solvent-free condition [5,6], Scheme. In fact, we used a new solid polymeric acid dopant (silica sulfuric acid) in doping polyaniline.

The resulting composite was characterized by FT-IR and UV-vis spectroscopy and its doping was confirmed by means of comparison with prepared polyaniline emeraldine base. In other words, the doping process has been proved via FT-IR and UV-vis spectroscopy. The morphology of composites was determined using Scanning Electron Micrographs (SEM). The conductivity of the synthesized samples was measured by means of a four-probe device.

$$SiO_2 \xrightarrow[\substack{\text{solid-state} \\ \text{-HCl}}]{\text{ClSO3H}} SiO_2\text{-}OSO_3H \xrightarrow[\substack{\text{solid-state} \\ \text{R.T}}]{\text{PANI-EB}} \text{Composite SSA-PANI}$$

Scheme

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Silica-Supported Sulfuric Acid as Effective Solid Dopant Acid in Doping of Polyaniline Emeraldine Base for Synthesis of a New Composite of Polyaniline in Solid-State

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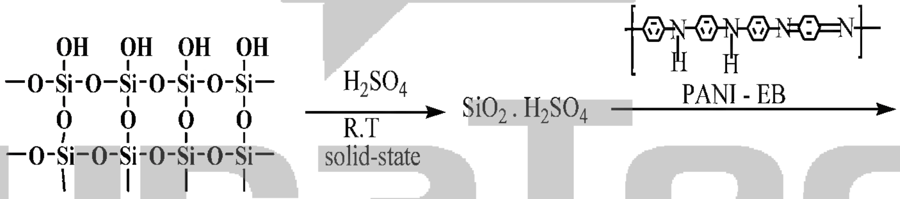
Polyaniline (PANI) is one of the most promising conducting polymers due to its straightforward polymerization and excellent chemical stability combined with relatively high levels of conductivity [1]. The conductivity of PANI can lead to change and increase when PANI is doped or protonated with acidic compounds such as HCl, H_2SO_4, or some organic sulfuric acids such as silica-supported sulfuric acid (SSSA) [2]. Also it is possible to modify the electrical properties of PANI by adding inorganic particles within the polymer matrix. So composites containing organic polymers and inorganic particles such as silica (SiO_2) provide a new class of materials with novel properties [3].

In the present work, a new composite of PANI-EB with SSSA was synthesized under solid state or solvent-free condition. The solvent–free reactions are industrially important due to reduced pollution, low costs, and simplicity in process and handling [4,5], Scheme.

The resulting composite was characterized by FT-IR and UV-vis spectroscopy and its doping was confirmed by means of comparison with prepared polyaniline emeraldine base. In other words, the doping process has been proved via FT-IR and UV-vis spectroscopy. The morphology of composites was determined using Scanning Electron Micrographs (SEM).



Composite PANI-EB-Silica supported sulfuric acid

Scheme

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Investigating the effects of starch phosphates on flowability of Portland cement slurries

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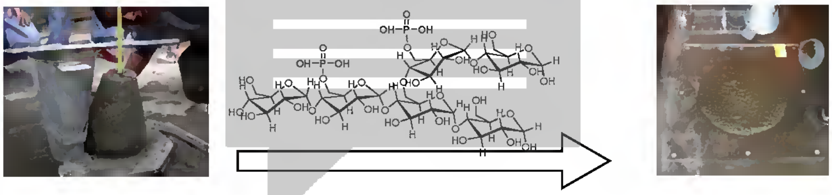
In the construction industry, it is very important for fresh concrete to be fluid enough to provide facile transportation and placing. To achieve this, the so-called water-reducing agents are used, which interact with the surface of cement particles and decrease their natural tendency to coagulate in aqueous systems [1]. Many conventional water-reducing agents are the condensation or addition polymers of synthetic origin. To avoid undesirable environmental effects of these petrochemical based materials, many investigations on water reducing agents based on the starch or cellulose were carried out [2,3].

In this study, an attempt has been made to enhance the flow and stability of Portland cement slurries by utilization of phosphorylated starch [4]. Consequently, we directed our efforts toward studying the rheological parameters of cement slurries, investigating the influence of molecular weight and DS value upon viscosity and yield stress of slurries, and also explored the possibility of using the starch phosphate as a stabilizer to enhance the paste stability and reduce bleeding.



Commercial cornstarch was acid hydrolyzed to yield various number-average molecular weights depending on the conditions of hydrolysis. The products were then phosphorylated using sodium dihydrogen phosphate and sodium hydrogen phosphate.

The phosphorus content of the starch phosphate was determined by a spectrophotometric method and the degree of substitution of the modified starch was calculated from the phosphorus content. It was shown that DS has an important role in enhancing the paste stability and flowability, so that bleeding rate and yield stress are reduced with increasing DS values.

Measurement of viscosity and yield stress of slurries by a rotary rheometer (Physica MCR-300) with shear rates from 0.01 to 100 S^{-1} suggested that best results were obtained only when the hydrolysis is mild. The progress of hydrolysis severely deteriorates the flow of the slurries.

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Synthesis, Characterization, and Properties of Novel Polyamides with Preformed Ester Structure

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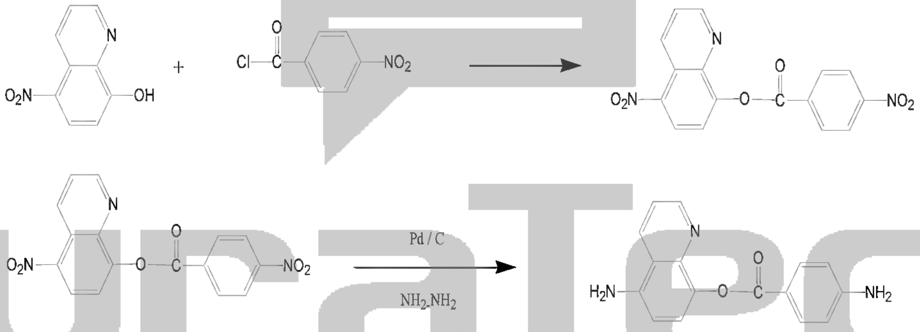
Aromatic polyamides are one of the most important classes of high temperature polymers that have good chemical and physical properties. But their industrial uses are limited by their difficult processability due to their high melting point, high glass transition temperature and limited solubility in most organic solvents [1,2]. Some certain properties could be introduced to the polymers by structural modification. Copolycondensation is one of the possible ways for modification of polymer properties. Modification of the properties of polyamides by incorporation of ester groups has been investigated and poly (ester amide) s have been studied extensively [3]. Therefore, much attention has been paid to different synthetic methods in this area for improving their solubility and processability (including introduction of flexible groups, bulky groups and disruption of symmetry and regularity of main chain) through the design and synthesis of new and specific monomer to obtain polymers with improved solubility while maintaining thermal stability. In this research, a new diamine was prepared via reaction of 8-hydroxy-5-nitro quinoline with 4-nitrobenzoyl chloride and subsequent reduction of nitro groups, and used as a monomer for the preparation of related polyamides with preformed ester unit.



Polycondensation reaction of this monomer with different aromatic diacid chlorides in the presence of propylene oxide (as an acid scavenger) led to preparation of different polyamides.

The prepared monomer and all the polymers were characterized by conventional methods. Thermal and physical properties of the polyamides including thermal stability, thermal behavior, solution viscosity, and solubility behavior in addition to crystallinity, and molecular weights were studied. They showed nice balance of properties including enhanced solubility, and heat-resistant that extends their application in various industries. Structure-property relations of the prepared polyimides were also studied.

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Novel poly(keto ether imide)s: as a new generation of soluble, heat-resistant polymers

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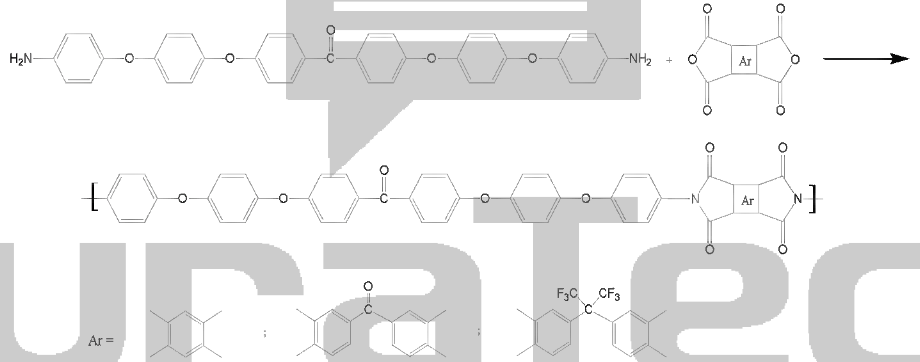
Aromatic polyimides are thermally stable polymers that generally show excellent mechanical strength and stability. Due to the increased performance characteristics demanded on polymers in various fields including the aerospace, automobile, and microelectronic industries, the use of these aromatic polymers in growing steadily [1]. However, one of the drawbacks to the employment of these high performance polymers is the difficulty in processing due to their high melting temperatures or high glass transition temperatures.[3] Therefore, some significant synthetic efforts, in the area of high-temperature resistant polymers, have been focused on improving their processability and solubility through the design and synthesis of new monomers [2,3]. Aromatic polyimides that contain aryl ether linkage generally have greater tractability, lower glass transition, and greater chain flexibility than their corresponding polymers without these groups in the repeat units. The improved solubility and lower glass transition temperatures are attributed to the flexible linkages that provide a polymer chain with a lower energy of internal rotation.

The present article deals with preparation a new diamine monomer containing ether and carbonyl flexible units and resulting poly(keto ether imide)s there from.



Monomer and polymers were fully characterized and the physical and thermal properties of the polymers including thermal stability and behavior, molecular weight, crystallinity, solubility, and mechanical properties were studied. As expected, polymers were high heat-resistance that was related to the fully aromatic nature of these polyimides and avoid of any weak linkages. Also, enhanced solubility of these polyimides was attributed to the high contribution of flexible groups (ether and ketone) in the backbone of these poly(keto ether imide)s.

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The effect of titanium dioxide nanoparticles on their physical and thermal properties of heterocyclic polyimides

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Nowadays, polymer-inorganic hybrid materials have become a popular topic in material science because of their unique properties [1-3]. This is related to their diphasic structure, leading to multifunctional materials. However, increasing interest in nano-size systems (ie systems of size range 0.5-100 nm) in recent years seems to be determined both by some distinctive properties of nanoparticles themselves and by anomalous cooperative properties of systems consisting of these moieties [4]. Polyimides (PI)s, which can be prepared from a variety of starting materials by a variety of synthesis routes and posses high thermal stability, high chemical resistance and excellent mechanical properties are a promising candidate type for the matrix of these hybrids [5,6]. The high glass-transition temperature of PIs would be expected to further stabilize the nanoparticles by decreasing their mobility, thereby preventing their agglomeration into large particles. In this study, the titanium alkoxide is incorporated into PI matrix through a simpler process and good quality and well-dispersed PI/titania hybrid films with relatively high titania content are prepared. Moreover, the characteristics of morphology, optical, mechanical, and thermal properties for the hybrid films are also investigated.

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The Role of Silica-Supported Camphor Sulfonic Acid in Doping and Synthesis of a New Composite under Solid-State Condition

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Conductive polymeric materials containing conjugated bonds have attracted much interest in scientific and technological areas in recent years. The conducting polymers such as polypyrrole, polythiophene, poly(p-phenylene), polyaniline and poly(o-methoxyaniline) have commonly been used in scientific and industrial studies and in various applications as rechargeable batteries [1,2], sensors [3-6], diodes, in transistors and microelectronic devices [7]. Among all the conducting polymers, polyaniline has received a great deal of attention owing to its simple synthesis, good environmental stability ability to dope with protonic acids and moderately high electrical conductivity [8]. The conductivity in thesepolymers can be varied by doping them with different protonic acids or by using functionalized protonic acids,these functionalized acids make polymer conducting as wellas render the resulting polymer complex soluble in common organic solvents such as m-cresol, toluene, xylene and chloroform[9,10].

In this work, a new composite was synthesized by doping of poly(o-methoxyaniline – emeraldin) base (POMA-EB) using of silica-supported camphor sulfonic acid. This method differs from the in situ polymerization because POMA-EB was prepared in a separate step and then doping was done by solid acid above . The resulting composite was characterized using Fourier transform infrared (FT-IR) and Ultraviolet-visible (UV-vis) spectroscopy. The morphology of composite was determined using scanning electron microscopy (SEM).

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Influence of nano-ZnO on polycondensation of UV-curable unsaturated polyester

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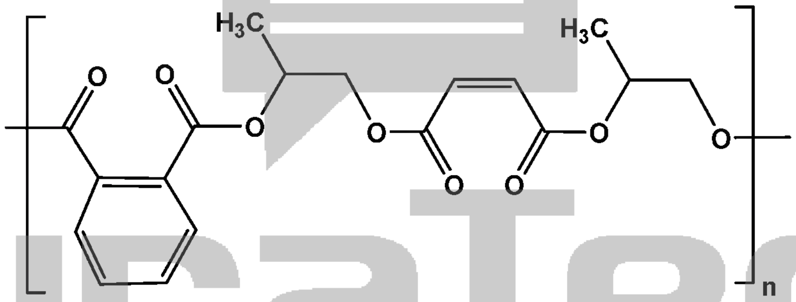
We have been synthesized UV-curable unsaturated polyester that can be used for wood coatings. The polyesterification of phetalic anhydride, maleic anhydride and propylene glycol was achieved in the presence of nano-ZnO. Unsaturated polyester was diluented by trimethylol propane triacrylate (TMPTA) and hexandiol diacrylate (HDDA). The diluented unsaturated polyester was formulated by benzophenone and N-methyl diethanol amine as photoinitiator and coinitiator, respectively. The formulated resins were cured by ultraviolet radiation. The effects of nano-ZnO on the mechanical properties of film coatings after UV radiation were evaluated by hardness, adhesion and gloss.



UV-curable linear unsaturated polyester

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Effect of nanosilica on the morphology and mechanical behavior of epoxy nanocomposite

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Among polymeric materials, thermosetting epoxy resins are commonly used in adhesives, coating, optical components and etc. due to their superior properties and low cost [1]. Depending on the specific desires for certain physical and mechanical properties, combinations of epoxy resin and some filler can usually be formulated. In the past decade, spates of research activities have been reported for improving mechanical properties of epoxy composites. Nanoparticles can significantly alter the mechanical properties of the polymer close to the particle surface due to changes in polymer chain mobility. Several recent investigations on nanocomposites of glassy polymer matrices reported enhance of strength and toughness [2-5]. As the matter of fact, silica has played an important role in reinforcement components due to nanoscale effects [6].

In this study, the mechanical properties of epoxy resin based on bisphenol A (DGEBA) with amine curing agent, in the presence of silica filler in comparison of different nanoscale concentrations were determined. Ultrasonic cavitation technique is one of the well-organized tools to disperse nanoparticles into a polymer [7]. Ultrasonic processor (Sartorius Labsonic® P, 105 W/cm2) was used to obtain a homogeneous mixture of epoxy resin/fumed silica and thereby helped to increase their interfaces. The mechanical properties of epoxy nanocomposites were measured via tensile test that were performed on dog-bone specimens (ASTM D3039 with crosshead speed of 1mm/min). Scanning electron microscopy (SEM) analysis was shown the agglomeration event in higher percentage of nanofiller. On the basis of obtained results, the epoxy nanocomposite contains 1 Wt. % of nanosilica showed sufficient disparity and highest strength and yang modulus.

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Investigation of plasticizing properties of ABA triblock copolymers based on PEG in cementitious systems

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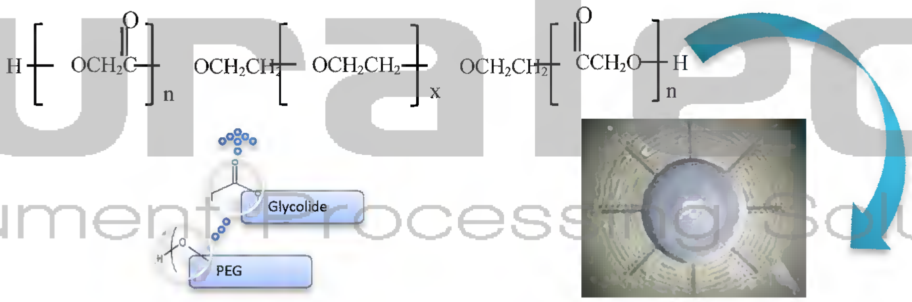
Plasticizers in cementitious systems are additives that uppon addition at a low dosage can change the workability, mechanical strength and other properties of cement paste effectively.[1] Plasticizers cause dispersion of cement particles and increase their mobility by two mechanisms: steric hindrance and electrostatic repulsion between cement particles by adsorption of negative functional groups on the plasticizer molecules.[2]

Slump retaining agents control the rate of setting of cement paste, so they can retain the workability of cement long enough for placing and finishing operation.

In this study, triblock copolymers based on poly ethylen glycol (PEG) was synthesised and their applications in the cementitious systems was investigated. The main purpose was verification of plasticizing effects of these copolymers in the cement paste. Ability of plasticizers depends on their structure, dosage and the water to cement ratio (W/C).[3]

ABA triblock copolymers with PEG (1000 and 1500 g/mol) as B block, poly caprolactone (PCL) and poly glycolide (PGA) (with different weigth ratio) as A block was synthesised via ring opening polymerization with stannous octanoate as catalyst. Their plastisizing effects and rheological properties was studied by mini-slump test and cylinder-cup rheometer. The Results show that by adding these copolymers to cement paste, the flowability increases, with PGA-PEG-PGA showing the highest performance. In this case the time of setting of hydraulic cement was also determined by Vicat Needle instrumen

Although these copolymers are not as efficient as commercial superplasticizer, they provide more insight into possibility and mechanism of plasticizing effects by non-ionic copolymers.



$$H\left[OCH_2\overset{O}{\overset{\|}{C}}\right]_n OCH_2CH_2\left[OCH_2CH_2\right]_x OCH_2CH_2\left[\overset{O}{\overset{\|}{C}}CH_2O\right]_n H$$

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Kinetics and Thermodynamics of Isothermal Curing Reaction of Epoxy - 4, 4'-Diaminodiphenylsolfon Reinforced with MWCNT Epoxy Functional

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Multiwall carbon nanotubes were functionalized with epoxy groups by chemical modification in four stages [1]. At each stage the compound was characterized by Fourier transform infrared spectroscopy and scanning electron microscopy. Epoxy composite samples were prepared by mixing diglycidyl ether of bisphenol A-based epoxy resin and synthetic epoxy functionalized multiwall carbon nanotube (E-MWCNT) with different percentages (1, 3, 6, 9, 12, 15 %) in acetone. Ultrasonic dispersion was used to produce homogenous blends. The optimum ratio of the reacting components (9%) was investigated by total enthalpy of the curing reaction from differential scanning calorimetry (DSC) thermograms. The kinetics of the curing reaction for epoxy composites with 4, 4'-diaminodiphenylsolfon as a curing agent was studied by means of a DSC isothermal technique [2]. The Kamal autocatalytic-like kinetic model was used to estimate the reaction orders (m, n), rate constants (k_1, k_2), and active energies (E_a) of the curing reaction [3]. However, the existence of E-MWCNT with hydroxyl groups in the structure catalyzes the cure reaction and influence the rate of reaction and therefore kinetics parameters. The E_a of cure reaction of DGEBA/DAS systems showed a decrease when E-MWCNT were present, therefore the rate was increased. Using the rate constants from the kinetic analysis and transition state (TS) theory, thermodynamic parameters such as enthalpy ($\Delta H^{\#}$), entropy ($\Delta S^{\#}$) and Gibbs free energy ($\Delta G^{\#}$) changes were also calculated [4]. The thermodynamic functions were shown to be very sensitive parameters for evaluation of the cure reaction.

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Small-Bandgap Conducting Polymers Based on Poly(heteroarylene methylenes) and Poly(heteroarylene methines). Synthesis, and Properties

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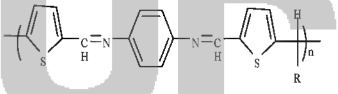
Currently known conducting polymers are prepared from π-conjugated polymers by a chemical or electrochemical process called doping which enhances the electrical conductivity of the pristine conjugated polymer by many orders of magnitude from the semiconducting to the metallic range (10^{-7} to 106 S/cm) [1]. However, it was also thought that control of the E_g value of a polymer by molecular design would allow the control of its optical, electronic, and optoelectronic properties [2]. There are a number of theoretical [3] and experimental [4] approaches to achieving small-bandgap conducting polymers. Along this, we wish to focus on the novel conjugated poly(N,N'-Bis(2-thienylmethylene)benzene-1,4-diamine methines) (I) and poly(N,N'-Bis(2-thienylmethylene) benzene-1,4-diamine methylenes) (II). Thus herein we report the synthesis and characterization of the poly(N,N'-Bis(2-thienylmethylene) benzene-1,4-diamine methines) and poly(N,N'-Bis(2-thienylmethylene)benzene-1,4-diamine methylenes). The theoretical and experimental characterization of relatively small band gap methines and methylenes –bridged derivatives is performed. AM1 and the modified extended Hückel theory were used to explore the ground-state geometric and electronic structures of these polymers.



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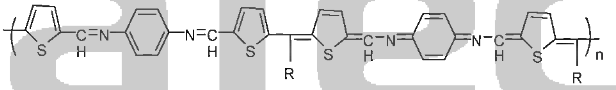

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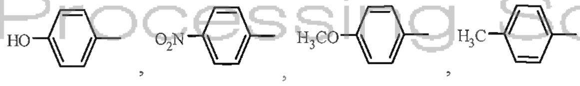

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Synthesis of salep phosphates and superabsorbent hydrogel networks based on Poly(acrylic acid) grafted onto salep phosphate for Controlled Release of Fertilizers

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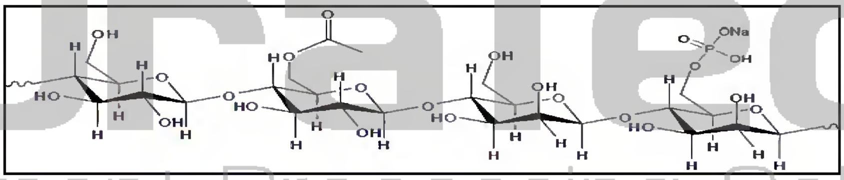
The preparation and applications of functional polymers is one of the most important research areas in polymer science. Incorporation of specific functional groups into polymers influences the physical, chemical, mechanical and rheological properties of materials [1]. Incorporation of vinyl monomers onto the backbone of natural polysaccharides helps in improving some properties of the polysaccharides and also allows the product copolymers to be used in novel applications, for example, as hydrogels. A hydrogel is a superabsorbent macromolecular compound that can absorb pure water up to hundred or thousand times of its dried weight [2].

Agrochemicals are bioactive agents that improve production of crops both in quality and quantity. contamination of ground water by agrochemicals becomes a great problem. One of the most alarming problems is nitrate leaching and subsequent pollution of ground water. Thus, the application of nitrate loaded carrier with a technology based on the controlled release of nitrates by the swelling of a polymeric carrier could prove to be a suitable technology against pollution of ground water [3].

In this study, salep phosphates with different phosphorus contents were prepared via reacting salep with a mixture of primary and secondary sodium phosphates under weak acidic conditions in a semi dry process. Effect of phosphorylaion of salep in swelling behavior and controlled release potential of superabsorbent hydrogels based on salep phosphates grafted with Poly(acrylic acid) is described. For a structural characterisation of salep phosphates FTIR spectra were recorded. The phosphorus contents of modified salep were determined using a standard wet chemistry method. The new superabsorbent hydrogel biopolymer was synthesized via radical crosslinking and graft copolymerization of acrylic acid monomer onto salep phosphates backbones. In our procedure, ammonium persulfate (APS) as a water-soluble initiator and methylenebisacrylamide (MBA) as a suitable crosslinking agent were used and the best synthesis conditions described.



Salep phosphates:

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Synthesis and characterization of novel chiral nanostructured poly(amide-imide)s from N-trimellitylimido-L-amino acids and 3,5-diamino-N-(thiazole-2-yl) benzamide under green condition

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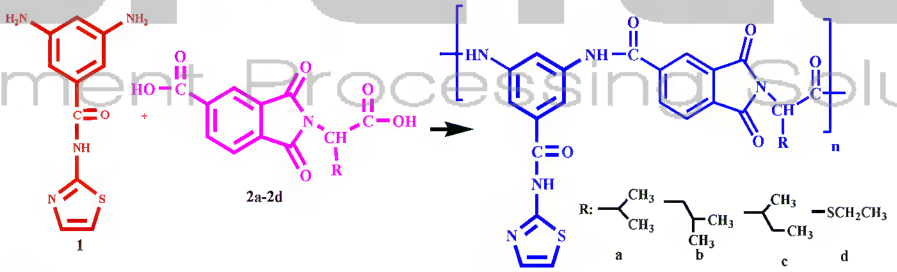
Recently poly(amide–imide)s (PAIs) have received much attention due to their favorable balance between process ability and performance. The PAIs have excellent thermal, physical and mechanical properties [1]. Functional macromolecular materials using biological chiral resources such as amino acids have been drawing much interest due to their biocompatibility and biodegradability easing the ecological trouble because amino acid residues can be targeted for leaving by different enzymes [2]. Thiazoles are reported to possess a broad range of antitumour, antibiotic, antibacterial, antifungal and antiinflammatory activities [2]. In the study a new series of optically active PAIs with moderated inherent viscosities in the range of 0.25-0.35 dL/g were synthesized from the direct polycondensation reaction of N-trimellitylimido-L-amino acids (2a-2d) with 3,5-diamino-N-(thiazole-2-yl)benzamide (1) in green medium consisting of tetra-n-butylammonium bromide and triphenyl phosphite (Scheme 1). At first N-trimellitylimido-L-amino acids were synthesized by the condensation reaction of trimellitic anhydride with two equimolars of various L-amino acids in acetic acid solution. Then, 3,5-dinitro-N-(thiazole-2-yl) benzamide (1) was prepared from the 3,5-dinitrobenzoyl chloride and 2-aminothiazole and it was reduction by using FeOOH/ hydrazine monohydrate. The resulted materials were fully characterized by means of by fourier transform infrared spectroscopy, ^{1}H-NMR spectroscopy thermogravimetry analysis, X-ray powder diffraction, UV-Vis spectroscopy and field emission-scanning electron microscopy.



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Synthesis and characterization of new aromatic polyesters

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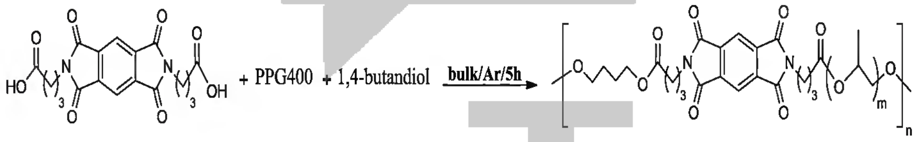
Polyesters are one of the most versatile polymers. They contain widely different materials with large applications, which are produced by a variety of manufacturing techniques [1]. They have in common the ester group –CO–O– in the main chain, which is a polar group and brings about inter and intramolecular chain interactions that may reflect in some properties such as low solubility, mobility of the chain and melting characterizations.[2]

Aromatic polyesters are of considerable interest both scientifically and commercially because of their excellent mechanical properties, chemical resistance and thermal stability [3, 4]. Dicarboxylic acid monomers were synthesized from the reaction of amino acids with anhydrides. Different polyesters with various molecular weights were synthesized from these carboxylic acids and diols with different stoichiometric molar ratios by polycondensation reaction. The obtained polymers were characterized by Fourier transform infrared spectroscopy (FT-IR), GPC, H-NMR and differential scanning calorimetric (DSC).



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Synthesis of N-methyl imidazol grafted poly(styrene-alt-maleic anhydride) copolymer and its application in phenol adsorption from aqueous solution

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Contamination of surface water and groundwater with aromatic compounds is one of the serious environmental problems human being today [2]. Phenol and phenolic compounds were listed as priority pollutants by the environmental protection agency (EPA) of United States and other countries and commonly present in industrial wastewater from oil refineries, petrochemical plants, ceramic plants, coal conversion processes, phenolic resin industries, pharmaceuticals, etc[1]. The permissible concentration of phenolic contents in potable water is 1 μg L^{-1} according to the recommendation of world health organization (WHO) so it is toxic even at low concentration [3]. Various treatment methods have been applied to remove phenolic compounds from aqueous solution. In this work we select the adsorption method for removing of phenol from aqueous solution. For this propose the poly(styrene-alt-maleic anhydride) was synthesized by free radical polymerization. Then the alternative copolymer were modified by step by step grafting reaction of N-methyl imidazole and ethylene diamine as crosslinking agent on the poly(styrene-alt-maleic anhydride) backbone. The various ratio of N-methyl imidazole to poly(styrene-alt-maleic anhydride) were used in preparation of modified copolymers. Fourier transform infrared spectroscopy (FT-IR) was used for characterization of prepared polymers. The prepared copolymers were investigated in phenol adsorption from aqueous solutions. The prepared copolymers showed good capacity in adsorption of phenol.

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Synthesis of a New Chiral Composite of Poly(aniline-*co*-(±)-2-*sec*-butylaniline) in the Presence of Silica Sulfuric Acid in Solid-State

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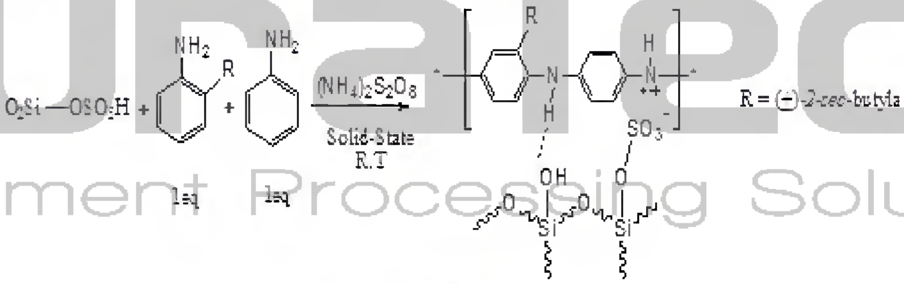
Conducting polymers and silica (SiO_2) are very important materials for a wide range of technological applications [1]. Enormous works on conducting polymers have been performed to enhance conductivity of conducting polymers by doping with inorganic and organic acids. Electrical properties of polymers are modified by adding inorganic particles within the polymer matrix. Among them, many PANI/inorganic polymer composites have been prepared recently. These composites based on polyaniline have been harvesting several intriguing properties within themselves due to the mutual influence of the individual constituents and synergism of their properties [1].

It has been found that ring-substituted (alkyl and alkoxy) and *N*-alkyl-substituted PANI are more soluble than unsubstituted PANI [2]. The most common method of chemical synthesis includes oxidation of the monomer with an oxidizing agent, e.g. ammonium peroxydisulfate, which is added to monomer solution [3].

In this work, a new chiral composite of poly(aniline-*co*-(±)-2-*sec*-butylaniline) with silica sulfuric acid has been synthesized at room temperature by chemical oxidation of monomers in presence of ammonium peroxydisulfate (APS) as oxidant [4]. In fact, copolymerization of mixture (1/1) of aniline and (±)-2-*sec*-butylaniline and doping of the obtained copolymer by silica sulfuric acid (SSA) has simultaneously been carried out in solid-state. The resulting composite was characterized by FT-IR and UV-vis spectroscopy. The morphology of composite was determined using scanning electron microscopy (SEM).



Scheme

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Cyanomethyl propane derivatives as pesticidal intermediates

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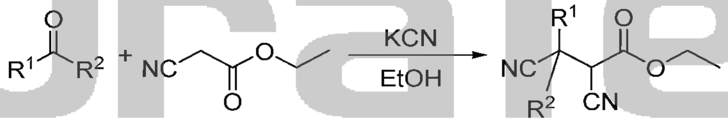
This research relates to a process for preparing certain cyanomethyl propane derivatives and the use of these compounds in the synthesis of pesticides and pesticide intermediates. Ethyl 2,3-dicyanopropionate was prepared and characterized by several methods.[1] However, many of these methods suffered from some drawbacks, that it is first necessary to isolate the intermediate formaldehyde cyanohydrins; These highly water soluble cyanohydrins are obtained by lengthy continuous extraction and have a limited stability, often decomposing violently upon attempted distillation. Furthermore, this reaction requires care given the risk of formation of dimeric side-products. In one aspect the present research seeks to provide a process for preparing cyanomethyl propane derivatives satisfying one or more of the following criteria:

- avoiding the use of formaldehyde cyanohydrins;
- avoiding the dimerisation side reaction;
- obtaining the required product directly in high yield and with high purity.



R^1, R^2 = Alkyl & Aryl

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How Analytical Chemistry Helps Organic Chemists to Understand Physical Chemistry?

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The massive use of analytical techniques, especially molecular spectroscopy, on the research methods of organic chemists has done much to condition universities to teach them a couple of modern physical (organic) chemistry courses. The commercial availability and widespread use of instrumentation for NMR, UV and IR spectroscopy has rendered an understanding of the theoretical bases of such techniques indispensable to the modern organic chemistry students and professors. On the other hand, all organic synthesis includes a separation (chromatography) step, which is primarily depends on physical chemistry theories.

In this article, it is described that there is a strong connection between (qualitative) organic analysis and physical chemistry. There will be an approach in this presentation between the theoretical concepts of physical chemistry and what are involved in the practical aspects of interpretation essential to the student who will be using chromatography and/or spectroscopy as an analytical tool in his undergraduate or graduate research.

Alumina Supported Acidic Ionic Liquid: Preparation, Characterization and Its Application as Catalyst in the Synthesis of 1,8-Dioxooctahydroxanthenes

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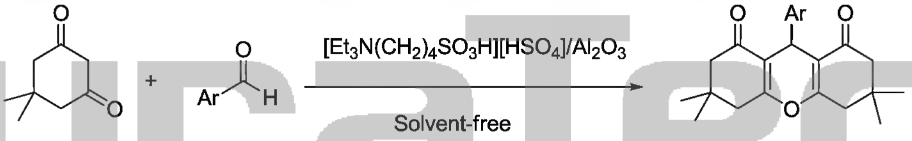
Xanthenes are important class of organic compounds with a large number of naturally occurring, as well as synthetic derivatives, and occupy a prominent position in medicinal chemistry.[1]A number of these compounds have been considered as dyes and fluorescent visualization materials for biomolecules and laser technologies.[2] Furthermore, these compounds have been investigated for their agricultural bactericide activity,[3] anti-inflammatory effect,[4] and antiviral activity.[5] Recently, many synthetic methods for preparing xanthenediones have been reported by the condensation of aromatic aldehydes and active methylene carbonyl compounds in the presence of various acid catalysts.[6-9] Many of these procedures suffer from lack of selectivity, unsatisfactory yields, being costly, toxicity of the reagents, or required special conditions.

Thus,we report herein an efficient synthesis of 1,8-dioxooctahydroxanthenes by the reaction of dimedone with aryl aldehydes using $[Et_3N(CH_2)_4SO_3H][HSO4]/Al_2O_3$ as a new solid acid supported catalyst. Reusability, easy work up, inexpensive, ready availability of the catalyst makes the procedure an attractive alternative to the existing methods for the synthesis of 1,8-dioxooctahydroxanthenes.



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Synthesis, lipophilicity studies and antibacterial properties of some novel indolecontaining pseudopeptides

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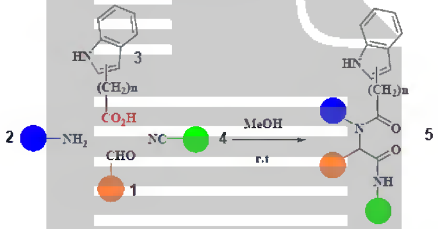

Indole nucleus is a substructure found in numerous natural products and pharmaceuticals possessing anti-inflammatory, antimalarial, antidepressant, antitumor and various other activities. Among the large family of indoles, indole carboxamides have recently attracted a great deal of attention of chemists and biologists due largely to their various pharmacological activities such as antioxidant, hypocholestrolemic, antihistaminic and Immunosuppressive.

Furthermore, in recent years, peptides and pseudopeptides especially those containing tryptophan have gained popularity as promising building blocks for design and development of novel materials with potential application areas ranging from drug design to biotechnology [1].

Considering all above, we`ve been greatly encouraged to synthesis novel indole-containing pseudopeptides via Ugi-4CR by the importance of indole carboxamides and the fact that although functionalized indole ring systems have been found frequently in biologically active compounds, indole derivatives as MCR partners are rather under-represented[2].

The compounds have been screened for their antimicrobial activity and they are found to exhibit moderate antimicrobial activities. The lipophilicity studies showed that most of the compounds possess optimum range for oral absorption and cell membrane permeation, as well as blood brain barrier permeation.

Keywords : Indole-containing pseudopptides, Antimicrobial activity, Lipophilicity

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The synthesis of 6-substituted-2-oxo-2H-chromene-3-carbohydrazides

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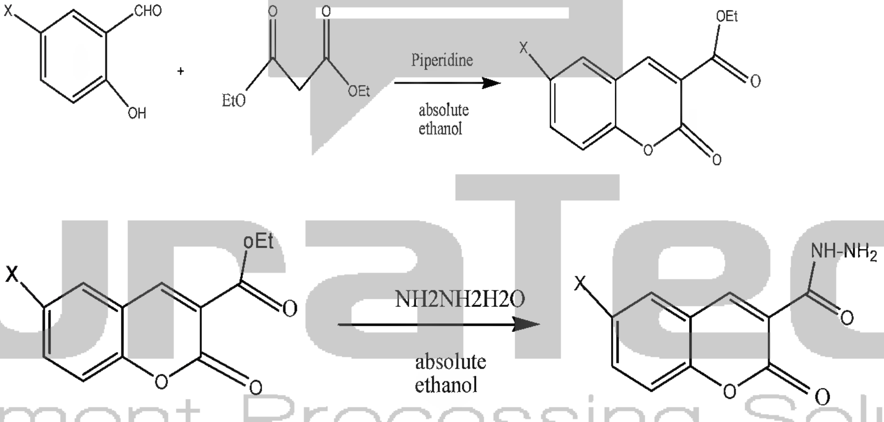
Abstract

Coumarins possess a variety of bioactivities including anticoagulant and antimicrobialeffects [1]. Some drug derivatives ofcoumarins are coumaromycin ,novobiocin and charteusin.[2-4]. 6-substituted-2-oxo-2H-chromene-3- carbohydrazides have been synthesized by the reaction of the 6-substituted-2-oxo-2H-chromen-3-carboxylate with hydrazine hydrate in the presence of ethanol under reflux condition after 5 hours.6-substituted-2-oxo-2H-chromen-3-carboxylate obtained from reaction of substituted 2-hydroxy benzaldehyde and diethylmalonate inabsolute ethanol usingpiperidine as base under reflux.The structures of novel synthesized compounds have been established by IR , H-NMR and Mass spectral data .

Keyword: chromene – hydrazine hydrate– diethylmalonate – carbohydrazid



X= -Br , -OH

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Palladium-Catalyzed intermolecular decarboxylation and Arylation of coumarin-3-carboxylic acids with Aryl bronic acid

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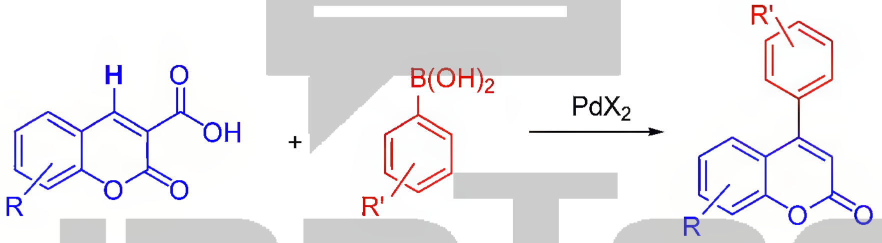
4-Arylcoumarins have attracted considerable attention as a result of their interesting biological and pharmacological activities and their presence in a variety of natural products. Depending on the substitution pattern, their antiprotozoal,[1] anticancer,[2] anti-HIV,[3] and cytotoxic properties[4] have been recognized. The transition-metal-catalyzed functionalization of C-H bonds is a powerful method for generating carbon-carbon bonds. Moreover palladium catalyzed cross-coupling reactions between organometallic and arene moieties are among the most employed methodologies for the synthesis of biaryls[5]. In this work a palladium catalyzed C-H activation of coumarin-3-carboxylic acids following decarboxylation with boronic acids is synergistically combined to synthesize coumarins arylated exclusively in the C-4 position (Scheme1).



Scheme1. Arylation of coumarin-3-carboxylic acids with aryl bronic acid derivatives

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Facile access to polysubstituted indoles via three component one – pot reactions in the presence of p-TSA

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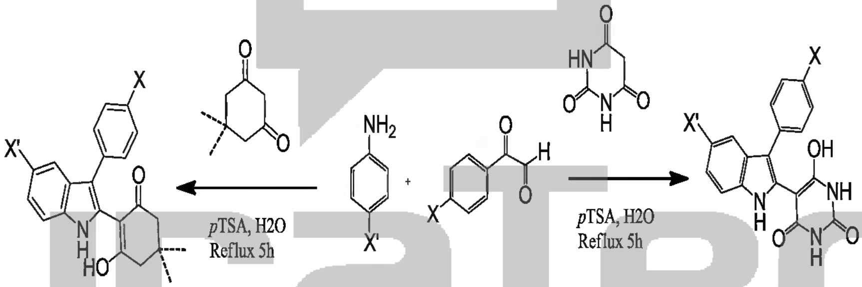
Multi-component reactions (MCRs) play an important role in organic chemistry. The significant contribution of MCRs is in the state of modern organic chemistry and their potential use in syntheses of complex organic [1]. Indole and its derivatives are known as important intermediates in organic synthesis and pharmaceutical chemistry [2]. Here, we report a new, simple and general synthetic method of substituted Indoles in high yields from three-component one-pot reaction of p-anilines, the phenylglyoxals and barbituric acid or dimedon in refluxing water in the presence of p-TSA for 5 h.



The simplicity of this experiment and work up are noteworthy. The structures of compounds were deduced from their ^{1}H NMR, ^{13}C NMR, mass and IR spectral data.

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An efficient method for synthesis two brominated derivatives of 4-nitroaniline without protection amine group

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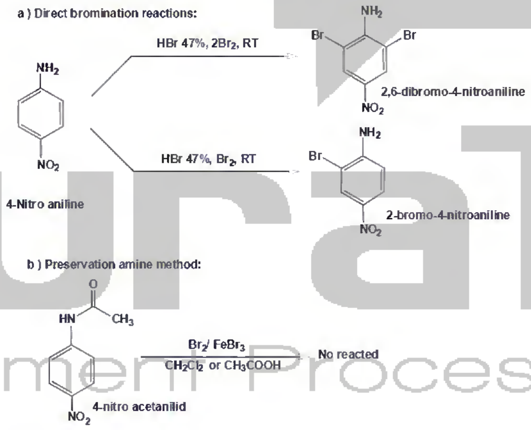
Organic molecules containing halogen atoms are found in many products. They are important intermadiets in reaction and in this type bromination and chlorination are straight forward processes . In aromatic molecules, electrophilic aromatic substitution reaction dependence to inductive and resonance effects that impressible from activator and deactivator groups. By protection of some functional group, slake these reactivity [1, 2]. In this research, 4-nitroaniline selected because it applied for very consumptions such as dyes and pigments synthesis, special antioxidant, corrosion inhibitor, pharmaceuticals, venom and gasoline intermediates [3, 4]. At present study in connection with our previous reports on the benign synthetic methods in organic chemistry, we wish to introduce an efficient protocol for the synthesis of new derivatives of brominated 4-nitroaniline by acid solvent. First, 4-nitroaniline powder was added in enough hydrobromic acid 47% in round-bottomed flask and warmed until completely dissolved, next solution cooled and wetted crystals formed the suspension. Then, cooled bromine was added dropwise to suspension and temperature is controlled for 4hr. Product powder extract from aqueous phase and recrystalized in ethanol [5]. These have been characterized with FT-IR and Melting point and solubility tests.



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Simple Synthesis of Amido coumarinyl furans Using A Multi–Component Reaction in Water

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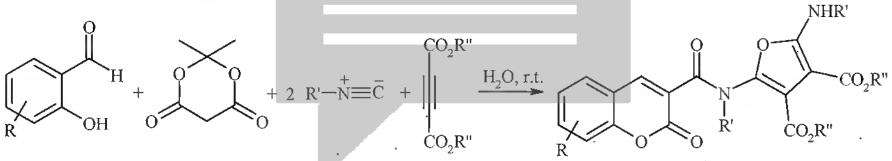
Furans, benzofurans, and their reduced forms are important core structures in functional materials and many biologically active natural products. Moreover, they are useful building blocks in total synthesis of natural products and pharmaceuticals.[1–4]

Coumarinyl compounds have been extensively used in medicinal chemistry. Some examples have been shown to be highly potent human β-secretase inhibitors and are used in the treatment of Alzheimer's disease. Most of the synthetic medicines containing coumarin, are prepared by the reaction between coumarin-3-carboxylic acids and amines.[5]

In recent decades green chemistry is a generally accepted term to describe the movement towards more environmentally acceptable chemical processes and products. Being nontoxic, readily available, nonflammable, inexpensive and environmental friendly, water has clear advantages as a solvent for use in green chemistry.[6,7]

Herein, we present a new synthetic method for the construction of potentially bioactive amido coumarinyl furan derivatives via a one–pot, isocyanide–based MCR involving commercially available starting materials. Thus a mixture of 2-hydroxy aromatic aldehydes **1**, meldums's acid **2**, dialkyl acetylenedicarboxylates **3** and isocyanides **4** afforded 2-(alkylamino)-5-{alkyl[(2-oxo-2H-chromen-3-yl)carbonyl]amino}-3,4-furandicarboxylates **5**.



1 **2** **3** **4** **5**

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Pure and doped boron nitride nanotubes: A computational NMR study

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Abstract

Carbon and non-carbon nanotubes have been came into special focus of researches and received increasing attention during the past 10 years, due to their unique and fascinating properties, and wide potential applications [1] .

The electronic and structural properties of BNNTs have been investigated by either computational or experimental [2] studies.

We have investigated the properties of the electronic structure of the Disiline-doped boron nitride nanotubes (Disiline-BNNTs) by density functional theory (DFT) calculations. The structural forms are firstly optimized and then the calculated CS tensors in the optimized structures are converted to chemical-shielding isotropic (CS^I) and chemical shielding anisotropic (CS^A) parameters. The shielding values of B and N atoms are calculated by, continuous set of gauge transformations (CSGT) and individual gauges for atoms in molecules (IGAIM) methods, using B3LYP/6-311+G*. The B3LYP theory level with IGAIM method is the best choice to evaluate theoretical chemical shifts for compounds studied. The results reveal the significant effect of Disiline doping on the chemical shielding tensors at the sites of those 11B and 15N nuclei located in the nearest neighborhood of the Disiline -doped ring. Furthermore, in comparison to the pristine model, the values of dipole moments and LUMO–HOMO gap are changed in the Disiline -doped models.

Keywords: Disiline, DFT, Boron nitrid nanotube, Chemical shielding, Anisotropic, Isotropic.

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7-9 March 2012

Synthesis and characterization of bis and tetrakis [tris(trimethylsilyl)silyl]borylferrocene

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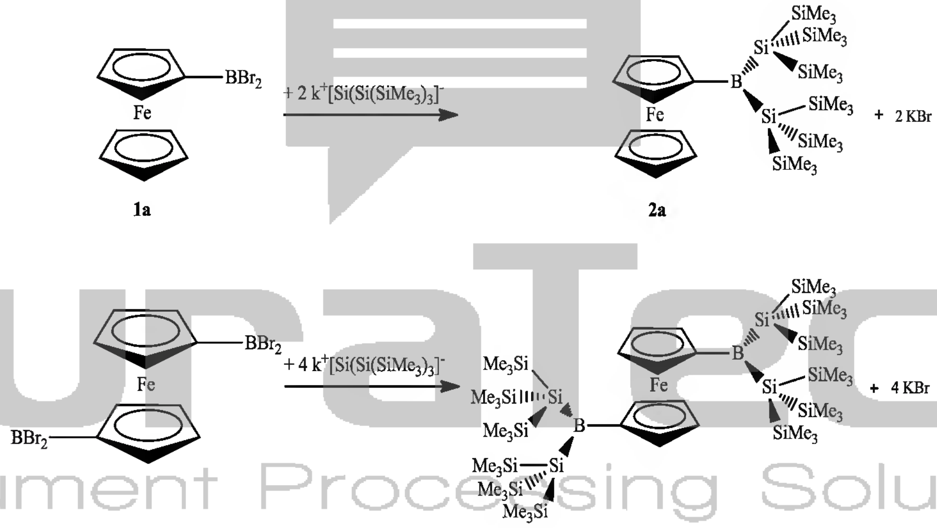
In the course of our studies of the synthesis of highly borylated aromatic systems, we report on the synthesis of bis and tetrakis [tris(trimethylsilyl)silyl]borylferrocene **2a** and **2b**.
The Compounds (dibromoboryl) ferrocene **1a**, and 1,1′- bis(dibromoboryl) ferrocene **1b** [1,2] were synthesized as the precursors for the synthesis of ferrocenylboran derivatives.
The first bis[tris(trimethylsilyl)silyl]borylferrocene (**2a**) and tetrakis [tris(trimethylsilyl)-silyl]borylferrocene **2b** were synthesized from the reaction of **1a** and **1b** with K$^+$[Si(SiMe$_3$)$_3$]$^-$ and characterized by ^{11}B-, ^{1}H- and ^{13}C-NMR spectroscopys. The Correctness of the proposed structures for the compounds **2a** and **2b** were discussed by the comparison of spectroscopic data of **2a** with the reported spectroscopic data and theoretical computations [1,3].



1a **2a**

1b **2b**

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Silica supported polyphosphoric acid (SiO_2 -PPA) Catalyzed three-component Synthesis of 1-(α-aminoalkyl) naphthols

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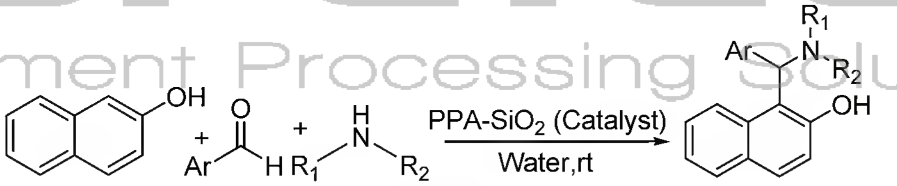
Multi-component reactions (MCRs) have been proven to be a very elegant and rapid way to access complex structures in a single synthetic operation from simple building blocks, and show high atom-economy, high selectivity and procedural simplicity due to the formation of carbon–carbon and carbon–heteroatom bonds in one pot procedure [1].

Compounds bearing 1,3-amino-oxygenated functional groups are ubiquitous to a variety of biologically important natural products and potent drugs including a number of nucleoside antibiotics and HIV protease inhibitors, such as ritonavir and lipinavir [2,3]. Thus, 1-(α-aminoalkyl) naphthols are important and the developing of new MCRs for their synthesis under mild reaction conditions is currently interest. In this research, we report a simple and environmentally benign methodology for the synthesis 1-(α-aminoalkyl) naphthols from the reaction of 2-naphthol, benzaldehydes, and amines in the presence PPA-SiO_2 was carried out in water as green solvent at room temperature (Scheme1).



Scheme1

References:

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Dual activation approach: $CaCl_2$ as a bifunctional and reusable catalyst for the one-pot three component synthesis of 4H-pyran derivatives

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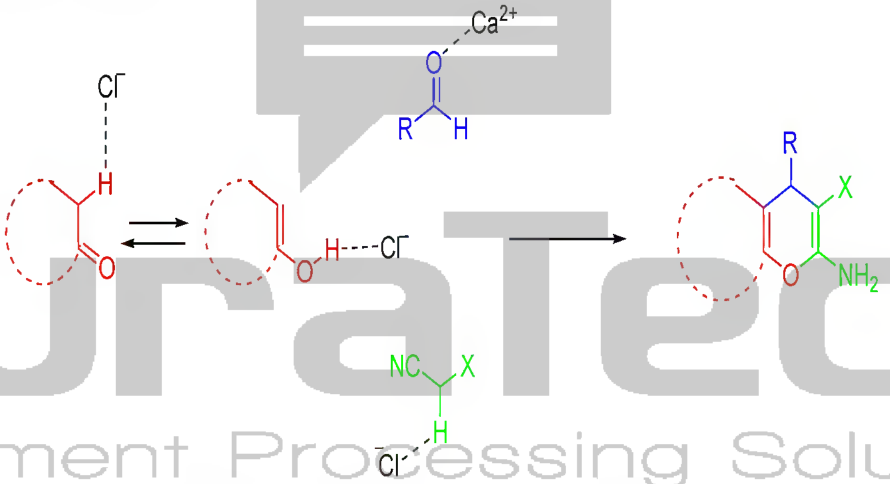
Reactions promoted by Lewis acids and Lewis bases are fundamental in organic synthesis; however, most such reactions are merely stoichiometric. Therefore, the development of catalytic reactions that use Lewis acid and Lewis base catalysts under neutral and mild conditions is particularly important; society needs forward-looking technology, which is based on environmental acceptability. The criteria include atom efficiency, formation of little inorganic waste, and selective synthesis of desired products. $CaCl_2$ is an inexpensive, water stable, environmentally benign and commercially available reagent that is able to act as a Lewis base [1] as well as Lewis acid [2] in organic transformations. A survey of literature shows that the one-pot three component synthesis of 4H-pyrans can be catalyzed successfully in the presence of acid as well as base catalysts. Based on the above facts and as a part of our research program to develop selective, efficient and green methods and catalysts in organic synthesis we report here the application of $CaCl_2$ as an efficient, inexpensive, water-tolerant and bifunctional catalyst for the synthesis of 4H-pyran derivatives. (Scheme 1)



Scheme 1. Bifunctionality of $CaCl_2$ in the synthesis of 4H-pyrans

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An efficient one-pot three-component synthesis of dihydropyrido[2,3-d]pyrimidines

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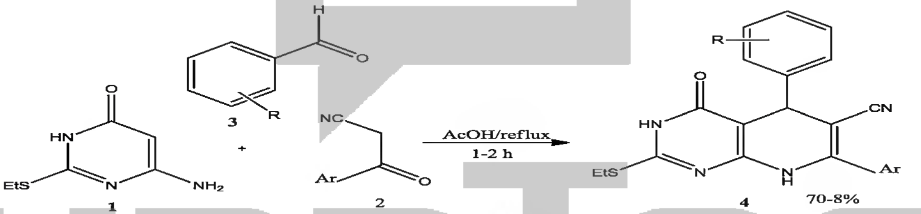
Multicomponent reactions (MCRs), in which several reactions are combined into one synthetic operation, have been used extensively to form carbon-carbon bonds in the synthetic chemistry. Such reactions offer a wide range of possibilities for the efficient construction of highly complex molecules in a single procedure step, thus avoiding the complicated purification operations and allowing savings of both solvents and reagents [1].

On the other hand pyridopyrimidines and their oxo and thioxo derivatives have been recognized as important organic materials in drug design and showing interesting biological activities [2]. In particular pyrido[2,3-d]pyrimidines represent a wide range of biological properties such as antipyretic, antibacterial, antitumoral, antihistaminic and calcium-channel-antagonist activities [2-4].

Based on our continued program in developing biologically important heterocycles [5], we report here a convenient and practical method for the synthesis of new derivatives of pyrido[2,3-d]pyrimidines by the reaction of 6-amino-2-thiouracil **(1)** (1mmol), acylacetonitrile **(2)** (1 mmol) and aromatic aldehydes **(3)** in glacial acetic acid under reflux condition. The reaction furnished the desired products in reasonable reaction times (1-2 h) and high yields (70-80%) (Scheme 1).



Scheme 1

The structures of all products were confirmed by spectroscopic (IR, H NMR, C NMR) methods.

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Micro extraction using hollow fibers for determination of drug in biological samples

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Recently, the new concept of three-phase liquid micro extraction was introduced based on applying two immiscible organic solvents in lumen and wall pores of hollow fiber[1]. In the present work, this novel micro extraction technique combined with high performance liquid chromatography has been developed for determination of Omeprazole. The effect of different parameters, such as effect of hollow fiber length, effect of extraction time , Two immiscible organic phases as organic membrane and acceptor phase,the volume of acceptor phase at optimum conditions and interfering species were investigated. According to optimized conditions for HF-LLLME of Omeprazole was obtained by utilizing a 8cm porous hollow fiber impregnated with n-dodecane, an acceptor solvent of acetonitrile, 28mL donor aqueous solution and extraction time of 60min. The results demonstrated that three-phase hollow fiber micro extraction based on two immiscible solvents is a simple and accurate technique with very good pre concentration factor also served as a technique for sample clean-up[2].

Keywords:
Three -phase hollow fiber micro extraction, immiscible organic solvents, Omeprazole , High performance liquid chromatography ,detection.

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Graphite Oxide: A Efficient Carbocatalyst for Oxidation Reactions

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The oxidation of organic substances has received significant attention as it represents an important functional group transformation, from both fundamental and practical perspectives.[1] Thus far, a wide range of homogeneous transition metal-based catalysts has been developed for this purpose.[2] Carbon-based materials catalyze a variety of reactions in solution.[3] Because of their low cost and wide variety of reasonably well-defined physicochemical properties and morphologies, carbon-based materials are desirable catalytic agents.

In continuation of our investigations herein we report the use of graphite oxide (GO),[4] a readily available and inexpensive material, as a mild and efficient carbon catalyst for the generation of aldehydes or ketones from various alcohols and alkenes under ultrasonic irradiation. GO was demonstrated to catalyze the oxidation of various alcohols and alkenes. These reactions were found to proceed under relatively mild conditions and afforded the desired product (aldehyde or ketone) in good to excellent yields. The present method has many obvious advantages as compared to many previous reports, including the simplicity and the generality of the methodology.

$$\mathrm{ROH} \xrightarrow{\mathrm{GO,\ )))}} \mathrm{RCHO}$$

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A novel and efficient one-pot method for synthesis of 3,4-dihydropyrimidin-2-(1H)-ones by carbon catalyst

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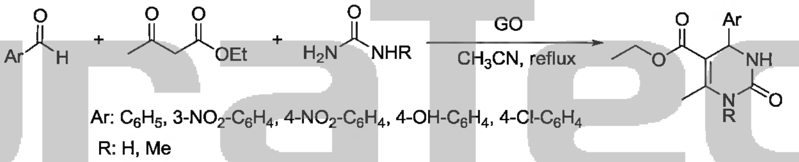
The multicomponent reaction (MCR) was considered as a powerful synthetic tool for preparing target molecules of biological relevance in an efficient manner.[1] The Biginelli reaction, one of the most useful multicomponent reactions, offers an efficient way to access multifunctionalized 3,4-dihydropyrimidin-2-(1H)-ones (DHPMs). Such heterocycles have proved to be efficient calcium channel modulators, mitotic kinesine inhibitors, adrenergic receptor antagonists, antibacterial and antiviral agents.[2]

Carbon-based materials catalyze a variety of reactions in solution.[3] Because of their low cost and wide variety of reasonably well-defined physicochemical properties and morphologies, carbon-based materials are desirable catalytic agents. However, little systematic attention has been given to their use and behavior as catalysts.

In continuation of our investigations on the synthesis of 3,4-dihydropyrimidin,[4] herein we describe a simple and efficient method for three-component cyclocondensation reactions of aldehydes, 1,3-diketones and urea derivative for the synthesis of 3,4-dihydropyrimidin-2-(1H)-ones derivatives using graphite oxide, a readily available and inexpensive material, as a mild and efficient catalyst under mild conditions. This new method has the advantage to give high yields, to be completed in short reaction times and simple product isolation procedure.



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Aza-Michael reaction of 5–Aryl 1–H–tetrazole

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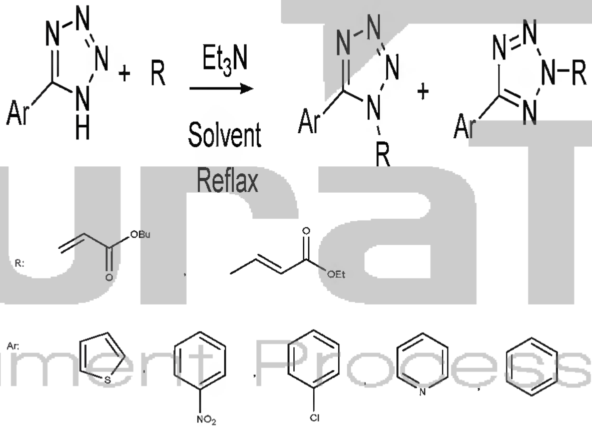
The Michael reaction is one of the most important reactions in organic chemistry. In general, conjugate addition reaction of nucleophiles to unsaturated carbonyl compounds requires basic conditions or acidic catalysts [1]. The Michael addition reaction proceeds even without a catalyst [2]. The addition of nitrogen nucleophilies to α,β-unsaturatedcarbonyl compounds or activated olefins, called aza-Michael reaction [3]. The aza-Michael reaction is an important step in the synthesis of bioactive natural compounds [4]. Most of the aza-Michael organocatalytic reactions are amine catalyzed and proceed via an enamine or iminium intermediate can avoid the possible competition between the nucleophile and the catalyst that can compromise the enantiomeric excess [5]. In the reaction of a series of 5-aryl 1-H--tetrazoles with α,β-unsaturated compounds, a series of alkylated tetrazoles obtained. Because of 1H-2H tautomerism of tetrazoles two alkylated isomers were identified. All prepared compounds characterized using IR, NMR, and MASS spectroscopy methods.



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One-pot multicomponent synthesis of piperidines using formic acide as catalyst

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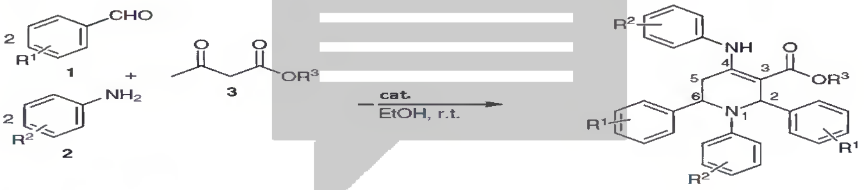
Multicomponent coupling reactions (MCRs) represent a highly valuable synthetic tool for the construction of novel and complex molecular structures with a minimum number of synthetic steps[1] and also offer potential advantages[2]. An essential tetrahydropyridine ring is building block for numerous natural products , synthetic pharmaceuticals and a wide variety of biologically active compounds [3].Among various method for synthesis of this compound MCR is the most efficient one.In this synthesis aromatic aldehydes, acetoacetic esters, and aromatic amines react in the presence of the catalyst . These reactions have improved recently by catalytical methodology [4],[5],[6],[7] and etc… .To extend methodology we use formic acide as catalyst of this reaction and get good result.the advantagouse of this reaction is easy work-up ,good yield ,mild condition and not expensive procedure.



cat=formic acide

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Hydrolysis chemistry of molybdocene dichloride: insights into the reaction mechanism

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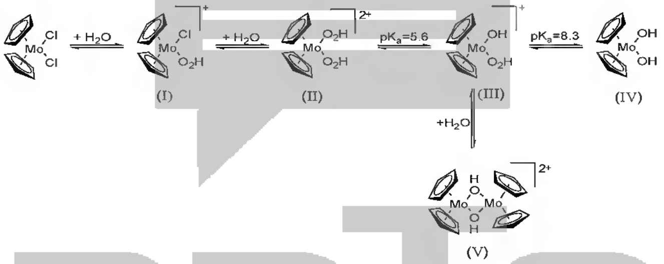
The interest in molybdocene dichloride and related metallocenes has dominated by their remarkable catalytic properties in organic synthesis and as anticancer agents [1]. Testing of a range of metallocene dichlorides identified Cp_2MCl_2 (M=Ti, V, Nb and Mo) as cytotoxic agents with potential as anticancer agents [3]. The hydrolysis chemistry of these compounds is complex, typically involving the formation of a number of dimeric and oligomeric species. The structure of the hydrolysis products is highly dependent on the pH and is often inferred only from titration studies. In most cases, hydrolysis of the coordinated halide or pseudo-halide ligands occurs first and affords aquated metallocene complexes, with OH or OH_2 ligands replacing X .The dissociation rate of the second X^- is dependent of X in Cp_2MoX_2. Taking into account the kinetic parameters and finding the most favorable reaction mechanism, has promoted us to investigate the hydrolysis chemistry of molybdocenes in a detailed theoretical calculation at B3LYP level of theory using aug-cc-pVDZ (cc-pVDZ-pp for Mo) and aug-cc-pVTZ (cc-pVTZ-pp for Mo) basis sets.



Three paths were found in the first and the second hydrolysis step in which, the water molecule attacks to the Mo atom and the chloride atom goes out spontaneously. In summary, the first hydrolysis step exhibits similar geometric features to the second hydrolysis step. Another plausible mechanism in the first and the second hydrolysis steps includes the cleavage of the Mo-Cl bond in the first time and adding of the water molecule to the structure in the next time. This process will repeat for adding of the second water molecules in the second hydrolysis step. The energetic properties, including the relevant thermodynamic quantities and the estimation of the rate constants, were obtained from the computations. Results indicate that S_N1 mechanism is the concerted mechanism of the hydrolysis processes. The computed values of free energy barriers and rate constants (k) in aqueous solution, for the first and second hydrolysis steps, are in excellent agreement with the experimental results under the same conditions.

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Hydrogen-bonding interactions between glycine and nitrosamine: A theoretical study

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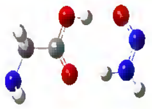
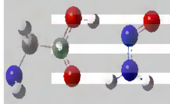
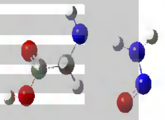
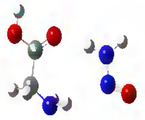
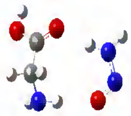
Amino acids are building blocks of proteins (polypeptides), which are the most important class of biological macromolecules. The primary attention has, however, been paid to glycine (Gly) which is the simplest amino acid. Since it represents a small and highly polar organic molecule containing several functional groups, its studies are of fundamental importance for understanding chemical bonding and evaluating links between modern theories and experimental observations [1,2]. Most of nitrosamines are carcinogenic compound and play an important role in the development of tumors and cancer in animals. N-nitrosamines are believed to require metabolic activation to exert their carcinogenic effect [3]. For the study of interactions between glycine and nitrosamine, computations were carried out using B3LYP, B3PW91 and MP2 methods with the 6-311++G (2d,2p) basis set. The counterpoise procedure (CP) was used to correct for basis set superposition error (BSSE) in the calculation of binding energy.

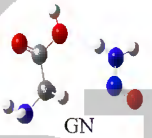

GN1

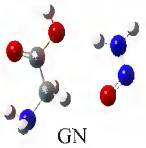

GN2


GN3


GN4


GN5


GN6


GN7

First of all, we considered all sites for interaction between glycine and nitrosamine. We found seven minima structures. All optimized complexes have cyclic structures with two H-bonds involved in the interaction. The GN5 structure is nine membered cyclic complex, GN2, GN3 and GN6 structures are seven membered cyclic complexes and GN1, GN4 and GN7 structures are eight one. The GN1,GN5 and GN7 structures contain two H...O hydrogen bond interactions, while GN2, GN3, GN4 and GN6 structures contains two H-bonds type interactions (O...H and N...H). The electronic binding energies (D_e) range from -50.99 to -12.76 kJ/mol. The relative stability order of the seven complexes is GN1> GN2> GN3> GN4> GN5> GN6> GN7. The structure GN1 is the most stable and cyclic structure GN7 is the less stable.

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Solvent-assisted catalysis mechanism on keto-enol tautomerism of trithiocyanuric acid

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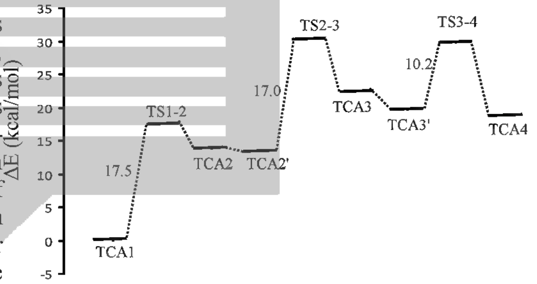
The first theoretical paper showing the catalysis of tautomeric processes by a water molecule published by Lledos and Bertran [1]. Tautomers are structural isomers that are conceptually related by the shift of hydrogen and one or more π bonds [2]. Many biomolecules may exist as a variety of tautomers. Since the energy difference between some of these tautomers is very small, their thermal energy may be easily transformed from one tautomer to another at room temperature. Moreover, for other tautomers with relatively high energy differences, solvent molecules which certainly act as catalysts are used to facilitate the tautomerization process.

In this present work, we will discuss the isomerization reaction process, in which, enthalpies, free energies and reaction rates in each step has been computed. B3LYP/6-311++g(2d,2p) method has been used to study the tautomerization of Trithiocyanuric acid (TCA) both in gas phase and water solution. For tautomerization in gas phase, the reaction path goes through three steps with three transition states. All these transition states contain an S-H-C-N 4-membered ring, in which the S-H-C-N torsion angles are all 0.00°. For tautomerism in H_2O solution, the reaction path also goes through three transition states. All the transition states contain 6-membered ring formed by C-N-H-O-H-S due to the forming of H-bonding complex between Trithiocyanuric acid and the solvent molecule. The presence of the solvent reduces considerably the energy barrier of the reaction. It is clear that methanole is a better catalyst than water. NBO analysis shows that there is a strong interaction between Trithiocyanuric and solvent molecules in transition states. AIM charge analysis indicates that the tautomerism shows a certain degree of proton transfer character. From the reaction enthalpy and reaction rate, tautomerism in water and methanole solvated system is easier than that in gas phase. Results indicate that the tautomerisms are endothermic both in gas phase and in solution.



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Synthesis and characterization of novel amide-benzothiazole copolymers

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Aromatic polyamides are one of the most important classes of high performance polymers, as they possess well mechanical properties, high thermal stability, chemical resistance, and low flammability [1]. Aromatic poly(benzothiazole)s (PBTs) also are a class of heterocyclic polymers that have been well-known for high thermal and thermoxidative stability and also are identified to have high-mechanical properties, and the high degree of molecular stiffness in the backbone [2-4]. Here in two aromatic monomers containing preformed bisbenzoheterocyclic groups connected by a meta and para-phenylene ring was synthesiszed. Then both bisbenzothiazoles were converted to dinitro by usual method using nitric acid and sulfuric acid and reduction of dinitro compounds with Tin(II)chloride in concentrated hydrochloric acid produced in bisaminobenzothiazoles. The structures were confirmed by ^{1}H-NMR, ^{13}C-NMR, FT-IR and also elemental analysis data. Then a series of new amide-benzthiazole copolymers containing meta and para-phenylene rings have been prepared from the reaction of simple terephthaloyl and isophthaloyl chloride, with both aromatic diamines at room temperature by low temperature solution condensation in high yield. Polymers structures were characterized by FT-IR, ^{1}H-NMR and elemental analysis. High molecular weight copolymers were obtained based on intrinsic viscosity and thermal stability of polymers investigated with thermogravimetry analysis (TGA) and diffraction scanning calorimetry (DSC) that showed high thermal stability.

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One-Pot Synthesis of 2,4-Diaminopyrimidine-5-carbonitrile Derivatives Using Sodium Acetate Supported on Alumina as Catalyst

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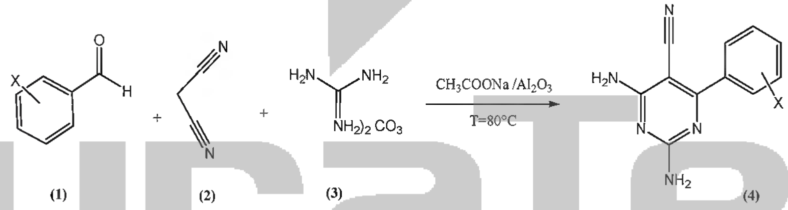
The one-pot condensation of aromatic aldehydes, malononitrile, and guanidine carbonate, in the presence of sodium acetate supported on basic alumina under solvent-free conditions, was reported. Looking for new efficient synthetic procedures toward heterocyclic compounds is one of the most widespread areas of research in organic chemistry. Pyrimidines, as the most important nitrogen-containing heterocyclic compounds, are of chemical and pharmacological interests that often play an essential role in medicinal chemistry. They are core constituents of analgesics, antihypertensives, antipyretics, and anti-inflammatory drugs [1]. They are also used in some pesticides, herbicides, and plant growth regulators [2]. Therefore we were prompted to find an ecofriendly procedure for the direct synthesis of 2,4-diamino pyrimidine-5-carbonitrile derivatives. In comparison to methods employing molecular solvents, the solvent-free approach proceeds more cleanly and provided better yields [3].
Herein, we reported the synthesis of 2,4-diamino-6-arylpyrimidine-5-carbonitrile derivatives **4,** through a one-pot cyclocondensation reaction of aromatic aldehydes **1**, malononitrile **2** and guanidine carbonate **3**, using simple and inexpensive sodium acetate supported on alumina as the catalyst under solvent-free condition (Scheme 1).



Scheme 1

Sodium acetate used in this process has important role in the reaction. First, it releases guanidine carbonate from its salt. Then, as an acidic catalyst, it activates the reactants to react with each other to form the diaminopyrimidine product. Excellent yields of products, simple work-up and performing the reaction under solvent-free conditions are the advantages of the present study.

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Synthesis of novel pyrimido[4,5-b]quinolines using ionic liquid as catalyst

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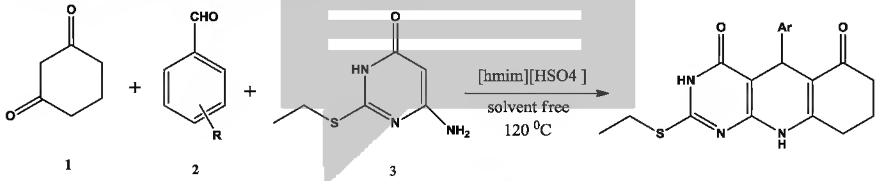
Multi-component reactions (MCRs) by virtue of their convergence, productivity, ease of execution and generally high yields of products have attracted considerable attention from the point of view of combinatorial chemistry [1]. On the other hand pyrimido[4,5-b]quinolines are important compounds because of their biological properties which are known to depend mainly on the nature and position of the substituent [2]. Quinoline derivatives display a broad range of biological activities such as anti-malarial [3], anti-tumor [4] and anti-bacterial [5]. Thus, considerable attention has been focused on the development of new methodologies to synthesize many kinds of pyridoquinoline systems.

Following our continued interests in the synthesis of biologically important heterocycles [6], in this research, we wish to report a very simple and highly efficient one-pot method for the synthesis of novel pyrimido[4,5-b]quinolines via a three-component cyclocondensation of equimolar amounts of 1,3-cyclohexadiene، aromatic aldehydes and 6-amino-2-(ethylthio)pyrimidin-4(3H)-one derivatives in the presence of ionic liquid [hmim][HSO4] (Scheme 1).



Scheme 1

This efficient method furnished the desired products (4) in high yields (75-95%) and short reaction times (10-30 min). High yields and ease of recovery and reusability of ionic liquid with consistent activity, makes this protocol efficient and environmentally benign.

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N-sulfonic acid poly(4-vinylpyridinium) chloride as a efficient solid acid catalyst for the chemoselective N-Boc protection of amines

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Protection of organic functional groups is an important process during multi-step organic synthesis.[1] Among the many protecting groups for amines $(Boc)_2O$ is used with high frequency. Activation is commonly achieved by the use of nucleophilic agents [2] and Lewis acids [3]. Although various N-Boc protection methods are available, most have one or more drawbacks including long reaction times, harsh conditions, harmful organic solvents, and tedious work-up procedures.

In recent years, use of solid acid reagents in organic reactions is attracted the attention of many organic chemists. In continuation of our studies, to protect the functional groups,[4, 5] we decided to use N-sulfonic acid poly(4-vinylpyridinium) chloride [NSPVPC] as a new solid acid reagent for acetylation of alcohols, phenols, amines, and thiols (Scheme 1).

$$R^1R^2NH \xrightarrow[\text{Solvent free, r.t.}]{(Boc)_2O\text{ (1mmol), NSPVPC (5mg)}} R^1R^2NBoc$$

Scheme1.

NSPVPC is superior proton source considering convenience, cost effectiveness and simplicity of their production procedure. Also, they are insoluble in most of the organic solvents and are excellent proton mediated sources for the organic reactions under heterogeneous conditions.

To explore the scope and limitation of the reaction we applied a wide range of substrates. All reaction yields were good to high (80-97%). So, we have developed an efficient method for N-Boc protection of the amines. In contrast to some existing methods using potentially hazardous catalysts/additives, this new method offers the following advantages: (i) low cost, availability and reusability of the reagent, (ii) no side reactions (iii) relatively short reaction times, (iv) easy and clean work-up.

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One-pot synthesis of indol-3-yl(alkanes)benzenamine in the presence of iron oxide nanoparticles

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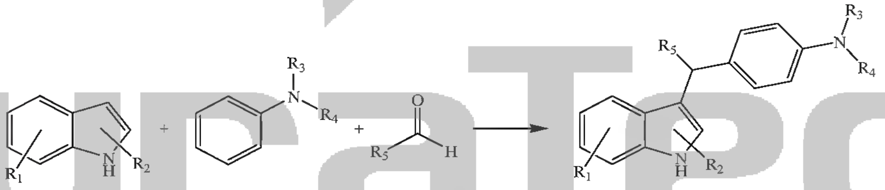
Indoles are important structural units in many natural products and their derivatives are known to possess various biological properties [1], such as, antibacterial, antioxidative, and insecticidal activities, and some indole derivatives have been used as antibiotics in pharmaceuticals [2]. Among indole derivatives, bis-indolyl alkanes, 3-alkyl indoles, and 3-diarylmethyl indoles are important class of bioactive metabolite [3]. Although the synthesis of 3-alkyl indoles has been studied extensively, the synthesis of other unsymmetrical indole derivatives is still highly desirable in synthetic community due to it need more practical procedures and mild reaction conditions[4].The nanocatalysts with high dispersion and narrow size can work under milder conditions with higher activities and selectivities compared with conventional heterogeneous catalysts [5].The magnetic nature of magnetic nanoparticles (MNPs) allows a convenient method for removing and recycling MNPs catalysts by applying an appropriate magnetic field. This kind of separation is not time-consuming and prevents the loss of solid catalyst in the process [6].In this paper, we wish to report one-pot three-component aza-Friedel-Crafts reactions of indoles, aldehydes and tertiary aromatic amines in presence of iron oxide nanoparticles as a magnetic, green and interphase catalyst.



Scheme

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synthesis of tetrahydrobenzo[b]pyran in the presence of succinic acid efficient catalyst in ethanol

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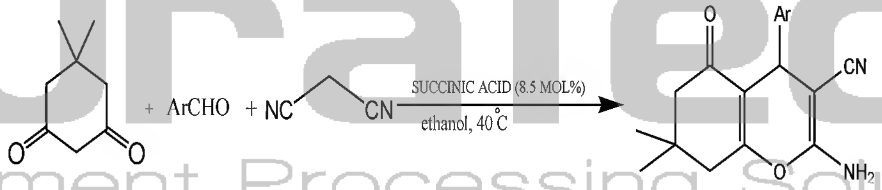
Tetrahydrobenzo[b]pyrans derivatives have attracted strong interest due to their useful biological and pharmacological properties. Several methods have been reported for the synthesis of tetrahydrobenzo[b]pyrans.[1]
In continuation of our research on green chemistry method by succinic acid catalyst and ethanol.an efficient, one-pot three –component tandem knoevengel-cyclocondensation reaction of an aromatic aldehyde, An active methylene compound and dimedone in the presence of catalytic amounts of succinic acid (10 mol%) as a catalyst in ethanol. In these conditions the reaction affords the title compounds in high to excellent yields in short reaction times.[2]



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Fast, efficient and convenient method for the preparation of arylazo sulfones and arylazo sulfides using stable aryl diazonium salts

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Arylazo aryl sulfones (arenediazosulfones) and arylazo sulfides have been studied from their thermal and photochemical [1, 2] behavior as well as their applications in organic synthesis [3]. For example, it is known that the thermolysis of these compounds is an important method for the preparation of arydiazenyl radicals [2]. Moreover, arylazo sulfides are one of the important precursors for $S_{RN}1$ reactions to produce a number of variously functionalized aromatic compounds [4]. Arylazo aryl sulfones are prepared by the reaction of arenediazonium salts with sulfinic acid salts [5] and one of the useful procedures for the preparation of arylazo sulfides is the reaction of aryl diazonium salts with aryl mercaptans [6]. Aryldiazonium salts are useful intermediates in organic synthesis due to their ready availability and high reactivity. These compounds, however, have a serious drawback in their intrinsic instability. Therefore, these salts are usually synthesized at around 10 °C and, to avoid their decomposition, they are handled below 0 °C. Moreover, because of this instability, subsequent reactions with diazonium salts must be carried out under the same conditions.Thus, new diazonium salts with high stability and versatility that can be easily made and stored under solid state conditions with explosion proof properties, are desired and necessary. We report herein an efficient, fast, and convenient procedure for the synthesis of arylazo aryl sulfones using sodium arenesulfinates in the presence of some stable aryldiazonium salts (arenediazonium o-benezenedisulfonimides, aryldiazonium silica sulfates and arenediazonium arylsufonates). Moreover, a number of arylazo sulfides were synthesized by employing these aryl diazonium salts in the presence of sodium thiolates. Unlike the traditional methods, these reactions were carried out at room under solvent-free conditions and there was no need to employ low temperature. The notable advantages of this methodology were operational simplicity, availability of the reactants, short reaction times, high yields and easy work-up.

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Microwave-assisted one-pot synthesis of dibenzo [a,j] xanthenes using phosphorus pentoxide on solid supports

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Phosphorus pentoxide has been frequently used in various types of organic reactions as a dehydration reagent, but it is difficult to handle due to its moisture sensitivity at room temperature. This problem is not solved by replacement of P_2O_5 with polyphosphoric acid (PPA) because this compound is extremely viscous and is almost impossible to stir effectively or use conveniently at temperatures below 60-90 °C. Moreover, it is difficult to handle on a large scale, even at elevated temperatures. Furthermore, some organic compounds are only sparsely soluble in PPA. Finally, hydrolysis of PPA in work-up procedures is always tedious and time-consuming. Recently, the use of P_2O_5 on solid supports has been developed because these reagents are easy to prepare and to handle and can be removed from the reaction mixture by simple filtration [1-2].

It is known that Xanthenes, especially benzoxanthens, are important intermediates in organic synthesis due to their wide range of biological and therapeutic properties [3]. Moreover, these compounds can be used as dyes, pH-sensitive fluorescent materials for visualization of biomolecules and in laser technology [4, 5]. The reported methods for the synthesis of 14-aryl or alkyl-14H-dibenzo [a,j] xanthenes involve the mixing of 2-naphthol with aldehydes in the presence of an acidic catalyst [6]. It is known that changing a support may completely alter the course of reaction or prevent catalysis. Therefore, the careful choice of a support is frequently critical if satisfactory results in a synthetic application are to be achieved. In this work, we studied the synthesis of benzoxanthens using catalytic amounts of phosphorus pentoxide on various supports (SiO_2, acidic alumina, montmorillonite, ZSM-5, and TiO_2). Using this method, different kinds of aromatic and aliphatic aldehydes were reacted with 2-naphtol to produce the corresponding 14-aryl or alkyl-14H-dibenzo [a,j]xanthenes under microwave irradiation. These reactions were carried out under solvent-free conditions in good to high yields. The notable advantages of this methodology were operational simplicity, availability of the reactants, short reaction times, high yields and easy work-up. Moreover, using inexpensive, easily available, non-corrosive and environmentally benign catalysts are the other advantages of the present work.

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Photocatalytic degradation of organic dyes by mixed oxide ZnO-Fe_2O_3

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A mixed semiconductor ZnO-Fe_2O_3 was synthesised using inorganic salts as precursors by sol-gel method. The catalyst ZnO-Fe_2O_3 was synthesized at pH 7 turned out to be superior than sol-gel and commerical ZnO under similar conditions. The powders were characterized by X-ray diffraction, scanning electron microscopy and FTIR spectroscopy [1]. Many research works have focused on mixed oxide semiconductor due to an efficient charge separation can be obtained by coupling two semiconductor particles with different energy levels. The improvement in efficiency of photocatalytic reaction is explained as result of a vectorial transfer of photo-generated electrons and holes from a semiconductor to another [2-7]. The photocatalytic degradation of organic dyes was studied on ZnO-Fe_2O_3 nano particales. The heterogeneous photocatalytic water purification process has gained wide attention due to its effectiveness in degrading and mineralizing the recalcitrant organic compounds as well as possibility of utilizing the solar UV and visible light spectrum [8]. The effects of irradiation time, amount of photocatalyst, oxygen, pH and temperature were examined.

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Synthesis and structural study of a new tetradentate Schiff base ligand derived from 4,5-dimethyl-1,2-phenylenediamine

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The condensation of primary amines with carbonyl compounds yields Schiff base that are still now regarded as one of the most potential group of chelators for facile preparations of metallo-organic hybrid materials [1]. This is due to the fact that Schiff bases offer opportunities for inducing substrate chirality, tuning the metal-centered electronic factor and enhancing the solubility and stability of either homogeneous or heterogeneous catalysts. In comparsion to the Schiff base metal complexes, only a relatively small number of free Schiff base ligands have been characterized [2]. The title Schiff base ligand was synthesized by adding 3-ethoxysalicylaldehyde (2 mmol) to a solution of 4,5-dimethyl-1,2-phenylenediamine (1 mmol) in methanol (10 ml). The mixture was refluxed with stirring for half an hour. The resultant red solution was filtered. Orange single crystals of the title compound were re-crystallized from methanol by slow evaporation of the solvents at room temperature over several days. This ligand was characterized by 1H NMR, IR and its solid state structure was determined using single crystal X-ray diffraction.In conclusion, the molecule of the title compound (Fig 1), crystallizes as an ethanol and water solvate. Strong intramolecular O—H … N hydrogen bonds generate S(6) ring motifs. The crystal structure is stabilized by intermolecular C—H… O and π … π interactions.

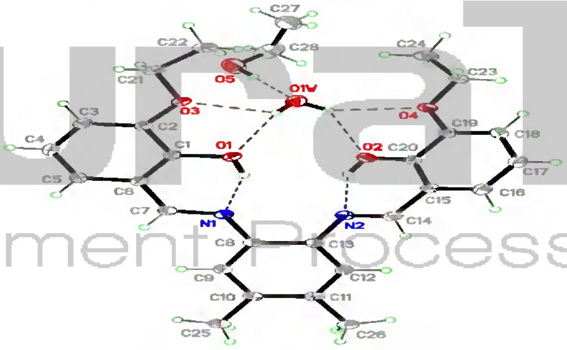

Fig. 1. ORTEP diagram of the ligand with atom numbering and 50% of ellipsoid probability.

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Three-component reaction between triphenylphosphine, dialkyl acetylenedicarboxylates and theophiline

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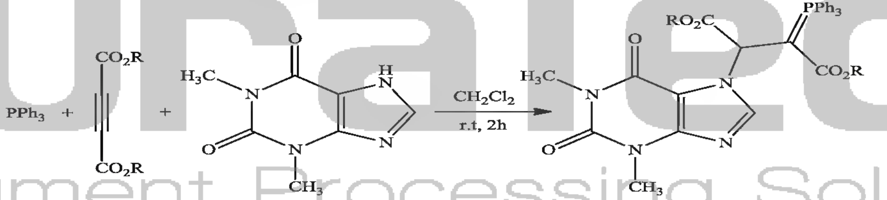
Phosphorus ylides are reactive systems, which take part in many reactions of value in organic synthesis [1]. Several methods have been developed for the preparation of phosphorus ylides. These ylides are usually prepared by treatment of an appropriate phosphonium salt with a base; the corresponding phosphonium salts are usually obtained from the phosphine and an alkyl halide [2]. Phosphonium salts are also prepared by Michael addition of phosphorus nucleophiles to activated olefins. Reaction of acetylenic esters with triphenylphosphine in the presence of an organic compound containing an acidic hydrogen has also been reported to produce phosphorus ylides.In continuation of our works on the reaction between triphenylphosphine and acetylene diesters in the presence of organic N-H, O-H or C-H acids[3], we herein report an efficient synthetic route to stable phosphorus ylides using three-component reaction between dialkyl acetylenedicarboxylates (DAAD's), triphenylphosphine and theophiline.



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The Study of Effect of Nano Basic Alumina as a Catalyst in Preparation of Semicarbazones in Solvent Free Condition

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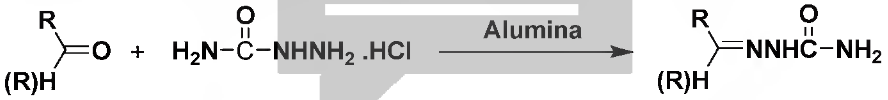
Alumina (Al_2O_3) is a key industrial material with numerous applications in refining and petrochemistry [1]. This metal oxide is widely used industrially as filler, adsorbent, drying agent, catalyst, catalyst support and reagent. γ-Alumina is the transition alumina with a basic property most commonly utilized to carry out surface organic chemistry [2]. On the other hand, Protection of carbonyl compounds as semicarbazones is of great interest to organic chemists as they are readily prepared and highly stable compounds [3]. Semicarbazones are extensively used for purification and characterization of carbonyl compounds. The most common method for the preparation of semicarbazone derivatives is the reaction of aldehydes and ketones with semicarbazide in the presence of base or acid as catalyst.



Very recently Kiasat et al. [4] reported protection of carbonyl groups as semicarbazone using γ-Alumina under solvent free conditions. In this research, we outlined the application of nano basic alumina as a catalyst for protection of carbonyl compounds as semicarbazone. The use of nanobasic alumina (confirmed by TEM) in this transformation, causes increasing yield of reactions (75-90%) and decreasing of time reaction (1.5-3 min.) in contrast with other methods.

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Efficient Solvent-Free Synthesis of Bete Bromo Acetates by $MgBr_2.OEt_2$-Catalyzed Ring-Opening Reaction of Epoxieds with Acetic Anhydride

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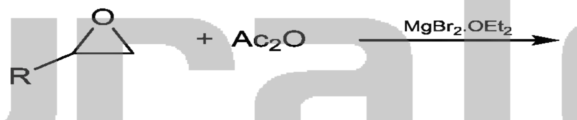
Introduction and Objective: Epoxides have been recognized among the most versatile intermediates in organic synthesis. They can be easily prepared and due to their ring strain, they react with different nucleophiles with high regioselectively, which lead to ring-opened products with various functional groups such as alcohols, diols, aldehydes, alkanes, alkenes and ketones [1-2]. In recent years, magnesium bromide ethyl etherate (MgBr2.OEt2) has found many applications as a mild Lewis acid to ease up various synthetic organic transformations [3]. The MgBr2 reagent, already successfully employed in the opening of epoxy- and aziridinoalcohols and derivatives [4]. In the present article, we introduce a MgBr2.OEt2-Catalyzed ring-opening reaction of epoxides with acetic anhydride nucleophile which leads to a new ring-opened product named Bete Bromo Acetates, have not been reported, in mild and solvent free conditions.

Method and Conclusion: The ring-opening reactions using different epoxieds and acetic anhydride in the presence of equivalent quantities of MgBr2.OEt2 catalyst is carried out which permits rapid and high yield formation of Bete Bromo Acetates derivatives in mild and solvent free conditions. Spectroscopic analysis of the products suggested the formation of the syn/anti mixtures of stereoisomers.



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Efficient synthesis of functionalized 2,4-diaminothiazoles from tetramethylguanidine, isothiocyanates, and α-bromoketones

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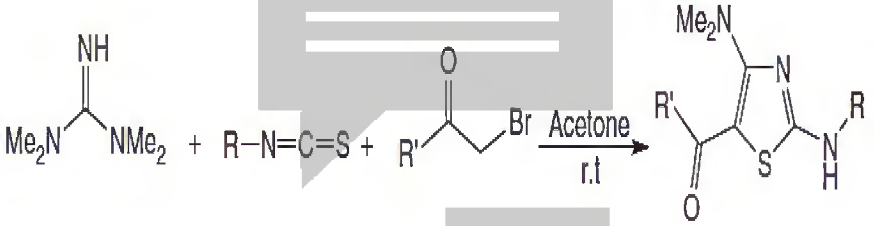
The thiazole ring system is commonly found in many pharmaceutically important molecules. Numerous natural products containing this heterocycle have been isolated and exhibit significant biological activities [1]. Among aromatic heterocycles, thiazoles occupy a prominent position in the drug discovery process [2] and this ring structure is found in several marketed drugs.

Several methods [4, 5] for the synthesis of thiazole derivatives have been developed, amongst which the most widely used method is Hantzsch's synthesis [6-8] (reaction between α-halocarbonyl compounds and thioamides, thioureas, thiocarbamic acids, or dithiocarbamic acids).

Recently, we described the Hantzsch method for thiazole synthesis is via the reaction of α-bromocarbonyl compounds with 2-(amidosulfanylenemethyl)-1,1,3,3-tetramethylguanidines (prepared in situ from tetramethylguanidine and aroylisothiocyanates), to afford functionalized 2,4-diaminothiazoles in good yields.



Conclusions

In conclusion, we have described a convenient route for the synthesis of functionalized 2,4-diaminothiazoles from tetramethylguanidine and isothiocyanates in the presence of α- bromoketones. The advantage of the present procedure is that the reaction is performed under neutral conditions by simple mixing of the starting materials. The procedure described here also provides an efficient one-pot methodology for the preparation of functionalized 2,4-diaminothiazoles.

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Synthesis and study of anthranilated collagen as sunscreen

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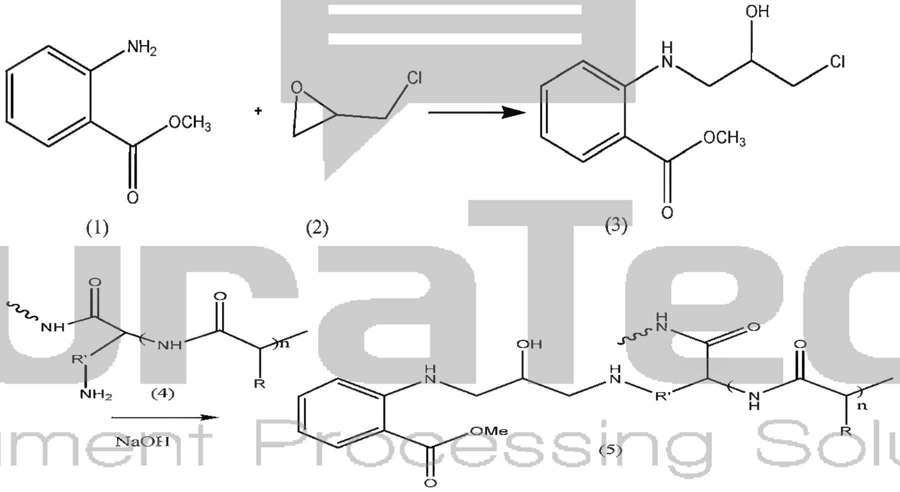
The reaction of methylanthranilate **(1)**, and epichlorohydrin **(2)** led to the synthesis of methyl 2-(3-chloro-2-hydroxypropylamino)benzoate **(3)**. Reaction continued with collagen **(4)** and collagen possessing anthranilate moiety **(5)** was obtained in good yield (Scheme 1). Structures of products were elucidated by IR and NMR spectroscopy.

The efficiency of products was studied by UV-spectroscopy as sunscreen. UV-spectrum of product showed strong and distinct absorption at 354 nm which was a proper evidence to sunscreen ability of product.



(Scheme 1)

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The insitu Copolymerzation of Aniline and o-Toluidine in the presence of Silica Under Solvent-Free Condition

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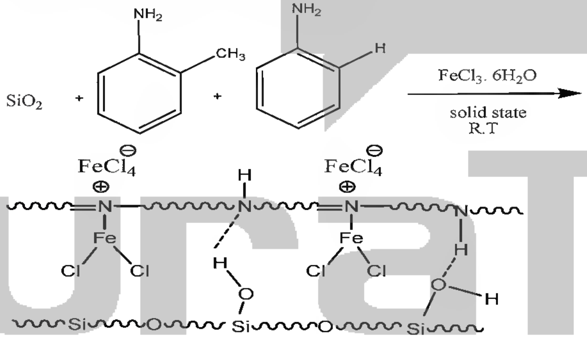
Polymers are generally used as insulators. However, the discovery that the organic polymers can also have conductivities comparable to metals and semiconductors has revolutionized this area of research especially in the electronics industry. The prospective utility of these conducting polymers or synthetic metals in electronic displays, telecommunication, electrochemical storage systems, biosensors and molecular electronics, etc. has further enhanced the interest in this important field [1–3].

In this work, we synthesized new copolymer composites of poly[aniline-co-(2-methyl aniline)] with 1/1 ratio of aniline and 2-methyl aniline on surface of silica and under solid-state condition. $FeCl_3.6H_2O$ was used as oxidant and with different ratios. We illustrated dpoing and oxidation state of these composites and their relationship with amount of oxidant. The FT-IR and UV-vis techniques have been used to investigate the doping process and structural transitions in the composites.



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PEG-SO_3H as a catalyst in tap water: A simple, proficient and green approach for the synthesis of spirocyclic (5,6,7,8-tetrahydro-4H-chromene)- 4,3′-oxindole derivatives

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The use of heterogeneous catalysis is often favoured for many synthetic reactions. The devlopment of heterogeneous methods with an activeacid species can result in improvement in the over all economical efficiency of the process and is usually preferable from an environmental point of view. The use of sulfonic acid immobilized inorganic materials has also attracted attention. The supported acidic PEG catalyst was prepared via anchoring chlorosulfonic acid onto polyethylene glycol by covalent bonds. This polymeric catalyst was used as an efficient bronsted acid catalyst for different organic functional group transformations either as reagent or as catalyst under heterogeneous and homogenous [1].

In recent times organic reactions in aqueous media have received high priority in view of green methodology. The use of water is also preferred due to its abundance, being economical and also due to its highly polar nature. Sometimes it shows higher reactivity and selectivity compared to other conventional organic solvents due to its strong hydrogen bonding ability [2].

The spirooxindole and its analogues are important heterocycles that are present in many naturally occurring alkaloids, biologically active synthetic molecules and organic fine chemicals. Some of them also act as pharmaceutical agents [3]. The development of new synthetic methods for the efficient preparation of heterocycles containing spirooxindole fragment is therefore an interesting challenge.

In this study, PEG-SO_3H as an efficient and reusable acidic catalyst have been used for the preparation of spirocyclic (5,6,7,8-tetrahydro-4H-chromene)- 4,3′-oxindole derivatives, an important class of potentially bioactive compounds, from condensation reaction of malonitrile, isatine and 1,3-dicarbonyl derivatives in aqueous medium. The compounds were isolated by simple filtration in good to high yields (85-98%).

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Aerobic oxidation of alkyl arenes using recyclable cobalt (II) tetrasulfophthalocyanine supported on modified nano silica

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In recent years, a lot of investigations have been done on artificial models of cytochrome p-450 such as phthalocyanines, porphyrins and schiff base complexes as catalyst in the oxidation of hydrocarbons [1].

Exploration of phthalocyanines (MPcs) goes back to almost one century ago; in which they were used as industrial dyes due to their deep blue to green colors [2]. Pcs have some advantages over porphyrins such as more stability and cheapness, therefore the use of these compounds that are able to control active form of O_2 as catalyst in redox reactions can be economical [1]. Pcs have a lot of applications in other technological domains such as: sensors, biosensors, semiconductors, solar cells, optical discs, PDT and etc. In addition, combination of MPcs with nano materials enhances their suitable properties [3-6].

In recent years, by the development of novel and green synthesis methods for preparation of MPcs and MTSPcs, they become noticeable. Microwave-promoted organic reactions are well known as environmentally benign number of chemical processes [7]. For this reason, we synthesized cobalt (II) tetrasulfophthalocyanine (CoTSPc) under solvent free condition using microwave irradiation [5]. For increasing the surface of catalyst, CoTSPc was supported on modified nano silica and in this way a heterogeneous catalyst was prepared and characterized by some techniques such as: FT-IR, SEM and DRS. Thereafter, we used this catalyst for aerobic oxidation of alkyl arenes using a combination of N-hydroxy phthalimide and recyclable cobalt (II) tetrasulfophthalocyanine supported on modified nano silica. Also we investigated the effect of solvent, amount of catalyst and temperature on oxidation times and yields of products.

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Synthesis and Study of the Solvent Effect on Self-Assembly in a Novel Tripeptide Molecule Contained Unusual Amino Acid Using Molecular Dynamics Simulations.

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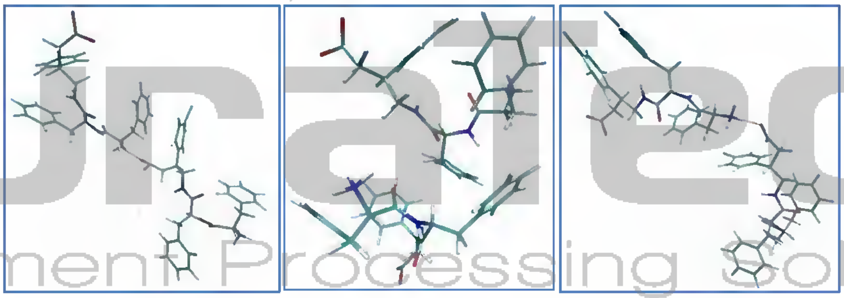
The diphenylalanine dipeptide is a suitable building block for molecular self-assembly. It is well reported that misfolding of the peptidic chain may produce unwanted processes that provoke fatal diseases. One of these problematic processes could be peptide assembly or aggregation. For instance, amyloid proteins may suffer conformational changes during folding processes leading to intermediate misfolded structures that can evolve into amyloid assemblies. These assemblies may precipitate as plaques over important parts of the body such as neural tissues and produce the so called amyloidogenic diseases[**1**]. We were encouraged to synthesis some novel peptides which contained γ- amino acids in their backbones. Gabapentin and baclofen were the best candidates for this approach. Baclofen is a muscle relaxer and an antispastic agent. In this article, we focused on the synthesis of some peptides. Between the synthesized peptides, H-Phe-Phe-Baclofen-OH was selected due to the existence of aromatic moiety in the structure of baclofen which is responsible for self-assembly via π-π stacking.

The realm of applications of computational chemistry is considerably expanding owing to steady advances in computer power. An ab initio quantum mechanical calculation was performed on H-Phe-Phe-Baclofen-OH tripeptide using Gaussian 03 package. The gas phase energy of the tripeptide was optimized at the HF/3-21G level. Molecular Dynamics Simulations were carried out with explicit solvent (water) using Gromacs 4.0.7 package. The details of simulations will be reported. Figure 1 shows screen captures in trajectory of the MD simulation of the tripeptide in bulk solvent. Different possible ways of self-assembly such as H-bonding, π-π stacking and T-Stacking can be seen in this Figure. The details about the self assembly of these compounds will discuss in the conference.



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Reaction of substituted N - (benzamido thiocarbonyl) phenylenediamine with benzaldehyde derivatives

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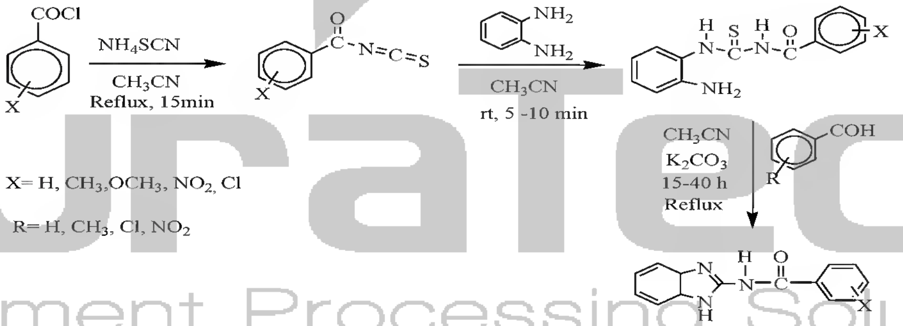
Benzimidazoles are very useful intermediates for the development of molecules of pharmaceutical or biological interest. These compounds are important class of bioactive molecules in field of drugs and pharmaceuticals. Benzimidazole derivativates have found applications in diverse therapeutic areas including anti-ulcers, anti-hypertensives, anti-virals, anti-fungals, anti-cancers, and anti-histaminics[1-4]. In this research, benzoyl isothiocyanates react with o-phenylenediamine to form their monothiourea derivatives. Benzaldehyde derivatives have been utilized as efficient desulfurizing agents for preparation of substituted 2-benzamido benzimidazoles from their corresponding thioureas. These products furnished in high yields at short reaction times.



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Conversion of mono (2-substituted benzamido thiocarbonyl) phenylenediamines to benzimidazoles in the presence of ethyl bromoacetate

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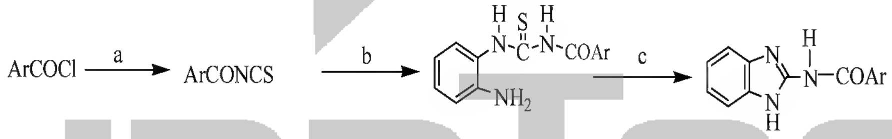
The benzimidazole nucleus is of significant importance to medicinal chemistry. Extensive biochemical and pharmacological studies have confirmed that benzimidazole molecules are effective against various strains of microorganisms. Benzimidazoles are regarded as a promising class of bioactive heterocyclic compounds that exhibit a range of biological activities. This ring system is present in numerous antioxidant, antiparasitic, antihelmintics, antiproliferative, anti-HIV, anticonvulsant, antiinflammatory, antihypertensive, antineoplastic, and antitrichinellosis activities [1-4]. In this research, benzoyl isothiocyanate derivatives react with o-phenylenediamine to form their monothiourea derivatives. An efficient method for the preparation of various substituted 2-benzamido benzimidazoles from their corresponding thioureas has been developed. Desulfurization of thioureas by ethyl bromoacetate furnished substituted 2-benzamido benzimidazoles in high yields and short reaction times.



Ar= Ph, 2-Me-ph, 3-NO_2-Ph, 4-Me-Ph

a) NH_4SCN, CH_3CN, Reflux, 15 min b) o-phenylenediamine, CH_3CN, rt, 5-10 min

c) Ethyl bromoacetate, CH_3CN, K_2CO_3, Reflux, 10-15 h

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Synthesis of 2-substiuted benzimidazoles in the presence of $HgCl_2$

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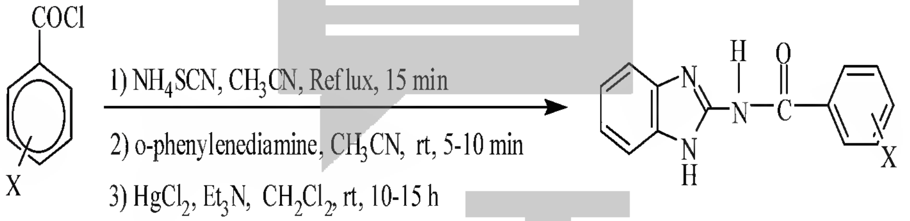
The benzimidazole ring structure is of particular interest especially within the realm of medicinal chemistry. Many of these compounds display a broad range of biological properties including antibacterial, anthelmintic, antiinflammatory, anticancer, and antiviral activity. There is still interest in the synthesis of benzimidazole derivatives for obtaining new biologically active compounds [1-5]. In this approach, benzoyl isothiocyanates react with o-phenylenediamine to form their monothiourea derivatives which on desulfurization with $HgCl_2$ led to the formation of corresponding 2-benzamido benzimidazoles in high yields at short reaction times.



X=H, CH_3,OCH_3, NO_2, Cl

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Synthesis and Characterization of Polymerizable Urethane Acrylic Photoinitiator for UV-Curable Coatings

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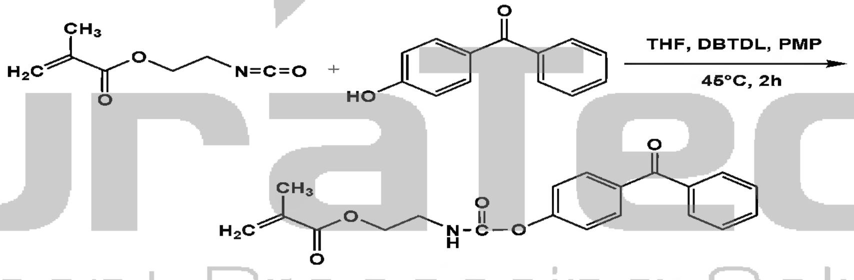
Polymerizable urethane acrylic photoinitiator (PUAP) was synthesized by 2-isocyanato ethylmetacrylate and p-hydroxy benzophenone in present of dibutyltin dilaurate (DBTDL) as catalyst, p-methoxy phenol (PMP) as radical scavenger and tetrahydrofuran (THF) as solvent at 45°C for 2h. PUAP was formulated in epoxy dimethacrylate as binder and N-metyl diethanol amine as co-initiator. Curing time and film properties such as hardness, gloss, impact and adhesion have been evaluated after ultraviolet radiation curing.



Polymerizable Urethane Acrylic Photoinitiator

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One-pot synthesis of pyrimidine-2-thiols in the presence of variety catalysts

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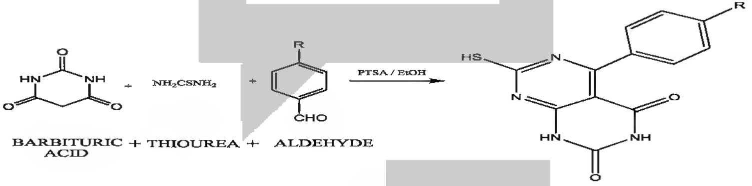
Introduction

The pyrimidine heterocyclic core is an important subunit because of its widespread abundance in the basic structure of numerous natural products [1]. A number of synthetic pharmacophores based upon the pyrimidyl structure exhibit antibacterial, antimicrobial, anticancer, anti-HIV-1 and antirubella virus activities [2]. On the other hand, A-ring heterosteroids are pharmaceutically important compounds due to their inherent biological properties [3, 4].

Results and Discussion

It has been reported that the synthesis of the title compounds requires a multi step process. We have developed a one-pot synthesis of these compounds in good yields when compared to alternative available methods. The condensation of barbituric acid with thiourea and aromatic aldehydes indeed gave corresponding pyrimidine-2-thiols



Conclusion

The IR spectrum of final products showed prominent peaks at 1216 (C–S) and 1619 cm^{-1} (C=N), consistent with the assigned structure. The ^{1}H NMR spectrum of these compounds showed signals at 2.51 (CH_3) 7.3 and 8.05 (aromatic H, J = 8Hz) 8.26 ppm (1H, SH), 11.23 (H-N) and 11.37 (H-N). These observations led us to one-pot synthesizes pyrimidine-2-thiols in very pure condition and excellent yields.

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Ultrasound-Promoted Preparation of Symmetrical Carboxylic Anhydrides Using p-Toluene Sulfonyl Chloride

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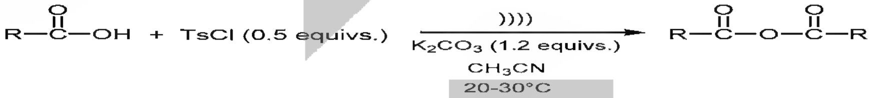
Carboxylic acid anhydrides are well recognized as important class of reagents frequently used for a wide range of organic synthesis. In addition, they act as acylating agent and active intermediate in preparation of other functional groups such as esters, amides and peptides [1]. Considerable efforts have been invested in the development of efficient methods for preparation of carboxylic anhydrides, also among of them preparation of carboxylic anhydrides by use of acid chlorides under ultrasound basic media is reported [2]. But most of these methods have associated problems, including limit their applications, toxicity, high cost, low yield, instability, high reaction temperature, harsh reaction conditions and necessary presence of a phase-transfer catalyst or tedious work-up [3]. Ultrasound-promoted synthesis has attracted much attention during the past few decades. A large number of ultrasonic reactions can be carried out in higher yield, shorter reaction time or milder conditions [4].

As a part of our efforts to developed novel methods for the preparation of carboxylic acid anhydrides [5], in this paper the preparation of symmetrical carboxylic anhydrides using carboxylic acids and p-toluene sulfonyl chloride (TsCl) under ultrasound irradiation is described.



$$R-\overset{O}{\overset{\|}{C}}-OH + TsCl\ (0.5\ equivs.) \xrightarrow[K_2CO_3\ (1.2\ equivs.),\ CH_3CN,\ 20\text{-}30^\circ C]{))))} R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$$

To demonstrate the effect of ultrasound, the synthesis of carboxylic anhydrides were investigated under stirring condition. The results showed that in most cases by using ultrasonic irradiation the rate of reactions related stirring condition is increased and better yield is produced.

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Water-assisted catalysis mechanism on tautomerism of 5-azauracil: A theoretical investigation

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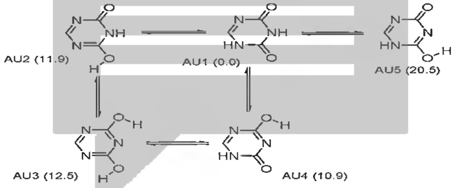
Tautomeric equilibrium in heterocyclic systems has been a significant interest and importance and has been studied theoretically using from semiemperical molecular orbital methods to more sophisticated calculations that may include electron correlation. As one important class of compounds, the effect of solvation on the tautomeric equilibrium of six-membered ring heterocyclic systems has been subject of many studies [1]. In studies of the tautomeric equilibrium in different environment it has been found that the environment is important for the relative stability of various tautomers. tautomeric equilibria in Uracil and its derivatives and those involved in some organic systems, have received all along great attention both from experimental and theoretical study [2].



The study in gas of five tautomers of 5-azauracil as isolated, monohydrated and bihydrated species and of their interconversion processes was performed at B3LYP/6-311++g(2d,2p) level of theory. All transition states were confirmed applying the intrinsic reaction coordinated (IRC) procedure Solvation energies were obtained as single point calculation using the self consistent reaction field polarizable continuum model (SCRF/PCM) procedure. resalts indicate that the tautomerization processes between isolated species cannot occure owing the high energetic barriers characterizing the involved proton shift. Microhydration with one water molecule causes a great number of monohydrated systems and a more pronounced energy separation between some of these with respect to dehydrated tautomers. In the presence of monohydrated species, the complexity of the tautomerization path increases. The activation barrier appears to be reduced by a big amount of energy. A quantity of about 15 kcal/mole is required for each single tautomerization from indication deriving from this study, the number of discrete water molecules to be coordinated to the base in order to have some benefits as far as the rate of tautomerization process is concerned, clearly depend on the structural characteristic of the base and on the type of transformation that occurs.

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Synthesis of Hindered 1,5-Disubstituted Tetrazoles from Secondary Amides in One-Step

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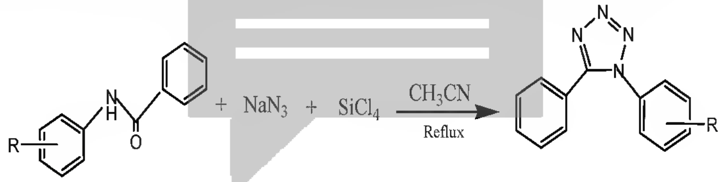
The class of tetrazole compounds has been recently used both as anticancer [1] and antimicrobial [2] agents. They have received increased attention due to their potential biological activity and industrial applications [3,4]. Furthermore, tetrazole fragment is a metabolically stable substitute for carboxy group and amide bond in the molecules of peptidomimetics [5]. The first amino acid derivatives containing a 5-tetrazolyl substituent were described by McManus and Herbst [6]. Later, Zabrocki et al proposed [7] to use tetrazole-1,5- diyl fragment for the synthesis of peptidomimetics with cis-block peptide bond. Growing demands for the tetrazole-containing components of peptides and peptidomimetics aroused extensive studies aimed at developing effective methods for the preparation of amides derivatives having a tetrazole moiety.In this work, hindered 1,5-disubstituted tetrazoles were synthesized by reflux of the mixture of amide, NaN_3 and $SiCl_4$ in CH_3CN. Although, Esikov and co-workers have mentioned that hindered 1,5-disubstituted tetrazoles cannot be synthesized from the aromatic secondary amides [8], but we synthesized the hindered tetrazoles from the secondary amides using the same method successfully. The obtained tetrazoles were characterized by ^{1}H-NMR, ^{13}C-NMR, ^{19}F-NMR, FT-IR and TLC.



R = CF_3, F, Cl

Scheme

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A clean and efficient one-pot three-component synthesis of novel dihydropyrido [2,3-d:6,5-d']dipyrimidines

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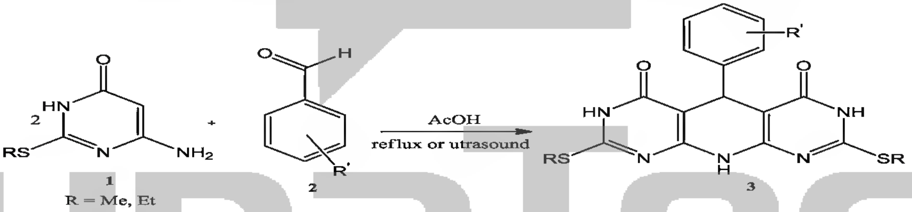
Dihydropyridine derivatives possess a variety of biological activities and drugs such as nifedipine, nicardipine and amalodipine are effective cardiovascular agents for the treatment of hypertension [1-3]. Several fused heterocyclic system incorporating a pyrimidine ring in their structure , play important roles as antihypertensive, antiviral, anti-inflamatory and antioxidant, antipyretic , antibacterial and antitumoral agents [4,5].

On the otherhand 6-Aminouracil and thiouracil derivatives find wide applications as starting materials for the synthesis of fused pyrimidines such as pyridopyrimidines. In continuation of our studies on the synthesis of medicinally important heterocycles [6], herein we report a clean and efficient three-component method for the preparation of novel dihydropyrido[2,3-d:6,5-d']dipyrimidines derivatives. In this protocol the reaction of 6-amino-2-thiouracil (**1**) with various aromatic aldehydes (**2**) in AcOH produced the desired producs (**3**) under both reflux and ultrasound conditions in good to high yields (70-90%) (Scheme 1). The reaction using ultrasonic irradiations gave the products in much higher yields and lower reaction times.



Scheme 1

The structures of all the prtoducts were established by spectroscopic (IR, ^{1}H NMR, ^{13}C NMR) analysis.

At this presentation the various aspects of this efficient method will be fully discussed.

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Amberlyst-15: an efficient and reusable catalyst for the oxidation of alkyl benzenes and alcohols with $NaBrO_3$

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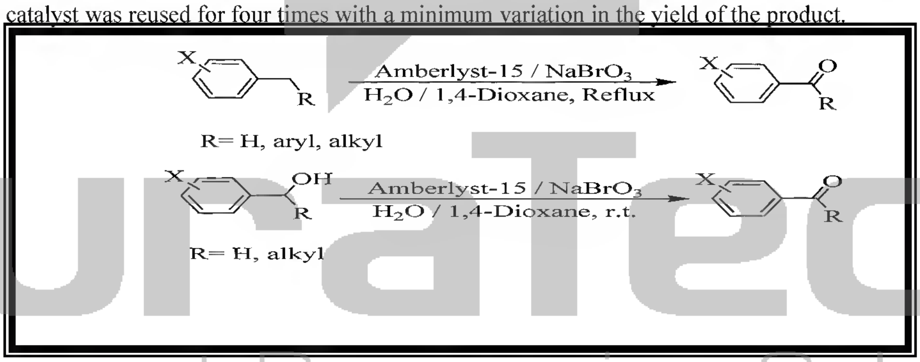
Oxidation of organic compounds is an important process in synthetic organic chemistry [1]. Although many reagents are available for the oxidation of organic substrate, they have certain limitations such as instability, the need of an excess amount of the reagent and poor selectivity to substrates. Therefore there still exists a need for highly efficient and mild oxidizing agents [2]. In recent years solid acidic catalyst has attracted considerable attention. In this regard, amberlyst-15 possesses unique properties to be used as a catalyst for the oxidation of organic compounds [3]. We report an effective procedure for the oxidation of alkyl benzenes and alcohols with Amberlyst-15 as a green and reusable solid acid catalyst and $NaBrO_3$ as an oxidant. A solution of the catalyst, substrate, oxidant and solvent was stirred. Oxidation of alkyl benzenes carried out in reflux condition and oxidation of alcohols carried out at room temperature in aqueous 1,4-Dioxane. The reaction was followed by TLC and GC. After the desire conversion, work-up has been done. The crude was separated on a silica-gel column chromatography. The recyclability of the catalyst was also checked. The recovered catalyst was reused for four times with a minimum variation in the yield of the product.



In conclusion, we have developed an efficient and simple procedure for the oxidation of alkyl benzenes and alcohols to the corresponding carbonyl compounds. The ease of set up and work-up of the reaction, and low cost and commercially availability of the oxidant and catalyst together with the excellent selectivity proposes method to be useful for environmentally safe oxidation of these compounds.

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A Green Protocol for Three-Component Synthesis of α-Aminophosphonates by succinic acid as a good catalyzed

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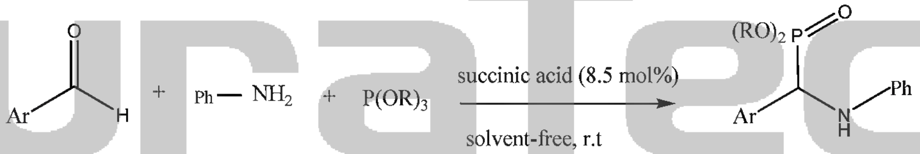
α-Amino phosphonates are of growing importance in biological processes, because they are considered to be structural analogues of the corresponding α-amino acids and transition state mimics of peptide hydrolysis[1]. In these connection, the utilities of α- amino phosphonates as enzyme inhibitors[2], HIV protease[3], anti-therombotic agents, peptid mimics, antibiotics, herbicides, fungicides, and insecticides, as well as important role for antibody generation are well documented[4].

A simple, efficient, and general method has been developed for the one-pot, three-component synthesis of α-aminophosphonates from a condensation reaction of trialkyl phosphite, aldehydes, and amines in the presence of catalytic amount of succinic acid (8.5 mol%) under solvent-free conditions.The advantages of this protocol are excellent yields,short reaction time,mild reaction conditions,more readily available ,inexpensive, more environmentally friendly, and simple work-up procedure. The structures of compounds were deduced from their m.p, IR and ^{1}H NMR spectra.



R=Me or Et

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One-pot multicomponent synthesis of highly substituted piperidines using tartaric acid as catalyst

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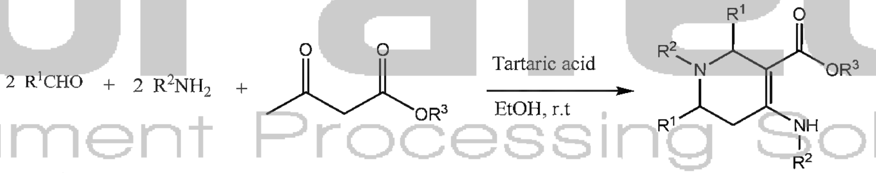
The piperidine ring is common in a number of biologically important natural products[1]. There are thousands of literature references, including patents, which utilize such compounds in medicinal research[2]. Of these, 1,4 disubstituted piperidine scaffolds are of particular importance, some as established drugs, and some bearing tetrahydropyridine (THP) frameworks (also convertible to the corresponding piperidines) are important in antiparasitic, antiviral, anticancer, antimicrobial, and antimalarial research as well as other fields[3].

Tartaric acid is a highly effective and efficient catalyst for the one-pot multicomponent condensation reaction of β-keto ester, two equivalents of aromatic aldehyde, and two equivalents of amine in EtOH at room temperature to give highly functionalized piperidines in high yields. This one-pot reaction has some important advantages such as the easy workup procedure, simple and readily available precursors, nontoxic and inexpensive catalyst, environmentally benign, and good to high yields.

The structures of compounds were deduced from their m.p, IR and ^{1}H NMR spectra.



R^1, R^2: ph, 4-Me-C_6H_4, 4-NO_2-C_6H_4, 4-F-C_6H_4, 4-OMe-C_6H_4
R^3: Me, Et

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Synthesis of α-Bromo ketones with the new, mild and efficient agent: DBU-hydro bromide-per bromide(DHPB)

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Halogenetad compound are widly used in chemistry synthesis, therfore synthesis of this compund is very important in chemistry.in this work we want to show DBU-hydro bromide-per bromide(DHPB)[1],[2],[3] as a stable, crystalline organic ammonium tribromides (OATBs) can be utilized as a new and efficient reagent for the synthesis of α-Bromo ketones. this new and mutiperpose reagent is very easy to prepare and can be use in room temprature.
The proposed mechanism for this new method of α-bromo ketones is depicted in figure 1.

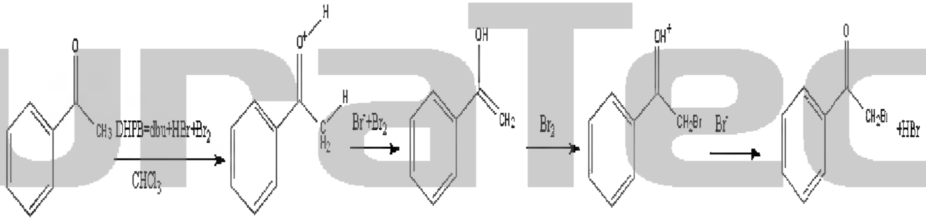

Figure 1

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Efficient synthesis of novel 9H-xanthen-9-yl derivatives by $Fe(HSO_4)_3$ as a heterogeneous acid catalyst

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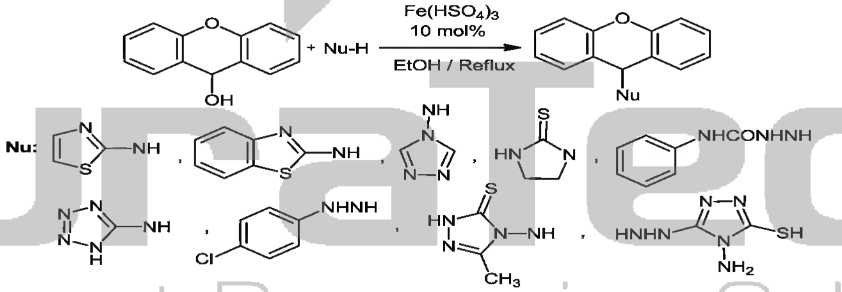
9H-Xanthen-9-ol falls in the group of non-specific reagents since it reacts with various natural products, urea, amino acids, ribonuclease and cytochrome [1]. The reactions of 9H-xanthen-9-ol with nucleophilic reagents such as thiol, imide, indoles, and thiophene promoted by acids or $BF_3.Et_2O$ have been reported [2-5]. We have previously reported that $Fe(HSO_4)_3$ as an efficient and recyclable catalyst for the one-pot synthesis of 14-aryl- or alkyl-14H dibenzo[a,j]xanthene derivatives by the reaction of 2-naphtol and aldehydes [6]. We have demonstrated the direct substitution of 9H-xanthen-9-ol with different nucleophilic reagents by ferric hydrogensulfate as a heterogeneous acid catalyst through S_N1 type reaction in high yields. The products were obtained in high yield in short reaction times, the reactions complete within 0.5-2 h with high regioselectively. These high nucleophilic selectivities are due to stability of pyrylium cation and strength of new C-N bond formation. The simplicity, together with the use of inexpensive, non-toxic, recyclable and environmentally benign nature of catalyst, are other remarkable features of the procedure.



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DBU as an efficient catalyst for one-pot, novel three component of Synthesis of hydroxyl naphthalene-1, 4-dione derivatives

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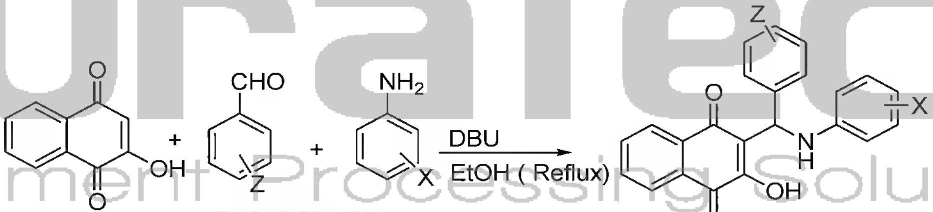
ABSTRACT

Molecules with the quinone structure constitute one of the most interesting classes of compounds in organic chemistry, due to their biological properties such as antitumor, molluscicidal, leischmanicidal,anti-inflammatory, and antifungal activities [1].herein, we use 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) as efficient organic base for synthesis of 2-hydroxy-3-[aryl (arylamino)methyl]naphthalene-1,4- drones. DBU have been used as catalyst for several reactions [2]. We are currently investigating the synthesis of hydroxyl naphthalene-1,4-dione derivatives via a facile, atom economical, and three-component condensation reaction of 2-hydroxynaphthalene- 1,4-dione , aromatic aldehydes, and anilines derivatives in the presence of a catalytic amount of DBU in refluxing ethanol .



Z=Cl,OCH_3,CN,
X=Cl,CH_3,OCH_3

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2-Hydroxy ethyl ammonium format as an efficient ionic liquid for as an efficient ionic liquid for efficient one-pot synthesis of ß-hydroxyphosphonates

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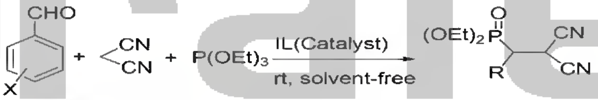
A mongst phosphonates, β-hydroxyphosphonates are an important class of compounds. They exhibit a variety of interesting and useful properties that make them attractive as herbicides, pesticides, antioxidants and horticulture agents. [1]

As we know, inorganic acids can cause equipment corrosion and bring serious environmental pollution. Solid acids have the disadvantages of less active site, requiring extended reaction time, having low thermal stability and rapid deactivation from coking. Bioenzymes are generally expensive for commercial use and difficult to recycle without activity. As an alternative, Brönsted acidic ionic liquid (IL) is becoming a popular choice of both solvent and catalyst for the Fischer esterification's and the other acidic catalyzed reactions [2]. This is because the Brönsted acidic ionic liquids have many unique properties including tunable acidity from different acid functional groups, low melting point, negligible vapor pressure, good solubility for most organic and inorganic compounds, and high thermal stability [3].



X=Br,Cl,OCH3

IL=[HO-CH2-CH2-NH3]⊕[HCO2]⊖

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Four-component synthesis of 1, 4-dihydropyrano [2, 3-c]pyrazoles using cellulose and starch sulfate as biodegradable and reusable catalysts

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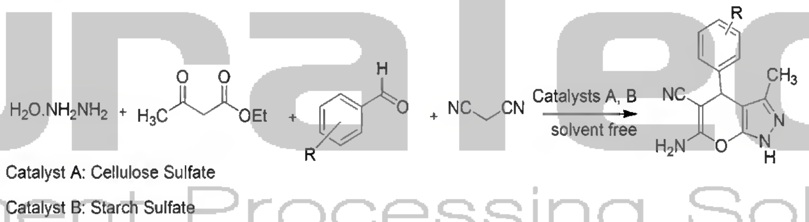
Heterogeneous solid acid catalysts for the synthesis of fine chemicals have attracted considerable attention from both environmental and economical points. The solid acids generally have high turnover numbers so that heterogeneous catalysts can be easily separated from reaction mixtures [1].In continuation of our research on the solid heterogeneous acidic catalysts [2], we herein report a practical method for the synthesis of 1,4-dihydropyrano[2,3-c]pyrazoles by employing four-component reactions of hydrazine hydrate, ethyl acetoacetate acetoacetate, aryl aldehyde and malononitrile under thermal solvent-free conditions in the presence of cellulose and starch sulfate (Scheme 1).



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Synthesis and characterization of aqueous anionic polyurethane dispersions based on polyether polyols

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A series of aqueous polyurethane dispersions were synthesized by the reaction of polytetramethylene glycol (PTMG) and isophorone diisocyanate (IPDI) and then extended with diol chian extender dimethylol propionic acid [1-2]. In order to synthesis aqueous polyurethane dispersions, polytetramethylene glycol was charged into the reactor under N_2 atmosphere and mechanical stirring. IPDI was added dropwise to polyol and the temperature was increased to 100°C until the prepolymer with NCO terminated groups was obtained. Then a proper amount of Dimethylol propionic acid (DMPA) was dissolved in N-Methylpyrrolidone to obtain a clear solution. As the next step, prepared solution of DMPA was added into the reactor. After that, in order to neutralize of carboxylic acid groups of DMPA, TEA base was added into the mentioned system and the temperature was decreased. Finally to create a stable emulsion of polyurethane, the required amount of deionized water was added dropwise to obtain aqueous dispersions PUs with 30 wt % solid content. Chemical structure of synthesized polyurethanes was characterized using FTIR, ^{1}HNMR, and ^{13}CNMR spectroscopy methods. FTIR spectrum of polyurethane extended by dimethylol propionic acid performed to verify the disappearance of the NCO at 2265 cm^{-1}[3]. Prepared polyurethanes were characterized with stretching vibrations N−H at 3322 cm^{-1}, C=O at 1713 cm^{-1} and NH for Amide II band at 1537 cm^{-1} by FTIR spectroscopy. Weak peaks in ^{1}HNMR which were appeared at 6.88–7.09 ppm, were attributed to cis and trans conformers of urethane NH groups that proved the urethane groups of prepared polyurethane. ^{13}C NMR spectrum of prepared samples with peaks at 156–158 ppm which related to carbonyl groups of urethane bonds, proved the formation of polyurethane polymer structure.

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Synthesis and characterization of terminally functionalized and epoxidized hydroxyl-terminated polybutadiene

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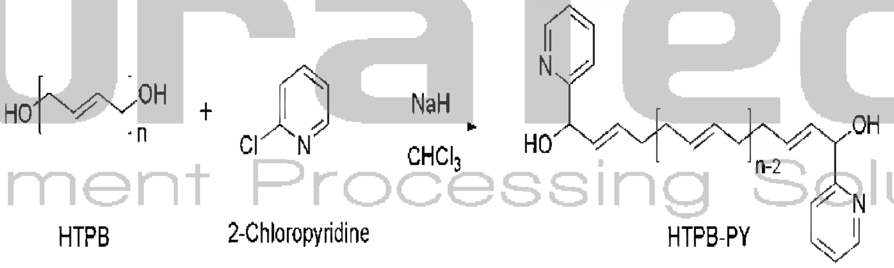
The study of terminal-functionalized polymers, where a polar or ionic functional group is attached to a non-polar polymer chain, has recently gained much interest thanks to their unique properties in solutions, bulks, and solid–solution interfaces [1, 2].This paper aimed at functionalization of hydroxyl-terminated polybutadiene (HTPB) by covalently attaching 2-chloropyridine to the terminal carbon atoms of the polymer. The product (HTPB-PY) was then converted to Pyridyl N-oxide (HTPB-PY-NO) using in situ-generated dimethyl dioxirane (DMD). In situ-generated DMDs are powerful, reactive, and efficient cyclic peroxides, usually obtained from the reaction between acetone and aqueous Oxone® ($2KHSO_5$, $KHSO_4$, K_2SO_4) in buffered conditions [3]. The data from characterizing the products by ^{1}HNMR, ^{13}CNMR, ^{14}N-NMR, and FT-IR techniques demonstrated the covalent attachment and the formation of HTPB-PY-NO. The spectral data also revealed that the terminal hydroxyls of the polymer were preserved in both processes without using any conditional controls. This modification, while not changing the unique properties of HTPB, resulted in the structural diversity of the polymer and enhanced its physical and chemical properties. HTPB-PY-NO can be considered a new generation of modified polymers with special capabilities.



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Synthesis of New Additive for Polymeric membranes based on Nanosupramolecule particles

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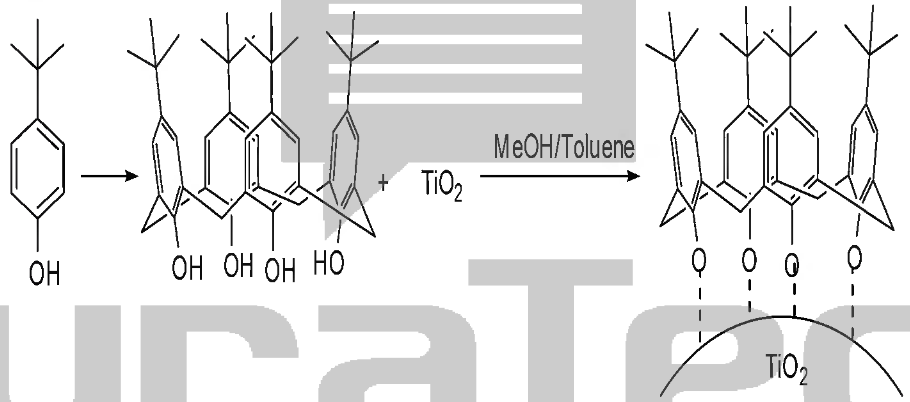
Polymeric membranes, because of the new application on selective separation of industrial gas mixture, have a great attraction [1]. According to the literature, using of the additive on the structure of polymeric membrane can raise the selectivity and efficiency. In this work, we have synthesized a new hybrid compounds such as nano supramolecular compounds as a new additives for polymeric membrane.

For this aim, at fist we have prepared the supramolecule via the following reactions (Scheme 1).



After the synthesis of supramolecules, these have been coated on the surface of various nanoparticles [2-3]. For preparation of new polymeric membrane, we have used different additives on various weight percent. We hope that, the new modified membrane could be separate the industrial gas mixture very impact.

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Synthesis Nano silver soap in industrials

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Laboratory responsible, Technical director, Directing Manager of Gol Narges Company

Abstract:

Nanoparticles show novel physicochemical properties compared with larger size particles of the same substance such as greater surface area, greater chemical and biological reactivity and bio availability [1]. Recently another property of silver, known for a long time, has gained interest: the property of killing microorganisms [2]. The release of silver ions from different silver compounds can cause damage to fungi, algae, bacteria and viruses. Therefore it is favored in cosmetic products. In this abstract, for the first time in Iran and after a long term study, R & D experts of GoleNarges Company succeed in producing nano silver soaps.

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Design and Control of n-Butyl Acrylate Reactive Distillation Column System in Pilot Plant Scale

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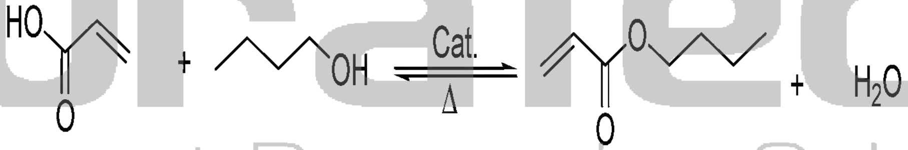
Reactive distillation has demonstrated its potential for capital productivity improvements, selectivity improvement, reduced energy use and the reduction or elimination of solvents in the process. Esterification process is utilized in a wide range of organic chemical industries. Esters of acrylic acid with various alcohol components such as methanol, ethanol, butanol, 2-ethylhexanol, etc. are commercially important as different monomers for typs of polymerization processes.[1] Butyl acrylate is widely used in industry as a precursor for varnishes, paints, adhesives, finishes of papers, fibers, rubbers, electronic and optical materials. Various production processes include esterifying acrylic acid with *n*-butanol in liquid phase in adjacent with acid catalyst conditions reported. They are include several reaction columns and drying columns.[2] Self polymerization of acrylic acid and *n*-butyl acrylate was one of the most important problems ahead during production. In this study some of polymerization inhibitors through gelation test were investigated. Also an improved method is chosen for production of *n*-butyl acrylate using batch esterification techniques that can be economically justified for use in downstream petrochemical industries. We have designed a special column for drying and purifying of *n*-butyl acrylate after first reaction column. Purity and concentration of product measured with Gas Chromatography and Refractometery Spectroscopy and set at its optimal value.



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Green and efficient oxidation of alcohols catalyzed by Mn(II) salen complexes immobilized on celloluse in ambient condition

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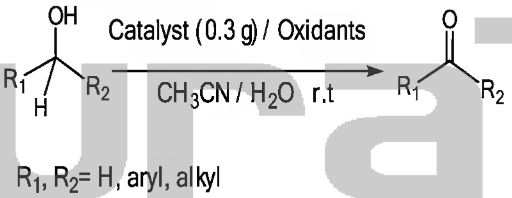
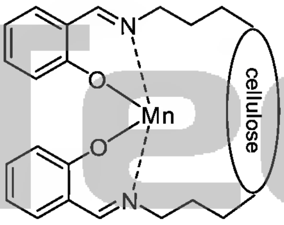
The oxidation of alcohols is currently a significant issue in many important fields such as organic synthesis, hydrogen storage/release, and transformation of renewable biomass resources. For this purpose, manganese complexes of the Schiff base (Salen complexes) have long been used as efficient homogeneous catalysts in asymmetric catalytic reactions due to their high oxidation ability [1].

The preparation of new heterogeneous catalysts by immobilizing catalytically active metal Salen complexes on an insoluble polymer support, porous materials such as zeolites, MCM-41 and analogous materials or intercalation in clays has received a lot of attention [2]. Development of new strategies for the recovery and recycling of catalysts, which minimizes the consumption of auxiliary substances, energy and time used in achieving separations, can result in significant economical and environmental benefits [3].

In this work, new active and stable immobilized salen complexe catalysed oxidation reaction of alcohols with various oxidants can be performed under ambient condition in acetonitrile water providing the corresponding products in moderate to high yields (60-85%).Using environmentally friendly bio-supported proton source catalyst and easy work up procedure are the other merits of our method.





Catalyst

Reference

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Applications of a monomeric orthopalladate complex containing mixed phosphorus–nitrogen donors in the Suzuki–Miyaura cross coupling reaction

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Transition metal-catalyzed cross-coupling reactions are one of the most important processes in modern organic synthesis for the formation of carbon-carbon and carbon-heteroatom bond [1].

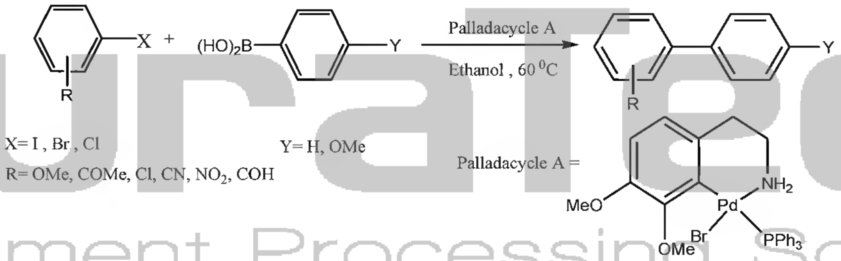
Organopalladium compounds play an important role in homogeneous catalysis due to their versatility and nontoxicity.

There are various cross coupling reactions and among them the Suzuki–Miyaura cross-coupling of aryl halides with aryl boronic acids is one of the most useful method for synthesis of biaryl and hetero biaryl derivatives [2]. Biaryls are applied as the building block of a wide range of herbicides, conducting polymers, and liquid crystal materials [3].

In continuation of our investigations on the synthesis and applications of palladacycles in Heck reactions,[4] and cyanation reactions,[5] we report herein the synthesis of the monomeric orthopalladate complex $[Pd\{C_6H_2(CH_2CH_2NH_2)\text{-}(OMe)_2,3,4\}Br(PPh_3)]$. The activity of this complex was investigated in the Suzuki–Miyaura C–C cross-coupling and compared with a dimeric $[Pd\{C_6H_2(CH_2CH_2NH_2)\text{-}(OMe)_2,3,4\}(l\text{-}Br)]_2$ palladacycle. The monomeric complex contains mixed phosphorus–nitrogen (P–N) donors and was found to be more active in Suzuki-Miyaura cross coupling reactions than the dimer, which contains only a single nitrogen donor.

This complex had been demonstrated as an active, efficient, stable and non-sensitive to oxygen and moisture catalyst for the Suzuki-Miyaura cross coupling reaction of various aryl halides with aryl boronic acids in Ethanol as solvent and K_2CO_3 as base at 60 °C.

This catalytic system promoted the desired coupling products in moderate to excellent yields and short reaction times(scheme 1).



Scheme 1

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An Efficient Dimeric Ortho-Palladated Complex of 2-Methoxyphenethylamine for Suzuki-Miyaura Cross-Coupling Reaction under Microwave Irradiation and Conventional Heating

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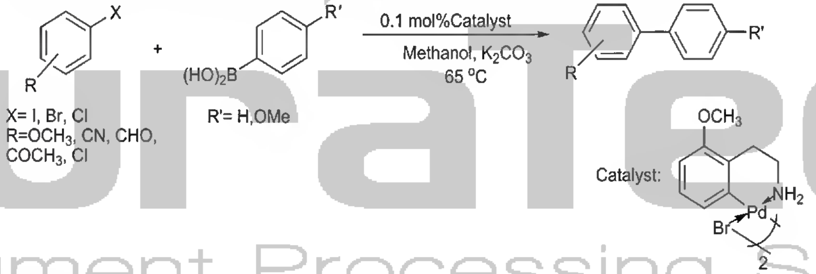
The Suzuki–Miyaura cross coupling reaction between organoboronic acids and organic halides or triflates is one of the most extensively used protocols for the synthesis of biphenyls due to the good tolerance of various functional groups [1,2]. In the last decade, the rapid growth studies in this field is mainly due to excellent tolerance of various functional groups, low toxicity and high stability of organoboranes towards air and moisture along with wide applications of Suzuki products in the synthesis of various useful intermediates such as natural products, pharmaceutical intermediates and agriculture (pesticides and herbicides) [3-5].

In this study, Suzuki cross-coupling reaction was successfully carried out in methanol utilizing an *ortho*-palladated complex of 2-methoxyphenethylamine. High isolated yields to biaryls were obtained using different aryl halides, and arylboronic acids with a small loading of the palladium catalyst. Reactions were performed with both electron donating and electron withdrawing groups and results clearly showed that there is not any sensitivity to substituents on the aryl ring. Application of this catalytic system under obtained optimized reaction conditions caused to produce the desired coupling products and application of microwave irradiation improved the yields of the reactions and reduced the reaction times compared to traditional heating conditions. The $[Pd\{C_6H_3(CH_2CH_2NH_2)\text{-}4\text{-}OMe\text{-}5\text{-}\kappa^2\text{-}C,N\}(\mu\text{-}Br)]_2$ complex of 2-methoxyphenethylamine exhibited very good activity in the Suzuki reaction of aryl iodides and bromides and was partly less reactive in aryl chlorides. This catalyst was stable under this couling conditions without using inert atmosphere due to its inherent air and moisture resistances.



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Application of Novel Dimeric Ortho-palladated Complex of Tryptamine in the Heck Coupling Reaction

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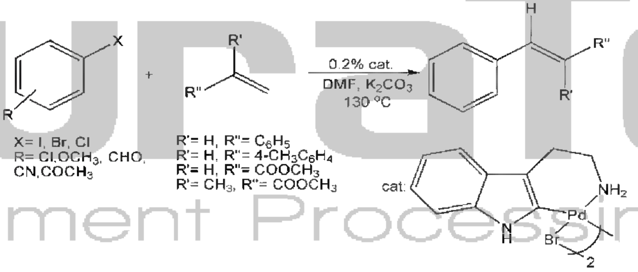
The Heck coupling reaction is one of the most powerful tools in synthetic chemistry for constructing aromatic carbon–carbon bonds between complex organic molecules with potential industrial or pharmaceutical applications [1,2]. Various forms of palladium have been reported to be useful catalysts or precatalysts [3]. Palladacycles emerging as a new family of palladium catalysts have been widely used in the Heck reaction because of their facile synthesis, thermal stability, and structural versatility [4,5].

The $[Pd_2\{(\kappa^2\text{-}C,N\text{-}C_8H_5NCH_2CH_2NH_2\text{-}2)_2\}(\mu\text{-}Br)_2]$ complex of tryptamine was synthesized and successfully applied to the Heck reaction of various aryl halides with olefins The effects of various parameters such as solvent, base, and amount of catalyst were studied. The reaction is suitable for a wide variety of substituted aryl iodides, bromides and even chlorides with different electronic properties. This complex converted different aryl bromides and iodides to the corresponding products in high yields and short reaction times, but aryl chlorides were changed to products with moderate yields in *N,N*-dimethylformamide (DMF) at 130 °C. Based on the results, production of exclusively the *trans* isomers by this method is great advantage of the presented catalyst. Other advantages of this catalyst are its easy preparation, handling, stability, and moisture insensitivity.

In this study, Hg poisoning experiments proposed that the Heck reaction catalyzed by this complex proceeded through a classical Pd(0)/Pd(II) cycle and such palladacycle was only a reservoir of the catalytically active Pd(0) species.



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Microwave Promoted Hiyama Coupling Reaction using Arylphosphite Ligand Contain Imino Functional Groups

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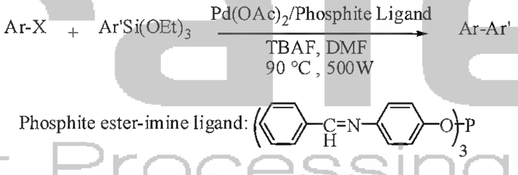
Palladium catalyzed-transformations are among the most potent and convenient tools of modern organic synthesis for C-C bond formation [1]. There are various cross coupling reactions and among them the Hiyama coupling reactions using organosilicon reagents have been developed and utilized as a synthetic method for the production of biaryl compounds [2-3]. Biaryls are as the building block of a wide range of pharmaceuticals, natural products, herbicides, and liquid crystal materials [4]. The key benefits of the Hiyama coupling reactions are the mild reaction conditions, commercial availability, low cost, very easily preparation of nontoxic organosilicon reagents, and the stability of them to other functionalities and to the reaction conditions [5]. The Hiyama cross coupling reactions usually are mediated by a palladium–phosphine complex as a catalyst. Most research has developed to obtain high catalytic activity with efficient ligands. Generally, sterically bulky and electron-rich alkyl and aryl phosphine ligands showed high activities in the cross-coupling reactions [6]. In contrast to the phosphine ligands, sterically hindered phosphite ligands are less expensive and more stable to air and moisture.

In continuation of our recent investigations on the synthesis of the palladium catalysts and application of these complexes in cross coupling reactions [7], herein an efficient, stable and non-sensitive to air and moisture catalytic system based on palladium-Schiff base tri-ester phosphate [8] is described for the Hiyama reaction of various aryl halides with triethoxysilylbenzene under microwave irradiation. The products were produced in excellent yields and short reaction times using palladium acetate-tris(parabenzylidine amino phenyl) phosphite with 1:2 ratios in DMF at 90 °C and 500 W. (Scheme 1).



Scheme 1. The cross-coupling reaction of triethoxysilylbenzene with aryl halides

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$(BeDABCO)PdCl_3$ as a highly active catalyst for the microwave-assisted Stille cross coupling reaction

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The palladium-catalyzed cross-coupling of nucleophilic organostannanes with electrophilic organic halides and triflates, known as Stille reaction has emerged as a powerful and versatile tool for the formation of C-C coupling reactions in the construction of new materials [1-2]. This cross coupling reaction has gained importance due to the growing availability of the organostannanes, their stability to moisture and air that leads to convenience in purification and storage of these reagents, and excellent compatibility with a large variety of functional groups thereby eliminating of the protection and then deprotection strategies which are a necessity with most organometallic reactions [3-4]. The Stille coupling is a powerful route to the formation of biaryls as building block of a wide range of pharmaceuticals, natural and bioactive products, conducting polymers, and liquid crystal materials. In view of the importance of biaryls, a number of effective palladium catalytic systems have been developed for the Stille cross coupling reaction. In continuation of our recent investigations on the synthesis of the palladium catalysts and application of these complexes in the microwave assisted cross coupling reactions [5-6], we now wish to report the extension of $(BeDABCO)PdCl_3$ homogeneous complex for the cross-coupling reaction of various aryl halides with phenyltributyltin under microwave irradiation.

An efficient catalytic system using $(BeDABCO)PdCl_3$ was developed for the Stille cross-coupling reaction. The substituted biaryls were produced in excellent yields in short reaction times using catalytic amount of this catalyst in DMF at 90 °C (Scheme 1).

$$\text{Ar-X} + \text{Ar'SnBu}_3 \xrightarrow[\text{CsF, DMF} \\ 90\ ^\circ\text{C , 500W}]{(\text{BeDABCO})\text{PdCl}_3} \text{Ar-Ar'} + \text{XSnBu}_3$$

Scheme 1. The Stille cross coupling reaction by $(BeDABCO)PdCl_3$

The ionic character of homogenous catalyst and microwave irradiation and also DMF as microwave-active polar solvent gave higher yields in shorter reaction times under microwave irradiation. Benzyl dabco as an efficient ligand and also a quaternary ammonium salt had efficient stabilizing effect on the Pd(0) species. The use of homogeneous metal catalyst in conjunction with microwave irradiation lead to an increased lifetime of the catalyst, saving time and energy, produce high yields, and decrease of discarded byproducts from thermal side-reactions.

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Novel Cyclodextrin Trimer via Tri-branched Benzimidazole Core: Synthesis and Characterization

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Cyclodextrins (CDs) are natural nanocapsule connected through α-(1-4)- linked glucose units in a rigid $^4C_1$ chair conformation, that most important properties of CDs is their inclusions with guest molecules into their hydrophobic cavities [1,2]. Amphiphilic CDs are good candidates to functionalize natural membranes as well as synthetic vesicles [4]. The preparation of new cyclodextrin trimer compounds with using the tri-branched benzimidazole molecules contain six free amine groups as core and β-CD as branch is reported here. Unimer entities have three hydrophilic sites (CDs) and hydrophobic site (benzimidazole derivative core). For the preparation of β-CD trimer, first, tri-branched benzimidazole was synthesized thorough reacted the 1,3,5-benzene tri-carbonyl chloride monomer with excess of 3,3`-diaminobenzedine (DAB) in polyphosphoric acid and mono-6-deoxy-tosyl-β-CD by reaction of β-CD in aqueous solution with tosyl chloride in the present of $CuSO_4$ and NaOH. Then tri-branched benzimidazole core was reacted with mono-6-deoxy-tosyl-β-CD in dry DMSO at 70 °C. Finally for the purification, the obtained mixture was precipitated in deionized water, filtrated and three time washed by water. From investigation the data it seems that these new trimer could show amphiphilic properties [3], and has potential to form stable Langmuir-Blodgett films [4]. Structure determination of obtained compounds was performed using spectroscopic methods and all of the collected data were in accordance with the proposed structures.

Chemical structures of cyclodextrin trimer

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Application of silica supported Lewis acids in organic synthesis

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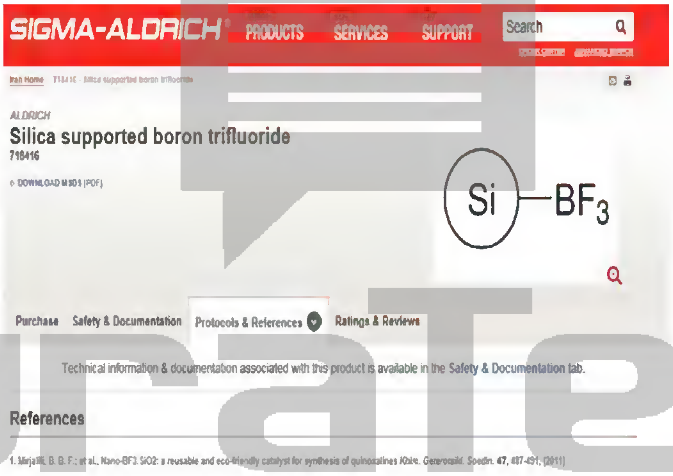
$BF_3 \cdot Et_2O$, $TiCl_4$, $SnCl_4$ and $SbCl_5$ as strong Lewis acids are corrosive, toxic, and volatile, and they also generate considerable amounts of waste. The handling of them is difficult and they are hydrolyzed to producing HCl in the presence of moisture.Nano-$BF_3 \cdot SiO_2$ [1,2], $BF_3 \cdot SiO_2$ [3-5], $SnCl_4 \cdot SiO_2$ [6], nano-$SnCl_4 \cdot SiO_2$ [7], nano-$TiCl_4 \cdot SiO_2$ [8], and nano-$SbCl_5 \cdot SiO_2$ [9] are bench-top catalysts that have many advantages such as simple preparation, reusability, easy handling or storage and being environmentally benign. They can be stored at an ambient temperature for months without losing its catalytic activity. We are investigating the application of silica supported Lewis acids as catalyst for promotion of organic reactions such as tri- and four-substituted imidazoles, β-acetamidoketones, benzimidazoles, , azo dyes, thioacetals, tetrahydrobenzo[*a*]xanthenes-11-one, 14-Aryl or alkyl-14*H*-dibenzo[*a,j*]xanthenes, and 1-amidoalkyl-2-naphthols under various conditions. These protocols have significant advantages such as high conversions, easy handling, cleaner reaction profile and shorter reaction times, which makes it a useful and attractive process for the rapid synthesis of many products.



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An Atomistic Interpretation of Calcium Induced Order in a Lipid Monolayer

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Membranes at physiological conditions are in contact with electrolyte solutions, so their specific interactions with ions are a matter of substantial interest. Experimental investigations show that ions play an essential role, not only in the structure, dynamics, and stability of membranes, but also for the binding and insertion of proteins, membrane fusion and transport across membranes. [1] Atomistic molecular dynamics simulations of phospholipid monolayers, as model systems, provide a detailed picture of the interactions and processes in biological membranes, which can be considered as two weakly coupled monolayers. Interactions between lipid membranes and ions can be investigated by changing the subphase composition (i.e. pH, ionic strength). Previously we have investigated the liquid condensed (LC)-liquid expanded (LE) phase transitions in DPPC monolayers, using molecular dynamics simulation approach. [2]

Observing obvious LC-LE phase transition in 293.15 K, revealed the ability of chosen force-fields (Berger *et. al* force filed for DPPC monolayer and Tip4p-2005 model for water layer) in representation of physical characteristics of studied phospholipid monolayer. An atomistic description of water and phospholipids provides a route to analyze the influence of electrostatic effects on the monolayer phase transition, from a microscopic point of view. An amphiphile head group of the DPPC, contains two moieties, that are spatially separated and oppositely charged, resulting in the zwitter-ionic head group with zero total charge.

Starting from the resulting structure files of our previous study [2] at different surface pressures, we added five different concentrations (0.1, 0.5, 0.75, 1.0 and 1.5 moles/liter) of $CaCl_2$ salt to the water subphase and investigated the effect of added ions on the structure, phase transition and ordering of the DPPC monolayer. All of the calculations were performed with the code GROMACS 3.3. [3] The surface-pressure area isotherms were calculated for the five different salt concentrations after 50 ns simulation time and compared with the isotherm in the vicinity of pure water layer. It was found that the effects are negligible for the solid (LC) phase, where they are enhanced for the fluid (LE) phase, resulting in the movement of isotherm coexistence region to the higher surface pressures and smaller area per phospholipids.

The radial distribution function, $g(r)$ was used to attain information on coordination between different atoms. The RDF for Ca^{2+} around a phosphate oxygen atom of the lipid head group was computed. Integrating the first peak of the $g(r)$, enabled us to define ion binding. Ions closer than the cutoff distance were considered as bound. We analyzed the number density plots of the ions (Ca^{2+} and Cl^{-}), phosphorus and nitrogens to specify the preferred atomic locations and the extent of ions penetration in the lipid head group. Although the divalent Ca^{2+} cations do not penetrate so deeply into the DPPC monolayer, they perturb the lipid organization significantly. The lipid tails experience conformational changes followed by an increase in the lipid-tail order, due to binding of cations to the monolayer.

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C-N formation of Buchwald-Hartwig amidation type for substituated thiophenes and furans

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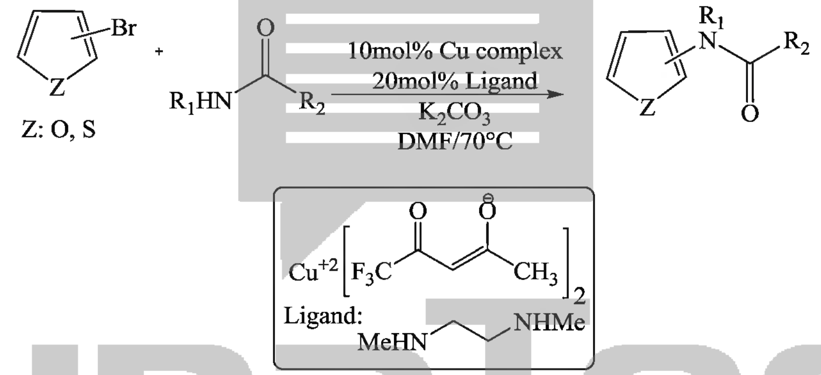
C-N cross-coupling of aryl halides with amides has been the subject of intense studies in recent years, primarily by the groups of Buchwald[1] and Hartwig[2]. Application of this methodology to various heteroaromatic compounds is still a relatively unexplored process.
Herein cross coupling reactions are applied between amides and aromatic halides. With using commercial available copper(II) trifluoroacetylacetonate and K_2CO_3 as base in presence of DMEDA as ligand, amidation of 2 and 3 Bromo thiophenes and furan rings has been completed. In 70^0C temperature and DMF as the solvent good yields of products obtained.



In concolusion, the route disscused here is mild and high yeilding with available starting material and catalytic system and allows for the preparation of highly substituted amido heteroaromatic substrates.

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A New Methodology approach for coupling of pyridin-2-ones with aryl bromides Catalyzed by Palladium(II)

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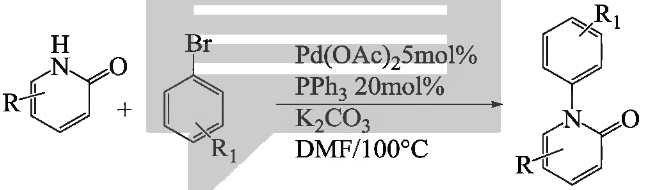
Pyridin-2-one is an important component of many pharmacological active substances and N-aryl substitution is frequently a key structural feature[1].N-arylation of amines under the copper-catalyzed Ullmann reaction usually requires drastic reaction conditions and produces moderate yields of the desired products[2-3].

We have reported coupling of pyridin-2-ones with aryl bromide with palladium acetate as catalyst and triphenylphosphine as ligand.This catalytic system shows excellent reactivity and stability in C-N cross-coupling reactions.



In concolusion,we have developed an efficient, general, catalytic system for C-N coupling of aryl bromides with pryridin-2-one which good yields of products obtained in short reaction times. Availability of starting materials and the low catalyst and ligand loading are also appealing features that make the proposed synthetic path advantageous.

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Regioselective synthesis of N-Aryl Hydrazide with copper(II) catalyst

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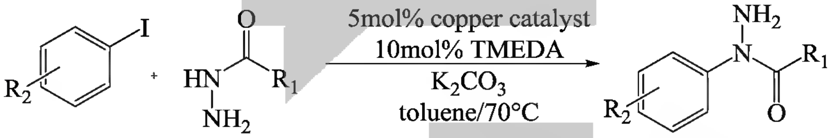
N-Aryl hydrazides form an important class of organic compounds with many applications in organic synthesis and in industry[1]. They are useful starting materials for the synthesis of biologically active heterocycles, such as indoles, carbazoles, pyrazoles, triazines, indazolones, and indazoles[2]. A method for regioselective synthesis of *N*-aryl hydrazide with using *para*- and *meta*- substituated aryl iodides and *N*-protected hydrazine is reported. In presence of catalytic amounts of copper(II) trifluoroacetylacetonate and Tetramethylethylenediamine as ligand and K_2CO_3 as base good yields of products obtained.



In concolusion,we have developed an efficient, inexpensive, general, catalytic system for regioselective coupling of aryl iodides and benzoic hydrizide with good yields in short reaction times.

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Synthesis of pyrimido[5,4-e]tetrazolo[5,1- b][1,3,4]thiadiazine Derivatives.

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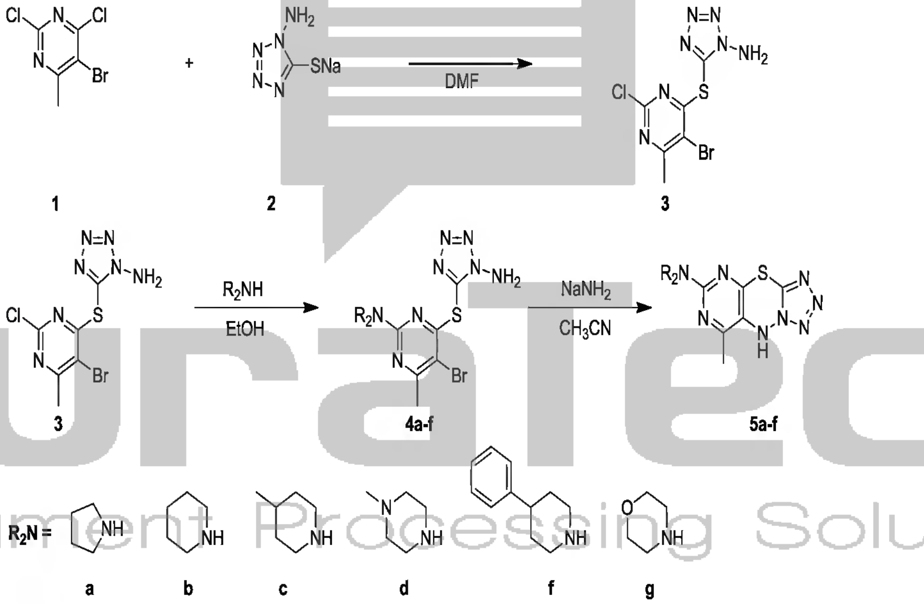
Pyrimido thiazines are interesting compounds because of their biological activities[**1**]. Significant lipoxygenase inhibition activity are observed for certain 2-substituted pyrimido[4,5-b][1,4]benzothiazines, e.g 4-methyl-2-(4-methylpiperazin-1-yl)-5H-benzo[b]pyrimido[5,4-e][1,4]thiazine, which were synthesized in our laboratory[**2**]. This interesting results prompted us to continue our research in the Pyrimido thiazine area.
In this study, six novel 2-substituted pyrimido[5,4-e]tetrazolo[5,1-b][1,3,4]thiadiazine **5a–f** were synthesized.



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Design and Synthesis of New Potent Peptides and Investigation of Their Activities

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Peptides are known as natural drugs. Peptide Chemistry has reached a considerable level of maturity, and apparently almost with complex structure. Designing and synthesis of novel peptides as biologically active compounds is a central goal in drug discovery. [1]
In continuation of our recent research about the synthesis of novel peptides;[2-5] in this lecture designing, synthesis, and investigation of biological activities of some novel peptides will be presented. Since addition of hydrophobic moiety to a peptide sequence increase the peptide's ability to penetrate plasma membrane, in this way some peptides were synthesized with adding a hydrophobic moiety in the end of N- or C-terminus of peptides. Meanwhile, recently unusual amino acids are increasingly becoming important substrates in modern drug synthesis and discovery research. With these points in mind, some novel peptides were designed and synthesized using combination of known SPPS and SIS approaches.
In this lecture, the three main sections are as follows:
a) Synthesis of LH-RH analogues via Ugi-4CR and investigation of their anti-cancer activities.
b) Synthesis of novel analgesic and opioid peptides and comparison of their activities.
c) Combination of unusual amino acids with di- or tri-peptides, and investigation of their structure.

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Comparison of the essential oil composition of three population of Ziziphora clinopodioides Lam. From Iran

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The genus *Ziziphora* L. belongs to the family Labiateae ,consists of four species,widespread all over Iran. *Z. clinopodiodes* Lam. is one of the valuable and medicinal species of the genus[1]. *Ziziphora* species have been used as infusion for various purposes such as sedative,stomachache and carminative ,also used to treat various ailments such as antiseptic and wound healing[2].
The essential oils obtained by hydrodistillation using a Clevenger type apparatuse from the aerial parts of three populations of *Z. clinopodiodes* collected from (Malard,Dizin, Garmabdareh)around of Tehran, were analyzed by GC and GC/MS.99.81%,98.23%and 97.63% of the oils were identified respectively.Qualitative and quantitative differences were seen in the essential oils.
The individual constituents were identified by their identical retention indices,refering to known compounds from the literature [3] and also by comparing their mass spectra with either the known compounds or with the Wiley mass spectral database.
Oxygenated compounds were predominated in the oils as well. P-mentha-3-en-8-ol(7.00%,24.71%.12.41%) , menthol (12.09%, 4.24%,14.54%) and 1,8-cineole (2.74%, 4.50%,12.46%) were found as the major components in all three oils respectively.A high amount of neomenthol (30.48%, 25.09%),piperitone(11.55%,6.53%)and pulegone (7.29%,11.44%)were found in the oils of Malard and Dizin specimens while the components were not seen in the oil obtained from the collected plant from Garmabdareh . Menthone(7.70%) was another major component which was found only in the oil obtained from the Malard species.As it is seen the Malard and Dizin species showed more similarities.

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Tandem bis-aza-Michael addition reaction of amines in aqueous Medium catalyzed by Poly(ethylene glycol)-bound Sulfonic acid (PEG-SO_3H)

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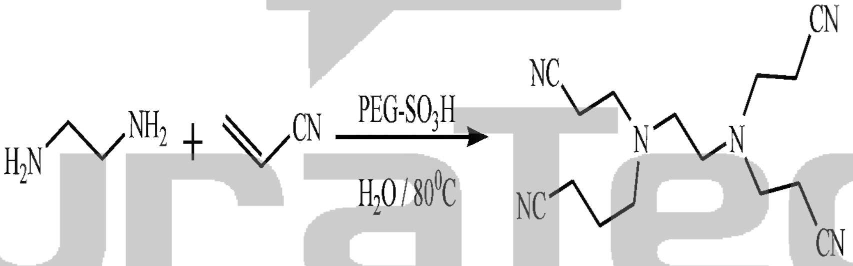
The development of new methodologies aimed at improving synthetic efficiency is an important goal in contemporary organic synthesis. A domino process, which involves several bond-forming reactions in a single manipulation, represents an attractive strategy in the facile assembly of molecular architecture. These operationally simple processes are atom economic, and minimize the generation of chemical waste and the use of energy. In this context, aza-Michael addition is an important class of carbon-nitrogen bond-forming reactions, and has been intensively explored and demonstrated to be a powerful tool in organic synthesis. Several methods have been developed for Michael addition using a variety of reagents such as various Lewis acids, $Cu(acac)_2$/ionic liquid, and boric acid [1-4].

In conclusion, we have demonstrated a sustainable and operationally simple the Tandem bis-aza-Michael addition reaction of amines to electron-deficient olefins to form the corresponding Michael adducts under mild conditions using PEG-SO_3H, which proceeds efficiently in an aqueous medium without the use of an organic solvent. Also the use of polymer supported, relatively low toxic, and inexpensive PEG-SO_3H as a catalyst renders this method greener and eco-friendly.

A simple process, short reaction time, green conditions, availability and use of inexpensive reagents makes the procedure novel and unique, and high yields (68-96%) are other advantages of our method.



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PEG-SO_3H-catalyzed three-component coupling of naphthol, alkyne and aldehyde: a novel synthesis of 1,3-disubstituted-3H-benzo[f] chromenes

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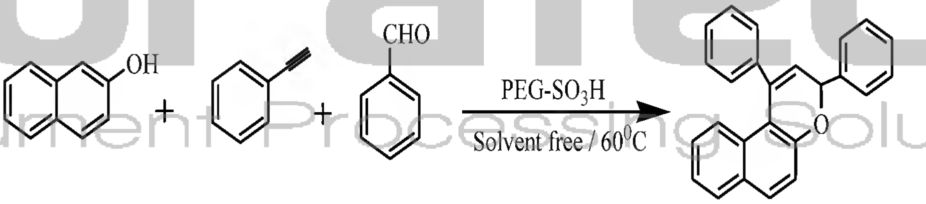
Multicomponent reactions (MCRs) are special types of synthetically useful organic reactions in which three or more different starting materials react to give a final product in a one-pot procedure [1,2].

There has been considerable interest in chromenes and their benzo-derivatives, not least because of their value for a variety of industrial, biological and chemical synthetic uses. In particular, benzo[f]chromenes (naphthopyrans) are of special interest as photochromic compounds, which have a wide variety of applications such as ophthalmic glasses, electronic display systems, optical switches and temporary or permanent memories. [3,4].

Consequently, there have been some reports on the preparation of benzo[f]chromenes So, In this project, we report a novel protocol for the one-pot synthesis of 1,3-diaryl-3H-benzo[f]chromenes by means of coupling of naphthol, alkyne and aldehyde using a catalytic amount of PEG-SO_3H. Accordingly, we first attempted a three-component coupling of 2-naphthol, phenyl acetylene and benzaldehyde using PEG-SO_3H at solvent free condition.

In this research, we report a new, simple, mild, and effective procedure for the one-pot synthesis of benzo[f]chromenes derivatives via a multi-component condensation in the presence of PEG-SO_3H as catalyst with high yields (72-95%) and short time. In conclusion we have developed a facile, convenient and environment-friendly multicomponent protocol for the synthesis of benzo[f]chromenes under green condition.



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One-step, three-component synthesis of novel 3-substituted indoles using Poly(ethylene glycol)-bound Sulfonic acid (PEG-SO_3H) as reusable catalyst

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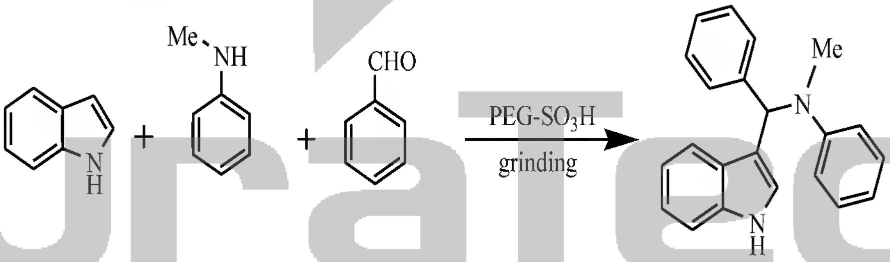
Concepts such as 'atom economy' and 'green chemistry' have focused significant interest on multicomponent reactions [1]. (MCR), wherein at least three simple partners are added together to result in a single diverse complex structure which allows the formation of several new bonds. The strategy of multicomponent reactions has been instrumental in playing a significant role in the preparation of structurally diverse chemical libraries. The utility of MCR is well represented in the synthesis of privileged medicinal scaffolds such as 1,4-dihydropyridines, dihydropyrimidines, decahydroquinolin- 4-ones [2] or substituted indoles [3]. Recently, indole derivatives have become increasingly useful and important in the field of pharmaceuticals[4]. Their biological properties have attracted many synthetic chemists to explore different methods suitable for the synthesis of substituted indoles. Despite several methods present in the literature for the synthesis of substituted indoles [5]. The development of simple, efficient and environmentally benign approaches for indole derivatives is highly desirable. In our previous reports, we have demonstrated that Poly(ethylene glycol)-bound Sulfonic acid (PEG-SO_3H) works efficiently for organic transformations . In continuation of our efforts for exploring PEG-SO_3H as an acid catalyst for multicomponent coupling reactions, herein we describe a one-pot multicomponent condensation reaction of indole, aldehydes and N-methylaniline to form a novel skeleton of 3-substituted indoles in the presence of 5 mol % PEG-SO_3H as a reusable catalyst at room temperature, with high yields (70-94%) and short time (Scheme 1).



Scheme1

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One-step, three-component synthesis of highly substituted pyridines using PEG-SO_3H as reusable catalyst

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The synthesis of 'privileged medicinal scaffolds' is highly important as these compounds often act as ligands for a number of functionally and structurally diverse biological receptors, and consequently, serve as a platform for developing pharmaceutical agents for diverse applications.

Among them, 2-amino-3,5-dicarbonitrile-6-sulfanylpyridines exhibit various pharmacological activities and are useful as antihepatitis B virus, antiprion, antibacterial, and anticancer agents, and as potassium channel openers for treatment of urinary incontinence. Moreover, some of these compounds were found to be highly selective ligands for adenosine receptors, implicated Parkinson's disease, hypoxia/ischemia, asthma, kidney disease, and epilepsy.

These vast applications have inspired the development of a number of methods for the preparation of pyridine derivatives. however, literature studies reveal that most of the methods involve multistep sequences and low isolated yields, use of toxic and expensive catalysts, and lack generality. The synthesis of pyridines a through multicomponent reaction (MCR) of aldehydes, malononitrile, and thiols has recently attracted much attention owing to excellent synthetic efficiency, intrinsic atom economy, high selectivity, procedural simplicity, and environmental friendliness [1-4].

In conclusion, we have demonstrated an efficient and general procedure for the synthesis of 2-amino-3,5-dicarbonitrile-6-sulfanylpyridines via multicomponent reaction of aldehydes, malononitrile, and thiols using PEG-SO_3H as a very mild , effective, environmentally benign, and reusable catalyst.

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One pot synthesis of β-amino ketones via direct Mannich-type reaction catalyzed with Poly(ethylene glycol)-bound Sulfonic acid (PEG-SO_3H)

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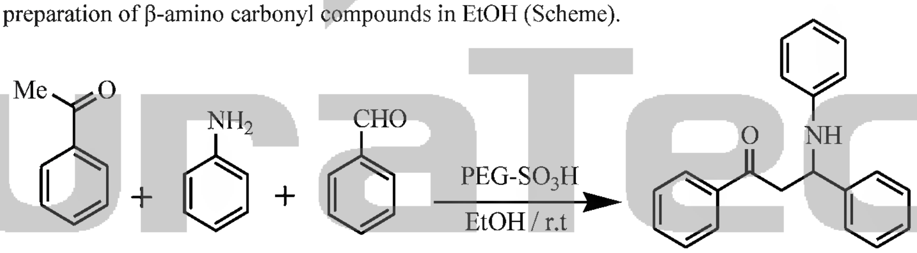
Mannich reactions are among the most important carbon– carbon bond forming reactions in organic synthesis [1]. They provide b-amino carbonyl compounds, which are important synthetic intermediates for various pharmaceuticals and natural products [2]. Therefore, the development of new synthetic methods leading to β-amino carbonyl compounds or their derivatives has attracted much attention. However, the classic Mannich reaction has limited applications. Attempts have been made in the past to improve methodologies based on two-component reactions, where the imine as electrophile is pre-formed and then reacted with nucleophiles such as enolates, enol ethers, and enamines [3]. However, in most cases these protocols use hazardous organic solvents, costly and non-recoverable catalysts, and requirement of special effort for catalyst preparation, and suffer from long reaction time with low yields [4]. Therefore, the development of modern versions of the reaction that work under mild conditions is of great importance. Poly(ethylene glycol)-bound Sulfonic acid (PEG-SO_3H) is an excellent acidic catalyst, which is frequently used to promote some important reactions.

We report herein full details of a novel, convenient, and simple procedure to realize a one-pot three-component reaction of aldehydes, amines, and ketones, catalyzed by PEG-SO_3H, for the preparation of β-amino carbonyl compounds in EtOH (Scheme).



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Synthesis and Characterization of Biodegradable Multiblock Copolymers of L-Lactide, ε-Caprolactone and PEG

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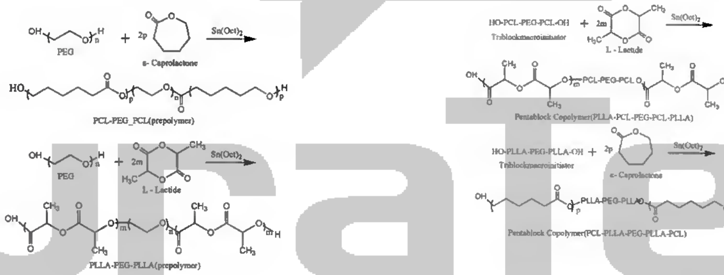
Biodegradable polymers have been in use for many applications like surgical sutures, encapsulates, scaffolds, and other advanced bio- medical and pharmaceutical devices [1]. The properties of Polylactide (PLA) and poly(ε-caprolactone) (PCL), such as, non toxicity, degradability, remoldability, permeability and cytocompatibility make them more suitable for biomedical applications, especially as cardiovascular assist devices, controlled drug release, biodegradable sutures, artificial skin, absorbable prostheses and tissue engineering scaffolds [2-3]. In this research two multiblock copolymers from polyethylene glycol (PEG), L-lactide (LLA) and ε-caprolactone (CL) were synthesized and characterized. Triblock prepolymers were first synthesized from PEG with molecular weight (M_n) of 15,000 Daltons, ε-caprolactone or L-lactide in the presence of $Sn(Oct)_2$ as catalyst.



The two triblock prepolymers(PCL-b-PEG-b-PCL and PLLA-b-PEG-b-PLLA) were used for the synthesis of two pentablock copolymers(PLLA-PCL-b-PEG-b-PCL-PLLA and PCL-PLLA-b-PEG-b-PLLA-PCL). The molecular structures of the copolymers were characterized by ^{1}H-NMR and ^{13}C-NMR analyses. Thermal behavior and thermal stability of these copolymers were evaluated by DSC and TGA thermograms, respectively.

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Silica-based scandium (III) as an efficient and recyclable interphase catalyst for acetylation of alcohols and phenols

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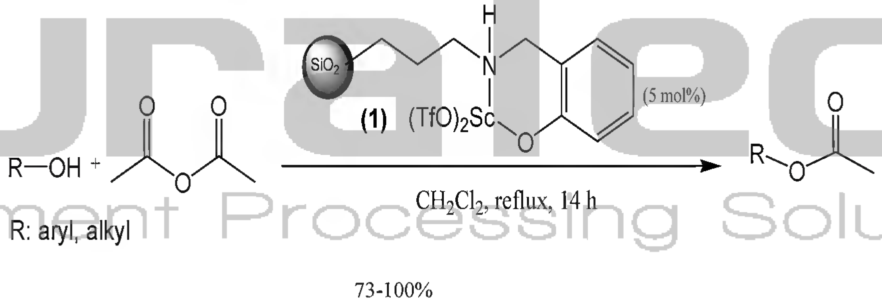
The acetylation of hydroxyl group is one of the most frequently used synthetic procedures in organic chemistry that is normally carried out with acetic anhydride or acetyl chloride in the presence of acid or basic catalyst [1]. Most of existing protocols for acetylation of alcohols or phenols are associated with one and more drawbacks involve the use of expensive or unrecoverable catalyst, harsh reaction conditions, unsatisfactory yields and tedious work-up procedure. One way to solve these problems is to immobilize one or more components of the catalytic systems onto a large surface area solid carrier to create new organic-inorganic hybrid (interphase) catalysts. Herein, silica-based scandium (III) interphase catalyst was prepared and quantitative determination of the functional group contents of the surface bound compound **1** was performed with thermogravimetric analysis (TGA) and Atomic Absorption Spectroscopy (AAS) [2]. In continuation of our study, to the development of new applications [3] of efficient and recyclable catalyst **1**, the acetylation of alcohols and phenols has been investigated. The alkyl and aryl alcohols and phenolic compounds undergo smooth acetylation with acetic anhydride in the presence of a catalytic amount of **1** under mild reaction condition to furnish the corresponding acetates in good to excellent yields. The catalyst shows high thermal stability (up to 300 °C) and it could also be recovered and reused for at least 4 reaction cycles without considerable loss of reactivity.



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New Applications of Imidoyl Chlorides in Heterocyclic Synthesis

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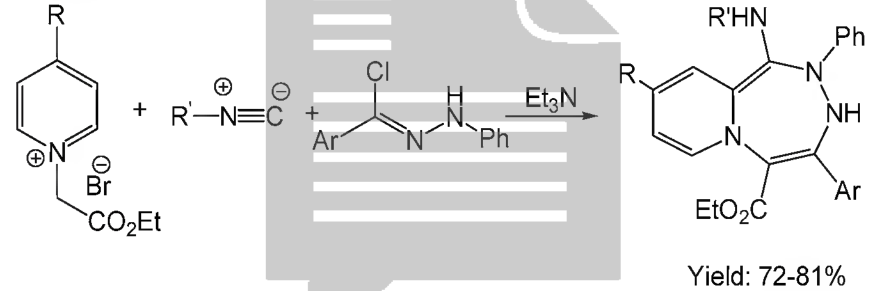
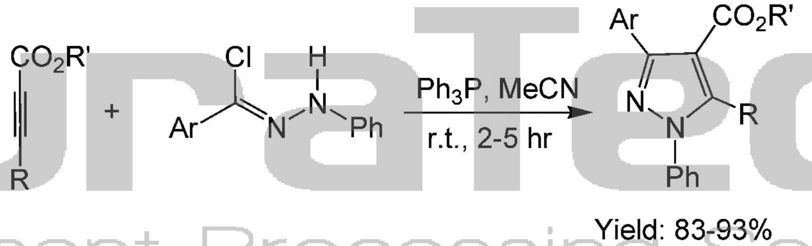
Imidoyl chlorides (prepared *in situ* from the corresponding amides, Ph_3P and CCl_4), are employed in multi-component condensation reactions with nucleophiles and electron-deficient acetylenic esters to give new heterocyclic compounds. Thus, a sequential reaction between pyridinium ylides, alkyl isocyanides, and 1-[chloro(aryl)methylene]-2-phenylhydrazines in CH_2Cl_2, afford functionalized 1-(alkylamino)-4-aryl-2,3-dihydro-2-phenylpyrido[2,1-*d*][1,2,5]triazepines in good yields.



The reaction of zwitterionic intermediates derived from triphenylphosphine and acetylenic esters with 1-[chloro(aryl)methylene]-2-phenylhydrazines, constitutes a synthesis of functionalized 3-(aryl)-1-phenyl-1*H*-pyrazoles in good yields.



Various features of these transformations will be presented and discussed.

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Preparation and Properties of Novel Polyimides Bearing Triazole Units in Backbone by Click reaction

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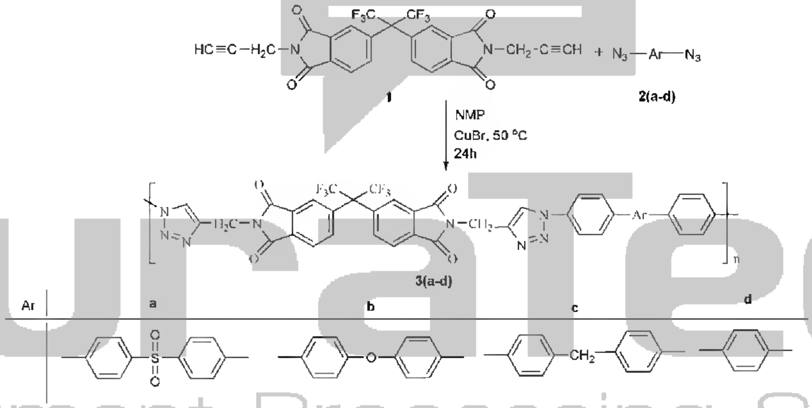
Click chemistry has found a vast number of applications in different research fields, such as material sciences [1,2], polymer chemistry [3,4], and pharmaceutical sciences [5]. It has been extensively used in the synthesis of polymers with different composition and topology [6]. In spite of the importance of polyimides (PI), click chemistry has not been widely employed for the preparation of these compounds.

In this study, some polyimides containing triazoles units in the main chain was prepared from the polymerization of dialkyne including imide linkages and diazides in the presence of Cu (I) catalyst. Condensation of propargyl amine with 4,4′-(hexafluoroisopropylidene)diphthalic anhydride in *N*-methyl-2-pyrrolidinone (NMP) provided *N,N′*-dipropargyl(4,4′-hexafluoro- isopropylidene) bisphathalimide (**1**). The polymerization of dialkyne (**1**) and diazides **2(a-d)** was earsily carried out under mild conditions in presence of CuBr in NMP at 50°C. The chemical structures of the resulting novel polyimides **3(a-d)** were characterized by FT-IR, ^{1}H NMR and elemental analysis techniques. Because of the flexible groups in the polymer backbone, these polymers exhibited good solubility in common polar organic solvents such as NMP, *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformide (DMF) and dimethylsulfoxide (DMSO). The resulting polyimides showed a decomposition temperature (at 5% weight loss) of 237–250 °C in nitrogen atmosphere and inherent viscosities (0.42-0.53 dL/g).



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Microwave-promoted homo-coupling reaction of aryl halides using TBA-ortho-palladated complex

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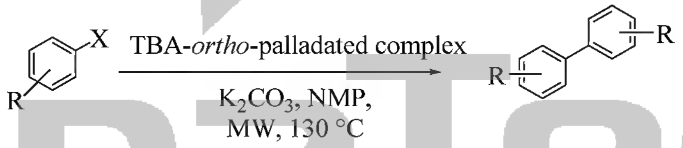
Transition metal catalyzed homo-coupling of aryl halides is a very efficient catalytic process for biaryls synthesis. Palladium [1], nickel [2], indium [3], copper and rhodium [4] have been used in these reactions. The most convenient method for the synthesis of symmetrical biaryls is a reductive homo-coupling of aryl halides by Ullmann reaction [5], which requires harsh conditions such as equimolar amounts of copper, high temperature and strong bases. The symmetrical biaryls also synthesized by oxidative coupling of aryl boronic acid, aryl zinc, aryl stannanes and aryl mesylates [6-7]. The most researches have performed considerable efforts to development milder reaction conditions using new catalysts and reaction systems. In order to develop catalysts that can operate at low metal loading and mild reaction, the palladacycle complexes have been considered as efficient catalysts for this purpose in organic synthesis, material science, biologically active compounds and macromolecular chemistry [8-9].

The activity of $[Pd\{C_6H_4(CH_2N(CH_2Ph)_2)\}(\mu\text{-}Br)]_2$ complex was investigated in the synthesis of symmetrical biaryls under both conventional and microwave irradiation conditions, and their results were compared together. This complex is an efficient, stable and non-sensitive to air and moisture catalyst for the homo-coupling reaction of aryl iodides, bromides and even chlorides. The products were produced in excellent yields in short reaction times using a catalytic amount of this *ortho*-palladated complex in NMP at 130 °C. In comparison to conventional heating conditions, the reactions under microwave irradiation gave higher yields in shorter reaction times. (Scheme 1).



TBA-*ortho*-palladated: $[Pd\{C_6H_4(CH_2N(CH_2Ph)_2)\ (\mu\text{-}Br)]_2$

Scheme 1. The homo-coupling reaction by *ortho*-palladated complex

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Microwave-assisted cyanation of aryl halides using TBA-ortho-palladated complex

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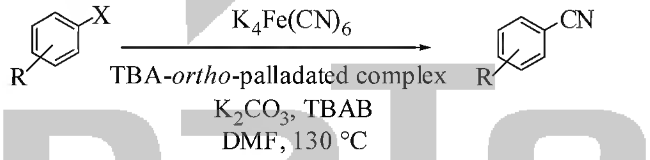
As aryl nitriles can be used in both laboratory and industrial scales in the synthesis of a vast range of commercial compounds [1], development of new synthetic methods for cyanation of aryl halides and aryl triflates are attractive subject in organic synthesis. The cyanide functional group serves as an important intermediate for many of the possible transformations into other functional groups such as carboxylic acids and their derivatives, aldehydes, amines, amidines, and heterocycles contain thiazoles, triazoles, tetrazoles, oxadiazoles, and etc [2-3]. A refined method for the preparation of benzonitriles is the transition-metal-mediated cyanation of aryl halides using inorganic or organic cyanide sources. The palladium-catalyzed cyanation of aryl halides using $K_4[Fe(CN)_6]$ as an inexpensive, non-toxic, and efficient source of cyanide is a useful and powerful method to obtain substituted benzonitriles [4-5]. The use of microwave irradiation in homogeneous transition metal-catalyzed reactions leads to the reduction of reaction times, production of high yields and higher selectivity, the decrease of discarded byproducts from thermal side-reactions, and increased lifetime of the catalyst [6].

In continuation of our recent investigations on the synthesis of the palladium catalysts and application of these complexes in the microwave assisted cross coupling reactions [7], we now wish to report the extension of *ortho*-palladated complex of tribenzylamine as homogeneous catalyst for the cyanation reaction of various aryl halides using $K_4[Fe(CN)_6]$] as a safe cyanating agent under microwave irradiation. The substituted benzonitriles were produced in excellent yields in short reaction times using catalytic amount of this catalyst (Scheme 1).



TBA-*ortho*-palladated: $[Pd\{C_6H_4(CH_2N(CH_2Ph)_2)\ (\mu\text{-}Br)]_2$

Scheme 1. The cyanation reaction by *ortho*-palladated complex

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CN-dimeric and monomeric ortho-palladated complexes catalyzed microwave-promoted Heck coupling reaction

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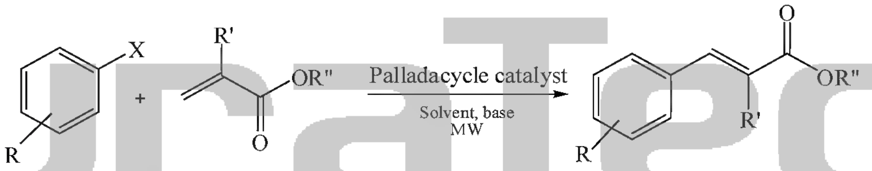
Olefin arylation described as the Heck coupling reaction is one of the most important palladium catalyzed C–C bond formation [1]. The Heck reaction has received considerable attention, primarily due to the enormous synthetic potential to generate sp2-sp2 carbon-carbon bonds. However, the reaction suffers from limitations such as relatively large amount of catalyst (>1 mol%) for reasonable conversions and hampered catalyst recycling. Various approaches towards catalyst improvement have been described [2]. Among the new methods the palladacycles catalysts are the most important classes of catalysts that used as very efficient catalysis with very low concentration in organic synthesis [3]. Transition metal-catalyzed reactions represent one of the most important and well-studied reaction types in microwave-assisted organic synthesis [4].T hese reactions typically need hours or days to reach completion with traditional heating under reflux conditions and often require an inert atmosphere. The use of microwave irradiation in transition metal-catalyzed reactions, which are usually time consuming, has assumed great importance due to the reduction of the reaction times to minutes and the decrease of discarded byproducts from thermal side-reactions [5].

In continuation of our recent investigations on the synthesis of the palladium catalysts and application of these complexes in the microwave assisted cross coupling reactions [6-7], in this report, the catalytic activity of dimeric $[Pd\{C_6H_2(CH_2CH_2NH_2)\text{-}(OMe)_2,2,3\}(\mu\text{-}Br)]_2$ and monomeric $[Pd\{C_6H_2(CH_2CH_2NH_2)\text{-}(OMe)_2,2,3\}Br(PPh_3)]$ complexes as efficient, stable and non-sensitive to air and moisture catalysts was investigated in the Heck coupling reaction. Vinylation of various aryl halids with olefins using a catalytic amount of these complexes led to production of the cross-coupled products in excellent yields in short reaction times (Scheme 1).



X= Br, I, Cl, SO_2Cl
R= OMe, COMe, COH, Cl, CN
R', R": H, Me

Scheme 1. The Heck cross coupling reaction by CN-palladacycle complexes

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TBA-ortho-palladated complex catalyzed microwave-enhanced copper-free Sonogashira cross coupling reaction

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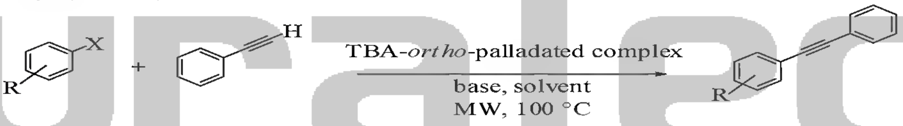
The Sonogashira coupling reactions of acetylenes with aryl or alkenyl halides or triflates have been developed in organic chemistry and material science for the production of internal alkynes and enynes [1]. Alkynes are as the building block of a wide range of pharmaceuticals, natural products, and biological active molecules, conducting polymers, non-linear optical and liquid-crystal materials [2-3]. The Sonogashira cross coupling reactions usually are mediated by phosphane-based palladium complexes. Generally, sterically hindred phosphine ligands showed high activities in the cross-coupling reactions such as Sonogashira couplings [4]. Most research has developed to obtain high catalytic activity with efficient catalytic systems. Moreover, a number of important studies have focused on the development of phosphine-free ligands such as *N*-heterocyclic carbenes [5]. Phosphine ligands suffer some drawbacks such as sensitivity to air or moisture and requirement for an inert environment and large amounts of palladium source for carrying out the reaction. Although carbene ligands are more stable than phosphines, they must be synthesized through multi-steps. Among the advanced catalysts the palladacycle catalysts are the most important classes of catalysts that used as very efficient catalysis with very low concentration for C-C bond formation in organic synthesis, material science, biologically active compounds and macromolecular chemistry [6]. Oxime [7] and ferrocenylimines [8] palladacycles as effective catalysts were found to promote the Sonogashira reaction.

In continuation of our recent investigations on the synthesis of the palladium catalysts and application of these complexes in the microwave assisted cross coupling reactions, we now wish to report the extension of *ortho*-palladated complex of tribenzylamine as homogeneous catalyst for the copper-free Sonogashira cross coupling reaction of various aryl halides under microwave irradiation. The substituted diphenylethynes were produced in excellent yields in short reaction times using catalytic amount of this catalyst (Scheme 1).



TBA-*ortho*-palladated: $[Pd\{C_6H_4(CH_2N(CH_2Ph)_2)\ (\mu\text{-}Br)]_2$

Scheme 1. The Sonogashira cross coupling reaction by *ortho*-palladated complex

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Comparison of essential oil composition of *Mentha longifolia* var. *chlorodictya* Rech.f. from two localities of Iran

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The family Labiatae , which is rich in essential oil, have commercial and medical values , among this rich array of plants yielding essential oils, the genus *Mentha* including 20 species that spread all over the world[1]. *Mentha longifolia* (L.) ,commonly known as wild mint is a perennial herb common in wet places. *M. longifolia* is one of the species which is used in folk medicine for the treatment of cold,cough,asthma and chest inflammations. It is also used externally to treat wounds and swotten glands.[2]

The aerial parts of *Mentha longifolia* var. *chlorodictya* were collected during flowering stage from Namak-dareh and Dailaman, two high localities of north of Iran in June 2010.The essential oils were obtained by hydrodistillation using a Clevenger type apparatus from the air dried plants. 97.0%, 98.5% of the total oils were identified respectively.

Identification of the constituents was made by comparison of their retention indices (RI)relative to n-alkanes,computer matching with Wiley library, and confirmed by comparison of their Mass spectra with those of authentic samples, or with data already available in the literature [3].

The oil composition of Dailaman and Namak-dareh species were found to be characterized by monoterpenes (83.59%,70.01%) respectively with high amount of oxygenated monoterpenes.Both samples showed cis-piperitone oxide (40.51%,36.41%),piperitenone oxide (37.33%, 22.58%), caryophyllene oxide (7.43%,13.65%) and thymol (3.98%,3.19%)as the major components.other main constituents in Namak-dareh species were:trans-caryophyllene(8.02%),1,8-cineole (4.74%)and germacrene D (2.13%).while in Dailamn specimen these components were found with small amount.

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7-9 March 2012

Investigation of the acylation reaction of (thio)barbituric acid derivatives for the synthesis of new type of micelle

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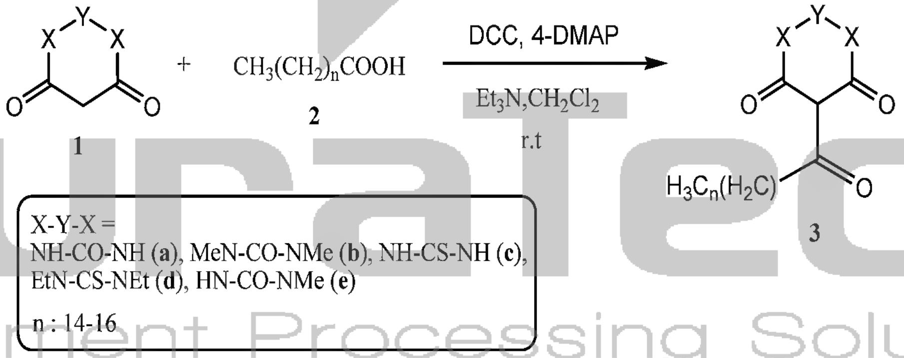
In aqueous solution, molecules having both polar or charged groups and non polar regions (amphiphilic molecules) form aggregates called micelles. In a micelle, polar or ionic heads form an outer shell in contact with water, while non polar tails are sequestered in the interior. Hence, the core of a micelle, being formed of long non polar tails, resembles an oil or gasoline drop.Micelles are widely used in industrial and biological fields for their ability to dissolve and move non polar substances through an aqueous medium, or to carry drugs which are, often, scarcely soluble in water. The carrying ability of micelles can be altered if parameters determining their size and shape are changed [1].The use of DCC, triethylamine, and 4-dimethylaminopyridine in dichloromethane provides a general and standard one-pot procedure for the C-acylation[2] of (thio)barbituric acid derivatives (1) with a wide range of carboxylic acids which have long hydrocarbons tail, use to synthesis of new type of micelle in good to excellent yields (Scheme 1).



Scheme 1

Refrencese
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New spiro[bicyclo] barbiturates based on cyclohexanone by nonconcerted [1+5] cycloaddition reaction

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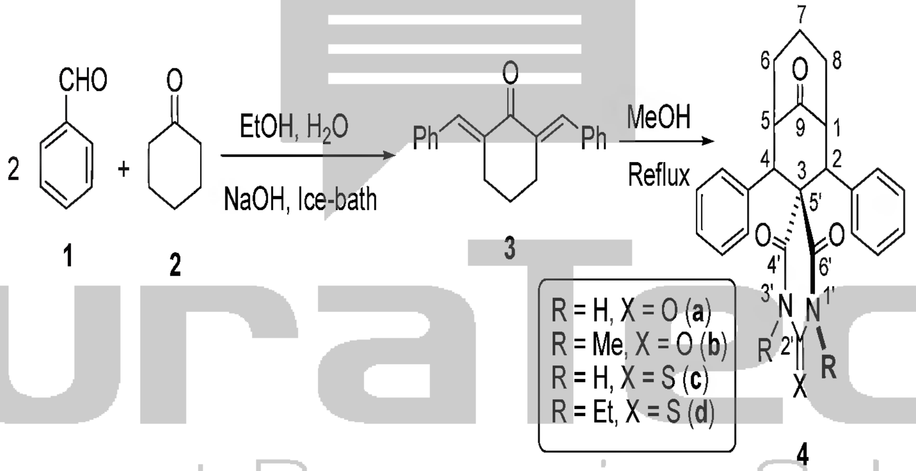
Spiro [bicycle] barbiturates are well-known as biological and pharmaceutical effects [1]. Several works have been reported for the synthesis of other spiro barbiturates (except spiro[bicyclo] barbiturates based on cyclohexanone) [2-4]. As we searched in the literature, there is no report about spiro[bicyclo] barbiturates based on cyclohexanones. Based on these concepts, we report the new rout for the synthesis of novel spiro[bicyclo] barbiturates based on cyclohexanones.

The intermolecular and then intramolecular Michael addition reaction of α,β-unsaturated ketones derived from cyclohexanone with (thio)barbituric acids lead to synthesis new type of 2,4-diaryl-1'*H*-spiro[bicyclo[3.3.1]nonane-3,5'-pyrimidine]-2',4',6',9(3'*H*)-tetraone. Structure elucidation is carried out ^{1}H NMR, ^{13}C NMR, FT-IR, UV-visible and mass spectroscopy techniques (Scheme 1).



Scheme 1

References

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One-pot, crossed multi component reaction for selective formation of spiro dihydrofuranes and spiro furo[2,3-*d*]pyrimidines in the reaction of dimedone, barbituric acids, BrCN and aldehydes

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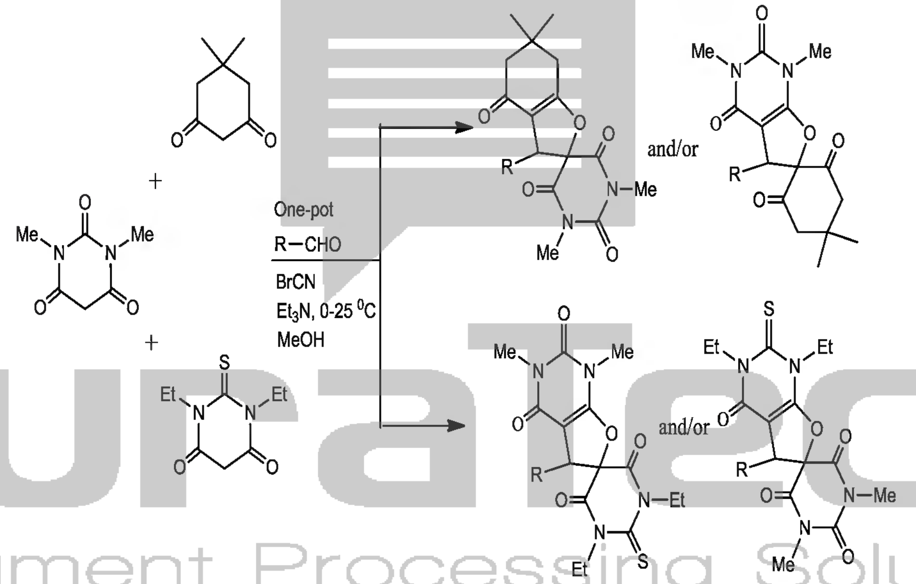
Substituted dihydrofurans in numerous natural compounds, showing important biological activities and wide variety pharmaceutical applications[1]. Large variety of 2,3-dihydrofuran compounds are of interest because they constitute important class of compound and natural products, many of which exhibit useful biological activities and clinical applications[2]. Also many of heterocyclic furo[2,3-d]pyrimidines [3] and spirobarbituric acids [4] are well known for their importance.

In this work, one-pot reaction of cyanogen bromide with 1,3-dimethyl barbituric acid and dimedone or 1,3-diethyl thio barbituric acid and various aldehydes in the presence of triethylamine were afforded spiro dihydrofuranes with 1,3-dimethyl barbituric acid or 1,3-diethyl thio barbituric acid ring moiety and/or spiro furo[2,3-*d*] pyrimidine with dimedone ring moiety. All structures were characterized by IR, ^{1}H-NMR, ^{13}C-NMR and Mass analysis.



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A New Methodology Approach for Synthesis of Aryl Sulfides Catalyzed by Palladium

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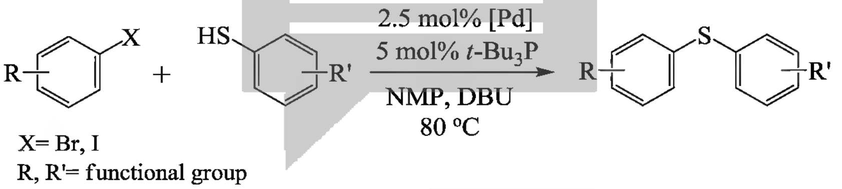
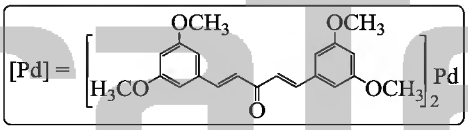
Aryl sulfides are a common functionality found in numerous pharmaceutically active compounds and are useful intermediates in organic synthesis.[1] A number of synthetic methods have been developed to prepare them from aryl halides.[2]

Herein, we describe a convenient and efficient procedure for the synthesis of aryl sulfides using a new palladium catalytic reagent system. In this new methodology we introduce commercially available Bis(3,5,3',5'-dimethoxydibenzylideneacetone)palladium(0) as catalyst and tri-*tert*-butylphosphine as ligand in formation of Carbon-Sulfur bond for first times.

Our studies shows that this catalytic reagent system is very efficient and fairly mild in compared to other reported catalytic systems for synthesis of aryl sulfides.





In conclusion, we have developed mild, convenient and high yielding route for synthesis of aryl sulfides. Moreover, the availability of starting materials and the low catalyst loading of the employed palladium sources and ligand are also appealing features that make the proposed synthetic path to sulfides pharmaceutically advantageous.

Acknowledgment. We thank "National Elite Foundation" for financial support of this work.

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A Mild and Efficient Palladium-Catalyzed of benzo[e]-1,2,4-triazines by Reaction of 2-Haloanilines and Benzohydrazides

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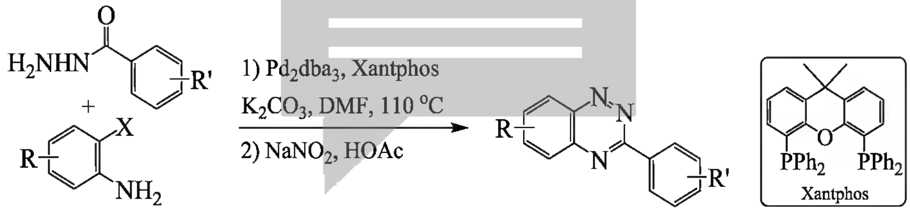
1,2,4-Triazines and their derivatives have been widely studied in terms of their synthetic methodologies and reactivity since some of these derivatives were reported to have promising biological activities.[1] The most common method for synthesis of this compounds is reaction of 1,2-diketones and amides in the presence of hydrazine.[2]

In this letter we report a new and efficient strategy for the synthesis of benzo[e]-1,2,4-triazines based on the reaction of 2-Haloanilines and Benzohydrazides using coupling reaction by palladium as transition metal catalyst and xantphos as ligand. For this purpose we performed reaction in two steps. In first step a coupling and then cyclization reactions occurred using Pd_2dba_3/Xantphos catalytic system. In second step the target molecule is produced using sodium nitrite as oxidizer. The yields of products were between 65-92% and the purity of products was very high.



X= Br, I

R, R'= functional group

In conclusion, we have demonstrated a new and efficient method for preparation of 1,2,4-tetrazines via palladium catalyst. This method is a new path for synthesis of benzo[e]1,2,4-triazines and there is no any reported publications for synthesis of these target molecules by palladium catalyzed until now. Excellent yield and fairly short reaction times are the main advantages of this method.

Acknowledgment. We thank "National Elite Foundation" for financial support of this work.

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A New Strategy for Buchwald-Hartwig Coupling of Aryl and Hetroarylhalides with Primary Amines Catalyzed by Palladium(0) Complex

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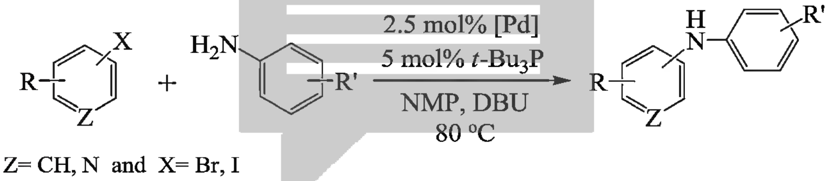
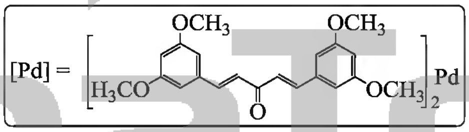
Palladium-catalyzed C-N cross-coupling reactions are an important technology both in industry and academia. Over the past decade great progress has been made in improving the efficiency and applicability of palladium catalyzed C-N cross-coupling reactions. Despite these recent advances, many limitations of these methods remain.[1]

Herein, we report a Bis(3,5,3',5'-dimethoxydibenzylideneacetone)palladium(0) as a new catalyst composed of a tri-*tert*-butylphosphine ligand that shows excellent reactivity and stability in C-N cross-coupling reactions and overcomes many restrictions that previous catalyst systems have possessed. Also we can synthesis of aryl and hetroaryl amines according to Buchwald-Hratwig coupling reaction using this new catalyst.





In conclusion, We use of commercially available Bis (3,5,3',5'-dimethoxydibenzylideneacetone) palladium(0) as a catalyst and tri-*tert*-butylphosphine as a ligand for performed of this protocol. Our observations show that this catalytic reagent system is a powerful tool for the synthesis of substituted anilines. High yields and short reaction times compared to other reported *N*-arylation reactions[2] are the most advantages of this methodology.

Acknowledgment. We thank "National Elite Foundation" for financial support of this work.

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A New Methodology for Synthesis of *N*-arylamides: Palladium-/Copper Catalyzed *N*-Arylation of Amides and Aryl Halides

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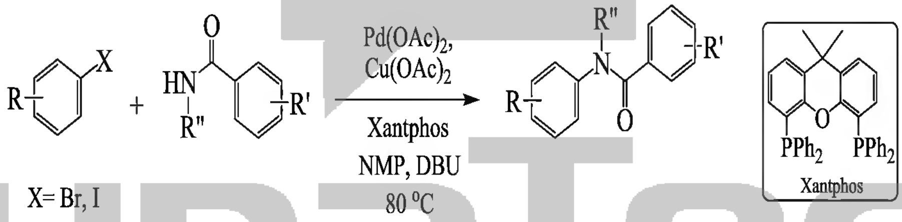
Metal-catalyzed amidation reactions of aryl halides are an attractive method for synthesizing *N*-arylamides. Previously, the amidations of aryl halides have been performed using Ullmann-type conditions using stoichiometric metal and high reaction temperatures. Recent advances in this area have allowed for the reactions of amides and aryl iodides or aryl bromides to be performed using catalytic amounts of metal under milder conditions.[1-3]

We have developed the Pd-Cu catalyst systems using phosphine ligands such as xantphos, which allow for the coupling of amides with aryl halides. This catalyst reagent system easily catalyzed the coupling reaction between nitrogen of amide and aryl halide. Amides are weak nucleophiles and without metal catalyst couldn't participate in the coupling reactions. We use of palladium acetate with xantphos for synthesis of *N*-arylamides. Copper acetate also use in this reaction for complete of the catalytic cycle and recovery of Pd(0) in the reaction. When copper acetate wasn't use, the reaction times and yields of products were long and low, respectively. Also a lot of palladium acetate must be applied for complete the reaction.



In conclusion, use of Pd-/Cu acetates as the catalyst, xantphos as the ligand, *N*-methylpyrrolidone (NMP) as the solvent, and 1,8-Diazabicycloundec-7-ene (DBU) as the base allows for the first general intermolecular C-N bond-forming reactions between aryl halides and amides. The amidations proceed at 80 °C with 1 mol % of Pd catalyst in good to excellent yields, and various functional groups are well tolerated.

Acknowledgment. We thank "National Elite Foundation" for financial support of this work.

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Synthesis of 2-Pyrone derivatives from (chlorocarbonyl)phenyl ketene with β-ketoamids and 4-hydroxy-2H-thiochromen-2-one

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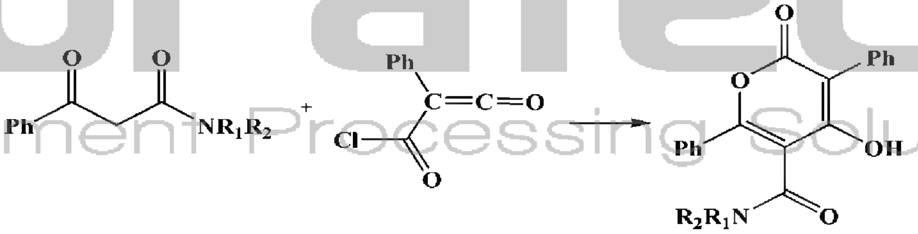
2-Pyrone derivatives were prepared in a one step procedure from readily available (chlorocarbonyl)phenyl ketene and β-ketoamids. A mechanism is presented to account for the formation of the products. In 2004 we reported the synthesis of substituted 2-pyrane derivatives by the reaction of (chlorocarbonyl)phenyl ketene and 1,3-diketons[1]. we describe an investigation of the cycloaddition of (chlorocarbonyl)phenyl ketene to β-ketoamids to prepare 2-pyrone derivatives and also synthesis of 4-hydroxy-3-phenylthiochromeno[4,3-b]pyran-2,5-dion derivatives using the reaction of 4-hydroxy-2H-thiochromen-2-one derivatives with (chlorocarbonyl)phenyl ketene in good yields.

In a this article, we have shown that the condensation of (chlorocarbonyl)phenyl ketene [2] with 1, 3-bisnucleophilic β-ketoamids derivatives [3] provides a convenient and rapid synthesis of 2-pyrones in high yields.



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New method For reduction of nitrate by Photocatalytic Reduction in presence of a hole scavenger

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The reduction of nitrite ions is of importance for many reasons, such as remediation of pollutants and production of useful intermediate chemicals (for e.g. hydroxylamine). Although many studies have been reported on the electrochemical reduction of nitrite ions [1-3] studies on the photocatalytic reduction of nitrite ions to ammonia are limited [4-6].

In this study, Photocatalytic reduction of nitrate ions was examined by using Bi^{3+}-TiO_2 catalyst in the presence of sodium oxalate as hole scavenger to enhance the photocatalytic reduction reaction.. Many factors such as, different hole scavengers and different concentrations of sodium oxalate were tested to search for the optimal reaction conditions.. Our results indicated that nitrate degraded effectively in aqueous Bi^{3+}-TiO_2 suspension by more than 83% within 150 min. The experimental results indicate that the presence of Bi^{3+} in TiO_2 catalysts substantially enhances the photocatalytic reaction of nitrate reduction. It was found that the optimal dosage of 1.5 wt% Bi^{3+} in TiO_2 achieved the fastest reaction of nitrate reduction under the experimental condition. Therefore a series of Bi^{3+}-doped TiO_2 (Bi^{3+}-TiO_2) catalysts with a doping concentration up to 2 wt% were prepared by a sol-gel method.. Bismuth ions deposit on the TiO_2 surface behaves as sites where electrons accumulate. Better separation of electrons and holes on the modified TiO_2 surface allows more efficient channeling of the charge carriers into useful reduction and oxidation reactions rather than recombination reactions.

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Design, construct and recycling of a new varnish and paint remover in silk screen printing industries which is used for glass and ceramic decoration.

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*Iran, Mashhad, Toos Industrial Estate, Maghsoud Factories Group. Ferdowsi university of mashhad**

Abstract:

ALN Cleaner has been designed to remove paint, varnish and also to clean the underlying surface. The principle of this product is penetration of the paint film by the molecules of the active ingredient, causing its swelling; this volume increase cause internal strains, which, together with the weakening of the layers adhesion to the underlying surface, lead to separation of the layer of the paint and varnish from the substrate.

Various co-solvents are added to the primary active ingredient such as activators, surfactants, thickeners, corrosion inhibitors, sequestrates and chelating agents.

Flocculation is a process which clarifies the used solution. Clarifying means removing any turbidity so that the solution is clear. Clarification is done by causing a precipitation to form in the ALN cleaner which can be removed using simple physical methods. Initially the precipitate forms as very small particles but as the solution is gently Stirred, these particles stick together to form bigger particles.

Many of the small particles that were originally present in the solution adsorb on to the surface of these small precipitate particles and so get incorporated into the larger particles that coagulation produce. In this way the coagulated precipitated takes most of the suspended matter out of the ALN cleaner and is then filtered off. flocculating agents that used in this work are Fe_2SO_4 ,$Na_2S_2O_7$,$AlCl_3$ and $NaCl$. only $NaCl$ can be considered the coagulants for the varnish. The aim of this study was to construct suitable varnish and paint remover for silk screen printing that used for glass and ceramic industries, and then to develop an efficient approach for recycling.

The advantages :

100% removal of all paints and varnish types from screen surfaces in few seconds, there would be no any damages on the screen, flash point of +80°C, Clear appearance , Mild pine oil odour, Its raw material is easy access, Low economical price, recyclable, possibility of recycling noble metal from device drainage, Possibility of automatic and manual operation, having proper viscosity to use in device, Minimum environmental toxicity effects.

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Electrocatalytic oxidation of silyl ethers using N-hydroxyphthalimides as catalyst

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Introduction

A new organocatalyst, *N*-hydroxyphthalimide (NHPI), has recently been introduced as an effective system for C-H activation by hydrogen abstraction. NHPI is a cheap, nontoxic catalyst easily prepared by the reaction of phthalic anhydride and hydroxylamine[1]. Grochowski and co-workers reported the first free radical reaction in the presence of NHPI in 1977[1]. In the 1980s, Masui's group published a series of papers describing reactions in which NHPI mediated the electrochemical oxidation of alcohols, benzylic compounds, olefins, amides, lactams, and acetals to obtain the corresponding oxygen-containing derivatives [2]. Silyl ethers are extensively used as protective groups for alcohols in synthetic chemistry [3] Because of its low cost, efficiency of preparation, stability under the intended reaction conditions and easy and selective removal and in many cases; it is necessary or convenient to achieve the direct transformation of Silyl ethers to the carbonyl compounds. Electrochemical deprotection of silyl ethers by NHPI as a catalyst follows the green and sustainable chemistry.

Experimental

Cyclic voltammograms (CV) were carried out using a potentiostat PGSTATE. A standard three-electrode electrochemical cell was used for the analytical experiments. An Ag/AgNO3 0.01 M+0.1Mm Ethoxytrimethylsilane+CH_3CN+tetra-butylammonium bromide 0.1 M electrode was used as a reference. A glassy carbon disk (diameter 5 mm) was used as working electrode.

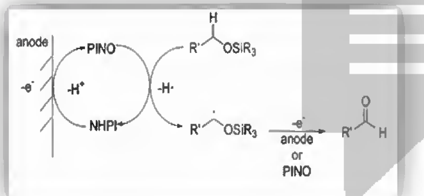
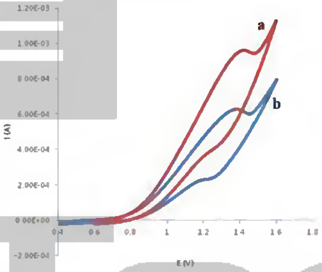


Fig 2-electrocatalytic oxidation of silylether

Fig 1-cv, in the(a)presence of NHPI,(b)absence of NHPI



Result and discussion

Figure 1, exhibits an anodic peak at E_{pa} corresponding to the one-electron oxidation of NO-H, leading to N-O˙. The reduction of this radical occurs on the reverse scan at E_{pc}. The PINO radical would be able to abstract the hydrogen R to the oxygen to generate a carbon centered radical which would lead in the
Presence of oxygen to the formation of carbonil compound (Fig2).

Conclusion

We now find a novel electro- oxidation method of silylethers by using NHPI as a catalyst. This method will provide a possibility of a new industrial technology for the electro oxidation of a variety of organic substrates.

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Biogas production from organic fraction of municipal solid waste (OFMSW) in an experimental reactor anaerobic digester

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Treatment of organic fraction of municipal solid waste (OFMSW) is an important component of an integrated solid waste management strategy and reduces both the toxicity and volume of the MSW requiring final disposal in a landfill. This study explores the anaerobic digestion technology (AD), in the absence of oxygen, as one of the main options for processing the biodegradable organic materials in MSW.

The AD process has been traditionally used for excess sludge digestion in wastewater treatment plants or for treating manure, achieving a biogas to produce energy [1]. The AD process is characterized by a series of biochemical transformations brought on by different consortia of bacteria: firstly, organic materials of the substrate-like cellulose, hemicellulose, lignin must be liquefied by extracellular enzymes, then is treated by acidogenic bacteria; the rate of hydrolysis depends on the pH, temperature, composition and concentration of intermediate compounds. Then soluble organic components including the products of hydrolysis are converted into organic acids, alcohols, hydrogen and carbon dioxide by acidogens. The products of the acidogenenesis are converted into acetic acid, hydrogen and carbon dioxide. Methane is produced by methanogenic bacteria from acetic acid, hydrogen and carbon dioxide and from other substrates of which formic acid and methanol are the most important [2]. Typical reactions during AD are [3]:

$$C_6H_{12}O_6 \longrightarrow 2\,C_2H_5OH + 2\,CO_2$$

$$2\,C_2H_5OH + CO_2 \longrightarrow CH_4 + 2\,CH_3COOH$$

$$CH_3COOH \longrightarrow CH_4 + CO_2$$

$$CO_2 + 4\,H_2 \longrightarrow CH_4 + 2\,H_2O$$

The AD is carried out in large digesters that are maintained at temperatures ranging from 30°C - 65°C. As digestion reaches the methanogenesis stage, the concentration of ammonia increases and the pH value can increase to above 8. Once methane production is stabilized, the pH level stays between 7.2 and 8.2. Optimum C/N ratios in anaerobic digesters are between 20 – 30. The retention time for wastes treated in mesophilic digester range from 10 to 40 days.The gas obtained during AD comprises of methane, carbon dioxide, some inert gases and sulfur compounds. Usually 100-200 m^3 of total gas are produced per ton of organic MSW digested. AD is a net-producing process, with around 75-105 KW of electricity created per ton of MSW input [4].

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Milli-sized sorbent based on calcium alginate-anhydride functional silane hybrid for adsorption of dye contaminants

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A new type of milli-sized sorbent based on calcium alginate-anhydride functional silane hybrid was synthesized by controlled gellification method. Calcium alginate as a biopolymer has been attracted more attention due to biological and industrial applications [1, 2]. Anhydride functional silane (AFS) was prepared by reaction of maleic anhydride and mercaptopropyltriethoxysilane in organic media and characterized by FTIR and ^{1}HNMR spectrometers [3]. The prepared AFS was dispersed in deionized water at ambient temperature. Proper amount of sodium alginate was dissolved in deionized water to obtain a semi-viscous solution of alginate. Then, dispersed AFS was added to the solution of alginate at room temperature while mentioned system was stirred by mechanical stirrer. After good mixing, a solution of calcium chloride with concentration (1.0 % w/v) was added to the previous mixture by controlled addition rate. Synthesized hybrid beads were filtrated by filter paper and dried at 50°C. Chemical structure of calcium alginate-anhydride functional silane hybrid beads was studied by FTIR spectroscopy. These beads are excellent sorbents to dye contaminants and therefore their adsorption capacity for adsorbing of malachite green dyestuff were tested by placing of these beads in a solution of malachite green with proper concentration. For comparison of adsorption capacity of these hybrids with neat calcium alginate beads, later materials were synthesized by addition of calcium chloride to sodium alginate solution. It was observed higher adsorption percentage of hybride beads than calcium alginate beads, about 63% and 36% for hybride and calcium alginate beads respectively in 25 ppm concentration of dyestuff.

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Novel Composite of Cellulose Acetate/Graphene oxide /Polyaniline(CA/GO/PANi): Preparation and investigation of their properties

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In the wake of increasing pollution and depleting of traditional energy resource, the development of renewable energy production and hybrid electric vehicles with low CO_2 emission have been attracting much attention since the end of last century[1]. Biopolymers such as cellulose acetate with high DS is considered because of sustainable and renewable biopolymer resource which holds very attractive properties such as biocompatibility, biodegradability, thermal and chemical stability and mechanical properties[2]. Graphene oxide (GO) is an oxidized state of graphene with oxygen functional groups (epoxide, hydroxyl, carbonyl and carboxyl groups) on the basal planes and edges, but the low electrical conductivity and acidic groups of GO are disadvantages in many investigations[3]. Therefore, using PANi which is considered as one of the most promising conducting polymers due to its unique acid-base doping–dedoping process can solve low electrical conductivity of GO[4].

The aim of this work is the preparation of conductive and biocompatible composites with desired properties to improve electrochemical performance which potentially could be used for supercapasitor electrodes. The electrically conductive composites of acetylated cellulose nanocrystals (ACN), graphene oxide (GO) and polyaniline (PANi) with different ratio of acetylated cellulose nanocrystals were prepared in the aqueous media for the first time. The composites were characterized using infrared spectroscopy, UV-Vis spectroscopy, tensile strength analysis test and electrochemical test .The results of these analysis showed that the electroactivity of these composites were improved in comparison with cellulose/ polyaniline composites. Also the tensile strength of these composite films showed a remarkable increase in comparison with graphene/polyaniline composites.

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A Green Protocol for Reduction of Aromatic Nitro Compounds to Amines with $NaBH_4/Cu(dmg)_2$ System in Water

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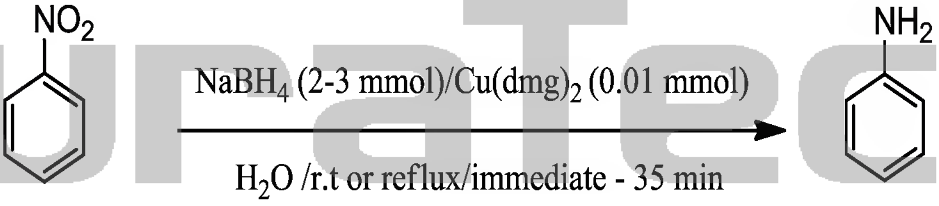
Aromatic amines are important starting materials and intermediates for manufactureing a great variety of chemicals, such as dyestuffs, pharmaceutical products, agricultural chemicals, photo graphic chemicals, surfactants, textile auxiliaries, chelating agents and polymers.

They are generally synthesized by reduction of nitro arenes. Aromatic amines can be prepared by a great variety of reduction methods. Probably the oldest industrially applied method is the reduction of nitrobenzenes with metal (usually iron, but also tin, zinc and aluminium can be employed) and water in the presence of small amounts of acid, first described by Bechamp in 1854[1].

In this investigation, we want to show that the combination system of $NaBH_4/Cu(dmg)_2$ in water as a green protocol for the efficient reductive of varieties of aromatic nitro compounds to their corresponding amines in high yields (Scheme).



(Scheme)

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Artificial Neural Network and Genetic Algorithm Approach for Modeling of Cr(VI) Adsorption from Aqueous Solutions Using Carbon Nanotubes

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Heavy metal pollution represents an important environmental problem due to its toxic effects and accumulation throughout the food chain and hence in the human body. Water pollution by chromium ions is a considerable concern, as this metal has found widespread use [1]. Chromium exists in both hexavalent and trivalent forms. Hexavalent form is more toxic than trivalent and requires more concern [1, 2, 3, 4].

In this study, an artificial neural network and Genetic algorithm based classification technique is applied for the prediction of adsorption efficiency for the removal of Cr (VI) ions from aqueous solutions by CNTs. The effect of operational parameters, such as initial pH, adsorbent dosage, contact time, and temperature, were studied to optimize the conditions for maximum removal of Cr (VI) ions.

Experiments were conducted in 250 mL Erlenmeyer flasks containing known Cr (VI) synthetic solutions. Known quantities of the adsorbents were added to the solutions. The carbon nanotubes were dispersed perfectly in the solution using an ultrasonic bath. The removal percentage is measured at three temperatures (17, 27 and 37°C). The suspension was filtered through a 0.2 μm Biofil syringe filter and the filtrate was analyzed to evaluate the concentration of Cr (VI) metal in the solution. Metal analysis was carried out by using a Cary 50 model UV visible spectrophotometer [2].

The solution pH, CNT dosage and initial concentration of Cr (VI) in the experiments were varied from 1 to 10, 0.02 to 0.15 g/L and 20 to 80 mg/L respectively to study the effect of these main parameters on the removal percent. The contact time effect on Cr (VI) removal and the kinetic were also studied. The samples were taken and analyzed at regular intervals [2].

The input variables were the pH, adsorbent dosage, contact time and temperature. The topology of an artificial neural network (ANN) is determined by the number of layers, the number of nodes in each layer and the nature of the transfer functions. Optimization of ANN topology is the next important step in the development of a model. The number of neurons in the hidden layer is determined according to the minimum prediction error of the neural network [3]. The ANN model here was developed using a three-layer feed forward back propagation network with 5, 4 and 1 neurons in the first, second, and third layers, respectively. A comparison between the model results and experimental data gave a high correlation coefficient (MSE = 0.06) and showed that the model is able to precisely predict the removal of Cr (VI).

Genetic algorithms are useful for complex and nonlinear optimization problems and generation of correlation. So it was used, with the available experimental data set, to establish a correlation to predict the Cr concentration on different situation. As result a relation was derived to predict the Cr removal efficiency in the scope of our study.

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Synthessis Nano-copper chromite catalysts ($CuCr_2O_4$) for employe in the several organic reaction

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The copper chromite ($CuCr_2O_4$) is one of the most efficient materials, has wide commercial application as catalysts being used in the unit processes of organic synthesis such as hydrogenation, dehydrogenation, hydrogenolysis, oxidation, alkylation, cyclization, etc. It can be used in the pollution abatement as the catalyst to remove aqueous organic wastes, volatile organic compound (VOC) and vehicular primary emissions such as CO, unburned hydrocarbon, NO x and soot[1]. In addition it has been used in various composite solid propellants as one of the efficient combustion supporting catalysts in the domain of space vehicles (rockets) and weapon industries (high explosives, ballistic missiles). Furthermore, copper chromite has been proved as promising catalyst for the production of H_2 a clean energy carrier, by photo-catalytic phenomena, conversion of alcohols, water gas shift reaction, through sulphur based thermo-chemical water splitting cycles, etc. The next application of $CuCr_2O_4$ is catalyst for alternative fuels preparations[2], synthesizing methanol, an important hydrogen carrier; high alcohol synthesis (HAS) by hydrogenation of CO or CO_2[3] , and fast pyrolysis of biomass to bio-oil products[4]. The catalyst is also helpful in the production of drugs and agro chemicals. In fine chemicals industry for perfumery and synthesis of fragrances[5] . In this article we present the synthesis of Cu-Cr-O nanocomposites via a citric acid (CA) complexing approach. Techniques of thermo-gravimetric/differential thermal analyzer (TGe DTA), X-ray diffraction (XRD), transmission electron microscopy (TEM) as well as scanning electron microscopy (SEM) have been employed to characterize the thermal decomposition procedure, crystal phase, microstructural morphologies and grain size of the as-synthesized materials, respectively. The results show that well-crystallized Cue Cr e O nanocomposites can be produced by using a temperature as low a s 600 ^{0}C. Phase structure of the as-obtained Cu-Cr -O nanocomposites depends on the Cu/Cr molar ratio in the starting reactants.

Keywords: Copper chromite composite oxide; Sole gel chemistry; Citric acid; Nanomaterials; Catalysts;

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A convenient and green synthesis of novel α-pyrones from Baylis-Hillman adducts

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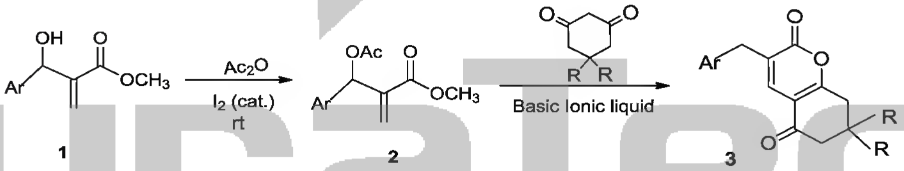
Various derivatives of α-pyrone, have been synthesized and evaluated for their biological activities in recent years. Some of these products have exhibited a broad range of activatives such as anti-HIV, antimicrobial, antifungal, anti-alzheimer and anti-inflamatory activities [1-5].

Based on our contnued interests in the development of benign methods in the synthesis of heterocycles of medicinal importance [6], we studied the synthsis of fused α-pyrones [3] from Baylis-Hillman adducts, using green chemistry protocols. The required Baylis-Hillman adducts **(1)** were prepared and then acetylated by acetic anhydride in the presence of catalytic amount of iodine at room temperature, under solvent free conditions. The adduct acetates (**2**) were reacted with cyclohexa-1,3-diones using basic ionic liquid. The reaction provided the desired fused α-pyrones in exellent yields and reasonable reaction times. In this study we have developed a simple, efficient and green method for the synthesis of various fused α-pyrone derivatives from Baylis-Hillman adducts and cyclic β-diketone derivatives in exellent yields (80-91%) (Scheme1).



Scheme 1

R = Me , H

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New process in Adsorption of organic pollutants and soil pollutant element, surface and ground water

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Abstract

With notice to publish records, more than 20 percents of world earth is exposed to pollution with chemical materials. When pollution composition is poured on soil surface or is added to soil, some physical and chemical phenomena with some soil features are adequate on soil fate and environment[1] For example, about oil hydrocarbon these pollution composition maybe evaporate or they exit with spontaneous oxidation, thermal, light and bio decomposition from soil[2]. In the other hand there is possibility of this composition transmission in soil and arrive to ground water surface. For mineral polluted composition is possible this reaction in soil: 1- surface adsorption with soil ingredient 2- exclusion of composition with same electrical capacity with soil ingredient 3- breakup and sediment reactions and 4- decomposition and degradation reactions. In any way presence of this polluted composition in soil can damage to soil quality and healthy and finally can influence on human health[3-4]

In this study is evaluated new process for pollution elimination from soil and then is evaluated the advantages and disadvantages of any method. Evaluation results are shown that between these methods, physical purge process has special place. Advantages of this process in comparing with present purges methods are: simplicity system design and its implementation, requirement to short time for purge (6 month to 2 years with notice to qualification of present pollution), very slightly cost than another purge methods (30 to 60 dollars per purge of 1 ton polluted soil), increasing in purge destroying of organic composition in areas with low bio decomposition, requirement to low equipments and facilities and additive to soil and low lateral effects on environment.

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Aldol Condensation of Cycloalkanones and Aromatic Aldehydes with Phosphomolybdic Acid (PMA) under Solvent-Free Conditions

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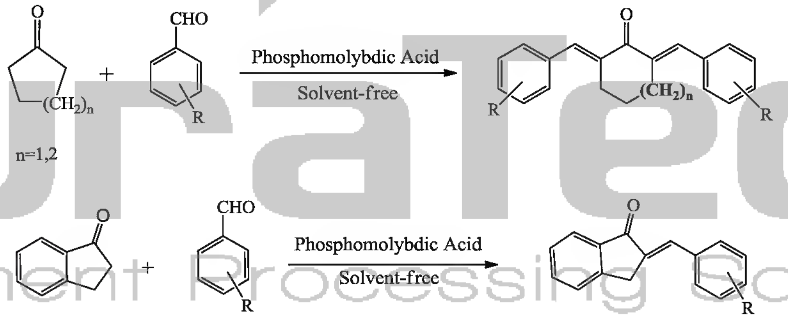
The aldol condensation of cycloalkanones and aromatic aldehydes is one of the most important methods for the preparation of α,α′-bis(substituted benzylidene) cycloalanones. Although this method has been introduced over than 100 year ago, however, because of the importance of aldol condensation, this subject still attract more in industrial and academic studies. In addition, solvent-free reactions because of advantages such as high yields, costless, simplicity and environmentally benign conditions have attracted a great deal of attentions.

In this project, bis(benzylidene) cycloalkanones and 2-benzylidene-1-indanones were synthe-sized by solvent-free condensation of cycloalkanones and aromatic aldehydes in the presence of catalytic amounts of phosphomolybidic acid in high yields (86-100%) under oil bath conditions (70-80 °C). The simplicity, high yields, short reaction times and easy work-up procedure as well as the benefits of solvent-free conditions are the major advantages of this protocol (Scheme 1).



scheme 1

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Synthesize of protein biofilter via extracted hemoglobin from sheep blood.

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Biological filters (Biofilters) are important synthesized compounds that can used in Filtration mask in industrials Contaminated gases and cigarette smoke[1-3] . Hemoglobin(Hb) has a ring structure of porphyrin and a hem structure in the centre of the ring, which has the ability to adsorb specific compounds. in this study (Hb) extracted from sheep blood via Hemolysis method . then 0.5 g solution extracted Hb added to Dialysis bag and Purified from salts impurities in 72h by Continuous control of EC . Then Hb extracted from solution by Centrifuge . Purified Hb solved again in 50ml DW and filtration by vacuum filter . Then added active charcoal (AC), mineral perlite and humic acid (HA) in three Solutions with fixed concentration of Hb and shaker along 48h . the change of concentrations of Hb were controlled by this formol : mg/ml Hb = 1.55 OD_{280} – 0.76 OD_{260}. Result after Optimization showed reduction of Hb concentrations in solution until constant concentrations and coat on AC , mineral perlite and HA .study of concentration changes showed coated Percent of Hb on absorbance were for AC with 95% , mineral perlite with 66.4% and HA with 78% . then absorbance washed via DW and Pure methanol and dry in 40°c . SEM , XRD and FTIR studies of AC, mineral perlite and HA befor and after adsorption of Hb were showed Hb coat on absorbance .These absorbance (synthesized biofilter) have ability to adsorption of harmful chemical composition in chemical industrials and Contaminated air .

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One-pot, water-medium green synthesis of the Hantzsch product by PEG-SO_3H

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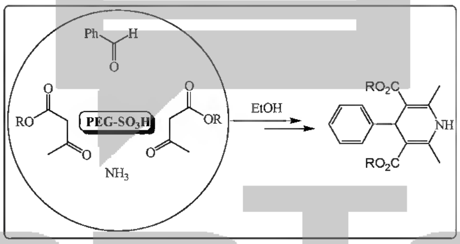
Recently, due to the vast medicinal utility of 1,4-dihydropyrimidine (Hantzsch product) and its derivatives, various methods to prepare these compounds have been reported. [1] Based on recent efforts to use eco-friendly reagents in chemistry, we choose the modified Polyethylene glycol (PEG) as the catalyst for synthesis of Hantzsch product. This product is obtained from a multi-component organic reaction between an aldehyde, 2 equivalent of a β-ketoester a nitrogen donor such as ammonium acetate.



In this project we prepare the sulfonic acid modified polyethyleneglycole as a recyclable and environmentally-friend catalyst, then we investigated the operation of this catalyst in Hantzsch reaction. The products were obtained in high yield, but the catalytic activity of PEG-SO_3H reduced after 3 cycles.

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Eco-friendly chemical decomposition of polycarbonate: Bisphenol-A recoverying

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Polycarbonate (PC) is an important engineering plastic and widely used to produce compact disc, computer parts, construction materials, etc. It is mainly produced by polycondensation reaction by using bisphenol A (BPA) and carbonyl dichloride or dimethyl carbonate (DMC) as the raw materials. The chemical recycling of waste PC has been gaining greater attention in recent years to obtain valuable products. For chemical recycling of waste PC to recover raw materials, the methods such as thermal decomposition, alcoholysis, methanolysis and hydrolysis have been reported. The results reveal that it is difficult to recover pure BPA by thermal decomposition and only BPA can be recovered by hydrolysis. However, due to the insolubility of PC in methanol, the reported methanolysis methods require high temperature and pressure and in presence of a lot amount of concentrated bases or acids.

In this report we would like to introduce an eco-friendly and simple method using glycerol as a safe and green solvent by minimum of volume and time, without applying high pressures and long reaction times. In our method polycarbonate (PC) has been glycolyzed to recovering bisphenol A (BPA) and the method was developed in order to finding an adequate safe method by using a base catalyst at minimum concentration.

The results showed that by using materials balance (pbw) as (PC/ gly/ water = 1:0.5:0.5, PC/ NaOH = 100:2) and at reflux conditions, PC is decomposed in 100% and BPA has been recovered in > 90% yields without any side reactions namely phenol formation as well as other overoxidation reactions.

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Efficient protection of aldehydes by their conversion to 1,1-diacetates catalyzed by silica foam supported molybdophosphoric acid

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Protection of functional groups plays an important role in multi-step synthesis of natural products. However, selective protection and deprotection of carbonyl groups are substantial steps in synthetic organic chemistry [1]. Acylals (1,1-diacetates) are appropriate candidates to this aim due to their stability in basic and neutral reaction media as well as in aqueous acids [2]. Meanwhile, gem-diacetates derived from □□□-unsaturated aldehydes are useful as dienes for Diels–Alder cycloaddition reactions. Moreover, acylals are used as cross linking reagents for cellulose in cotton [3].

One important class of solid catalysts is heteropoly acids (HPAs), having both redox and acid properties [4-6]. Among heteropoly acids, polytungstic acids are the most widely used catalysts due to their high acid strengths, thermal stability and low reducibility. Heteropoly acid catalysts have many advantages over the liquid acid catalysts, which are harmless to the environment with respect to corrosiveness, safety and quantity of waste.

Here, a mild and highly efficient method for protection of aldehydes with acetic anhydride in the presence of silica foam supported molybdophosphoric acid at room temperature is reported. Under these conditions, different aldehydes bearing electron-withdrawing and electron-donating substituents were reacted with acetic anhydride and the corresponding 1,1-diacetates were obtained in good to excellent yields. The catalyst was reused several times without loss of its catalytic activity.

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Microsynthesis and gas chromatography electron ionization mass spectrosmetry analysis of O(*S*)-alkyl *N,N*-dimethylamino methylthiophosphonates (methylthiophosphonothiolates) for verification analysis of the Chemical Weapons Convention

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The availability and understanding of mass spectrometry data of chemical agents is important for their successful identification in environmental complex matrices [1]. Large number of chemical weapons convention (CWC) related chemicals puts more complexity to the analytical activities under CWC verification requirements which need unambiguous identification of chemicals in complex environmental samples [2]. Unambiguous identification of these convention-related chemicals is achieved by gas chromatography-mass spectrometry (GC-MS) analysis of collected samples after sample preparation considering MS spectra and GC retention indices. *O*(*S*)-alkyl *N,N*-dimethylamino methylthiophosphonates (methylthiophosphonothiolates) are included in the schedule 2.B.4 list of the CWC annex of chemicals. To the best of our knowledge, no general microsynthesis protocol and investigation is reported describing the electron ionization mass spectral (EI-MS) fragmentation of title compounds. Herein, we wish to report a general microsynthesis protocol for a pool of these chemicals. The microsynthesis of the *O*(*S*)-alkyl *N,N*-dimethylamino methylthiophosphonates (methylthiophosphonothiolates) generally involves five steps (Fig. 1). Based on fragment ions of chemicals and density function theory calculation, the fragmentation routes were rationalized.

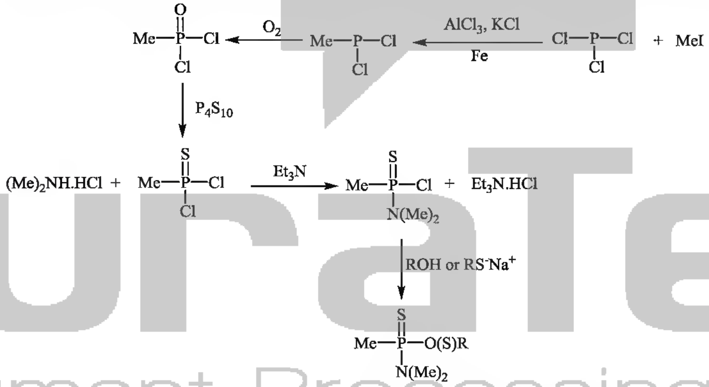

Fig. 1. Microsynthesis route of *O*(*S*)-alkyl *N,N*-dimethylamino methylthiophosphonates (methylthiophosphonothiolates)

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Synthesis, characterization and photocatalytic activity of MCM-41/ZnO and MCM-48/ZnO

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Since the discovery of the M41S family of ordered mesoporous adsorbents by scientist at Mobil Oil, the two most investigated materials, MCM-41 with a 2-D hexagonal structure and MCM-48 with a 3-D cubic structure, are synthesized. A larg number of preparation methods have been developed to synthesize mesoporous materials[1].

In this study, the impregnation synthesis of Zn-doped MCM-41 & MCM-48 was done by using direct and indirect solvothermal method. The mesoporous materials of MCM-41 and MCM-48 were synthesized hydrothermally at ambient temperature conditions from ethyl orthosilicate as Si source and cetyltrimethylammonium bromid (CTAB) as template. The reaction mixture was stirred vigorously at room temperature and then the solid produced was filtered, washed, dried and calcined in air for 6 h. The obtained substrates were characterized by XRD and FT-IR techniques. A comparative study in structural properties of ZnO/MCM-41 & MCM-48 materials was evaluated. The performance of these substrates toward the photocatalytic degradation of congo red in aqueous solution was studied. The photocatalytic activity is in relation with their structural properties and aggregation. The nanocrystals of ZnO has attracted considerable attention as a photocatalyst for the degradation of organic pollutants in water and air.The results show that all the samples produced by direct synthesis method, are used as the active components of catalyst [2,3].

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$Al(DS)_3$ efficiently catalyzed condensation of 1,4-dicarbonyl compounds and amines in water at room temperature: a green Pall-Knorr pyrroles synthesis

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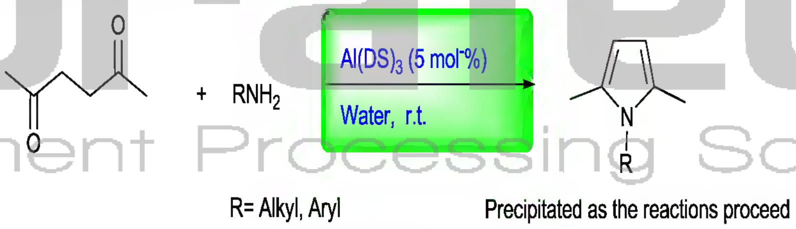
'Click chemistry', a term recently coined by Sharpless and co-workers,[1] denotes a growing family of powerful chemical reactions that are based on 'spring-loaded' energy-intensive substrates that can, under the right conditions, unload their energy to form stable products in high selectivity. Water is a desirable solvent for click chemistry for reasons of cost, safety, and environmental concerns [1].

Pyrrole derivatives are important intermediates not only in the synthesis of drugs, pigments, and pharmaceuticals, but also for the development of organic functional materials [2]. Substituted pyrroles are an important class of compounds displaying remarkable pharmacological properties such as antibacterial, antiviral, anti-inflammatory, antitumoral, and antioxidant activities. Consequently, a wide range of procedures has been developed for the construction of pyrroles. Nevertheless, the Paal–Knorr reaction remains one of the most attractive methods for the synthesis of pyrroles; wherein 1,4-dicarbonyl precursors are converted to pyrroles by the reaction with primary amines or ammonia in the presence of various promoting agents.

In this study micellar solution of anionic, cationic and neutral surfactants was used as a green media for the Paal–Knorr reaction of 1,4-dicarbonyl compounds, and amines at room temperature. Among them Aluminium dodecyl sulfate $Al(DS)_3$ efficiently catalyzed the reaction in neat water and the corresponding desired pyrroles were precipitated as the reactions proceed (Scheme 1). This method provides a novel and improved modification of the Paal–Knorr reaction in terms of mild reaction conditions and clean reaction profiles, using a simple workup procedure and improved yields.



Scheme 1

References

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Antibacterial activity of *Salvia reuterana* Constituents

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Within the Lamiaceae family, the oil rich genera are mainly in the subfamily Nepetoidea,. *Salvia* is one of the members of tribe Menthae of subfamily Nepetoidea with about 700 species distributed all over the world.*Salvia reuterana* is one of the widespread species in Iran and Iraq[1]. *Salvia* species have shown the presence of flavonoids [2]and diterpenoids[3]as the components which have biological activities. Flavonoids and terpenoids are characteristic constituents of green plants .

In this investigation Two flavonids: 5-hydroxy-6,7,4′-trimethoxy flavone (salvigenin), 5-hydroxy-7,4′-dimethoxy flavone (thitonine) and a labdane type diterpenoid: 8,13-epoxy-14 labdene (manoyl oxide) isolated from the solvent extract(n-hexan,ethyl acetate, methanol)(1:1:1) of the aerial part of *Salvia reuterana* Boiss which was collected from Khoram Abad province of lorestan(1920m high).The proposed structure were stablished by ^{1}HNMR, ^{13}CNMR, ^{2}DNMR(C-H-Cosy, HMQC),DEPT and Mass spectroscopy and confirmed in accordance with bibiliographic data and computational chemistry results.

The three components were evaluated against 7 microorganisms including gram(+/-)bacterias by measurment of growth inhibitory zone. They showed significant effect specially on gram(-) bacteria: *Salmonella para A, Escherichia coli ,Shigella flexneri.* and in this way the most effective component was thitonine which was even more effective than Gentamicine as standard antibiotic.

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Evaluation of antioxidant and antimicrobial activity of the leaves and fruits of *Ferula ovina* Boiss from Kashan area

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Genus *Ferula* belongs to the family *Umbelliferae* and has about 133 species distributed throughout the Mediterranean area and central Asia [1-3]. The Iranian flora contains about 30 species of *Ferula* of which some are endemic [2,5]. The popular Persian name of the most of these species is "Koma" [5]. *Ferula ovina* Boiss. is one of these species distributed in different regions of Iran [2]. Anti-spasmodic, anticholinergic and smooth muscle relaxant activities of the aqueous extracts of *F. ovina* have previously been reported [6, 7]. This research reports the *in vitro* antioxidant and antimicrobial potentials of the leaves and fruits of *Ferula ovina* Boiss. Methanol extracts from the leaves and fruits showed weak antioxidant activities in 1,1-diphenyl-2-picrylhydrazyl (DPPH) test (IC_{50} values= 395.7 ± 1.3 and 259.2 ± 2.1 μg/ml, respectively) and β-carotene/linoleic acid assay (inhibitions percentages = 49.4 % and 48.6 %, respectively). Total Phenolic compounds content of the extracts was 14.80 ± 0.22 and 20.25 ± 0.35 μg/mg, respectively [8]. The plant extracts also showed considerable antimicrobial activity against two strains of tested microorganisms[9].

Keywords: *Ferula ovina* Boiss., Extracts, Antioxidant activity, Antimicribial activity, Total phenolic

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Identification of chemical compounds in essential oils from seeds, leaves and stems of ferula hezarlalehzarica Y.Ajani

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Abstract

The genus *Ferula*, which belongs to the Umbelliferae family, has 133 species distributed throughout the Mediterranean area and Central Asia [1]. The Iranian flora consists of 30 species of *Ferula*, including 15 endemics, and the popular Persian name of most species is "Koma" [2]. Many reports on phytochemical analyses of this genus, including essential oil analysis, can be found in the literature [3–7]. In this study, after collecting plant material, in May 2011 from Kerman province botanical identification and suitable drying, the essential oils of Seeds, leaves, and stems of *Ferula hezarlalehzarica* Y.Ajani were separately extracted using hydrodistillation method and analyzed by GC and GC/MS. Identification of the constituents of the oils were done by comparison of their mass spectra and retention indices with those given in the literature and those authentic samples[8]. Nine compounds (100%) were identified in the Seed oil, with Myrcene (68.0%), β-Phellandrene (22.5%) as the main constituents. Also, among the 18 identified compounds (92.7%) in the leaf oil, 7-Methoxy-2,5-dimethyl-chromone (36.2%), (*Z*)-β-Ocimene (21.3%) were found to be the major components. Furthermore, 7-Methoxy-2,5-dimethyl-chromone (44.5%), Thymol, methyl ether (14.5%), were the main constituents among the 22 compounds (87.5%) characterized in the Stem essential oil.

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Constituents of The Essential Oil of Achillea eriophora From Baluchestan

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Abstract

The Achillea species is a chemically polymorphic perennial herb from a genus of complex taxonomy and is widespread throughout Europe, Asia, and North America [1]. Bumadaran is a popular name for several species of Achillea in the Persian language. They have been used as anti-inflammatory, antispasmodic, diaphoretic, diuretic, and emmenagogue agents and for treatment of hemorrhage, pneumonia, rheumatic pain, and wounds since ancient times [2]. Achillea has a mythological background dating back to Achilles in the Trojan war who used this plant for curing his wounds [1,3]. These species are also used as medicinal plants for feverish conditions, common cold, and digestive complaints, and are topically used for slow healing wounds, skin inflammations [1], and as veterinary remedy [4]. The aims of this study were to extract the essential oils only from the A.eriophora. The plant were collected during the flowering priod from Khash. Aerial parts of the plants were dried in shade and ground in a grinder. The dried plant samples (500 g) were subjected to hydrodistillation for 4 h using a Clevenger-type apparatus. The oil was dried over anhydrous sodium sulfate and stored at 4-5° C before analysis. The essential oils were obtained by Clevenger distillation and analyzed by GC/MS. About 34 compounds were determined in the flower and leaf of A.eriophora. The major constituents identified by this method were Camphor (21.59%), Artemesia ketone (13.84%), α-Thujone (11.85%), Yomogi alcohol (7.74%), 1,8-cineole (5.19%), Terpinene-4-ol (4.23%).

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Synthesis of benzofurans derivatives through oxidation of catechol derivatives in the presence of ethyl acetoacetate.

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Abstract -The organic compounds, catechols can be easily oxidized to the corresponding reactive o-benzoquinons. Catechols are used in a variety of applications including photography, dying, rubber and plastic production and pharmaceutical industry. Catechol is known as a polyphenol in which two hydroxyl groups are substituted onto benzene ring. Benzofurans have attracted much attention due to their broad spectrum of pharmacolohical activities such as anticancer, antimicrobial , antioxidant, and anti-HIV-1 activities[1].Therefore, the synthesis of benzofuran derivatives have been extensively investigated. High reactivity of o-benzoquinone , the most coupled chemical reactions are following nucleophilic attacks and , thus, the nature of nucleophilic plays an important role in these reaction. In the presence of oxidant, several 5,6-dihydroxylated benzofuran derivatives were synthesized via oxidation-Michael addation of acetyl acetoacetate with catechols (catechol,3-methylcatechol ,3-methoxy catechol) in one-pot procedure .This reaction was carried out under air at room temperature in aqueous medium.

In a round-bottom flask ethyl acetoacetate, acetho nitril , sodium acetate buffer pH 7.0 and catechols derivatives were mixed. Potassium hexa cyano ferat (III) was added at room temperature and stirring was main faired for the 2h.After the reaction was finished ,the reaction mixture was then filtered and washed with water .The resulting crude products were purified by silica column chromatography, using ethyl acetate and coloform as the eluent to obtain the benzofuran product .The final products were confirmed by IR,^{13}CNMR,^{1}HNMR,MS study.

The presence of poor leaving groups or bulky groups on the reactive positions of chemically generated o-benzoquinine, C-3 and C-4, inhibitor slowdown the coupled chemical reactions. The presence of a methyl or methoxy group at the C-3 position of catechols probably causes the Michael acceptors to be attacked by anion enolate ethyl acetoacetate at the C-4 or C-5 position to yield two types of products in each case, but one type product. The electronic effect of C-3 substituent on catechols was investigated and different pathway from that of electrochemical method was proposed based on NMR spectrum. Although the oxidation of final products in this system caused they yield decrease, the described method held promise in the synthesis of 5,6-dihydroxylated benzofuran derivatives due to the facile procedure and the readily available material .

The result of this work show that catechols are oxidized in water to their respective o-quinones. The quinines are then attacked by the enolat anion of ethyl acetoacetate to form benzofuran derivatives .According to our results, it seems that the 1,4-Michael addation of this nucleophile to o-quinones leads to the formation of new benzofuran derivatives as final products [2].The optimization of this method and reaction of various substituted catechols with β-dicarbonyl compounds are in progress.

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Study of Hydrophobic Mismatch Alleviation Mechanism By Molecular Dynamics Simulation of $KALP_{15}$ Peptide in DPPC Bilayer

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Membrane proteins need to undergo conformational changes such as tilting, turning or shifting of one or more α-helices to perform their function. All these changes are as a result of partial reorientation of protein within the membrane, so the surrounding lipid environment has significant influence on the functioning of membrane proteins. A recent review by Hot and Killian [1] has shown the ability of simplified model membranes and peptides as a tool to investigate complex lipid/protein interactions.
We have previously investigated phase transitions of DPPC monolayers at different temperatures and could see obvious liquid condensed-liquid expanded transitions in simulation time scales of 60 ns. [2]
This work is devoted to explore the hydrophobic mismatch alleviation mechanism, using molecular dynamics simulations, for trans-membrane $KALP_{15}$ peptide (Aminoacid sequence: Ac-GKK $(LA)_4$L KKA-NH_2) in DPPC bilayer. Hydrophobic mismatch occurs if the hydrophobic length of the membrane protein does not match the hydrophobic thickness of the membrane.
The DPPC bilayer was constructed from fully equilibrated DPPC monolayer of our previous work [3] at liquid expanded (fluid) phase and 293.15 K which contained 64 lipids and 3655 water molecules, so the resulting bilayer has 128 lipids and 7310 water molecules. The $KALP_{15}$ peptide was created as ideal helix using the software Swiss PDB viewer. [3] The C-terminus was acetylated and the N-terminus amidated and the peptide was solvated in a bath of water and a 2-ns simulation was performed with restraints on the backbone atoms, to ensure that the side chains were relaxed. The peptide was then inserted into the well equilibrated DPPC bilayer using the methodology developed by Faraldo-Gomez *et al.* [4]
After peptide insertion, equilibration simulation was performed on peptide/lipid system for 5 ns, with position restraints on the peptide backbone atoms. Then the system was simulated in production run with no restraints, for 50 ns. The united atom Berger *et al.* force field was adopted to model the lipid bilayer, where the peptide was simulated using the GROMOS force field. The average hydrophobic thickness of 28 A° for DPPC bilayer and the length of hydrophobic stretch of 13.5 A° for $KALP_{15}$ peptide, gives rise to negative hydrophobic mismatch of -14.5 A°.
Inspecting the resulting structure, reveals that the mismatch alleviation dominantly takes place by combination of local bilayer bending and snorkeling of the lysine residues of the peptide. $KALP_{15}$ peptide has four lysine residues that under negative mismatch condition, increase the effective length of the trans-membrane segment by snorkeling. During the simulation time, the peptide remains largely α-helical, and does not undergo significant structural changes, but the adjacent lipids that immediately border the peptide, show drastic structural changes due to peptide addition. This corresponds to the idea of a hard peptide in a soft lipid environment.

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Spectroscopic and conductometric investigation of the interaction of amoxicillin (antibiotic drug) with Zn(II) and Mn(II) ions

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B-lactam antibiotics (e.g., amoxicillin) are traditionally used for the treatment of common bacterial infections in both human and food-producing animals[1,2].Zinc and manganese are so-called biometal since it inters into the composition of some metalloenzemes necessary for the normal course of biochemical processes. Small amount of zinc should be constantly taken in by the human body with food[3-5].
Spectroscopic methods were used for the determination of Amoxicillin using complex formation with Zn (II) and Mn (II) ions.The complexation of reaction between Zn^{2+} and Mn^{2+} metal cations with amoxicillin were studied in aqueous solution at different temperatures using the conductometric method.
The value of log k_f calculated from the absorption spectra and conductivity measurement for Zn(II)-amox and Mn(II)-amox complexes at $25^{\circ C}$. Enthalpy and entropy of complexation were determinate from the temperature dependence of the complextion Constance[6,7]. The interaction of amoxicillin with Zn(II) and Mn(II) ions has been found to form one complex with metal to ligand composition of 1:1.The results show that the complexation formation is affected by the nature of solvents, time, PH, temperature.

Key words: amoxicillin, Zn (II), Mn(II), conductometry and Spectroscopic methods

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The effects of temperature and relative humidity on the extracted compounds from the leaf of flue-cured tobacco

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Most of the chemical and biochemical changes begin during the chlorophyll degradation stage and continue through the early phases of leaf drying. The rates of chemical changes and moisture removal are controlled by varying time, air and leaf temperature, relative humidity, and air velocity in the curing barn, because these variables along with pH, influence enzymatic reactions. Important changes that occur during the flue-curing of tobacco include hydrolysis of starch to free sugars and partial respiration of those sugars to carbon dioxide, hydrolysis of proteins into free amino acids and the conversion of nitrate into nitrite and its subsequent reaction with tobacco alkaloids to form tobacco specific nitrosamines[1,2,3,4]. This study carried out in Tirtash Research and Education center in order to evaluate and determination of the chemical factors and compounds such as: Nicotine, nitrite, total nitrogen, reducing sugar, protein, pH, acidic number, total ash and nitrosamines from tobacco plant. The consideration from 2009 to 2010 showed that the extracts of tobacco at temperature of (36, 42, 48, 54 and 68), relative humidity (85% -15%) and air velocity were different by aspect of the chemicals composition. For this study the tobacco samples were taken based on the same curing conditions, and then analyzed for nicotine (by spectrophotometer), total nitrogen, reducing sugar, protein, pH, acidic number, base salts and nitrite. Finally the amount of nitrosamines (NNN, NNk, NAB and NAT) was determined by using of techniques with liquid chromatography Mass spectroscopy (LC/MS/MS) with follow program: column Waters.XterraMSc182.54um 2.1×5.mm (P/N186…..594), column temperature 65C0, injection volume 5 µL and flow rate 0.25 ml/min.The results showed that the changes of chemical compositions were between 2% - 50%. The reduce sugar and nitrosamines were determined in percentage of 33 and 50 that had the highest changes to other constituents. But the changes of pH and total N (2% - 6 %) were the lowest. In conclusion the studies showed that the temperature and relative humidity regimes change the chemistry and quality of the leaf tobacco.

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Chemical Composition of The Essential Oil of Teucrium orientale From Dehbakri Jiroft

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Abstract

The genus Teucrium (Lamiaceae) is comprised of about 340 species widespread over the world. In the Flora Iranica, this genus is represented by 12 species [1]. Various species of the genus Teucrium are used as antiseptic, antipyretic, antiinflammatory, antispasmodic, antinociceptive, anti-rheumatic, anthelmintic, diuretic, hypoglycemic, diaphoretic, and tonic in folk medicine [2]. Phytochemically, several diterpenoids, diterpenelactones, triterpenoids, flavonoids, and minor phenolic compounds have already been isolated from this plant and analyzed [3-4]. The aims of this study were to extract the essential oils only from the T.orientale. The plant were collected during the flowering priod from Jiroft. Aerial parts of the plants were dried in shade and ground in a grinder. The dried plant samples (400 g) were subjected to hydrodistillation for 5 h using a Clevenger-type apparatus. The oil was dried over anhydrous sodium sulfate and stored at 4-5° C before analysis. The essential oils were obtained by Clevenger distillation and analyzed by GC/MS. About 40 compounds were determined in the flower and leaf of T.orientale. The major constituents identified by this method were Bis (2-ethylhexyl) phthalate (15.42%), β-Cubebene (6.91%), Trans-caryophyllene (6.3%), Camphor (5.9%), Caryophyllene oxide (5.79%).

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Antioxidant, Antimicrobial and Antitumor Activity Evaluation of Total Methanolic Extracts from *Perovskia Abrotanoides Karel* from Kashan

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Aromatic plants have been used since ancient times for their preservative and medicinal properties, and to impart aroma and flavor to food. The pharmaceutical properties of aromatic plants are partially attributed to essential oils. In this research, *Perovskia abrotanoides* Karel from Lamiaceae family from Kashan was investigated. The present study was conducted to evaluate the in vitro antioxidant properties of total methanol extract from aerial part of *Perovskia abrotanoides* Karel. The antioxidative potential of the samples were evaluated using two different methods: a) inhibition of 2,2-diphenyl-1-picryl hydrazyl (DPPH) stable free radical, b) β-carotene-linoleic acid assay. The methanolic extract showed major effectiveness in DPPH assay with an IC_{50} value of 37.88 ± 0.03 μg/ml, comparable to that of synthetic standard antioxidant butylated hydroxy toluene (BHT, IC_{50} = 17.06 ± 0.5 μg/ml). In the β-carotene/linoleic acid assay, the methanol extract was exhibited good linoleic acid oxidation inhibition percentage (80.29%) which was only slightly lower than that shown by BHT (102.34%). Total phenolic contents of methanolic extract of *P. abrotanoides* was (92.92 μg), showing a direct relationship between antioxidant activity and phenolic compounds contents. The methanol extract of the plant also showed considerable antimicrobial activity against most of tested microorganisms but the plant essential oil was inactive in this test [1-2]. The methanol extract was screened by the brine shrimp lethality assay and showed week toxicity in this test (LC_{50}= 583 μg/ml) [3].

Keywords: *Perovskia abrotanoides Karel*, Antioxidant Activity, β-Carotene-Linoleic Acid Assay, DPPH Assay, Antimicrobial Activity, Brine Shrimp Lethality Test

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Interaction of Calf Thymus DNA with [μ-octylen bis(dithiocarbamato)-bis(bipyridine) Palladium(II)] Nitrate. Thermodinamic, Cytotoxic and Spectroscopic Studies

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The design of small transition metal complexes that can interact at specific sequences of DNA is an important research line.
Thus the interaction of Calf Thymus DNA with a new palladium(II) anticancer complex of [μ-octylen bis(dithiocarbamato)-bis(bipyridine) Palladium(II)] Nitrate was studied by isothermal titration method in 30mM Tris_HCl buffer solution (pH=7.0) at 300 and 310K.
There is a set of 26 binding sits(g) for the complex on the DNA with positive cooperativity in binding. n,the Hill coefficient (as a criterion of cooperativity) find out to be 5.6 at 300 K and 7.3 at 310K respectively. K_{app} the apparent equilibrium constant are 21.4 mM^{-1} and 39.3 mM^{-1} at 300K and 310K respectively.
The above compound can denature the DNA and the concentration of this ligand in the midpoint of transition ($[L]_{1/2}$), is decreased by improving temperature, from 0.25 mmol/L at 300K to 0.19 mmol/L at 310K. the conformational stability of DNA in the interaction with ligand (ΔG^0_{H2O}) determined to be 24.5 kJ/mol and 26.7 kJ/mol at 300K and 310K respectively.
Presence of ligand led to less stability of the DNA . values for m, (a measure of ligand strength for DNA denaturation) are 0.61 and 0.74 $(kJ/mol).(mol/L)^{-1}$ at 300K and 310K respectively.
Enthalpy of DNA denaturation by the complex ($\Delta H^0_{coformation}$ or $\Delta H^0_{denaturation}$) in the range of 300K and 310K is find out to be 6.5 kJ/mol. In addition, the calculated entropy (ΔS^0_{H2O}) of DNA denaturation by complex is -0.23 kJ/mol at 300K. the negative value of entropy change is related to the more disorder of denatured DNA with respect to the native DNA.

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Thermodynamics of Binding in the interaction of [μ-hexylen bis(dithiocarbamato)-bis(bipyridine) Palladium(II)] Nitrate with Calf Thymus DNA

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The interaction of Calf Thymus DNA with a new palladium(II) anticancer complex of [μ-hexylen bis(dithiocarbamato)-bis(bipyridine) Palladium(II)] Nitrate was studied by isothermal titration method in 30mM Tris_HCl buffer solution (pH=7.0) at 300 and 310K.

There is a set of 24 binding sits(g) for the complex on the DNA with positive cooperativity in binding. n,the Hill coefficient (as a criterion of cooperativity) find out to be 5.1 at 300 K and 6.9 at 310K respectively. K_{app} the apparent equilibrium constant are 20.9 mM^{-1} and 38.8 mM^{-1} at 300K and 310K respectively.

The above compound can denature the DNA and the concentration mproving temperature, from 0.22 mmol/L at 300K to 0.18 mmol/L at 310K. the conformational stability of DNA in the interaction with ligand (ΔG^0_{H2O}) determined to be 23.4 kJ/mol and 25.9kJ/mol at 300K and 310K respectively.

Presence of ligand led to less stability of the DNA . values for m, (a measure of ligand strength for DNA denaturation) are 0.59 and 0.71 $(kJ/mol).(mol/L)^{-1}$ at 300K and 310K respectively.

Enthalpy of DNA denaturation by the complex ($\Delta H^0_{coformation}$ or $\Delta H^0_{denaturation}$) in the range of 300K and 310K is find out to be 6.3 kJ/mol. In addition, the calculated entropy (ΔS^0_{H2O}) of DNA denaturation by complex is -0.20 kJ/mol at 300K. the negative value of entropy change is related to the more disorder of denatured DNA with respect to the native DNA.

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Binding Propertise of a New Anti-tumor Component [μ-buthylen bis(dithiocarbamato)-bis(bipyridine) Palladium(II)] Nitrate with Calf Thymus DNA

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Metal- based drugs have been used in therapeutic medicine for several hundreds of years and are used in contemporary society for the treatment of a large variety of human ailments, e.g., cancer, diabetes, and rheumatoid arthritis, as well as in diagnostic medicine.

Dithiocarbamates have also been investigated for anti-cancer potential, must notably platinum and palladium dithiocarbamates. Based on cytotoxicity assays, often the metal-containing dithiocarbamate compounds show greater potency than cisplatin but, are not as cytotoxic as other standard drugs.

Thus the interaction of a new palladium(II) antitumor complex of [μ-buthylen bis(dithiocarbamato)-bis(bipyridine) Palladium(II)] Nitrate with Calf Thymus DNA was studied by isothermal titration method in 30mM Tris_HCl buffer solution (pH=7.0) at 300 and 310K.

There is a set of 23 binding sits(g) for the complex on the DNA with positive cooperativity in binding. n,the Hill coefficient (as a criterion of cooperativity) find out to be 4.9 at 300 K and 6.8 at 310K respectively. K_{app} the apparent equilibrium constant are 21.0 mM^{-1} and 39.2 mM^{-1} at 300K and 310K respectively.

The above compound can denature the DNA and the concentration of this ligand in the midpoint of transition ($[L]_{1/2}$), is decreased by improving temperature, from 0.21 mmol/L at 300K to 0.18 mmol/L at 310K. the conformational stability of DNA in the interaction with ligand ($\Delta G^0{}_{H2O}$) determined to be 24.3 kJ/mol and 26.2 kJ/mol at 300K and 310K respectively.

Presence of ligand led to less stability of the DNA . values for m, (a measure of ligand strength for DNA denaturation) are 0.55 and 0.72 $(kJ/mol).(mol/L)^{-1}$ at 300K and 310K respectively.

Enthalpy of DNA denaturation by the complex ($\Delta H^0{}_{coformation}$ or $\Delta H^0{}_{denaturation}$) in the range of 300K and 310K is find out to be 5.6 kJ/mol. In addition, the calculated entropy ($\Delta S^0{}_{H2O}$) of DNA denaturation by complex is -0.16 kJ/mol at 300K. the negative value of entropy change is related to the more disorder of denatured DNA with respect to the native DNA.

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Identification of bioactive compounds in *Scilla Persica HAUSSKN and Scilla Natalensis*

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ABSTRACT

The presence of some chemical substances in medicinal plants results in a definite physiological action on the human body. The most important of bioactive compounds in plants consist of alkaloids, flavonoids, tannins and phenolic compounds [1]. Knowledge of the chemical constituents of plants is desirable, not only for the discovery of therapeutic agents, but also such information may disclose new sources for bioactive compounds and precursors in the synthesis of complex chemical substances [2-3]. In the present study, the bulbs of *Scillapersica HAUSSKN* and *Scillanatalensis* were obtained from university of Golestan (Gorgan, Iran) and university of Natal Botanical Garden (Pietermaritzburg, Africa), respectively. The bulbs were cut into pieces, dried overnight for a week, and shaken in 80% MeOH (100 ml) and EtOAC (100 ml) for 72 h. The solvent was then evaporated at 72^0C until a very concentrated extract was obtained. Identification tests were carried out to investigate the presence of alkaloids, anthocyanosides, anthraquinones, flavonoids, glycosids, phlobatannins, reducing suger, saponins, tannins, terpenoids and steroids. The results indicated that only, the MeOH extracts of two species showed alkaloids, anthraquinons, glycosides, reducing sugars and saponins. Flavonoids were found in both extracts while steroids only existed in EtOAC extract for both species. For the study of anthocyanosides, 20 g of the fresh plant was boiled in distilled water. Then, 1 mL of the filtered solution was mixed with 5 mL diluted HCl. A pale pink color was observed only for *S. Percica HAUSSKN* (positive test). The identification test for phlobatannins showed red precipitate (positive test) only for MeOH extract of *S. Natalensis*. Tannins were also observed in both extracts of *S. Percica HAUSSKN.* The results showed that terpenoids did not occur in two species.

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Comparative study of solvent polarity effects on radical-scavenging activity of fractions obtained from column chromatography for *Pterocarya fraxinifolia* L.

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Pterocarya fraxinifolia L.from Juglandaceae Family, plant found in southern shores of the Black and Caspian Seas [1]. This plant is used as a good dyeing and antifungal agent by local people [2]. There is only one report about evaluating of antioxidant activity of *P. fraxinifolia* L. in the literature [3]. In this research work, methanol extract of the mentioned plant was obtained by using soxhlet. According to high antioxidant potential of methanol extract, in order to achieve effective fraction of the extract, column chromatography was performed; the sequential extraction was realized with four solvents of different polarities (methanol, chloroform, ethyl acetate, hexane) to achieve four fractions. Antioxidative potential was tested by measuring their ability to scavenge stable 2,2-diphenyl-1-picrylhydrazyl (DPPH). Results demonstrated that the radical inhibitory depends on type and concentration of applied extracts and increases in the following order: ethyl acetate > methanol > chloroform > hexan. This is also stablished that radical inhibitory increases with increasing concentration for all extracts.

Keywords: *Pterocarya fraxinifolia* L., radical-scavenging, column chromatography

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Phytochemical analysis of *Pterocarya fraxinifolia* L. from Guilan

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Knowing about chemical constituents of plants is desirable, not only for discovery of therapeutic agents, but also because such information may be of value in disclosing new sources of economic materials for example tannins, oils, gums, as precursors for synthesis of complex chemical substances. In addition, knowledge of chemical constituents of plants would further be valuable in discovering actual value of folkloric remedies [1].

P. fraxinifolia is an indigenous plant found in southern shores of the Black and Caspian Seas [2]. Juglone, a naphthoquinone compound, is established in the leaves and hulls of *P. fraxinifolia* [3,4].

This report is about first study of phytochemical analysis of *Pterocarya fraxinifolia* L. leaves (Juglandaceae family). Methanol extract was prepared using perculation method, phytochemical analysis was carried out, major identified constituents of extract exhibits high amounts of tri-terpenes and tannins in methanol extract of *P. fraxinifolia*. However, the extract contained low concentration of flavonoids, anthraquinones, heart glycoside.

Keywords: Phytochemical analysis, *Pterocarya fraxinifolia* L, Juglandaceae

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Microwave-assisted and conventional hydrodistillation of essential oils from *Zhumeria majdae* Rech. f. & Wendelbo

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The monotypic and endemic Iranian *Zhumeria majdae* Rech. f. & Wendelbo, belonging to the Labiatae family, was recently described as the first member of a new genus of *Zhumeria* [1]. It has a limited geographical range in southern Iran [2]. In folk medicine, the leaves of the plant have been used for many years as a curative for stomach aches, as an antiseptic, and for the treatment of painful menstruation [3]. Also, the antinociceptive, anti-inflammatory, and acute properties of the extract of *Z. majdae* were reported [4]. There are many methods to obtain essential oils from the plant materials. Microwave-assisted hydrodistillation (MAHD) is an advanced hydrodistillation (HD) technique, in which a microwave oven is used in the extraction process [5]. In this study, *Z. majdae* was collected from Geno mountain, Hormozgan province, south of Iran, in May 2011. HD and MAHD methods have been compared for their effectiveness in the isolation of essential oils from aerial parts of the plant. The MAHD method was superior in terms of saving energy and extraction time (20 min, compared to 3 h in HD). The composition of the extracted oils was investigated by GC and GC/MS. GC analysis was carried out using a Shimadzu 15A instrument coupled to a flame ionization detector (FID). An Agilent 5975C mass spectrometer coupled to an Agilent 7890A gas chromatograph equipped with a HP-5MS capillary column was used for GC/MS analysis. The components of the essential oils extracted by both HD and MAHD methods were similar and the two oils contained the same dominant constituents: linalool (39.2% and 42.6%), camphor (25.7% and 27.1%), limonene (8.7% and 5.8), and camphene (5.6% and 4.2%), respectively. As a result, in order to reduce the extraction time, MAHD can be used for the extraction of metabolites from the herbs instead of conventional HD. In addition, compared to many solvent extraction techniques, MAHD can be suggested as an "environmentally friendly" and green extraction method [6].

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((Organic chemistry/ phytochemistry))

Investigation and determination of carbohydrates, nutrient content and heavy metals in Scorzonera paradoxa plant

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Carbohydrates are a group of polyhydroxy aldehydes, ketones, acids or their derivatives, together with linear and cyclic polyols. Sometimes, carbohydrates are referred to simply as sugars and their derivatives. Carbohydrates are found abundantly in nature, both in plants and animals, and are essential constituents of all living matter [1]. In the other hand understanding the nutrient content of a plant body will be a useful way for determining rangeland capacity, the most proper time of utilization of range plants, prediction of malnutrition and evaluation of nutrition requirements of plants [2].Scorzonera paradoxa Fisch. & C.A. Mey. with native name "Naghoodeshk, a member of Asteraceae or compositae family [3], is used as vegetable in east of Iran, and is an adaptable plant of central sandy areas of Iran.

The current research, we evaluate Naghoodeshk properties including carbohydrates, crude protein (c.p) and fat content using Deriaz (1961), Kjeldahl (1965) and Soxhlet extraction methods respectively, crude fiber, neutral detergent fiber (NDF), acid detergent fiber (ADF) according to the method of Goering and Van Soest (1970) and heavy metals such as Ag, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, Zn, P using Korouri et al (1982) method.

$$\text{Plant} \xrightarrow[\text{2) HCl 37\%} \quad \text{3) } \Delta \text{ /5 min}]{\text{1) 550 } ^{0}\text{C/ 8h}} \text{Solution of Ash for Ana. Heavy Metal}$$

$$\text{Plant} \xrightarrow[\text{2) NaOH 40\%} \quad \text{3) } H_3BO_3 \quad \text{4) HCl}]{\text{1) } H_2SO_4 / K_2SO_4 / CuSO_4 / SeO_2 / 420\ ^{0}\text{C}} \text{Determination of Crude Protein}$$

The results showed that a higher quantity of the above elements exist in the leaf compared to the root. The leaves are rich in Fe, Mg, Mn and Zn in concentrations of 25-500 ppm whereas the quantity of Fe and Mn are considerable in the root. Amount of ash, crude protein (c.p) and fat content in leaf were higher than root and amount of crude fiber, ADF, NDF and energy have a higher quantity in the root compared to the leaf.

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((Organic chemistry/ phytochemistry))

The study of phenolic compounds, flavonoids and tannins in Scorzonera paradoxa Fisch. & C. A. Mey native of south khorasan province

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Phenolic Compounds are large group of structurally diverse naturally occurring compounds that possess at least a phenolic moiety in their structures. These compounds encompass various structural types such as tannins and flavonoid [1]. It has been reported that phenolic compounds display a wide range of pharmacological activities, such as anti-inflammatory, anti-neoplastic and anti-oxidant [2]. So, the identification and determination of phenolic compounds in Scorzonera paradoxa Fisch. & C. A. Mey. will play an important role in the further development and use of this herb.The Scorzonera paradoxa Fisch. & C. A. Mey, a member of Asteraceae or compositae family, with native name "Naghoodeshk" is used as vegetable in east of Iran. Plant prennial, herb; tuber clubform, long ovate; leaves ovate, acute, light green to blue or silver, rarely red, flower purple to violet and flowering time is May – June [3].

In this study we have determind Phenolic Compounds, Flavonoids in five different extracts (Et_2O, $CHCl_3$, EtOAc, n-BuOH, and H_2O) and Tannins in the acetone extract using Singleton et al. (1999), zhuang et al. (1992) and Mak Car et al. (1992) methods, respectively.

$$\text{Sample Extract} \xrightarrow[\text{2) } Na_2CO_3 \text{ 10\% / 1h}]{\text{1) Folin- Ciocalteur reagent / 3min}} \begin{matrix}\text{Total Phenolic Contents}\\ \text{(The Absorbance in 760 nm)}\end{matrix}$$

$$\text{Sample Extract} \xrightarrow[\text{2) } AlCl_3 \text{ 10\% /6min} \quad \text{3) NaOH 1M}]{\text{1) } NaNO_2 \text{ 5\% /5min}} \begin{matrix}\text{Flavonoid-Aluminium Complex}\\ \text{(The Absorbance in 510 nm)}\end{matrix}$$

A significant amount of these compounds has also been observed in the H_2O extracts of both examined plant tissues. The smallest quantity of these compounds was found in the Et_2O and $CHCl_3$ extracts.

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Synthesis and Thermodynamics of Binding in the interaction of a water soluble and anti-cancer Platinum (II) complex with Calf Thymus DNA

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A new platinum (II) anticancer complex of [Pt(phen)(pyr-dtc)] (where phen is 1,10 phenanthrolin and pyr-dtc is pyrrolidindithiocarbamate) was synthesised and the interaction of this complex with Calf Thymus DNA was studied by isothermal titration method in 30mM Tris_HCl buffer solution (pH=7.0) at 300 and 310K.
There is a set of 6 binding sits(g) for the complex on the DNA with positive cooperativity in binding. n,the Hill coefficient (as a criterion of cooperativity) find out to be 3 at 300 K and 5at 310K respectively. K_{app} the apparent equilibrium constant are 42.5 mM^{-1} and 49.5 mM^{-1} at 300K and 310K respectively.
The above compound can denature the DNA and the concentration of this ligand in the midpoint of transition ($[L]_{1/2}$), is decreased by improving temperature, from 0.093 mmol/L at 300K to 0.087 mmol/L at 310K. the conformational stability of DNA in the interaction with ligand (ΔG^0_{H2O}) determined to be 23.4 kJ/mol and 25.9kJ/mol at 300K and 310K respectively.
Presence of ligand led to less stability of the DNA . values for m, (a measure of ligand strength for DNA denaturation) are 0.65 and 0.79 (kJ/mol).$(mol/L)^{-1}$ at 300K and 310K respectively.
Enthalpy of DNA denaturation by the complex ($\Delta H^0_{coformation}$ or $\Delta H^0_{denaturation}$) in the range of 300K and 310K is find out to be 6.3 kJ/mol. In addition, the calculated entropy (ΔS^0_{H2O}) of DNA denaturation by complex is -0.17 kJ/mol at 300K. the negative value of entropy change is related to the more disorder of denatured DNA with respect to the native DNA.

Keywords: Thermodynamic Studies, anti-cancer Palladium (II) complex

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An Efficient Synthesis of 1,2-Diarylethanes by Iron Nanoparticles Promoted Cu(I) Catalyzed Homocoupling of Arylmethyl halides

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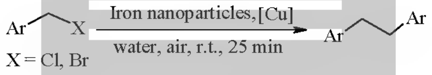
The development of useful reagents and efficient catalysts which enable carbon-carbon bond formation, is a key part of contemporary organic synthesis. The reductive coupling of organic halides is an important method for C–C bond formation where Wurtz and Ullmann reactions are classical methods for the preparation of bialkyl and biaryl compounds. Transition metal catalyzed coupling reactions between organic electrophiles and organometallic compounds constitute the most straightforward approach for the formation of C–C bonds.[1]

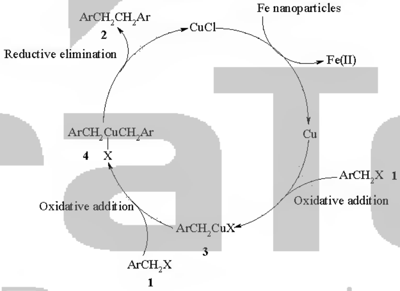
Recently transition-metal nanoparticles have attracted a great deal of attention; their preparation, structure determination, and applications are topics of current interest.[2] One of these applications is their use in reactions generating C–C bonds.[3]

We report herein an improvement of homocoupling of benzylic halides under mild conditions. Thus a mixture of an arylmethyl halide **1**, iron nanoparticles and a catalytic amount of CuBr in air and water undergo a reductive homocoupling reaction at room temperature to afford 1,2-diarylethanes **2** in excellent yields.



1 2

A mechanistic rationalization for this reaction is provided below.



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N-Heterocyclic carbenes related to quinazoline at DFT

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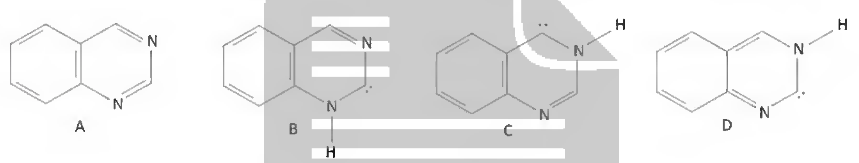
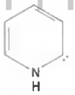
There is some scattered information about pyridine derived N-heterocyclic carbenes (NHCs) first proposed as a reaction intermediate 70 years ago by Hammick [1, 2]. Close to pyridine the quinazoline ring as an unstable compound, **A** (Scheme1), along with many alkaloids, is a widely recognized moiety in organic syntheses and medicinal applications [3].

Scheme 1. Three carbenic tautomers of quinazoline



The current work covers both thermodynamic and kinetic aspects of three carbenic tautomers of quinazoline **B**, **C** and **D** based on a DFT (B3LYP/6-311++G**) approach (Table 1). All carbene isomers are found to be planar. In these carbenes, the singlet states more stable than their corresponding triplets. Among these carbenes, **C** appears to be the most stable one. Also the highest amount of HOMO-LUMO gap is obtained for **C** indicating higher stability. In contrast, the heat of hydrogenation is less negative for **D**. The aromaticity of rings is estimated using NMR calculations. In these structures, all phenyl rings are considerably aromatic with large negative NICS(1)zz, while pyrimidine rings appear less aromatic. Interestingly, the pyrimidine ring of **D** is more aromatic than those of **B** and **C**. The beauty of our results is in the structure **D** both electrophilicity and nucleophilicity are the largest. Comparison of these data with those of pyridine-2-ylidene shows a comparable stability and/or viability.

Table 1. Calculated thermodynamic data for the three carbenic tautomers of quinazoline at B3LYP/6-311++G**.

Structure	$\Delta E_{s\text{-}t}$ (kcal/mol)	ΔE_H (kcal/mol)	E_{HOMO} (au)	$\Delta E_{H\text{-}L}$ (kcal/mol)	N (eV)	ω (eV)	$NICS(1)_{ZZ\ (phenyl\ ring)}$ (ppm)	$NICS(1)_{ZZ\ (pyrimidine\ ring)}$ (ppm)
B	30.6	-46.6	-0.199	67.77	4.02	2.66	- 28.6	- 17.6
C	44.9	-43.4	-0.214	89.73	3.62	1.92	- 29.0	- 17.7
D	28.6	-34.1	-0.190	58.36	4.27	3.00	- 26.8	- 23.9
	38.4	-41.2	-0.197	87.9	4.09	1.57	-	-

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DFT study of alkaline metals interactions with some diazabicycloalkanes, structure and stability constant

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Numerous natural and physiologically active compounds contain a substituted diazabicycloalkanes (Figure 1) fragment in their molecules. Examples are alkaloids of the tropane [1] and calystegine series [2]. (–)-Cocaine (**I**) is the most known alkaloid of the tropane family [3]. In order to importance of these compounds we have been studied the structures of some Diazabicycloalkanes by quantum mechanics theoretically methods. All the calculations have been performed using the GAUSSIAN 09 quantum chemical package. Method of B3LYP in combination with basis set, 6-311++g (d,p) has been employed in searching for the most stable structures. In all the cases, the steady-state nature (minimum on the potential energy surface) of the optimized ligands, complexes and cation has been confirmed by calculating the corresponding frequencies at the same computational level. Calculations were carried out at gas phase, H_2O solvent, CCl_4 solvent separately and standard conditions (P=1atm, T=298.15K).the free Gibbs energy of complex formation reaction and stability constant have been determined as: K_P = stability constant

$L + M^+ \rightarrow LM^+$ (L=Diazabicycloalkanes , M^+=Li^+ and Na^+)

$\Delta G^o(298) = G^o(298)(LM^+) - [G^o(298)(M^+) + G^o(298)(L)]$

$\Delta G(298) = \Delta G^o(298) + RTLnK_P$ and $\Delta G(298) = 0$ SO $\Delta G^o(298) = -RTLnK_P$

The results show in gas phase the complexes are formed very favoritely, but in presence of H_2O as solvent these complexes are not formed, meanwhile in CCl_4, these complexes have K_P>> 1.

(R=H, CH_3)

Figure 1

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Covalent Immobilization of α -amylase onto Covalent immobilizationof alpha amylase on activated organo-montmorillonite (Cloisite 30B) as a new and efficient support

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Abstract:

activated cloisite is described. The effect of hydrophilic or hydrophobic nature of the support, the reuse efficiency, and kinetic behavior of covalent immobilized α-amylase were studied. The effect of substrate concentration on enzymatic activity of the free and covalent immobilized enzymes showed a good fit to the Michaelis–Menten plots. The covalent immobilization of enzymes onto insoluble supports is a topic of active research in enzyme technology and is essential for their application to industrial processes. Various methods exist for immobilization of enzymes, and these may be divided into two main categories: (1) physical methods based on molecular interactions between the enzyme and support, and (2) chemical methods based on formation of covalent bonds. The hydrolysis of starch to products with low molecular weight,catalyzed by a-amylase (1,4-a-D glucan glucanohydrolase; E.C.3.2.1.1), is one of the most important commercial enzymic processes . Conversion of starch into sugars,syrups and dextrins forms the major part of the starch processing industry. Immobilization of amylase on, mainly,water insoluble carriers, seems to be the most promising way to obtain more stable and reusable forms of enzymes. The activity of α-amylase on activated cloisite at the optimum pH was 58.9%. The adsorptiherm was modelled by the Langmuir equation. The amounts of the covalent α-amylase immobilized on activated cloisite at highest activity were 68.6%.

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Computational Analysis on the Barrier to Rotation about the C-N Bond in P-methylphenylcarbamate

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Carbamates are of particular interest due to their usefulness in various industries as agrochemicals (herbicides, fungicides and pesticides), in the pharmaceuticals industry as drug intermediates, and in the polymer industry in the synthesis of polyurethane and also in peptide syntheses. In addition, among the various amine-protecting groups, carbamates are commonly used due to their chemical stability toward acids, bases, and hydrogenation. In particular, the pharmacological activity and the importance of syn and anti rotamers of carbamates in their biological activities motivated detailed investigations of the energetic properties of these systems as conformational switches in molecular devices [1].

Carbamates have conjugated C-N bond with fairly high barriers to rotation [1-3] because the strength of the interaction between the nitrogen lone pair and carbonyl group is reduced by the competing interaction between the opposing oxygen atom and the same carbonyl. One of the oxygen lone pairs is able to donate into the carbonyl л system and thereby partially compensate for the loss of л interaction with the nitrogen lone pair when C-N bond rotation takes place [1-3].

The present investigation included several levels of calculation at the HF/6-311++G(d,p), B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p). Transition states (TS1 and TS2) generated by rotation over the central C-N bond of the planar ground state (GS) and activation parameter ($\Delta H^{\neq}$) were determined computationally.

Table: Calculated Barrier to Rotation about the C-N Bond in P-methylphenylcarbamate (kcal/mol)

	HF	DFT	MP2
$\Delta H^{\ddagger}_1$	15.905	15.309	11.447
$\Delta H^{\ddagger}_2$	15.489	15.658	14.695

$\Delta H^{\ddagger}_1$= TS1-GS, $\Delta H^{\ddagger}_2$= TS2-GS

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Structural analysis of tetra acetyl dibenzyl hexaaza isowurtzitane (TADBIW) by DFT method

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High-energy density materials play an important role in aeronautics, the weapons industry and other high-tech fields in which cage structural compounds have raised popular interest due to high density, high energy and high tension. The 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane(HNIW or CL-20) was first synthesized in 1987 by Nielsen [1] and was applied by military and industry. Several experimental works including studies of synthesis pathways [2], properties [3,4] of CL-20 have been carried out. The compound of tetraacetyldibenzyl hexaazaisowurtzitane (TADBIW) is an important precursor of synthesizing the high energetic dense compound of CL-20[4]. The basic structure of TADBIW is shown in Fig.1.

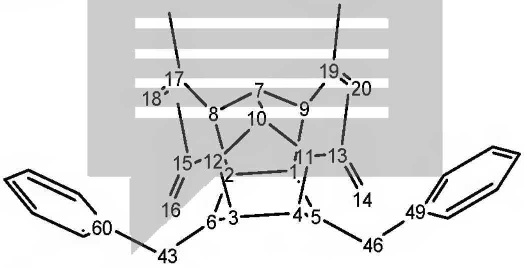

Figure 1. The atom numeration for tadbiw molecule used for calculations.

The conformational analysis and electronic structure of tetraacetyldibenzyl hexaazaisowurtzitane (TADBIW) were studied by density functional theory (DFT) .Six conformers for TADBIW were obtained. Full geometry optimization, AIM and NBO analysis for the conformers were performed at the B3LYP/6-311++G (d,p) level. The results show that the C–C bond linking two five-membered rings and the boat shaped six-membered ring are important factors in stabilizing molecular structure. Furthermore, computational results reveal that skeleton tension, repulsive interactions and steric hindrance are three superior factors that determine the most stable conformer of TADBIW.

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Conformational analysis, intramolecular hydrogen bonding and investigation of solvent effect on the β-dinitroso compounds as dithionitrosamine

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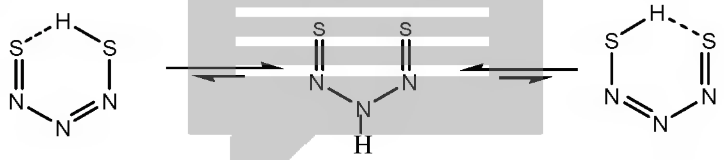
The nitrosamines constitute a family of potent carcinogens, which are formed readily from a diverse set of nitrogen compounds and nitrite or its derivatives [1, 2]. Similarly, N-thionitrosoamines, which are organic compounds that contain a new functional group, the thionitroso unit (-N=S), have been prepared by reaction of 1, l-dialkylhydrazines with sulfur and by reduction of thionylhydrazines. The thionitrosoamines are highly colored compounds. Spectral evidence suggests that a dipolar resonance structure contributes to their over-all electronic structure [3].By substituting a thionitroso group in the one of hydrogen atoms of thionitrosamine(DTA), a new compound called dithionitrosamine, is introduced. This compound can participate in the di thionitrosamine (DTA) ↔ 2-mercapto1-thionitrosodiazene (MTD) tautomeric equilibrium (Fig. 1), which two tautomers interconvert to each other in tautomeric equilibrium.



DTA MTD DTA

The conformational analysis for different conformers of dithionitrosamine were carried out at B3LYP and MP2 levels with the standard basis set, 6-311++G (d,p). In general, the thionitrosamine(DTA) tautomers are more stable than the 2-mercapto1-thionitrosodiazene (MTD) ones . Surprisingly, the chelated MTD form with S-H···S intramolecular hydrogen bond (IHB) is not a conformation in equilibrium. In spite of this instability, the IHB for this form (MTD-11) was comprehensively studied to evaluate the effect of hetero atom (N) on the characteristic of IHB system. The evaluation of hydrogen bond energy by different methods clearly predicts that the hydrogen bond strength in MTD-11 is lower than the malonaldehyde(MA). In addition, the solvent effects on the properties of DTA tautomers are estimated by continuum solvent (PCM, IPCM, and SCIPCM), discrete and mixed models. Theoretical results clearly show that the potential energy surface of DN, especially global minimum, is strongly affected by the solvent.

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Hammett equation in the rate and equilibrium constant of keto-enol Tautomerism

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Free energy relationships can be used to provide simple methods for calculation of useful molecular parameters and to understand the mechanism of reactions [1]. One of the most famous relations in this area is Hammett equation [2]. Since 1937, many kinds of organic reactions have been treated by the Hammett equation or its extended form and many studies especially in chemistry and biology have been reported in this area. For example, protein linkages and interaction with enzymes [3], antitumor properties [4], and many other biologic purposes [5] of organic molecules were reported using these equations. Therefore, in continuation of our interest on the theoretical study of tautomerism in organic compounds, we have decided to study of relation between Hammett constants and energetic parameters of tautomerism.

We have selected a usual keto-enol system (para-acetophenone derivatives) to apply a Hammett equation. The optimizations of all structures (isomers and transition states) and frequency calculations were carried out using B3LYP/6-311++G** level of theory [6]. Calculations were carried out using the Gaussian 98 program package [7]. First ten para-substituted acetophenone derivatives were selected and the structures of their keto and enol tautomers and transition state were optimized using DFT calculations. Then, thermodynamic data for optimized structures were calculated using frequency calculations and atomic charges were calculated from NBO calculations. From the outputs of calculations, graphical representation of optimized structures, molecular parameters, atomic charges, energy values and diagrams of relation between Hammett constants and energy values of tautomerism were shown. Moreover, the effects of different solvents (methanol, chloroform, tetrahydrofuran, acetone and water) on the equilibrium constants, rate constants and Hammett relations were calculated and the results were shown in tables and figures. Details of computations and the results obtained in this work are presented below.

The results show linear relations between $\log(Keq/Keq_H)$ (logarithmic ratio of equilibrium constants) and σ_p, σ_R or R values. Moreover, the same relations between $\log(k/k_H)$ (logarithmic ratio of rate constants) and σ_p, σ_R or R values were found in the gas phase and five different solvents. The best correlation was observed when σ_p values were used as substituent constants. The other diagrams using σ_m, σ^+, σ^-, σ_I, σ^+_m or F as substituent constants were not shown acceptable regressions or appropriate correlation coefficient. The diagrams of $\log(Keq/Keq_H)$ (versus substituent constants) showed positive slopes (ρ) while diagrams of $\log(k/k_H)$ showed negative slopes. In other words, by the increase of electron-withdrawing property of para-substituent, the equilibrium constant increases while the rate constant decreases.

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Dynamic ^{1}H NMR Study Around the Carbon–Carbon Double Bond in the Stable Phosphorus Ylides Derived from the Reaction Between Triphenylphosphine and Dimethyl Acetylenedicarboxylate in the Presence of SH-Heterocyclic Compound

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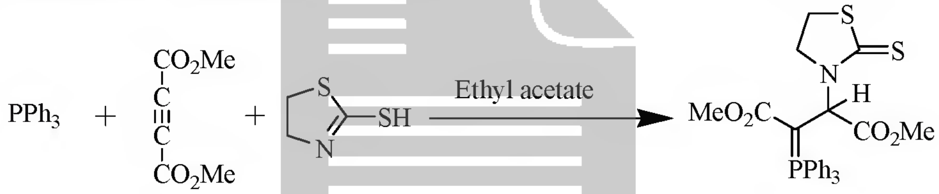
Phosphorus ylides are reactive systems which take part in many valuable reactions of organic synthesis [1]. Stable crystalline phosphorus ylides were obtained in excellent yields from the 1:1:1 addition reaction between triphenylphosphine **1** and dimethyl acetylenedicarboxylate 2 in the presence of strong SH-acid 2-thiazoline-2-thiol **3** [2] (scheme 1).



1 **2** **3** scheme 1 **4**

These stable ylides exist in solution as a mixture of two geometrical isomers as a result of restricted rotation around the carbon–carbon partial double bond resulting from conjugation of the ylide moiety with the adjacent carbonyl group. Dynamic effects are observed in the ^{1}H NMR spectra that are attributed to the restricted rotation around the carbon–carbon double bond. The experimental energy barrier ($\Delta G^\#$) and other activation parameters ($\Delta S^\#$, $\Delta H^\#$) on the basis of the ^{1}H NMR study for the rotational interchangeable process of major and minor isomers in ylides **4** are reported (scheme 2).

Z-4 scheme 2 **E-4**

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Theoretical Study on Thermal Stability of Novel Poly (amide-imide) s based on ab Initio Method

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Aromatic poly (amide–imide) s (PAI) s as high performance polymeric materials has been noted for their excellent characteristics such as thermal stability [1, 2]; there are relationship between structural parameters (such as bond lengths and donor-acceptor electronic delocalization, bonding, nonbonding and antibonding orbital occupancies and energies) and thermal stability [3]. In this project, a novel diacid as monomer was prepared successfully by condensation reaction of 3, 3'-diamino diphenyl sulfone and trimellitice acid in a medium consist of acid acetic solution at refluxing temperature, the structure of monomer was determined by FTIR, elemental analysis and melting point. In continuation tree kind of poly (amide-imide) s were synthesized by polycondensation reaction between new diacid and tree different diamine (4, 4'-diamino diphenyl sulfone, 4, 4'-diamino diphenyl ether and 3, 4-diamino benzophenone) in high yield 95%, 97% and 76%, respectively, in presence of triphenyl phosphite, $CaCl_2$ and pyridine in N-methyl-2-pyrolidone (NMP) as solvent, these (PAI) s were characterized by FTIR, elemental analysis, inherent viscosity, UV-visible spectroscopy, thermal properties of new PAIs were evaluated by DSC and TGA. The structures of the smallest common units of (PAI) s have been optimized and analyzed by HF/3-21G level of theory and natural bond orbital (NBO) interpretation. NBO results indicate that there is a direct relationship between the structural parameters (especially bond lenghts) and the electron delocalizations. In addition, there is a direct relationship between the thermal stability and the stabilization energies associated with the electron delocalizations.

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Theoretical descriptors response to the calculations of the pK_a values of some boronic acids in aqueous solution :A DFT study and NBO analysis

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With the specific target of calculating the pK_a value of boronic acids ($RB(OH)_2$) in aqueous solution we inquired the solute-solvent interactions of these acids and their corresponding conjugated bases. Relative pK_a values were computed for each boronic acid using methylboronic acid ($CH_3B(OH)_2$) as a reference point. All gas phase computations were performed at level (MP2/6-311++G (d,p) // B3LYP/ 6-31+G (d)). Solvation was included in the calculations using the polarized continuum model (PCM) at the HF/6-31G (d, p) level. The geometry optimization of studied structures performed with DFT computation and these are used to carry out Natural Bond Orbital (NBO) analysis. NBO analysis performed at level (B3LYP/ 6-31+G (d) of theory. A part of Natural Bond Orbital (NBO) analysis was examined as indicator for the variations observed in the calculated pK_a, including natural population analysis charges (Qn) on atoms of the dissociating boronic acid group. The results reveal that difference in acid strength is more relevant to the type of substituent and namely electron withdrawing substituent will increase the acidic nature and donor group to act quite contrary and decrease the acidity character. In the different isomers of a one type substituent (Para, Meta and Ortho), spatial effects was dominant on electronic effects and it had the most dominant role in determining the acid strength. Natural resonance theory (NRT) is used to calculate of natural bond order and prediction polarity of bond. The NRT result indicates that the O-H bonds in all studied cases have an electrovalency character.

There are good agreement between theoretical values and experimental results for this series of compounds, the average error has been demonstrated to be less than 1.2 pK_a unit.

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Photochromic; solvatochromic and electrical behaviour of new synthesized 1,3-diazabicyclo[3.1.0]hex-3-enes based on chalcones

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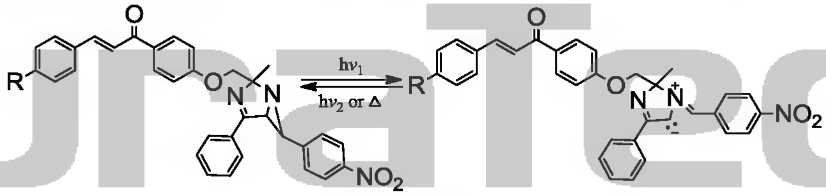
Study of photochromic materials has drawn great attention to their significant application in optical data storage, holographic storage, solar cells and as sensitizers [1-4]. Chalcone derivatives are known to exhibit excellent cytotoxic, antioxidant, antibiotic, and anticancer, activities [5]. In this article, new type of photochromic 1,3- diazabicyclo[3.1.0] hex-3-enes derivatives having a chalcone unit, were synthesized (Scheme 1). The final compounds was isolated, purified and charactrized utilizing IR, ^{1}H NMR, ^{13}C NMR and UV spectra. Their optical and electrochemical properties, such as photochromism, solvatochromism, photochromic kinetics and cyclic voltammetry were investigated in detail. The photochromism and photochromic cycloreversian-cyclization kinetics from closed photo-isomer to open photo-isomer form of target photochromic in EtOH were investigated by UV light (254 nm). For investigation of solvatochromism, several protic and aprotic solvents were used the concentration of all solutions was chosen 10^{-4} mol / lit. and the resulting absorption maxima wavelength was obtained via UV-VIS spectrophotometry. A conventional parameter in solvatochromic studies is absorption maximum λ_{max}. In this work the ring-opening and ring-closing for the bicyclic aziridin moieties were considered by us. The electrochemical behaviour was tested by oxidative cyclic voltammetry. The closed photo-isomer is always easier to oxidize than the open photo-isomer one. The results show that all of these compounds contained good photochromism, high quantum yield, interesting solvatochromic effect and electrical properties.



Scheme 1

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Theoretical Investigation Regarding the Kinetics and Mechanism of the Reaction Between Triphenylphosphine, Dialkyl acetylenedicarboxylates and C-H Acid

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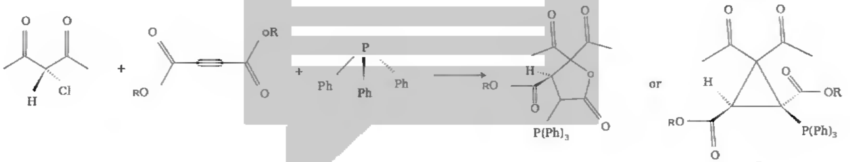
In the recent work, quantum mechanical calculations have been performed for proposed mechanism of the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of C-H acids such as 3-chloroacetylacetone in the gas phase (following Figure). All calculations were carried out at the HF/6-311G(d,p) level by using gaussian03 in gas phase. The results showed that the first and third steps of mechanism reactions are rate determining and fast steps, respectively. Moreover, activation parameters ($\Delta G^{\neq}$, $\Delta S^{\neq}$and $\Delta H^{\neq}$) along with kinetics parameters (k and Ea) were calculated for each step and overall reactions. Theoretical data had a good compatible with the experimental data.



1 2 3 4 5

R	product
Me	4
T-Bu	5

Figure. Synthesis of reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of C-H acids such as 3-chloroacetylacetone in the gas phase.

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Induced effects on the stability enol-keto forms and intra molecular hydrogen bond strength in the ethyl-2 ,4-dioxo-4-phenyl butanoate and dimethyl oxaloacetate

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Abstract:

β-Dicarbonyls are capable of enol-keto tautomerism. The position of the enol-keto equilibrium for this class of compounds differs according to electronic characteristics of the substituents. Comparision stability of enol-keto forms and the hydrogen bond strength were investigated by electron-withdrawing and electron donation effects in ethyl-2,4-dioxo-4-phenyl butanoate (EDPB) and dimethyl oxaloacetate (DMOA) by means of density function theory (DFT) at B3LYP/6-311G++ level. We applied the calculations in Gaussian program package. Depending on the position of the enolated proton, the occurrence of two classes of cis-enol forms is possible for EDPB and DMOA. Considering the theoretical calculation of HF (absolute energy in Hartree), E_{IHB} in EDPB and DMOA we understand that electron-withdrawing (such as –COOEt) in β position, weakens the IHB(Intra molecular Hydrogen Bond) while increasing the enl content.On the other hand, electron donation groups (such as –OMe and phenyl)) make the IHB stronger and increase the keto content. This results demonstrate enol form in EDPB and DMOA is more stable than keto form which is in agreement with HF values obtained for enol and keto forms of EDPB and DMOA.

EDPB DMOA

Fig.1. compristion enol-keto forms stability and the hydrogen bond strength of EDPB & DMOA by induced effects

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A Comprehensive Computational Study on the Kinetics and Mechanism of 4-methyl- 1-Pyrazoline

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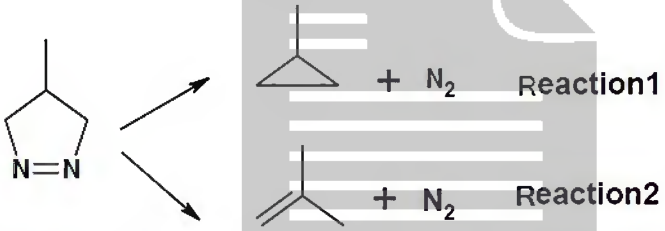
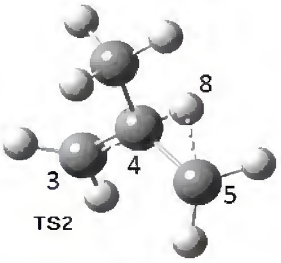
kinetic and mechanisms of nitrogene elimination from 4-methyl-1-pyrazoline (4M-1-PZ) and it's deuterated derivatives have been investigated in the gas phase with the B3LYP, B3PW91, MP2 and PBEPBE methods, using the 6-311++G(d,p) basis sets[1-3]. According to the type of products and their percentages (methyl cyclopropan=53% and 2-methyl-1-propene=43%) in the experimental work [4], we consider two main trajectories for 4M-1-PZ pyrolysis:





a) Methyl cyclopropan formation is occurred according to one of C-N bonds cleavage. Because of its high activation energy (72 kCal.mol^{-1}) rather than the experimental value (42 k Cal.mol^{-1}) this pathway is rejected.

b) Second possibility is the cleavage of two carbon-nitrogen bonds in a synchronous manner in the first stage, then reaction proceeds through a four-membered cyclic transition state (TS2). The activation energy in this case obtained 41 kCal.mol^{-1} and 71 kCal.mol^{-1}, respectively, which is accordance to the experimental results.

After obtaining the energetic understanding of the TSs, full investigation of the nature, structure, charges and electron density were done, using the NBO and AIM analysis. In these concepts for computing the bond orders in the reactant and TSs Weiberg bond indices were used. All molecular computations give us information which confirmed the nature of the TSs and the reaction mechanism. The natural charge value of C3 has a positive and C4 has a negative character which describes the H8 transmission from C4. Kinetic isotope effects confirmed the H migration during the reaction.

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Ab initio calculation of absolute pK$_b$ value in aqueous solution for nicotine.

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Abstract

Nicotine is the principal alkaloid in Nicotiana tabacum. Alkaloids are a group of basic substances which contain a cyclic nitrogenous nucleus. Alkaloids are present in animals as well as in plants. In Nicotiana tabacum plants most alkaloids are 3-pyridyl derivatives. Among the many alkaloid materials found in nicotiana, nicotine is considered to be the principal alkaloid in commercial tobaccos.

The reaction mechanism of the nicotine was investigated using ab initio quantum mechanical (at the HF/ 6-31+G level) and density functional theory calculations in the gas phas and in solution. A thermodynamical cycle is proposed to calculate absolute pk$_b$ values for nicotine in aqueous solution.

$$\Delta G^0 = -\Delta G_{solv}(RN) + \Delta G_{vap}(H_2O) + \Delta G^0_{vac} + \Delta G_{solv}(RNH^+) + \Delta G_{slv}(OH)$$

The polarizable continuum model (PCM) was used to describe the solvent, and absolute pk$_b$ values were computed for different classes of organic compounds. The model furnishes pk$_b$ values in good agreement with the experimental results for some classes of compounds. Calculation of absolute pK$_b$ value in aqueous solution for nicotine was 5.06838*10^{-22}.

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DFT study of molecular switch based on dibenzo[1,2]dithiine

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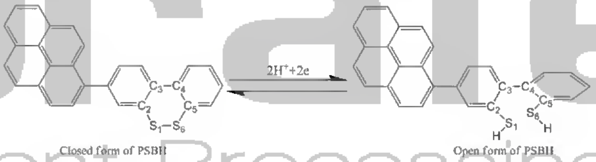
Organic compounds containing redox centers are attractive materials for molecular electronics because the current can be influenced either by electrochemical gating or by the presence of oxidizing or reducing agents [1]. Biphenyl unit is a good example of bistable molecular systems to switch because a bond break and twisting in biphenyl unit can modify the electron flux [2]. Dibenzo[1,2]dithiines are one of the most important materials for making molecular nano-switches. In this system, disulfide bonds are easily cleaved by electrochemical reduction (i.e., 2ē, $2H^+$). In the present study, physical properties of 3-(pyren-1-yl)dibenzo[c,e][1,2]dithiine (PSBH) and open form of its (a bistable redox-responsive molecular switch) are theoretically investigated in order to understand its switching behaviors in details. All calculations were performed using Gaussian 03[3] package of programs at DFT-B3LYP/6-31G* method. The calculated values of the frontier molecular orbital energies confirmed that the closed form of PSBH has lower HLG. This is in agreement with the higher electrical conductivity of closed form of PSBH in comparison of that in its open form. The polarizability calculation results confirmed that α_{xx} is the important component of polarizability tensor, and the lower α_{xx} in the open form of PSBH indicates that the electrical conductivity in this form is lower than that in the closed form and is parallel to the HLG results. Paying attention to the standard Gibbs free energy change (ΔG^o) of electrochemical reduction of PSBH showed minimum polarizability principle (MPP) followed by this reaction. The NBO electric charges on heavy atoms of biphenyl unit revealed that the $S_1^{\delta+}$–$C_2^{\delta-}$ and $S_6^{\delta+}$–$C_5^{\delta-}$ bonds are highly polarized and positive charges on sulfur atoms are reinforced, which caused the collapse of S–S bond.



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DFT study of external electric field on the switching of 1,2-bis(5-methyl-2,2-bithiophen-4-yl)cyclopent-1-ene

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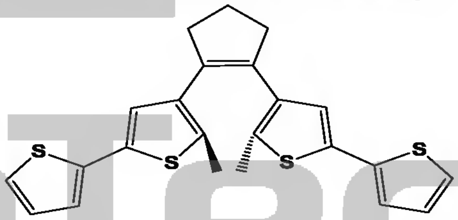
In this work, the effect of external electric field on the switching of 1,2-bis(5-methyl-2,2-bithiophen-4-yl)cyclopent-1-ene is considered. All calculation were performed using Gaussian 03 [1] software and the B3LYP/6-31G* method. The quantities of external electric fields on open and closed molecules are: 0, $10*10^{-4}$, $20*10^{-4}$, $30*10^{-4}$, $40*10^{-4}$, $50*10^{-4}$ (a.u.). Results show that in both open and close form, ESE increased with increasing in external electric field and increased with switching of molecule. On the other hand, total dipole moment of molecules increased with increasing in external electric field. Open and closed form of molecules is extended in 3 dimensions (x،y،z) but μ_x is the main component of total dipole moment and is more sensitive to external electric field. With increasing in the external electric field, HOMO level will become more unstable and LUMO level will become more stable. Therefore, energy gap and frequency of excitation of electron decreased. Switching of open form to close is accompanied with increasing in the dipole moment, decreasing in the energy gap, increasing in the polarizability and finally increasing in the electric conduction. In other view point, with increasing in external electric field, dipole moment, polarizability, and electric conduction increased, but energy gap decreased. This switching is not spontaneous, but with increasing in the external electric field, the tendency to closing the molecules will increase. After closing the molecule, Gibbs free energy, enthalpy, and entropy will decrease and equilibrium constant will be increase. The theoretical results confirmed that switching of open form to close can be done by UV light and its backward process by Vis light. Required frequency for switching of open form to closed form decreased with increasing in external electric field, also, in higher external electric field, switching of open form to close done in Vis frequencies.



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Theoretical Study of the Kinetics and Mechanism of the Reaction Between Dialkyl Acetylendicarboxylates, Triphenylphosphite and NH Acid for Generation of Phosphonate Esters

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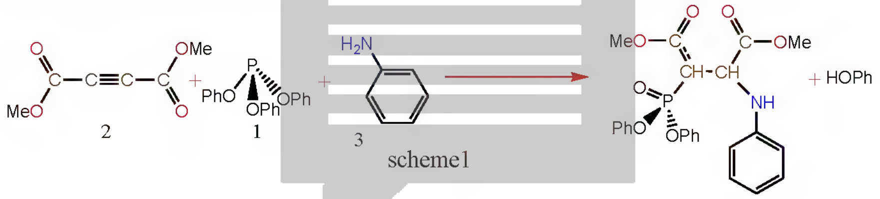
In the recent work, the variable mechanism were investigated for the reaction between triphenylphosphite, dialkyl acetylenedicarboxylates in the presence of N-H acids such as aniline in the gas phase (see scheme 1). Suitable mechanism was determined with respect to the potential energy surface. All calculation were performed by the Gaussian09 in HF/6-31G (d,p) level. In addition, extra basis set 6-31+G(3df,3pd) was employed for the phosphorous atom and also single point energy calculations were achieved at B3LYP/6-31G(d,p) level. Two dimensional scanning techniques were applied to determine the transition state structures. With respect to the rate determining step and Gibbs free energy ($\Delta G^{\#}$), rate constant of reaction was calculated by the Eyringe equations.



scheme1

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Complexation study of 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (kryptofix5) with Ni^{2+} metal cation in some binary mixed organic solvents

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Abstract

Kryptofixes are macrobicyclic amines with polyether linkages connecting the bridgehead nitrogen atoms. They are usually spherical and capable of encapsulating metal ions in their cage-like cavities to form stable complexes. Since their discovery by Lehn and co-workers, a considerable amount of work has been published on the interactions of these molecules with metal cations in aqueous and non-aqueous media [1,2]. Among several factors influencing the formation of macrocyclic complexes, the ability of solvent molecules to solvate metal ions and, thus, to compete with the donating groups of the ligands for the coordination sites of the central cation plays a fundamental role [3,4].

The goal of this investigation is to study the effect of the nature of the cation and also the composition of the mixed solvents on selectivity and thermodynamic of complexation reaction of 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (kryptofix5) with Ni^{2+} metal cation in some binary solvent solutions of methanol (MeOH), ethylacetate (EtOAc) and methylacetate (MeOAc) with acetonitrile (AN) using the conductometric technique.

The stability constant of the resulting 1:1 complex was calculated from computer fitting of the molar conductance-mole ratio data. A non–linear relationship was observed between the stability constants ($\log K_f$) of this complex with the composition of binary solutions, which was explained on the basis of changes occurring in the structure of the mixed solvents and also the preferential solvation of the cations, ligand and the resulting complexes in solutions. The corresponding thermodynamic parameters (ΔH°_c, ΔS°_c) were obtained from temperature dependence of the stability constants using the van't Hoff plots. The results show that both parameters are affected by the nature and composition of the solvent systems.

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Aromaticity of a group of heterocyclic compounds with one ring-junction atom

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Aromaticity is one of the most important concepts in chemistry, but there is still a lot of debate about the extent to which reactivity, energetic, magnetic, and geometric criteria can evaluate this single, unifying property of molecules [1]. In this study, the aromaticity of a series of heterocycles containing a common atom to the fused rings (**Figure 1**) has been evaluated by using magnetic criteria– nucleus-independent chemical shifts (NICS), magnetic susceptibility exaltations (χ), HOMO-LUMO gap and computed ^1H and ^{13}C chemical shifts. The structures were optimized at B3LYP/6-311+G** and aromaticity indices were also calculated at the same level of theory [2]. Of the parent systems containing the ring-junction atom only indolizine **1** has a neutral structure similar to indole.In comparison, the conjugated structure of **2**(X=CH+) has a positive charge on the ring-junction atom. Despite the rarity of such systems in nature, there is much interest in their chemistry due to the structural similarity to parent systems indoles, purines and naphthalenes. The study indicates that the position of the substituents significantly influences the extent of cyclic electron delocalization.

1) X=N, O

2) X=CH+, O, S, NH

Figure 1. Two series of the heterocycles with one ring-junction atom.

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An Ionic Liquid Based on α-Amino Acid Anion and N7, N9-Dimethylguaninium Cation ([dMG][AA]): A Theoretical Study on the Structure and Electronic Properties

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Ionic liquids (ILs) are a class of novel compounds composed of organic cations and inorganic anions. They are used as catalyst, extraction solvents, and electrolyte materials due to their remarkable properties. In terms of the new RTILs, ionic constituents and the size of IL seem to be critical. However, recent studies have shown that the cationic constituent of ILs is important to the thermal stability of the IL [1]. The bulkier cations and dicationic salts [2] rather than monocationic salts vastly improve the thermal stability of ILs. Thus, a bulkier cation seems to be another crucial factor to be considered for the design of new ILs [3]. In this work, we focus on the molecular interaction of several AAILs which are composed of N7, N9-dimethylguaninium cation and amino acid anions ([dMG][AA] (AA = Gly, Phe, His, Try, and Tyr) ILs). Then, the effects of side-chain length of aromatic amino acid functional group on the nature of interaction have been investigated. Moreover, properties extracted from quantum theory of atoms in molecules (QTAIM) and natural bonding orbital analysis (NBO) were used to determine the nature and strength of intermolecular hydrogen bond interactions. All of the calculations are done using Gaussian 03 software. Geometry optimization and frequency calculation are done using B3LYP/6-311++G(d,p) method. This kind of IL has the advantage of being green and can be introduced easily in synthetic processes.

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Kinetics and mechanistic studies of the reaction between acetylenedicarboxylic acid and triphenylphosphine in the presence of carbazole

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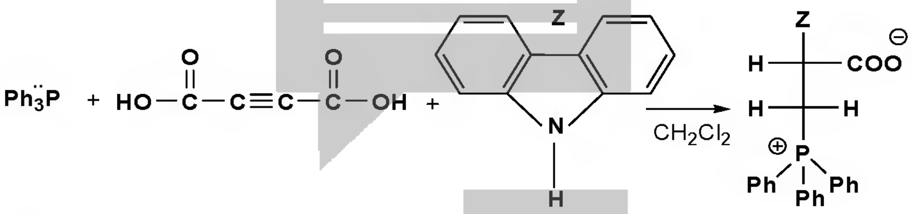
The kinetics of reaction between triphenylphosphine, acetylenedicarboxylic acid in the presence of carbazole has been spectrophotometrically studied in dry organic solvents at different temperatures. The observed overall second rate constant (k_2) for reaction decreases with decreasing solvents dielectric constant and media temperature; k_2, on reciprocal temperature is in a good agreement with Arrhenius equation and overall reaction is first order in both the acetylenedicarboxylic acid and the triphenylphosphite. The Proposed mechanism has been evaluated, and activation parameters involving $\Delta G^{\#}$, $\Delta S^{\#}$ and $\Delta H^{\#}$ for the first step (rate determining step), as an elementary reaction, on the basis of Eyring equation have been determined.



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A DFT study for different regioselectivity of 1,3-dipolar cycloaddition reactions of an azomethine ylide toward vinyl ether and vinyl sulfide

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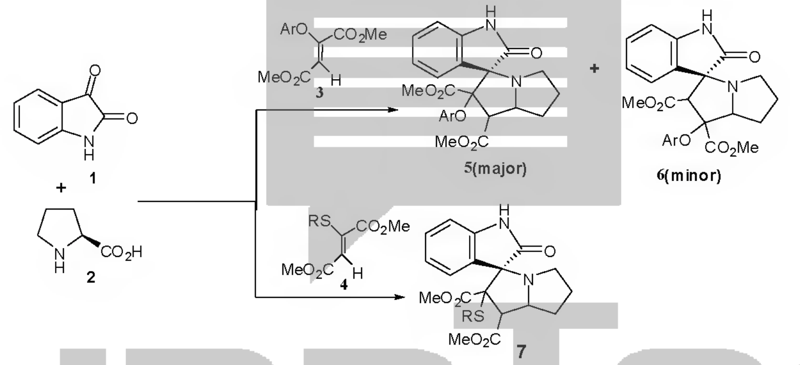
In principle, the regioselectivity could be rationalized in terms of the more favorable FMO interactions between the coefficient centers. The large–large and small–small interactions are more favored than the large–small and small–large ones [1,2]. Regioselectivity also can be analyzed in terms of the HSAB principle which indicates that the interaction between A and B is favored when it occurs through those atoms having approximately equal softness values [3].



In this work, the observed different regioselectivity in the reaction of an azomethine ylide, which was generated by decarboxylation condensation of isatin **1** and proline **2**, with vinyl ether **3** and vinyl sulfide **4** has been studied using density functional theory (DFT) at B3LYP/6-31G** level. The regiochemistry of two reactions has been elucidated in terms of global and local reactivity indices, FMO analysis and HSAB (Hard and Soft Acids and Bases) principle.

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A theoretical study on the [1,5]-prototropic generation of an azomethine ylide and regioselectivity of the 1,3-dipolar cycloaddition using DFT-based reactivity indices

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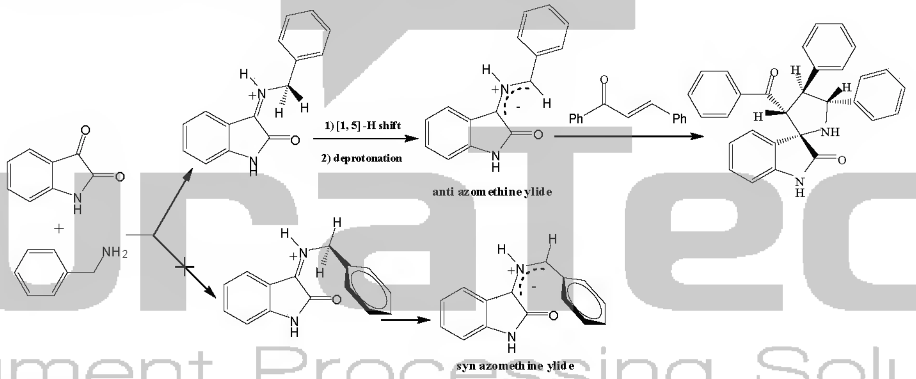
Azomethine ylides are a class of powerful reagents, which react readily with various dipolarophiles to afford pyrrolidines and pyrrolizidines [1]. A particularly mild method for the generation of nonstabilized azomethine ylides involves the [1,5] prototropic shift. The concept of the [1,5]-H shift in the iminium ion to form an azomethine ylide was proposed by Grigg [2]. However no theoretical studies on the mechanism aspects have been reported [3].

Herein, the molecular mechanism of the cycloaddition reaction between an azomethine ylide, generated from isatin and benzylamin, with chalcone as a dipolarophil has been investigated by means of a density functional theory (DFT) method. The energy path in preparing the azomethine ylide via a [1,5]-H shift in the iminium ion was evaluated. The regio- and stereoselectivity were explained on the basis of transition states stabilities and global and local reactivity indices of the reactants.



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β- and γ-Isotope effect a useful method for the elucidation of predominant tautomeric forms and structure backbones in organic compounds

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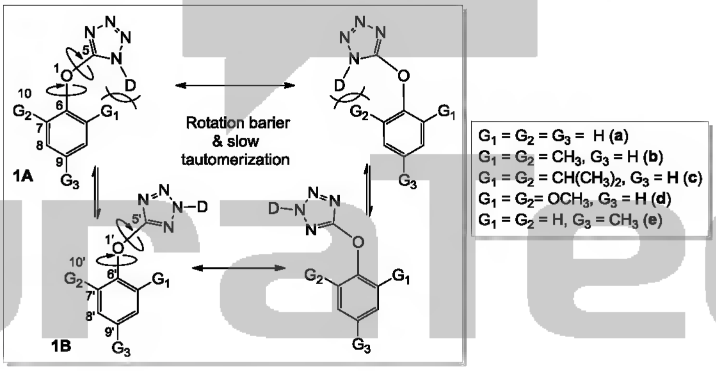
Deuterium isotope effects on carbon-13 chemical shifts are of great potential use for spectral assignments and structure determination. These effects unambiguously reveal the chemical shifts of the carbons in the neighborhood of the deuterium atom [1]. Deuterium isotope effects have also been reported for polyols [2a], amines [2b], amides [2c,d], amino acids [2e], proteins [2f], ammonium derivatives [2g], azo dyes [2h] and heterocyclic pyridazine systems [2i]. Recently, we have investigated the β- and γ-isotpe effect of tetrazoles (**1**) for elucidation of their predominant tautomeric forms [2j]. In general, the β- and γ-isotope effect is a useful method for the elucidation of predominant tautomeric forms and structure backbones in organic compounds.



$G_1 = G_2 = G_3 =$ H (**a**)
$G_1 = G_2 = CH_3$, G_3 = H (**b**)
$G_1 = G_2 = CH(CH_3)_2$, G_3 = H (**c**)
$G_1 = G_2 = OCH_3$, G_3 = H (**d**)
$G_1 = G_2$ = H, $G_3 = CH_3$ (**e**)

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Configurational behaviors of 1, 2-diphenyldiazene, -diphospene and –diarsene. A hybrid-DFT study and NBO interpretation

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Abstract:

Hybrid-density functional theory (B3LYP/Def2-TZVPP) based method and NBO interpretation were used to study the configurational behaviors of 1, 2-diphenyldiazene (**1**), 1, 2-diphenyldiphospene (**2**) and 1, 2-diphenyldiarsene (**3**). The results obtained showed the Gibbs free energy difference ($G_E–G_Z$) values (i.e. ΔG_{E-Z}) at 298.15 K and 1 atm between the E- and Z-configurations decreases from compound **1** to compound **3**. The NBO analysis of donor-acceptor ($LP\rightarrow\sigma^*$) interactions showed that the generalized anomeric effect (i.e. $GAE_{total}=GAE_E-GAE_Z$) associated with the LP $M_1\rightarrow\sigma^*_{M2-Cphenyl}$ and $\sigma_{M1-Cphenyl}\rightarrow\sigma^*_{M2-Cphenyl}$ increases from compound **1** to compound **3**. The variation of the GAE can be controlled by its corresponding off-diagonal elements [i.e. resonance integral (S)]. On the other hand, there are no the same trends between the calculated total dipole moment and Gibbs free energy difference values between the E- and Z-configurations (i.e. $\Delta\mu_{Z-E}$) of compounds **1-3**. Accordingly, the GAE succeeds in accounting for the increase of the E-configuration stability from compound **1** to compound **3**. Therefore, the GAE associated with the electron delocalization, not the total dipole moment changes (i.e. $\Delta\mu_{Z-E}$), is a reasonable indicator of the total energy difference in compounds **1-3**. There is a direct correlation between the calculated GAE and $\Delta\ [r_{M1-Cphenyl}\ (E)–(Z)]$ parameters. The correlations between the GAE, bond orders, total steric exchange energies (TSEE), ΔG_{E-Z}, $\Delta\mu_{Z-E}$, structural parameters and configurational behaviors of compounds **1-3** have been investigated.

Keywords: 1, 2-diphenyldiazene, stereoelectronic effect, molecular modeling, ab initio, NBO

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Kinetics and Mechanism of the Reactions Between Triphenylphosphite and Dialkyl Acetylenedicarboxilates in the Presence of Chloro-and Fluoro-Aniline

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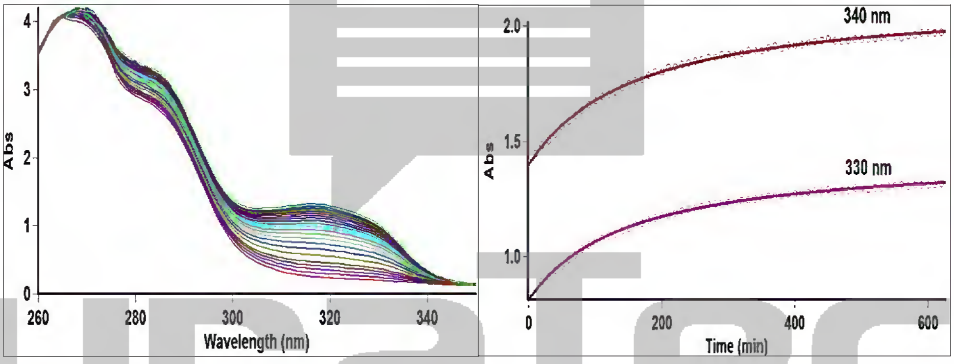
Kinetic studies were made of the reactions between triphenylphosphite and dialkylacetylenedicarboxylates in the presence of chloro-and fluoro-Aniline. To determine the kinetic parameters of the reactions, the reaction progress was monitored by UV spectrophotometry. The second-order fits were automatically drawn and the values of the second-order rate constant (k2) were automatically calculated using standard equations. In the temperature range studied, the dependence of ln k2 on the reciprocal temperature was consistent with the Arrhenius equation. Furthermore, useful information was obtained from studies of the effect of solvent, structure of the reactants (different alkyl groups within the dialkylacetylenedicarboxylates), and also the concentration of reactants on the rate of reaction. The mechanism was confirmed to involve a steady-state condition with the first step of the reaction being the rate-determining step.



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Comparison of the various methods on estimation of halobenzenes aromaticity based on aromatic stabilization energies

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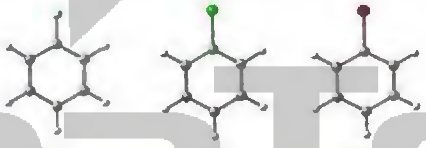
Aromaticity can be described by different quantitative criteria, based on geometric, energetic and magnetic. In some cases, these various criteria do not agree [1]. In this work, methods of aromaticity have been compared in three classes of molecules including fluorinated, chlorinated and brominated benzenes based on aromatic stabilization energies (ASEs). All molecules were optimized at the MP2/6-31G(d,p) level of theory by GAUSSIAN09 program package [2]. Delocalization index was calculated on the base of results of population analysis using AIM2000 program [3]. The harmonic oscillator model of aromaticity (HOMA) as a geometric-based index, average two center index (ATI) which is in sense based on extracting the information from the molecular electron density and electron delocalization index, and nucleus-independent chemical shifts (NICS) as a magnetic-based index which is obtained from the NMR data [4] were used on estimation of aromaticity.



1 2 3

Figure 1. Structures 1-3 correspond to 1-fluorobenzene, 1-chlorobenzene, and 1-bromobenzene, respectively.

In all cases aromaticity increases by the increase in ASEs index. Generally, aromaticity increaes with the increase in HOMA, ATI and absolute values of NICS, The values of ASEs indicate that the brominated benzenes are the most and fluorinated benzenes are the less aromatic compounds. The trend in the values of ATI is in agreement with the trend in the values of ASEs for these compounds. ATI is expected to be the best method for estimation of aromaticity in these molecules.

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L-Proline as an efficient catalyst for the multi-component synthesis of 1,3-thiazolidin-4-one under solvent free condition

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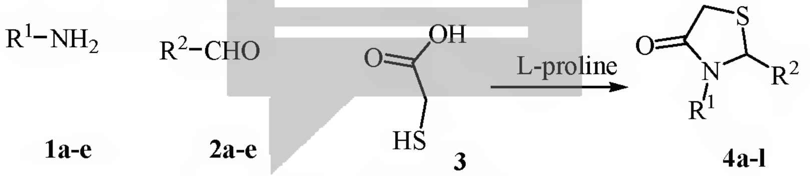
The thiazolidin-4-one ring system is a core structure in various synthetic pharmaceutical compounds, displaying a broad spectrum of biological activities. Several synthetic methods have been developed for the synthesis of 4-thiazolidinones [1]. The main synthetic routes to thiazolidin-4-ones involve cyclocondensation of azomethines (Schiff's base) with mercaptoacetic acid [2]. There are also reports using chemical agents such as N,N-dicyclohexyl carbodiimide (DCC) [3] as desiccant to assist the formation of thiazolidinone derivatives. The use of ionic liquid [4] and baker's yeast [5] has also been reported to expedite the cyclocondensation of the azomethines and thioglycolic acid. However these methodologies suffer from one or more disadvantages such as costly dehydrating agents and require prolonged heating and tedious work-up. Therefore it was thought worthwhile to develop a new method for the cyclocondensation



Scheme 1. Synthesis of Thiazolidinon-4-one **4a-l**

Herein, we report a simple and facile synthesis of 1,3-thiazolidin-4-one in good yields. In a one-pot procedure, compounds 4a–l were obtained in the course of a three component reaction with amine, aromatic aldehyde 2a-j and mercapto acids 3 using L-proline at an ambient temperature under solvent free condition. We examined awide variety of aromatic aldehydes with various substituents to establish the catalytic importance of L-proline for this reaction. (Scheme1). Compared to the previously reported methods, mild reaction conditions, easy work-up, clean reaction profile, shorter reaction time, and wide range of substrate applicability are the key advantages of this methodology.

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Thermal curing comparison of epoxy resin with amine and amide curing agents

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Abstract

Epoxy composites have extensive applications, for instance in adhesive, medical devices, optical component owing to their admirable resistance compared many materials [1-3]. The type of curing agent for modifications of epoxy resins can influence the curing chemistry, the curing rate, crosslink density, morphology, etc. So the choice of curing agent is very essential and requires to be considered very carefully. Epoxy resins can be cured with a wide variety of curing agents. Aliphatic and aromatic polyamines, polyamides, and their derivatives are the commonly used amine type curing agents. In this study, influence of different curing agents on thermal curing process of epoxy composite is investigated. Therefore the curing process of epoxy resin based on diglycidyl ether of bisphenol F (DGEBF) in the presence of amine and amide curing agent is determined through differential scanning microscopy (DSC) that were performed from 25 to 250 ^{0}C at rate of 10°C/min. Moreover, Fourier Transform Infrared Spectroscopy (FT-IR) was used to discuss the complete curing of composites.

The FTIR results revealed that epoxy resin cross linked with amine curing agent more completely than amide curing agent. Because the epoxide ring is strained (unstable), and polar groups (nucleophiles) can attack it. After completing the curing process of DGEBF the amine groups react with matrix and the peroxides ring peak is disappeared.

DSC results showed higher glass transition temperature (Tg) and total reaction enthalpy (the maximum produced heat of reaction during curing) of polyamine system. Therefore polyamine system has more thermal stability than polyamide system. Furthermore crosslinking decrease is due to increasing flexibility of epoxy/polyamide that depends on lower Tg. On the basis of obtained results, the curing behavior of epoxy composite depends on the type of curing agent.

Keywords: epoxy resin, thermal curing, polyamine, polyamide

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An investigation on the curing behavior of epoxy resin based on bisphenol A (DGEBA), in the presence of nano filler

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Epoxy resin has been developed rapidly since invented, and are widely used in modern life [1–3]. The most important and industrialized epoxy is bisphenol A. In this study, the cure process of epoxy resin based on bisphenolA (DGEBA) with polyamine hardener in presence of nano silica investigated through Differential Scanning Calorimetry (DSC) and Fourier Transform Infrared (FT-IR) [4].

In this study, the cure process of epoxy resin based on bisphenol A (DGEBA) with polyamine hardener in presence of nano silica investigated through Differential Scanning Calorimetry (DSC) and Fourier Transform Infrared (FT-IR) [1]

The total reaction enthalpy (the maximum produced heat of reaction during curing) and glass Transition (Tg) was measured by DSC scans from 25 to 200 °C at rate of 10°C/min. All results were compared to those of bare epoxy resin and a decrease in ΔH and slight increase in Tg were observed.

In curing process, the reaction occurs between amine active hydrogen and epoxy groups. Reduction in total reaction enthalpy in presence of nano silica indicates lower degree of cure. Therefore, some of epoxy rings residue in the matrix and FT-IR spectra shows epoxy ring peak (the band at 914 cm^{-1}). These results indicate that some amine active hydrogen covered with nano particles [5,6].

As a matter of fact Tg depends on crosslinking and increases with higher crosslinking. DSC curves show slight increase of Tg upon addition of nano silica. This increase happens because of large surface area that enhances the crosslinking.

Nano composites with a 1 wt% in SiO2 and a good dispersion of silica nano particles, within fully cured DGEBA matrix were easily produced through the proposed synthesis route. Silica addition reduces cure kinetics. Cure activation energy is not influenced by the silica presence.

The nano composite glass transformation temperature depends on the heating rate of cure process, at higher silica content there is no difference in Tg values between plain polymer and nano composite.

It is known that properties of nano composites depend on both interfacial interactions and nano composites structure, that is on the nano particle size, size distribution, and surface chemistry. Therefore, the new route may allow projecting the nano composite.

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A New Strategy for the Chemoselective Sulfonamide N-Alkylation of Sulfonyl Ureas under Neutral conditions

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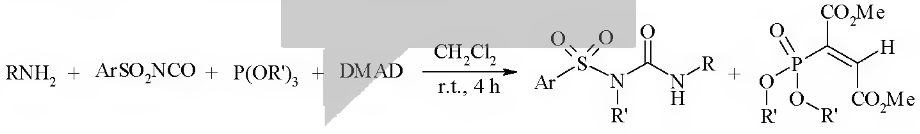
N-Alkylation is an important reaction in synthetic organic chemistry. The N-alkylation reaction with alkyl halides is well known,[1] but the use of alkyl halides is undesirable from an environmental point of view. Other alkylating reagents and conditions for N-alkylation include: alcohols/metal catalysts,[2] alcohols/Ph_3P/DDQ,[3] highly active methylating reagents such as Me_2SO_4, Me_3PO_4, and Me_2CO_3,[4] and also reductive amination of carbonyl compounds.[5] However, most of these methods have disadvantages such as high reaction temperatures, long reaction times, use of strong reducing reagents or hydrogen gas, and in some cases, use of very hazardous reagents.

The sulfonyl urea unit is an important structural motif found in biologically active organic compounds. These compounds, first discovered by Janbon et al.,[6] have been shown to be highly active herbicides, antidiabetics, and antitumor agents.[7]

Chemoselectively alkylated sulfonyl ureas are important compounds in medicinal studies. An important procedure for acquiring these compounds was reported by Roth et al. in 1995 in which sulfonyl ureas were alkylated with alkyl halides in the presence of DBU in acetonitrile.[8]

Herein, we report a new reagent for the chemoselective sulfonamide N-alkylation of sulfonyl ureas under neutral and mild conditions. Thus, a mixture of an amine **1** and an aryl sulfonyl isocyanate **2** was converted into the corresponding sulfonyl urea in dry CH_2Cl_2 at ambient temperature. The reactions reached completion within a few minutes, which was indicated by TLC monitoring. After addition of a trialkyl phosphite **3**, a solution of dimethyl acetylenedicarboxylate **4** in dry CH_2Cl_2 was slowly added to the reaction mixture and stirring was continued at ambient temperature for further two hours to afford the alkylated sulfonyl ureas **5** in excellent yields.



1 **2** **3** **4** **5** **6**

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New heterogeneous oxidant based on permanganate supported on aminated silica-gel for oxidation of alcohols

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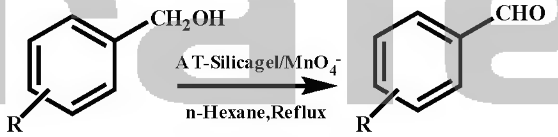
Abstract

Oxidation of alcohols to the corresponding aldehydes and ketones remains one of the most important reactions both from fundamental research as well as synthetic point of view [1]. Oxidation by homogeneous systems has many problems; such as tedious work-up, acidic media, and safety problems [the presence of toxic transition metal cations, e.g., Co(II), Pb(IV), Hg(II), Mn(IV and VII), Ag(I), Zr(IV)] [2]. Thus, developing an environmentally friendly and efficient heterogeneous oxidant is of paramount importance. In this work amino functionalized triazine supported on silica-gel was prepared by reaction of silicagel with cyanoric chloride in dry tetrahydrofurane in the presence of triethylamine followed by ethylene diamine treatment. This amino functionalized silicagel was reacted with CH_3I in dioxane. Subsequent reaction of this material with $KMnO_4$ gives AT-silicagel/MnO_4^-. This novel reagent was applied as an effective heterogeneous reagent for the oxidation of alcohols to the corresponding carbonyl compounds in the presence of n-hexane as a solvent and reflux conditions in high yield and excellent selectivity (Scheme 1). Our goals in undertaking this work were: (a) to overcomethe reported limitations and drawbacks such as tedious work-up, acidic media, e.g., (b) to devise a heterogeneous system, especially useful for industry, with many advantages such as reduced pollution, lower costs and simplicity in processing and handling. (c) to develop a high-yielding synthesis of benzaldehyde and its substituted homologues using a recyclable reagent. Different parameter such as type of solvent, reaction temperature, reaction time and amount of reagent were examined and it was found that the best results were obtained in the presence of n-hexane as a solvent in its reflux temperature. In conclusion, our studies showed that potassium permanganate heterogeneous reagent supported on aminated triazine rings linked on silica gel serve as highly active heterogeneous oxidant reagent for the oxidation of benzyl alcohol and its substituted homologues. This reagent exhibited excellent activity and selectivity under mild conditions and can be recyclable.



Scheme 1.

References:

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Room–Temperature Synthesis of Monoarylidenes of Piperidin-4-one under Solvent-Free Conditions

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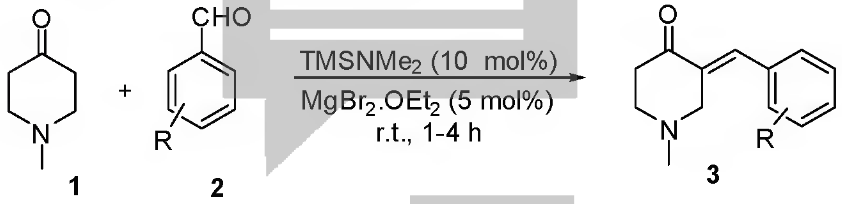
α,-β unsaturated ketones are of great importance in synthetic organic chemistry since they are key component of many natural and biologically active structure [1]. The chemistry of piperidin-4-one is of current interest due to potential medical and biological applications of its derivatives [2].

In addition, they could serve as convenient precursors for other nucleophylic synthetic transformations[3]. Several strategies are offered so far for the preparation of these compounds[4]. However, many of them usually incorporate more than one step reaction or need the use of commercially unavailable starting materials.

In the present work, an efficient synthesis of monoarylidenes of piperidin-4-one **3** was achieved by the reaction of 1-methyl 4-piperoidone **1** and aromartic aldehyde **2** in the presens of $MgBr_2.OEt_2$ under solvent free condition [5]. High yields of products are obtained at room-temperature and the procedure is applicable to the reactions with aromatic and aliphatic aldehydes.



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Synthesis of Poly N-isopropyl acrylamide as Thermosensitive Polymer

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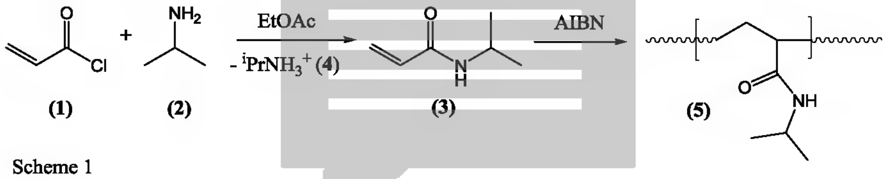
The linear poly (*N*-isopropylacrylamide) (PNIPAAm) is a thermoresponsive polymer whose aqueous solutions exhibit at reversible transition with a lower critical solution temperature LCST [1]. In this project we try to report a facial method to synthesize monomer and polymers of *N*-isopropyl acrylamide.

The reaction of acroleyl chloride (0.2 mol) (**1**), and isopropyl amine (0.4 mol) (**2**) in ethyl acetate led to the formation of N-isopropyl acrylamide (**3**) and isopropylammonium chloride (**4**). Precipitated salt **4** was filtered, the solvent of filtrate was evaporated at reduced pressure, and the residual was solidified after staying for 24 h at 0 °C after which monomer **5** obtained as white precipitate (Scheme 1). Monomer **3** polymerized in THF at 70 °C in the presence of AIBN, as free radical initiator, during which PNIPAAm formed as colloid, solvent was evaporated at reduced pressure, and polymer (**5**) obtained as colorless crystals.

The structure of monomer and polymer elucidated by IR spectroscopy. Thermosensitivity of polymer was studied at 25-40 °C. Measured LCST (32 °C) of synthesized polymer was in good agreement with reported one [2, 3]. This method may be a facile method for the synthesis of acrylamide thermosensitive polymer as well related monomers.



Scheme 1

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Facile Method for the Synthesis of 2-substituted Quinazolin-4(1*H*)-one Derivatives Catalyzed by SiO_2-$H_3PW_{12}O_{40}$

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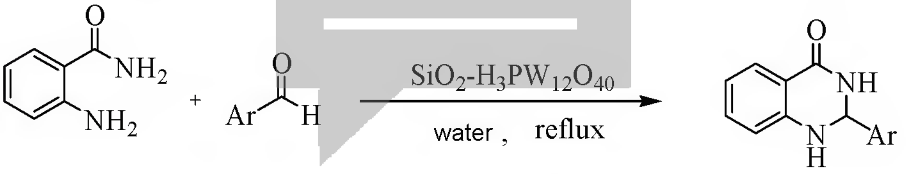
Among the various classes of heterocyclic compounds, quinazolin-4(1*H*)-ones form important component of pharmacologically active compounds, as they are associated with a wide spectrum of biological activities such as antiinflammatory, antihypertensive, anticancer, antitumor and antibacterial [1]. Various methods for the synthesis of 2-arylquinazoline were based on the reaction of 2-aminobenzamide with aromatic aldehyde catalyzed by some catalysts such as NH_4Cl, $AlCl_3/ZnCl_2$, *p*-TSA, and asymmetric Bronsted acids or one-pot condensation of isatoic anhydride, amines and aldehydes in organic solvent [2]. These reported methods involve various disadvantages, such as low yields, prolonged reaction times, and the use of toxic organic reagents and catalysts. Silica-supported 12-tungstophosphoric acid (PW/SiO_2) is a cheap, noncorrosive, easily available and reusable catalyst [3].

Herein, we report an efficient, mild, high yield and simple workup synthesis of quinazolin-4(1H)-one derivatives by cyclocondensation of *o*-aminobenzamide with different aldehydes or ketones in the presence of PW/SiO_2 in wather (Scheme 1).



Scheme 1

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Aldol Condensation of 2*H*-Thiopyran-4(3*H*)-one Using DMAP as Organocatalyst in Aqueous Media

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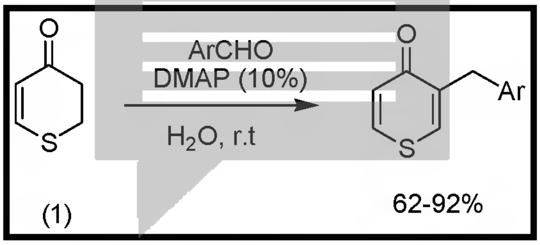
Thiopyran structures are one of the most important classes of sulfur containing heterocycles [1-3] with many applications in the preparation of natural and unnatural products such as the synthesis of polypropionates by aldol reactions [4]. Based on our previous related investigations [5], we were encouraged to study aldol condensation of dihydrothiopyran-4-one (1) in aqueous media. In this work we successfully achieved the expected products by using catalytic amounts of DMAP (4-Dimethylaminopyridine) as an organocatalyst, under very mild conditions. Reactions proceeded in good to high yields at room temperature with a very straightforward and easy workup procedure. The structure of the products is assigned based on their spectroscopic data. As a result of this work, reactions products were obtained rapidly and under relatively environmentally benign conditions.



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Preparation of semi-aromatic polyamides and investigation of structural parameters on their UV absorption

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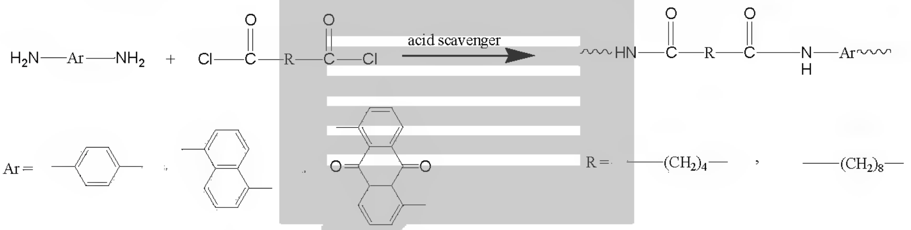
Polyamides have attracted many attentions since they were synthesized, characterized, and applied as commercial development of synthetic fibers, known commonly as nylons. It is known that aromatic polyamides are a class of high temperature resistance polymers with good chemical resistance, thermal stability, low flammability, and very good mechanical properties [1,2]. Polyamides are widely used in different products and industries including textile, automobile, aerospace, military, electronic, and other industries. So, their colors and their ability to absorb UV radiation strongly affect their applications in the mentioned industries [3,4].
In the present research, semi-aromatic polyamides with different aromatic groups (bulkiness) and different aliphatic units (methylene chains) were prepared through solution polycondensation method in the presence of an acid scavenger.



$$H_2N{-}Ar{-}NH_2 + Cl{-}\overset{O}{\overset{\|}{C}}{-}R{-}\overset{O}{\overset{\|}{C}}{-}Cl \xrightarrow{\text{acid scavenger}} \sim\sim HN{-}\overset{O}{\overset{\|}{C}}{-}R{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{N}{-}Ar\sim\sim$$

All the six polymers were characterized by conventional methods including FT-IR, NMR, and elemental analysis. Physical and thermal properties of the polymers including inherent viscosity, solubility, thermal stability and behavior, flame-retardancy and crystallinity of the polymers were studied. were studied. Also, UV absorption of polyamides was investigated and the effects of structure on it were studied. Incorporation of phenyl, naphthyl, and anthraquinoyl groups from one side, and size of aliphatic chain from another side (significant structural modifications that affected UV absorption) were studied.

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Heterogeneous palladium porphyrin as an efficient catalyst for the Heck reactions

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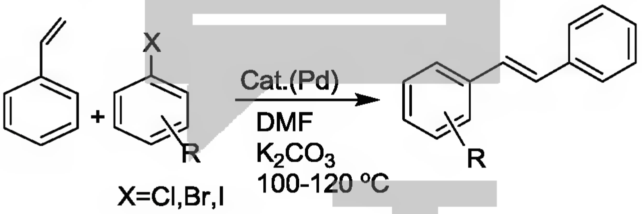
Palladium-catalyzed coupling of aryl halides with alkenes, Heck cross-coupling reaction, is an extremely valuable method for carbon-carbon bond formation [1-4]. It is now widely used in the special chemical and pharmaceutical manufacturing industries, because it is simple, versatile, and relatively mild. It is interesting to note that in the absence of catalyst, the reaction did not proceed. Heterogeneous palladium complexes having high activity and selectivity, offer several significant practical advantages in synthetic and industrial chemistry; among those, the ease of separation of the catalyst from the desired reaction products is most important [5-8].

In the present work, we report the preparation of heterogeneous *tetrakis*(4-pyridyl)porphyrinato-palladium(II) and its application in the Heck reaction of aryl halides in the presence of inorganic or organic bases. The effects of the various reaction parameters on the catalytic activity were studied [9]. Due to insolubility of this Pd(II) complex in all common organic solvents, its structural investigations were limited only to its physicochemical properties such as SEM, TGA, IR and UV-vis spectral data.



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Poly(ester imide)s as a New Kinds of Heat-resistant Polymers with Enhanced Solubility

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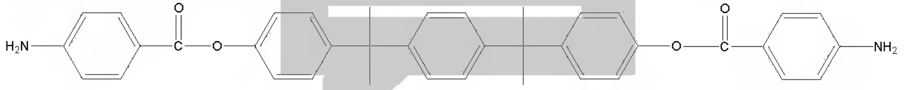
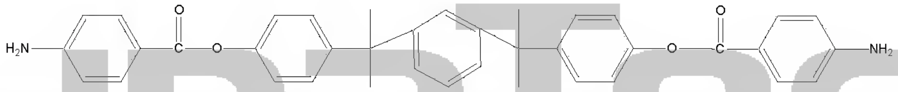
Among various polymers, polyimides received more attention due to their favorable balance of physical and chemical properties. Wholly aromatic polyimides are engineering plastics and are gaining wide acceptance by different industries because they contain a number of unique features. These include excellent physical properties, retention at elevated temperature and in wet environments, almost constant electrical properties over a wide range of temperatures, good chemical resistance and non flammability properties [1]. However, one of the drawbacks to the employment of these high performance polymers is the difficulty in processing due to their high melting temperatures or high glass transition temperatures [2]. Strong interaction between polyimide chains and their rigid structure are the main reasons for these behaviors. Copolycondensation is one of the possible ways for modification of polymer properties. Thus, for the processing of polyimides many copolyimides, such as poly(amide-imide)s, poly(sulfone-imide)s, poly(ether-imide)s, poly(ester-imide)s and other copolymers have been prepared [3, 4].

In this research, two new diamines were prepared via reaction of bis-phenol-p and bis-phenol-m with 4-nitrobenzoyl chloride and subsequent reduction of nitro groups. Monomers were fully characterized and used for the preparation of related polyimides.





Two-step polycondensation reaction of this monomer with different aromatic dianhydrides resulted in preparation of poly(ester imide)s. Polymers were characterized by FT-IR, H-NMR, and elemental analysis methods. Thermal and physical properties of the polyamides including thermal stability, thermal behavior, solution viscosity, and solubility behavior in addition to crystallinity, and molecular weights were studied. Polymers prepared from bis-phenol-p showed higher thermal stability and lower solubility in comparison to the similar polymers prepared from bis-phenol-m. It was related to the para-oreintation of bis-phenol-p polymers and better close packing and dipole-dipole interaction of the polymeric chains.

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New types of poly (amide-imide)s: synthesis, characterization, and properties

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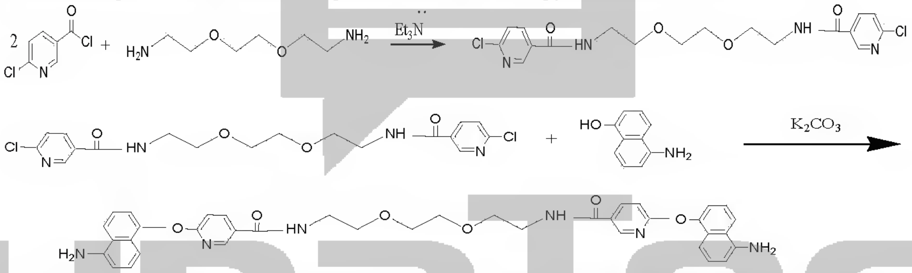
Aromatic diamines are valuable building monomers for the preparation of different types of high-performance polymers including polyamides, polyimides, and their copolymers. Copolycondensation is one of the possible ways for modification of polymer properties. Modification of the properties of polyamides by incorporation of imide groups and more hydrogen-bonded amide groups has been investigated and poly(amide imide amide)s have been studied extensively [1–3]. The incorporation of rigid segments in the polymer chain is an effective method to enhance the thermal stability. Thermal resistance of polyimides is higher than that of polyamides, but polyamides have better solubility and processability than polyimides. Poly(amide imide)s are known as valuable polymers among high-performance polymers due to the fact that they combine and inherit desirable features from both polyamides and polyimides [4].

In this research, a new diamine monomer containing pyridine, ether, amide, and aliphatic units was prepared via two step reactions. Nucleophilic chloro displacement reaction of 6-chloronicotinoyl chloride with two moles of 1,8-diamino-3,6-dioxaoctane afforded a dichloro compound. Subsequent reaction of dichloro compound with 5-amino-1-naphthol resulted in a new pyridine-based diamine.



The diamine containing preformed amide group was polycondensed with different dianhydrides to produce related poly(amide imide)s. The prepared monomer and all the polymers were characterized by conventional methods. Different physical and thermal properties of the polymers were studied. According to the obtained results, these polymers showed nice balance of properties including high thermal stability and improved solubility. Incorporation of aromatic and imide units was the main factor for enhancing thermal stability. Introduction of ether, aliphatic, pyridine, and bulky groups were significant structural modifications for improving solubility of the poly(amide imide)s.

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The Synthesis of Arylquinoxalines and Arylnaphthodiazepine Derivatives

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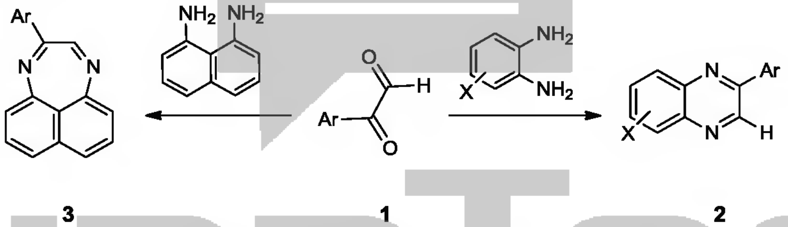
Quinoxaline and its derivatives are important nitrogen containing heterocyclic compounds of various biologically interesting properties with several pharmaceutical applications. Substituted quinoxalines are an important class of benzoheterocycles, which constitute the building blocks of wide range of pharmacologically active compounds having antibacterial, antifungal, anticancer, antitubercular, antileishmanial, and antidepressant activities activities [1-3].

Diazepines are interesting from the point of view of their chemical structure [4]. The diazepines constitute an important group of psychotherapeutic drugs and have been extensively studied because of their sedative-hypnotic, muscle relaxant, anxiolytic, and anticonvulsant properties [5]. The discovery of specific receptors in mammalian brain tissue for diazepines has led to a useful screening procedure to evaluate the interaction of various diazepines with the binding site. Due to their success and safety, diazepines have been amongst the most widely prescribed drugs during the last two decades.

Here, we report the synthesis a series of arylquinoxalines (**2**) and arylnaphthodiazepines (**3**) in good to excellent yields by reaction of 1,2-diaminobenzene derivatives and 1,8-diaminonaphthalene with arylglyoxals (**1**) respectively.



Ar = ph, 3-BrC_6H_4, 4-BrC_6H_4, 3-OMeC_6H_4, 4-OMeC_6H_4
X = H, CH_3, NO_2

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The Synthesis of Quinoxalinophenazine Derivatives

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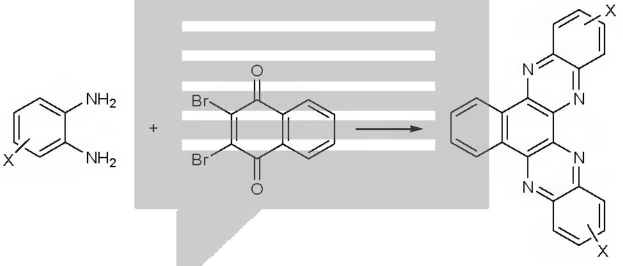
Phenazine derivatives are generally water-soluble and coloured compounds that often have antibiotic activity [1]. These compounds are produced by bacteria from diverse general including Streptomyces, Pseudomonas, Pelagiobacter and Vibrio [1-3]. Some bacterial isolates produce more than one type of phenazine, each composed of a heterocyclic, nitrogen-containing phenazine nucleus. The diversity of phenazines arises from the varied type and number of functional groups attached to this nucleus.
Here, we report the synthesis of a series of quinoxalinophenazine (**3**) by reaction of 1,2-diaminobenzene derivative (**1**) with 2,3-dibromo-1,4-naphtaquinone (**2**) in DMF/EtOH under reflux conditions, with high yield. These compounds were confirmed by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy determinate.



1 **2** **3**

X =H, Me, NO_2

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Solvent-free Diastereoselective Synthesis of Dicyanotetrahydropyrrolo Phenanthrolines

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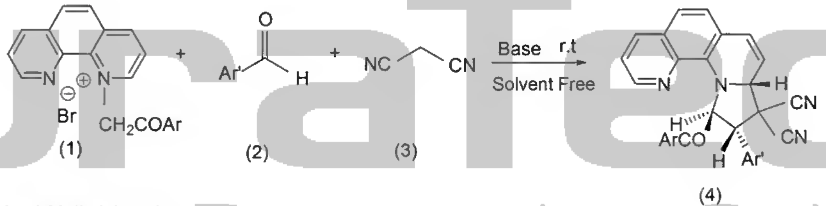
The solvent-free approach to the synthesis of molecules is an attractive one, since the majority of solvents are either toxic or flammable and add considerably to the cost of an overall synthesis. In many instances, the solvent-free approach allows shorter reaction times, improved selectivity and easier separations and purifications than conventional solvents [1].

Grindstone chemistry is a branch of green chemistry for solvent-free chemical reactions which can be probably conducted in high yield by just grinding solid/solid, solid/liquid, or even liquid/liquid together .There are several advantages to performing synthesis in dry media: (i) short reaction times, (ii) increased safety, (iii) economic advantages due to the absence of solvent[2]. In the last decade, interest in substituted [1,10]phenanthrolines has been increased and, as result, chemistry, synthetic methods and properties of these *N*-heterocycles have been studied by several group[3]. Owing to the increasing importance of these N-heterocycles in the field of biology and technology we now report an efficient and clean synthetic route for pyrrolo phenanthrolines in good yield.

We observed that three-component reaction of 1-***phenacyl***-1,10-phenanthrolinium bromide **1**, aromatic aldehydes **2** and malonitrile **3** in the presence of triethylamine as base, in green methodology, afforded chiefly a single diastereoisomer of tetrahydropyrrolo[1,2-*a*][1,10] phenanthroline derivatives **4** as new macromolecules in excellent yields .

It's clear that Lewis base such as triethyl amine and DABCO are good basic catalyst. Also NaOH is good basic catalyst but the reaction took about one hours to complete.

The isolated product was completely characterized by IR and ^{1}H NMR . The melting point of the compound was in agreement with those of literature reported[4].



Ar=4-Methylphenyl
Ar'=Phenyl, 3-Chlorophenyl,1-Naphthyl

Base: Et_3N , DABCO, NaOH

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$Fe(ClO_4)_3/SiO_2$-catalyzed synthesis of ß-amido carbonyl compounds through Dakin-west reaction

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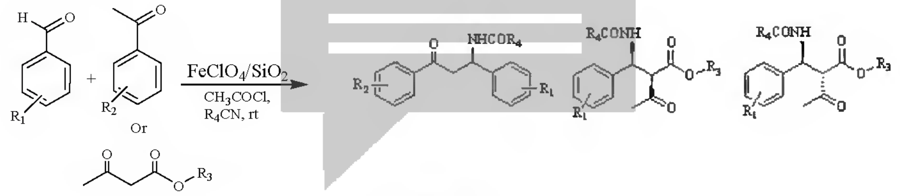
β-Acetamido ketone skeletons exist in a number of biological and pharmaceutical compounds makes them valuable building blocks [1,2] and there have been intensive attempts to synthesize β-amido ketones. The best-known route for the synthesis of these compounds is the Dakin–West reaction,[3] which involves the condensation of an α-amino acid with acetic anhydride in the presence of a base to afford the β-acetamido ketones.[4]Another procedure for the formation of these compounds from condensation of enolizable ketones, an aryl aldehyde, and acetyl chloride in nitriles in the presence of heterogeneous and homogeneous acid catalysts have been reported. Iron catalysts in organic reactions have recently received much attention in view of their cheapness and environmental friendliness. Amoung them ferric perchlorate and ferric perchlorate adsorbed on silica gel are ranked as powerful Lewis acids for affecting various organic transformations.[5]

In this communication we wish to report synthesis of β-amido ketones with enolizable ketones, acetonitrile, benzonitrile and acetyl chloride in the presence of $Fe(ClO_4)_3/SiO_2$ at room temperature (Scheme 1).



Scheme 1

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The Synthesis of (3-(2, 5-dimethoxyphenyl)isoxazol-5-yl)methanol

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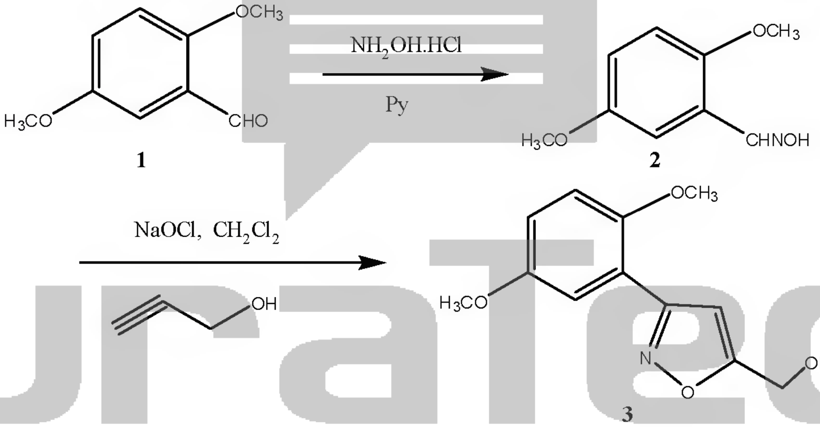
Compounds with isoxazole moiety have pharmacological, biological and industrial applications; specifically these compounds show antiviral activity [1]. Recently, the synthesis of isoxazole 4- and 5-carbaldehydes and their conversion to isoxazolyl-1, 4-dihydropyridines were studied [2].
In this research work, first, 2, 5-dimethoxybenzaldehyde (**1**) was transformed to 2, 5-dimethoxybenzaldoxime (**2**) by using NH_2OH in pyridine. The in-situ generated nitriloxide from reaction between **2** and NaOCl, was reacted with propargylalcohol to produce (3-(2, 5-dimethoxyphenyl) isoxazol-5-yl) methanol (**3**) in a cycloaddition procedure.
The structure of all the synthesized compounds was characterized and confirmed by FT-IR and NMR spectroscopy techniques.



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Glutamic Acid: A New Catalyst for One-Pot Synthesis of 7-aryl-11,12 dihydrobenzo[h] pyrimido-[4,5-b]quinolone-8,10(7H,9H)-diones

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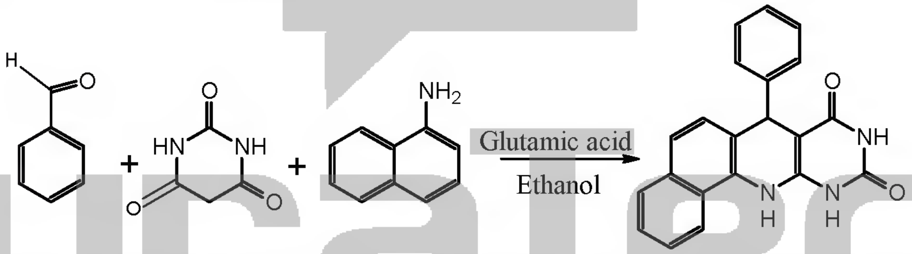
Abstract

Aseries of new 7-aryl-11,12-dihydrobenzo[*h*]pyrimido-[4,5-*b*]quinoline-8,10(7*H*,9*H*)-diones were synthesized via three component reaction of aldehydes, 1-naphthylamine and barbituric acid in Glutamic Acid Catalyst. The method provided several advantages such as easy work-up, high yields and environmentally benign procedure.7-Aryl-11,12-dihydrobenzo[*h*]pyrimido-[4,5-*b*]quinoline-8,10(7*H*,9*H*)-diones, a novel class of fused heterocyclic compounds, are incorporated by pyrimido-[4,5-*b*]quinoline-2,4(1*H*, 3*H*, 5*H*, 10*H*)-dione and [4,7]-phenantroline motifs, both of which possess various important bioactivities. For example, not only are pyrimido-[4,5-*b*]quinoline-2,4(1*H*, 3*H*, 5*H*, 10*H*)-dione derivatives antitumor, anticancer, antihypertensive, and antibacterial, they are also inhibitors of Kaposi's sarcoma-associated herpesvirus (KSHV) and topoisomerase, useful for the treatment of topoisomerase associated disease sand disorders[1–2].At the sametime,[4,7]-phenantroline derivatives exhibit antitumor,anticancer,antiviral, antimalarial, antiinfective, cytotoxic activities, as well as being triple-helix DNA stabilizing agents [3–4]. Hence, it is promising that the fused scaffolds of pyrimido-[4,5-*b*]quinoline-2,4(1*H*,3*H*,5*H*,10*H*)dionewith[4,7]phenanthroline,7-aryl-11,12-dihydrobenzo[*h*]pyrimido-[4,5-*b*]quinoline-8,10(7*H*, 9*H*)-diones, may display novel or enhanced significant bioactivities.



A typical rocedure for the preparation of 4a_4l: Aldehyde (1.2 mmol), 1-naphthylamine (2.2 mmol), barbituric acid (3.2 mmol) were added to a 20 mL round bottom flask containing 20%mol Glutamic Acid. The mixture was then stirred at 90 °C for appropriate time (monitored by TLC).

After completion of the reaction, the reaction mixture was added with 5 mL water. The precipitate was collected by suction and purified by recrystallization from EtOH to give products 4. The filtrate was concentrated under reduced pressure and dried at 100°C to recover the ionicliquid for subsequent use. Some selected data:

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Synthesis of spiro[pyrazolo[3,4-*b*]pyridine-4′,3-oxindoles]*via* one-pot three component condensation reaction in water

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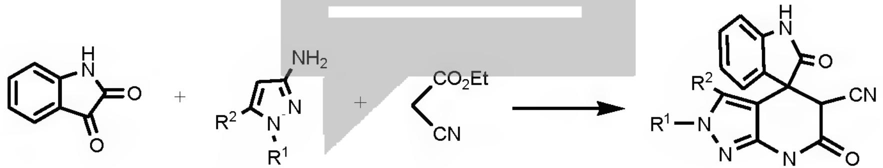
Multi-component reactions (MCRs) are special types of synthetically organic reactions in which three or more starting materials react to give a final product in a one-pot procedure. Such reactions are one of the best tools in modern organic synthesis to generate compounds libraries for screening purpous because of their productivity, simple procedure and facile execution [1]. Pyrazolo[3,4-b]pyridines are attractive compounds for drug discovery since many of such scaffolds exhibit a wide range of biological and pharmaceutical activities. These include HIV reverse transcriptase [2], anti-tumor and anti-proliferative [3], as well as compounds for treatment of Alzheimer's disease [4].

The other important structural fragment presents in our final products includes oxindole substructure, exists in many alkaloids (e.g., spirotryprostatin B, alantrypinone, and citrinadin A) [5]. In general compounds carring the indole moiety exhibit antibacterial and antifungal activities [6].

Aqueous media is an important advantage of this reaction. As water (green solvent) is the most environmentally acceptable, safest, and most abundant solvent [7]. In addition, water enable facile work-up protocols, as most organic compounds, being lipophilic, are readily segregated from aqueous media. Furthermore, water, as our reaction medium, processes conferring uniqe selectivity and reactivity [8].

Therefore, this work is devoted to the synthesis of new spiro-oxindoles by one-pot three component reaction of derivatives of isatin in aqueous media. The product which is gained has oxindole, pyridinone and pyrazole rings.



R^1 = Me, Ph
R^2 = H, Ph

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Effect of different diol and diamine chain extenders on aqueous anionic polyurethane dispersion properties

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A series of aqueous polyurethane dispersions were synthesized based on prepolymer mixing process by reaction of polytetramethylene glycol (PTMG) and isophorone diisocyanate (IPDI) which were extended with different diol and diamine chain extenders [1]. Anionic waterborne polyurethanes were obtained based on hydrophilic dimethylol propionic acid (DMPA) monomer in this research [2]. Aqueous polyurethane dispersion samples were prepared by placing polytetramethylene glycol into the reactor under N_2 atmosphere and mechanical stirring. The prepolymer with NCO terminated groups was obtained by addition of IPDI to polyol and increasing the temperature to 90°C [3]. This prepolymer was extended by proper amounts of DMPA solution in N-Methylpyrrolidone. Then the required amounts of different diol or diamine chain extenders were added to the reactor in chain extension step. In order to neutralize of the carboxylic acid groups of DMPA, triethyleneamine was added into the mentioned system. Finally stable emulsion of polyurethane samples were synthesized by adding the required amount of deionized water into the reactor to obtain aqueous dispersions PUs with 30 wt % solid content. Characterization of chemical structure and thermal-mechanical properties of these polymers were performed by FTIR and DMTA respectively. Chemical structure of polyurethanes extended by different chain extenders were proved with the disappearance of the NCO band at 2270 cm^{-1}. It was observed that with changing of the chain extender from diol to diamine, melting temperature of soft segment increases to upper temperatures significantly. The hydrophilicity of the prepared samples was measured by contact angle test and observed that diamine chain extenders afford lower contact angles.

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Preparation and characterization of novel chiral poly(amide-imide)/organoclay/TiO_2 bionanocomposites

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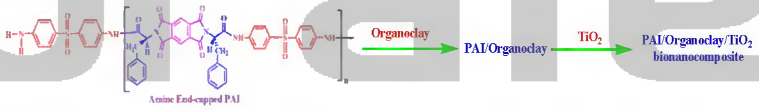
Composite materials represent one of the most active fields in the polymer industry. Many different types of fillers and nanoparticle have been added to polymers to provide an improvement of the final products. In recent years, it has been observed that the addition of just a small quantity of nano-sized layered silicates greatly improved the properties of virgin polymers without affecting their processability [1,2]. Also among many nanocomposite precursors, TiO_2 nanopowder is increasingly being investigated because it is non-toxic, chemically inert and has a high refractive index, UV filtration capacity and high hardness. Such materials on the nanoscale level show significant improvements in mechanical properties, heat distortion temperatures, thermal stability and enhanced barrier properties [3]. In the present investigation, novel series of poly(amide-imide)(PAI)/organoclay/TiO_2 bionanocomposites (BNC)s has been synthesis. At first, Cloisite Na^+ and protonated form of *L*-phenylalanine amino acid were used for the preparation of the novel chiral organoclay via ion-exchange reaction. Then, PAI containing phenylalanine amino acid was synthesized via solution polycondensation of *N,N'*-(pyromellitoyl)-bis-phenylalanine diacid with 4,4'-diaminodiphenylsulfone in the presence of tetrabutylammonium bromide as a green solvent. Then, this polymer was end-capped with amine end groups of diamine in the final polymerization process. In the next step, PAI/organoclay BNC films containing 5% of organoclay was prepared via solution intercalation method through blending of organoclay with the PAI solution. Then, different percentages of modified TiO_2 were added to PAI/organoclay for study the synergetic effect of both nanoparticles. The nanostructures and properties of the PAI/organoclay/TiO_2 BNCs were investigated using fourier transform infrared spectroscopy, X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and thermogravimetry analysis (TGA) techniques. XRD, FE-SEM and TEM results revealed the formation of exfoliated and intercalated organoclay platelets in the PAI matrix. TGA results indicated that the addition of organoclay and TiO_2 into the PAI matrix increases in the thermal decomposition temperatures of the resulted BNCs.



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Synthesis and Characterization of Chitosan-Agar Full-Polysaccharide Biodegradable Films by Reductive Amination

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During the last two decades, significant advances have been made in the development of the biocompatible and biodegradable materials for various applications such as drug delivery systems and tissue engineering [1,2]. Polysaccharides are the main part of the natural based biodegradable materials, because of their biocompatibility, biodegradability, and nontoxicity. Chitosan, a natural polymer obtained by alkaline deacetylation of chitin, is biocompatible and can be completely digested by the colonic bacteria [3]. Agar consists of a mixture of agarose and agaropectin. The predominant component of agarose is a linear polymer, made up of the repeating monomeric unit of agarobiose [4].

This work focuses on the synthesis of the chitosan-agar full-polysaccharide hydrogel by crosslinking of chitosan with periodate activated agar and subsequent reductive alkylation. Agar activated molecule prepared by periodate oxidation of the agar and then applied as a crosslinking agent to form a new hydrogel network. The effect of chitosan/agar weight ratio on the swelling behavior of the hydrogel at various pH solutions was investigated. The swelling of the hydrogel decreases with decreasing the acidity of the solution. A preliminary study was conducted on the hydrogel swelling and deswelling kinetics. The equilibrium swelling was achieved after 25 min. The data may be well fitted with a Voigt-based equation. The structure of the hydrogel was confirmed by FT-IR spectroscopy, scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and solubility test. Swelling measurements of the synthesized hydrogel showed good swelling capacity especially in acidic solutions. The polymers may have potential application in tissue engineering and drug delivery systems.

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Silzic-catalyzed synthesis bisamides

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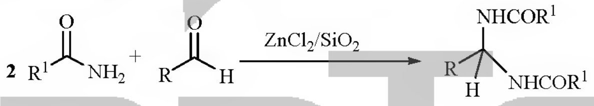
Multicomponent reactions (MCR) are chemical processes where three or more reagents combined to give the final product retain significant portions of all starting materials. Therefore, they lead to the connection of the starting materials in a single synthetic operation with high atom economy and bond-forming efficiency, thereby increasing molecular diversity and complexity in a fast and often experimentally simple fashion. For this reason, MCR are particularly well suited for oriented synthesis of pharmaceuticals and agrochemicals.

Gem-bisamides can be easily transformed into other useful materials such as gem-diaminoalkyl and aminoalkyl compounds and are of considerable interest in the synthesis of pharmacological materials such as peptidomimetic compounds. They could be synthesized via direct condensation of two moles of amides with aldehydes in the presence of acidic catalysts [1-4].

In this work, we have reported their synthesis in the presence of $ZnCl_2/SiO_2$ (silzic) under solvent-free conditions (Scheme 1).



Scheme 1.

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A convenient method for synthesis of new formyl coumarines derivatives

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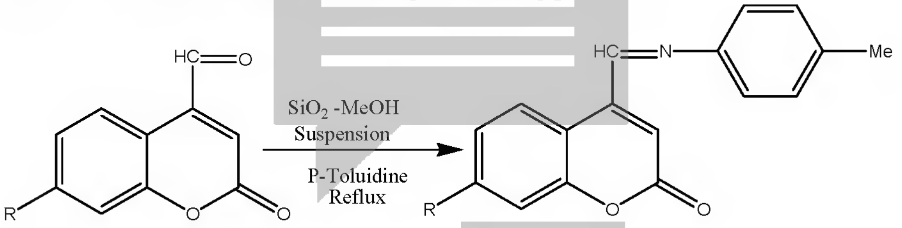
Abstract

In our efforts some substituted coumarine 4-carbaldehydes were prepared in moderate to good yield using dioxin as appropriate solvent .[1] for these important transformations 4-methyl coumarines were used as starting materials and SeO_2 was used as oxidizing agent of choice.[2,3] The molecular structure of the so-called composition was verified through some techniques of spectroscopy such as ^1H NMR, FT-IR, and mass after measuring the melting point.[4]



Keywords: coumarine -aldehyde –SeO_2-Synthesis-Oxidation.

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Study of Integral Skin PUFs Degradation Using Green Solvents

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Abstract

Since the last 40 years, polyurethanes have been used in an ever increasing range of application. For example Polyurethane integral skin foams are widely used in the automotive industry.with polyurethane production volumes increase, The amount of PU waste is also on the rise. For decrease the amount of waste disposal of these foams, chemical recycling is preferred as a useful method to achieve both targets: 1) making the industry more compatible with the environment, 2) defining an economic progress. Many scientists reported the glycolysis of PUF [1-3]. In this work, the one of the main goals was using the green solvent for glycolysis (DEG and EG / Sorbitol/water) and to reduce the energy and material losses. The materials used for the glycolysis were integral skin foam prepared with the formulation of Polyol/MDI in the ratio of 100:41 respectively. Two necked round bottom flasks were used for all reactions. The flasks were equipped with a condenser, a thermometer and an agitator. The scraps of Integral skin foam (15 g), NaOH (1 % w/w) and various systems (DEG and EG/Sorbitol/water) in which glycolysis reactions were running, were placed in the flaks. The reactor was heated up to 195±5℃ with the difference of 5 ℃ and rpm 1000 at atm. The reaction extends to complete dissolution of foams. The reaction mixture transferred to a decanted funnel and was left to be cooled in room temperature. After several minutes, it was separated into clear upper and dark brown lower phases. The separated phases were analyzed by classical and instrumental methods. We have investigated that with the increasing sorbitol content, reaction time increased. This was possibly due to increasing viscosity of the reaction media as well as difficulties in nucleophilic attack of destroying agent to the polyurethane bonds (Figure1). The different catalysts were employed in the solvent system in order to decrease the dissolution time .NaOH had the greatest decreasing effect on the dissolution times. The ^{1}H_NMR ,^{13}C_NMR and FT_IR spectra showed that the processing of the chemical recycling of PU integral skin by solvent (DEG and EG / Sorbitol/water) and catalyst NaOH resulted good yield.

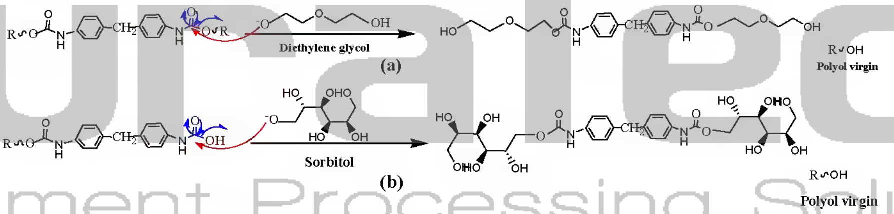

Fig.1. Mechanism reaction PUF by destroying solvent DEG(**a**),sorbitol(**b**)

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Ionic metal adsorption by hydrogels containing citric acid and imino diacetic acid

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The contamination of water resources by industrial effluents is a serious issue [1]. The determination of trace toxic metal ions and their removal with chelating polymers have gained great importance in environmental applications because of their high degree of selectivity, high loading capacity, versatility, durability, and enhanced hydrophilicity [2-4]. The necessity of reducing the concentration of heavy metals to acceptable levels in wastewater and the need for more highly specific metal-recovery processes in both hydrometallurgical and environmental applications have led to increasing interest in polymer-based adsorbents. In this work poly(styrene-alt-maleic anhydride) was grafted by citric acid or iminodiacetic acid in different molar ratios. The prepared polymers characterized by FT-IR and NMR spectroscopy. The prepared graft polymers have a pH sensitive properties and their pH of cloudy point in aqueous solution were determined. The graft copolymers was examined in ionic metal adsorption such as Pb^{2+}, Cr^{2+}, Ni^{2+}. The adsorption results of aforementioned metallic ion were high, so the prepared polymers show good ability in adsorption of metallic ion from aqueous solutions.

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$SbCl_5/SiO_2$: an efficient and facile heterogeneous catalyst for preparation of azo dyes based on β-naphthol at room temperature under solvent-free conditions

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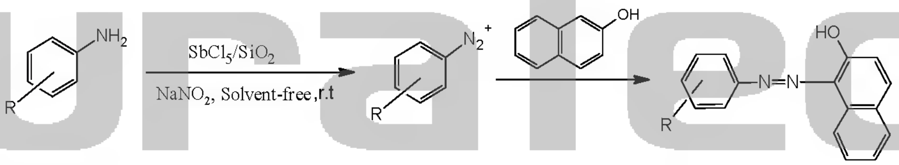
Supported-metal catalysts are widely used in the chemical industry and environmental protection. It is well known that the support has a great influence on the catalytic performance of catalysts [1]. Antimony pentachloride ($SbCl_5$), a thin, colored and fuming liquid, is used in industry and organic synthesis. This catalyst can be easily separated from the reaction products by simple filtration and quantitatively recovered in the active form [2]. Almost 10^6 tons of dyes are produced annually around the world, of which azo dyes, characterized by one or more azo groups linking substituted aromatic structures, represent more than 50% by weight. These dyes are widely used in a number of industries such as textile, food, cosmetics and paper printing. Approximately 10–15% of dyes are released into the environment during manufacturing and usage [3]. Diazonium salts are useful synthetic building blocks in organic synthesis because these compounds can be linked to methine or aromatic sp^2-hybridized C-atoms [4]. Herein, we wish to report a convenient and rapid one-pot method for diazotization and diazo coupling reactions using $SbCl_5/SiO_2$ under solvent-free conditions at room temperature. The reaction is clean and the purification of product is straightforward with excellent yield, especially solid anilines. These are azo dyes based on coupling of the β-naphthol and diazonium salts. $SbCl_5/SiO_2$ is friendly with respect to corrosiveness, safety, reduced waste and ease of separation and recovery. Spectroscopic methods such as ^{1}H- and ^{13}C-NMR, FT-IR, UV-Vis were used for identification of azo dyes.



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Highly efficient one-pot synthesis of trisubstituted imidazoles in the ionic liquids(ILs)

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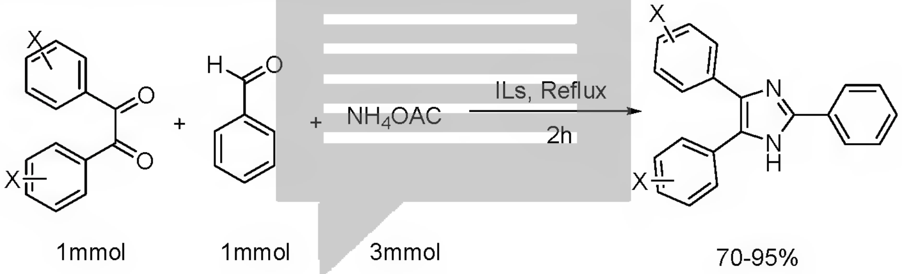
Operationally simple, atom economical, and scalable synthesis of 2,4,5-trisubstituted imidazoles from benzil, aldehydes, and ammonium acetate is shown to proceed readily in the ionic liquids with high yield. The scope of the reaction is quite broad; a variety of aromatic and aliphatic activated and unactivated aldehydes have all been shown to be viable substrates for this reaction. Excellent yields and purity were obtained by washing the products with hot ethanol.



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Catalyst-free synthesis of dihydropyridine from ***Barbituric acid in water***

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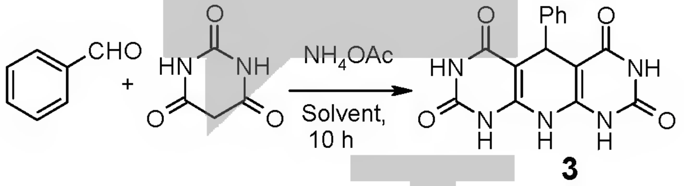
Operationally simple, atom economical, and green procedure has been developed for the synthesis of dihydropyridine derivatives by a simple condensation of barbituric acid, aldehyde and ammonium acetate in water under catalyst free conditions. Excellent yields and purity were obtained with only filtration and washing with hot water and ethanol.



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An efficient procedure for the one-pot synthesis of dihydropyrimidinones and 1,4-dihydropyridines catalyzed by $FeCl_3.SiO_2$ nano particle

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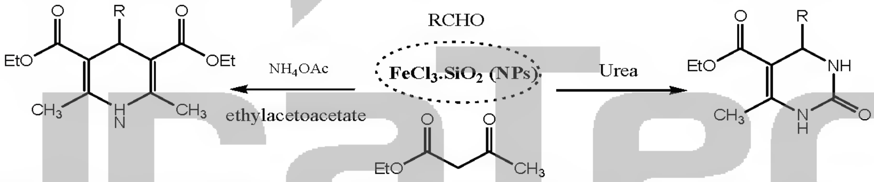
Multicomponent reactions, have become very popular in the discovery of biologically active novel compounds due to its simple experimentation, atom economy and high yields of the products [1]. Recently, a number of modified methods have been developed [2-4]. Solid acids and especially those based on micelle-templated silicas and other mesoporous high surface area support materials are beginning to play a significant role in the greening of fine and speciality chemicals manufacturing processes [5]. An economical and recyclable nano silica supported ferric chloride was prepared as heterogeneous catalyst for the synthesis of various substituted such as 1,4-dihydropyridines (DHP) and dihydropyrimidin-2(1H)-one (DHPM) via condensation of aldehydes with ethyl acetoacetate and ammonium acetate urea in ethanol. All the synthesized compounds have attracted large interest due to pharmacological and biological activities[6]. The products could be separated from the catalyst simply by filtration and the catalyst could be recycled and reused for several times without noticeably decreasing the catalytic activity. The structure of products are confirmed by IR and1H NMR spectroscopic methods.



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Efficient Synthesis of Functionalized Thiazolidines Containing Highly Polarized Carbon-Carbon Double bonds

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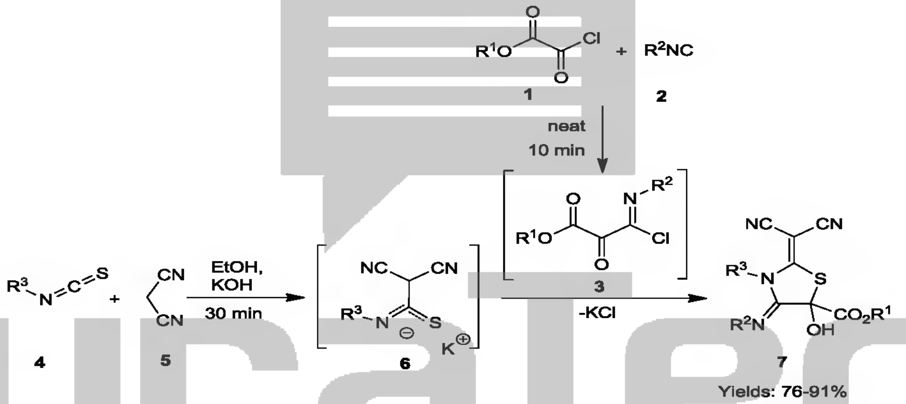
Thiazolidines and their derivatives are an important class of five-memberd heterocycles, which have found applications as analgesics, anti-inflammatory, antimicrobial, and antioxidant drugs.[1] We report on the reaction of Nef-isocyanide adducts **3**, obtained from alkyl chlorooxalates **1** with alkyl isocyanides **2** at room temperature, with potassium (2,2-dicyano-1-mercaptovinyl)(alkyl)amides **6**. This reaction leads to the formation of the thiazolidine derivatives **7**, in good yields.



The structures of compounds **7** were deduced from their IR, ^{1}H NMR and ^{13}C NMR spectral data. Various features of these transformations will be presented and discussed.

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One-pot three Component Synthesis of Benzo[b]pyran-3-carbonitrile Derivatives in Aqueous Glucose Solution as Medium and Promoter

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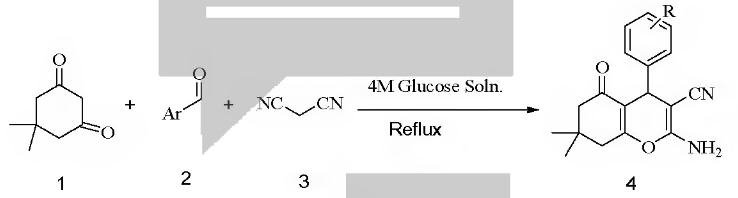
Benzo[b]pyran derivatives have been found as structural motif in the structure of some drugs which show various pharmacological properties such as peroxisome proliferator-activated receptor r and -γ (PPARr and γ) antagonists [1], and novel anti-ischemic agents [2]. So, the search for more environmentally benign and versatile synthetic methods is still an active area of research in organic chemistry. The well-known process for the synthesis of benzo[b]pyran derivatives includes a three-component reaction of cyclic 1,3-diketones, aryl aldehydes, and malononitrile which is carried out under various reaction conditions. Conditions such as microwave and electrogeneration of base were also employed in this process [3,4]. Because the idea of green chemistry has shifted somehow toward employing biobased materials with diverse structures, such as sugars, for the purposes of synthesis and catalysis, we have already reported the synthesis of 2-arylbenzimidazoles in aqueous glucose solution [5]. So, we herein wish to report a novel methodology for the synthesis of benzo[b]pyran-3-carbonitrile derivatives via a one-pot three-component reaction of dimedone (1), aromatic aldehydes (2) and malononitrile (3) in 4M aqueous glucose solution (Scheme 1).



Scheme 1

All of the products were obtained in less than a half an hour with excellent to quantitative yields. The products were precipitated completely after formation and can be isolated easily and washed by sitirring in water for half an hour. This reaction did not proceed well in pure water inferring to the role of glucose in the process. In summary, this methodology seems to be a good alternative to the present methodologies because of using an ecofriendly carbohydrate aqueous solution as a medium and catalyst.

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Synthesis of New Polyether-Diester Podands Containing A 4*H*-pyran-4-one Unit

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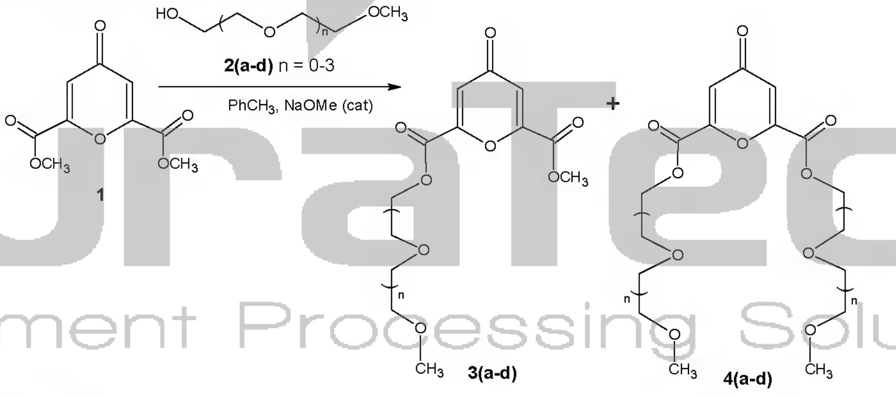
The synthesis and cation complexing characterization of noncyclic polyethers were reported in past decades. Until now a large variety and number of podands have been prepared and their properties have been studied extensively. Some of the properties of the synthetic noncyclic polyethers are similar to those of certain macrocyclic polyethers, however the synthesis of these are very simpler than them [1]. Heteroaromatic components can assume donor position in podands. 4*H*-pyran-4-one derivatives constitute a useful class of heterocyclic compounds which are widely distributed in nature. 4*H*-pyran-4-one and corresponding derivatives have been the subject of much research due to their importance in various applications and their widespread biological significance.

In continuation of our studies in the chemistry of 4*H*-pyran-4-ones [2-4], we have investigated the synthesis of new noncyclic polyether-diester ligands containing the 4*H*-pyran-4-one derivatives subcyclic unit. These compounds have been prepared by treating various glycols monomethylether (2) with dimethyl chelidonate (1) *via* transesterification reaction in toluene using sodium methoxide as catalyst. The reaction was driven to completion by the removal of methanol through its absorption onto molecular sieves. The proposed structures for the noncyclic polyethers-diesters (3-4) are consistent with data obtained from Mass, IR, ^{1}H and ^{13}CNMR spectra and elemental analyses.



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Highly efficient, solvent-free, one-pot synthesis of trisubstituted imidazoles using $SbCl_5/SiO_2$ as a novel catalyst

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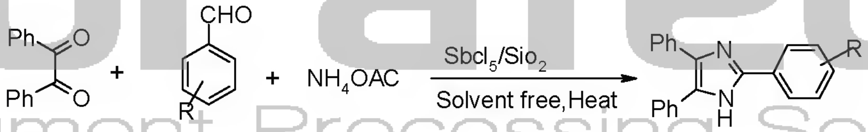
Multicomponent reactions enjoy an outstanding status in organic and medicinal chemistry for their high degree of atom economy and application in the diversity-oriented convergent synthesis of complex organic molecules from simple and readily available substrates in a single vessel [1]. One such reaction is the synthesis of imidazoles. Imidazole and their derivatives, which usually possess diverse biological activities, play important roles as versatile building blocks for the synthesis of natural products and as therapeutic agents [2]. Nowadays, solid-supported reagents have improved the activity and selectivity more than can individual reagents, because the surface area of the reagent is increased manifold. Antimony pentachloride ($SbCl_5$), a thin, colored and fuming liquid, is used in industry and organic synthesis. Since antimony pentachloride is a liquid with a high specific gravity that fumes in air and reacts with the moisture to form HCl, and since its handling and usability in the liquid form is laborious, the supported form is indeed preferable. It has been claimed that the supported $SbCl_5$ is a solid super acid. $SbCl_5$ is used extensively in organic synthesis as a Lewis acid for enhancing a variety of organic reactions [3]. Herein, we wish to report a mild and efficient methodology for the synthesis of tri-substituted imidazoles via direct tri-component condensation reaction between benzil, various aldehydes and ammonium acetate using catalytic amounts of $SbCl_5/SiO_2$. The key advantages of this process are short reaction times, high yields, reusability of catalyst, easy work-up and purification of products. Final products were fully characterized by IR, ^1H- and ^{13}C-NMR spectroscopic methods.



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The Synthesis of 5-(bromo methyl)-3-(3, 4, 5-trimethoxy phenyl) isoxazole as a new compound

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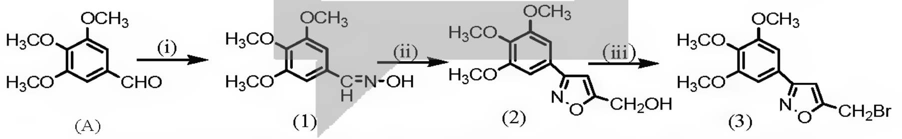
Isoxazole derivatives have been used as key intermediates in synthesis and have been investigated intensively for the last several years. Isoxazoles attract great interest because of their wide reaching application in the medicinal chemistry and material science [1]. For example in year 2010, A series of novel 2, 5–bis (3-indolyl) isoxazoles were synthesized as antitumor agent [2], In 2010 year, a seriese of isoxazole-based histon deacetylase (HDAC) inhibitors structurally related to SAHA were designed and synthesized [3] and in 2007 year, a set of new enantiopure isoxazoles derivatives were prepared and tested for their affinity and efficacy at human β_1-, β_2-, β_3-adernergic receptor subtype [4]. This research work describes the synthesis of new compound of isoxazole family. First, 3, 4, 5-trimethoxybenzaldehyde (A) was transformed to 3, 4, 5-trimethoxybenzaldehyde oxime (1) by using NH_2OH in pyridine. The in situ generated nitriloxide from reaction between (1) and NaOCl, in a cycloaddition procedure then was reacted with propargylalcohol and [2+3] cycloaddition to produce (3-(3,4,5-trimethoxyphenyl)isoxazol-5-yl) methanol (2), in final 3-(3,4,5-trimethoxy phenyl)-5-bromomethyl isoxazole (compound 3) prepared by reaction of PBr_3 and compound 2 in $CHCl_3$ (**scheme 1**).The structure of all the synthesized compounds was characterized and confirmed by FT-IR, ^{1}HNMR and ^{13}CNMR spectroscopy techniques.



Scheme1. Reagent and conditions: i) py, NH_2OH, reflux, ii) CH_2Cl_2, NaOCl, propargylalcohol, iii) PBr_3, $CHCl_3$.

In conclution, a series of isoxazole synthesized. We have successfully developed an other method for synthesis of disubstituted isoxazole from benzaldehyd with propargylalcohol that synthesis compound is useful as key intermediates for the synthesis of other compounds.

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Synthesis of 14-alkyl- or aryl-14H-dibenzo [a,j]xanthenes using $SbCl_5/SiO_2$ as an facile catalyst in conventional and solvent-free conditions

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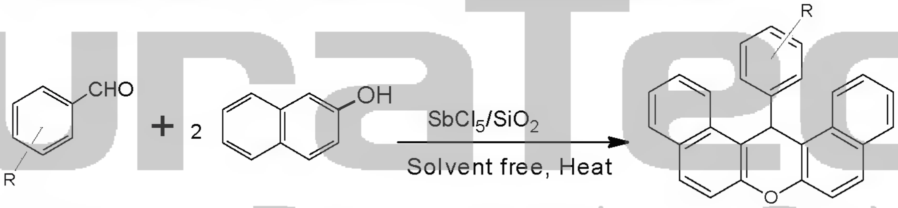
Organic syntheses involving greener process and under solvent free conditions have been investigated worldwide due to stringent environment and economic regulations[1]. Antimony pentachloride ($SbCl_5$), is used in industry and organic synthesis and since its handling and usability in the liquid form is laborious, the supported form is indeed preferable. It has been claimed that the supported $SbCl_5$ is a solid super acid. $SbCl_5$ is used extensively in organic synthesis as a lewis acid for enhancing a variety of organic reactions [2]. In recent years, much attention has been directed towards the synthesis of 14-substituted-14-H-dibenzo [a,j] xanthene derivatives[3]. Xanthene's heterocycles and derivatives are interest because they are an important class of natural compounds such as Bikaverin and Guayin which exhibiting a wide range of pharmaceutical and biological properties such as antiinflamatory, antitumor, and applied in photodynamic therapy[4].In continuation of our research program directed toward the synthesis of xanthenes, we wish to describe the synthesis of xanthenes, from β-naphthol and various aldehydes in the presence of a heterogeneous solid acid catalyst in high yields. Final products were fully characterized by IR, ^{1}H- and ^{13}C-NMR spectroscopic methods.



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An efficient three-component tandem reaction for the synthesis of pyrazolo[3,4-*b*]pyridine

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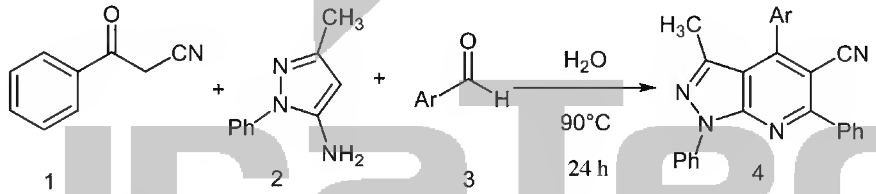
One-pot multi-component reaction (MCR's) strategies offer significant advantages over conventional linear-type syntheses by virtue of their convergence, productivity, facile execution and high yield [1]. In addition, the use of water as the reaction media has several benefits; water is a cheap, plentiful, nontoxic, nonflammable, green, neutral and natural solvent [2]. Also, by carrying out of the tandem MCRs in water and/or without any harmful organic solvents have increased importances [3]. The pyrazolo[3,4-b]pyridines in general, represent a unique class of compounds due to a wide range of medicinal uses reported in the literature [4]. In this work, we have reported the one-pot three-component condensation reaction as tandem of benzoyl acetonitrile (**1**), 3-methyl-1-phenyl-1*H*-pyrazol-5-amine (**2**) and aldehyde (**3**) in water in the absence of any organic solvent and catalyst at 24 hours that lead to pyrazolo[3,4-b]pyridine derivatives in good yield.



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Synthesis of 2-((4-chloro-2-oxo-2H-chromen-3-yl)methylen) amino)carboxylicacid

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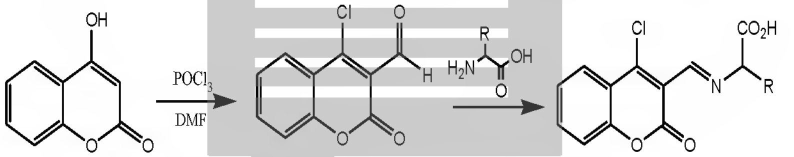
There are number of reports that natural and synthetic coumarin derivatives possess antimicrobial activity [1-2].Amino acids have found extensive application in the life sciences as components of biologically active peptides and small molecule pharmaceuticals[3].Schiff bases are the important compound owning to their wide range of biological activities industrial application[4].They have been found to possess the pharmacological activities such as anticancer, antibacterial, antifungal and antimicrobial[5-9].In the present work, we report the synthesis of Schiff'sbases of 4-chloro-3- coumarinaldehyde.

A number of novel 2-((4-chloro-2-oxo-2H-chromen-3-yl)methylen) amino)carboxylic acid in situ of reaction of amino acid with 4-chloro-2-oxo-2H-chromen-3-carbaldehyde were synthesized.



R = -CH3 , $-CH(CH_3)_2$, $-CH(CH_3)(C_2H_5)$, $-CH_2CH(CH_3)_2$, $-CH_2Ph$

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Synthesis of N,N′-bis benzamido thiocarbonyl phenylenediamine derivatives

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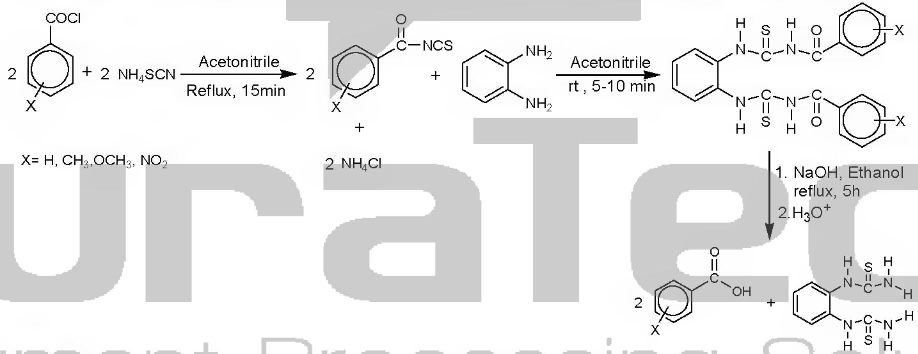
It is well known that thiourea derivatives exhibit potent antibacterial [1], fungicidal, antitubercular,
antitumor, antiviral, analgesic bioactivities and are also useful as insecticides, fungicides, herbicides [2], and plant-growth regulators [3]. The compounds containing thiourea as structural fragment in their molecules are suitable candidates for chemical modeling as precursors in the synthesis of heterocyclic active derivatives. The thioureides compounds are useful ligands in coordination chemistry, being studied their complexation behavior, general characterization and biological activity, especially as cancerostatic agents [4].

In this research, reaction of benzoyl isothiocyanates with *o*-phenylenediamine was studied. The results show products of the reaction are derivatives of N,N′-bis benzamido thiocarbonyl phenylenediamine in high yields and short reaction times. Hydrolysis of these products produce thiourea derivative of phenylenediamine.



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Polymeric nano-structures based on carbon nanotubes

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Polyethylenimine and their derivatives,especially poly(2 -oxazoline),are known as key compounds, opening up new aspects of polymerization chemistry of cyclic iminoethers and materials science. In this study, polyoxazoline bease on carbon-nanotube synthesized. functionalization nanotubes reaction as a macro-initiator in the polymerization cationic 2 - methyl -2 - oxazoline to be applied. Carbon nanotubes (CNTs) are ideal fillers for polymer composites due to their high Young's modulus combined with good electrical and thermal conductivity. The very high aspect ratio makes it likely that the addition of a small amount of CNTs strongly improves the electrical [1], thermal [2] and mechanical [3] properties of the polymer matrix. Thus, CNT/polymer composites combine the good processability of the polymers with the excellent mechanical and other functional properties of the CNTs. Polyoxazoline polymers with methyl (PMOZ), ethyl (PEOZ), and propyl (PPOZ) side chains were prepared by the living cationic polymerization method. In this contribution, we report a novel functionalization that follows the approach of the diazonium salts [4,5]. we have employed 4-(bromomethyl)aniline as the regentfor the generation of the diazonium salt . The resulting composite was characterized by TGA and DSC. The TGA were conducted in a Shimadzu TGA-50, under air at a heating rateof 5 °C/min, from room temperature to 800 °C. Nanostructured poly oxazoline were studied with the various methods, such as IR, TEM, SEM, HNMR, RAMAN. The PMOZ-modified nanotubes show a markedly increased suspendibility in chloroform due to the high solubility of PMOZ in this solvent. The impact of PMOZ as a biodegradable and biocompatible polymer, and its applications in tissue engineering give significance to these results, which could lead to the incorporation of nanotube-based advanced materials for biomedical purposes. At the same time, these results can be generalized to other monomers that polymerize via the same mechanism as PMOZ as well as to the generation of copolymers by using appropriate combinations of monomers.

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Synthesis and characterization of two tridentate imine compounds with diketone base as initial reactant

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In recent years, some important potential applications, such as catalysis, magnetism, gas storage of the functional coordination complexes have been drawn considerable attention [1-3].

Some of the organic compounds consist of imine groups act as coordinated ligands. The Schiff bases ligands with the imine group derived from the condensation of primary amines and carbonyl compounds [4-5]. Herein, we report the synthesis of two distinct Schiff base organic compounds; L_1: 3-(2-hydroxyethylimine)-1-phenylbutane-1-one and L_2: 4-(2-hydroxyethylimine)pentane-2-one.

These two synthesized organic compounds; Schiff base ligand; with three sites for coordination are connecting as a chelate to the metal centers as nodes. So, these organic structures have best potential for some biological applications. Also, these structures are characterized by IR, ^{1}HNMR and ^{13}CNMR spectroscopies.

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Synthesis of some new tetrazolo pyrimidine derivatives

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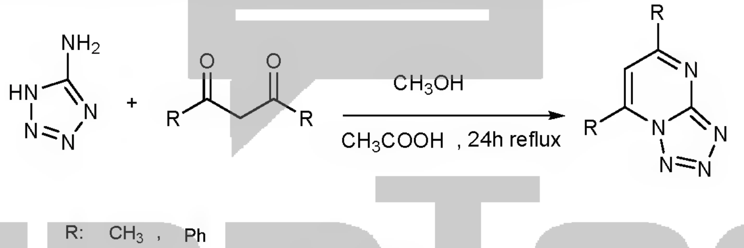
Pyrimidine is a heterocyclic aromatic compound containing two nitrogen atoms at positions 1 and 3 of the six-member ring. Pyrimidine nucleotides are of fundamental importance as precursors of DNA and RNA biosynthesis in all living organisms[1]. The regulation of pyrimidine biosynthesis in plants is poorly understood, relative to what is known in other organisms[2-4]. The fused derivatives by heterocyclic compounds display good antifungal

activity[5]. Tetrazoles have important applications in major areas, such as medicine, agriculture and food chemistry[6]. Tetrazoles have also important uses in organic synthesis[7]. In The present study reaction of 5- amino tetrazole with β- di- ketone derivatives produce some new tetrazolo pyrimidine derivatives.



Scheme 1

Structural characterization of these new compounds was carried out using IR, NMR, and MASS spectroscopy.

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Development of heterogeneous catalyst based on modified triazine ring supported on silica-gel for the Knoevenagel condensation

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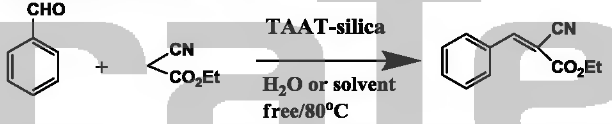
Heterogenization of homogeneous catalysts is an important topic in organic chemistry [1]. While some advantages of the homogeneous catalysts such as catalytic activities and selectivity are retained, other properties like easier work-up, recyclability and stability of the heterogeneous systems will be obtained. Knoevenagel condensation is a well-known organic reaction largely employed for C–C bonds formation [2]. The Knoevenagel adducts, in fact, are useful intermediates for further transformations, such as Diels–Alder and Michael additions. The classical Knoevenagel condensation has been carried out by reacting of a methylene active compound with an aldehyde or a ketone in the presence of a base. Methylene active compounds carrying two electron with drawing groups, such as malononitrile, cyanoacetates, malonates, and β-ketoesters, are generally used in the known condensations [3]. In this work, silica gel surfaces were modified with diethylenetriamine (DETA) via two step chemical reaction. Cyanuric chloride was chemically bound to the surface hydroxyl groups of silica-gel to give cc-silica. In the second step cc-silica was reacted with DETA to give diethylenetriamine on triazine ring bounded to silica-gel (TAAT-silica). This heterogeneous catalyst was used as a basic catalyst for the Knoevenagel condensation reaction of aromatic aldehydes and ethyl cyanoacetate in water as a solvent (Scheme1). The green and mild reaction conditions, medium to short reaction times, simple work-up, low cost and easy preparation of catalyst are the obvious advantages of the present catalyst. Finally, this catalyst can be recovered by washing with aqueous solution and used again at least three times without negligible loss in its activity.



Scheme 1. Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate using TAAT-silica as a heterogeneous catalyst.

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Radiation crosslinking of poly (butylene terephthalate) and its effects on thermal properties and flame properties

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Engineering plastics like polybutylene terephthalate due to its desirable properties as have various industrial applications such as in automotive, electric and electronic component industries. One of the ways to improve more these properties for special applications is crosslinking.[1] There are different methods to crosslink polymers, among which radiation cross linking method has more advantages than that of chemical methods. Major advantages are: process takes place at room temperature and under normal pressure; also irradiation takes place after the moulding process without presence any chemicals, substantial time and cost savings.[2,3] In this work the effect of radiation crosslinking on the thermal and flammability properties of polybutylene terephthalate (PBT) has been investigated. For this aim ROHDOTRON TT200 accelerator has been used. PBT/additives samples were prepared by using internal mixer 350-E made by Brabender Company. The mixing was carried out at 80 rpm and 240 °C. Rang dose of crosslinking the polymer was between 200 - 400 kGy. Thermal and fire tests such as heat distortion temperature, Thermogravimetric analysis and UL-94 test in vertical and horizontal position have been carried out on irradiated and non-irradiated samples. Result of TGA revealed that radiation crosslinking has effective role on the enhancement of thermal stability and increased char formation. According to the results of UL 94, irradiated samples burned with lower speed and less dripping.

Key words: radiation crosslinking, electron beam, polybutylene terephthalate, flammability, thermal properties

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Fast and Efficient Method for Reduction of Carbonyl Compounds with $NaBH_4/Fe_3O_4$ Nanoparticles System

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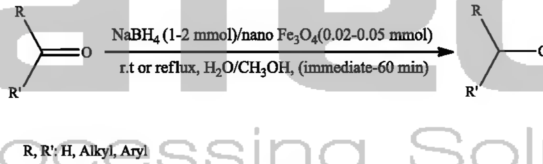
Increasing attention to the environmental concerns and the requirement for efficient and green catalysts have attracted chemists to use new and environmentally benign catalysts. Recently, nano- particles have been used in organic synthesis. Fe_3O_4 nano-particles are one kind of the most important nano-particles. Because excluding the normal nano behavior, they impact a characteristic magnetism which is helpful for its recycle. The catalyst can be recovered by the use of an external magnet and reused (Scheme 1)[1].

Reduction of carbonyl groups to the corresponding alcohols is one of the most important functional group inter-conversions in organic synthesis. On the other hand, metal hydrides are valuable reagents in modern organic chemistry. The most frequently used hydride is the $NaBH_4$ reagent. It is a mild, inexpensive and invaluable reagent for applications in a wide range of reduction processes. The reducing capability of $NaBH_4$ greatly could be accelerated by using many of additives [2,3]. In this investigation, we introduce a new combination system of $NaBH_4$ with catalytic amounts of magnetic Fe_3O_4 nano-particles (16.81 nm)[4]. as reusable and green catalyst for reduction of variety of carbonyl compounds such as aldehydes, ketones, acyloins, α-diketones and conjugated enones to their corresponding alcohols in high to excellent yields (Scheme 2).

Scheme 1



Scheme 2

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Synthesis of optically active 1,2,4-triazolo-[3,4-b]-1,3,4-thiadiazole derivatives containing L-amino acid moieties

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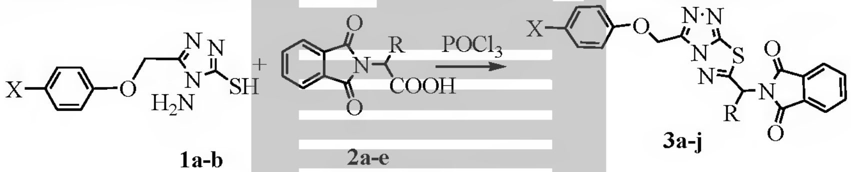
The recent literature is enriched with progressive findings about the synthesis and pharmacological activity of fused heterocycles. The [1,2,4]-triazolo-[3,4-b]-[1,3,4]-thiadiazole derivatives obtained by fusing the biolibale [1,2,4]-triazole and [1,3,4]-thiadiazole ring together, are reported to possess antimicrobial and antitubercular agents.[1] A literature search revealed which the preparation of these compounds have been extensively studied in the recent years, as followed from data of the most convenient procedure for the synthesis of [1,2,4]-triazolo-[3,4-b]-[1,3,4]-thiadiazole derivatives is based on the reaction of 5-substituted 4-amino-(4H)-1,2,4-triazole-3-thioles with carboxylic acids.[2]



Scheme 1. Synthesis of compounds **3a-j**

In continuation of our effort to develop the synthesis of new optically compound derivatives,[3-5] we report herein, a simple and efficient method for the synthesis of substituted triazolothiadiazole 3a-j **via reaction between of amino triazole with N-aroyl L-amino acid. 5-substituted 4-amino-(4H)-1,2,4-triazole-3-thiole** 1a-b **was prepared by heating substituted 4-substitueted phenoxy acetic acid with one equivalents of carbonothioic dihydrazide in an oil bath at 170 °C. The resultant triazole** 1a-b **was further converted to 1,2,4-triazolo-[3,4-b]-1,3,4-thiadiazoles** 3a-j **through one pot reaction by condensation with N-phethaloyl L-amino acids** 2a-e **in the presence of $POCl_3$ respectively. Our synthetic approaches are depicted in Scheme 1. In Conclusion we have been able to synthesize some N-aroyl-L-amino acids having a free terminal carboxyl function, which can react with amino triazole. This reaction may be useful for combinational synthesis of type** 3 **compounds having various R substitutions with a view to test for biological activities**.

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18th Iranian Seminar Of Organic Chemistry
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Using 1-(1-buthyl sulfonic)-3-methylimidazolium nitrate and phosphorouspentoxide as a green solvent for the oxidation of benzylic alcohols to the corresponding carbonyl compound.

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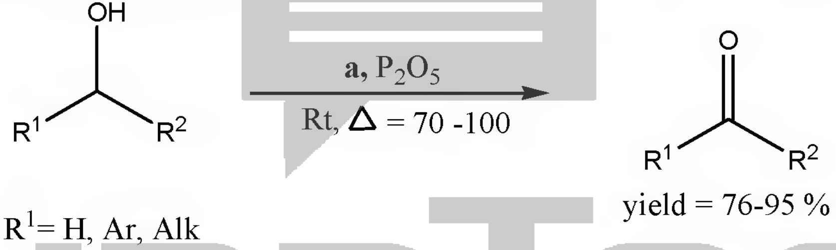
Ionic liquids, nowadays, have been using as green solvents in reaction media. Their safety, recyclability and ease of handling and etc are some of the outstanding characteristics of them [1]. Using ionic liquids having dual effects as solvent and reagent or catalyst have received considerable attention in recent years [2]. These applications eliminate the use of some toxic reagents such as transition metals, strong acids and especially high temperatures. On the other hand oxidation of benzylic alcohols to corresponding carbonyl compounds has been extensively studied and lots of catalysts and reagents have been envisioned for this procedure [3]. Ionic liquids, also, have been applied as green solvents and reagents for this transformation. Here in, we wish to report a green and versatile procedure for the oxidation of benzylic alcohols to carbonyl compounds via new nitrate – base ionic liquid in the presence of P_2O_5. Some of the benefits of the process are: the reagent is cheap and easy to handle in comparison with previous procedures. The ionic liquid is stable for long time. The byproducts are harmless to environment and the extraction is straightforward and the ionic liquid could be recovered completely. The reaction results in no yield for aliphatic alcohols.



R^1= H, Ar, Alk
R^2= Ar, Alk

a =

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Solvent free azo dyes synthesis via coupling of α-naphthol in the presence of $SbCl_5/SiO_2$ at room temperature

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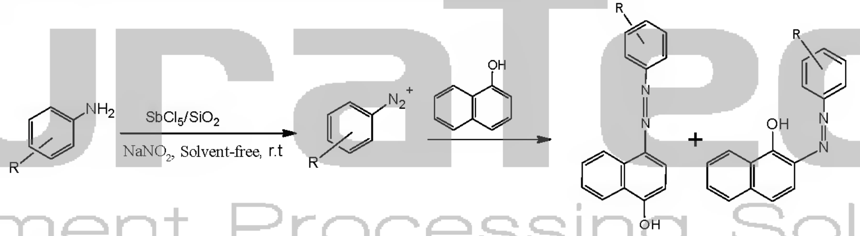
In recent years, the use of solid acids as heterogeneous catalysts has received significant interest in different areas of organic synthesis. Heterogeneous solid acids are advantageous over conventional homogeneous acid catalysts as they can be easily recovered from the reaction mixture by simple filtration and can be reused after activation or without activation, thereby making the process of N-donor solvents have been reported [1]. Diazonium salts are precursors of azo compounds which are very useful in the fields of dyes, pigments and advanced materials. Azo dye compounds are widely used as colorants in the textile industries but they have several other applications, for example, colorants for digital printing and photography; dyes for drug, food and cosmetic applications. Azo dyes are compounds that contain azo groups linked to methine or aromatic sp^2-hybridized C-atoms [2]. These azo dyes have two different products that separated with column chromatography. It is noted that lewis acid sites on silica-supported antimony (V) chloride ($SbCl_5$:SiO_2) act as highly efficient catalyst, even for low activity substrates, in the preparation of azo dyes in solvent free condition. The fact that $SbCl_5$ did not leach makes $SbCl_5/SiO_2$ as alternative heterogeneous acid catalyst to the conventional homogeneous acids at room temperature [3]. The formation of the diazotizing reagent starts with protonation of nitrous acid under strongly acidic conditions, and azo coupling occurs at room temperature in the presence of nucleophilic components and heterogeneous catalyst. Spectroscopic methods such as ^{1}H- and ^{13}C-NMR, FT-IR, UV-Vis were used for identification of azo dyes.



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One-Pot synthesis of hexahydroquinoline derivatives using $AlPW_{12}O_{40}.XH_2O$ catalyst

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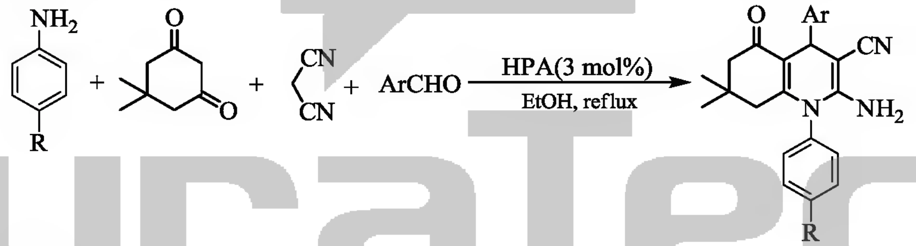
In recent years, an increasing interest has been focused on the synthesis of 1,4-dihydropyridine (DHP) compounds owing to their significant biological activities.[1] Quinolines having a 1,4-dihydropyridine nucleus are very important compounds because of their pharmacological properties such as antitumalarial, anti-inflamatory, antiasthamatic, antibacterial and antihypertensive.[2] Alternative strategies for their synthesis involving different catalysts and conditions have been developed.[3,4] However, some method suffer from drawbacks like some longer reaction times, unsatisfactory yields, harsh reaction conditions.

In continuation of our investigations on the synthesis of 1,4-dihydropyridine,[5] herein we describe a novel and efficient one-pot method for the preparation of 2-amino-7,7-dimethyl-5-oxo-1,4-diaryl-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile derivatives from cyclo-condensation of aldehydes, malononitrile, anilines and dimedone in reflux of ethanol as solvent and HPA($AlPW_{12}O_{40}.XH_2O$) as catalyst. This new one pot method has the advantages to give high yields, to be completed in short reaction times, with simple product isolation procedure.



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Design and Synthesis of New Potent Peptides and Investigation of Their Activities

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Peptides are known as natural drugs. Peptide Chemistry has reached a considerable level of maturity, and apparently almost with complex structure. Designing and synthesis of novel peptides as biologically active compounds is a central goal in drug discovery. [1]

In continuation of our recent research about the synthesis of novel peptides;[2-5] in this lecture designing, synthesis, and investigation of biological activities of some novel peptides will be presented. Since addition of hydrophobic moiety to a peptide sequence increase the peptide's ability to penetrate plasma membrane, in this way some peptides were synthesized with adding a hydrophobic moiety in the end of N- or C-terminus of peptides. Meanwhile, recently unusual amino acids are increasingly becoming important substrates in modern drug synthesis and discovery research. With these points in mind, some novel peptides were designed and synthesized using combination of known SPPS and SIS approaches.

In this lecture, the three main sections are as follows:

a) Synthesis of LH-RH analogues via Ugi-4CR and investigation of their anti-cancer activities.

b) Synthesis of novel analgesic and opioid peptides and comparison of their activities.

c) Combination of unusual amino acids with di- or tri-peptides, and investigation of their structure.

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Synthesis and characterization of a new bidentate Schiff base ligand

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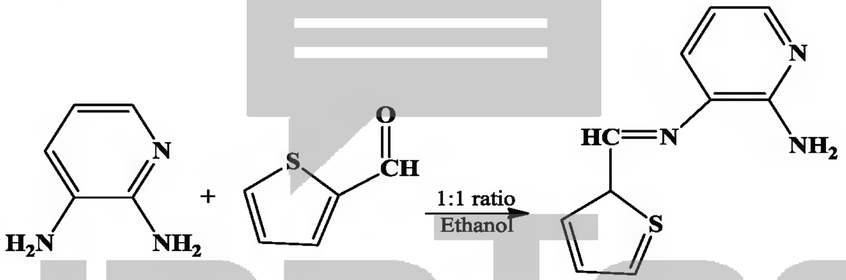
Abstract

Compounds with C=N functional group are known as Schiff base, which are usually synthesized from the condensation of a primary amines and active carbonyl groups. A large number of Schiff base compounds are often used as ligand in coordination chemistry by considering their metal binding ability [1]. These compounds may serve as models of relevance for biologically important species or as catalysts for various organic transformations, and are promising materials for optoelectronic applications and the design of biosensors [2-4].

The new unsymmetrical Schiff base ligand (*E*)-N^3–(thiophen-2-yl-methylene)pyridine-2,3-diamine (L_1H), was prepared by condensation of 2,3-diaminopyridine and thiophen-2-carbaldehyde in ethanol at -4 °C. The synthesized Schiff base ligand has been characterized with common physical methods such as elemental analysis (CHN), FT-IR, ^1H, and ^{13}C NMR.



The FT-IR spectrum of the ligand shows a sharp band at 1600 cm^{-1}, attributable to the imine group, but no bands due to m(C=O) vibrations. Observed bands at 3452 and 3286 cm^{-1} are assigned to NH_2 group. The ^1H NMR spectrum of Schiff base displayed nine resonances in the downfield region of the spectrum that can be assigned to protons of L_1H. One singlet at 5.41 ppm is assigned to NH_2 of the ligand. All aromatic protons and $-CH_{imine}$ resonate in 6.68-8.66 ppm. The ^{13}C NMR spectrum of the ligand display 10 distinct resonances assigned to the aromatic and imine carbons. All of obtained data confirms the formation of tridentate Schiff base ligand.

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Gewald and Ugi One-pot Multicomponent Reactions to Synthesis of Polysubstituted 2-Aminothiophens and Isocoumarins respectively Catalyzed by [HMIM]Br Ionic liquid

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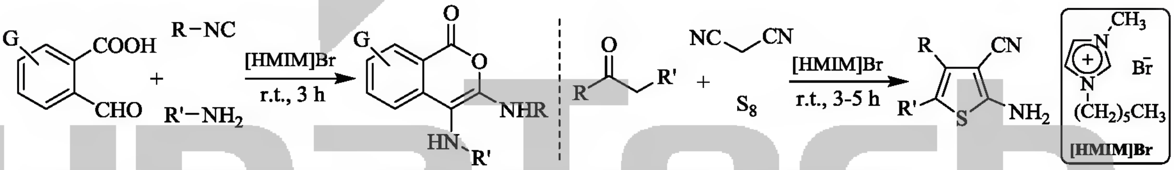
Substituted 2-aminothiophenes are important intermediates in the synthesis of a variety of agrochemicals, dyes and pharmacologically active compounds.[1] The most convergent and well-established classical approach for the preparation of 2-aminothiophenes is Gewald's method, which involves multicomponent condensation of a ketone with an activated nitrile and elemental sulfur in the presence of morpholine as a catalyst.[2]

Ugi four-component condensation (Ugi-4CC) usually refers to the reaction between amines, carbonyl compounds, carboxylic acids, and isocyanides. Really, there are many kinds of Ugi reactions since large variations of the nature of the components are possible.[3]

Ionic liquids, as environmentally benign solvents, offer an attractive alternative to conventional organic solvents because they are non-volatile, non-flammable, non-explosive, and can be recycled.[4]

The high yields, and ease of product isolation prompted us to investigate the Gewald and Ugi reaction but replacing the organic base with ionic liquid 1-hexyl-3-methylimidazolium bromide [HMIM]Br and using room temperature for heating.



In conclusion, we have introduced an efficient and environmentally friendly approach for the synthesis of polysubstituted 2-aminothiophenes via Gewald reaction and isocoumarins via Ugi-4CC using [HMIM]Br in good to excellent yields at room temperature. Also, the reaction workup is simple and the ionic liquid can be easily separated from the product.

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Theoretical Study on the Mechanism of Ugi Reaction

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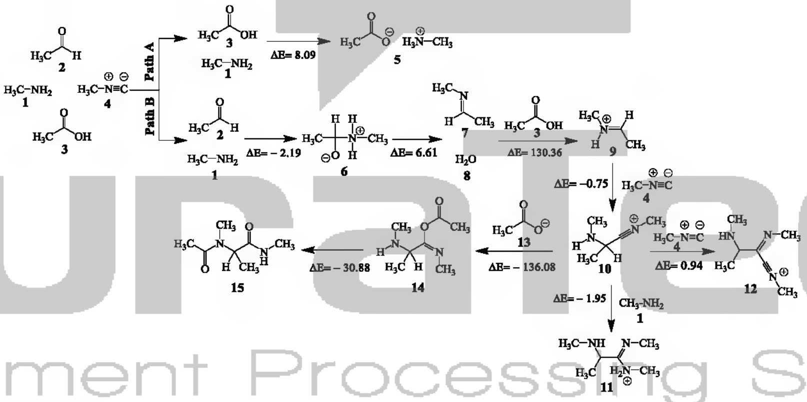
The Ugi reaction is a multi-component reaction in organic chemistry involving a ketone or aldehyde, an amine, an isocyanide and a carboxylic acid to form a bis-amide[1,2]. In this paper we try to report on the mechanism of Ugi reaction from theoretical point of view. Reagents, products and possible intermediates of Ugi reaction were designed and optimized at HF/6-31G* level of theory without any constrains. Heats of formation (HF, in Hartree) and relative stabilities (ΔE, in kcal/mol) were calculated and summarized in Table 1 and Scheme 1. The results were in agreement with experimental findings so that as well in experimental considerations, formation of **15** was kinetically the best choice to reaction proceeding.

Compound	HF	Compound	HF	Compound	HF
1	-95.140929	6	-248.000453	11	-399.356145
2	-152.856033	7	-172.002152	12	-436.005625
3	-227.743781	8	-75.987772	13	-227.172921
4	-131.845649	9	-172.365261	14	-531.601888
5	-322.871823	10	-304.212105	15	-531.651108

Table 1.



Scheme 1.

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Computational study of some 1, 3-dipolar cycloadition reactions

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Introduction: The chemistry of 1,3-dipoles has attracted great interest more than a century [1]. This kind of cycloaddition reaction is one of the most useful reactions for the synthesis of heterocyclic compounds [2].In the present work, we investigated reacting ethyl diazoacetate (4) with various alkynes (1-3) in gas phase (Fig.1).These reactions gave the 3- and 4-isomers [3].

Computational details: All calculations were performed with the Gaussian98 program [4]. For DFT calculations, the B3LYP/6-31G* level of theory was employed. The optimizations of equilibrium geometries of all products were obtained by full optimization at the ground states of products. Thermodynamic calculations are performed with the same method. Also we calculated the chemical hardness, η , and the global electrophilicity index, ω, that μ is the electronic chemical potential and are given by: $\eta \approx \varepsilon_L - \varepsilon_H$, $\omega = \left(\mu^2 / 2\eta \right)$, $\mu \approx (\varepsilon_H - \varepsilon_L)/2$

Results and discussions: In this work, at first, the maximum hardness principle (MHP) which was introduced by pearson [5] were used to predict the stability sequence of regioisomeres products in selected reactions(Fig.1). Our results reveal that MHP principal correctly predict the 3-isomer (5) is more stable than 4-isomer (6). Then the electronic chemical potential, μ, of reactants are used to indicate direction of charge transfer (CT) at these 1,3DC reactions. The results revealed that the three dipolarophiles with the electronic chemical potential values, μ, between -0.0947 a.u. and -0.1033 a.u., are lower than of their common dipole with value -0.1568 a.u. .Therefore CT at these reactions will be from the dipolarophile to dipole. Also, electrophilicity,ω, for reactants were calculated. Three dipolarophiles (1, 2, 3) presented electrophilicity,ω, with values 0.918 eV, 0.774 eV and 0.802 eV respectively. With the absolute of scale of electrophilicity based on the ω index these compounds can be classified as marginal(2,3) or may be moderate(1) electrophilies. On the other hand, electerophilicity,ω, of dipole (4) has values 3.82 eV, So, dipole classified as a strong electrophile. Results show that dipole has a lower chemical potential (-0.1568), which is the index that determines the direction of the electronic flux along the cycloadition. Furthermore, along this series of 13DC reactions the more favorable interaction will take place between the less electrophilic specie 2, namely the dipolarophiles in the present case, and the electrophilic dipole (4).At the end, thermodynamic results show that all pathways are exothermic. Computed reactions energies for 2 pairs of reactions (Gibbs free energy difference, ΔG) suggest that the pathway with 3-isomer product is thermodynamically the most favorable.

Fig.1. The considered reactions [3] (3 pairs reactions)
R= **1)** –CH2CH2OH **2)**-CH2CH2CH2OH
3) –CH2-CH2-C H(CH3) –OH

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A recyclable protocol for aza-Michael addition of amines to α,β-unsaturated carbonyl compounds using Hydroxy sodalite

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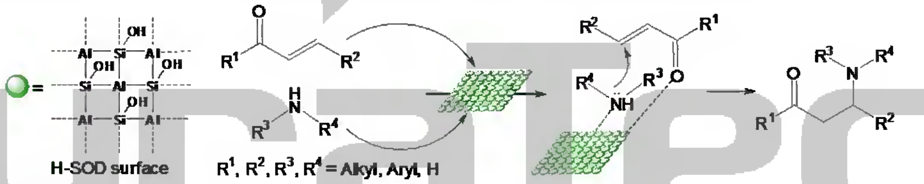
The aza-Michael addition is one of the widely used reactions for carbon-nitrogen bond formation in modern organic synthetic chemistry. Conjugate reaction of various amines with α,β-unsaturated carbonyl compounds provides β-amino carbonyl ingredients, which have attracted great attention for their use as key intermediates of anticancer agents, antibiotics and other drugs [1]. Generally, aza-Michael additions have been catalyzed by strong bases and acids [2]. However, many of these methods suffered from some drawbacks, for example, the requirement for a large excess of reagents, substrate selective for some catalysts, often involvement of some toxic solvents and occurrence some side reactions. Therefore, chemical researchers have paid more attentions to the development of more mild catalytic systems for the aza-conjugate reaction. Hydroxy sodalite (H-SOD) is a compact and stable kind of alumino silicate (zeolite) that have active surface of alumina and silica with ability of hydrogen bonding in dehydrated form. In this work, we have used hydroxy sodalite as a new catalysts for aza-Michael addition of amines to α,β-unsaturated carbonyl compounds. In this reaction Lewis acid site of H-SOD can active the carbonyl group of unsaturated ketone and hydroxyl group of its surface will adsorbed the amine on through hydrogen bonding. This protocol also has some advantages, such as readily work-up of the reactions, good to excellent yields, excellent reaction selectivity and good recyclability of the hydroxy sodalite.



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Determination of organosolphor pesticide residues in tobacco plant by spectrophotometery and GC-MS method.

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pesticide residues are one of most important problems in environmental chemistry and human safety[1-3] . In this article studied determine of pesticide residues (dithiocarbamates) in tobacco by GCMS and spectrometric method. In spectrometric method for determination of dithiocarbamates in tobacco, the dithiocarbamates are decomposed on heating with hydrochloric acid in the presence of stannous chloride. The carbon disulfide (CS_2) which is formed, is transferred with a current of nitrogen, into a trap containing concentrated sulphuric acid to remove interfering substances, and then into a trap containing a methanolic solution of potassium hydroxide. The concentration of potassium o-methyl dithiocarbamat formed under these condition was measured by spectrophotometry, then results were expressed as carbon disulphide, and the values obtained using this method were taken to indicate the dithiocarbamate residue level. In this study, carbon disulfide which is formed at the end of the extraction stage is solution into a trap containing isooctane. The concentration of carbon disulfide was measured by GCMS. The GCMS response was calibrated using carbon disulfide standard solutions. 30 samples of tobacco and sodium diethyldithiocarbamate were determined amount of carbon disulfide by spectrometric method and GCMS method. The two series of results were compared by using analysis of variance or t-test method for p= 0.05, and correlation statistical calculation.

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Effect of Ca^{2+} on mnemiopsin structure and dynamics

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Mnemiopsin is a protein that belongs to the EF-hand superfamily of calcium-binding photoproteins [1]. They have been widely used as probes of intracellular Ca^{2+}, biosensors, bioanalysis, lables for highly rapid immunoassay and etc. [2]. All members of EF-hand superfamily exhibit a common structural motif (helix-loop-helix) [3]. In this study, at the first time the conformational changes of mnemiopsin were investigated in the addition of Ca^{2+}. Mnemiopsin was expressed in *E. coli* BL21 and obtained after purification on Ni-NTA Agarose and dialysis with a solution containing 50 mM Tris-base, 5 mM NaCl and glycerol 5% pH 9.0. Calcium is removed during the dialysis by EDTA [4] or TCA (trichloroacetic acid) precipitation (apo-form) [5]. The far-UV CD and fluorescence (intrinsic, extrinsic and quenching) measurements were carried out with Jasco-715 spectropolarimeter and LS55 fluorescence spectrophotometer, respectively. The far-UV CD spectra of all Ca^{2+}-loaded form are nearly similar to that of apo-form. In addition, the low calcium concentration (µM) induced changes of the molar ellipticity are distinguishable from that of the high calcium concentration (mM). Trp fluorescence intensity of the protein decreases in a concentration-dependent manner of Ca^{2+} added, whereas its ANS fluorescence increases. These results indicate that the apo-form of the protein adopt a closed conformation when compared to the Ca^{2+}-loaded once. Ca^{2+}-loaded mnemiopsin was also quenched more than apo-form, revealed increasing flexibility of the protein in the presence of Ca^{2+} in contrast to other EF-hand proteins.

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Synthesis and characterization of novel soluble polyimides from diamine having xanthene and various dianhydride

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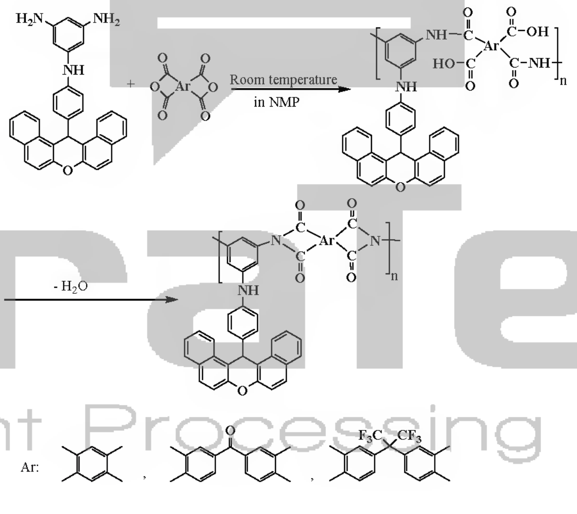
Polyimides have been of great interest in engineering and microelectronics for a number of applications owing to their unique property combinations [1,2]. Although exceptional thermal stability is complemented by excellent mechanical and electrical performance, their in-solubility in common organic solvents and their high glass transition and softening temperatures make these systems difficult to process and fabricate.therefore,considerable research has been undertaken in order to identify new ways to circumvent these limitation. Consequently, polyimide processing is generally carried out from poly(amic acid) solution, i.e., a processable precursor, and can be subsequently converted to intractable polyimide through thermal treatment. However, this manufacturing method has several inherent problems such as the hydrolytic characteristic of the poly(amic acid); moreover, voids and stresses can be generated in the final product after thermal treatment [3,4]. Therefore, much effort has been concentrated on synthesizing soluble and tractable polyimides. This paper relates the synthesis and characterization of new soluble polyimides derived from the novel diamine bearing xanthene unit and conventional aromatic dianhydrides.



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Synthesis of highly-substituted fluorenes by reaction of Inden-3-yliden malononitrile with acetylenic esters

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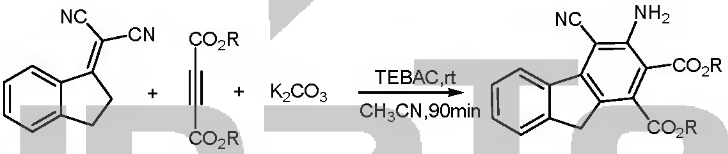
Fluorene and fluorene derivatives are important compounds and have different types of biological activities, such as anti-inflammatory[1] and antitumor activates.[2] The literature reports that the tetrahydrobenzo[a]-fluorine compounds also inhibit bone loss or bone desorption.[3] Besides, 9H-fluorene derivatives have a strong inhibitory effect on cholesterol biosynthesis and anti-inflammatory activity.[4] The considerable research effort is justified by the potential applications of these molecular systems, which are the basis for artificial photosynthetic systems,[5] materials presenting semiconducting or nonlinear optical properties[6] and molecular electronic devices.[7] They have been reported to be prepared from arylidenemalonodinitriles and 1-arylethylidenemalonodinitriles in the presence of piperidine [8] or under microwave irradiation.[9]

In the light of the above mentioned chemistry and properties of fluorenes, the development of new approaches, which enable access to these entries, are desirable. As part of our ongoing studies on the development of facile methods for synthesis of organic compounds from readily available starting materials,[10] herein we found that Inden-3-yliden malononitrile, can react with dialkyl acetylenedicarboxylates in the presence K_2CO_3 and TEBAC (triethylbenzylammonium chloride) as catalyst, leading to highly-substituted fluorene via condensation-cyclization process. The structures of the products were deduced from their IR, mass, ^{1}H NMR, and ^{13}C NMR spectra.



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A new tetradentate Schiff base ligand derived from 6-methoxysalicylaldehyde: Synthesis, characterization and crystal structure determination

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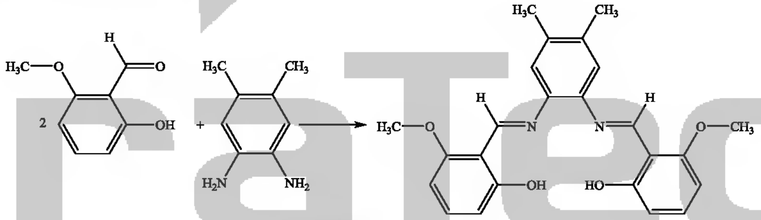
Schiff bases are one of the most prevalent ligands in the field of coordination chemistry. The importance of Schiff bases is related to the frequent presence of a C=N bond in natural systems as well as to the fact that their easy formation gives the opportunity of building ligands of different structures [1-3].

The title Schiff base ligand was synthesized by adding 6-methoxysalicylaldehyde (4 mmol) to a solution of 4,5-dimethyl-1,2-phenylenediamine (2 mmol) in ethanol (20 ml). The mixture was refluxed with stirring for half an hour. The resultant yellow solution was filtered (Scheme 1). This ligand was characterized by ^{1}H NMR, IR and its solid state structure was determined using single crystal X-ray diffraction.

In conclusion, the asymmetric unit of the ligand comprises two crystallographically independent molecules A and B. The dihedral angles between the central dimethylsubstituted benzene ring and the two outer benzene rings are 49.5 (1) and 5.06 (11)° in molecule A, and 42.55 (8) and 5.77 (9)° in molecule B. In each molecule, two strong intramolecular O—H⋯N hydrogen bonds generate two *S(6)* ring motifs [4]. The crystal structure is further stabilized by intermolecularπ–π interactions.



Scheme 1

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Synthesis and characterization of surface modified superpamagntic iron oxide nanoparticles with thiodiglycolic acid and sodium alginate

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Abstract

Superparamagnetic iron oxide nanoparticles (SPION) with appropriate surface chemistry have been widely used experimentally for numerous in vivo applications such as magnetic resonance imaging contrast enhancement, tissue repair, immunoassay, detoxification of biological fluids, hyperthermia, drug delivery and in cell separation, etc. All these biomedical and bioengineering applications require that these nanoparticles have high magnetization values and size smaller than 100 nm with overall narrow particle size distribution, so that the particles have uniform physical and chemical properties [1]. In this study superparamagnetic iron oxide nanoparticles were surface-modified with thiodiglycolic acid and sodium alginate as two different kinds of surfactants to attain ultrafine and well-dispersed (water-base) Fe_3O_4 nanoparticles. These nanoparticles were synthesized by controlling chemical co-precipitation method from the solution of ferrous/ferric mixed salt-solution in alkaline medium. For comparison, Fe_3O_4 nanoparticles without surfactant were also synthesized under the same condition and method. The result revealed that addition of surfactants affected on the size and morphology of the nanoparticles.Their structure and morphology were characterized by X-ray powder diffraction (XRD), atomic force microscopy (AFM), scanning electron microscope (SEM), energy dispersive spectrometer (EDS) and Fourier transform infrared spectroscopy (FT-IR). Furthermore, magnetic properties of the products were studied by vibrating sample magnetometer (VSM), the result showed that the two different surface modified nanoparticles posses superparamagnetic properties at room temperature because the remanence and coercivity of the particles is negligible in absence of external magnetic field. The crystallite size of the two samples was calculated using Debye–Scherrer equation.

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Synthesis and characterization of polyurethane elastomers with different thio compounds as chain extender

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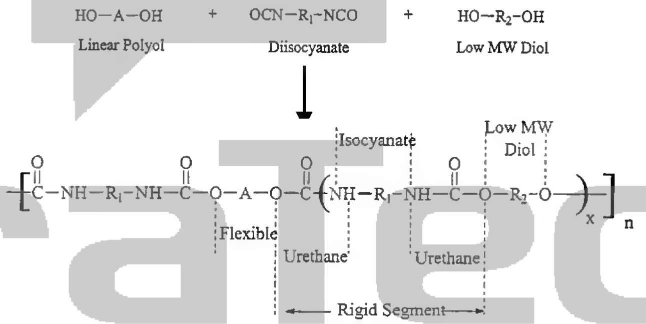
Polyurethane (PU) elastomers as a unique material class and occupying a special place in the materials-properties spectrum are defined in terms of their physical properly and chemical structure relationships .Their traditional application fields are defined followed by the great upthrust of PUs Into new fields in the aerospace, surface coatings and automotive industries [1]. This study reports the synthesis and characterization of polyurethane elastomers using prepolymer method, with emphasis on the effect of different sulfur containing chain extender on thermal and mechanical properties of polyurethanes. Tree types of Polyurethane elastomers using polytetramethylene glycol (PTMG-1000), Isophorone diisocyanate (IPDI) and tree sulfur containing compounds, thiodiglycol, thiodiglycolic acid (TDGA) and *thiodipropionic* acid (TDPA) as chain extender were synthesized. Chemical structure of PUs was confirmed by Fourier Transfer Infrared (FTIR) analysis. FTIR results confirmed the presence of amide group for acid-based chain extenders. The effect of chain extenders on thermal stability have been investigated by studying the Dynamic Mechanical Thermal Analysis (DMTA) and thermogravimetrlc analysis (TGA). The physical and mechanical properties of prepared polyurethane elastomers are measured. The obtained results are investigated and discussed.



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Recognize Organic Pollutions by Bioindicators and Measurement methods them in Aquatic Environments

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Abstract:

Persistent organic pollutants (POPs) are featured with low and high solubility in water and some organic solvents and fast respectively.[2] These compounds are poisonous and possess accumulative property in live tissues as well as long-term storage / transmition capability that can create deleterious effects on aqua ecosystems (water, sediments, aquatics) and man's health.[1] On the other hand, existence, status, and number of variety of fishes, invertebrates, insects, algae, and vegetation's (bioindicators) suggest accurate information on health or pollutions of an aquatic environment such as rivers, lakes, and marshes.[3]

In this study, the method of using bioindicators has been compared with the method of chemical analyses upon tracing persistent organic pollutants in aquatic environments. In addition, its superiority in fields such as specifying pollution level, sampling methods, low-cost method, unnecessity for advanced lad-equipment, method convenience, prompt conclusion, variety of measurement methods for pollution, classification of pollution level, and accumulative effects of pollutions have been reviewed.[1][2][3][4]

There are great deals of organic matters in aquatic environments. Some of them are known as oxygen-demanding residue. Pollutants ratio in specific volume of water could be estimated and measured by oxidation of current carbon atom in the residue as well as calculating biochemical oxygen degree (BOD), chemical oxygen demand, and total organic carbon analysis (TOC).[1][2]

This paper attempts to compare the three methods to one another with respect to measurement methods, advantages and disadvantages of the methods, their use cases, their accuracy, measurement instruments, time and cost.[1][2][4][5][6]

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Preparation and characterization of semi-synthetic hydrogels based on poly (NIPAM) inserted onto collagen sponge

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Abstract

The preparation of a semi-synthetic hydrogel based on poly(N-isopropyl acrylamide-co-diethylene glycol diacrylate) inserted onto a collagen porous membrane, it was previous presented[1]. The synthesis of the hydrogels was performed through radical copolymerization of N-isopropyl acrylamide (NIPAM) with diethylene glycol diacrylate (DEGDA) also as crosslinking agent, using ammonium persulfate as initiator and N, N, N', N'- tetramethylethylene diamine activator, and it was achieved in the presence of the collagen matrix. In this paper the thus prepared hydrogels are characterized by Differential Scanning Calorimetry, Scanning Electron Microscopy and for their swelling capacities. A kinetic model was studied to investigate the swelling mechanism of the semi-interpenetrated polymeric network[2].

The swelling behaviour was found dependent on the hydrogel composition and to the external stimuli such as temperature and pH of environment. This manner of acting recommends these materials as smart materials with potential applications in tissue engineering and pharmaceutical field as for example bioproducts carrier matrices[3].

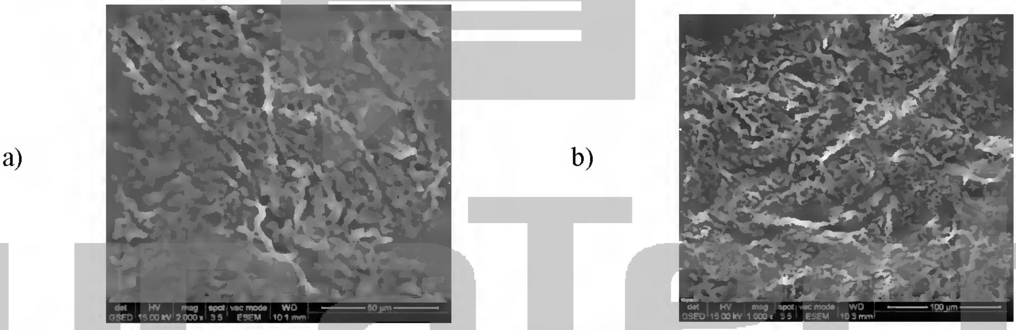

Figure 1. Morphological aspect of the hydrogel based on 50% collagen and 6.5% DEGDA (a) and 13.5% DEGDA (b) swelled in buffer solution of pH 2.4.

Keywords: semi-synthetic hydrogel, poly(N-isopropyl acrylamide-co-diethylene glycol diacrylate), collagen.

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Preparation and properties of new pyridine-based poly(ether-urea)s with improved thermal stability

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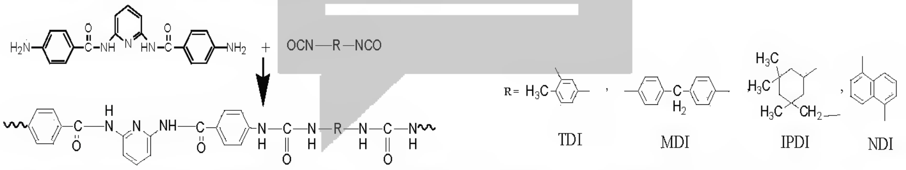
Polyureas are one of the most important classes of polymers that possess many uses for different industrial applications. They are unique polymers with a broad range of physical and chemical properties such as abrasion resistance, water repellency, leather appearance, etc. Polyureas are polyamides of carbonic acid, and like most of conventional polyamides, they are suitable for elastomer and fiber applications due to their tough and high melting point. Several methods have been reported to prepare polyureas including reaction of diamines with phosgene, carbonate esters, carbonate alkali metals, carbon dioxides, and ureas [1-3]. But the best method includes the reaction of diamines with diisocyanates. In this research, a new diamine monomer containing pyridine and ether units was prepared via two step reactions. Nucleophilic chlorodisplacement reaction of 2,6-diaminopyridine with two moles of 4-nitrobenzoyl chloride afforded 2,6-bis(4-nitrobenzamido)pyridine and subsequent reduction of the nitro groups led to 2,6-bis(4-aminobenzamido)pyridine. Solution polyaddition reaction using NMP as a solvent was successfully achieved for preparation of new poly(ether urea)s from the reactions of new pyridine-based diamine (DA) with four different diisocyanates.



The prepared monomer and all the polymers were characterized by conventional methods.
Different physical and thermal properties of the polymers were studied. According to the obtained results, these polymers showed high thermal stability. Incorporation of ether, pyridine and bulky groups were significant structural modifications for preparation of these thermally stable polyureas.

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Poly(3-methylthiophene)/SiO_2 nanocomposite prepared via an inverted emulsion technique

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Organic semiconductors have similar physical characteristics to inorganic semiconductors, which can be used in the manufacture of OLEDs [1], photovoltaic cells [2], lasers [3] and transistors [4]. Semiconductor polymers have advantages when compared to inorganic semiconductors, such as: (a) greater flexibility and adaptability, (b) possibility and ease to make small structural changes in the monomer of the polymer to modify its physical and chemical properties, (c) simplicity manufacturing techniques and (d) low cost of production. The poly(3-alkylthiophene) (P3ATh s) are derivatives of polythiophene, differing by an alkyl group attached to carbon 3. The P3AThs, due to the presence of alkyl group, show a significant increase in solubility, fusibility and luminescence compared to polythiophene. This class of materials has electrochromism, thermochromism and solvatochromism properties. On the other hand, it has been demonstrated that many characteristics of semiconductor polymers can be improved by the presence of nanosized particles such as TiO_2 and SiO_2 [5].

In the present work, we investigated the synthesis of poly(3-methylthiophene)/silica (P3MTh/SiO_2) nanocomposite by an inverted emulsion pathway for the first time. In this new method, toluene and chloroform were separately used as the reactions solvents. Therefore, an inverted emulsion was prepared, which had an organic solution of host polymer and surfactant as continuous phase and aqueous solution of oxidant as dispersed phase. Firstly, into a 100-mL round-bottomed flask, toluene or chloroform (40 mL), sodium dodecylbenzenesulfonate (SDBS) (1.4 mmol, 0.500 g) and nanosized SiO_2 (0.050 g) were poured, respectively while stirring at room temperature. In the second step, the solution of 3-methylthiophene monomer (7 mmol, 0.6871 g) in toluene or chloroform (10 mL) was added dropwise to the vessel. Finally, the solution of $FeCl_3$ oxidant (7 mmol, 0.6871 g) in deionized water (10 mL) was added too. After these additions, the mixture was then stirred for another 3 h at room temperature to yield a greenish black mixture. Methanol (100 mL) was added to the system to precipitate the product, which was then filtered, washed with methanol four times, dried in the fume hood overnight. In this strategy, the oxidative polymerization occurs at the interface between the aqueous and the organic phases, since the oxidant $FeCl_3$ is present in the aqueous solution and 3-methylthiophene in the organic phase. Consequently, the larger the interface area between the two phases, the more uniform dispersion of the two substances in composite will be. Herein, the preparation conditions such as the nature of surfactant and solvent as well as the mole ratios of the matters used had significant effect on some important properties of the resulting nanocomposite such as optical and thermal behavior. To characterize the nanohybrid obtained, in addition to FT-IR, UV-vis and thermogravimetric analysis (TGA) some other analyses including X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were also done. From this study it could be demonstrated that the inverted emulsion method is an efficient alternative for the former reports of P3MTh/SiO_2 nanocomposites preparation.

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Dehydrogenation of imidazoline derivatives with *tert*-butyl hydroperoxide catalyzed by polystyrene-bound Mn(III) tetraphenylporphyrin in water

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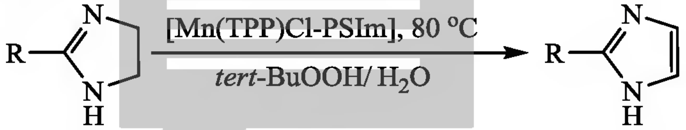
Synthetic metalloporphyrins have been known as active catalysts in a wide range of oxidation reactions. These catalysts have attracted much attention because their structures are similar to cytochrome P-450, a natural catalyst which oxidizes foreign organic compounds and metabolizes drugs in our bodies [1]. Dehydrogenation of 2-imidazolines to their corresponding imidazoles is biologically and pharmaceutically very important, since many imidazole derivatives possess antihypertensive, antiinflammatory, antibacterial, and antidiabetic activities [2]. Dehydrogenation of imidazolines by an oxidizing agent should provide an efficient method for the preparation of imidazole derivatives. Several reagents such as $KMnO_4@SiO_2$, $KMnO_4@K10$, $KMnO_4@Al_2O_3$, and the homogeneous $Mn(TPP)Cl/NaIO_4$ catalytic system have been previously reported for this purpose [3-4].

In the present work, the dehydrogenation of 2-substituted imidazolines with *tert*-butyl hydroperoxide in the presence of tetraphenylporphyrinatomanganese(III) chloride supported on polystyrene-bound imidazole, [Mn(TPP)Cl@PSI] is reported (Scheme 1). A wide variety of 2-imidazolines were efficiently converted to their corresponding imidazoles by the [Mn(TPP)Cl@PSI] catalytic system in water. The reaction parameters such as catalyst amount and effect of temperature were optimized in the dehydrogenation of 2-phenyl imidazoline.



(Scheme 1)

In conclusion, this catalytic system is a highly efficient system for dehydrogenation of imidazolines with *tert*-butyl hydroperoxide under reflux conditions. Finally, this catalyst is a robust and recoverable catalyst.

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Biomass alkali-rich ash as catalyst for one-pot synthesis pyridine derivatives under solvent-free condition

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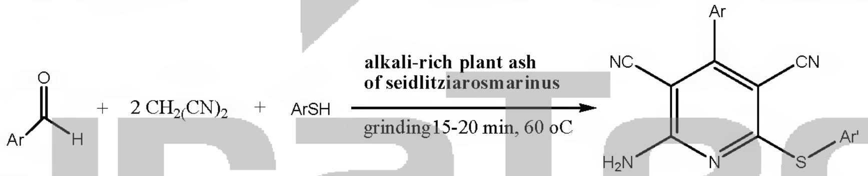
The pyridine ring systems represent the major class of heterocycles and their analogues exhibit diverse biological and physiologicalactivities.[1] In particular, 2-amino-3,5-dicarbonitrile-6-thio-pyri-dines serves as 'privileged scaffold' due to their potential therapeutic applications.[2-7]These compounds were reported to inhibit PrPScaccumulation in scrapie-infected mouse neuroblastoma cells(ScN2a),[2a] MAPK-activated PK-2,[2b] IKK-2 and modulate androgen receptor function.[2c] In addition, they serve as potassium channel openers for the treatment of urinaryincontinence.[3] 2-Amino-3,5-dicarbonitrile-6-thio-pyridines skeleton is often used as anti-prion,[2a,4] anti-hepatitis B virus,[5] anti -bacterial,[6] and anti-cancer[7] agents.

Herein, we attempt to develop a facile one-pot solvent-free protocol via alkali-rich plant ash of seidlitziarosmarinus as catalyst. The ash of this plant is a source of alkaline materials such as carbonates.[8] In summary, we have found a green and efficient procedure for the synthesis of pyridines compounds.

The structures of the products were deduced from their IR, ^{1}H NMR, ^{13}C NMR and Mass spectroscopic data.



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Synthesis of 2-substituted perimidines catalyzed using $FePO_4$

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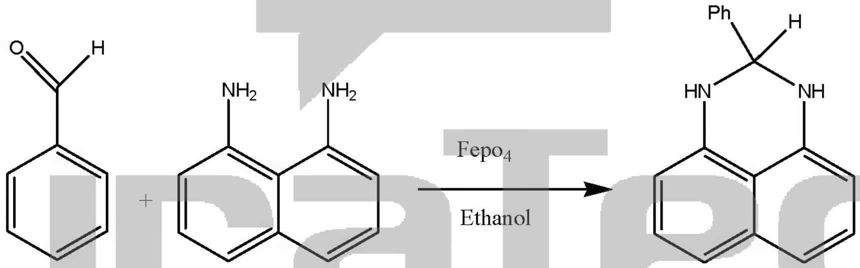
Multi nuclear *N*-hetrocyclic compounds like perimidines are of wide interest because they exhibited a diverse range of biological activities [1]. Owing to their biologically activities, there are several preparative methods for the synthesis of perimidine derivatives [2-7]. The most commonly method for the preparation of perimidines is the condensation reaction of 1, 8-diaminonapthaalene with a carbonyl group which need special reagent or force reaction condition. due to the versatile biological properties of perimidine derivatives and as a continuation of our studies on synthesis of heterocyclic compounds, we wish to report a clean and simple synthetic method for the preparation of dihydroperimidines using $FePO_4$ as an efficient catalyst that was employed as green catalyst for reaction between 1,8-diaminonaphtalene and aromatic aldehydes. The attractive features of this procedure are good conversion, reusability of the catalyst and easy work up make good way in this synthesis.



Scheme 1

Reference:
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Interaction Studies of Pt(II) Antitumor Complex with Calf Thymus DNA

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Numerous strategies have been developed in an attempt to reduce the toxicity of cis-diaminedichloroplatinum (II), which is an important cytotoxic drug. platinum complex of the type [Pt(bpy)(pyr-dtc)](NO_3) has been synthesized. This water soluble complex has been characterized by spectroscopic and non spectroscopic methods. This complex has been interacted with Calf Thymus DNA using UV-Visible isothermal titration method in 30mM Tris_HCl buffer solution (pH=7.0) at 300 and 310K.

There is a set of 7 binding sits(g) for the complex on the DNA with positive cooperativity in binding. n,the Hill coefficient (as a criterion of cooperativity) find out to be 4 at 300 K and 5 at 310K respectively. K_{app} the apparent equilibrium constant are 132 mM^{-1} and 78 mM^{-1} at 300K and 310K respectively.

The above compound can denature the DNA and the concentration of this ligand in the midpoint of transition ($[L]_{1/2}$), is decreased by improving temperature, from 0.08 mmol/L at 300K to 0.067 mmol/L at 310K. the conformational stability of DNA in the interaction with ligand (ΔG^0_{H2O}) determined to be 35.2 kJ/mol and 30.7 kJ/mol at 300K and 310K respectively.

Presence of ligand led to less stability of the DNA . values for m, (a measure of ligand strength for DNA denaturation) are 0.7 and 0.57 (kJ/mol).$(mol/L)^{-1}$ at 300K and 310K respectively.

Enthalpy of DNA denaturation by the complex ($\Delta H^0_{coformation}$ or $\Delta H^0_{denaturation}$) in the range of 300K and 310K is find out to be 34 kJ/mol. In addition, the calculated entropy (ΔS^0_{H2O}) of DNA denaturation by complex is -0.11 kJ/mol at 300K. the negative value of entropy change is related to the more disorder of denatured DNA with respect to the native DNA.

Keywords: Interaction Studies, anti-cancer Palladium (II) complex

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Synthesis and Binding Propertise of a New Anti-tumor Component [Pt(bpy)(n.pro-dtc)]NO_3 with Calf Thymus DNA

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Metal- based drugs have been used in therapeutic medicine for several hundreds of years and are used in contemporary society for the treatment of a large variety of human ailments, e.g., cancer, diabetes, and rheumatoid arthritis, as well as in diagnostic medicine.
A new platinum(II) antitumor complex of [Pt(bpy)(n.pro-dtc)]NO_3 (where bpy is 2,2'-bipyridine and n.pro-dtc is n-propyldithicarbamate) was synthesised and interaction of this complex with Calf Thymus DNA was studied by isothermal titration method in 30mM Tris_HCl buffer solution (pH=7.0) at 300 and 310K.
There is a set of 5 binding sits(g) for the complex on the DNA with positive cooperativity in binding. n,the Hill coefficient (as a criterion of cooperativity) find out to be 4 at 300 K and 6 at 310K respectively. K_{app} the apparent equilibrium constant are 39.2 mM^{-1} and 31.8 mM^{-1} at 300K and 310K respectively.
The above compound can denature the DNA and the concentration of this ligand in the midpoint of transition ($[L]_{1/2}$), is decreased by improving temperature, from 0.42 mmol/L at 300K to 0.34 mmol/L at 310K. the conformational stability of DNA in the interaction with ligand (ΔG^0_{H2O}) determined to be 20.7 kJ/mol and 25.2 kJ/mol at 300K and 310K respectively.
Presence of ligand led to less stability of the DNA . values for m, (a measure of ligand strength for DNA denaturation) are 0.15 and 0.24 (kJ/mol).$(mol/L)^{-1}$ at 300K and 310K respectively.
Enthalpy of DNA denaturation by the complex ($\Delta H^0_{coformation}$ or $\Delta H^0_{denaturation}$) in the range of 300K and 310K is find out to be 43 kJ/mol. In addition, the calculated entropy (ΔS^0_{H2O}) of DNA denaturation by complex is -0.12 kJ/mol at 300K. the negative value of entropy change is related to the more disorder of denatured DNA with respect to the native DNA.

Keywords: Binding Property , anti-cancer Palladium (II) complex

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Antimicrobial Activities of Methanol Extract of Ziziphora Tenuior L. from Qamsar

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Recently, a number of antibiotics have lost their effectiveness due to development of resistant strains of bacteria, which has primarily occurred through the expression of resistance genes [1,2]. In addition to inducing resistance, antibiotics are sometimes associated with opposing effects such as hypersensitivity, immune-suppression and allergic reactions [3]. Therefore, there is a need to develop alternative antimicrobial drugs for treatment of infectious diseases [4,5]. Z. tenuior is a traditional herbal medicine widely used as a mild sedative, spasmolytic and antibacterial agent [6]. This study was designed to in-vitro examination of antimicrobial activities of methanol extract of Z. tenuior. Inhibitory effects of methanol extracts of Ziziphora Tenuior L. was tested against gram-positive and garm-negative bacteria by using disc-diffusion method. Mentioned plant shows sensitivity to one of the gram-negative bacteria (Candida albicans) and has not high sensitivity to gram positive.

Keywords: Ziziphora Tenuior L., antimicrobial activity, Methanol Extract, Candida albicans

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Free radical scavenging activities of methanol extract of Ziziphora clinopodiodes Lam. and Ziziphora tenuior L. from Qamsar

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The genus Ziziphora is in the family Lamiaceae in the major group Angiosperms (Flowering plants). Z. Clinopodioides is widely used in Iranian traditional medicine for treatment of common cold, gastrointestinal disorders and inflammations, is a member of Labiatae family [1]. Several effects such as antibacterial [2], antifungal [3], antioxidant [4] and anti-inflammatory [5] have been reported as medicinal effects of this plant. Z. tenuior is another species of this plant which is widely used as a mild sedative, spasmolytic and antibacterial agent [6]. To the best of our knowledge there is no report about antioxidant activity of these mentioned plants from Qamsar. In this research we have evaluated antioxidant activity of methanol extract from aerial parts of Z. Clinopodiodes and Z. tenuior growing wild in Kashan, central Iran. Antioxidant activity was measured via DPPH test [6]. Z. tenuior extracts exhibit beter ability to scavenging of DPPH radical (IC_{50}=63.78 μg/ml) in comparing of Z. Clinopodiodes (IC_{50}=66.44 μg/ml).

Keywords: Ziziphora Tenuior L., Ziziphora clinopodiodes Lam., DPPH, Methanol Extract,

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Inhibition of lipid peroxidation ability of Ziziphora tenuior L. and Ziziphora clinopodiodes Lam. extract

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Clinical trials and epidemiological studies have established an inverse correlation between the intake of fruits and vegetables and occurrence of diseases such as inflammation, cardiovascular disease, cancer, and aging-related disorders [1]. Dietary antioxidants, including polyphenolic compounds, vitamins E and C, and carotenoids, are believed to be effective nutrients in the prevention of these oxidative stress related diseases [2]. Antioxidants have thus become a topic of increasing interest recently. A literature search revealed that the number of publications on antioxidants and oxidative stress has nearly quadrupled in the past decade (1684 in 1993; 6510 in 2003; 9032 in 2011) [3].

β-Carotene bleaching assays are the most important antioxidant assay was used to determine inhibition of oxidant stress. At this research we have used of this test to investigated the antioxidant activity of methanolic extract of Z. Tenuior and Z. clinopodiodes. Z. tenuior extracts exhibit beter ability to Inhibition of lipid peroxidation ability (75.24 %) in comparing of Z. Clinopodiodes (47.22 %).

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Preconcentration and Determination of Dopamine , Adrenaline and Histamine by Dispersive Liquid Liquid Microextraction in Combine with Gas Chromatography and Flame Ionization Detector (DLLME-GC-FID)

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Abstract

In this study two kind of biogenic amines i.e. dopamine (DA) , adernaline (AD) and histamine (HA) were derivatized and extracted from aqueous sample and then were introduced to gas chromatography system with flame ionization detector (GC-FID) . The catecholamines dopamine and adrenaline are important biological compounds and act as neurotransmitters in mammals [1] and histamine introduces as a food spoiling indicator specially in sea food. In this study we used ethyl chloroformate as a derivatizing agent. Dispersive liquid liquid microextraction (DLLME) method was applied for preconcentration of analytes . After derivatization of analytes, 5ml of analyte sample were placed on a glass tube after that 1ml disperser solvent and 40µl chloroform as extraction solvent were mixed and rapidly injected to the aqueous sample in glass tube [2]. After formating cloudy solution it was sentrifuged for 1 minutes and then a portion of sediment phase (1µl) injected to GC system and separated on a 30 m × 0.32 mm i.d. CP-Sil column by temperature programming. Nitrogen was used as carrier gas at a flow rate of 4 mL min^{-1} and detector was FID. The calibration curves were linear in the range 0.1-10 ng per ingection (1 µL injection) with detection limits 0.001–4.0 ng per injection (1 µL injection).

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Can Arsenic Trioxide As2O3 delivered by Human Serum Albumin?

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Abstract

Human serum albumin (HSA) is a principal extracellular protein with a high concentration in blood plasma and carrier for many drugs to different molecular targets [1]. Human serum albumin (HSA) with high affinity binding sites is a major transporter for delivering several endogenous compounds and drugs in vivo[2]. Drug binding to HSA can alter the protein biophysical and biochemical properties of protein. Arsenic trioxide is an anticancer. Arsenic can inhibit proliferation in many different cancer cell lines in vitro and in vivo, and promotes apoptosis affecting tumor growth [3]. It apparently affects numerous intracellular signal transduction pathways and causes many alterations in cellular function. As_2O_3 Chemotherapeutic drug has been shown in treating both newly diagnosed and relapsed patients with acute promyelocytic leukemia (APL). Arsenic trioxide reduced multiple myeloma and solid tumor activity. The aim of this study was to examine the interaction of As_2O_3 with Human Serum Albumin (HSA) in aqueous solution at physiological conditions[4]. UV–visible, Fourier transform infrared (FTIR) spectroscopic methods were used to determine these interactions [5]. The protein secondary structure analyzed by FTIR spectroscopy showed major decrease of α-helix from 60% (free HSA) to 51% for As_2o_3 high concentrations (0.5Mm) and increase of β Turn from 5% (free HSA) to 16% and random coil 3% (free HSA) to 21% occurred in the As_2O_3 –HSA complexes. Structure analysis (UV-Vis date) showed As_2O_3 bind HSA via both hydrophilic and hydrophobic interaction. Stronger As_2O_3 –HSA complexes formed with overall binding content of $K=1.7 \times 10^4$. These result suggest that Human serum albumin can be good carrier for delivering As_2O_3 drug to target tissue.

Keywords: Human Serum Albumin (HSA), Arsenic trioxide (As_2O_3), FTIR spectroscopic, UV-visible spectroscopic.

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Repair of O6-methylguanine to guanine by O6-alkylguanine-DNA Alkyltrasferase in the presence of the water solvent

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Several methylating agents in the cells and environment such as S-adenosylmethionine and methylmethane sulfonate [5] can methylate different sites of DNA bases. O6-methylguanine (O6mG) is the most toxic, mutagenic and carcinogenic base modification among the different methylated DNA bases [6]. The repair of O6mG by O6- Alkyl guanine-DNA alkyltransferase (AGT) protein is a great interest subject from the anti-cancer therapy point of view [7]. O6mG is repaired by the transferring of the methyl group from the O6 site of guanine to the thiol group of cysteine residue (Cys145). The energy barrier of methyl transfer has been calculated equal to 34.20 kcal mol^{-1} [3]. In this work, the effect of water solvent (see Fig. 1) on the repair mechanism of O6mG has been investigated by the quantum mechanical calculation. All structures have been optimized at the B3LYP/6-31G* level of theory by Gaussian09 program package [8].

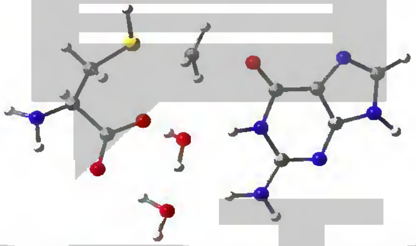

Figure 1. O6-methylguanine-cystiene complex in the presence of the water solvent

Methyl transfer from guanine to Cys is accompanied with the proton transfer from Cys to guanine such that the repair follows the S_N2 mechanism. In the presence of two water molecules, the energy barrier of methyl transfer from guanine to Cys reduces to 25.71 kcal mol^{-1} in the presence of water solvent.

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Utilization of modified montmorillonite as a support material for immobilization of lipase

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In this study, modified montmorillonite used as a support material for immobilization of lipase. Montmorillonite with monolayer surfactant was successfully used for immobilization of lipase and the relative activity of immobilized enzyme was examined under varying experimental conditions. The effects of various factors such as concentration of enzyme solution, pH and temperature of immobilization medium and magnetic stirring were evaluated. Lipases (EC 3.1.1.3) are a very important class of enzymes for applied biocatalysis. The high degree of stability of lipases in organic solvents makes them suitable for reactions at the intermediate stages of conventional organic chemical processes and for the catalytic transformation of substrates that are insoluble in aqueous media [1,2]. Lipases have been widely used for biotechnological applications in the dairy industry, oil processing, production of surfactants, and preparation of enantiomerically pure pharmaceutical [3]. In this work, a solution of lipase was added to modified or unmodified montmorillonite. The immobilized lipase was then used for the hydrolysis of olive oil at 37 °C in an incubator under stirring. The free fatty acids produced were measured by titration of the sample with NaOH in ethanol. The present work demonstrated a promising application potential of the unmodified montmorillonite for enzyme immobilization.

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Antioxidant activity of Seidlitzia Rosmarinus leaf extracts –A powerful antioxidant source

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Abstract:

The number of methods to measure the antioxidants in botanicals, foods and other dietary supplements has increased considerably in the last decade [1]. Seidlitzia rosmarinus is a perennial woody plant grown mostly along the banks of salt marshes and in soils with high saline water tables. This plant being a halophyte is very well adapted to grow in dry and salt affected desert soils. The dried leaves powder is used as detergent for washing cloths and dishes. It has also many industrial applications such as dyeing, making soaps, pottery and ceramics among others [2]. In the present study, two different antioxidant tests such as 2,2-diphenyl-1-picrylhydrazyl free radical (DPPH) and ferric reducing-antioxidant power assay (FRAP) were employed in order to evaluate the antioxidant activities of Seidlitzia rosmarinus leaves. The results were obtained in comparison with butylated hydroxytoluene (BHT). Leaves powder extracted using ethanol, chloroforms, n-hexane and ethylacetate in soxhlet extractor. The levels of total phenolics, total flavonoids of the extracts were also determined. All extracts had good total phenolic and flavonoid contents, inhibited lipid peroxidation, showed radical scavenging activities. The extracted solution with ethanolic, chloroform, ethyl acetate, n-hexane solvents showed IC_{50}: 14.53, 17.41, 18.45 and 20.03 respectively. IC_{50} of BHT is 26.64 as control a plus.We observed that ethanolic extracted solution showed the most antioxidant activity. In summary, the leaves of the Seidlitzia rosmarinus could be considered as a significant natural antioxidant source.

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The chemical composition of the essential oils of Matricaria recutita extracted with Soxhlet extraction using different solvents

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Chamomile, Matricaria recutita L., is a well-known medicinal plant in folk medicine cultivated all over the word. Chamomile essential oil is widely used in pharmaceutic, cosmetic, and food industries [1, 2]. It is a spontaneous herbaceous perennial plant and its drug is largely used, as an infusion, for its anti-inflammatory properties, especially for respiratory and gastroenteric tracts [3].

In this work the aerial parts of Chamomile was subjected to Soxhlet extraction with different solvents such as n-pentane, dichloromethane and ethanol. Plants were also extracted with water under reflux and then the yields of reflux were fractionated by liquid-liquid extraction with two organic solvents (n-pentane, dichloromethane). The extracts were then analyzed by capillary gas chromatography/flame ionization (GC/FID) and capillary gas chromatography/mass spectrometry (GC/MS). As expected, significant differences were seen in terms of extraction yields. The data analysis showed that the main compounds of the extract were bisabolol oxid A and B, 7-methoxy coumarine, en-yn-dicycloether and hexadecanoic acid.

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cytotoxic activity of Tanacetum pinnatum DC. from kashan

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The Asteraceae or Compositae (commonly referred to as the aster, daisy, or sunflower family), is an exceedingly large and widespread family of vascular plants [1]. Among the plants that could become a potential source of usable substances is the Tanacetum genus comprising about 150 species, about 30 of them have been also practically utilized. Some of the most popular ones are T. vulgare, T. parthenium, T. pinnatum and T. balsamita. The Tanacetum spieces are rich in essential oils, bitter components and sesquiterpene lactones. Many studies have been published about the composition of essential oils at this genus [2-5].

Artemia salina was first described (as Cancer salinus) by Carl Linnaeus in his Systema Naturae in 1758. The resilience of these creatures make them ideal test samples in experiments. Artemia is one of the standard organisms for testing the toxicity of chemicals [6]. The brine shrimp lethality assay is considered a useful tool for preliminary assessment of toxicity [7,8].

At this research we have evaluated the cytotoxic activity of methanolic extract of this plant. The results exhibited that this plant has no significant toxicity.

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Determination of Some Chemical Constitutes of methanolic extract Tanacetum pinnatum Boiss. from Kashan

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The genus Tanacetum (Compositae) is represented by 26 species in the flora of Iran, 12 of them are endemic. An information of the chemical constituents of plants and fruits are desirable, not only for the discovery of therapeutic agents, but also because such information may be of value in disclosing new sources of such economic materials as flavonoids, alkaloids, tannins, oils, gums, precursors for the synthesis of complex chemical substances, etc. Analysis of chemical constituents of plants would be valuable in discovering their chemical or biological activities [1-4].

To the best of our knowledge there is no report about chemical constituents of mentioned plant in the literature. The aim of this study is qualitative phytochemical analysis for the flavonoids, alkaloids, tannins and saponins existence in T. pinnatum via in-vitro phytochemical assays using general reagents [2,3].

Results confirm that T. pinnatum contains tannin and has no considerable Alkaloid. flavonoids and saponins were not exhibited due our assays.

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Essential oil composition and antioxidant of Achillea wilhelmsii C. KOCH from kermejegan

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A. wilhelmsii with the local name, “Boomadaran” is a traditional medicinal plant which has been used by Iranian people from ancient. The composition of the volatile oil of A. wilhelmsii grown in Kerman, Mazandaran [1-3] and the constituents of the oil from Egypt and Turkey have been reported previously [4].

This report refers to composition of the essential oil and antioxidant activity of A. wilhelmsii collected from kermejegan, central Iran. Extraction of the oil was performed by simultaneous steam distillation-solvent (SDE apparatus), dried using sodium sulphate, the oil was yellow in color (more than 2%).

In vitro antioxidant activity of methanol extract of T. pinnatum was also evaluated. Screenings of antioxidant activity of the extract was performed using 2,2-diphenyl-1-picrylhydrazyl (DPPH) and beta-carotene-linoleic acid assays. GC/FID and GC/MS analysis of the plant essential oil resulted in the identification of 28 compounds representing 88.93% of the oil. α-Pinene (16.32%), 2,3,6-trimethyl-Anisole (12.52 %), Chrysanthenone (9.73%) and E-nerolidol (8.46%) was detected as the major components consisting 47.03 % of the oil.

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Thin–Layer Chromatographic Separation of Atenolol Enantiomers using Cellulose Triacetate as Chiral Stationary Phases

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Several drugs are produced as racemic mixtures even though the therapeutic activity often resides in a single enantiomer and the second enantiomer can be less active or even harmful. Enantiomerically pure pharmaceuticals account for approximately one third of all drug sales worldwide and over 50 percent of the top selling drugs are chiral [1]. Atenolol, as one of these Chiral drugs, is utilized for treatment of blood pressure and shortness of breath anomaly. Investigation has shown that left and right (±) enantiomers attribute different pharmacological behaviors. In the present study, separation of enantiomers of Atenolol by Thin-layer Chromatographic with Cellulose triacetate micro sphere as Chiral Stationary Phases is investigated. Thus, aqueous solution of methyl cellulose (0.25%) and polyvinyl alcohol (3 %) were prepared and aged for 4 h. Then, 21 mL of methyl cellulose solution was mixed with 14 mL of polyvinyl alcohol to which Cellulose triacetate (4 g), calcium sulphate (1g) and silica gel (1 g) were added to form a suspension solution [2]. This suspension was spread on glass plates (5 x 10 cm) and are allowed to dry at RT to form a layer with thickness of 0.2 mm. Separation of Atenolol enantiomers by these kind of plates afforded the R_f of 0.47 and 0.69 with a separation factor of 1.47 using mobile phase constituted of n-hexane/ethanol (60:40).

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Chemical Composition of Volatile Constituent of Salix aegyptiaca L. Water stored for Forty Days

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Different types of herbs used in pharmaceutical, cosmetic, food and drink industry were extracted and then analyzed by gas chromatography – mass spectrometry by using a rapid extraction method. The composition of active principles in herbs has been used for a long time both in folk medicine and in therapeutics. Recently, the use of volatile oils has increased [1-3].

Historically, the Iranians did not used most types of herbal water immediately after distillation (according to an ancient experience) alternatively, stored it for a given time in a calm and quiescent place to access its maximum consistency and get its taste and odor balanced; Salix aegyptiaca L water is one of these mentioned herbal water. Therefore we were investigated the compositions of volatile compounds of Salix aegyptiaca L. water stored for about forty days. Volatile oils were isolated by simultaneous hydrodistilation and extraction (SHDE) with xylene as solvent using modified Clevenger's apparatus. The extracts were then analyzed by capillary gas chromatography/ flame ionization (GC/FID) and capillary gas chromatography/mass spectrometry (GC/MS).

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Evalution of total phenolic contents of two enflorence extracts of Rheum ribes L.

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Rhubarb (Rheum ribes L.) belongs to the Polygonaceae family, commonly found in eastern Turkey, Lebanon and Iran[9]. Many bioactive natural molecules, especially those with plant origin, have at least one benzene ring with a hydroxyl functional group in their skeleton. Such compounds are collectively known as phenolics and, due to their hydrogen or single electron donating potentials, usually play important roles in the antioxidant activity of the plant extracts[10].

In this study Folin-Ciocalteu assay[11] was used to determine total phenolic content of Rheum ribes L. and amount of phenolics was reported as gallic acid equivalent (standard phenol), see eq. 1

$$\text{Absorbance}=0.0012*\text{gallic acid}(\mu g)+.0033 \qquad (1)$$

Measured total phenols of methanol and water extracts, shows higher amount of phenolic compounds for methanol extract. Considering the results, it seems that despite being water as common solvent in local and traditional uses for extraction of food or medicinal plants, type of solvent must be considered more careful to have the best qualities especially for industrial applications.

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Essential oil composition of the leaves and flowers of Phlomis olivieri Benth. and Phlomis persica Boiss. From Iran

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The genus Phlomis (Labiatae) consists of about a hundred species in the world and seventeen in Iran ,of which ten species are endemic[1]. Some of Phlomis species are used in folk medicine. Various biological activities have have been reported of phlomis species like:anti-inflammatory,immunosuppressive,antimutagenic,antinociceptive, antifibrel,free radical scavenging and antimicrobial effects[2].

The essential oil of the leaves and flowers of Phlomis olivieri and Ph. persica which were collected from the north of Yasooj (Province of Kohkiloe and Boyerahmad) were isolated by hydrodistillation using a Clevenger type apparatus. The oils were subjected to the GC and GC/MS .The components were identified by comparison of retention indices (RI)with those reported in the literature and by comparison of their mass spectra with the Wiley library or with the published mass spectra[3].

The essential oils were rich in sesquiterpens with typical major component of phlomis species germacrene D ,which was found (37.59%,19.53%) ,(26.48%,19.48%)respectively in the leaves and flowers of Ph. olivieri and Ph. persica. Bicyclogermacrene was another major component in the corresponding oils(7.98%,5.71%) and (18.68%, 20.38%)respectively. The other main components in the leaves of Ph. persica were 9,12,15-octadecatrien-1-ol(11.18%),and 6,10,14-trimethyl-2-pentadecane(9.00%).Germacrene B (9.95%)was another major component in the flowers of Ph. persica. β-caryophyllen (9.97%,12.02%),β-selinene(6.75%,8.92%)and 6,10,14-trimethyl-2-pentadecanone(3.92%,8.60%)were found as the major constituents in the oils obtained from the leaves and flowers of Ph. olivieri.

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Comparison of Ultrasonic Bath Method with Soxhlet Method in Caffeine Extraction from Black and Green Persian Tea

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Green and black tea has been one of the popular drinks in Asian countries and now is widely used all over the world due to its beneficial health effects. Green tea has many components such as caffeine, catechins, fats, amino acids, aroma chemicals, vitamins, chlorophyll [1]. Moreover, chemical analysis of caffeine in tea leaves is used as an additional tool for evaluating tea quality [2]. Caffeine is a purine alkaloid and is a major constituent of tea, coffee and other beverages. It acts as a Central Nervous System Stimulant and also has negative withdrawal effects. Decaffeinated beverages are being used to overcome its negative effects. Decaffeinations by different methods like solvent, water and super critical fluid extraction have been done [3]. In this research the soxhlet and ultrasonic bath methods have been employed to extract caffeine from green and black tea. Then, the caffeine has gained from tea by solid–liquid extraction using water and dichloromethane as effective solvents. The caffeine extraction has been performed at isothermal conditions of 97° c for water and 20° c for dichloromethane [4]. In this method the soxhlet was heated for 48 h at 130 ° c .Caffeine efficiency was obtained after purification from black and green tea, 78% and 66% respectively. The Soxhlet method has a disadvantage like the long time reaction. The caffeine efficiency purification from black and green tea by ultrasonic bath method for 4 h at 60 ° c and 46 kHz, were respectively, 75% and 63%. The advantages of this method are shorter extraction times and lower energy consumption in comparison with soxhlet method. Spectroscopic methods such as ^{1}H- and ^{13}C- NMR, UV-Vis were used for identification of caffeine.

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Chemical composition of essential oils of leaf two Eucalyptus species

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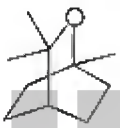
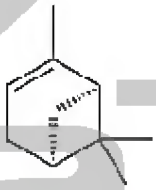
Eucalyptus is a genus of Myrtaceae family which these trees are cultivated world over for its oil, gum, pulp, and timber, medicine value [1]. The essential oil found in its foliage is the most important one and use in food, perfumery and pharmaceutical industries [2, 3]. In this work, the leaves of two species of Eucalyptus from Zahedan (E. viminalis, E. viridis) that were during period flowering, E. viminalis from Sirjan and another E. viridis from island gheshm have been given in hydrodistillation and then their extracted essential oils subjected to GC-MSS analysis. Oils components were identified according to their retention indices and by the comparison of their mass spectral fragmentation pattern and the MS library data base.

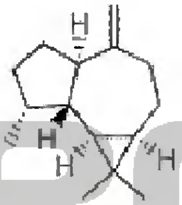
In the essential oil extracted of E. viminalis from Zahedan 40 compounds were identified, with the dominant compounds being 1,8-cineole(58.06%), α-pinene(9.01%), globulol(6.90%) and aromadendrene (5.85%). In essential oil of leaf E. viridis from Zahedan were detected 44 compounds that the majour components were 1,8-cineole(53.35%), α-pinene(17.52%) and aromadendrene(6.63%). For species from Sirjan 41 with 1,8-cineole(41.77%), spathulenol(7.11%), aromadendrene(5.94%), gamma-terpinene(5.84%) and aromadendrene(5.53%) and also for essential oil of species from island gheshm 32 that main constituents were 1,8-cineole(54.02%) and α-pinene(16.78%). There were 19 compounds similar in leaves of four sample analyzed in this study. Note that there is a combination of 1,8-cineole as the main compound, with the majority value among all four samples.



1,8-cineole



α-pinene



aromadendrene

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Antioxidant activity and chemical composition of volatile oils of flowers from two Eucalyptus species from Zahedan

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Eucalyptus is a genus of Myrtaceae family which these trees are cultivated world over for its oil, gum, pulp, and timber, medicine value [1]. The essential oil found in its foliage is the most important one and use in food, perfumery and pharmaceutical industries [2, 3]. But there are a few reports on the composition of volatiles chemical compositions from flowers [4]. In this work, flowers of two species of Eucalyptus (E. viminalis and E. viridis) from Zahedan have been submitted to hydrodistillation and its extracted essential oils have been subjected to GC-MSS analysis. Compounds were identified by comparing their GC retention times and mass spectral fragmentation pattern and the MS library data base. The antioxidant activity of essential oils of flower, two species of eucalyptus were measured by DPPH assay [5].
In the essential oil extracted from flowers of E. viminalis 34 compounds were identified. There were such as major components 1,8-cineole (35.73%), aromadendrene (11.05%), α-pinene (7.75%), globulol (7.30%), phellandrene (6.10%) and α-terpinolene (6.11%). For E. viridis number of all components were 30 and the most abundant components were 1,8-cineole (41.67%), α-pinene (9.44%), aromadendrene (8.94%), globulol (6.14%), phellandrene (6.07%). Essential oil of both species showed a weak antioxidant activity, almost one-third times compared to the BHT. There were 25 components which are in common in two samples in this work. Because of similarities between essential oils of leaf and flower in investigated by us, one can use the flowers of E. viminalis and E. viridis instead of its leaves.

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Determination Antioxidant activity of Mentha longifolia from Birjand

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Mentha longifolia plant of the Lamiaceae family region of Birjand located in East Iran is collected. The antioxidant activity of the different extracts of aerial parts of Mentha longifolia was investigated[1]. The antioxidant potentials of the extract compounds were established by using three radical-scavenging assays, namely, DPPH scavenging, besides β-carotene bleaching assay and FRAP assay. The antioxidant activity is compared with synthetic antioxidant, namely BHT[3]. The demonstrated modified spectrophotometric method makes use of the 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical and its specific absorbance properties. The absorbance decreases when the radical is reduced by antioxidants[2]. In contrast to other investigations, the absorbance was measured at a wavelength of 517 nm. for β-carotene bleaching assay the absorbance was measured at a wavelength of 490 nm. And FRAP assay wavelength of 593nm. IC_{50} ethanolic extract in DPPH and β-carotene assay were 62.32 and 748.023. Ethanolic extract of this plant in the three methods had the most antioxidant activity. Three extracts the antioxidant activity were very little demonstrated and the chloroform extract has antioxidant activity was lowest.

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GC-Mass analysis of the volatile components from stem and fruit of

Mindium laevigatum(Vent.) Rech.f. & Schimman-Czeika

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Genus Mindium (family campanulaceae) has three species in Iran and 7 in the world.The old name of this plant is Michauxia laevigata Vent.It is two or more years old.Including morphological characteristics; long stem is erected to 0.5-2 meters in height and branched from the base,the fruit is dehiscent and capsule. [1,2].In the warm season of 2011 Mindium laevigatum was collected from Shahsavaran valley of Kashan. Volatile constituents of the plant extracted through SDE apparatus was analyzed qualitatively and quantitatively in this research. Analysis was performed using gas chromatography-mass spectroscopy technique.The main volatile components of the stem and fruit were hexadecanoic acid, linoleic acid, ethylepalmitate, pentacosane, myristic acid, lauric acid,eugenol, n-hexanol, Linalool, methyl linoleate and perhydrofarnesyl acetone.

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Investigation of effective parameters on enzymatic machining as a novel technique for nanomachining of metals

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Abstract

In this present investigation, the influence of various parameters on enzymatic machining has been studied. All specimens were initially prepared, and then enzymatically machined. Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and other quantitative analyses were utilized for the examination of morphological properties of the surface. The determined results were compared with the results of mechanical, chemical and microbial machining methods. Results of the SEM micrographs illustrated that roughness of the surface was qualitatively reduced using enzymatic machining. Also, roughness of the surface was changed in the range of 0 to 10 nm quantitatively, according to AFM topographs. The extraordinary nanometric quality of surface finishing, simplicity of experimental proceeding and its controllable nature could be regarded as the significant advantages of enzymatic machining process.

Keywords: Enzymatic machining; Nanometric roughness; Surface finishing

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Essential Oil Composition of Different Parts of Ligularia persica Boiss.

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Ligularia persica Boiss. is an important genus of the Compositae family (tribe Senecioneae). In according to flora Iranica, there is only one species of Ligularia in Iran that is endemic to northern Iran [1]. It is well-known that Ligularia species are used in traditional medicines such as treatment of coughs, inflammations, jaundice, scarlet fever, rheumatoidal arthritis, and hepatic diseases [2]. Up to now, several phytochemical studies have identified the presence of various compounds such as steroids, alkaloids, flavonoids, lignans, sesquiterpenoids, and terpenoids [3]. Ligularia persica were collected during the flowering stage in July 2011. The air dried parts were subjected to hydrodistillation using a Clevenger-type apparatus for 2 h. To our knowledge, there is no report that detail chemical composition of various essential oil of Ligularia persica.

The present study was conducted to examine the chemical composition of essential oil of leaves, stems and flowers of Ligularia persica. The GC and GC/MS analysis of the oil resulted in detection 92.16%, 87.95%, 86.84%, of the total essential oil respectively of flowers, stems and leaves that is main components of flowers oil were cis-ocimene (11.46%), 2-ethyl-4-methylthiophene (6.68%), γ-terpinene (6.32%), β- myrcene (5.94%), β-pinene (5.94%), 2,4,6-octatriene (5.58%), germacrene-D (2.61%). The major constituents of stem oil were sabinene (6.39%), cis-ocimene (4.46%), γ-selinene (4.44%), β-myrcene (3.76%), α-pinene (3.62%), α-phellandrene (3.6%), β-pinene (3.5%), benzoxepin (3.29%), cyercene (2.93%), naphthalene (2.46%). The main compounds of leave oil were cis-ocimene (5.25%), cadinene (3.79%), valencene (3.18%), sabinene (3.03%), 1.3-cyclopentadiene (2.92%), β-myrcene (2.41%), naphthalene (2.36%), cyercene (3.72%), γ-terpinene (1.77%).

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A detailed view for the interaction studies between an anti-tumor agent and human serum albumin: an absorption spectroscopy approach

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Since many biological phenomena depend on the interactions of ligands to proteins, it is of importance to develop sensitive and simple studies for determination of binding parameters. Some techniques commonly used for this purpose are fluorescence spectroscopy, circular dichroism, equilibrium dialysis and calorimetery. UV-Vis spectroscopy is one of the most useful techniques for calculation of ligand-protein binding parameters [1]. So, electronic absorption titration experiments were performed with two methods at constant temperatures of 300 K and 310 K. Based on this experiments we determined binding parameters, the number of binding sites and the binding constant and the thermodynamic parameters, $\Delta G^{\circ}_{H_2O}$, molar Gibbs free energy of binding, $\Delta H^{\circ}_{H_2O}$, molar enthalpy of binding and $\Delta S^{\circ}_{H_2O}$, molar entropy of binding [2]. Results obtained from our present work would be useful to understand the mechanism of interactions of the small molecule compounds binding to HSA and helpful in the development of their potential biological, pharmaceutical and physiological implications in the future.

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Essential oil chemical composition and antioxidant and antimicrobial properties of Colligonum arborescens Litw. from Kashan area

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Essential oil composition and antioxidant and antimicrobial activity of the methanol extracts of the *Colligonum arborescens*[1] were evaluated in this research. GC and GC/MS analysis of the plant essential oil resulted in the identification of 21 compounds representing (100%) of the oil, the major components lauric acid (44.36%), p-mentha-1,4(8)-dien-3-one (8.49%), β-ionone (5.89%), liguloxide (4.26%) and geranylaceton (4.66%) constituted 67.66% of it [2]. Various methanol extracts of the plant were also evaluated for their antioxidant activity using 2,2-diphenyl-1H-picrylhydrazyl (DPPH) and β-carotene-linoleic acid tests. Methanol extract from the stem of the plant was considerably active in DPPH (IC50 = 46.79 ± 0.34 µg/ml) and β-carotene-linoleic acid (inhibition percentage: 60.31%) tests and its total phenolic compounds content was about (83.12 µg/ml). Methanol extract of the fruit showed moderate activity in DPPH (IC50=89.32±0.34 µg/ml) and β-carotene-linoleic acid (inhibition percentage: 68.3%) tests and its total phenolic compounds content was about (67.66 µg/ml) [3]. The plant also showed a week antimicrobial activity against tested microorganisms [4].

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(Organic Chemistry/ PhytoChemistry)

Investigation of solvent polarity effect on secondary metabolites extraction in berberis

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Abstract:

Plants are a source of large amount of drugs comprising to different groups such asantispasmodics, emetics, anti-cancer, antimicrobials etc. A large number of the plants areclaimed to possess the antibiotic properties in the traditional system and are also usedextensively by the tribal people worldwide. Extraction methods used pharmaceutically involves the separation of medicinally active portions of plant tissues from the inactive/inert components by using selective solvents. During extraction, solvents diffuse into the solid plant material and solubilize compounds with similar polarity[1].

The purpose of standardized extraction procedures for crude drugs (medicinal plant parts) is to attain the therapeutically desired portions and to eliminate unwanted material by treatment with a selective solvent known as menstrum. The extract thus obtained, after standardization, may be used as medicinal agent as such in the form of tinctures or fluid extracts or further processed to be incorporated in any dosage form such as tablets and capsules. These products contains complex mixture of many medicinal plant metabolites, such as alkaloids, terpenoids, flavonoids and etc[2]. Extraction of the bioactive plant constituents has always been a challenging task for the researchers[3].

In this study, we evaluated the effects of various solvents with different polarity on the extraction of secondary metabolites of barberry, such as alkaloids, terpenoids, flavonoids and tannins.

Doing qualitative phytochemical tests on the extract, in addition to secondary metabolites quality determination, which is extracted by any solvent, by comparison the results, it was reported that mehtanol is the best solvent for secondary metabolites extraction in berberis.

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Chemical Composition of the Essential Oil of Elaeagnus angustifolia L. from Kerman Province in Iran

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The plants belonging to the genus Elaeagnus (Elaeagnaceae) are distributed widely from the northern regions of Asia to the Himalayas and Europe. One species of this genus, Elaeagnus angustifolia is reported in Iranian folk medicine to be used for its anti-inflammatory and analgesic effects[1,2].

In this study, essential oil from flowers of Elaeanus angustifolia L. from Mehdiabad in Kerman province, an endemic to Iran, was extracted using hydrodistillation method.

The oil were analyzed by capillary gas chromatography, using flame ionization (GC / FID) and capillary gas chromatography mass spectrometry (GC / MS) detection. Fifty Six components were identified in the essential oil of Elaeanus angustifolia L. with ethyl cinnamate (28.3%), hexafarnesyl acetone(17.3 %), 2, 6, 14, tetramethyl hexadecane (10.2%), nonanal(4.4%), phenyl 2-methylbutyrate(2.7%), and phytane (2.7%) as the main constituents. The results showed that the amount of ethyl cinnamate is remarkably high in the oil of Elaeanus angustifolia L.

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Composition of the first and the second residues of rose water composition of Rosa damascena Mill. by gas chromatography mass spectrometry (GC/MS) identification.

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Roses have been used since ancient time in rituals, cosmetics, perfumes, medicines and aromatherapy [1, 2]. Turkey, the main rose oil producer in the world, uses R.damascena Mill .for rose oil production [3].

When the rose water was obtained by hydrodisttilation, the first essential oil was extracted. But yet, much of it is present in rose water. Therefore, rose water was redistilled for the second essential oil and what remains is the first residue. After passing it through the resin column, what leaves the column is the second residue.

In this work the first and the second residue composition of rose water were extracted with different solvents and the extracts were then analyzed by capillary gas chromatography/flame ionization (GC/FID) and capillary gas chromatography/mass spectrometry (GC/MS).

The result showed that, phenyl ethanol in the first residue as the main constituent and in the second residue with lower content. In all of solvents benzyl alcohol is another constituent in both first and second residue. Linalool, eugenol and methyl eugenol are just in the first residue. Geraniol and citronellol are in both residues. So , it is important to know the first and the second residue composition for using some these constituent.

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Determination of total phenolic and flavaonoid compounds content in ethyl acetate extract of different parts of Ruscus hyrcanus

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Abstract

The active nitrogen and oxygen species may induce some damage to the human body. Over production of various forms of activated oxygen species, such as oxygen radicals and non-free radical species is considered to be the main contributor to oxidative stress, which has been linked to several diseases like atherosclerosis, cancer, and tissue damage in rheumatoid arthritis [1]. Antioxidants are vital substances which possess the ability to protect the body from damage caused by free radical induced oxidative stress. Recently, there have been great efforts to find safe and potent natural antioxidants from various plant sources [2]. Numerous crude extracts and pure natural compounds from plants were reported to have antioxidant and radical-scavenging activities [3].

The genus *Ruscus* is used both as a medicinal and ornamental plant steroid saponins extracted from rhizomes possess anti inflammatory and vasoprotective properties and are used both in conventional and traditional medicine [4].

Thus, present study was undertaken to evaluate the in vitro antioxidant effect of leaf, stem and root extracts of *Ruscus hyrcanus* (Liliaceae). In this investigation various parts of this plant were successively extracted with ethyl acetate using a soxhelet extractor for 8 h. The content of total phenolic and flavonoid compounds were measured in the plant extracts. The data obtained in the in vitro models clearly establish the antioxidant potency of all extracts.

The total phenolic contents of ethyl acetate extract of leaf, stem and root were 91.86 ± 8.0, 99.40 ± 7.9 and 75.60 ± 6.4 mg gallic acid equivalent/g of extract, respectively. Also, total flavonoid contents of ethyl acetate extract of leaf, stem and root were in order to: 30.67 ± 2.0, 29.83 ± 3.1 and 33.29 ± 1.3 mg quercetin equivalent/g of extract powder, respectively, by reference to standard curve ($y = 0.0063x$, $r^2 = 0.999$).

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Extraction of the Essential Oil from Plant with Three Methods

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Abstract

The genus Ferula, which belongs to the Umbelliferae family, has 133 species distributed throughout the Mediterranean area and Central Asia [1]. The Iranian flora consists of 30 species of Ferula, including 15 endemics, and the popular Persian name of most species is “Koma” [2]. Many reports on phytochemical analyses of this genus, including essential oil analysis, can be found in the literature [3–7]. In this work, the essential oils from aerial parts of Ferula hazarlalehzarica. Y.Ajani, separately obtained by Conventional hydrodistillation (HD) , microwave-assisted hydrodistillation (MAHD) and Solvent free microwave (SFM) and analyzed by GC and GC/MS. Air-dried aerial parts of the plant were hydrodistilled for 3 h using a Clevenger-type apparatus and at 600 W for 30 min (MAHD) and 5min (SFM) using an adapted microwave distillation. GC analysis was carried out using a Hewlett-Packard 6890 instrument coupled to a flame ionization detector (FID). Compounds were separated on a HP-5 capillary column. GC/MS analysis was performed using a Hewlett-Packard 5973 mass spectrometer coupled to a HP 6890 gas chromatograph equipped with a HP-5MS capillary column. All constituents of the oils were identified on the basis of their mass spectra characteristics and retention indices [8]. Eighteen compounds (90.9%) were identified in the essential oil obtained through HD,7-methoxy 2,5-dimethyl-chromone (21.29%),z-β-ocimene(18.52%), myrcene(12.87%) were the main constituents. Furthermore , 22 compounds (94.2%) were characterized in the oil extracted by MAHD. The major component were 7-methoxy-2,5-dimehyl-chromone(26.32%),z-β-ocimene(15.02%),myrcene(6.95%) were the main constituents among the sixteen compounds (83.3%) characterized in the essential oil obtained by SFM method. 7-methoxy-2,5-dimethyl-chromone(37.29%), z-β-ocimene(13.12%), myrcene(4.64%) were the main constituents.

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Comparsion and Determination Ascorbic Acid in The Fresh and Dried Fruit of Jujube

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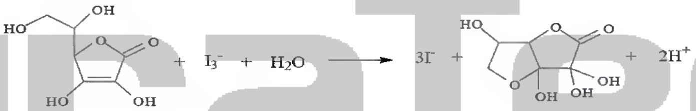
Abstract:
Jujube trees called jujube is a species of Ziziphus in the buckthorn family Rhamnaceae. with elongated leaves and tiny feet to 8 feet in height. Jujube is native to tropical regions and has a different shape and size. Jujube fruit contains acids, sugars, triterpenes, alkaloids,flavonoids, tannins, mucilage, and vitamins like vitamin C (ascorbic acid) .Vitamin C or L-ascorbic acid or L-ascorbate is an essential nutrient for humans and certain other animal species[1]. Vitamin C helps regulate the immune system It also is needed in the manufacture of collagen and norepinephrine and helps to benefit the skin, teeth, and bones [2][3].

In this study the amount of vitamin C in fresh and dried fruit of the jujuba determined.first the powder of fruits soaked in water for about 30 hours then the sample solutions titrated with standard iodine solution to reach the endpoint. The endpoint indicates by the reaction of iodine with starch suspension,which produces a blue-black product[4]. Repeated this titration at least three times and Recorded the averages of volumes. The results compared with together. Specified that the value of ascorbic acid in dried jujube is more than the fresh one of jujube. that meanes when the fruits ripe value of vitamin C decreases[5].



Keywords: jujube, ascorbic acid, titration

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Using of Ultrasonic Waves for Extraction Active Biological Agents of Dried and Fresh Jujube Plant

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Abstract:
Jujube trees with autumn leaves the scientific name of Zizyphus jujube lam Rhamaceae family,medium, Jujube is native to tropicalregions and has a different shape and size. Jujube tree has been too early.leaves are oval orelliptical.Jujube fruit contains: acids,sugars,triterpenes, peptide alkaloids, isoquinoline alkaloids, flavonoids, tannins, mucilage, and triterpenesaponins. Alkaloids are a group of naturally occurring chemical compounds that contain mostly basicnitrogen atoms. They often have pharmacological effects and are used as medications, Flavonoids are a class of plantsecondary metabolites. flavonoids also have anti-allergic, anti-inflammatory,anti-microbial,anti-cancer,and anti-diarrheal activities.Saponins are a class of chemical compounds, one of many secondary metabolites found in natural sources.they produce soap-like foaming when shaken in aqueous solutions [1][2].

The purpose of this work is extraction important active agents like alkaloids-flavonoids and saponin by ultrasonic waves from dried and fresh fruit of jujuba. At the firstthe nucleus of fresh and dried fruits of jujube plant was removed and crushed in a ball mill so need to remove the fat of the plant samples with petroliumether.Some of the samples prepared for investigationthe value of alkaloids-flavonoids and saponin byultrasonic-assisted extractionat different times and powerwhile other samples analyzed without ultrasonic-assisted extraction [3]. The results show samples that prepared by ultrasonic-assisted extraction has more value of the active agents than the others. In fact ultrasonic irradiation has increased the yield of the active agents in extraction [4].

Keywords: jujube, active agents, extraction

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Insight into the reaction of Erythromycin with Pb^{2+} ion in non aqueous solution

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Abstract

Erythromycin,an antibiotic belonging to the family of macrolides, is consisting of a 14 member ring, a keton group, two glycosidic bonds and a dimethylamino group [1]. The drug targets at ribosome and inhibits the protein synthesis of Gram positive bacteria such as Mycoplasma and chlamydia [2,3].

Heavy metals often have direct physiologically toxic effects and are stored or incorporated in living tissues, sometimes permanently [4].Lead is a cumulative poison and Neurotoxin that binds to essential enzymes and several other cellular components and inactivates them [5] .

The transfer of genetic information for the synthesis of a specific protein is influenced by metal ion, that may bind with the nucleotide fragment, enzyme, protein or the drug itself [6,7]. Thus, these interactions may be responsibl for the alteration of antibiotic level in humanserum and tissue. These changes and the formation of new compounds can effect the antibacterial activity of erythromycin . Therefore, in this work was studied interaction of erythromycin with $Pb(No_3)_2$ in methanol solvent . Via Job's methode of continuous variation and Mole – ratio method has been founded that the interaction of erythromycin with Pb^{2+} ion forms one complex with metal to ligand composition of 1:2. The influence of pH, time, temperature, interferences on stable of complex has been tested.

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Synthesis of New 3-methoxybenzyloxy coumarin Derivatives As Potential cytotoxic and antioxidant

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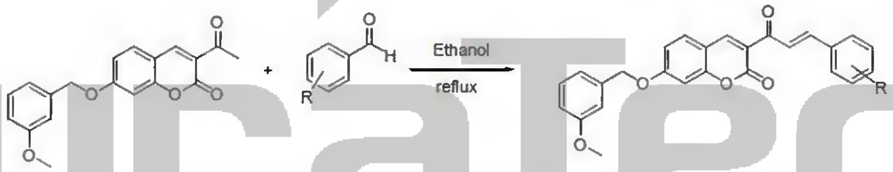
Coumarins are nowadays an important group of organic compounds that are used as additives to food and cosmetics, optical brightening agents and laser dyes. Coumarin derivatives are usually occurring as secondary metabolites present in seeds, roots and leaves of many plant species. Chalcone derivatives of coumarin exhibit several biological activities such as antioxidant [1], anti-inflammatory [2], antitumor [3], antibacterial activity [4], anticoagulating and anti-HIV activity. Also, it has been found that the presence of a reactive unsaturated keto function in chalcones to be responsible for their antimicrobial activity which may be altered depending on the type and position of substituent on the aromatic rings [5]. In these work a series of novel coumarin–chalcone hybrids have been synthesized as the shown in scheme 1 as potential for antioxidant and anticancer activities.



Scheme 1. A simple procedure for the synthesis of new coumarin derivatives

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Simple Method Direct Amination of Multi-Walled Carbon Nanotubes

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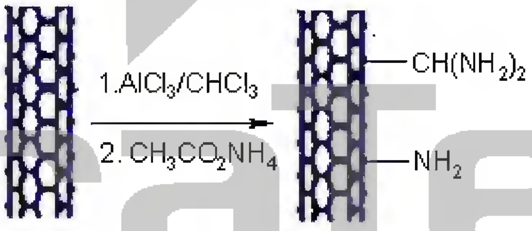
Among the various functional groups attached to CNTs, amines are added in a relatively simple procedure. In fact, the nitrogen atom of the amino group (–NH_2) has a lone valence electron,which is easily available for bonding to other molecules. Because of this reactivity, the amine-functionalized CNTs are frequently used in fabrication of electrodes [1-2], composites [3-4], and membranes [5].We report one pot electrophilic addition of Multi-Walled Carbon Nanotubes(MWCNTs) with chloroform using Lewis acid as catalyst followed by amination with ammonium acetate. The results confirmed the presence of high concentrations of –NH_2 groups on the surfaces of MWCNTs treated by the method of the present work.

The resulting materials characterized with different spectroscopic techniques such as infrared spectroscopy, elemental analysis (CHN), Raman and thermo gravimetric analysis (TGA).

The process has proved to be very effective, safe and easy to operate. It is also very clean and the scale up of this method is easy.



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18th Iranian Seminar Of Organic
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7-9 March 2012

Design and synthesis of novel acetylcholinesterase inhibitory with coumarin motif

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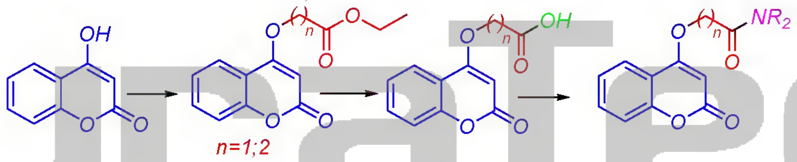
Alzheimer's disease (AD) is considered as a common neurodegenerative disorder mostly observed in aged populations [1]. Decrease of acetylcholine level in the hippocamp and cortex is the one of the most important causes of AD; therefore acetylcholinesterase (AChE) inhibitors are effective agents for treatment of AD's symptoms [2].

In an attempt to find novel agents against AD, a series of coumarin derivatives have been reported as compounds able to inhibit acetylcholinesterase enzyme [3]. On the other hand synthesis and AChEI activity of phenyl pipirazine structures have been largely discussed [4]. In pursuit of the described studies in this area and to obtain novel AChEI compounds, two hybrid structures of these structures would be synthesized in this study. The synthetic pathway for synthesis of our designed compounds is shown in Scheme 1.



Scheme 1

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Highly efficient Suzuki Cross-Coupling Reactions catalyzed by heterogeneous palladium porphyrin

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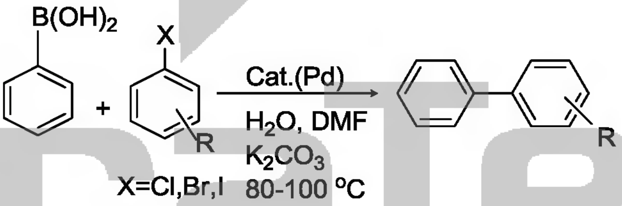
Suzuki cross-coupling reaction represents a powerful method for the C-C bond formation [1-3]. Construction of biaryl compounds via the palladium-catalyzed Suzuki reaction is an interesting area in organic synthesis. The importance of biaryl units as molecular components in pharmaceuticals, herbicides and natural products, as well as in engineering materials such as conducting polymers, molecular wires and liquid crystals, has attracted enormous interest [4-6]. The reaction represents an attractive alternative over other methods using organometallics because organoboranes are air- and moisture-stable with relatively low toxicity. With various metals being employed in coupling reactions, palladium is the most versatile metal in promoting or catalyzing reactions involving C-C formation due to its excellent catalytic efficiency in this type of reactions [7-10]. A control experiment indicated that the coupling reaction did not occur in the absence of catalyst.

In the present work, we have prepared heterogeneous tetrakis(4-aminophenyl)porphyrinatopalladium(II) and its catalytic activity was tested for the Suzuki cross-coupling reactions under various conditions. The catalyst exhibits high catalytic activities for the coupling of various aryl halides with organoboronic acid providing excellent yields of desired product [11]. The catalyst was characterized by various physicochemical and spectroscopic techniques.



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DFT Study and NBO Analysis of Nanotubes Containing Anti-HIV and Anti-Cancer Drugs

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Abstract:

Scientists have expressed their hope to develop the use of carbon Nanotubes to release vaccines. It is important to release drug in cell without damaging healthy cells of tissue under studying. [1]. For this aim, some anticancer and anti-HIV drugs were selected to react to a same nanotube. Emtricitabine is a synthetic nucleoside analog of cytosine with activity against immunodeficiency type 1 (HIV-1). Emtricitabine is the (-) enantiomer of 2',3'-dideoxy-5-fluroro-3'-thiacytidine. It differs from Lamovudine only by the presence of a flouro atom at 5-position of the cytosine ring. Emtricitabine was the first reported to show anti-HIV activity comparable to Lamivudine [2]. Gemcitabine (2',2'-dioxocytidine) (Gemzar) is used in various carcinomas. Common side effects are Vomiting, Poor appetite, … [3]. This work is carried out by a pc computer which has Intel (R) 2 quad CPU 8400 with 4 GB RAM. A Nanotube (6,6) including 84 atoms is selected which react with Emtricitabine, Lamiduvine and Gemzar drugs. The DFT Calculations have been performed using Gaussian 03 [4] by B3LYP method [5] and standard 6-31G(d) basis set. Then complexes between Nanotube/Emtricitabine (composite 1) and Nanotube/Lamiduvine (composite 2) are formed by an etheric bond and optimized by B3LYP/6-31G(d) method. Gemzar has two sites for reacting to Nanotube. On the first head, an etheric bond is formed (composite 3). On the second head, an amine bond is formed (composite 4).The Natural Bond Orbital (NBO) [6] analysis calculations have been also performed for all structures using B3LYP method and the standard 6-31G(d) basis set. For optimized composites, bond lengths and O, C and N Mulliken charges, hybrid and occupancy of them were calculated. The results show the complex formed between Nanotube and Emtrictitabine (composite 1) has lower energy than composite 2. So this composite is more stable than the other agent. Also the results show that both composites are more stable than the single agents and the composite 3 is more stable than composite 4. From hybrid of donor atoms, it is obtained that by increasing p share in hybrid, the occupancy reduces. In this work, a study of hyperconjugative interactions has been completed, too. The results show hyperconjugation effect in composite 1 and 3 (from lone pairs of Oxygen to σ^* or π^* orbitals of Carbon atom of Nanotube) is more than composite 2 and 4 (between lone pair of Nitrogen to σ^* or π^* orbitals of Carbon), respectively. Also it becomes clear that occupancy in lone pair of Nitrogen atom is less than lone pairs of Oxygen atom. The obtained energies of HOMO and LUMO orbitals show lower amount for HOMO and more amount for gap of these energies in composite 1 and 3. These are two reasons for composite 1 and 3 being more stable than composite 2 and 4, respectively.

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Nano-$SbCl_5.SiO_2$: An Efficient Heterogeneous Alternative Reagent for Synthesis of bis indole methan derivatives

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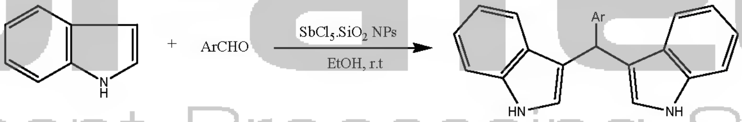
Since, Antimony pentachloride is a liquid with a high specific gravity that fumes in air and reacts with the moisture to form HCl. The handling and the usability of $SbCl_5$ as a liquid form is laborious and the supported form is indeed preferable. $SbCl_5$ supported on SiO_2 nanoparticles has been prepared and has been used effectively as a catalyst.

Indole moiety is present abundantly in various natural plants and its derivatives find applications in the field pharmaceuticals, agrochemichals and material sciences [1]. Bis (indole)methanes, important derivatives of indole, are present widely in bioactive metabolites of terrestrial and marine origin [2-4]. They are also the most active cruciferous substances for romoting beneficial estrogen metabolism and inducing apoptosis in human cancer cells. Moreover, vibrindole-A was demonstrated to exhibit anti-bacterial activity against staphylococcus aureus, S. albus and B.subtilis.

We report, herein, the synthesis of different derivatives of bis (indolyl) methanes from condensation of aldehydes and indole in the presence of Antimony pentachloride supported on nano silicagel. The reactions were carried out at room temperature in ethanol. This methods have some advantages such as good to excellent yield, mild reaction condition, ease of operation and workup, short reaction time and high product purity.



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Identification and absorption of enantiomer compounds in cigarette smoke via synthesized multiwalled carbon nanotube (MWCNT)

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Cigarette smoke content the more than 4000 derived compounds . In this study researched the identification and absorption of enantiomer compounds on Carbon nanotube (CNT) with 8-10 nm diameters. First CNT put in cigarette filter and burned via smoking machine (FILTRONA, CSM)., then filters were shaken for 6 hours in 100 cc pure methanol, the final solution was then injected into a GC/MS, with a QP detector, under the following conditions: Column J&W, DB-5ms. temperature program : (60°C for 0.5 min, 250°C at 5°C /min, 250°C for 20 min, 300°C at 30°C/min, 300°C for 7min). Oven temperature: 60°C, flow: 0.8 ml/min, Ion source temperature: 200°C, interface temperature: 270°C. The substances were identified by comparing the retention times of each compound with the retention time in mass spectrometry libraries (NIST and WILLY229). result show the absorption of 99 enantiomer compounds on CNT. Most important compounds that absorbed on CNT concerned to : (S)-(+)-4-sec-butylpyrazole , (+-)-[4.a.alpha,5,beta.(E)]-4-methyl-5-(1-propenyl)-2-imidazolidinone , (+-)-Cis-3,4-dimethyl-2-phenyltetrahydro-1,4-thiazin , (S)-(+)-2-phenyl-3-oxa-5-hexenoate , S)-(+)-4-sec-butylpyrazole, L-(-)-Asparagin , (S)-(-)-3-N-methylamino-2-phenylpropan-1-ol , (+)-3-carbomethoxy methylene -2-bornanone , (1E) – 8 – (4- morpholiny) – 4 cycloocten – 1 – one oxime , (2S,3R)-(+)-3-(Benzylsulfonyl)butan-2-ol , (+-)-5-Hydroxy-6-(1-ethoxyethyl)-2,7-dimethoxynaphthoquinone , (S,S)-(+)-4,4′-Bis(2-methylbutyl)azoxy benzene.

Also MWCNT was studied by SEM , TEM and FTIR before and after absorption .

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Three-component and solvent free synthesis of 2,4,6-triarylpyridines using guanidine as an environmentally friendly source of ammonia

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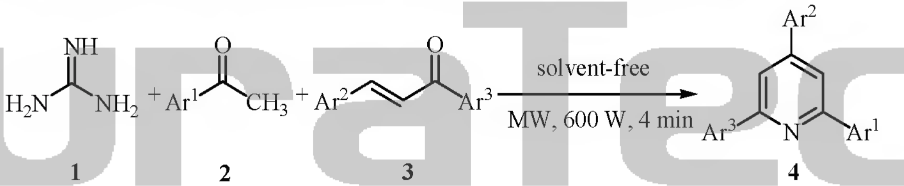
In this research, the main aim is providing a reliable, with excellent yield method for synthesis of 2,4,6-triarylpyridine derivatives by the reaction of guanidine, acetophenone, and chalcone. This reaction was carried out under economical one-pot reaction conditions and green reagents (catalyst and solvent free). Also, in this method, guanidine was introduced as a good and useful source of ammonia. Microwave irradiation has become an effective tool for synthesis of organic compounds, in both academic and industrial laboratories[1,2]. In recent years, many reviews have been published on the application of microwaves to solvent-free reactions, fullerene chemistry, heterocyclic chemistry, carbohydrates, homogeneous and heterogeneous catalysis, medicinal and combinatorial chemistry and green chemistry. Therefore, the application of microwave irradiation in organic synthesis for conducting reactions at highly accelerated rates and high yields is an emerging technique [3].

The procedure is: a mixture of guanidine **1**, acetophenones **2**, and chalcone **3** were irradiated in a microwave oven at 600 W for 4 minutes under solvent-free conditions to produce the corresponding pyridines **4** in 92-98% yields. All the reactions went to completion within 4 min. ^{1}H NMR analysis of the reaction mixtures clearly indicated the formation of the corresponding 2,4,6-triarylpyridines **4a–m** in good to excellent yields. All products were characterized by ^{1}H and ^{13}C NMR spectroscopy and by comparison of their spectral data and melting point values with those of the authentic samples reported in the literature. As a result, the reaction between guanidine, acetophenone and chalcone provides a simple one-pot entry into the microwave-assisted synthesis of 2,4,6-triarylpyridines of potential synthetic and pharmaceutical interest. Solvent-free conditions, short reaction times, excellent yields of the products and use of simple starting materials are the key advantages of this method. The simplicity of the present procedure makes it an interesting alternative to complex multi-step approaches[2,3].



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Versatile synthesis of substituted imidazoles using calcium nitride as a source of ammonia

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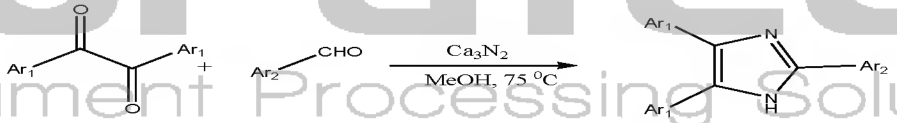
In this research, The main aim is evaluating the application of calcium nitride (Ca_3N_2) as a suitable source of ammonia for the synthesis of 2, 4, 5-trisubstituted imidazoles. The tests revealed that heating a mixture of a benzaldehyde, a benzyl, and calcium nitride in methanol leads to the formation of functionalized imidazoles in good to excellent yields[1-3]. Regarding the unrivaled pharmacological properties of imidazols, a convenient protocol, using calcium nitride as the ammonia source and different aldehydes and benzyls, for the synthesis of these heterocycles is described. the reaction between benzyl , benzaldehyde and calcium nitride has been used as a efficient method to produce 2, 4, 5-trisubstituted imidazoles in yields of 70–82% (Scheme 1).The reactions were carried out at 75^0C and were completed within 22 hours. The structure of the products were established by ^{1}H NMR, ^{13}C NMR spectroscopy and by comparison of their spectral data and melting point values with those of the authentic samples reported in the literature. As a result, we have shown that the simple method introduced in this work can be effectively used for the synthesis of 2,4,5-three substituted imidazoles based on the application of Ca_3N_2 as an eco-friendly, inexpensive and efficient source of ammonia, enjoying the advantage of having high yields, and simple and easy work-up operations.

$$Ca_3N_2 + 6H_2O \longrightarrow 2NH_3 + 3Ca(OH)_2$$

$$Ca_3N_2 + 6MeOH \longrightarrow 2NH_3 + 3Ca(OMe)_2$$



1 2 3

70-82% yield

Scheme 1

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A ONE-POT TANDEM METHOD FOR THE SYNTHESIS OF QUINAZOLINONES FROM ARYL IODIDES

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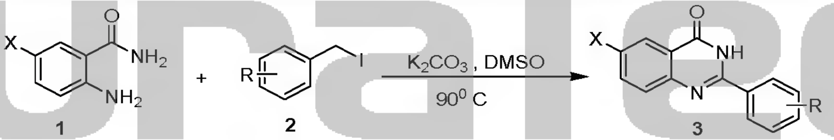
In this paper ,a new ,one-pot, with a good yield is introduced. This method explores a one-pot tandem procedure for the synthesis of quinazolinones from ARYL iodides and o-Aminobenzamides leading to the production of quinazolinones with high yields under mild conditions in DMSO without requiring an additional oxidant [1]. The work also showed that according to this method, ARYL iodides bearing a range of substituents tend to be suitable substrates. General Procedure for the preparation of 2-Phenylquinazolin-4(3H)-one is described as :A mixture of benzyl iodide (0.218g, 1 mmol) and K_2CO_3 (1.5 mmol) in DMSO (1 mL) was stirred for 4 h at 90 °C. Next, ortho-Aminobenzamides (0.136 g, 1 mmol) were added to the reaction mixture and stirring was continued at 90 °C for 2 h. The reaction mixture was cooled to room temperature and H_2O (5 mL) was added. Stirring was continued for 1 h at ambient temperature[2]. The resulting white precipitate was filtered, washed with H_2O (5 mL), dried, and recrystallized from n-hexane/EtOAc (3:1) to give 2-Phenylquinazolin-4(3H)-one as colorless crystals, m.p 235-237 0C.1H NMR (DMSO-d6, 300 MHz) δ12.55, 8.12–8.20 (m, 3H), 7.80–7.88 (m, 1H), 7.70–7.76 (m,1H), 7.55–7.62 (m, 4H) ppm; As a result, we report a novel and efficient procedure for the synthesis of 4(3H)-quinazolinones. In this method, a mixture of an ARYL iodide and ortho-aminobenzamides is used to afford 4(3H)-quinazolinonesin good yields of 78–86%. The reactions were performed at 90°C by mixing the two components. The structures of the products were established by ^{1}H NMR ,^{13}C NMR spectroscopy and by comparison of their spectral data and melting point values [1,2].



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The Study of Synthesis and Cyclising Reactions of 2-(4-Chloro-3,3-dimethyl-7-phenoxyindolin-2-ylidene)malonaldehyde

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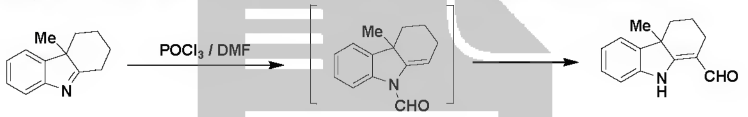
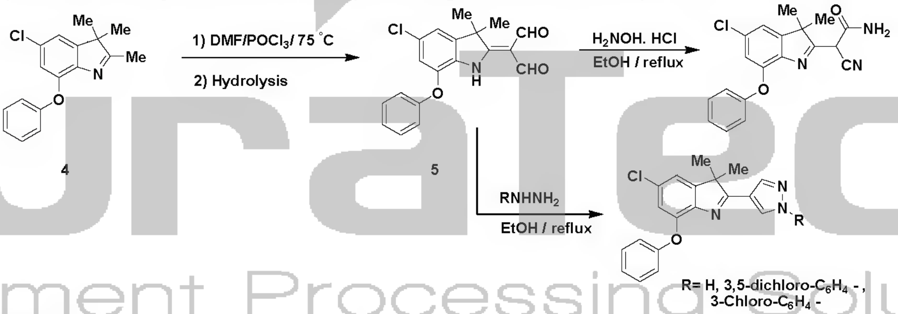
In 1959, Fritz [1] reported the N-formylation of the 3,3-disubstituted 3H-indole **1** (indolenine) using the Vilsmeier reagent from DMF and $POCl_3$. Further reaction of **1** with the Vilsmeier reagent, and hydrolysis produced **3**. Formation of this product probably involves the intermediacy of **2**, from which the N-formyl group is hydrolytically removed:



1 2 3

We previously described the reaction of 3-H-indoles with the Vilsmeier reagent to produce aminomethylene malondialdehydes, additionally, we described a simple and straightforward preparation of substituted pyrazoles by condensation of dialdehyde with hydrazine and arylhydrazines [2,3]. In this study, we first synthesis indolenine **4** via Fischer reaction. Exposure of the indolenine **4** to the vilsmeier reagent at 75°C produced β-diformyl compound **5**. The malondialdehyde **5** was reacted with arylhydrazines, hydroxylamine hydrochloride to give various heterocyclic compounds in excellent yields:



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Efficient Synthesis of Polyfunctional N-substituted 1,4-Dihydropyridines

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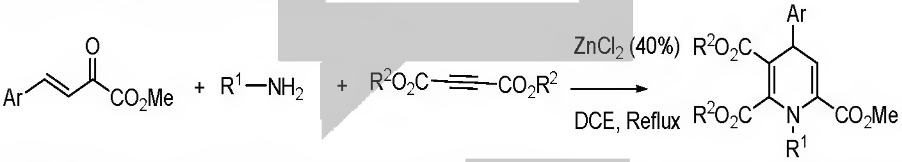
1,4-Dihydropyridine derivatives (1,4-DHPs) have interesting pharmacological and biological properties. It is clear that 1,4-DHP nucleus serves as the scaffold of important cardiovascular drugs and act as calcium channel blockers. It was shown that the activities of these compounds are related to the substituents and especially the number of ester functional groups [1]. Due to the biological activity of DHPs, we wish to report herein an efficient approach for the synthesis of polyfunctional 1,4DHPs with three alkyl ester groups.

Aryl methylidene alkyl pyruvates were used as starting material which could be synthesized via reaction of pyruvic acid and aromatic aldehydes in the presence of potassium hydroxide. Three-component reaction of aryl methylidene pyruvates, dialkylacetylene dicarboxylates and primary amines in the presence of Zinc Choloride (40 %) as lewis acid, leads to form polyfunctional N-substituted 1,4-dihydropyridines in 42-87 % yields.

The synthesized novel 1,4DHPs bearing three alkyl ester groups at C-2, C-5, and C-6, which could be used for further transformation.



It seems that the existence of more alkyl ester functional groups could add the interaction activity of these compounds with lipase enzymes[2]. The investigation of the biological activity of these compounds is in progress. Reaction could follow via these procedures:

a) Formation of enaminone via reaction of dialkyl acetylene dicarboxylate.
b) Addition of enaminone to activated aryl methylidene pyruvates.
c) Cyclization and finally dehydration.

In conclusion, this work describes a convenient and efficient process for the synthesis of functionalized 1,4-dihydropyridines via 3-MCR.

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An efficient one-pot synthesis of 5,5-disubstituted hydantoins in the presence of SiO_2 functionalized carbon nanotubes

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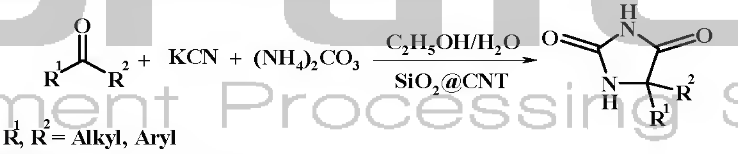
Abstract

Hydantoins (Imidazolidine-diones) are a class of bio-active molecules that have broad medicinal such as anticonvulsants, anti-tumor, antiarrhythmic, antimicrobial, antidiabetic, and agrochemical (herbicidal and fungicidal) applications [1-3]. Several method are used for synthesis of 5,5-disubstituted hydantoins [4]. These heterocycles are often made by the Bucherer-Bergs reaction. It is a four-component reaction (4-CR) that involves the condensation of a ketone (or aldehyde) with cyanide, ammonia and carbon dioxide with the latter reagents conveniently generated from ammonium carbonate. Organic chemical syntheses involving multi-component condensation strategy attained greater value, as the target molecules are often obtained in a single step rather than multiple steps which minimize the tedious work-up procedures and environmental hazardous wastes [5]. On the other hand, in the development of industrial processes, efficient separation of reagents and catalysts to enable their reuse for subsequent reaction cycles is a key challenge [6].Herein we wish to report a mild, efficient, and facile one-pot synthesis of 5,5-disubstituted hydantoin derivatives by the multi-component reaction of ketone (or aldehyde), potassium cyanide and ammonium carbonate in the presence (SiO_2@CNT) as a catalyst. This procedure is very simple and affording good to excellent yields. Structures of hydantoins were identified by spectroscopic methods such as FT-IR, UV-Vis, ^{1}H- and ^{13}C-NMR.



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New Method for Hydroxylation of Multi-walled Carbon Nanotubes and Study on Dispersion Stability in Organic Solvents

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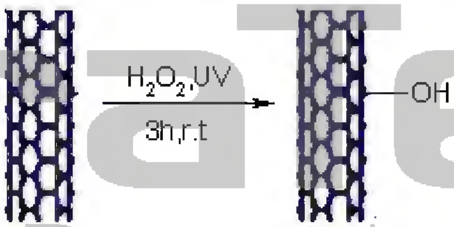
Carbon nanotubes, a new form of carbon allotropes, were discovered by Iijima, has stimulated great research interest, due to their unique physical properties and potential practical applications such as materials science ,physics, and engineering [1-2]. On the other hand, the application of CNTs has been hindered due to their poor dispersion and homogeneity within polymers. Chemical or physical functionalization of CNTs may increase the interfacial binding between CNTs and polymer matrices and increasing their dispersion stability and solubility [3].

In this research, we present the systematic investigation of the effect of hydroxyl radical ($HO^{\bullet}$) on the surfaces of carbon nanotubes. The possible mechanism indicated that introduction of those functional groups into the structure of MWCNTs could be regarded as the results of attacks of $HO^{\bullet}$ with double properties of oxidizability and electrophilic addition on defect sites and unsaturated bonds of C=C in the MWCNTs sample. [4].

In this study, a new, easy and highly efficient low cost method was employed for hydroxylation of MWCNTs by use H_2O_2 under the UV light. The workup of reaction products is very easy and the hydroxylated MWCNTs with high concentration of hydroxyl groups were produced. Obtained functionalized MWCNTs characterized in detail using XRD, FTIR, TGA and Raman spectroscopy also the dispersion of multi-walled carbon nanotubes in various common organic solvents was investigated.



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Galactopyranosylation and Glycopyranosylation of 1,3,4-Oxadiazole-2(3H)-thiones

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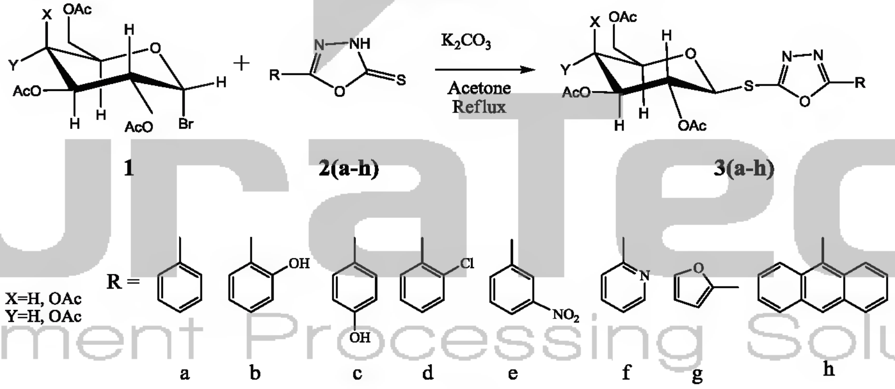
The 1,3,4-oxadiazole ring has been found in the skeleton of potent biological activity.[1] On the other it was known that carbohydrates and their derivatives have a significant biological role and occur widely in all living matter and function even appear to be essential to the process of infection by certain pathogenic species [2]. The carbohydrate moiety can be expected to play the role of drug carrier and improve the selectivity of compounds for cancerous cell lines. For example, vaccination using synthetic tumor-associated antigens such as carbohydrate antigens, holds promise for generating a specific antitumor response by targeting the immune system to cancer cells [3]. Recently, we became interested in the synthesis of thiogalactoside and thioglycoside compounds. Reaction of 1,3,4-oxadiazole-2(3H)-thiones **2(a-h)** with 2,3,4,6-tetra-O-acetyl-α-D-galactopyranosyl bromide or 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl bromide **1** in the presence of potassium carbonate gave the corresponding S-galactosides or S-glycosides **3(a-h)** Scheme 1.



Scheme 1

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Aniline to polyaniline/TiO_2 nanocomposites in a water-based nanofluid in the presence of sodium dodecyl sulfate emulsifier

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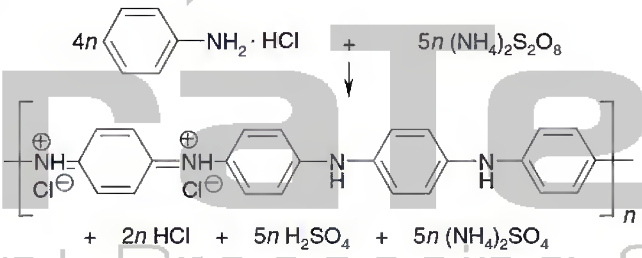
Environmental decontamination using semiconducting material photocatalysts has attracted a great deal of attention in recent years [1]. The main advantages of the photocatalytic process include mild operating conditions and the fact that it can be powered by sunlight, thus significantly reducing the electric power required and therefore the operating costs. Owing to the strong oxidation ability, nontoxicity and long-term photostability, nano-TiO_2 exhibits many advantages over the other photocatalysts, even bulk TiO_2 [2]. However, there are still some disadvantages, such as the lack of visible light response and no so much photocatalytic activity. In order to overcome these problems, some strategies have been investigated, including noble metal deposition, doping of metal or nonmetal ions, mixing with another metal oxide, surface photosensitization with dye and preparing composites with organic polymer [3]. Hence, the aim of this study is designation of a novel method to prepare PANI-based TiO_2 nanocomposites with unique characteristics. At first, a homogenized mixture of TiO_2 nanopowder in deionized distilled water was prepared using ultrasonic bath in the presence of sodium dodecyl sulfate (SDS) as the nanofluid stabilizer. HCl was then added to the colloid obtained so that the final solution was 0.1 N with respect to the acid concentration. Next, aniline monomer and then ammonium peroxydisulfate (APS) as the reaction oxidant were slowly added to the polymerization vessel. Structure of the nanocomposite was confirmed by IR and UV-vis. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and thermogravimetric analysis (TGA) showed nanoparticles exact size using Scherrer's equation, type of morphology, distribution quality of the two matters in the bulk, and heat stability of the product (Scheme 1).



Scheme 1

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A simple and efficient procedure for the synthesis of 1H-Pyrazolo[1,2-b]phthalazine-5,10-dione Derivatives

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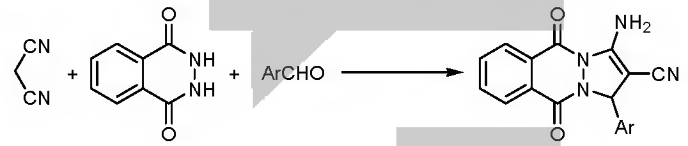
Multi-component reactions (MCRs) have attracted the attention of synthetic organic chemists for building highly functionalized organic molecules and pharmacologically important heterocyclic compounds, MCR are the preferred techniques due to high throughput synthesis of compounds in a cost- and time-effective manner.[1,2]

Multicomponent reactions of malononitrile, aldehyde and nucleophilic compounds have recently attracted the interest of the synthetic community because the formation of different condensation products can be expected on the specific conditions and structure of the building blocks.

Heterocycles containing the pyrazole rings are important targets in synthetic and medicinal chemistry because this fragment is a key moiety in numerous biologically active compounds, among them such prominent drug molecules as celecoxib, pyrazofurine, and many others. Similarly, heterocycles containing a phthalazine moiety are of interest because they show some pharmacological and biological activities.[3,4]



we report the synthesis of 1H pyrazolo[1,2-b]phthalazine- 5,10-dione derivatives via the simple, efficient, one-pot, and three-component condensation reaction of malononitrile, phthalhydrazideand aromatic aldehydes in the presence of a catalytic amount of **TFA** in ethanol as solvent at 70 °C.The structures of all products were confirmed using physical and spectral (NMR and IR) data.

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Efficient and facile nucleophilic aromatic substitution of Nitro groups with alkyl- or arylthiols by Magnesium Methoxide

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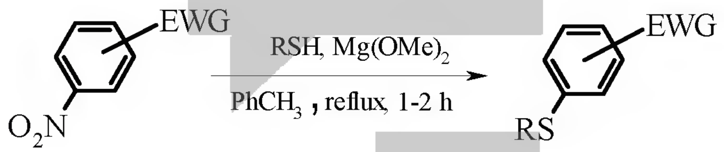
Nucleophilic aromatic substitution reactions (S_NAr reactions) of nitroarenes that have strong electron-withdrawing groups at the ortho or para positions are well known processes [1]. The use of the nitro function as a leaving group in such reactions facilitates the synthesis of novel substituted benzene derivatives and simplifies the synthesis of a wide variety of heterocycles [3]. In the previous report [2], the success of the displacement is crucially due to the use of hexamethylphosphoramide (HMPA) and the use of DMSO resulted in lower efficiency.

Here, we report an improved method for S_NAr reactions of activated nitroarenes with thiols. Treatment of nitroarenes having electron-withdrawing groups at the ortho or para position with alkane or arylthiols in the presence of magnesium methoxide in toluene under reflux condition leads to nucleophilic displacement of the nitro group with the alkylthio group. The present Mg(OMe)-mediated reaction is high-yielding and rapid, compared with similar reactions mediated by other bases, [4, 5] and will be an extremely useful tool for conjugation chemistry through the formation of a sp^2 carbon–sulfur covalent bond [6].



EWG = COOMe, COR, CHO, CN
R= Ph, Alkyl, carboxylic acids

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Sulfur Salen Organocatalysis in mild and highly regioselective ring opening of epoxides to halo alcohols by elemental halogen

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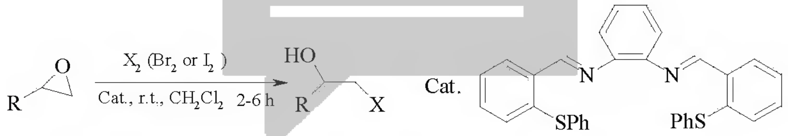
Oxiranes are among the most versatile intermediates in organic synthesis, they can be easily prepared from a variety of other functional groups [1] and due to their ring strain and high reactivity, their reactions with various nucleophiles lead to highly regio and stereoselective ring opened products [2]. The vicinal halohydrins have found wide applications in organic transformations and in the synthesis of marine natural products. A variety of reagents are known to convert epoxides to halohydrins; the ring opening of unsymmetrically substituted epoxides with Li$_2$[NiBr$_4$] [3], LiX-[Bmim]PF$_6$ [4], haloboran reagents [5], Br$_2$/PPh$_3$ [6], SmI$_2$ [7], Ti(O-ipr)$_4$ [8], and BF$_3$-Et$_2$O [9] has been reported.

We would like to describe herein, that new synthetic sulfur salens are highly reactive to cleavage of the epoxide rings to relative vicinal halohydrins in the presence of elemental iodine and bromine, more efficient and regioselective in high yield under mild conditions that would be highly desirable. The catalysts are easily recovered and can be reuse several times.



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Efficient Transformation of Carbonyl Compounds by Polymer Supported Periodic acid as a New Polymeric Oxidizing Agent

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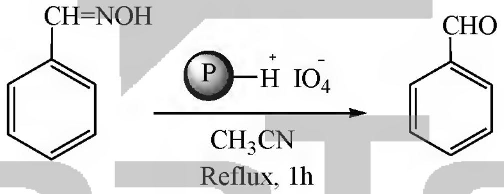
Oximes are extensively used as preferred and readily prepared derivatives for purification and characterization of carbonyl compounds [1]. Furthermore they play an important role as protecting [2] and selectively activating [3]. Regeneration of ketones and aldehydes from their oximes has assumed added importance since the discovery of the Barton reaction in which oximes are produced at non-activated hydrocarbon sites [4]. Many oxidizing agents have been used, only a limited number of methods are efficient because of the low solubility of these metallic reagents in most organic solvents [5]. The applications of this catalyst is in the oxidation of alcohols, sulfides and hydroquinone [6]. Herein, we wish to report an efficient transformation of Oximes to the corresponding carbonyl compounds using polymer-supported periodic acid as a new polymeric oxidizing agent under aprotic conditions. The product has been obtained in high yields and short reaction times. The structure of product has been assigned by physical and spectroscopic date.



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Polymer-Supported Periodic Acid: An Efficient Reagent for Oxidation of Hydroquinones into Quinones under Aprotic Solvent

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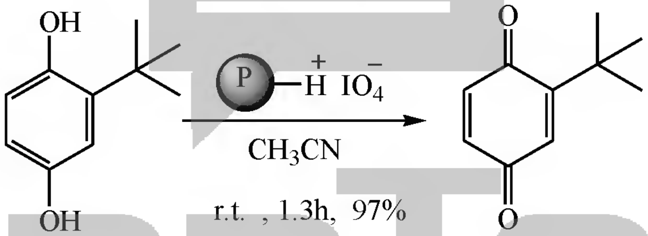
The oxidation of hydroquinone to quinone (Q) is a very important physiological reaction and copper metal is found to be the most efficient catalyst for this reaction [1]. A general method for the preparation of quinones is the oxidation of HQ and its derivatives [2]. A number of oxidants, for example, mineral acids [3], Fermy's salt [4], lead tetraacetate , cerium ammonium nitrate [5] and other transition metal ions have been employed, but most of these suffer from drawbacks such as homogenous reaction conditions and the generation of toxic wastes. In this research, we report the oxidation of some hydroquinones into quinins by using polymer-supported periodic acid as a polymeric oxidizing agents under aprotic conditions. The product has been obtained in high yields and short reaction times. The structure of products has been assigned by nuclear magnetic resonance (NMR) and infrared (IR) together with physical and spectroscopic data.



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Theoretical study of a set of chiral Cyclophanes

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Cyclophanes are the hydrocarbons containing one or more benzenoid rings or other large aromatic systems combined with an aliphatic chain bridging two nonadjacent carbons. Although the chemistry of cyclophanes has been extensively investigated [1], the studies on chiral cyclophanes are rather limited. Apart from their role for studying the electronic interaction between the aromatic moieties, they have also been used as chiral ligands in asymmetric catalysis.

In this research, the structures and magnetic properties of a set of chiral cyclophanes(**Figure 1**) were studied computationally at the B3LYP/6-311+G** level of density functional theory (DFT).The local aromaticity of benzenoid moieties is examined by means of nucleus independent chemical shifts (NICS) as quantifier of magnetic anisotropy[2]. The NICS values obtained over a distance inside and outside of the cage give a clear indication of diamagnetic and paramagnetic ring currents.

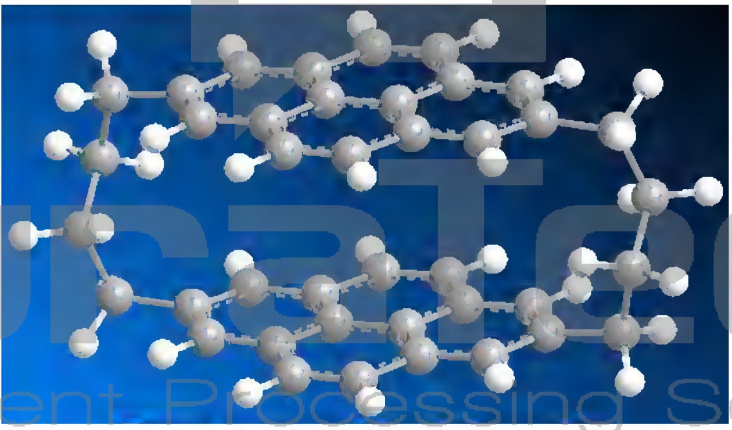

Figure 1. A prototype of the cyclophanes studied.

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Aniline to Polyaniline/silver nanocomposites via emulsion polymerization in the presence of p-phenylenediamine

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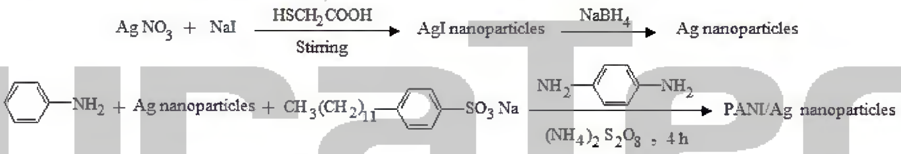
Deposition of metal or metal oxide nanoparticles into a conducting polymer matrix is an attractive area of science [1]. The Polyaniline/silver (PANI/Ag) nanocomposites have been accelerated in the presence of a few amount of p-phenylenediamine (PDA) in acidic media [2,3]. This study deals with the novel synthesis of PANI/Ag nanohybrids via emulsion polymerization using PDA.

Experimental: Ag nanoparticles were prepared as follows: 7.5 mL of $AgNO_3$ solution (0.01 M) was added to 225 mL deionized water with stirring. After 10 min of mixing, 15 mL of 2-mercaptocarboxylic acid solution (0.01 M) was added to the mixed solution and 7.5 mL of 0.01 M NaI solution was dripped into the mixed solution under vigorous stirring immediately. After 20 min of further reaction, a light yellow solution of AgI nanoparticles was obtained. Then, (0.06 g, 1.06 mmol)$NaBH_4$ as reducing reagent was added to AgI colloid and the mixture was kept stirred for another 30 min until AgI was thoroughly reduced and a light red colloid of Ag nanoparticles can be obtained and then acidified with HCl to 0.1 N. Aniline (0.582 g, 6 mmol), sodium dodecylbenzene sulfonate (21.78 g, 60 mmol), PDA (0.006 g, 0.06 mmol) and ammonium peroxydisulfate (1.854 g, 8 mmol) were added to the above colloid. PANI/Ag hybrid was prepared after 4 h stirring at room temperature. Acetonitrile was then added to destroy micelles and precipitate the product.



Results: A nanocomposite of PANI/Ag was successfully synthesized by a novel strategy starting from aniline via emulsion polymerization in the presence of p-phenylenediamine. The hybrid prepared was fully characterized using IR, UV–vis, SEM, TEM, XRD, and TGA analyses. A uniform core-shell surface could be detected by SEM. Nanoparticles of Ag (~ 2% w/w) with size of about 20 nm were dispersed into the polymer matrix. In addition, thermo-stability of the product was not affected by this dispersion. Conductivity measurements were also done and compared with that of pure PANI.

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Synthesis of formyl Coumarines Using Selenium Dioxide as oxidant

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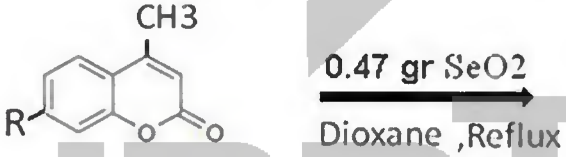
Abstract

The present project, by using 0.47 gr (0.0084) Seo$_2$ as oxidant and 20ml Dioxane as reaction solvent tries to oxide a sequence of Coumarine derivatives in the presence of oxidants to the related aldehyde.[1] In the next step the oxidation output was changed to the related imine by a condensation reaction with aldehyde.[2] After purifying the imine products by TLC (quantitative), the molecular structure of the so-called composition was verified through some techniques of spectroscopy such as ^{1}H NMR, FT-IR, and mass after measuring the melting point.[3]



Keywords: coumarine- aldehyde- SeO2- synthesis- selective.

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Synthesis of new Bis phenanthrimidazole from 9,10-phenanthraquinone and aldehydes drivatives

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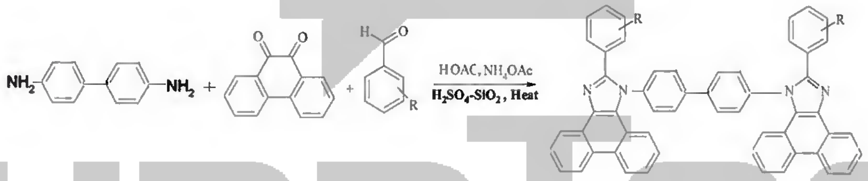
A new convenient, efficient, and cost-effective one pot synthesis of bis phenanthrimidazole from 9,10-phenanthraquinone, benzidin and aldehydes, using sulfuric acid immobilized on silica as a catalyst is described. The peresent methodology offers several advantages in excellent yields, simple procedure, shorter reaction times.the use of inexpensive reagents, easy recovery and eco friendly . It was found that when 9,10-phenanthraquinone and an aldehyde were refluxed in glacial acetic acid solution containing ammonium acetate, excellent yields of bis phenanthrimidazol resulted. In this work, We found that treatment of 9,10 phenanthraquinone with stoichiometric aldehydes in ethanol, in the presence of sulfuric acid immobilized on silica as catalyst, leads to bis phenanthrimidazole in excellent yields. In addition, we used triethyl orthoesters instead of aliphatic aldehydes. We found that our methodology works very well for triethyl orthoesters.a mixture of an aldehyde (2mmol), a phenanthraquinone (2mmol), ammonium acetate (2mmol), sulfuric acid immobilized on silica(5 mol%) and 5 ml glacial acetic acid was heated at 80C.the progress of reaction was mainted by TLC.



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Preparation of Novel Photo and Optically Active Poly(ester-imide) by Direct Polycondensation Reaction

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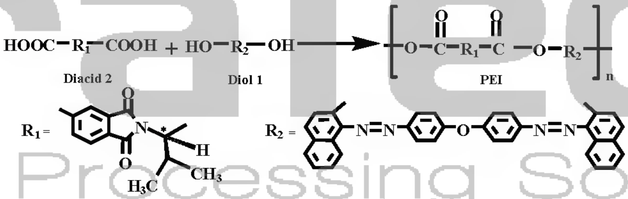
Polyester (PE) is an example of polymers that degrade during a long period. Recycling of this polymer helps the environment as well as preventing the wasting of energy. PEs often have limited heat and flame resistance, so these materials are inappropriate for many important applications [1,2]. Aromatic polyesters have good thermal and mechanical properties, and therefore they belong to the class of high performance engineering plastic [3]. Azo compounds are highly colored and have been used as dyes and pigments for a long time. They have also been used in many practical applications such as coloring fibers, photoelectronic applications, and analytical chemistry. [4].

In this research, the direct polycondensation reaction of N-trimellitylimido-L-valine (2) as a diacid with 4,4′-bis-[(2-hydroxy naphthalene)1-azo]diphenyl ether (1) as a novel diol containing azo groups was carried out in a system of tosyl chloride (TsCl), pyridine (Py) and N,N-dimethylformamide (DMF) (scheme 1). The effect of the amount of DMF, aging time, reaction temperature, and reaction time on the reaction yields and polymer viscosities were studied.

The resulting poly(ester-imide) (PEI) was characterized by FT-IR, ^{1}H-NMR spectroscopy and thermal gravimetric method. PEI has azo and naphthalene groups as well as chiral center in the main chain, so it is photo, florescence and optical active. In addition because of the existence of L-valine in the polymer chain, it is expected to be biodegradable and classified under environmentally friendly polymers.

Keywords: poly(ester-imide)s; direct polycondensation; condensing agent; optically active polymers; azo compounds.



Scheme 1. Synthesis of PEI.

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A New One-Pot Reaction for the Synthesis of Highly Substituted Thiophenes Using α-Halo acetopheneones

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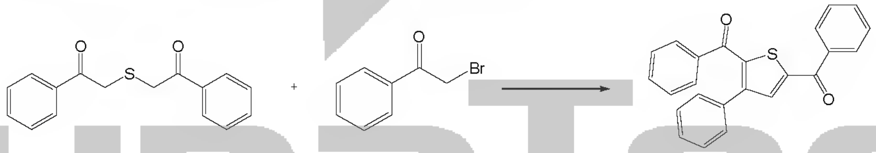
Thiophene is an important heterocyclic organic material and a large number of methods have been devised to prepare this heterocycle. Thiophene has been used extensively in the synthesis of anticancer drugs [1], anti inflammatory [2], anti-tuberculosis [3].

Thiophenes have been synthesized by the well known Paal –Knorr reaction, involving the cyclization reaction of 1,4-diketones with hydrogen sulfide P_2S_5 [4]. However, the application of Paal–Knorr reaction for the synthesis of thiophene derivatives is limited due to less commercial availability of wide range of 1,4-dicarbonyl compounds. The most known approach for the preparation of highly substituted thiophenes is the Gewald method in which, elemental sulfur is reacted with equimolar amounts of an activated acetonitrile and a carbonyl compound in the presence of base [5]. Another method has been used the reaction of 3-thiapentanedioic acid diethyl esters with 1,2-dicarbonyl compounds in the presence of a suitable base [6].

Herein we wish to report for the first time to our knowledge a simple procedure for the construction of highly substituted thiophenes using the reaction of α-haloketones with inorganic sulfide salts in the presence of a base.

Meanwhile the effective parameters in the reaction course such as the type of organic base, solvent, temperature and the reaction time were optimized. Also, all new compounds were characterized by FT-IR, ^{1}H-NMR, ^{13}C-NMR and the low resolution Mass spectroscopy.



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Common surface polymerization to prepare polypyrrole/silver nanocamposites in various kinds of organic solvents in the presence of surfactants

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Incorporating nanosized metal particles into the matrices of inherently conducting polymers such as polypyrrole (PPy) is of current interest for many purposes. On one hand, the polymer can be a matrix for stabilizing the growth of nanoparticles and avoiding the agglomeration process. The stabilized nanoparticles then can be studied for their catalyses, optical, magnetic, mechanical and electrical properties. On the other hand, the nanoparticles can be deposited into polymer matrices to enhance some of the polymer properties, like Raman activities, conductivity, etc. or to modify the polymer structures, electronic, mechanical and electrical properties [1]. For the first time, in 2007, Petridis et al. have reported the synthesis of PPy/Ag nanocamposites by interfacial technique [2]. Three years later, a similar study was reported by Li et al. to prepare the mentioned nanohybrid [3].

Alongside these studies, this article too, describes the polymerization of pyrrole in the boundary of two immiscible solvents, which can be applied for the synthesis of PPy/Ag nanocamposites. To our knowledge, no previous work has been reported to describe the important role of organic solvents in the presence of surfactants (Figure 1). Moreover, two anionic surfactants, i.e. sodium dodecylbenzene sulfonate (SDBS) and sodium polystyrene sulfonates (SPSS) were employed. In all systems, $AgNO_3$ dissolved in the aqueous phase was used as the reaction oxidant, and the reduction of Ag^+ to metallic silver is accompanied by oxidative polymerization of pyrrole, leading to the formation of nanocomposite particles. FTIR, UV-vis, XRD, SEM, TEM and TGA analyses were used to study the morphology and the structure of the nanocomposite. In summary, the oxidation of pyrrole and the formation of silver occurred simultaneously via employing $AgNO_3$ at the interface of water and tested organic solvents in the presence of surfactants. As a key conclusion, it should be stated that the further solubility coefficient difference, the more morphological order and the more thermostability will be.

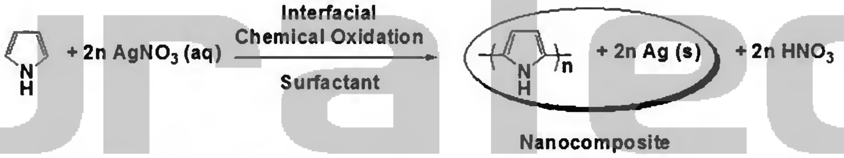

Figure 1. Synthesis of polypyrrole/Ag nanocomposite by interfacial polymerization in the presence of surfactant

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Physicochemical Modification of Polyaniline by graft reaction on PSMA

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Polyaniline (PANI) as a conductive polymer has attracted much attention because of its electronic, electrochemical and optical properties and especially good environmental and thermal stability [1]. The main disadvantage of this conducting polymer, however, is its poor processability both in melt and in solution due to the stiffness of its backbone [2]. This disadvantage can be minimized, however, by doping PANI with functional protonic acids. Another effective manner is chemical modification of PANI on its structure. Indeed, the structure of PANI could modified by graft reactions with other polymers in order to enhance mechanical properties and conductivity [3,4].

In this work we prepared PANI in nano scale by chemical oxidation method in presence of ultrasonic irradiation. The PANI was dedoped and grafted onto poly (styrene–alt– maleic anhydride)(PSMA) copolymer in various ratios. The UV-Vis studies were carried out on prepared graft copolymers in acidic and basic media. The characterization of prepared polymers was carried out by FT-IR and DSC analysis.

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Formation of 2H-Pyran-2-ones from 1,3-Dicarbonyl Compounds, Acetylenic Esters and Sodium O-Alkyl Carbonodithioates

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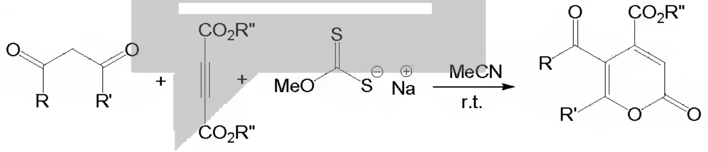
The pyran-2-one motif is found in a large number of naturally occurring compounds, many of which have interesting pharmacological properties [1, 2]. For this reason, pyran-2-ones have long been recognized as important synthons for organic synthesis and medicinal chemistry and their reactivity has received substantial attention. Pyran-2-ones are useful as Diels-Alder dienes, and therefore cycloadditions comprise much of the literature pertaining to these compounds. Deils-Alder reactions with pyran-2-one are facile with alkynes in addition to alkenes [3, 4].
As part of our current studies on the development of new routes in heterocyclic synthesis [5], we report an efficient synthetic route to 2H-pyran-2-ones. Thus, the reaction of 1,3-dicarbonyl compounds **1** with dialkyl acetylenedicarboxylates **2**, in the presence of sodium O-methyl carbonodithioate (**3**) at room temperature in MeCN as a solvent, produced 2H-pyran-2-ones **4** in good yields



1 2 3 4

In conclusion:
we have developed a convenient, one-pot method for the preparation of functionalized 2H-pyran-2-ones from 1,3-carbonyl compounds and dialkyl acetylenedicarboxylates in the presence of sodium O-methyl carbonodithioate. The simplicity of the present procedure makes it an interesting alternative to complex multistep approaches.

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Monolayer growth of polyacrylamide and hydroxyethylacrylate on starch surface by atom transfer radical polymerization

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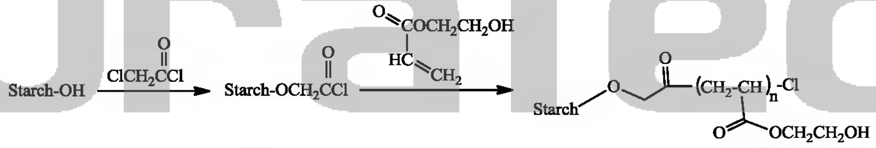
Recently, the studies of polysaccharides to obtain derivates that have better operating properties increased, because polysaccharides are an important class of natural biomacromolecules with low toxicity, good biocompatibility, and are biodegradable [1]. Starch, as one of the most abundant polysaccharides in nature which is easily available and cheap. Starch consists of two types of molecules amylose (normally 20–30%) and amylopectin (normally 70–80%). Both consist of polymers of a-D-glucose unit in the $^4C_1$ conformation. In the last years there has been increasing interest in the derivatization of polysaccharides such as starch to obtain derivatives showing improved functional properties as a function of environmental conditions (pH, temperature, salinity) [2]. The main problems of natural polymers were their poor processing and low mechanical strengh. Therefore new efforts have been made to improve these two properties.

The aim of this work is modification of starch structure chemically to achieve a polymer with better ability in swelling in water which can be used as drug carrier. For this propose the hydroxyl groups of starch was chemically reacted with cloroacetyl chloride or bromoacetyl bromide to achieve starchacetyl chloride and starchacetyl bromide respectively. Then modified starch was used as macroinitiator in polymerization of acryl amide and hydroxyl ethyl acrylamide by atom transfer radical polymerization (ATRP) [3]. The growth of acrylamide or hydroxyl ethyl acrylate on starch backbone was done as monolayer which can be seen in AFM images.The prepared polymers show good swell ability in water. The charachterization of prepared polymers was done by FT-IR and NMR spectroscopy and AFM.



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Direct polycondensation reaction of 4,4'-bis-[(4-hydroxyphenyl)azo]diphenyl ether with various optically active diacids

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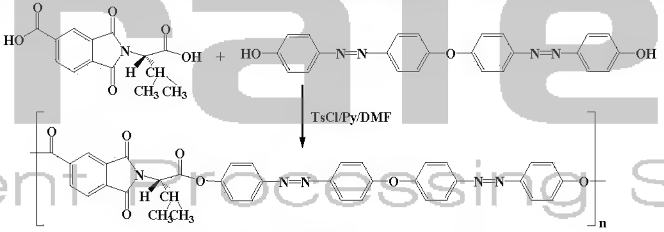
Aromatic polyimides and their copolymers are well known as high-performance polymer materials for their excellent mechanical and electrical properties, high thermal and thermo oxidative stability, and outstanding solvent resistance. However, most aromatic polyimides are intractable materials that do not melt before thermally decomposing, therefore, would be difficult for processing. One way to decrease the melting point of polyimides is introducing flexible spacer which have been reported in the synthesis of poly (ester-imide)s (PEIs) [1]. The synthesis and properties of azo dye based polymers has drawn a considerable amount of attention due to their applications as reversible optical storage media, chioptical switches, electrooptic modulators, and chemical sensors [2-4].

Different optically active diacids were prepared by reaction of 1,2,4-benzenetricarboxylic-1,2-anhydride (TMA) with L-valine, L-histidine, D-alanine, L-phenyl alanine, L-lucine, L-methioninein in N,N-dimethylformamide (DMF). 4,4'-Bis-[(4-hydroxyphenyl)azo]diphenyl ether was synthesized by reaction of 4,4′-diaminodiphenyl ether with phenol in the presence of $NaNO_2$ and hydrochloric acid. Novel PEIs were prepared by the reaction of these diacids monomer with 4,4'-bis-[(4-hydroxyphenyl)azo]diphenyl ether via direct polyesterification in a system of tosyl chloride /pyridine / DMF as a condensing agent. PEIs containing amino acids and azo moieties. It is worth noting that the most important and diffused biological polymers are optically active. The formations of PEIs were confirmed by FT-IR and ^{1}H-NMR spectroscopy analysis. The solubility of PEIs were tested quantitatively in various solvents, the PEIs were soluble in organic solvents such as DMF, DMAc, DMSO, NMP at room temperature, and are insoluble in solvents such as chloroform, methanol, ethanol, and water.



Scheme 1

References

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Synthesis polyhydroquinolines using $Fe(ClO_4)_3/SiO_2$

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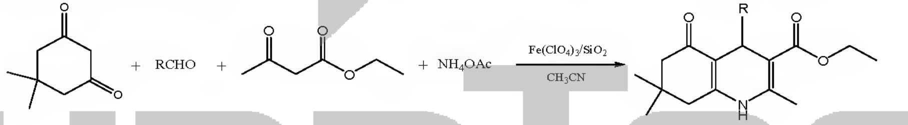
Ferric perchlorate adsorbed on silica gel has been found to be effective for the rapid organic functional group transformations such as dimerization of alkynes, aromatic hydrocarbons, selective oxidation of thiols to disulfides, and transannular reaction in 1,5-cyclooctadienes on grinding using pestle and mortar in the solid state and alumina-supported iron (III) perchlorate [$Fe(ClO_4)_3{\cdot}Al_2O_3$] have been effectively used as a Lewis acid catalyst for Nazarov cyclization/Michael addition of pyrrole derivatives [1].Substituted polyhydroquinoline and 1,4-dihydropyridines (1,4-DHPs) have attracted considerable interest because they possess various biological activities.[2] They are generally prepared by classical Hantzsch method, which involves condensation of an β-ketoester aldehyde, as well as ammonia in acetic acid or in refluxing alcohol. [3] Several catalysts such as bakers' yeast,[4] silica gel/$NaHSO_4$,[5] $Yb(OTf)_3$,[6] $Sc(OTf)_3$,[7] heteropolyacid, and [8] CAN have been used to improve the reaction yields. In this communication we interest to report a straightforward and general method for the synthesis of Substituted polyhydroquinoline by simply combining aldehyde,ethyl acetoacetate, dimedone, and ammonium acetate in the presence of a catalytic amount of $Fe(ClO_4)_3/SiO_2$ .This method gives remarkable advantages such as simple work-up procedure, environmentally friendly, inexpensive, non-toxic and recyclable catalyst, shorter reaction time along with excellent yields.



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The synthesis of 2-amino-4,5-diphenyl furan from a nitrile bearing active methylene and benzoin

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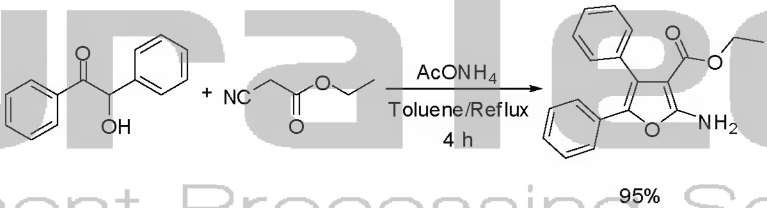
Polysubstituted furans play an important role in organic chemistry not only due to their presence as key structural units in many natural products [1] and in important pharmaceuticals, [2] but they can also be employed in synthetic chemistry as building blocks. For this reason the synthesis of polysubstituted furans continues to attract the interest of many synthetic chemists. We now report an efficient synthetic route to polysubstituted furans using Benzoin and active methylene compounds in the presence of ammonium acetate. This procedure offers significant advantages such as operational simplicity, mild reaction conditions, enhanced rates, ease of isolation of products, cleaner reaction profiles and eco-friendly nature of the solvent, which makes it useful and attractive strategy for the synthesis of 2-aminofuran derivatives.



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Environmentally Friendly Suzuki-Miyaura Synthesis of Biaryl Derivatives Mediated by Palladium/Choline Chloride System

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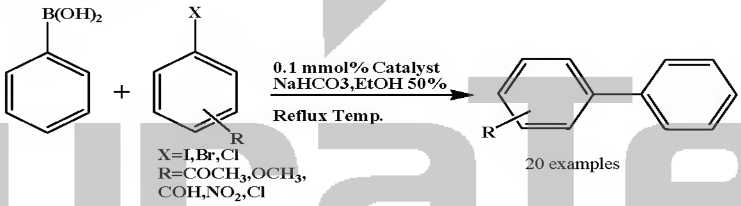
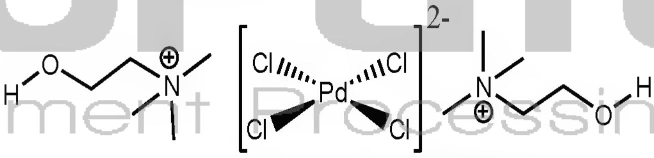
In recent years, transition-metal-catalyzed cross-coupling reactions are of powerful methods for synthesis of biaryls which are valuable materials in agrochemicals, natural products and pharmaceuticals. Among these reactions, Suzuki-Miyaura cross-coupling is mostly applied because of two reasons:1) Organoboron compounds are readily available, less toxic and highly stable.2)A wide range of functional groups are applicable in such reactions[1-2].

Generally, Suzuki-Miyaura reaction is performed in difficult conditions such as high temperature, oxygen-free atmosphere, use of organic solvents and long-time reactions [3]. Much attention has been paid in order to improve these conditions. Herein, a novel system of Pd-choline chloride is revealed. Choline Chloride is an essential nutrient needed for maintenance of normal life in human which is an organic salt with the cation of N,N,N-trimethyl ethanol amine that is very soluble in water[4]. So, with the aid of such additive, it is possible to have palladium solved in water and as the result, the reaction has the capability to be done under environmental conditions. This complex, $[PdCl_4][(CH_3)N^+CH_2CH_2OH]_2$, has good reactivity toward aryl halides even some of the aryl chlorides. The products were synthesized in $EtOH/H_2O$ medium at reflux temperature and $NaHCO_3$ as base. The isolated yields can be reported from good to excellent.





Activated catalyst

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Synthesis of Benzimidazoles With Different Heterogeneous Catalysts

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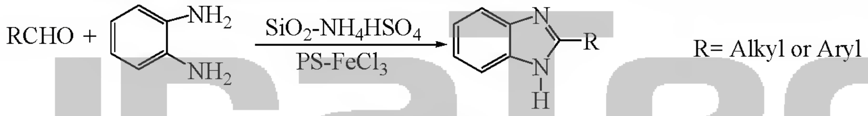
In recent years, the use of solid supported catalysts has received considerable attention in different areas of organic synthesis. The activity and selectivity of a catalyst dispersed on the surface of a support is improved as the effective surface area of the catalyst is increased manifold, and hence they are expected to perform more effectively than the individual catalysts [1].

The benzimidazole derivatives are potent biologically active compounds and exhibit antiviral, antiulcer, antihypertension, and anticancer properties [2]. Classical methods for synthesis of benzimidazole involve condensation of aldehydes with o-phenylenediamines. A variety of catalysts have been used for this purpose [3-6]. However, many of the reported methods suffer from the drawbacks such as strong oxidizing nature, generation of environmentally perilous waste material, tedious work-up, and the use of moisture-sensitive, hazardous, or unreusable catalysts.

In a continuation of our recent work on the use of heterogeneous catalysts, we now wish to introduce silica gel supported NH_4HSO_4 and polystyrene supported $FeCl_3$ as heterogeneous catalysts for the coupling of aldehydes and o-phenylenediamine to afford 2-aryl and alkylbenzimidazoles (Scheme 1).



Scheme1

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Barium chloride dispersed on silica gel nanoparticles ($BaCl_2$-nano SiO_2) as an efficient catalyst for the preparation of 2,4,5-triaryl imidazoles

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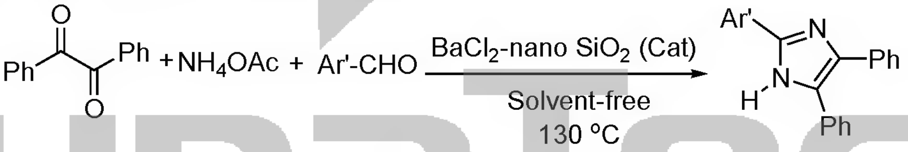
The use of heterogeneous solid supported Lewis acid catalysts instead of their unsupported salts have some advantages and they are desirable to achieve effective and catalyst handling, product purification and to decrease waste production. Some examples of them have been performed as inexpensive catalysts that can be easily separated, reused and is not contaminated by the products [1].
Compounds containing imidazole skeletons exhibit important biological activities and play important roles in biochemical process [2-4]. Also large classes of imidazole derivatives are used as ionic liquids [5]. Thus these properties have instituted a diverse collection of synthetic approaches to these heterocycles. A number of routes have been developed for synthesis of substituted imidazoles [6]
Herein $BaCl_2$-nano SiO_2 [34-35] was employed as useful catalyst for the synthesis and easy purification of 2,4,5-triaryl imidazole derivatives via one-pot three-component cyclo-condensation of benzil, ammonium acetate and aldehydes under thermal conditions in high yields (Scheme 1).



Scheme 1

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Synthesis of Novel Spirobenzofuran-3,3'-indolines

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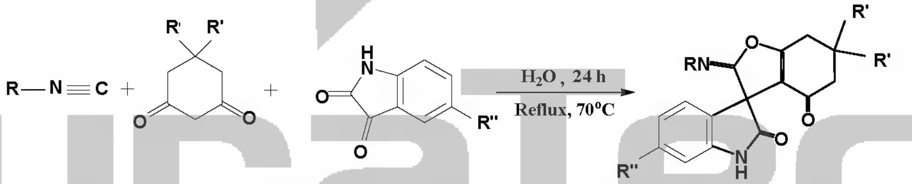
Spirocyclic systems containing one carbon atomcommon to tworings are structurally interesting.The asymmetric characteristic ofthe molecule due to the chiral spiro carbon is one of the importantcriteria of the biological activities. The presence of the satirically constrained spiro structure in various natural products also adds tothe interest in the investigations of spiro compounds.Spirocompounds represent an important class of naturally occurringsubstances characteristic by their highly pronounced biologicalproperties [1].In spite of extensive application of Spiro indolines, a few methods have been reported for the preparation of these interesting compounds. Nevertheless, most of these methods suffer from limitations such as moderate yields, long reaction times, harsh reaction conditionsand application of hazardous solvents. Therefore, finding an efficient and a capable protocol for the preparation of Spiro benzofuran-3,3'indolines is of obvious importance.In this work a simple and efficient one-pot three-component synthesis of the biologically important spiro[benzofuran-3,3'-indolines] scaffold was carried out by the reaction of isatin, dimedone, and isocyanide in aqueous medium. This method is of great value because of its environmentally benign character, high yield processing and easy handling. All the structures were confirmed by spectroscopic data such as ^{1}HNMR, ^{13}NMR and IR [2].



R=cyclohexyl, But R'=CH$_3$ R''=H ,Cl

In conclusion, we have developed a clean and simple one-pot three-component reaction for the synthesis of a series of spiro[benzofuran-3,3'-indoline] derivatives in water. The utility of the described methodology in MCRs is highly promising as it allows for the combination of the synthetic virtues of the conventional MCR strategy with the ecological benefits and convenience of the procedure [3].

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Ketalization of ketone with diols catalyzed by 1,8-Diazabicyclo[5.4.0]undec-7-ene-hydrobromide-perbromide

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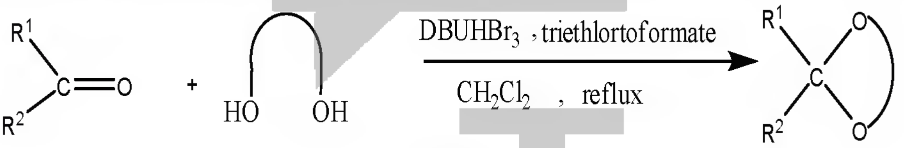
The protection of carbonyl group is sometimes necessary in the manipulation of organic molecules with multiple functional groups. Cyclic acetals and ketals are the most useful protective groups for the carbonyl functionality [1]. Acetals and ketals are generally prepared from carbonyl compounds and alcohols or diols in the presence of lewis acids such as $SbCl_3$ [2], DDQ [3], iodine[4], ion exchange resins such as titanium cation-exchange montmorillonite [5], transition metal complexes such as rhodium, ruthenium and iridium complexes [6]. We have applied DBU-hydrobromide-perbromide as solid acid catalysts for selective ketalization of carbonyl compounds under mild condition. Different kinds of diols and carbonyl compounds were subjected to the ketalization in the presence of $DBUH\text{-}Br_3$ in dichloromethane as a solvent and triethyl orthoformate under reflux condition. DBU-hydrobromide-perbromide can serve as an efficient catalyst for the ketalization of carbonyl compounds under mild condition (scheme 1). The yields are good to excellent and the procedure is simple and convenient. Morever, the availability of the reagent, easy and clean work-up and high yield make this method attractive for organic synthesis.



Scheme 1

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Synthesis, Characterization, and Thermal Properties of New Organosoluble Poly(ester-imide)s Containing Ether Group

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A new series of aromatic poly(ester-imide)s (PEIs) with 1,3-bis[4-aminophenoxy] propane moieties were prepared from the newly synthesized diacid monomer with various aromatic diols. Aromatic polyimides are heat resistant polymers that generally show excellent mechanical strength and stability. Aromatic polymers that contain aryl ether linkage generally have greater tractability, lower glasstransition, and greater chain flexibility than their corresponding polymers without these groups in the repeat units [1]. The improved solubility and lower glass transition temperatures are attributed to the flexible linkages that provide a polymer chain with a lower energy of internal rotation [2]. the present study deals with the synthesis and characterization of new diacid monomers containing ether and imide groups and related polyesters therefrom. Properties of the prepared polymers including inherent viscosity, thermal behavior and solubility were studied.

1,3-Bis[4-aminophenoxy]propane was synthesized by using a two-step reaction. At first 1,3- bis[4-nitrophenoxy]propane was prepared by the reaction of two equimolars 4-nitrophenol **1** and one equimolar 1,3- dibromo propane. Then dinitro compound was reduced by using 10% Pd-C, ethanol and hydrazine monohydrate. 1,3-bis[4-(trimellitimido)phenoxy] propane was synthesized through the condensation reaction of one equivalent of diamine with two equivalents of trimellitic anhydride in a mixture of acetic acid and pyridine (3:2). Dissolving the residue in cold water produced a gummy solid that provided a green solid with the addition of concentrated HCl.

TsCl was dissolved in Py to yield sulfonium salt and after a certain period of time the solution was treated with DMF for 30 min. The reaction mixture was added to a solution of diacid in Py to form activated acid. After 30 min a solution of diol in Py was added and the whole solution was maintained at room temperature and then at an elevated temperature for aobtained in good yields (61-96%), and the inherent viscosities were 0.18-0.90 dL/g, which were measured in DMF solutions.

A new series of thermally stable and organosoluble PEIs containing ether and methylene groups were prepared by direct polycondensation reaction. The presented results also clearly demonstrate that incorporating the imide group into the polymer main chain as well as combination of the wholly aromatic backbone and several functional groups remarkably enhanced the thermal stability of the new polymers. These polymers are expected to have higher solubility due to the presence of ether and alkyl groups in the polymer chain. These properties could make these PEIs attractive for practical applications such as processable high-performance engineering plastics.

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A versatile and facile method for the synthesis of benzimidazoles from o-nitroaniline and aldehydes in one step via a reductive cyclization

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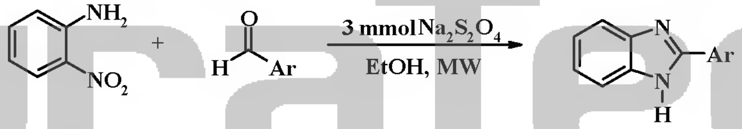
Benzimidazoles are very useful intermediates/subunits for the development of molecules of pharmaceutical or biological interest. Substituted benzimidazole derivatives have found applications in diverse therapeutic areas including antihypertensives, antivirals, antifungals, anticancers, and antihistaminics [1]. Due to their wide range of pharmacological activity, industrial and synthetic applications, a number of methods have been reported for the synthesis of benzimidazoles, which include the coupling of phenylenediamines and carboxylic acids or their derivatives (nitriles, imidates, or orthoesters) [2], the reaction between N-ethoxycarbonylthiomides with 1,2-diamines [3], and the reaction of aldehydes with 1,2-diamines followed by N-halosuccinimides (X = Cl, Br, I) [4]. Recently, azalactones [5], 2-aryl-1,1-dibromoethane and amino amides [6] have been used as starting materials for this synthesis of benzimidazoles. However, all of these methods have problems, including drastic reaction conditions, low yields and severe side-reactions.

In connection with our research program directed toward the synthesis of benzimidazole, we hope to describe the synthesis of benzimidazoles from several kinds of aromatic aldehydes and o-nitroaniline in the 3.0 mmol of $Na_2S_2O_4$ under reductant agent at microwave irradiation in short time reaction and high yields. The structure of products has been assigned by physical and spectroscopic data.



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Microwave-assisted synthesis of some novel imidazo-quinazolin derivatives

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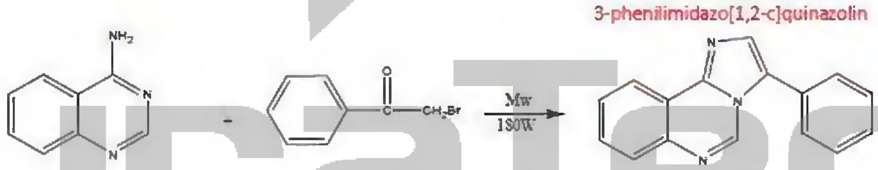
Heterocyclic chemistry comprises at least half of all organic chemistry research worldwide. In particular, heterocyclic structures form the basis of many pharmaceutical, agrochemical and veterinary productsquinazolines are classes of fused heterocycles that are of considerable interest because of the diverse range of their biological properties, for example, anticancer, diuretic, anti-inflammatory, anticonvulsant and antihypertensive activities.[1- 3].

In this research, we describe the new and improved methods for the construction of the imidazo-quinazolin derivatives by reaction of quinazolin-4-amin, phenacyl boromid derivatives under microwave irradiation.



This procedure was successfully applied to the synthesis of imidazo-quinazolin derivatives.(m.p:290 °C).

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Determination of The stability of Tautomeric form of Creatinine molecule in The Gas phase by using DFT method

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The purpose of This study is the determination of the stability of tautomeric forms of creatinine molecule in the gas phase

Creatinine is the degradation product of creatine, the very popular muscle-building supplement. Creatinine is produced (from creatine) inside the cell, in the blood stream, in your glass of creatine before drinking, or on the shelf in your creatine container. Basically, creatine will spontaneously convert to creatinine in almost any environment you can image.[1]

Investigation of tautomerism in creatinine is very important in biology.

The absence of experimental energetic and structural data of tautomeric equilibrium presents a challenge to quantum chemical methods to obtain an insight into the reactivity of these compounds. [2]The geometries of various tautomers and isomers of creatinine have been studied using the B3LYP/6-311++G** method. Relative Gibbs free energies can be used to obtain ΔG and K_{eq} between tautomers and $\Delta G^{\#}$ and rate constants for tautomerism interconversions of each molecule.،The structure of transition state between each pair of tautomers was optimized by appling Schlegels synchronous transit-guided quasi-newton (QST3) method started from the fully optimized structure of one tautomer and finished on the fully optimized structure of another tautomer.The transition states were verified with frequency calculations to ensure they were first order saddle points with only one negative eigenvalue. Additionally intrinsic reaction coordinate (IRC) calculations proved that each reaction linked the correct products with reactants.Rate constant were calculated by canonical transition state theory using eyring equation[3]. In the gas phase 2-imino-1-methyl imidazolidin -4-one (Keto-form) are computed to be more stable than the other tautomers.

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A Mild and Convenient Method for the Reduction of Carbonyl Compounds with $NaBH_4$ in the Presence of Catalytic Amounts of $NiCl_2(Pph_3)_2$

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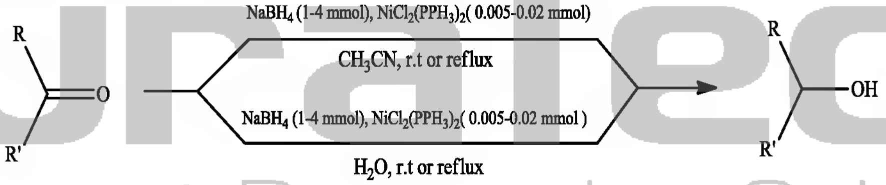
Reduction is one of the most fundamental and useful reactions in organic synthesis. The discoveries of sodium borohydride in1940s have provided an efficient route for the reduction of functionalized molecules and they are commonly used in organic laboratory nowadays. So, controlling the reducing power of $NaBH_4$ has been one of the main interests for organic chemists in many years.In this catalyst dichlorobis(triphenylphosphine)nickel(II) complex, $[NiCl_2(PPH_3)_2]$, as a stable olive green solid, was prepared quantitatively by complexation of an equimolar amount of nickel chloride hexahydrate and Pph_3 at room temperature. The combination System of $NaBH_4$ / $NiCl_2(Pph_3)_2$ can easily reduce variety of carbonyl compounds such as aldehydes, ketones, acyloins, □-diketones and □,□-unsaturated carbonyl compounds to their corresponding alcohols in good to excellent yields. Reduction reactions were performed in H_2O and CH_3CN at room temperature or under reflux conditions.



R, R': H, Alkyl or Aryl

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Investigation of pyridazinones and diazepinones synthesis in the presence of actived KSF

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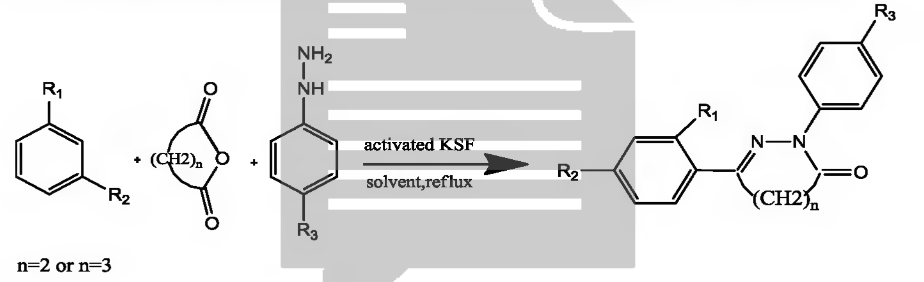
Pyridazinones and diazepinones are useful compounds with a broad array of biologically activities. They contain notable hypertensive, antiasthmatic, antidepressant, antibacterial, antifungal, antianemic, cardiotonic, anticancer, pesticidal and herbicidal properties [1-3]. Current development in the pyridazinone and diazepinones chemistry and our continue interest in the development of an efficient and environmentally friendly procedure for the synthesis of pharmaceutical compounds prompted us to explore the synthesis of pyridazinones and diazepinones in the three component procedure from arenes, anhydrides and $ArNHNH_2$ in the presence of an capable acidic active catalyst (Scheme1). For these reasons, we used KSF because of its environmental compatibility, reusability, and ease of isolation.



Scheme1

The general procedure for the synthesis of pyridazinones and diazepinones follows: A mixture of anhydride, arene, $ArNHNH_2$ and activatd KSF in appropriate solvent was refluxed for 18 hours. Subsequently, the catalyst was removed by filtration and the product was purified by either column or preparative chromatography (EtOAc: petroleum ether 1:4) to furnish the desired pyridazinones and diazepinones. The yield was obtained 37%.

In the future we want to explore the synthesis of pyridazinones and diazepinones in the presence of new activated KSF in order to optimise the yield and time of reaction.

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Solvent-free and efficient one-pot three-component synthesis of α-aminophosphonates using $MgBr_2$ recyclable Catalyst

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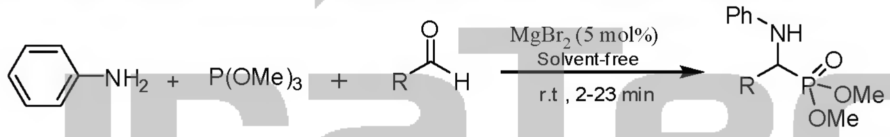
The synthesis of α-aminophosphonates as analogous of natural α-aminoacids has attracted a significant interest by organic chemists in recent years. They have been attracting a good deal of attention ever since the first compounds with a phosphorus–carbon bond were detected among natural products [1,2]. Their diverse applications include as enzyme inhibitors, antibiotics, pharmacological agents and many other applications are well documented [3,4]. Peptido mimetics made out of this class of compounds have shown promising pharmacological properties [5]. Thus, a variety of synthetic approaches are desirable to synthesize α-amino phosphonates [6].

We now describe a simple, general and efficient protocol for the synthesis of α-aminophosphonates via three- component reactions of aldehydes, amines, and trimethyl phosphite using $MgBr_2$ catalytic, solvent-free conditions at room temperature. $MgBr_2$ is an efficient catalyst which has been successfully utilized in numerous reactions. $MgBr_2$ is a readily available and inexpensive reagent and can conveniently be handled and removed from the reaction mixture. Thus, the remarkable catalytic activities together with its operational simplicity make it the most suitable catalyst for the synthesis of α- aminophosphonates.



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Efficient One-Step Synthesis of Benzazoles Bearing Sulfonamide Moiety

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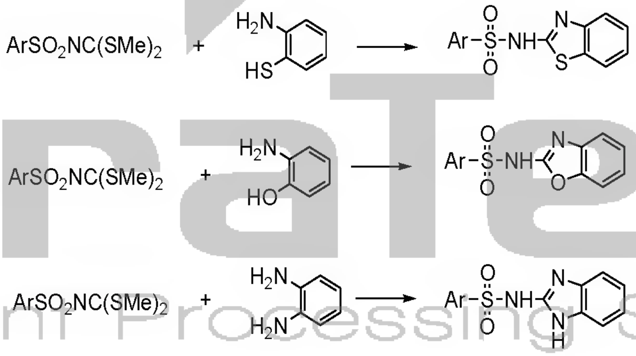
Benzazoles (benzimidazole, benzoxazole, benzothiazole) are strictly important compounds in organic chemistry and industry. These compounds have been shown wide applications in medical chemistry [1], as antitumor [2-4] and antibiotic [5]. The standard approach to the synthesis of benzazole derivatives is cyclo-condensation reaction of corresponding 2-aminophenol, 2-aminothiophenol, or 1,2-diaminobenzene with carboxylic acids or derivatives and in somewhat severe reaction conditions. Benzothiazoles can be also synthesized directly from the reaction of 2-aminothiophenol and an aromatic aldehyde in various reaction conditions. They are also prepared by means of oxidative cyclization of thiobenzanilides with a large number of oxidizing agents.

Here for the first time to our knowledge we wish to report a simple and efficient procedure for the preparation of benzazole derivatives bearing sulfonamide moiety. It was found that, when a mixture of dimethyl arylsulfonyl carbonimidodithioate and 2-aminophenol, 2-aminothiophenol, or 1,2-diaminobenzene was dissolved in a suitable solvent and treated with a mild base, the corresponding benzoxazole, benzothiazole, and benzimidazole bearing sulfonamide derivatives were obtained respectively in good to excellent yields.

The key dimethyl arylsulfonylcarbonimidodithioate starting material could be easily accessible from the parent sulfonamide in two simple steps. The simplicity of the method, short reaction time, mild reaction condition, easy work-up and separation of the products, alongside with the high yields of the product are some merits of the presented method.



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An Efficient One-Pot Synthesis of Pyrillium Perchlorate Derivatives

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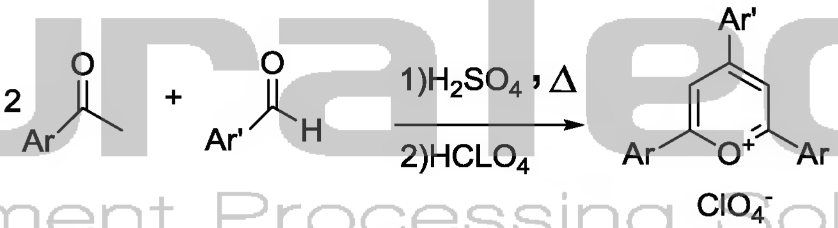
Multicomponent reactions (MCRs) [1] are very popular in modern synthetic organic chemistry since they offer one-pot combination of more than two reactants in one step and allow direct access to complex target molecules. In this context, the one pot cyclization of acetophenone derivatives with aromatic aldehydes followed by insitu oxidation of the product with an oxidant leads to the formation of cationic pyrillium rings which is accompanied with an anion and forms a solid product. These compounds are important because of their colors and dye and pigment properties [2].
In the present work, we have attempted to synthesize a variety of these compounds and try to offer a new procedure for their preparation with more environmentally acceptable features.



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Synthesis of novel thermo-stable and optically active poly(amide-imide)s derived from 3,5-diamino-N-(thiazol-2-yl)-benzamide and various amino acids-based diacids

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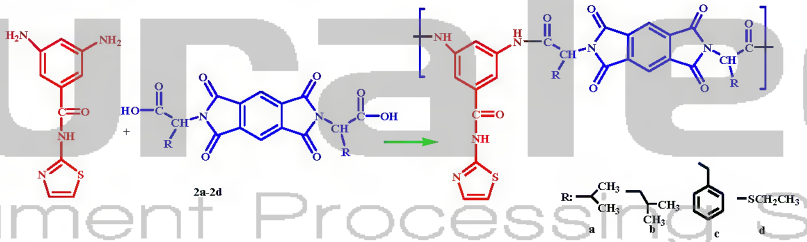
Polymers derived from diacid monomers containing chiral amino acids moieties are one kind of the important prepared amino acid based polymers owing to great potential applications as biocompatible materials, optical and chemical functional materials [1]. The unique structures and the potential applications of these polymers have attracted researchers to develop various polymerization techniques [2]. Herein, we wish to report, a green approaches toward the synthesis of novel optically active poly(amide-imide)s bearing amino acid moieties that condensed from the reaction of 3,5-diamino-N-(thiazol-2-yl)benzamide and diacids containing various amino acids in tetra-butylammonium bromide. Novel diamine monomer was synthesized via reduction of 3,5-dinitro-N-(thiazol-2-yl)benzamide by iron oxide hydroxide catalyst in methanol. This catalyst can reduce the sulphur and azo-containing aromatic nitro compounds rapidly to the corresponding amines in high yields by employing hydrazine hydrate as a hydrogen donor [3]. Chiral diacid monomers were synthesized in high yield from pyromellitic dianhydride and different natural amino acids (valine, luecine, isoluecine, and phenylalanine) in acetic acide. The direct polymerization reactions of these monomers provided optically active poly(amide-imide)s(2a-2d) with high yields and inherent viscosities in the range of 0.20-0.34 dLg^{-1}. The obtained polymers were characterized by FT-IR, specific rotation measurements, and representative of them by ^{1}H NMR and elemental analysis techniques.



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A green and metal-free oxidation of sulfides and thiols catalyzed by PEG-SO_3H in ambient condition

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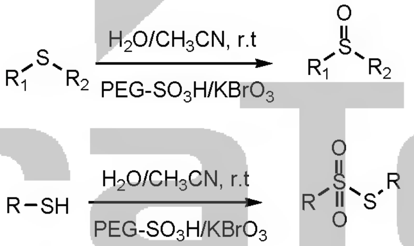
The oxidation of sulfides is the major method for the synthesis of sulfoxides which are versatile intermediates in organic synthesis and are useful for the preparation of biologically and medically important compounds [1,2].

On the other hand, organic reactions using reusable and recyclable catalyst also received much attention in recent years. They can conveniently be handled and removed from the reaction mixture, making the experimental procedure simple and ecofriendly. PEG-SO_3H is one of the examples of modified PEG which has been reported to be an efficient reagent or catalyst for the synthesis of organic compounds [3].

In this letter, we report a novel and efficient protocol for the oxidation of sulfides and thiols in the presence of potassium bromate as oxidant using PEG-SO_3H as an inexpensive and recyclable solid acid catalyst under ambient condition in acetonitrile/ water with good to excellent yields (75- 93%). This methodology is superior to the reported methods from point of view of yield, short reaction time, operational simplicities, and straightforward work-up of the products.



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Preparation of a novel energetic plasticizer 2,2-dinitro-1,3 propandiol-diformate(ADDF)

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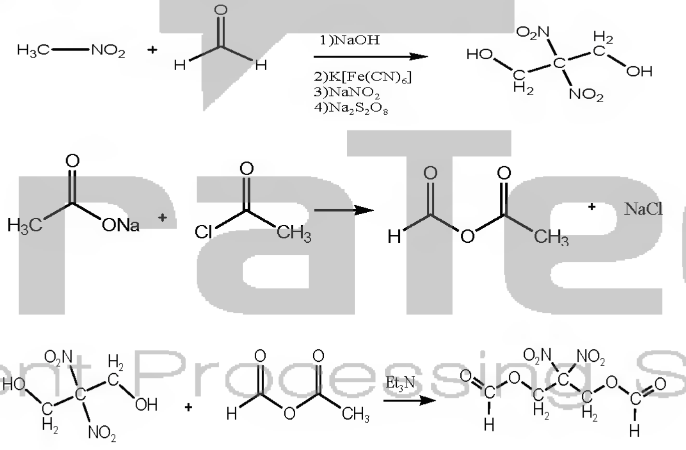
ABSTRACT

The primary role of energetic plasticizers in energetic material formulations is to modify the mechanical properties of the charge to improve safety characteristics. This is achieved by softening the polymer matrix and making it more flexible [1]. 2,2-Dinitro-1,3-propanediol-diformate (ADDF) is a novel low sensitive energetic plasticizer that is useful in explosive and propellant compositions and has -36% of oxygen balance [2].The main object of this research work is the preparation of 2,2-Dinitro-1,3-propanediol-diformate as an energetic plasticizer in 3 step. At first 2,2-dinitro-1,3-propanediol has been prepared from nitromethane and formaldehyde. Then the formic acetic anhydride was synthesized from sodium formate and acetyl chloride. At the end ADDF was synthesized by reacting 2,2-dinitro-1,3-propanediol with acetic formic anhydride in the presence of pyridine in dichloromethane as solvent. The structure of products has been established with FT-IR, ^{13}C-NMR and ^{1}H-NMR spectroscopic techniques.



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Electrochemical synthesis of amino-substituted 1,2benzoquinone derivatives(green chemistry method in Aqueous media)

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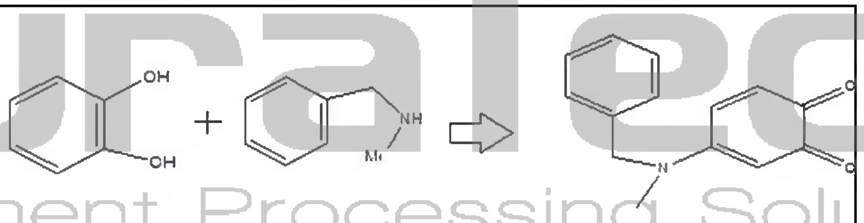
Abstract

The electrooxidation of 3-substituted catechols has been studied in the presence of N-methyl benzylamine in water + ethanol (90/10) solution. The o-benzoquinones derived from catechols participate in michael addition reaction with N-methyl benzylamine to form the corresponding monoamino-substituted o-benzoquinones. We propose a mechanism for the electrode process. An efficient electrochemical synthesis of amino-substituted 1,2-benzoquinone derivatives has been performed at a carbon rod electrode in a undivided cell and under EcE mechanism. The products has been charectrized with H-NMR and IR spectroscopy and TLC

Keywords: electrosynthesis- catechol- amine- benzoquinone- EcE mechanism

Experimental

All chemicals (catechol and N-methyl benzylamine) were reagent-grade materials and phosphat salts were of pro-analysis grade. A solution (80ml) of phosphatte buffer (0.15M, pH=6.8) in water+ethanol (90/10) solution, containing 1mmol of catechol and 1mmol of N-methyl benzylamine, was electrolysis in an undivided cell at 0.45V vs SCE. The electrolysis was terminated when the current decreased by more than 95%. At the end of the electrolysis, the precipitated solid was collected by filtration. The products were purified by column chromatography. After purification, Products were characterized by H-NMR, IR and TLC.



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Synthesies of 2,2'-((5-bromo-6-methylpyrimidine-2,4-diyl)bis(azanediyl))dipropanoic acid and 2-((4-methyl-6-morpholino-5-nitropyrimidin-2-yl) amino) propanoic acid and investigation on properties and stability constants of their complexes with some metals

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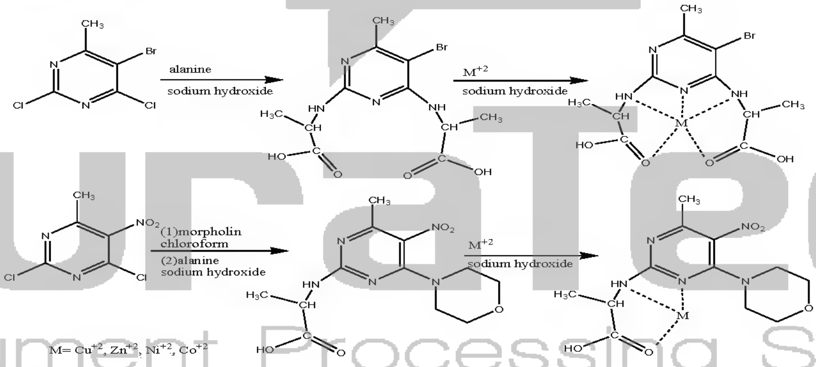
The interactions between metal inos and amino acids are of considerable interest as models for metal-protein reactions and models in a variety of biological systems. estimation of equilibrium concentrations of metal ion complexes as a function of pH provides a useful picture of metal ion binding in biological systems. In this research, ligands of 2,2'-((5-bromo-6- thylpyrimidine-2,4-diyl)bis(azanediyl))dipropanoic acid and 2-((4-methyl-6-morpholino-5-nitropyrimidin-2-yl) amino) propanoic acid synthesized[1] and complexes of them with Cu^{+2}, Zn^{+2}, Ni^{+2}, Co^{+2} metal ions were investigated by a potentiometric pH method in aqueous solutions. It was found that 2,2'-((5-bromo-6-methylpyrimidine-2,4-diyl)bis(azanediyl))-dipropanoic acid and 2-((4-methyl-6-morpholino-5-nitropyrimidin-2-yl) amino) propanoic acid behave as multiple dent ligand and strong complexes with these metal ions from $-NH_2$ and -COOH ends. Bjerrum's method was used for obtaining mean amount of ligand ($\bar{n}$) in the range of 0.2-1.0, which is a good evidence for the completion of complex formation in the first step. A solution was prepared by addition of 1.00×10^{-3} M metal ion, 1.00×10^{-2} M as ligand and 0.0169 M $HClO_4$ in volume of 100 distilled deionized water in a flask. Then it was titrated with standardized 0.1 M NaOH in low volumes until pH of the solution reached 12.0 and at the end the stability constants of complexes measuremented[2].



Scheme

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An efficient and facile synthesis of poly(3,4-ethylenedioxythiophene) using binary organic solvents

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Among different conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) has emerged in recent years, thanks to characteristics previously reported. PEDOT is a conducting polymer based on 3,4-ethylenedioxylthiophene (EDOT) monomer[1,2]. Two most commonly used oxidants of EDOT for preparing PEDOT are ammonium persulfate $(NH_4)_2S_2O_8$ and ferric chloride $FeCl_3$. A major limitation in chemical oxidative polymerization of EDOT is the low organo-solubility of oxidants in the reaction solvents. It has been demonstrated that in this class of polymers employing the oxidant in greater molar ratios results in a product with better optical, thermal and conductivity characteristics [3]. To overcome the mentioned limitation we tried to prepare the polymer through binary organic solvents including chloroform and acetonitrile. To the best of our knowledge, no study about the modification of PEDOT synthesis using binary organic solvents has been performed yet. Accordingly, we could dissolve $FeCl_3$ oxidant in CH_3CN up to five molar times relative to monomer, and this allowed us to synthesis PEDOT with improved characteristics. In fact, the present work deals with an efficient and facile route to synthesis PEDOT via a chemical oxidative manner using chloroform and acetonitrile binary solvents. To compare the results PEDOT was synthesized in its classical manner using single $CHCl_3$ solvent as well. Firstly, EDOT (1.60 mL, 15 mmol) was poured into a reaction flask containing chloroform (75 mL). Next, a solution of $FeCl_3$ (12.166 g, 75 mmol) in CH_3CN (40 mL) was added to the vessel slowly. The final mixture was then stirred at 0° C for 24 h. The product was filtered in reduced pressure, washed several times with deionized water and acetone. The product was fully dried in vacuum oven at 60° C. to prepare PEDOT in solely $CHCl_3$ solvent, both monomer and oxidant were dissolved in $CHCl_3$ with mole ratio of 1:2. Unfortunately, in this case, no further amount of $FeCl_3$ oxidant was dissolved in the reaction solvent. The IR spectra of the products are shown in Figure 1. The resulting PEDOT polymers were also characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and conductivity measurements.

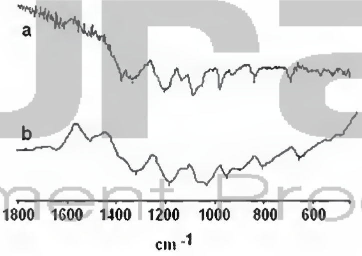

Figure 1. IR spectra of (a) PEDOT prepared in binary solvents $CHCl_3/CH_3CN$ (b)PEDOT prepared in single $CHCl_3$ solvent.

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Novel synthesis of 1,2,3,4-tetrahydroquinoline-fused quinoxalines

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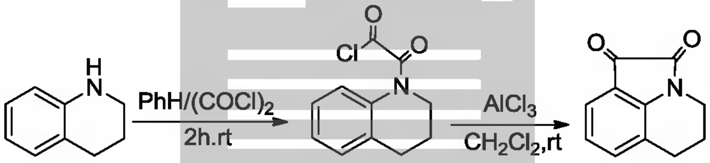
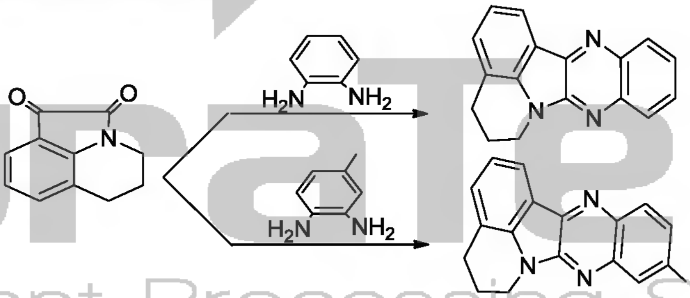
Quinoxaline structural units are found frequently in biologically active substances, as recently well summarised. Quinoxalines fused to other heterocyclic systems have been of particular interest. The quinoxaline framework also figures largely in materials chemistry again.[1,2] The standard route for the ring synthesis of quinoxalines involves the acid or Lewis acid catalysed double condensation of a 1,2-diketone with an ortho-phenylenediamine.
In this research, we synthesized 1,2-dione from 1,2,3,4-tetrahydroquinoline by the action with oxalyl chloride with good yield.



Scheme1

The reaction of various 1,2-diamines (ortho-diamines) with 5,6-dihydro-1H-pyrrolo[3,2,1-ij]quinoline-1,2(4H)-dione in acetic acid/reflux for 6 hours produced new quinoxaline fused tetrahydroquinolines in good yields .



Scheme2

Refrences:

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2. Shamsi, M.; Baradarani, M. M.; Afghan, A.; Joule, J. A. Arkivoc, 2011, ix, 252-260

Novel synthesise of 2-amino-7,7-dimethyl-2',5-dioxo-2',4',5,5',6,6',7,8-octahydrospiro[chromene-4,1'-pyrrolo[3,2,1-ij]quinoline]-3-carbonitrile

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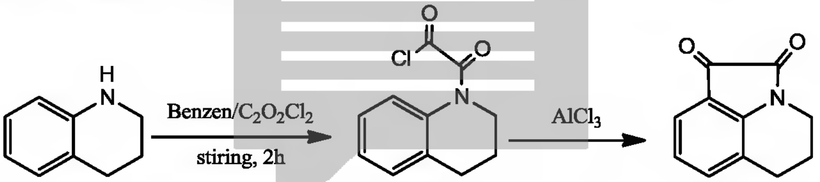
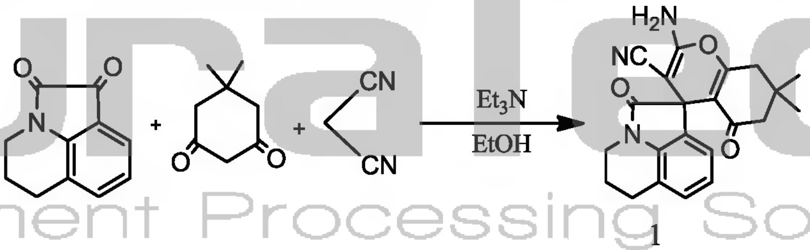
In multicomponent reactions (MCRs), three or more reactants come together in a single reaction vessel to form new products that contain structural units of all the components. This type of reaction becomes increasingly important in organic and medicinal chemistry .[1,2]
The synthesis of heterocycles by multicomponent reactions often involves classic carbonyl condensation chemistry and basic catalysts play important role in MCRs .
In this research, we synthesized 1,2-dione from 1,2,3,4-tetrahydroquinoline by the action with oxalyl chloride with good yield .



Scheme1

Then we design novel procedures in multicomponent reaction, that was successful to produced 1 and led to product in good yield .



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Scheme 2

Refrences:
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Synthesis of Novel Derivatives of Aryl Urazoles under Solvent- free Conditions

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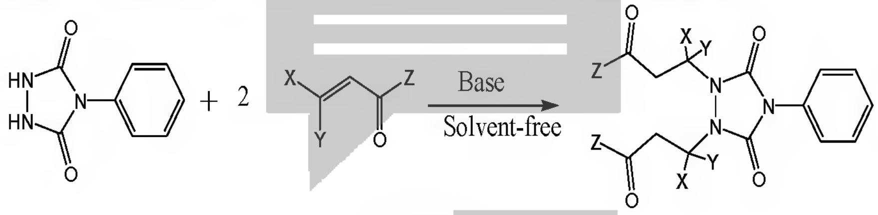
Abstract

Over the past decade, protection of the environment and waste prevention have been increasingly emphasized by researchers from both academia and industry [2]. In this regard, removing the organic solvent and replacing them by the green conditions have been considered. One of the most important and basic reaction in synthetic chemistry is the aza michael addition reaction that the Most of obtained products of this reaction have biological properties. Therefore extensively studies have been reported in this field [3]. Aryl urazoles are used as anticonvulsants, anti-bacterial and a vasodilator agents in medicinal clinic [1]. In this research, new derivatives of the 4-phenyl urazoles have been synthesized using the Michael addition reaction of 4-phenyl urazole on α-β unsaturated systems (Scheme 1).



Scheme (1)

This reaction is performed in the presence of, tetrabutylamonium bromide and an organic or inorganic base under solvent- free conditions. The effects of variety solvents as well as variety bases on this reaction was investigated. The structure of all compounds has been confirmed by FR-IR, ^{1}H-NMR, ^{13}C-NMR.

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Microsynthesis and mass spectrometric study on O(S)-alkyl N,N-dimethylamino alkylphosphonates (alkylphosphonothiolates) for Chemical Weapons Convention verification purposes

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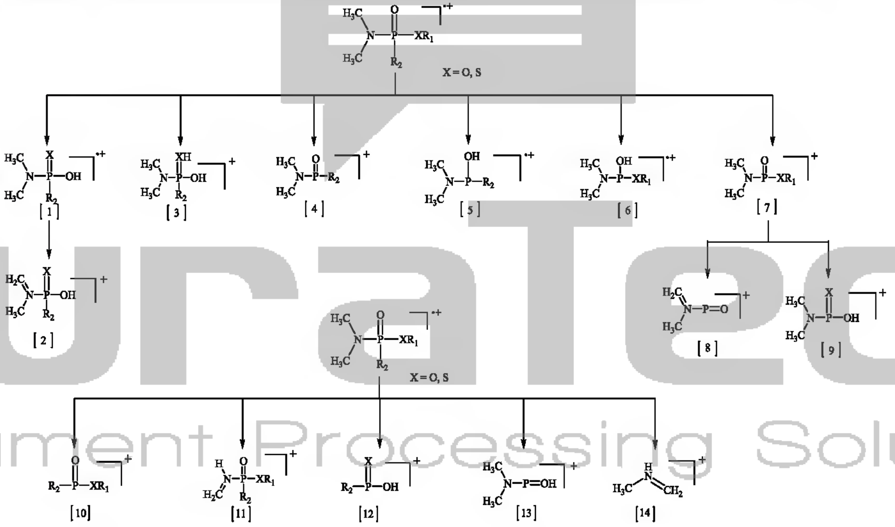
Large number of Chemical Weapons Convention (CWC) related chemicals puts more complexity to the analytical verification activities under CWC requirements which need unambiguous identification of chemicals in complex environmental samples [1]. For successful identification of the CWC-related compounds in real samples or samples of Organization for the Prohibition of Chemical Weapons (OPCW) official proficiency tests [2] the availability of mass spectra and interpretation skills are essential requirements. One of the CWC-related chemical groups is O(S)-alkyl N,N-dimethylamino alkylphosphonates (alkylphosphonothiolates). To the best of our knowledge, there is no general microsynthesis protocol and data in mass spectral libraries for such compounds. Herein, we wish to report a general microsynthesis protocol for a pool of the O(S)-alkyl N,N-dimethylamino alkylphosphonates (alkylphosphonothiolate). Their electron impact mass spectra with possible fragmentation routes are also investigated. The microsynthesis of the O(S)-alkyl N,N-dimethylamino alkylphosphonates (alkylphosphonothiolates) generally involves two steps: the initial addition of dimethylamine hydrochloride to alkylphosphonic dichlorides in the presence of triethylamine as a base to form N,N-dimethyl alkylphosphoramidic chlorides and subsequently reaction with alcohols/sodium thiolates to yield desired products. Mass spectrometry studies revealed that their fragmentations were dominated by alkene elimination, hydrogen rearrangement, McLafferty cleavage and amine elimination. Conclusions were confirmed using MS/MS experiments. The plausible fragmentation routes of title compounds are illustrated in Figure 1.



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Synthesis of Novel Pyrazolo [3,4-b] Pyridine Derivatives

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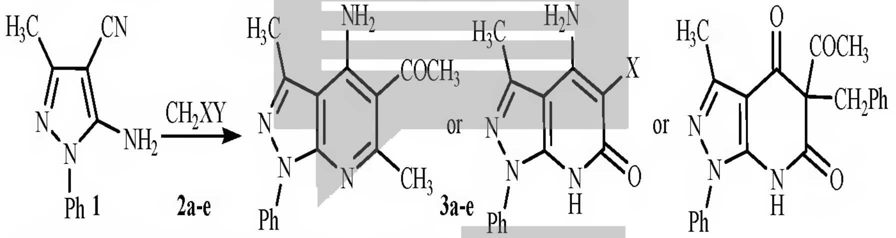
The pyrazolo[3,4-b]pyridine system has interesting biological and pharmacological properties [1-4], such as ACTH (adrenocorticotropic hormone) - releasing factor (CRF (corticotropin-releasing factor)) antagonist activity; CRF antagonists are believed to be effective in the treatment of a wide variety of stress-related illnesses, such as depression, Alzheimer's disease, gastrointestinal diseases, anorexia nervosa, hemorrhage stress, drug and alcohol withdrawal symptoms, drug addiction and infertility [2]. Our interest in the synthesis of heterocyclic compounds of biologically importance has encouraged us to study the synthesis of some new pyrazolo[3,4-b]pyridines. In this context we wish to report on the reactions of phenyl-1H-pyrazole 1 which on treatment with various active methylene compounds 2a-e in acetic acid or EtOH/EtOK afforded some new pyrazolo[3,4-b]pyridines 3a-e.



X= $COCH_3$, CN, CO_2Et, p-ClC_6H_4; Y= $COCH_3$, CO_2Et, CN

^{1}H NMR spectra of compounds 3a-e in DMSO-d_6 showed singlet signals due to CH_3-pyrazole groups at 2.23–2.75 ppm. Their IR spectra in KBr showed absorption bands at 1630-1700 cm^{-1} assignable to carbonyl groups. The eliminated absorption band attributed to nitrile group in addition to the other spectral data confirmed the structure of products. In conclusion, on the basis of spectroscopic analysis, pyrazolo[3,4-b]pyridines 3a-e were prepared in acidic or basic solutions depending on the type of active methylene compounds.

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Synthesis and Determination of the most stable 1,4-thiazepine's Tautomers

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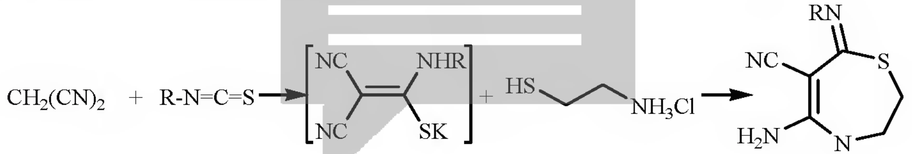
1,4-Thiazepine is a privileged structure because of its presence in a number of pharmacologically important compounds. Several derivatives of 1,4-thiazepin-5-one [1,2] and -2,4-dione [3] are being developed for the treatment of cancer and heart and inflammatory diseases. we previously described the synthesis of novel polyfunctionalized 1,4-thiazepines [4]. To extend the scope of this reaction, we have explored the reaction of other substituted (methylene)malononitrile potassium salts with 2-chloroethylamine hydrochloride to synthesize the new tetrahydro-1,4-thiazepine-6-carbonitriles 3a–f. A mixture of 2-((ethyl or arylamino)(mercapto)methylene)malononitrile potassium salts 2a–f (which were prepared as intermediates from malononitrile and isothiocyanates 1a–f) and 2-chloroethylamine hydrochloride in dimethylformamide (DMF) was first stirred at room temperature, then heated to afford the solid products 3a–f.



1a-f **2a-f** **3a-f**

R= C_2H_5, C_6H_5, p-ClC_6H_4, p-BrC_6H_4, p-$NO_2C_6H_4$, m-MeC_6H_4

The structures of compounds 3a–f were confirmed from their spectral and micro analytical data. Their ^1H NMR spectra in acetone-d_6 showed triplet signals due to S-CH_2 groups at 2.88–3.03 ppm (J~6.8 Hz) and doublet triplet signals due to N-CH_2 at 3.64–3.78 ppm (J~6.0 Hz). After adding D_2O, the latter signals appeared as triplets with the same coupling constants as their neighboring methylen groups. It implied that compounds with NH liked to methylen group are the most stable tautomeric structures. In conclusion, on the basis of spectroscopic analysis, 1,4-thiazepines 3a-f were prepared as the most stable tautomers in one-pot synthesis.

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Efficient One-pot Synthesis of Spirooxindole-dihydropyridine Derivatives in Aqueous Medium

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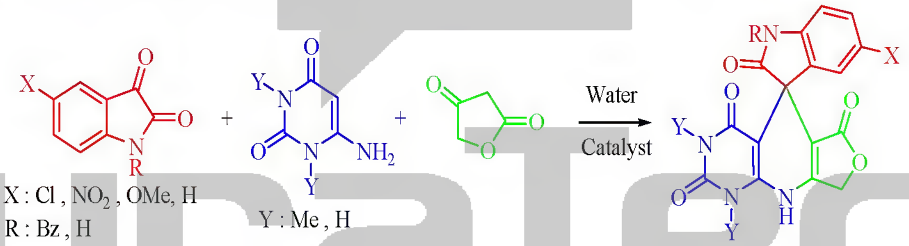
Compounds with spiro skeletons not only constitute subunits in numerous alkalouids, but are also templates for drug discovery and have been used as scaffolds for combinatorial libraries [1]. Among them, the spiro-oxindole framwork represent an important structural motif present in a number of bioactive natural products such as coerulescine, horsfiline and spirotryprosta-tine A [2]. In addition, spirooxindole ring systems identified to serve as inhibitors of the human NKI receptor [3]. Therefor, a number of methods have been reported for the preparation of spirooxindole derivatives [3,4]. Herein we explain a new rout for synthesis of some novel spiro-oxindole derivatives.

To achieve the suitable conditions for the syntheses of the desired spio[oxindole-dihydropyridine]s, we tested the reaction of indoline-2,3-dione **1**, 6-amino-1,3-dimethylpyrimidine-2,4(1H,3H)-dione **2**, and furan-2,4(3H,5H)-dione **3** as a simple model system in different solvents and with the aid of several catalysts. After detecting the more efficient condition, various substituted isatins **1** were used to react with 1,3-dialkyl-5-amino uracil **2** and tetronic acid **3** under the optimized conditions. Structures of all the products were determined by ^1H NMR, ^{13}C NMR, and mass spectral data as well as elemental analyses. Synthesis of several products of this class has reasonably proved the present rout as a reliable method for production of spiro-oxindole compounds.



1 2 3 4

Selected data for Spiro-2,4,5,6,8,9,2′,3′-Octahydro-1,3-dimethylforu[3,4-b]pyrido[3,2-d]pyrimidine -3,5′-indoline-2,4,6,2′-tetraone : δ_H 11.67, 10.34, 7.23, 7.04, 6.97, 6.95, 5.01, 4.95, 3.42, 3.06 ppm. δc 180.5, 171.9, 164.9, 159.7, 157.6, 151.6, 137.0, 129.1, 128.4, 128.0, 127.2, 124.0, 121.52, 117.16, 65.78, 50.00, 31.78, 27.57 ppm.

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Synthesis of new derivatives of isothiazolo[3,4-d]pyrimidine

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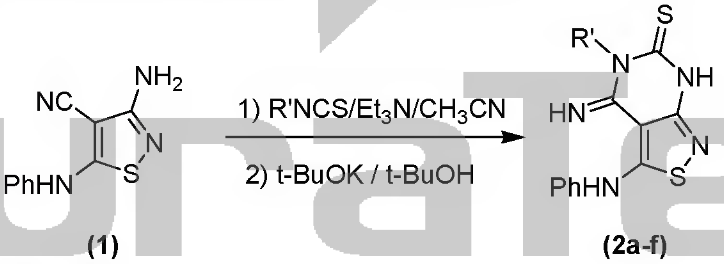
Pyrimidines and isothiazolopyrimidines are important materials for the synthesis of a number of compounds which have a broad spectrum of biological activities, in particular, anti-fertility, anti-inflammatory and anti-convulsant properties[1]. Various reactions for the synthesis of them have been reported in literatures, for example, condensation of aroylhalides with malononitrile to give the intermediate which in turn was converted to isothiazolopyrimidine via sequential treatment with PCl_5, diethyldithiophosphate and H_2O_2 [2], sulfonation and intramolecular cyclization of 4-mercapto-5-acetylpyrimidine derivatives[1], oxidative cyclization of a β-aminothioamide [3] and treatment of 6-amino-1,3-dialkyluracils with 4,5-dichloro-5H-1,2,3-dithiazolium chloride [4]. Also, some occasionally reports about the synthesis of fused isothiazolopyrimidine heterocyclic ring system were also found in literature [5].

The general synthetic strategy for the preparation of isothiazolopyrimidines is described here. We report the synthesis of new derivatives, 4,5-dihydro-4-imino-5-aryl-3-(phenylamino) isothiazolo[3,4-d]pyrimidine-6-(7H)-thione**(2)** from the condensation of 3,5-diaminoisothiazole-4-carbonitrile **(1)** with various arylisothiocyanates in the presence of Et_3N and subsequently refluxed in t-BuOK/ t-BuOH .



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Synthesis of novel heterocyclic systems of [1,2,4]triazolo[3′,4′:2,3]pyrimido [4,5-c] isothiazole

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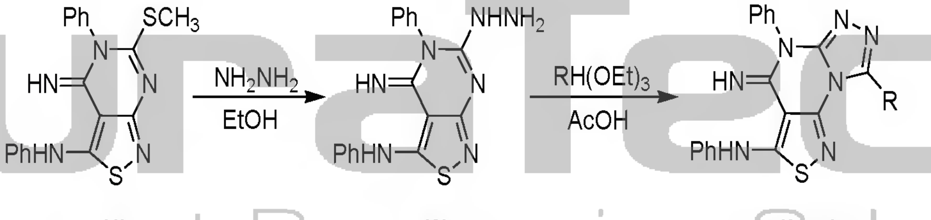
Isothiazolopyrimidines are of interest not only for the heterocyclic systems but also as compounds which uses as kinasin spindle protein (ksp) inhibitors, sedatives and anti-inflammation agents [1,2]. Some methods for the preparation of these heterocyclic system are involves treatment of 4-thiocyanatopyrimidine-5-carbaldehyde with ammonium acetate in the presence of 2-propanol [3] or condensation of 5-aminoisothiazole-4-carbonitrile with formamide [4] and also by the treatment of 5-amino-3-methylisothiazole-4-carbonitrile with orthoesters and acetic anhydride to give the related iminoethers. Ammonia in methanol converts iminoethers to the corresponding amidine which requires treatment with strong base (lithium methoxide) to effect cyclization to give isothiazolopyrimidine or reaction of 5-amino-3-methylisothiazole-4-carbonitrile with sodium methyl xanthat forms 3-methyl-5h,7h-isothiazoleo[5,4-d]pyrimidine-4,6-dithione.[5].

In this study, the reaction of 4,5-dihydro-4-imino-6-(methylthio)-N,5-diphenyl-isothiazolo[3,4-d]pyrimidin-3-amine **(1)** with hydrazine hydrate afforded the corresponding hydrazine derivative **(2)** in boiling ethanol. Further treatment of this compound with orthoesters in acetic acid gave the desired [1,2,4]triazolo[3′,4′:2,3]pyrimido[4,5-c]isothiazoles **(3a-c)**.



(1) **(2)** **(3a-c)**

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Synthesis of Novel Vanadyl Complex Based on Aminomethylene Phosphinic Acid Ligand as an Antidiabetic Agent

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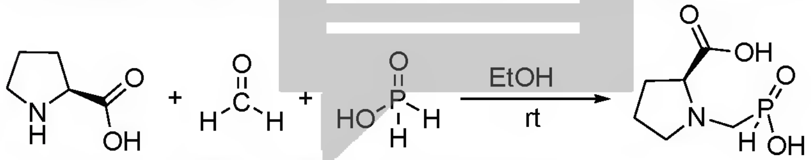
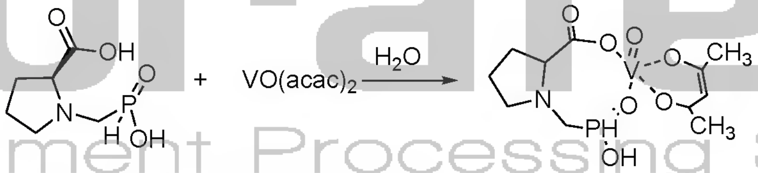
Diabetes mellitus is a heterogeneous disorder, which afflicts over 140 million people worldwide and can lead to cardiovascular disease, blindness, kidney disease, and death. It is characterized by hyperglycemia, alterations in carbohydrate and lipid metabolism, and vascular and neurologicalcomplications [1]. In recent years, oxovanadium(IV) complexes have been investigated as a potent antidiabetic agents [2]. Some papers have been reported on the synthesis of aminomethylene phosphinic acids [3]. Herein, we report synthesis of a new ligand (H_2L) based on this family of phosphinic acid compounds by the reaction of L-proline with hypophosphorus acid(30%) in the presence of paraformaldehyde (Scheme 1).



Scheme 1. Synthesis of L-proline derivative of aminoimethyle phosphinic acid

In continuous, a new acetoacetonate vanadyl(IV) antidiabetic complex of H_2L was prepared by the reaction of this ligand with vanadyl bis(acetoacetonate) complex (Scheme 2).



Scheme 2. Synthesis of oxovanadium(IV) complex of H_2L

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The useful utilization of coumarins in the synthesis of dihydropyran-2-ones containing coumarin scaffolds with drug applications

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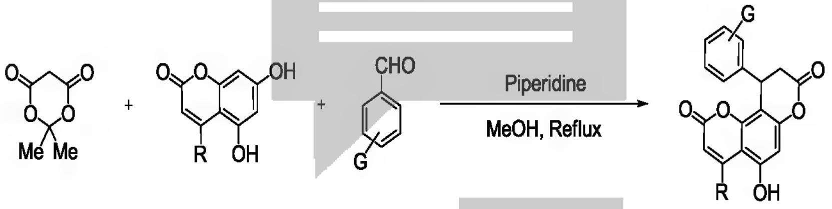
Multi-component reactions (MCRs) play an important role in combinatorial chemistry because of its ability to synthesize small drug-like molecules with several degrees of structural diversity. MCR is defined as three or more different starting materials that react to form a product, where most, if not all of the atoms are incorporated in the final product. This reaction tool allows compounds to be synthesized in a few steps and usually in a one-pot operation [1]. Coumarins are the benzo-2-pyrone derivatives mainly found in plants of the family of Rutaceae and Umbelliferae. They exhibit a broad range of biological activities including anticoagulation, antifungal, anti-psoriasis, and etc [2].

Dihydropyran-2-ones are an important class of heterocyclic structures that can be applied in drug and pharmaceutical fields [3].

In this study, we wish to report one-pot, three-component synthesis of dihydropyran-2-one derivatives which are fused with coumarin rings (Scheme 1).



Scheme 1

Herein, a new series of 4-aryl substituted pyran-2-one[2,3-h]coumarins have been synthesized via a MCR approach in the presence of coumarin derivatives, Meldrum's acid and aryl aldehydes which were characterized by elemental and spectral analysis. This synthetic strategy allows forming the complicated oxygen containing fused heterocyclic systems that have various pharmaceutical activities [3]. As well as, the introduction for the synthesis of various aromatic and heteroaromatic substitutions into 4-position of chroman-2-one systems were obtained. By this achievement, the scope of heterocyclic compounds was developed.

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$FePO_4$ catalyzed two consecutive aminomethylation at the α-position of the β-dicarbonyl compounds: an easy access to hexahydropyrimidines and its spiro analogues

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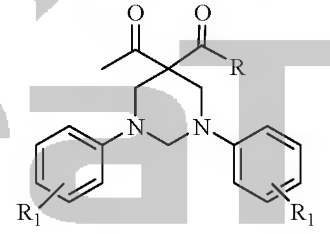
Hexahydropyrimidines containing various natural products and pharmaceutical agents show immense biological activities.[1] Different n-substituted hexahydropyrimidines are synthetic intermediates for spermidine nitroimidazole drugs for the treatment of A549 lung carcinoma.[2] They form structural units in the trypanothine reductase inhibitiny ligands for the regulation of oxidative stress in parasite cells.[3] n-(4-Aminobutyl) hexahydropirimidine and n-(3-aminipropyl) hexahydropirimidine are shown to compete with spermidinefor uptake by l1210 cells.[4].

Multicomponent synthesis of 1,3-diaryl-hexahydropyrimidines by a one-pot reaction of 1,3-dicarbonyl compounds, amines and formaldehyde catalyzed by $FePO_4$ in dichloromethane at room temperature has been reported. Double amino methylation occurs at the α-position of the 1,3-dicabonyl compounds and β-keto esters. The same methodology leads to spiro compounds with indane-1,3-dione. In this reaction, six molecules condense in one pot to form six new covalent bonds, thus, creating high atom economy. This is the first report of the synthesis of the substituted hexahydropyrimidines involving β-keto esters and its spiro analogues with indane-1,3-dione using $FePO_4$(Scheme 1).



Scheme 1

References

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7-9 March 2012

Solvent-free Preparation of Some Novel 2-Arylbenzimidazole Derivatives Using L-Tartaric Acid as Organocatalyst

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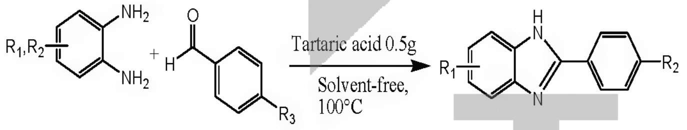
One of the very important heterocyclic building blocks which have emerged for many purposes in medicinal sciences until now is benzimidazoles and their fused analogs. Literature survey of scientific reports clearly shows the importance of this family from the medicinal point of view. We can refer to novel antimicrobial and antitubercular agents [1], novel inhibitors of hKSP [2], dipeptidyl peptidase III [3]. One of the most important methodologies for the preparation of benzimidazoles is the oxidative cyclodehydrogenation of Schiff bases prepared from the reaction of o-phenylenediamine with aldehydes using a suitable oxidizing agent. Few oxidant-free protocols have also been established so far which includes using prolinium nitrate as organocatalyst [4].

In addition, the impact of environmental concerns has attracted the researchers' interest into designing methodologies which exclude the application of toxic reagents, reactants and catalysts [5]. Herein, we reported a greener oxidant and solvent-free protocol for the synthesis of 2-arylbenzimidazoles from the reaction of o-phenylenediamine and benzaldehyde derivatives without application of any oxidant using L-tartaric acid as solid phase and catalyst (Scheme 1).



1-4 5-13 14a-q

1: R_1, R_2 = H; 2: R_1, R_2= Me; 3: R_1= COOH; R_2= H;4: R_1= Me, R_2= H. 5: R_3= H; 6: R_3= Me; 7: R_3= OMe; 8: R_3= Cl; 9: R_3= Br; 10: R_3= NO_2; 11: R_3= NHCOMe; 12: R_3= OCH_2Ph; 13 R_3= F

Scheme 1

The advantages of the present work are (i) performing the reaction under solvent-free condition, (ii) using tartaric acid as a green solid phase and catalyst, (iii) simple work-up, (iv) good to excellent yields, (v) high level of generality for different o-phenylenediamine and benzaldehyde derivatives and (vi) chemoselectivity.

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A Novel Method for Synthesis of Red-light Emitting Compounds by Cross-Coupling Reactions of 2-Pyran-4-ylidene-malononitrile Derivative

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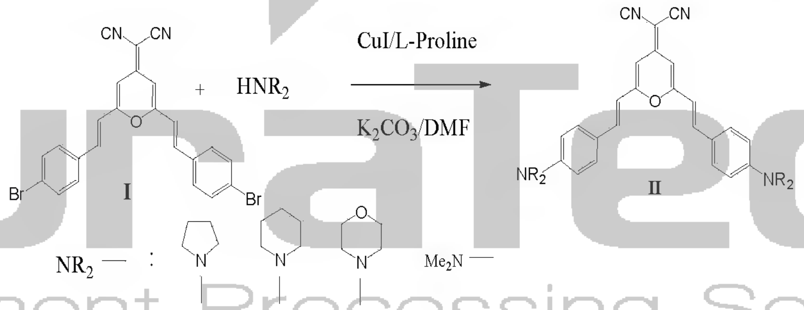
During the past decade, the study of the synthesis, structure, and chemical properties of organic light-emitting diodes (OLED) electronic materials has become one of the foremost topics in chemistry and physics. For the flatpanel and full color display, it is necessary to have a set of green, blue and red emitters with sufficiently high luminous efficiency and proper chromaticity. 2-{2,6-bis-[2-(4-dimethylaminophenyl)vinyl]-pyran-4-ylidene}-malononitrile (d-DCM) is a very efficient laser red dye which was used for a tunable light source in a broad spectral region. These types of compounds are usually synthesized by condensation reactions between donor-containing aldehydes and acceptor-containing dicyanomethylidenepyrans. Reactions between the two reactants, even in equivalent molar ratio for bis products, are inevitably accompanied by the presence of a considerable portion of the mono condensed products. Purification of this bis-condensed product was usually is so difficult.

Aryl-nitrogen bonds are prevalent in many compounds that are of pharmaceutical and materials interest. The development of synthetic methods to form these bonds has been widely studied. The Ullmann condensation has been a powerful method for the coupling of aryl halides with amines. Ullmann reactions require the use of copper metal or copper salts, base, and heating during the reaction. Usually these type of compounds were synthesized by Cu-catalyzed Ullmann coupling reaction of aryl halides with N-heterocycles.

In this work, we report a novel method for synthesis of d-DCM derivatives according to Ullmann coupling reaction. Series of novel bis-condensed derivatives of d-DCM synthesized by cross coupling reactions of 2-{2,6-Bis-[2-(4-bromophenyl)vinyl]pyran-4-ylidene}-Malononitrile with amines in the presence of copper iodide as catalyst. In this reaction we used from L-proline as ligand for increase activation of catalyst. The yields of products in the range of 68 to 76%. Our method offers some advantages over the previous one. For instance, it uses cheaper reagent, it is selective for synthesis of bis condensed products and has higher total yields with shorter synthetic steps.



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A Benign and Green Synthesis of Indenopyridopyrimidines under Ultrasonic Irradiations

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Green chemistry has become a major driving force for organic chemists to develop environmentally benign routes to a myriad of materials [1]. On the other hand multi-component reactions, an important class of organic tandem reactions, are one-pot processes with at least three components to form a single product, which incorporates most or even all of the starting materials [2]. Likewise, as evident from the literature, application of ultrasound in a so called "sonochemistry" has received enormous interests since it offers a versatile and challenging technique in organic synthesis. Nowadays, ultrasonic irradiation technique has been employed not only to decrease reaction times but also to improve yields in a large variety of organic synthesis [3]. In respect to our continued interests in developing benign synthetic protocols for biologically important heterocycles [4], several pyrido[2,3-d]pyrimidine derivatives (**4**) based on a three-component condensation reaction between aminopyrimidin-4-one (**1**), indanedione (**2**) and aryl aldehydes (**3**) under ultrasonic irradiation conditions. This method benifits the advantages of higher yields (94-98%) lower cost and easy workup (Scheme 1).

Scheme 1

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Utility of 6-amino-2-methylthiouracile as a precursor for the synthesis of bioactive pyrimidine derivatives.

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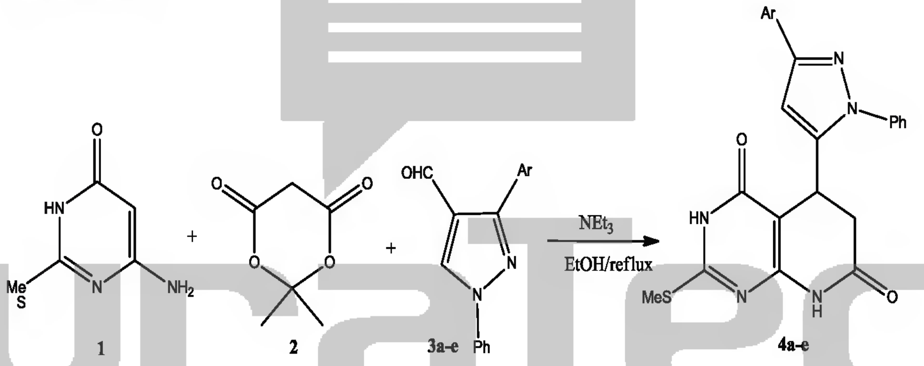
It is well known that many pyrido[2,3-d]pyrimidine derivatives possess interesting physiological properties. It has been proven that they posses antibacterial [1], antiviral [2], anti-inflammatory [3] and bactericidal [4] activities.

As part of our program aimed at developing highly expedient, selective and environmentally friendly methodologies for the preparation of heterocycles of biological importance [5], we describe here an efficient method for the regioselective synthesis of new derivatives of pyrimidine.

We investigated the reaction of 6-amino-2-(methylthio)pyrimidin-4(3H)-one (**1**), meldrum's acid (**2**) and heteroaryl aldehydes (**3**) for the synthesis of novel fused pyrido[2,3-d]pyrimidines (**4a-e**) in absolute ethanol and using triethylamine as catalyst. This one-pot three-component condensation reaction furnished the desired pyridopyrimidines regioselectivly in good to high yields. The easy work-up of the products, use of EtOH as a green solvent and mild reaction conditions are the notable features of this protocol. The antibacterial activities of the selected products were also tested. Some of them showed promising activities.



Ar = p-C_6H_5, p-ClC_6H_4, p-$CH_3OC_6H_4$, p-$NO_2C_6H_4$, m-$NO_2C_6H_4$

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Study on the Synthesis of Diethyl Hydroxylamine(DEHA)

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The synthetic method of diethyl hydroxylamine from diethylamine and hydrogen peroxide was studied.The effects of the kinds and amount of catalyst,solvent, reactant molecular ratio,reaction temperature,reaction time on the reaction yield were studied.

N,N-diethylhydroxylamine (DEHA) is used in water treatment chemical formulations for controlling corrosion, photographic chemicals, inhibitors and silicon rubber. (Scheme)

Key Words: diethyl hydroxylamine, hydrogen peroxide

$$NH(C_2H_5)_2 + H_2O_2 \xrightarrow[\text{solvent}]{\text{catalyst}} NOH(C_2H_5)_2$$

(Scheme)

References:
United States Patent 4918194,Process for the synthesis of a N,N-dialkyl-hydroxylamine

Synthesis of β-phosphonomalonates Catalyzed by Iodine

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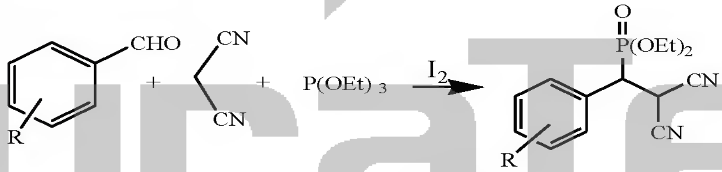
Phosphonates exhibit a wide range of notable biological properties, which expand their applications as enzyme inhibitors, metabolic probes [1], peptide mimetics [2], antibiotics, and pharmacologic agents [3], besides to their traditional roles as intermediates in organic synthesis [4]. Extensive efforts have been made to introduce convenient and efficient methods for the synthesis of phosphonates. Direct phosphorus-carbon bond formation represents one of the most versatile and powerful tools for the synthesis of phosphonates. Amongst the methods for P-C bond formation, phospha-Michael addition, has evoked remarkable attention by organic chemists [5,6,7,8]. Synthesis of β-phosphono malonates by this method commonly promoted by bases [5], Brønsted/Lewis acids [6], transition metals [7], radical initiators, such as microwaves [8]. Although these methods are valuable, they suffer from one or more of the following drawbacks, such as: low yields, high temperature, long reaction times, requiring a promoter, such as microwave, using toxic solvents or a large amount of catalyst and tedious work-up procedures. Therefore, the development of a new method to overcome these shortcomings still remains an ongoing challenge for the synthesis of these significant scaffolds.

In this paper, a new, convenient one-pot method for the synthesis of a variety of β-phosphonomalonates by a tandem Knoevenagel-phospha-Michael reaction of phosphite esters with aryl/heteroaryl/alkyl aldehydes and malonitrile in the presence of iodine as a catalyst is described.(Scheme). This method offers several advantages, such as using low loadings of iodine as a cheap catalyst and offers good yields of the products. Short reaction times, mild reaction conditions, ease of recovery and catalyst reusability make this method a new, economic and waste-free chemical process for the synthesis of β-phosphonomalonates.



Scheme

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Synthesis and characterization of new composite of poly(o-Toluidine)/silica with doping by camphor sulfonic acid under solid-state condition

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Polyaniline (PANI) is a very important polymer owing to its diversified chemistry and interesting physical properties [1]. Preparation of composites of conducting polymer (PANI) has been considered to provide a suitable solution to the processibility problem [2-3] and in addition, it has been found that ring-substituted (alkyl and alkoxy) and N-alkyl substituted PANI are more soluble than unsubstituted PANI. Therefore, many studies have been devoted to the synthesis of soluble PANI derivatives [4]. However, its insolubility in common solvents, which results in difficult processability, has restricted its applications. Recently, polytoluidines have attracted considerable attention since they exhibit better solubilities and hence better processability than polyaniline [5-7]

In the present paper, a new composite of poly(o-toluidine) have been synthesized. Poly(o-toluidine) emeraldine base (POT-EB) was doped with solid dopant acid (silica-supported camphor sulfonic acid) for preparation of the composite under solvent-free (solid-state) condition. The resulting composite was characterized using Fourier transform infrared (FT-IR) and ultraviolet-visible (UV-vis) spectroscopy, and its doping was confirmed by means of comparison with POT-EB synthesized in solution. The morphology of composite was determined using scanning electron microscopy (SEM).

$$\mathrm{SiO_2} \xrightarrow[\text{Solid-Sate}]{\text{CSA}} \mathrm{SiO_2.CSA} \xrightarrow{\text{POT-EB}} \text{Composite}$$

Scheme

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Doping of Poly(o-Toluidine) Emeraldine Base by Solid Dopant Acid (Silica-Supported Perchloric Acid) under Solvent-Free Condition

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The field of conducting polymers has been flourishing rapidly day by day and these materials are becoming indispensable for this century. Polyaniline, one of the most promising conducting polymers, is inherently brittle and poor in processibility due to its insolubility in common organic solvents [1-2]. This problem has been overcome to some extent by using substituted derivatives of aniline such as ring substituted [3]. The polymers of the substituted aniline exhibit greater solubility but the conductivity is found to be slightly lower. However, efforts have been made to improve the processibility of these polymers, in recent years, by using a functionalized protonic acid, which makes polyaniline conducting as well as renders the resulting polyaniline complex soluble in organic solvents. It is possible to modify the properties of polymers by adding inorganic particles within the polymer matrix. So composites containing organic polymers and inorganic particles such as silica (SiO_2) provide a new class of materials with novel properties [4].

In this work, a new composite was synthesized by doping of poly(o-toluidine) emeraldine base with solid dopant acid, silica-supported perchloric acid, under solvent-free condition [5-6]. The resulting composite was characterized by Fourier transform infrared (FT-IR) and Ultraviolet-visible (UV-vis) spectroscopy. The morphology of composite was studied through scanning electron microscopy (SEM).

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P_2O_5/SiO_2 as a Reusable Catalyst for the synthesis of 2,3-dihydroquinazolin-4(1H)

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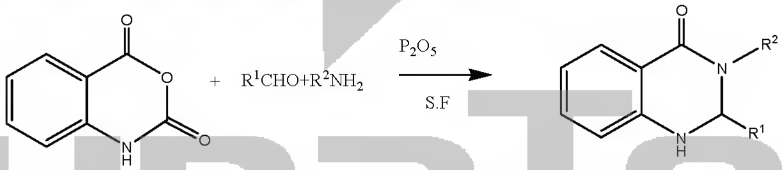
Multi-component reactions (MCRs) are emerging as useful tools for carbon-carbon and carbon-heteroatom bondformation and for the synthesis of important organic molecules with several degrees of structural diversity. Quinazolinones are a class of N-heterocycles that has attracted much attention because of their broad range of pharmacological activities such as anticancer ,anti-inflammatory antifertility, antifungle and mono amine oxidase inhibition these compounds can easily be oxidized to their quinazolin-4(3H)-one analogs,which are themselves important biologically active compounds. (1) Heterogenization of homogeneous catalysts has been an interesting area of research from the industrial point of view;this combines the advantages of homogeneous catalysts (high activity and selectivity, etc.)with the engineering advantages of heterogeneous catalysts (easy catalyst separation,long catalytic life, easy catalyst regenerability, thermal stability and recyclability (2). To a mixture of isatoic anhydridel(1 mmol), aromatic aldehyde (1 mmol), and p_2o_5-Sio_2(15 mol %) was added primary amine. The reaction mixture was then heated at 100 °C for an appropriate time until the completion of the reaction was achieved as monitored by TLC. Then, the reaction mixture was cooled, washed with ethanol (15 mL) and evaporated under vacuum to give the product, which was crystallized from ethanol to afford pure(3)



In conclusion, we have described a rapid and efficient method for the preparation of in high yield and short reaction time by a dihydroquinazolin-4(1H)-ones derivatives ensation reaction of aldehyde, isatoic anhydridel and primary amine under the catalytic effect of Silicaphos for short and solvent-free conditions

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A facile approach for the synthesis of 14-aryl-14H-dibenzo[a,e]xanthenes under solvent-free condition

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The synthesis of xanthenes, especially benzoxanthenes, has been of considerable interest to chemists because their oxygen heterocycles may contribute to potential antibacterial [1] antiviral and anti-inflammatory activities [2]. Furthermore, these compounds can be used as dyes, in laser technology [3] and pH-sensitive fluorescent materials for the visualization of bimolecular assemblies (Fig. 1). For the synthesis of benzoxanthenes, various methods have been reported including the reaction of 2-naphthol with formamide 2-naphthol-1-methanol [4] and carbon monoxide. However, these methods have drawbacks such as poor yields, prolonged reaction time, using of toxic organic solvents, excess reagents/catalysts, and harsh reaction conditions.

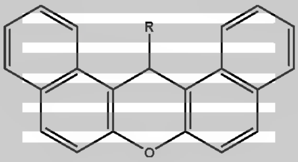
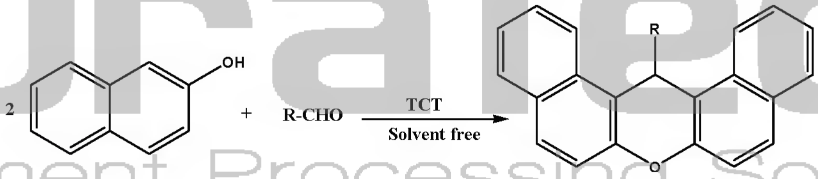


Fig.1. Benzoxanthenes

In connection with our research program directed toward the synthesis of xanthenes, we hope to describe the synthesis of xanthenes from several kinds of aromatic aldehydes and 2-naphthole in the presence of TCT as new catalyst at 110 °C under solvent free reaction in high yields. The structure of products has been assigned by physical and spectroscopic data.



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Application of Ni Catalysis in Synthesis of 8-chloro-N-(2-chlorophenyl)-4-methyl-1,2,3,4-tetrahydroquinolin-2-amine

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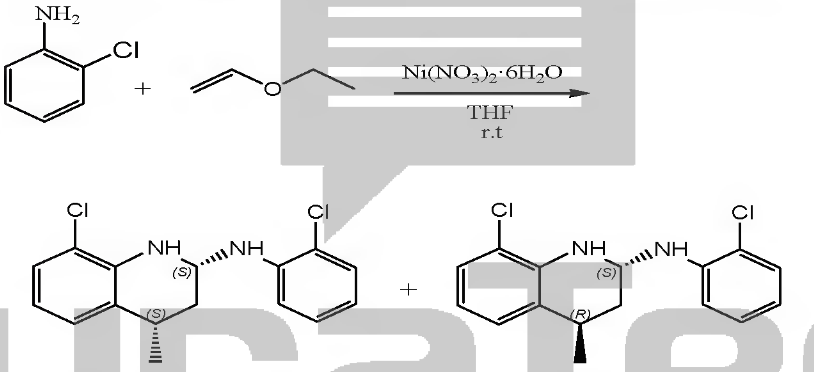
Substituted tetrahydroquinoline derivatives bearing various simple and complex substituents are of medicinal and industrial importance due to their pronounced activity in many physiological processes [1,2]. These core structures are present in numerous other pharmacological agents such as Sumanirole maleate (PNU9566 E), an anti-depressant agent for the treatment of Parkinson's disease, also tetrahydroquinoline-based inhibitors have also been found to be the most potent among several structural classes of protein farnesyl transferase inhibitors [3].

In a this article, we describe an efficient one pot procedure for the synthesis of 8-chloro-N-(2-chlorophenyl)-4-methyl-1,2,3,4-tetrahydroquinolin-2-amine in the presence of Ni(II) catalyst.



C: (2S, 4S) or (2R, 4R) enantiomer **D: (2S, 4R) or (2R, 4S) enantiomer**

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L-Hystidine/phenyl boronic acid catalyzed synthesis of azoloquinazolinones

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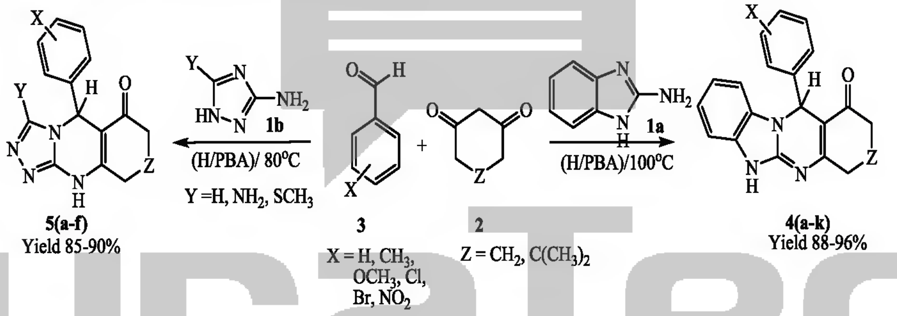
Quinazolines structures exist in skeleton of various natural products and compound that have a broad spectrum of biological activities [1]. In addition, heterocyclic compounds containing azoles rings have been extensively described in the literature as an important class of compounds with a wide variety of biological properties [2]. Quinazoline and its derivatives have recently been evaluated as antagonists of various biological receptors [3] and the synthesis of quinazoline derivatives is currently of great interest in organic synthesis. In recent years, there is a great interest for synthesis of new fused heterocyclic compound composed of two or more different heterocycles [4]. We developed an efficient method for the synthesis of tetrahydrobenzimidazo[2,1-b]quinazolin-1(2H)-ones ring systems **4** and tetrahydro-1,2,4-triazolo[5,1-b]quinazolin-8(4H)-ones ring systems **5** by a one-pot three-component condensation reaction of a cyclic β-diketone **2** with an aldehyde **3** and various aminoazoles **1** using Hystidine/phenylboronic acid (H/PBA) catalyst in ethanol under reflux conditions.



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Synthesis of chromene derivative and spiro[acenaphthylene:chromene] via one-pot three-component reaction in the presence of histidine catalyst

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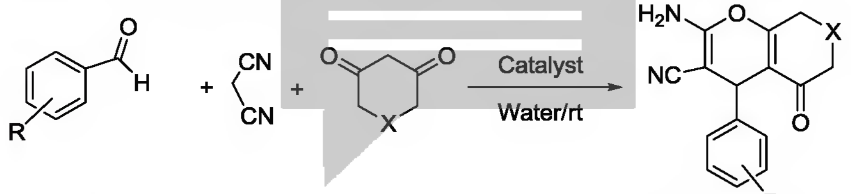
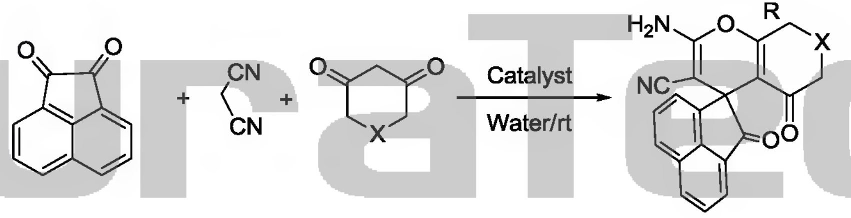
Chromenes as important classes of compounds are widely present in plants [1] and also exhibit remarkable effects such as pharmaceuticals [2], antifungal [3] and antimicrobial activities [4]. On the bases of biological studies, the existences of more than two different heterocyclic moieties in a single molecule often increase the biological activities [5]. L-amino acids are readily available natural organic molecules that are fundamental building blocks of biological systems such as proteins, enzymes, natural products and drugs [6]. These compounds have been utilized as asymmetric catalyst, chiral auxiliaries, chiral ligands, and chiral synthons in the asymmetric synthesis. They also recently have been used as organocatalyst and promoter in a wide range of organic reactions [7]. They also recently have been used as organocatalyst and promoter in a wide range of organic reactions [8]. Therefore these compounds have received much attention because of their advantages from chemical and environmental as well as a resource standpoint. In this mind, the use of these compounds as an efficient organocatalyst or promoter to catalyze organic multi-component reactions in water remains a challenging objective. On the other hands, MCRs in water and/or solvent-free with a suitable catalyst and without using harmful organic solvents are one of the current interests. This will complete the significant characters of MCRs to ideally satisfy the green chemistry's principles. In this research, a mixture of aldehyde or acenaphthoquinone with malononitrile and cyclic 1,3-diketone in water in the presence of histidine α-amino acid as a catalyst (natural catalyst) stirred at room temperature. The product showed good results.





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Convenient synthesis of dispiropyrrolidines pyrazolidinone through 1,3-dipolar cycloaddition reaction

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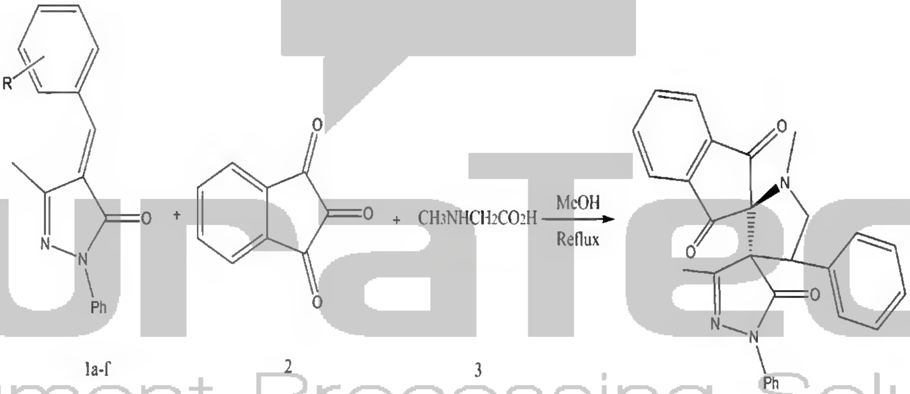
1,3-Dipolar cycloaddition reactions are efficient methods for the construction of heterocyclic units .One of the most important classes for 1,3-dipolar cycloaddition involves azomethine ylide,which is a powerful method for the construction of biologically active five-membered heterocycles especially substituted spiropyrrolidines rings [1]. High stereospecificity and stereoselectivity are the reasons why these reactions are synthetically so useful in organic synthetic field [2]. Pyrazoles are key structures in numerous compounds of therapeutic importance [3]. Compounds containing this ring system are known to display diverse pharmacological activities such as an tibacteria antifungal, anti-inflammatory, analgesic, and antipyretic. Spiro compounds represent an important class of naturally occurring substances characerized by highly pronounced biological properties [4].

In this report we used (E)-Arylidene pyrazolidinone as unusual dipolarophiles for dispiro-pyrazolopyrrolidine with potential biological significance. we observed that when the dipolarophile 1a-f were subjected to 1,3-dipolar cycloaddition with the azomethine ylide generated by decarboxylation condensation of ninhydrin (2) and sarcosin (3) in methanol and a mixture of cycloadducts 4a-f was obtained (scheme 1).



1a-f 2 3 4a-f

R:H,F,Cl,OMe,N(Me)$_2$,NO$_2$

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Synthesis of oxime from 2-(morpholino methyl)cyclohexanon

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Abstract

The aim of this paper is focused on synthesis of an oxime from 2-(morpholino methy) cyclohexanon.Numerous functional grop transformations of oximes make them very important in synthetic organic chemistry [1]. The oxime functional group by having medical and biological difference properties, apply in biosyn thesis, agricultural, pharmacy process and making paints in dustry.These agent is incorporated into many organic medicinal agents, including some antibiotics [2]. First step of synthesis is refluxing of morpholine and Hcl (10%) in presence of cyclohexanon, formaldehyde and Ethanol 96^0 up to 6 hours.Then after evaporation of Alchol, the obtaind viscose liquid made basic and extracted using ether . Now the substance called 2-(Morpholino methyl) cyclohexanon, which is a ketoAmine, has produced. IR spectra hasthe light bar 1708_{cm}^{-1} which indicates the presence of C=0 band.This substance will be refluxed with hydroxyl Amine hydrochloride and sodium acetat for 2hours and after completed cooling, water added to precipitate oximeoccurs.After filtering the solution, it was crystallized by Ethanol 96^0 to reach pure precipitate. In oxime synthesis, consumed Acetate Sodium Leads NH_2OH release from hydrochloride Salt.Released hydroxyl Amine executes electron increase by a nucleophilic attack from pair of free electrons to carbon of carbonyl [3] .Having protons in carbony l oxygen leads them more prepared against nuclear attack. For a material consisting carbonyle Acid strength reinforce increase of electrone. But not as much as acidity that low free nitrogen material. Caronyl material congestino will be done by a electrophilic cathalizor as proton. produced oxime has the melting point about 110-115c^0 . presence of 1708 $_{cm}^{-1}$ bar related to c=o and finally 3342_{cm}^{-1} bar related to oH / oxime indicates creation of that .

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Development of heterogeneous catalyst based on modified triazine ring supported on silica-gel for the Knoevenagel condensation

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Heterogenization of homogeneous catalysts is an important topic in organic chemistry [1]. While some advantages of the homogeneous catalysts such as catalytic activities and selectivity are retained, other properties like easier work-up, recyclability and stability of the heterogeneous systems will be obtained. Knoevenagel condensation is a well-known organic reaction largely employed for C–C bonds formation [2]. The Knoevenagel adducts, in fact, are useful intermediates for further transformations, such as Diels–Alder and Michael additions. The classical Knoevenagel condensation has been carried out by reacting of a methylene active compound with an aldehyde or a ketone in the presence of a base. Methylene active compounds carrying two electron with drawing groups, such as malononitrile, cyanoacetates, malonates, and β-ketoesters, are generally used in the known condensations [3]. In this work, silica gel surfaces were modified with diethylenetriamine (DETA) via two step chemical reaction. Cyanuric chloride was chemically bound to the surface hydroxyl groups of silica-gel to give cc-silica. In the second step cc-silica was reacted with DETA to give diethylenetriamine on triazine ring bounded to silica-gel (TAAT-silica). This heterogeneous catalyst was used as a basic catalyst for the Knoevenagel condensation reaction of aromatic aldehydes and ethyl cyanoacetate in water as a solvent. The green and mild reaction conditions, medium to short reaction times, simple work-up, low cost and easy preparation of catalyst are the obvious advantages of the present catalyst. Finally, this catalyst can be recovered by washing with aqueous solution and used again at least three times without negligible loss in its activity.

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An Efficient Synthesis of Bicyclo[3.3.1]nonane Systems via Tandem 1,3-Dinucleophilic Addition of 4-Hydroxy-2-Quinolinones to Quinolinium Salts

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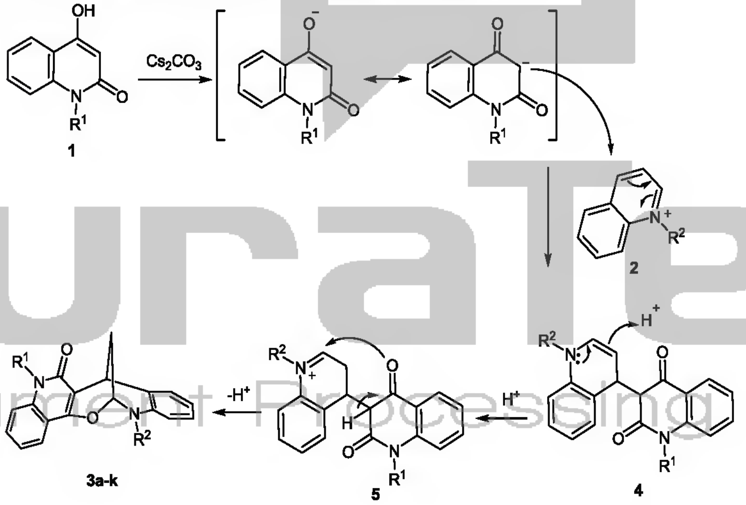
Quinolinones and annulated quinolinones are well-known for their remarkable biological activities. A large number of fascinating pharmaceutical activities have been recognized to be associated with quinolinones derivatives. The synthesis of such compounds has been the subject of several research studies which demonstrate the high importance of such class of compounds [1, 2]. Herein, we have developed an efficient protocol for the preparation of bicyclo[3.3.1]nonane systems. High yield and selectivity and low cost of the reagents are the salient features of this method. The reaction starts from easily accessible starting materials, which makes it a useful and interesting process for the preparation of quinolinones-annulated heterocycles in a one step operation. The reaction generally involves the initial addition of quinolinone to quinolinium salt to form enamine intermediate which can be trapped by intramolecular O-alkylation of quinolinone (Scheme 1).



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A simple and efficient synthesis of gem-dihydroperoxides from ketones using aqueous hydrogen peroxide and catalytic $Al(HSO_4)_3$

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gem-Dihydroperoxides have gained much importance in recent years due to their relevance to peroxidic antimalarial drugs(1). they are useful intermediates in the synthesis of tetraoxanes(2) and endoperoxides(3). Also,very recently.DHPs been utilized as oxidants(4). gem-Dihydroperoxides can be prepared by ozonolysis of ketone enol ethers or a-olefins in the presence of H_2O_2 or by hydroperoxide rearrangement of bicyclic alcohols. However, these methods suffer from disadvantages such as the requirement of suitable starting materials, use of concentrated H_2O_2 and excess acid and unsatisfactory yields. Recently, a method for the conversion of ketones into gem-dihydroperoxides using aqueous H_2O_2 in the presence of iodine was reported. The time required for this conversion was typically 24 h. In continuation of our work on the development of useful synthetic methodologies we have observed that gem-dihydroperoxides can be prepared from ketones on treatment with aqueous H_2O_2 (%۵۰)using a catalytic amount of $Al(HSO_4)_3$. Various ketones were successfully converted into the corresponding gem-dihydroperoxides at room temperature. The conversions were complete within 1–4 h.. Both acylic and cyclic aliphatic ketones afforded the desired products in excellent yields. Cyclododecanone was converted into the corresponding gem-dihydroperoxide in 1 h in 92% yield .Previously, the same conversion using H_2O_2 required 24 h to form the same product in only 60% yield. The high yields of products, mild reaction conditions, short conversion times and the use of less costly reagents are notable advantages of the present method

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N-formylation of amines under solvent-free conditions

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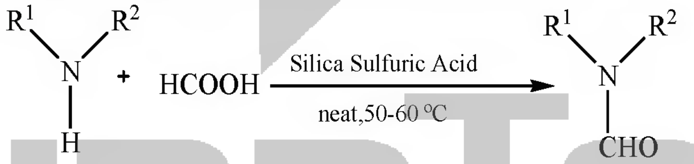
Abstract

The reaction of primary and secondry amines with formic acid in the presence of silica sulfuric acid under solvent-free conditions brings about highly and efficient N-formylation to give the corresponding formamides in excellent yield. The N-formylation reaction involves simple operation, short reaction time and high yields but also high chemoselectivity.

We have observed that the N-formylation of aniline can efficiently be accomplished in this reaction medium by treatment with formic acid at 50-60 °C. Herein we wish to report on the use of solid-supported reagents to produce formamides starting from primary and secondary amines. The reaction of amines with formic acid first appeared in 1955. [1]



R^1,R^2= alkyl or aryl

We have shown that efficient formylation of anilines by a cheap, and easily prepared silica sulfuric acid. The possibility of performing the reaction in formic acid, and the simple procedure and work up makes this method a useful addition to the present methodologies[2].

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Acetylation of phenols, anilines and thiols using heterogeneous catalyst under solvent-free conditions

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Abstract

The silica sulfuric acid was employed for the acetylation of a variety of phenols, amines and thiols under solvent-free conditions at room temperature. This method showed preferential selectivity for the acetylation of amino group in the presence of hydroxyl group. No, C-acylation was observed under the present conditions. Electron deficient phenols are efficiently acylated. Some of the major advantages of this method are high yields, short reaction times, ease of operation[1].

$$\text{RXH} \xrightarrow[\text{Ac}_2\text{O, neat, r.t}]{\text{Silica Sulfuric Acid}} \text{RXAc}$$

X= O/ S/ NH,
R= aromatic, aliphatic

We also investigated the reusability of the catalyst. The recycled catalyst was used for four reactions with the same substrate without observation of appreciable lost in its activity[2].

The catalytic activity of silica sulfuric acid for selective acylation of phenols and amines in the presence of other functional groups is worthy of mentioning. The advantage of this catalyst over some other catalysts for acylation of alcohols has also been shown.

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One-pot Synthesis of Stable Phosphorus Ylides by the Reaction of Ph$_3$P with Activated Acetylenes in the Presenceof NH-Acid Compounds.

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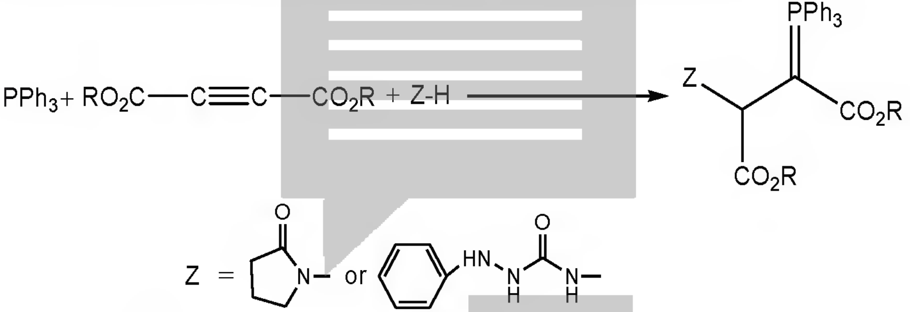
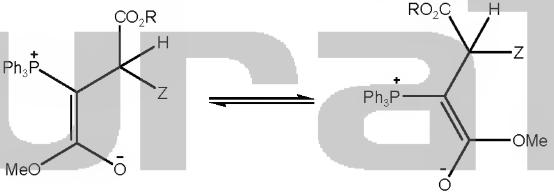
Reaction of triphenylphosphine with dialkylacetylenedicarboxylates in the presence of strong NH-acids such as 2-Pyrrolidin or Phenylkarbazid have been studied. In some cases, stable phosphorus ylides are obtained in excellent yields. The ylide moiety of thesecompounds is strongly conjugated with the adjacent carbonyl group and rotation about the partial double bond in (E) and (Z) geometrical isomers is slow on the NMR time scale at ambient temperature.Thus, these ylides exist as a mixture of geometrical isomers. From the reaction of 2-Pyrrolidin or Phenylkarbazid with dialkylacetylenedicar -boxylate in the presence of triphenylphosphine, stable phosphorus ylidesis obtained in good yields [1-3].





(Z) (E)

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Synthesis of functionalized furo[3,2-c]coumarins via three-component reaction in water

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Abstract

Furocoumarin derivatives can be found in many natural products and exhibit potent biological activity. They are inherently photosensitive and have many therapeutic uses [1]. The photo chemotherapeutic effect relies on their ability to intercalate with the pyrimidine bases of microorganism DNA. Neo-tanshinlactone is known as one of the furo[3,2-c] coumarins isolated from the rhizome of Salvia miltiorrhiza Bung, which is an anti-breast cancer agent. The important biological activities of furocoumarins such as anticoagulant, insecticidal, antitumor, antioxidant, antimicrobial and antifungal lead to high interest in the introduction of new synthesis methods for the construction of them [2]. There are several methods for the synthesis of furocoumarins with most involving a claisen rearrangement and a tandem alkylation / intermolecular aldolization reaction [3]. We report herein a highly efficient and straightforward synthesis of functionalized furo[3,2-c]coumarins via three-component condensation of aldehydes and 4-hydroxycoumarin in water in the presence of I_2 and co-oxidant. Finally, the structure of product was confirmed by single crystal X-ray diffraction. This protocol is a facile one-pot synthesis of furan annulated coumarins with in situ generated biscoumarins, which offers a convenient route to synthesis of multisubstituted furanocoumarin.

R= H, Me, Ph

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Three component reaction of tert-butyl isocyanide and dimethyl acetylenedicarboxylate in the presence of 4H-pyran-4-one drivatives

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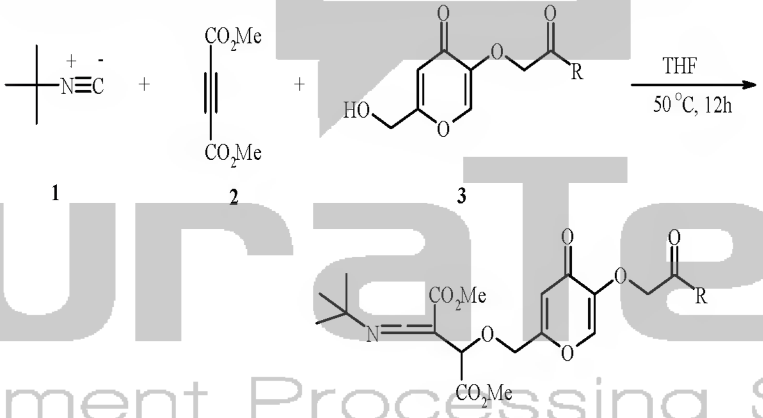
Multi-component reactions (MCRs), by virtue of the convergence, productivity, facile execution, and generally high yields of products, have attracted much attention from the point of combinatorial chemistry. Of pivotal importance in this area are the isocyanide based MCRs such as the versatile Ugi and Passerini reactions [1,2]. In recent years, the synthetic applications of multifunctional heteroallenes have been widely investigated [3]. In spite of extensive developments in the chemistry of modified ketenes and isocyanates, little attention has been paid to the synthesis of ketenimines [4]. In this work, we studied three-component reaction of tert-butyl isocyanide **1**, dimethyl acetylenedicarboxylate **2** and 4H-pyran-4-one derivatives **3**, that leads to ketenimine derivative of fused pyrone **4**.



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Microwave Assisted Synthesis of β-Enaminones Catalyzed by Chloroacetic acid

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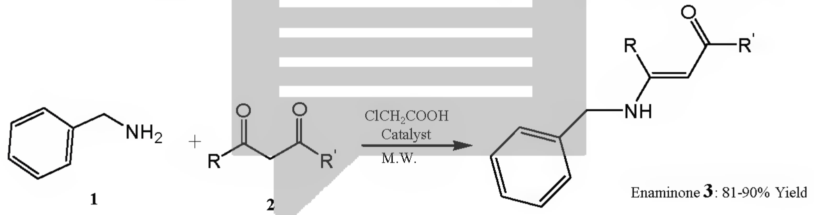
Abstract: β-enaminones contain the conjugated system O=C-C=C-N and are capable of reacting with a wide variety of both electrophilic and nucleophilic reagents. They have been greatly used as key intermediates in organic synthesis. In particular, they have been employed as synthetic building block of a wide variety of heterocycles and pharmaceutical compounds. Several improved precedures have been reported including the reaction of amines and 1,3-dicarbonyl compounds using $Zn(OAc)_2.2H_2O$, $COCl_2$-$6H_2O$, $Bi(OTf)_3$, $HClO_4$-SiO_2, clay K_{10}/ultra-sound, Cu-nanoparticle, and $NaAuCl_4$. As part of our current studies on the development of new routes in approach to the synthesis of organonitrogen compounds, we describe an efficient synthesis of derivatives of enaminones **3** from reaction of benzylamine **1** with 1,3-diketones or 1,3-ketoesters **2** by cloroacetic acid catalysis under microwave radiation (scheme 1). The advantage of the present procedure is that the reaction is performed by simple mixing of the starting materials using an inexpensive and available catalyst in a short time. So the products **3** are prepared in good yields according to a green chemistry procedure.

Keywords: β-Enaminones, Microwave Synthesis, 1,3-diketones, 1,3-ketoesters, benzylamine, Chloroacetic acid.



Scheme 1: Synthesis of N-benzyl enaminone using chloroacetic acid as a catalyst

Conclusions

In summary we describe an efficient solvent free synthesis of enaminone in the presence of of chloroacetic acid catalyst under microwave radiation. The advantage of the present procedure is that the reaction is performed by simple mixing of the starting materials using an inexpensive and available catalyst in a short time. So the products 3 are prepared in good yields according to a green chemistry procedure. This method was successfully applied to enamination of β-diketones and β-ketoesters.

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One Pot Synthesis of New Trisubstituted Bis-Pyrimidines From Corresponding Bis-Amidine Drugs

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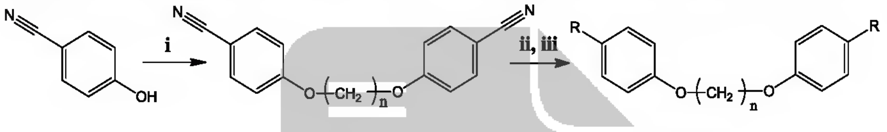
Introduction: Pentamidine and its analogs constitute a class of compounds that are known to be active against Plasmodium falciparum, which causes the most dangerous malarial infection. Malaria is a widespread disease known to affect hundreds of millions of people and presents a perceivable threat of spreading. Hence, there is a need for well-defined scaffolds that lead to new, effective treatment [**1-3**].

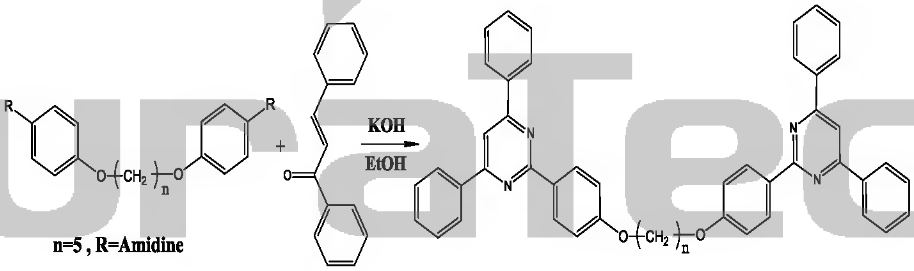


(A)

n=5 , R=Amidine

Reagents and conditions: (i) dibromoalkane, NaH, DMF, reflux; (ii) HCl gas, EtOH, dioxane, 0 °C-ambient temp; (iii) appropriate amine, EtOH, ambient temp.

Dinitrile (A) was prepared in one-pot from 2 equivalents of appropriate cyano phenols with 1 equivalent of dihaloalkanes by Williamson ether after refluxing for 1 h white powder was obtained. The resulting dinitrile (A) recrystallized from ethanol, with melting point 109-110 °C. lit. 108-110 °C [**2**]. Dinitrile A was converted to the appropriate pentamidine drugs following the general procedure and according to the above scheme. In other effort the prepared dinitrils (A) in the presence of base and 2equevalents of chalcones were converted to the new trisubstituted bis-pyrimidines compounds.



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HA Zeolite : An Efficient and Green Catalyst for One – Pot Synthesis of 14-Aryl or Alkyl – 14H – Dibenzo [a,j] xanthene.

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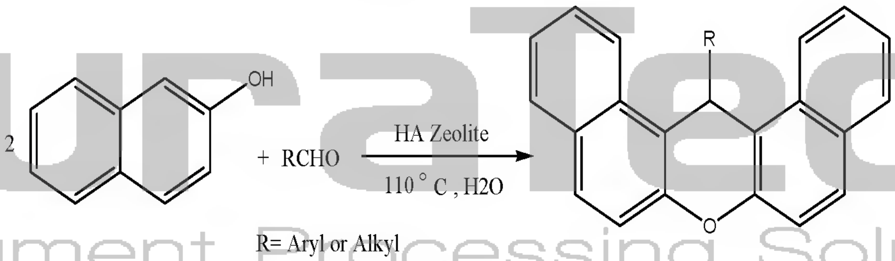
Xanthene and benzoxanthene have attracted considerable interests because of their wide range of antibacterial and anti-in flammatory activities as well as photo toxicity and antagonist activity [1]. Also, these compounds are used in industry, such as PH sensitive florescent material for the visualization of bio molecular assemblies, in laser technologies due to their useful spectroscopic properties [2]. Because of their wide range of pharmacological, industrial and synthetic applications, several methods have been reported for the synthesis of xanthenes and benzoxanthenes. Condensation reaction of 2-naphtols with aldehydes is one of the most simple and straight forward approaches for the synthesis of xanthenes derivatives [3]. Herein, we report a novel, green, facial, commercially, efficient and heterogeneous catalyst for one-pot synthesis of 14-Aryl or Alkyl-14H-Dibenzo [a,j] xanthenes.



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Formation of trialkyl quinoline-2,3,4-tricarboxylates by reaction of isatin, dialkyl acetylenedicarboxylates, and sodium O-alkyl carbonodithioates

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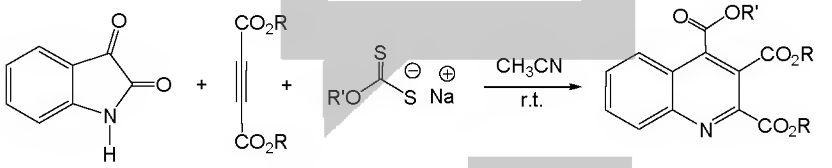
Introduction

Quinolines are an important group of heterocyclic compounds. Several quinoline derivatives have been found to possess useful biological activities such as antimalarial, antibacterial, anti-asthmatic, antihypertensive, and anti-inflammatory[1-4]. In addition, quinolines are valuable synthons for the preparation of nano- and meso-structures with enhanced electronic and photonic functions [5-7]. As a result of their importance as substructures in a broad range of natural and designed products, significant effort continues to be directed toward the development of new quinoline-based structures and new methods for their construction.

Experimental

As part of our current studies on the development of new routes in heterocyclic synthesis, we report an efficient synthetic route to quinoline derivatives. Thus, the reaction of isatin (= indolin-2,3-dione, **1**) with dialkyl acetylenedicarboxylates (**2**), in the presence of sodium O-alkyl carbonodithioates (**3**) at room temperature in acetonitrile as a solvent, produced trialkyl quinolin-2,3,4-tricarboxylates (**4**) in good yields.



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R= Me, Et R'= Me, Et, nPr, iPr, tBu, Bn, Allyl

Conclusions

In conclusion, we have developed a convenient, one-pot method for the synthesis of trialkyl quinolin-2,3,4-tricarboxylates using isatin, acetylenic esters, and sodium O-alkyl carbonodithioates. The present method may be considered as a practical route for the synthesis of quinoline-ring systems.

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Fast and Convenient Method for Reduction of Carbonyl Compounds with $NaBH_4/Cu(dmg)_2$ in Aprotic and Protic Solvents

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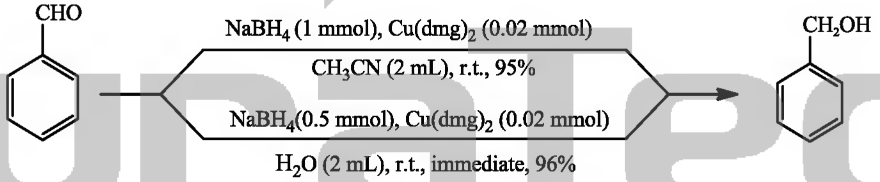
During the past decades, sodium borohydride as a key reagent has played an important roel in the reduction of organofunctional groups in modern organic synthesis. This reagent is a relatively mild reducing agent and mostly used for the reduction of aldehydes and ketones in protic solvents[1]. It is also know that the reducing capability of $NaBH_4$ greatly could be accelerated by using many of additives. Therefor, controlling the reducing power of sodium borohydride has been one of the main interests for organic chemists in many years. In this context, we wish to introduce a new combination system of $NaBH_4$ and $Cu(dmg)_2$ for fast and efficient readuction of carbonyl compounds such as aldehydes, ketones, α-diketones and conjugated enones to their corresponding alcohols in high to excellent yields (Scheme).



(Scheme)

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The investigation of the synthesis of 5-(bromomethyl)-3-(2- bromophenyl) isoxazole as a new compound

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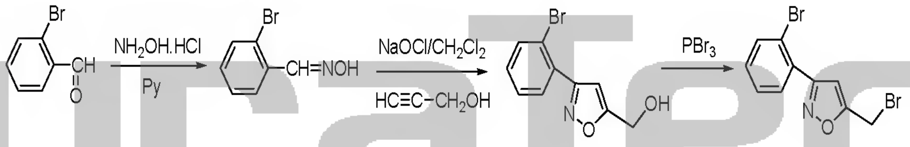
Among aromatic heterocycles, the isoxazole unit is present in anumber of pharmacological compounds. For example in 1995, some isoxazole derivatives which were used as muscle relaxants were synthesized [1]. In 2006, chemists synthesized 3,2-Benzyloxy phenyl isoxazoles and isoxazolines to evaluate them as CFTR activators on cancerous cells [2]. In 2009, researchers exhibited synthesis of 5-isoxazole-5-yl-2-deoxyuridine which was used in anti-herpes simplex ointment [3]. In 2011, an efficient one-pot synthesis of 3-aryl-5-methyl isoxazole-carboxylate from aryl aldehydes was explained that had pharmaceutical application [4]. In this research work, some new compounds of isoxazole family were synthesized and characterized. At first 2-bromo benzaldehyde changed into 2-bromo benzaldoxime (1) by using hydroxylamine hydrochloride in pyridine as a solvent.. By increasing sodium hypochlorite, compound (1) changed to nitrile oxide and simultaneously a [3+2] cycloaddition reaction was carried out using propargil alcohol and nitrile oxide. The result was (3-(2-bromo phenyl)isoxazole-5-yl)methanol (2).At the rest of the research 5-(bromo methyl)-3-(2-bromo phenyl)isoxazole (3) was prepared by reaction of PBr_3 and compound (2) in CH_2Cl_2. The structure of all the synthesized compounds was characterized and confirmed by FT-IR, ^{1}HNMR and ^{13}CNMR spectroscopy techniques.



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An efficient approach to the synthesis of polyfunctionalized amino acids

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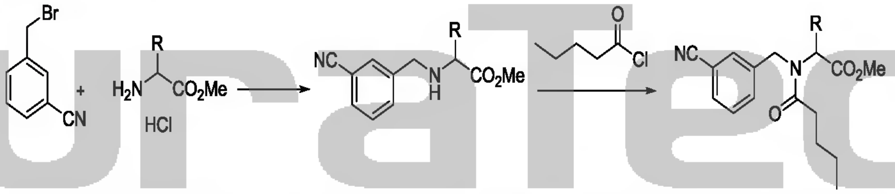
Functionalized amino acids are ubiquitous in many important biologically active molecules, synthetic drugs and drug candidates. For instance, Valsartan which is a nonpeptide, orally active, and specific angiotensin II receptor blocker acting on the AT_1 receptor subtype has been used in treatment of hypertension, heart failure and in left ventricular dysfunction post myocardial infarction (heart attack)[1,2]. The existence of the different functional groups can affect the chemical behavior of the molecule and may increase transforming potential of desired products.

In this approach we wish to report the synthesis of a series of amino acid methyl ester. The synthesized amino acid methyl esters are then carried to the next step to undergo coupling with aryl halides and carboxylic acids or acyl halides respectively. The products have different functional groups which could be used for further transformation. The general reaction is shown below.



The products could be used in different reactions, such as addition of azide, hydrolysis and reduction of nitrile groups.

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Free-radical scavenging activity & volatile oil constituents from Varthemia persica DC.

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It has now been established , that oxygen derived free radicals, primarily superoxide ($O_2^{\cdot-}$) anion and hydroxyl radical ($OH^{\cdot}$), play an important role in the pathogenesis of acute experimental gastric lesions induced by stress, ethanol and non-steroidal anti-inflammatory drugs [1]. Varthemia aromatic genus (Asteraceae) with having one species, V. persica DC, in Iran, distributed also in Afghanistan and Pakistan has three varieties including V. persica, squarrosula and V. stenocephalas [2,3]. In this research we have evaluated essential oil constituents and antioxidant activity of methanol extract from aerial parts of V. persica growing wild in Kashan, central Iran. The essential oil consisted of 22 identified components with α-pinene, caryophyllene and limonene as the major compounds. Antioxidant activity was measured via DPPH assay [4]; the extract shows moderate activity to scavenge of DPPH radical.

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Synthesis of New Quinolone Derivatives Under Thermal and Microwave Irradiation

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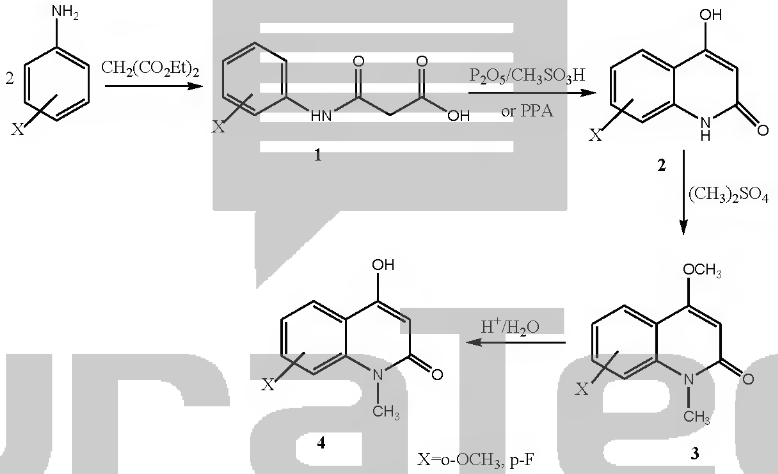
In this study, different procedures were used for the preparation of derivatives of 4-hydroxy-2-quinolones **2** from corresponding propanoic acid **1**. Then compound **2** was reacted with dimethyl sulfate to give methylated product **3** and subsequent hydrolysis afforded compounds **4** as summarized in scheme 1. Freeman reported that a mixture of aniline derivative and excess of diethyl malonate in diphenyl ether at 250 °C for 24 h afforded cyclic compound **4** directly[1]. In our study we irradiated a mixture of aniline derivative and diethylmalonate (10:1 molar ratio) under microwave and prepared corresponding 3-(aryl-1-ylamino)-3-oxopropanoic acid **1** in good yield. Heating prepared acid in polyphosphoric acid (PPA) or methansulfunic acid containing P_2O_5 at 140–150°C afforded the 4-hydroxy-2-quinolone **2** [2, 3]. Stirring compound **2** with dimethyl sulfate and subsequent hydrolysis provided compound **4** in good yield. The structures of the quinolone derivatives were confirmed by FT-IR, ^1H NMR and ^{13}C NMR spectroscopic techniques.



Scheme 1.

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Biomimetic oxidation of imidazolines with tert-butyl hydroperoxide in water catalyzed by manganese(III) porphyrin supported on silica

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Cytochrome P-450 monooxygenation enzyme can selectively catalyze the introduction of an oxygen atom to many substrates. The active site of this enzyme is an iron porphyrin which is surrounded by proteins [1]. Oxidation of imidazolines to their corresponding imidazoles is biologically and pharmaceutically very important, since many imidazole derivatives possess antihypertensive, antiinflammatory, antibacterial and antidiabetic activities [2]. Oxidation of imidazolines by an oxidizing agent should provide an efficient method for the preparation of imidazole derivatives. Several reagents such as $KMnO_4@SiO_2$, $KMnO_4@K10$, $KMnO_4@Al_2O_3$, and the homogeneous $Mn(TPP)Cl/NaIO_4$ catalytic system have been previously reported for this purpose [3-4].

In this report, manganese(III) porphyrin supported on silica was prepared and characterized by elemental analysis, FT IR spectroscopy, diffuse reflectance UV–Vis spectrophotometry (DR UV–Vis) and scanning electron microscopy (SEM). The prepared catalyst was used for the oxidation of imidazolines with tert-butyl hydroperoxide under reflux condition. First, reaction parameters such as catalyst amount and effect of temperature were optimized in the oxidation of 2-phenyl imidazoline.

In conclusion, this catalytic system is a highly efficient system for oxidation of imidazolines with tert-butyl hydroperoxide under reflux conditions. Due to the particle size of the silica, the catalytic activity of this heterogeneous catalyst is higher than our previously reported catalysts. Finally, this catalyst is a robust and recoverable catalyst.

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Study of reaction between triphenylphosphine and di-^{t}butyl-acetylene dicarboxylate in the presence of 3-choloroacetylacetone

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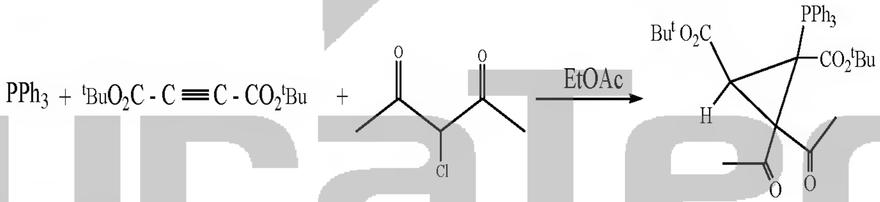
Phosphorus ylides are reactive intermediates, which take part in many valuable reaction in organic synthesis [1-5]. Several methods have been developed for the preparation of phosphorus ylides. These ylides are usually prepared by treatment of a phosphonium salt with a base, and phosphonium salts are usually prepared from the phosphine and an alkyl halide [1-5]. Phoshonium salts are also prepared by Michale addition of phosphorus nucleophiles to activated olefin and in other ways [1-5].

In the current work, Stable phosphorus ylides were obtained in good to excellent yilds from the 1:1:1 addition reaction between triphenylphosphine, di-^{t}butyl-acetylenedicarboxylate in the presence of CH-acids such as 3-choloroacetylacetone.



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A Green Procedure for the Three-Component Synthesis of Highly Substituted Pyridines in Water

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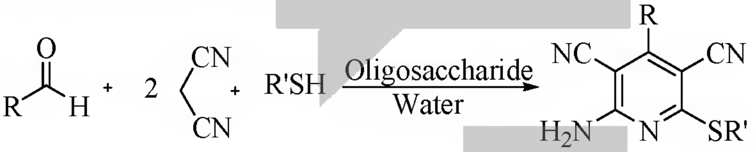
Multicomponent reactions (MCRs) have drawn high efforts in recent years owing to exceptional synthetic efficiency [1]. Compounds with 2-amino-3,5-dicarbonitrile-6-thio-pyridines ring system exhibit diverse pharmacological activities and are useful as anti-hepatitis B virus [2], anti-bacterial [3] and anti-cancer [4] agents and as potassium channel openers for treatment of urinary incontinence [5].
Use of heterogeneous solid catalysts is of current interest in chemistry and industry because solid offer many advantageous such as simplicity in handling, more environmentally safe disposal and less plant corrosion problems.
One of the fundamental challenges and ultimate goals in organic synthesis is to perform the reactions in water [6]. Water is cheap, safe and reduces the use of harmful organic solvents. Therefore, it leads to the development of environmentally friendly chemical processes [7]. Here, we report an efficient method for three-component synthesis of highly substituted pyridines in the presence of oligosaccharides in water (Scheme).



Scheme

Good to high yields, simple work-up procedure, ease of catalyst recovery, and re-usability of the catalyst without appreciable loss of activity make this method attractive and a useful contribution to the present methodologies.

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A Green and Efficient One-Pot Synthesis of 1,4-Dihydropyridines Using Nanoparticles Zno catalyst under solvent free conditions

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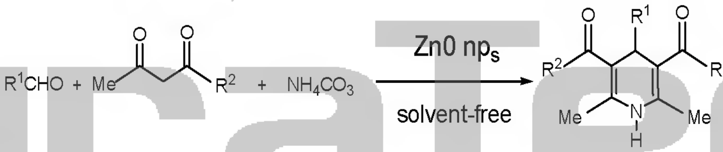
It is well known that 1,4-dihydropyridines are an important class of calcium channel blockers and have emerged as one of the most important classes of drugs for the treatment of cardiovascular diseases, including hypertension [1]. The preparation of 1,4-dihydropyridines by classical Hantzsch synthesis was developed more than 100 years ago [2]. When sterically hindered aldehydes are employed in classical Hantzsch synthesis, extended reaction times are needed, and still the yields are generally low [3]. Thus, Hantzsch's reaction for the synthesis of dihydropyridines has received renewed interest, and several improved procedures have recently been reported [4]. However, in spite of their potential utility, many of these methods involve expensive reagents, organic solvent, long reaction times, and unsatisfactory yields. Thus, the development of an efficient and versatile method for the preparation of Hantzsch's reaction is an active ongoing research area, and there is scope for further improvement toward milder reaction conditions, low reaction times, and improved yields. ZnO is an semiconductor material and has been used widely in pigments, cosmetics, chemical sensors, solar cell and optoelectronics.Recently,efficient Friedel-Crafts acylation as well as Beckmann rearrangement reactions and a facile synthesis of cyclic Ureas from diamines have been reported using ZnO catalyst [5]. In this work, we wish to report an efficient and green catalytic synthesis of 1,4-dihydropyridines using of ZnO nanoparticle in solvent-free.



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Zno nanoparticles as a green and Highly Efficient catalyst for synthesis of dihydropyrimidin-2(1H)-ones under solvent free conditions

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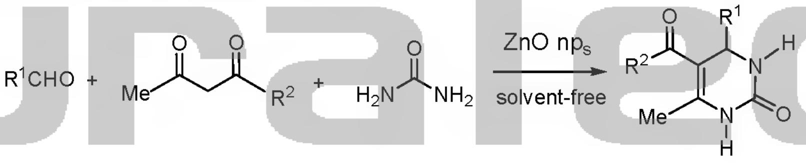
Dihydropyrimidinones derivatives have attracted considerable interest in recent years because of therapeutic and pharmacological properties such as calcium channel blockers, antihypertensive agents and α-1a-antagonist [1]. The classical biginelli reaction of an aldehyde, β-dicarbonyl and urea or thiourea requires strongly acidic conditions with relatively low yields. In order to improve the efficiency of biginelli reaction, a lot of catalysts have been used. Some of them are really fascinating from the synthetic chemist's points; however, some drawbacks still remain [2]. There are several disadvantages associated with the reported methodologies including unsatisfactory yields, long conversion times, difficult handling of reagents, toxic and inflammable organic solvents, and incompatibility with other functional groups in the molecules that limited these methods to small-scale synthesis. Thus, developments of facile and of facile environmentally friendly synthetic methods for preparation of the dihydropyrimidinones are yet demanded. Over recent years, nanometer inorganic oxides have attracted interest throughout the scientific community. Their electronic, magnetic, optical, biological, mechanical and catalytic properties make nanometer materials attractive alternatives to their bulky materials. Of them, the special catalytic activities of nanomaterials intrigued our interest. Because of the larger specific surface area, the metal oxide nanoparticles have a high surface activity, which results in a more robust catalytic activity than bulk metal oxide [3]. In this work, we wish to report an efficient and eco-bening procedure for the synthesis of 3,4-dihydropyrimidin-2(1H)-ones from the aldehydes using ZnO nanoparticles as catalyst under solvent- free.



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Synthesis of functionalized 2-iminothiazoles from reaction of pyridinylthiourea derivatives with α-bromoketones

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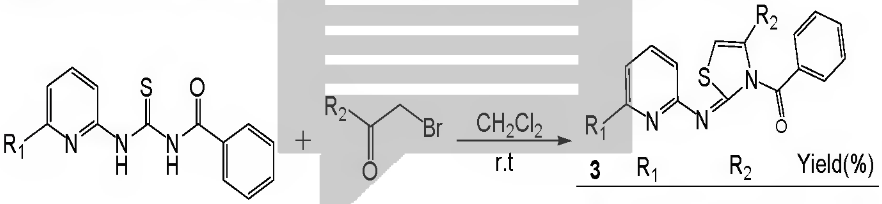
Abstract:

Thiazoles are one of the major scaffolds in heterocyclic chemistry, showing various pharmacological activities like antimicrobial [1, 2] or anti-inflammatory [3]. Numerous natural products containing this heterocycle have been isolated and exhibit significant biological activities [4]. Among aromatic heterocycles, thiazoles occupy a prominent position in the drug discovery process and this ring structure is found in several marketed drugs [5]. The classical method for the synthesis of thiazoles is the Hantzsch process, in which a α-haloketone is condensed with a thioamide. This method gives excellent yields for simple thiazoles [6]. As part of our continuing interest in synthesis thiazole reactions [7, 8], we describe an efficient synthesis of functionalized 2-iminothiazoles from 1-benzoyl-3-(pyridine-2-yl)thiourea **1**, prepared from 2-aminopyridine and benzoyl chloride, as a nucleophile, and α-bromoketone **2** at room temperature to produce the expected products **3** in 80-95% yields (scheme 1)



1

2

3	R_1	R_2	Yield(%)
3a	H	CO_2Et	86
3b	H	4-$MeOC_6H_4$	95
3c	H	4-Br C_6H_4	91
3d	NH_2	CO_2Et	80
3e	NH_2	4-$MeOC_6H_4$	92
3f	NH_2	4-Br C_6H_4	87

Scheme 1: synthesis of 2-iminothiazoles **3**

References:

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Succinic acid as a good catalyzed condensation reaction of β-naphthol and aldehyde: a green synthesis of aryl-14H-dibenzo[a, j]xanthenes

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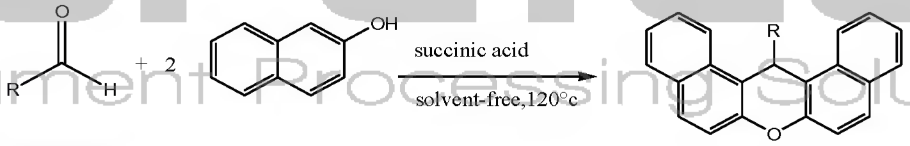
Xanthenes and benzoxanthenes are biologically important drug intermediates[1]. They are cited as active oxygen heterocycles possessing antiviral, antibacterial and antiflammatory activities [2] as well as efficacy in photodynamic therapy and antagonists for paralyzing action of zoxazolamine [3]. The other useful applications of these heterocycles are as dyes, fluorescent materials for visualization of biomolecules and in laser technologies [4]. In conclusion this paper describes a convenient and efficient process for the synthesis of 14-alkyl- or aryl-14H-dibenzo[a,j]xanthenes by one-pot reaction of alkyl or aryl aldehydes and β-naphthol in the presence of catalyst succinic acid at 120 °c under solvent-free conditions.

This method offers some advantages in terms of simplicity of performance, solvent-free condition, low cost, and it follows along the line of green chemistry. The catalyst is readily available and inexpensive and can conveniently be handled and removed from the reaction mixture.

The structures of compounds were deduced from their m.p, IR and ^{1}H NMR spectra.



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Rice husk: Introduction of a green, cheap and efficient catalyst for the acetylation of alcohols, phenols, amines and thiols

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Protection of organic functions are important processes during multi-step organic synthesis.[1] Among the many protecting groups for alcohols, phenols, amines and thiols, acetate is used with high frequency. The acetylation is typically performed using acetic anhydride in the presence of either base [2] or acid catalysts. [3] Although various acetylation methods are available, most have one or more drawbacks including long reaction times, harsh conditions, harmful organic solvents, and tedious work-up procedures. In recent years, use of green reagents in organic reactions is attracted the attention of many organic chemists.

Rice husk, as a thin but abrasive skin in nature, which covers the edible rice kernel, contains cellulose, hemicellulose, lignin, silica, solubles, and moisture. [4] In the course of decades, rice husk has found different applications in chemistry and industry.

In recent years, investigations on the application of silica-based reagents became an important part of our ongoing research program. [5] In continuation of these studies, and based on the morphology and components of the rice husk sample we concluded that this material, as a green reagent and a source of amorphous silica, [6] be able to catalyze acetyl protection of alcohols, phenols, thiols and amines with Ac_2O (Scheme 1).

$$\mathrm{RXH} \xrightarrow[\text{solvent-free, r.t. and/or } 80^{\circ}\mathrm{C}]{\mathrm{Ac_2O}\ \text{(3 mmol), RiH (0.15-0.3 g)}} \mathrm{RXAc}$$

$X = O, S, N$

Scheme1.

To explore the scope and limitation of the reaction we applied a wide range of substrates. All reaction yields were good to high (80-97%). So, we have developed an efficient method for acetylation of alcohols, phenols, thiols and amines. In contrast to some existing methods using potentially hazardous catalysts/additives, this new method offers the following advantages: (i) low cost, availability and reusability of the reagent, (ii) no side reactions (iii) relatively short reaction times, (iv) easy and clean work-up.

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Synthesis of 4- amino-6-oxo-6H-indeno[1,2-d][1,3]thiazepine-5-carbonitrile

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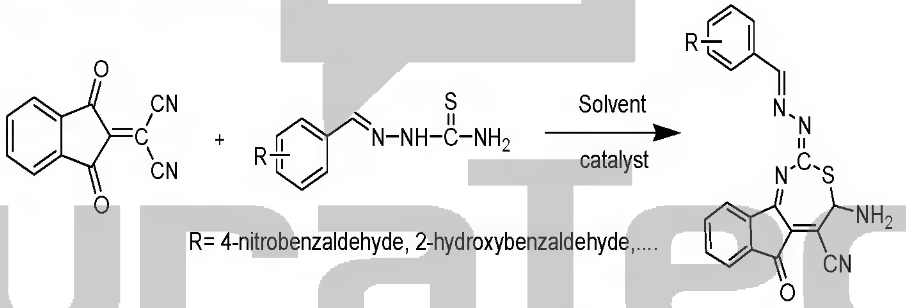
Developing new synthesis methods for novel nitrogen-containing molecules is an important area organic synthesis [1]. Among these compounds, thiazepine derivatives are of particular interest because of their diverse biological activities and clinical. Applications molecules incorporating a benzothiazepinone motif exhibit a wide and diverse range of biological activity. benzothiazepinones have been reported that are antipsychotics[1], antidepressants[2], suppressors of proliferation of the HIV virus[3], and cysteine protease inhibitors. we report in the present work the synthesis of a derivatives, as an intermediate, then these compounds are used for synthesis of dioxo-thioxo and trioxo-tetrahydrospiro(indenepyrrole) derivatives. The results of ^{1}H NMR, ^{13}C NMR, and FT-IR spectra and elemental analysis confirmed the formation of these products.



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Reinvestigation of alkali fusion of sodium p-chlorosulfonate

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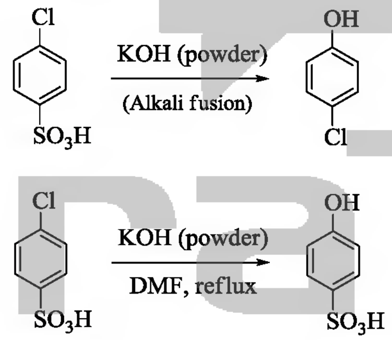
One of the most popular methods for the industrial scale preparation of phenols is alkali fusion of sulphonates. This reaction usually needs high temperature (350-500 °C) and harsh reaction conditions. Mono- and di- substituted aromatic sulfonates generate corresponding phenolic compounds.[1]
Also, nucleophilic substitution reaction of chlorobenzenes and hydroxide ion could be assigned to another classic pathway for the preparation of phenolic compounds. This reaction usually carries out in refluxing conditions in high boiling solvents and facilitates by electron withdrawing groups in chlorobenzenes.[2]
Herein, the competition of nucleophilic substitution reaction of chlorobenzene sulfonate and hydroxide ion in both alkali fusion condition and reflux in DMF was investigated. Results showed that the reaction in alkali fusion condition gives halophenol, while in refluxing DMF phenol sulfonate was obtained in good yield.



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Melamine trisulfonic acid (MTSA): a mild and efficient catalyst for the synthesis of quinoxalines at room temperature

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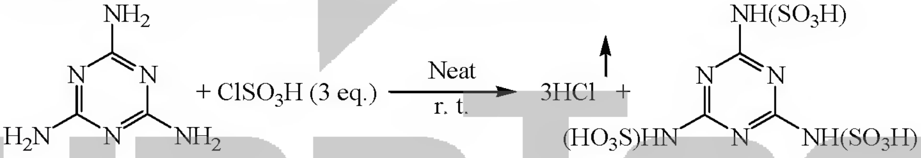
Recently we have reported the preparation of melamine trisulfonic acid (Scheme 1) and its application as a new, efficient and versatile catalyst in organic transformations that need the use of acidic reagents to speed up [1-5]. Herein, and in continuation of our studies, we wish to report the applicability of this reagent in the promotion of the synthesis of quinoxalines at room temperature (Scheme 2). The clean, mild acidity condition, quantitative yields of products, short reaction time and low reaction temperature are attractive features of this reaction which build a suitable method for heat- or acid-sensitive substrates, particularly in drug synthesis. In practice, this method is a combination of a satisfactory synthesis and, more significantly, easy product isolation and purification.

Keywords: diamines, diketones, Melamine trisulfonic acid



Scheme 1

Scheme 2

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A Simple One-Pot, Three Component Synthesis of 3-Amino-5-aryl-4-carbonitrile pyridazines In Water

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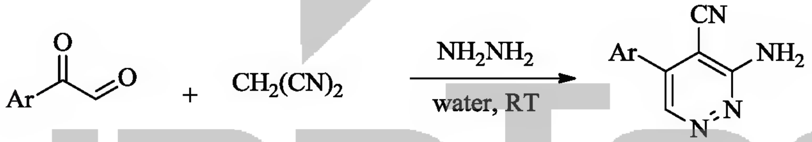
Pyridazine derivatives and heterocyclic annelated pyridazines continue to attract attention due to their wide variety of interesting biological activities. The synthesis and utility of many pyridazines as analgesics, insecticidals,[1] fungicidals,[2] cardiotonics,[3] a-d bacteriocides[4] have been reported. We have previously reported the synthesis of 3-arylpyrimido[4,5-]pyridazine-5,7-(6H,8H-diones and their sulfur analogues[5] as potential mono amine oxidase inhibitors. Here we report the synthesis of a series of novel 3-amino-5-aryl-4-carbonitrile pyridazines undue mild one-pot three component conditions.

Thus the reaction of a mixture of hydrazine hydrate (1 mmol), arylglyoxals (1 mmol), and malononitrile (1 mmol) in water (2 ml) at room temperature gave the corresponding 3-amino-5-aryl-4-carbonitrile pyridazines as a white precipitate in good yield. The products were then collected, washed with water (3×5 ml) and purified by recrystallization from ethanol.

The structure of pyridazines were confirmed by spectral data (^{1}H-NMR, ^{13}C-NMR and FT-IR).



Ar = C_6H_5, 4-FC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 4-$NO_2C_6H_4$, 4-$MeOC_6H_4$
3,4-$(MeO)_2C_6H_3$, 3-BrC_6H_4, 3-$MeOC_6H_4$

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Multi-wall carbon nanotube supported palladium nanoparticles for synthesis of TADBIW

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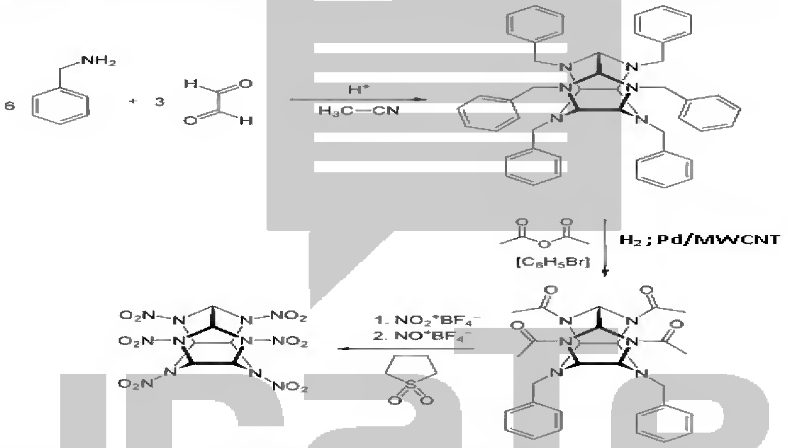
In the recent decades, much attention in the area of high energy materials chemistry has been given to investigation of the properties of 2,4,6,8,10,12_hexanitro 4,6,8,10,12 hexaazatetracyclo [5.5.0.0^{3,11}.0^{5,9}]dodecane (hexanitrohexaazaisowurtzitane, CL-20) and search for efficient methods for the synthesis of this polycyclic nitramine. The studies of the explosive and detonation properties of CL-20 and related compositions showed that presently this compound is the most powerful stable explosive [1]. The best known method for synthesis of CL-20 is combination of third steps. The first step is the construction of the HBIW (hexabenzylhexaazaisowurtzitan) from glyoxal and benzylamine. The second one is the substitution of the four benzyl groups of the HBIW with four acetyl groups to produce the TADBIW(tetraacetyldibenzylisowurtzitan). The third on is conversion of TADBIW to CL-20. In order to produce TADBIW from HBIW, the researcher, has to use proper hydrogenation catalysts. In this paper we synthesis and supported palladium nanocatalyst on a multi-walled carbon nanotube (MWCNT) and then applied for selective hydrogenation of HBIW to TADBIW .The process could be expressed by the following scheme [2,3].



Pd deposition on the functionalized MWCNTs was carried out via the incipient wetness impregnation technique using Pd (II) chloride The concentration of Pd in the solution was settoattain 0.5wt.% on the support [4]. The morphology of the Pd/MWCNT catalyst was characterized by SEM (Scanning electron microscope) and TEM (transmission electron microscope). The SEM and TEM images clearly showed that the Pd sediments were successfully dispersed over multi-walled carbon nanotube structure. This nanocatalyst gave a considerable yield, as high as 70%.Nano catalysts have much premium, such as high specific surface (200-1000) m^2/gr, and athwart active carbon have not macroporous and microporous, and impure such as sulfur. Reactions were designed by Fractional Design software in 30 levels with 5 parameters.

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Biginelli reaction under catalyzed by sodium carbonate as a basic catalyst

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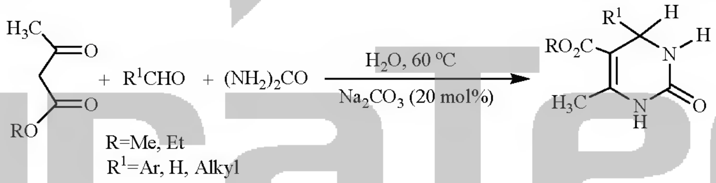
Biginelli reaction involves the single one-pot condensation of an aldehyde, a ketoester and urea, thiourea or guanidine to get dihydropyrimidin-2-ones and dihydropyrimidin-2-thiones (DHPMs) as pharmaceutically important multi functionalized molecules. The yield of traditional Biginelli reaction was very low, thus the use of a wide variety of Lewis or Bronsted acid catalysts, energy sources and solvents to perform the Biginelli reaction has been well reported [1-4]. There are also reports on the use of ionic liquids, microwave irradiation, solid phase reagents, and polymer-supported catalysts in recent literature. In spite of the importance of the Biginelli reaction, running of this reaction under basic conditions is still under debate.

We were interested in studying Biginelli and Hantzsch reactions in aqueous media using sodium carbonate with the aim to develop an operationally simple method for the synthesis of a range of DHPMs Therefore, the model reaction of benzaldehyde, ethyl acetoacetate and urea in water was optimized by investigating various parameters. The optimized conditions required heating with 20 mol% of sodium carbonate in water for three hours at 60 °C. The scope and generality of the base-catalyzed Biginelli reaction in water was demonstrated by synthesizing a series of DHPMs from the substituted aromatic and enolizable aliphatic aldehydes. In all cases, the desired products were isolated in excellent yields (Scheme 1).



R=Me, Et
R^1=Ar, H, Alkyl

Scheme 1.

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Synthesis of biological active 6-amino-4- aryl-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitriles by heterogeneous reusable catalysts

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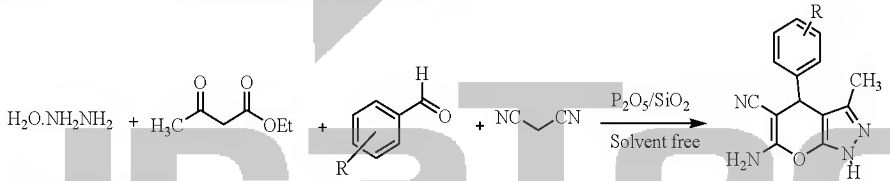
1,4-Dihydropyrano[2,3-c]pyrazole-5-carbonitrile are important compounds and show biological[1], anticancer[1],antimicrobial [2] , anti-inflammatory[3], insecticidal[4] and molluscicidal activities[5]. Pyranopyrazole was synthesized from the two component reaction of 3-methyl-1-phenylpyrazolin-5-one and tetracyanoethylene in the presence of triethylamine for the first time[6]. Later on, a number of two-component reactions involving pyran derivatives and hydrazine hydrate[7] or the reaction between 3-methyl-2-pyrazolin-5-one and benzylidenemalononitrile[8] to obtain pyranopyrazoles were established for preparation of this class of medicinal compounds.

We herein report a practical method for the synthesis of pyranopyrazole by employing four-component reactions of hydrazine hydrate, ethyl acetoacetate, aryl aldehyde and malononitrile under thermal solvent-free conditions in the presence of P_2O_5/SiO_2 (7% w/w) as catalyst (Scheme 1).



Catalyst A: P_2O_5/SiO_2

Scheme 1

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An Efficient Synthesis of 4H-Benzo[g]Chromene-5,10-dione Derivatives Using Ionic Liquid, 2-hydroxyethylammonium Formate Catalyzed Multicomponent Reaction Under Solvent-free Conditions

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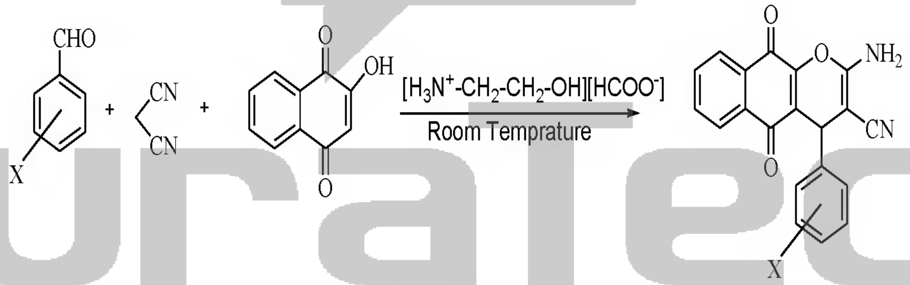
1,4-Pyranonaphthoquinone derivatives possessing pyran and 1,4-naphthoquinone motifs exhibit much more anticancer activities against KB, HeLa (human cervical carcinoma) and HepG2 (human hepatocellular carcinoma) cell lines[1]. Due to their diverse biological activities, the synthesis of 1,4-pyranonaphthoquinone derivatives has attracted considerable attention. So far, several methods tothese compounds have been reported[2].
Herein we shall report an efficient and green synthetic route to 4-aryl-5,10 dihydro-4H-benzo[g]chromene-5,10-dione derivatives by a three-component reaction(which consists of condensati, Michael addition, and cyclization) with aromatic aldehyde 1,2-hydroxy-1,4-dihydronaphthalene-1,4-dione and malononitrile in persense of a catalytic amount of 2-hydroxyethylammonium formate $[H_3N^+–CH_2–CH_2–OH][HCOO^-]$ as an inexpensive and available ionic liquid under solvent-free and ambient conditions.(Scheme 1).



Scheme 1

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Heterocyclization of 6-alkyl-3-propargylmercapto-1,2,4-triazin-5(2H)-ones and 5-alkyl-3-propargylmercapto-1,2,4-triazoles by heteropolyacids

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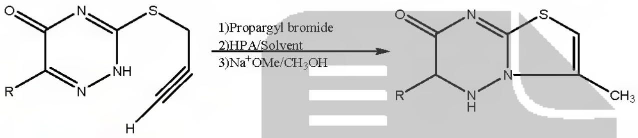
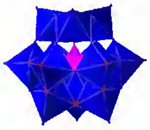
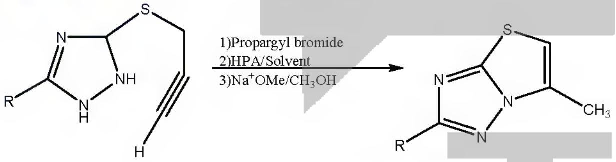
Cyclization of 6-alkyl-3-propargylmercapto-1,2,4-triazin-5(2H)-ones, (2) [1] and 5-alkyl-3-propargylmercapto-1,2,4-triazoles(4) in the presence of Keggin heteropolyacids, $H_3PW_{12}O_{40}$,$H_3PMo_{12}O_{40}$, $H_4SiW_{12}O_{40}$ and lacunary Keggin structure ($K_7PMo_2W_9O_{40}$) afforded (3) and (5) respectively in high yields and short reaction times.



(2) (3)



Figurl:Keggin structure



(4) (5)

Thiones of nitrogen-containing heterocycles have excited the attention of researchers because of their synthetic possibilities and useful properties. Many compounds containing sulfur and nitrogen atoms are anti-inflammatory[2], sedative[3], antibacterial[4,5] antiviral[6,7] or antitumor[8,9].The catalytic function of heteropolyacids (HPAs) have attracted much attention particularly in the last two decades[10]. HPAs as solid acid catalysts are green with respect to corrosiveness, safety, quantity of waste and separability and it is well known that the use of HPAs catalysts for organic synthesis reactions can give a lot of benefits. One of the unique features that make solid HPAs economically and environmentally attractive is their stability and bronsted acidity.

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Highly efficient and catalyst-free synthesis of 4H-pyran derivatives: Carbonyl activation in a neutral reaction medium

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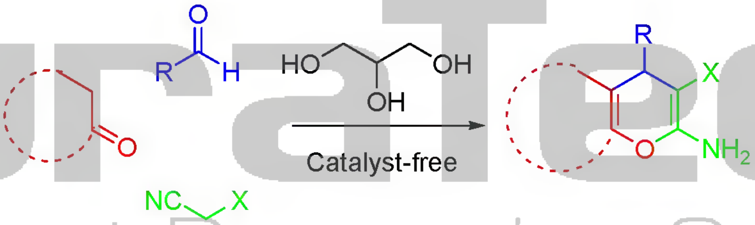
Now days demand for glycerol as starting biodiesel production influence remarkably the glycerol market in US and Europe. Glycerol is a green and biodegradable material that has a high boiling point and reactions in glycerol can be carried out at high temperatures, thus allowing acceleration of the reaction, or making possible reactions that do not proceed in low boiling point solvents. Beside these, glycerol is a nontoxic and non-flammable solvent for which no special handling precautions or storage is required. More recently Hei et al. demonstrate that glycerol is an effective promoting medium for electrophilic activation of aldehydes and some reactions that conventionally carried out using acid catalysts, can be performed under catalyst-free conditions in the presence of glycerol as a reaction medium.[1] Nowadays catalyst-free methodologies for the synthesis of organic compounds have attracted much interest because of their ease of experimental procedures as well as workup, low cost, possibility of using acid or base sensitive substrates, and environmentally benign nature. Considering above facts and as a part of our researches to develop efficient and environmentally benign synthetic methods in organic chemistry, we report here the application of glycerol as a green, biodegradable and very cheap medium for the synthesis 4H-pyrans under catalyst-free conditions.(Scheme 1)



Scheme 1. One-pot three component synthesis of 4H-pyrans in glycerol under solvent-free conditions

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Synthesis of 10-aryl-6,7,8,10-tetrahydo-9h[1,3] dioxolo [4,5-b] xanthen-9-ones using Iron(III) phosphate

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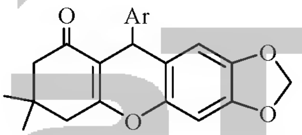
Multi-component reactions have emerged as an important tool for building of diverse and complex organic molecules through carbon-carbon and carbon-heteroatom bond formations taking place in tandem manner [1]. Particularly, in the last three decades a number of three and four-component reactions have been developed.[2]

On the other hand, iron (III) phosphate is relatively cheap and safe catalyst that is prepared using $Fe_2(SO_4)_3$ and disodium phosphate and purchased as commercially. It is not harmful to human health. Chemically, iron (III) phosphate is very stable and will not dissociate unless in the presence of concentrated acid, which is not present in natural surroundings, because of its low solubility in the aqueous agro ecosystem, there is little contamination beyond treated areas. As a consequence of our interest in the synthesis of heterocycles systems[3,4] and application of $FePO_4$ catalyst in organic synthesis, herein, we wish to report a facile, three-component one-port synthesis of novel 10-aryl-7,7- dimethyl-6, 7, 8, 10- tetrahydro-9H-[1,3]-dioxolo [4,5,-b]xanthen-9-ones from the condensation of 3,4- methylenedioxyphenol, aromatic aldehydes and dimedone in the presence of a catalytic amount of $FePO_4$ in ethanol under reflux conditions(Scheme 1).



Scheme 1

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Poly (styrene-4-sulfonic acid) coated magnetic nanoparticles as high effective acid catalyst

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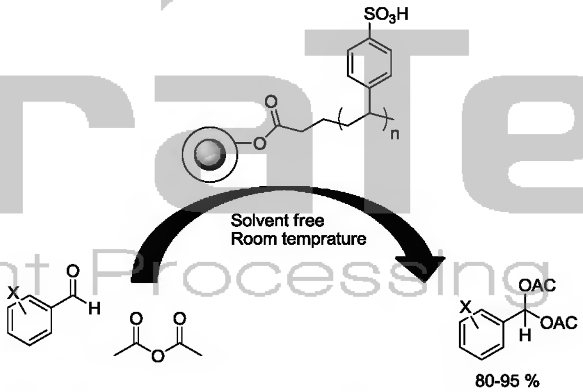
A restriction on the using of homogeneous catalysts in industry is difficulty in separating of catalyst from reaction mixture or separating the product continuously. It will be important economically and environmentally which in large-scale organic synthesis catalyst could be simply recycled [1]. Using of heterogeneous catalysts would be an attractive solution to this problem because of their easy separation and facile recycling. However, homogeneous catalysts show higher activity than heterogeneous catalysts but efforts to prepare the heterogeneous catalyst is still an active research field for chemists. To successfully achieve to the high active heterogeneous catalyst, a rational choice is immobilization of homogenous catalyst on a variety of insoluble support materials. Many support materials are often used for immobilization of active homogenous catalysts such as polymers [2], zeolite, silica [3] or metal oxides. Among these support materials, magnetic nanoparticles (MNPs) are very popular when used for immobilization of active homogenous catalyst because their magnetic responsibility causes simple separation of catalyst by using a magnet. Here in we report a new class of acid catalyst which MNP was coated with poly (styrene-4-sulfonic acid) and we used them for diacetylation of aldehydes. First we synthesized $Fe_3O_4@SiO_2$ by co-precipitation method in alkali medium. After that nanoparticles were modified by 3-(trimethoxysilyl)propylmethacrylate. Free radical polymerization was carried out by sodium styrene sulfate as monomer and modified magnetic nanoparticles in water/ethanol mixture. After polymerization was complete, MNP@polymer was neutralized by HCl 1*M*. Diacetylation raction was carried out by catalyst at room temperature and solvent free condition very well. Catalyst was separated by external magnet. Advantage of our catalyst is high loading of polymer chain in MNP than normally coating of MNP.



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Synthesis of 3,3-Disubstituted Oxindole Derivatives using Analcime Zeolite as an Eco-friendly Catalyst

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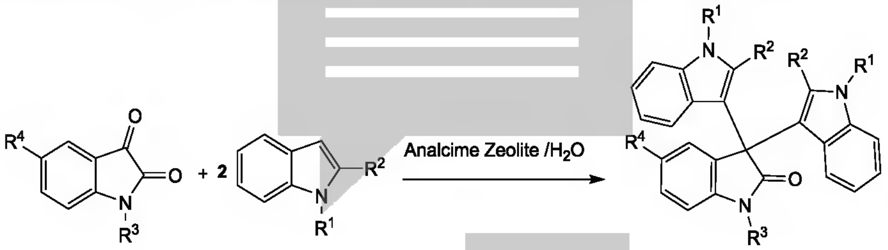
Many of the catalysts used by industries are based on aluminosilicates, which combine high stability with excellent activity in acid-mediated reactions. Zeolites, which are low in toxicity and recyclable, is important in fine-chemical and pharmaceutical manufacture and in petroleum refining. Over the past few years, a variety of acid-catalyzed reactions have been successfully conducted in the presence of Zeolites as efficient catalyst [1].

Oxindole derivatives are a privilege heterocyclic motif that forms the core of a large family of alkaloid and natural products with strong bioactivity profiles and interesting structural properties [2]. The 3,3-diaryloxindoles have been shown to possess antibacterial, antiprotozoal, and anti-inflammatory activities [3]. The 3,3-diaryloxindoles can be formed by the reaction of isatin and indols in acid conditions for long reaction times or promoted by heteropolyacid in mild reaction conditions [4-5]. However, synthesis of this class of compounds especially, 3,3-di(heteroaryl)oxindoles have not been widely explored.



Scheme 1

We wish to report an efficient route to the synthesis of 3,3-di(heteroaryl)oxindole derivatives using Analcime Zeolite as a green catalyst in water (Scheme 1). The notable features of this method are mild reaction conditions, simplicity in operation, cleaner reaction profiles and low cost of the catalyst, which make it as an attractive and very useful process for the synthesis of important biological oxindoles.

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Synthesis of Flavonoid Derivatives in the Presence of Ferric Hydrogensulphate

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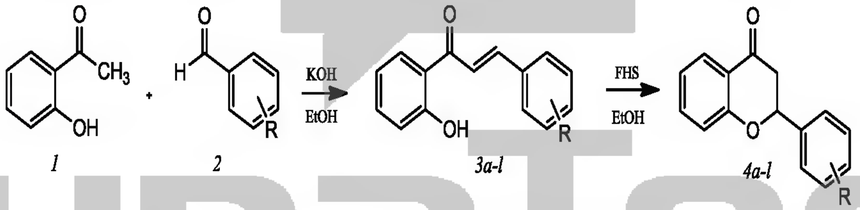
Flavonoids are among the most abundant plant secondary metabolites and are mostly biologically active compound. They are used as antimicrobial agent [1], anti-infection [2], antioxidant and anti-cancer [3], because of their pharmaceutical importance, there are many methods in the literatures purification and their structure elucidation [4,5].

In this paper, we would like to introduce new method for the synthesis of flavonoids using 2'-hydroxyacetophenon, benzaldehyde and ferric hydrogensulphate (FHS) as a new catalyst for their preparation **(4a-l)**.



R : H, *p*-Me, *p*-Et, *p*-iso-Pro, *o*-MeO, *m*-MeO, *p*-MeO, *o*-Cl, *p*-Cl, *p*-NO_2

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N-Alkylation of poor nucleophilic aniln and derivatives with alcohols by a hydrogen autotransfer process catalyzed by copper oxide nanoparticles-catalyzed

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Anilin and their derivatives are of fundamental importance as naturally occurring bio-active compounds such as alkaloids, amino acids and nucleotides contain amino groups, which are particularly useful for the development of new pharmaceuticals and agrochemicals.[1] Consequently, the development of improved methods for the synthesis of amines continues to be an intense focus of research.[2]. Traditionally, the alkylation of amines is achieved using conventional alkylating agents, such as alkyl halides. There can be selectivity problems in such reactions when control of multiple alkylation can be difficult and many alkyl halides have toxic or even mutagenic properties and an alternative to using such reagents is therefore advantageous.[3] Alternatively, in recent years a number of reports on the hydroamination[4] or hydroamino-methylation of olefins or alkynes[5] for the synthesis of anilin derivatives have been reported. Compared to the frequently applied N-alkylations with alkyl halides and reductive aminations, an economically and environmentally attractive method is the N-alkylation of anilin and their derivatives using primary and secondary alcohols. This domino reaction sequence involves in situ dehydrogenation of the alcohol to give the corresponding carbonyl compound, which on subsequent imination followed by reduction with the initially produced hydrogen leads to the formation of the N-alkylated anilin and their derivatives. The advantages of this method are the ubiquitous availability of alcohols and high atom efficiency, for example no salt formation and water as the only by-product. Moreover, compared to reductive aminations, it is possible to run these reactions in the absence of hydrogen pressure[6]. Typical procedure for the N-alkylation of anilin and their derivatives with alcohols**:** A mixture of amine (3 mol) alcohol (1.5 mol), K2 CO3(2.5 mol) and CuO NPs (5 mol %) in toluene (8 mL) was stirred at 140 ° C temperature for 6 h. After completion of the reaction as indicated by TLC, the reaction mixture was centrifuged to separate the catalyst, the solid residue was washed with ethanol to make the catalyst free of organic matter, and the reaction mixture was diluted with water and then extracted with ethanol. . All products were characterized by IR, ^{1}H NMR, ^{13}C NMR and mass spectroscopic techniques.

Key words: N-alkylation, benzyl alcohols, amines, copper chromite nanoparticles, reusability.

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Novel method for preparation of 2-naphthol azo dyes by [H-NMP] HSO_4 as a green acidic reagent

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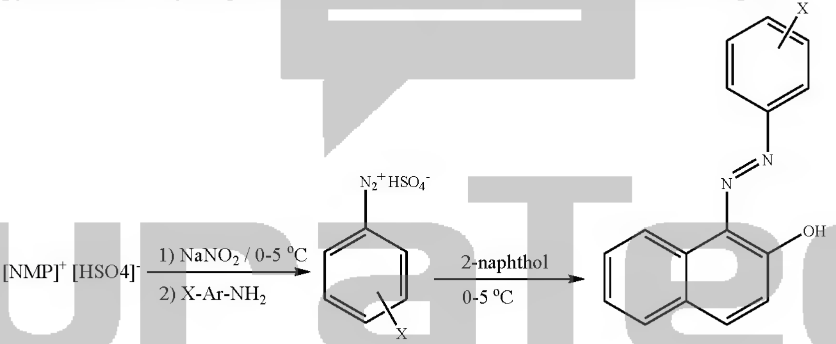
Ionic liquid or molten salts are compounds that are composed entirely of ions and exist in a liquid state. They usually consist of poorly coordinating ion pairs and a classical example is [bmim] BF_4, which is a colorless mobile but non-volatile liquid [1-3]. There is some reported in synthesis of azo dyes by using of ionic liquid [4]. Recently a mild and efficient method for preparation of azides from alcohols using acidic ionic liquid [H-NMP] HSO_4 has been reported by hajipour and co worker [5]. The aim of this manuscript was to describe reaction conditions for preparation of some phenylazonaphthols in acidic ionic liquid using a coupling reaction of aniline derivates with 2-naphthols.The reactions were carried out in N-methyl-2-pyrrolidonium hydrogen sulfate $[NMP]^+[HSO_4]^-$ as an acidic ionic liquid.



X=Br, Me,Cl, NO_2, OMe,....

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Synthesis and biological activity of novel derivatives of 2-benzylidene-1-(4-methyl-6-morpholino-5-nitropyrimidin-2-yl)hydrazine

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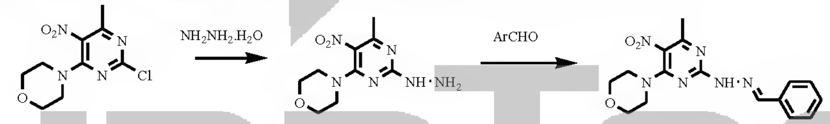
Pyrimidine and its derivatives are ubiquitous in nature. As such, the pyrimidine subunit has found widespread applications in therapeutically active compounds. Most importantly, pyrimidine bases are fundamental constituents of the building blocks of DNA and RNA and hence play a significant role in biochemical vital processes for human beings and animals [1,2]. The structural diversity and biological importance of pyrimidines have made them attractive targets for synthesis over many years. The pyrimidine is a widespread heterocyclic moiety, which is present in numerous natural products as well as synthetic pharmacophores with biological activities [3]. Substituted pyrimidines, particularly with amino-groups at 2 and 4 positions, are known pharmacophores in several structure-based drug design approaches in medicinal chemistry [4]. Schiff bases have often been used as chelating ligands in the field of coordination chemistry and their metal complexes are of great interest for many years. It is well known that N and S atoms play a key role in the coordination of metals at the active sites of numerous metallobiomolecules [5]. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer and herbicidal applications [6]. In this study, we report the synthesis and biological activity of a new series of 2-benzylidene-1-(4-methyl-6- morpholino-5-nitropyrimidin-2-yl)hydrazine.



Ar = C_6H_5, 4-$O_2NC_6H_4$, 4-ClC_6H_4,
4-$MeOC_6H_4$, 2-ClC_6H_4

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Ferric Hydrogensulphate a new Catalyzed for Synthesis of Derivative

2-aryl-2,3-dihydroquinolin-4(1H)-ones

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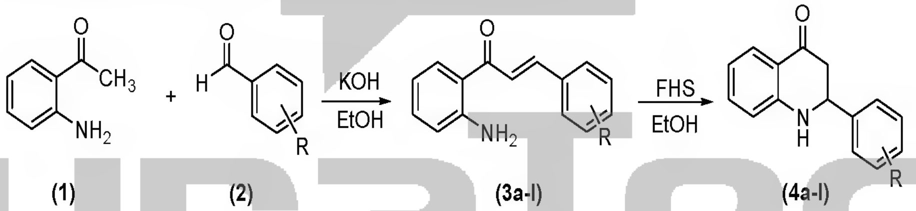
2-Aryl-4-quinolones and 2-aryl-2,3-dihydroquinolin-4(1H)-ones have been studied as potential treatments for a range of diseases because of their important biological properties, such as antiviral, antiplatelet, antitumor and positive cardiac effects[1]. Various methods have been reported for the synthesis of 2-aryl-4-quinolones and 2-phenyl-2,3-dihydroquinolin-4(1H)-ones[2]. Generally, their synthesis is carried out using acid- or base-catalyzed isomerization of substituted 2-aminochalcones, mainly using reagents such as orthophosphoric acid, acetic acid or strong base[3].
Herein, we describe a general strategy for the synthesis of aza-analogs of flavanones starting from o-aminoacetophenone. In this research, we demonstrated that 2-aminoacetophenone and aryl aldehydes undergo a smooth one-pot condensation cyclization in the presence of ferric hydrogen sulphate as catalyst to furnish 2-aryl-2,3-dihydroquinolin-4(1H)-ones **(4a-l)** in high yields.



(1) **(2)** **(3a-l)** **(4a-l)**

R = H, 4-Me, 4-Et, 4-iso-Pro, 2-MeO, 3-MeO, 4-MeO, 2-Cl, 4-Cl, 4-NO_2

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Studies on the synthesis of new derivatives of 1,4- dihydropyridines using cellulose-sullfuric acid catalyst

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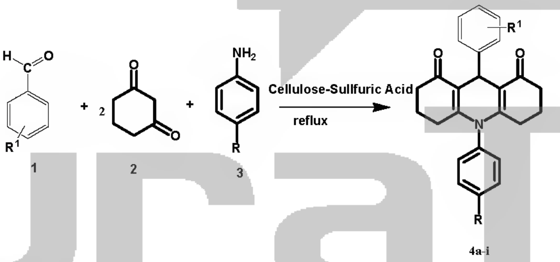
Current literature reveals that 1,4-dihydropyridines exhibit interesting pharmacological and biological properties.Thus, they have been used as calcium channel modulators for the treatment of cardiovascular disorders [1].

On the other hand solid acid catalysts for the synthesis of fine chemicals have attracted considerable attention from both environmental and economical points. The solid acid generally has high turn over numbers and can be easily separated from reaction mixture [2].

In continuation of our ongoing interest in the synthesis and use of N-heterocyclic compounds in organic synthesis [3], we have developed for the first time an efficient method for the synthesis of dihydropyridine derivatives namely dihydropyridones, via a one-pot three-component reaction of aldehyds (**1**), 1,3-cyclohexadione (**2**) and aniline derivatives (**3**) in the presence of premade and reusable cellulose-sulfuric acid as a bio-supported and heterogeneous catalyst. In this protocol the pyridone derivatives were obtained in high yields (85-95%) and reasonable reaction times (1-2 h).



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One-step Synthesis of 2-amino-6-(hydroxymethyl)-8-oxo-4-aryl-4,8-dihydropyrano[3,2-b]pyran-3-carbonitriles

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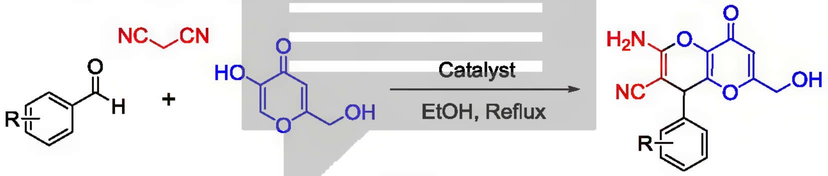
Multi-component, one-pot synthesis has received considerable attention because of its wide range of applications in pharmaceutical chemistry for the creation of structural diversity and combinatorial libraries for drug discovery. MCRs are extremely convergent, producing a remarkably high increase of molecular complexity in just one step. [1]
Kojic acid derivatives, one of the important kinds of fused heterocyclic compounds, possess significant bioactivities such as antifungal, anti-HIV, anticonvulsant, anti-inflammatory, antioxidative, antibacterial, anticonvulsant, and tyrosinase inhibitory activities. [2] Therefore, the synthesis of kojic acid derivatives has aroused great interest in the organic and medicinal communities. In addition, substituted 2-amino-4H-pyrans have been shown to exhibit biological activity as anti-cancer, antihypertensive and coronary dilating agents. [3]



Scheme1

A considerable effort has been made for the synthesis of pyran annulated heterocyclic derivatives due to their wide mentioned applications. Therefore, in this communication, we wish to describe our preliminary investigation for the reactions of various aldehydes, malononitrile and kojic acid, 5-hydroxy-2-(hydroxymethyl)-4H-pyran-4-one, in EtOH in the presence of catalytic amounts of Et_3N, providing a convenient method for the synthesis of new 2-amino-6-(hydroxymethyl)-8-oxo-4-aryl-4,8-dihydropyrano[3,2-b]pyran-3-carbonitrile derivatives.

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Synthesis and Characterization of a New 5-Boromo Salicyliden-2-Amino Benzimidazole Schiff base and its Complexes with Co(II), Ni(II), Hg(II) and Cd(II)

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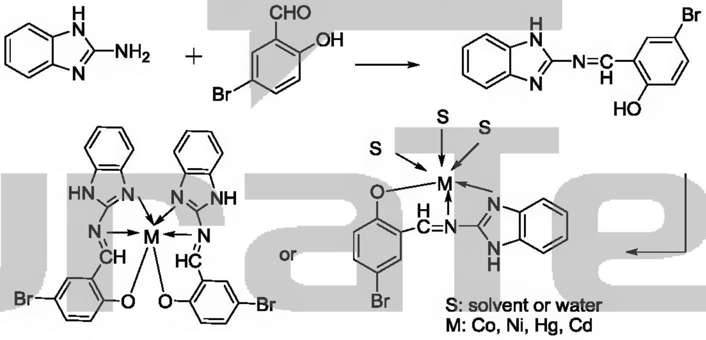
Compounds containing a benzimidazole moiety attached to a heterocyclic system are important chemical classes having a number of significant biological activities against several viruses such as HIV, herpes (HSV-1), influenza and Epstein-Barr [1].

Schiff bases containing polyfunctional groups have not only produced stable metal complexes, but these ligands and their metal complexes also have a significant role in the domains of stereochemistry, model systems of biochemical interest, drugs, herbicides and fungicides, catalysis, stabilizers, polymers, pigments and dyes, etc [2].

In view of the above-mentioned findings and due to continuation of our research for the synthesis of Schiff bases and their applications [3], we are going to report the synthesis of new Schiff base resulted from reacting of 2-amino benzimidazole and 5-Boromo Salicylaldehyde in ethanol and related complexes (Scheme **1.**). The structure of these complexes may be given in accordance with those previously which indicate the Schiff base ligand coordinated to metal ions through the N, O, N or N, O, S system according to the structure of the Schiff base used. Research on structural aspect is ongoing.



Scheme **1.** Structure of the ligand and Suggested structural formula of the complexes.

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Sr(DS)$_2$-catalyzed synthesis of 4,4'-diaminotriarylmethane

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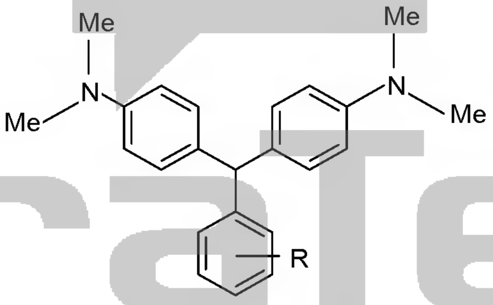
Dyes may be classified according to chemical structure or by their usage or application method. According to the chemical structure classification, triarylmethane dyes are among the most important dyes. Triarylmethane dyes are monomethine synthetic dyes with three terminal aryl groups, of which at least one, but preferably two or three, are substituted by a donor group para to the methane carbon atom. Due to the importance of DTM compounds, several reviews have disclosed on di- and triphenylmethane derivatives[1-5]. These compounds have a broad range of applications in color-forming, manufacturing of novel types of various colorless copying papers, pressure- sensitive heat-sensitive materials, high-speed photo duplicating copying papers, light-sensitive papers, ultrasonic recording papers, electrothermic heat-sensitive recording papers, inks, crayons, typewritten ribbons, and photoimaging systems[6]. Herein, we wish to report a green synthesis method for the preparation of DTMs using arylamines and aldehyde derivatives in the presence of stransium dodesyl sulphate.



R=H, NO$_2$, F, Cl, Br, Me, OMe

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An efficient synthesis of 9-aryl-1,8-dioxooctahydroxanthene derivatives by acetic acid as a solvent and catalyst

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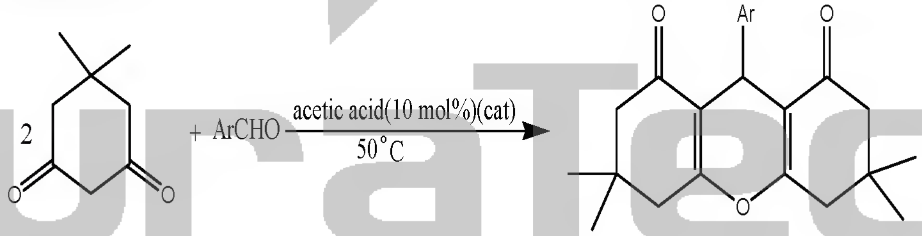
Xanthene's derivatives are parent compounds of a large number of naturally occurring and synthetic derivatives,and occupy a prominent position in medicinal chemistry.[1]

Efficient one-pot Knoevenagel condensation and Michael addition of dimedone with various aldehydes using acetic acid as a catalyst and solvent gave 9-aryl/alkyl-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-diones in excellent yields. The present approach offers the advantages of simple methodology, clean and mild reaction, low environmental impact, simple workup procedure, short reaction times, high product yields.[2]

Keywords:Dimedone. Aromatic, aldehyde, Condensation, Xanthenedione, acetic acid



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Addition of the acetic anhydride to aldehydes via activation of the $RuCl_3$ based on a ligandless method

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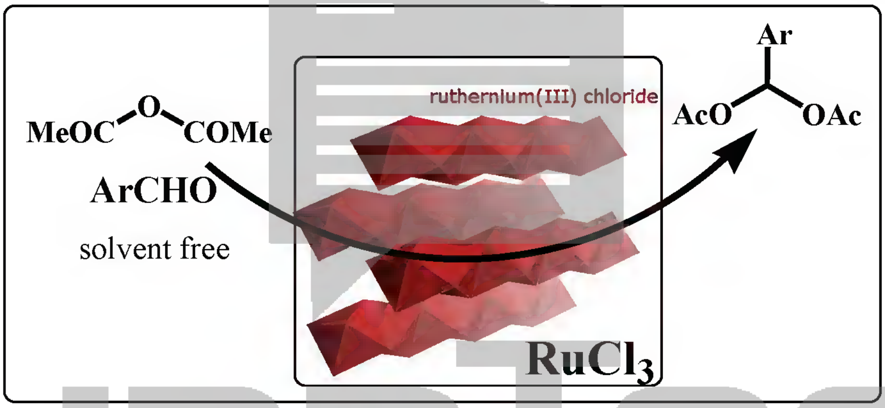
The protected carbonyl groups play an important role in various organic syntheses and in chemistry of drug design [1]. Acylal (1,1-diacetate) formation is one of the most widely used processes for protection of carbonyl compounds [2].



We now reported that Ruthenium (III) chloride is an efficient catalyst for conversion of aromatic aldehydes to diacylals under solvent-free conditions at room temperature. Good yields were obtained within short reaction times. The experimental procedure for the synthesis of the acylals is simple and involves stirring the aldehyde and the anhydride.

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A Green and Highly Efficient, One-pot Synthesis of α-Amino Phosphonates Using DBSA as a Bronsted Acid

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α-Amino phosphonates, analogues of α-amino acids, occupy an important place in organic chemistry with diverse biological, medicinal and agrochemical properties [1]. A number of synthetic methods have been developed for the preparation of α-amino phosphonates during the past two decades. Of these methods, the nucleophilic addition of phosphites to imines, catalyzed by a base or an acid, is the most convenient. In this respect, Lewis acids such as $SnCl_2$, $SnCl_4$, $BF_3.Et_2O$, $ZnCl_2$, and $MgBr_2$ have been used [2]. However, these reactions cannot be carried out in a one-pot operation with a carbonyl compound, amine, and dialkyl phosphite because the amines and water that exist during imine formation can decompose or deactivate Lewis acids. Recently, one-pot three-component reactions starting from carbonyl compounds, amines, and either dialkyl phosphites or trialkyl phosphites have been used for preparation of α-amino phosphonates.

Herein, we describe a new and highly efficient method for synthesis of α-amino phosphonates by a one-pot, three-component reaction utilizing p-dodecylbenzene sulfonic acid (DBSA) as Bronsted acid catalyst (Scheme 1).

Scheme 1.

References:
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One-pot Synthesis of 2-Amino-4H-chromenes by yttrium(III) nitrate supported on the silica gel as a catalyst

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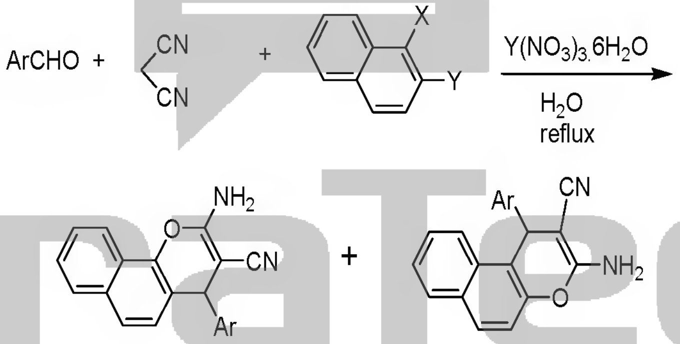
2-Amino-4-H-chromenes and their derivatives are of considerable interest as they possess a wide range of biological properties[1], such as spasmolytic, diuretic, anticoagulant, anticancer and antianaphylactic activity[2].

One of the tools used to combine economic aspects with the environmental ones is the multicomponent reaction (MCR) strategy[3]. this process consists of two or more synthetic steps which are carried out without isolation of any intermediate, thus reducing time and saving money, energy and raw materials. we performed the synthesis of 2-amino-4H-chromenes through a three-component reaction employing yttrium(III) nitrate supported on the silica gel as a catalyst.

A mixture of an appropriate benzaldehyde (1mmol), malononitrile (1mmol), α- or β-naphthol (1mmol) and yttrium nitrate supported on the silica gel (0.04g), in water were refluxed within 1-2h. After completion of the reaction and separation of catalyst, the residual solid was recrystallized to give the substituted 2-amino-4H-chromenes with high to excellent yields. The Products were characterized by physical and spectroscopic data (IR, NMR, etc).



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The effect of titanium dioxide nanoparticles on their physical and thermal properties of heterocyclic polyimides

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Nowadays, polymer-inorganic hybrid materials have become a popular topic in material science because of their unique properties [1-3]. This is related to their diphasic structure, leading to multifunctional materials. However, increasing interest in nano-size systems (ie systems of size range 0.5-100 nm) in recent years seems to be determined both by some distinctive properties of nanoparticles themselves and by anomalous cooperative properties of systems consisting of these moieties [4]. Polyimides (PI)s, which can be prepared from a variety of starting materials by a variety of synthesis routes and posses high thermal stability, high chemical resistance and excellent mechanical properties are a promising candidate type for the matrix of these hybrids [5,6]. The high glass-transition temperature of PIs would be expected to further stabilize the nanoparticles by decreasing their mobility, thereby preventing their agglomeration into large particles. In this study, the titanium alkoxide is incorporated into PI matrix through a simpler process and good quality and well-dispersed PI/titania hybrid films with relatively high titania content are prepared. Moreover, the characteristics of morphology, optical, mechanical, and thermal properties for the hybrid films are also investigated.

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Nano silica phosphoric acid an efficient catalyst for synthesis of tetrahydrobenzo[a]xanthenes-11-one derivatives

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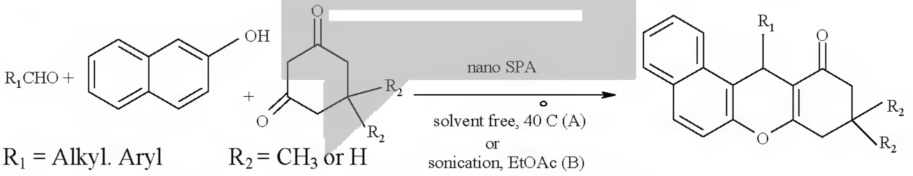
Tetrahydrobenzo[a]xanthenes-11-ones as benzoxanthene derivatives could be synthesized via one – pot condensation of 2-naphthol, aldehyde, and 1,3-diketone in the presence of an acidic catalyst. According to the literature, this protocol was catalyzed by indium(III)chloride [1], proline triflate[2] , p-toluenesulfonic acid [3], strontium triflate [4] , dodecatungstophosphoric acid [5], tetrabutyl ammonium fluoride [6] and $NaHSO_4.SiO_2$ [7].

In this work we hope to describe simple procedures for synthesis of tetrahydrobenzo[a]xanthenes-11-one using efficient and reusable nano silica phosphoric acid under solvent free condition or sonication in ethyl acetate



Simple work-up procedure, reusability of catalyst, short reaction time and high yields are some advantages of these protocols.

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Four component reaction for the synthesis of 2H-indazolo[2,1-b]phthalazinetriones

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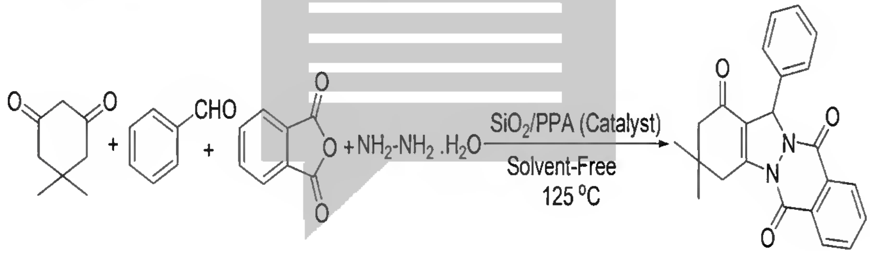
Creation of molecular complexity and diversity [1] from simple substrates, while combining economic aspects [2,3] with environmental ones [4], constitutes a great challenge in modern organic chemistry, both from academic and industrial points of view [5]. Multi-component reactions [6] (MCRs) involving domino processes [7] have emerged as powerful tools to reach this near ideal goal [8]. Looking for novel lead structures of pharmaceutical, catalytic, or even academic interests, we are involved in the development of new MCRs from 1,3-dicarbonyl compounds [9].

In this research, four component reaction between dimedone, aromatic aldehydes, hydrazinium hydroxide, and phthalic anhydride in the presence of PPA-SiO_2 under solvent-free conditions is described (Scheme 1). PPA-SiO_2 can be easily prepared from the reaction of PPA and SiO_2 (0.08 g, 0.04 mmol of H^+) [10]. This thermal solvent-free green procedure offers advantages such as short reaction time, simple work-up, environmental benignity and high to excellent yields.



Scheme 1

References:
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Synthesis of 1-(α-aminoalkyl) naphthols, the Betti bases, catalyzed by DBU under ambient conditions in aqueous media

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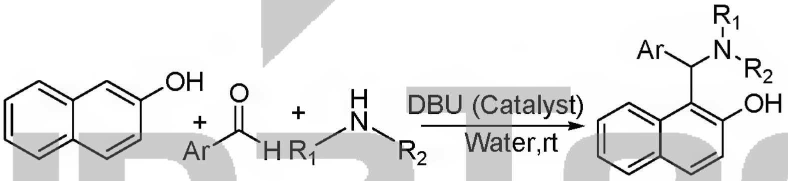
In recent years multi-component reactions (MCR) have become a powerful tool for atom efficient and waste-free synthesis of complex building blocks of 'drug-like' motifs. Generally MCR strategy affords time and cost advantageous, environmentally benign pathways leading to the synthesis of a library of compounds [1].

In this research, we report an efficient and direct protocol for the preparation of 1-(α-aminoalkyl) naphthols, the Betti bases, employing a multi-component, one-pot condensation reaction of 2-naphthol, aromatic aldehydes and amines in the presence of DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene) under ambient conditions in aqueous media (Scheme 1).



Scheme1

This method is devoid of expensive reagents and high temperatures. A wide variety of 1-(α-aminoalkyl) naphthols underwent three component reactions under mild reaction conditions to afford desired products in good to excellent yields.

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THF/Na an efficient mediate for cleavage of diselenide bonds and subsequent one-pot synthesis of organic selenides from alkyl halides.

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Introduction

Organoselenium compounds have been extensively applied in organic synthesis in particular selenol esters have been used in liquid crystals and other selenium derivatives have been investigated in a wide range of pharmacological responses, thus they have been evaluated as anti-inflammatory, anti-atherosclerotic, anti-cancer, anti-microbial and antiviral agents [3].

During the last few decades, cleavage of symmetrical diorganyl-diselenides have received much effort for preparation of selenide anions (RSe^-) and subsequently formation C-Se bond. Chemical cleavage of Se-Se bonds in symmetrical diselenides were achieved with reducing agents such as $NaBH_4$, Na/NH_3, Na/NMP and $LiAlH_4$. Especially, the use of various promoting agents, such as InI,[7] SmI_2, $Zn/AlCl_3$, , and $RhCl(PPh_3)_3/H_2$, $Zn/RuCl_3$, Mg/Cu_2O, $Mg/FeCl_2$, and rongalite have been reported to cleavage of Se-Se bonds and generate the selenide anions [1,2]. However, these reactions require strong base and harsh conditions, reagents with unpleasant odor, expensive and toxic materials, long reaction times, unsatisfactory yields, as well as elevated temperatures in the reactions.

Results and Discussion

In this work, we have explored one-pot method for subsequent synthesis of organic selenides by sodium-promoted cleavage of diphenyl-diselenide and subsequently, condensation with alkyl halides (Scheme 1). Sodium is an attractive, ready available, low price, environmentally friend and often advantageous alternative to other metals in the field of metal-promoted and catalyzed cleavage Se-Se bonds.

$$R^1Se\text{-}SeR^1 \xrightarrow[\text{THF, r.t.}]{\text{Na}} R^1\overset{\ominus}{Se}\ \overset{\oplus}{Na} \xrightarrow[\text{r.t.}]{R^2X} R^1SeR^2$$

(Scheme 1)

In summary, an efficient one-pot protocol was developed for synthesizing alkyl phenyl selenides by using sodium metal. The novel method has the advantages of a simple experimental procedure, mild and neutral reaction conditions, use of relatively non-toxic reagents and solvents, and high yields of the desired products.

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One-pot five-component synthesis of highly substituted piperidines using 1-methyl-2-oxopyrrolidinium hydrogen sulfate ([Hpyro][HSO_4])

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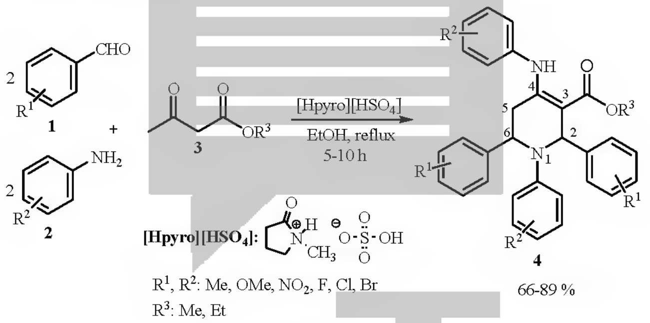
Synthesis of six-membered nitrogen heterocyclic compounds such as piperidine rings is very important because of their pharmacological and biological properties. The piperidines and their analogues exhibited diverse biological activities such as antimalarial [1], anti-hypertensive [2], antibacterial [3], anticonvulsant and anti-inflammatory agents [4]. Owing to the importance of piperidines from pharmaceutical and biological view, introduction of an efficient method for the preparation of these compounds is still in demand. In this work we report an efficient and convenient procedure for the synthesis of highly substituted piperidines via one-pot five-component reaction between aromatic aldehydes, anilines and β–ketoesters catalyzed by 1-methyl-2-oxopyrrolidinium hydrogen sulfate ([Hpyro][HSO$_4$]) in ethanol under reflux conditions (Scheme).



R^1, R^2: Me, OMe, NO$_2$, F, Cl, Br
R^3: Me, Et

Scheme.

Reference

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A simple synthesis of stable phosphorus ylides from reaction between triphenyl phosphine or trimethyl phosphite, acetylenic esters and NH-containing compounds

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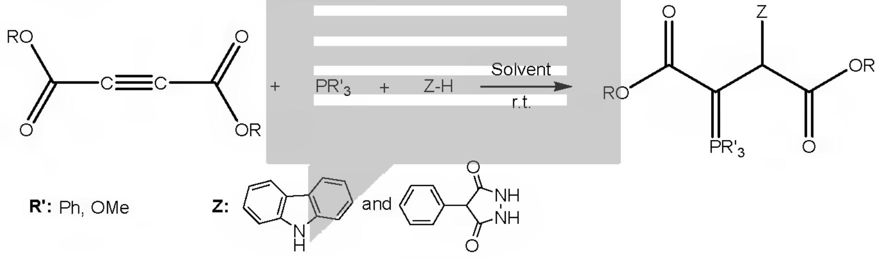
The synthesis of organophosphorous compounds is important in organic chemistry because of the application of these compounds in the synthesis of organic products, especially in the synthesis of naturally occurring products with biological and pharmacological activity [1]. As a result, numerous studies have been previously reported using the reaction between trivalent phosphorus nucleophiles and deficient carbonyl compounds, in the presence of a proton source, such as CH, NH, OH, or SH compounds [2, 3]. In the present work, we describe a mild and efficient protocol for the synthesis of stable phosphorus ylides from the reaction between triphenyl phosphine or trimthyl phosphite, dialkyl acetylenedicarboxylates, and N-H heterocyclic compounds such as carbazole and 4-phenyl urazole (Scheme). All products are stable solids and were characterized by melting point, elemental analyses, IR, ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and Mass spectroscopy.



Scheme.

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Synthesis, Characterization, Properties and Structure of Novel Pinacolophanes

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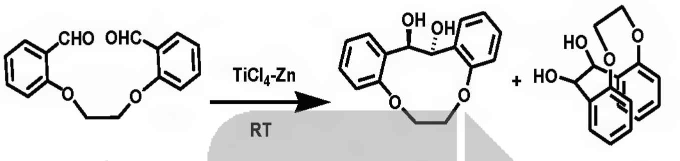
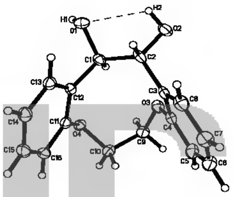
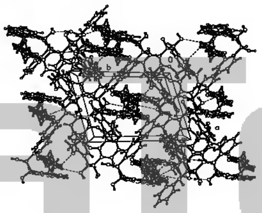
Pinacolophanes **2**, cyclophanes containing pinacol moieties, are of our future interest as both molecular hosts and potential asymmetric ligands for catalytic asymmetric reactions [1].
Here, we report on the synthesis of cis- and trans-pinacolophanes **2**.



1 **trans-2** **cis-2**

As shown in above Scheme, the intramolecular pinacol coupling of **1** with low-valent titanium at room temperature gave a mixture of trans- and cis-isomers of **2**. The stereochemistry of these cyclophanes was determined by NMR spectral data as well as by single-crystal X-ray analysis. The only differences between the ^{1}H-NMR spectra of cis and trans isomers of **2** are that both the aromatic resonances are further downfield and aromatic ranges are larger for trans isomers.
Upon slow evaporation at room temperature of $CHCl_3$–hexane mixtures containing trans-**2**, colorless crystals were obtained after several days and analyzed by X-ray diffraction on single crystals. The molecular structure of trans-**2** was established by X-ray crystallographic analysis.
Intramolecular hydrogen bondings in the crystal structure of the molecules play an important role in holding their configuration, while the intermolecular hydrogen bondings lead to a designed arrangement of the molecules.





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Three-Component One-Pot Synthesis of Novel 4-Aryl-3-methyl-4,5-dihydro-1H-pyrazolo[3,4-b]pyridin-6(7H)-ones without Catalyst

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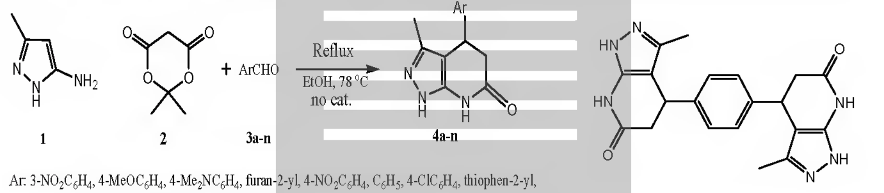
Multi-component reactions (MCRs) in which three or more reactants are brought together in a highly convergent approach to rapidly build up molecular structure and complexity, high atom economy and enviromentaly benign procedures, have occupied a prominent and advantageous position in pharmaceutical and synthetic chemistry [1,2]. On the other hand, pyrazole and its derivatives are key substructures in a large variety of compounds and pyrazole-containing compounds have received considerable attention owing to their diverse biological activities and pharmacological properties, some pyrazoles have been implemented as antileukemic, antitumor and anti-proliferative agents[3-7].

In this report we have devised a novel and efficient three-component one-pot synthesis of a series of novel 4-aryl-3-methyl-4,5-dihydro-1H-pyrazolo[3,4-b]pyridin-6(7H)-ones(**4a-n**) using Classical method with heating in refluxing EtOH without catalyst via the reaction of 5-amino-3-methyl-1H-pyrazole, Meldrum's acid and various arylaldehydes using one-pot three-component approach is described. This rapid method produced the products in short reaction times (1-2 h) and appropriate yields (50–80%).



Ar: 3-$NO_2C_6H_4$, 4-$MeOC_6H_4$, 4-$Me_2NC_6H_4$, furan-2-yl, 4-$NO_2C_6H_4$, C_6H_5, 4-ClC_6H_4, thiophen-2-yl, 2,4-$Cl_2C_6H_3$, 3,4-$(MeO)_2C_6H_3$, 4-FC_6H_4, 4-$^iPrC_6H_4$, pyridin-3-yl, 1,4-phenylene

Bis-pyrazolo[3,4-b]pyridin-6(7H)-one

Scheme 1. Synthesis of 3-methyl-4,5-dihydro 4-aryl- -1H-pyrazolo[3,4-b] pyridin-6(7H)-ones 4a-n.

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Synthesis of novel Spiro [furan-2,11'-indeno[1,2-b]quinoxaline]-3-carboxylate derivatives via a one-pot multicomponent reaction

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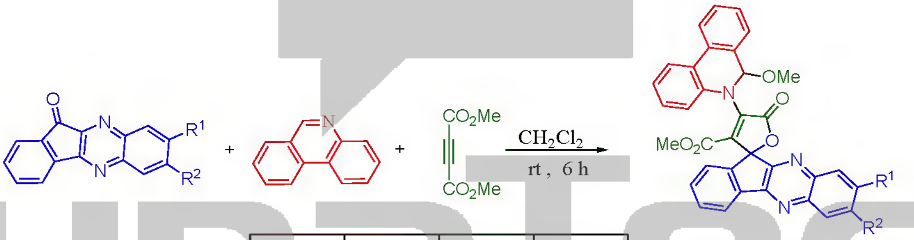
Quinoxaline derivatives are an important group of aza-polycyclic compounds which have many biological and pharmaceutical applications such as antibacterial [1], antifungal [1], antidepressant [2] and antitumor agents [3]. On the other hand spiro compounds represent an important class of naturally occurring substances characterized by highly pronounced biological properties. The spiro functionality has been found to be present in phytochemicals such as alkaloids, lactones, or terpenoids [4]. Multi-component reactions (MCRs) have attracted the attention of synthetic organic chemists for building highly functionalized organic molecules and pharmacologically important heterocyclic compounds [5]. In continuation of our research on the synthesis of quinoxalines[6] and the development of multicomponent reactions, we report herein a one-pot, three component method for synthesis of novel methyl 4-(6-methoxy-7,10-dihydrophenanthridin-5(6H)-yl)-5-oxo-5H- spiro[furan-2,11'-indeno[1,2-b]quinoxaline]-3-carboxylate derivatives from 11H-indeno[1,2-b]quinoxalin-11-one, acetylenic esters and phenanteridine. The structures of compounds were deduced from their mass, IR, ^{1}H and ^{13}C NMR spectra.



Entry	R^1	R^2	Yield(%)
1	H	H	90
2	Me	Me	85

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Synthesis of Novel Substituted 4H-furo[3,4-c]chromen-4-one derivatives

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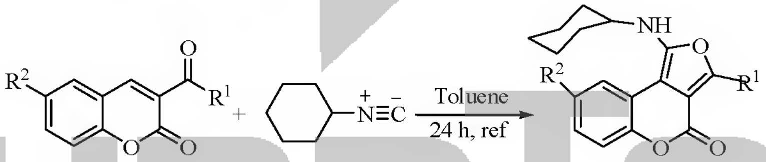
Chromen-2-ones (Coumarins) are very well known for their biological activity.[1] They exist in a variety of forms due to the various substitutions possible in their basic structure which modulate their biological activity.[2, 3] Coumarins possess anti-inflammatory, antioxidant, anti-allergic, hepatoprotective, antithrombotic, antiviral, antimicrobial, and anticarcinogenic properties. Moreover, the function of plant growth and growth regulators depends on them, as well as the control of respiration, photosynthesis and defense against infection.[4, 5] Furochromen-2-ones (furocoumarins), tricyclic systems in which a furan ring is fused to the chromen-2-one unit, are of particular interest since they exhibit potent biological and pharmacological activity.[6-7] Although several methods of synthesis are presently known,[8,9] new approaches for the rapid and selective construction of furochromen-2-one scaffolds are still highly desirable. Herein we report, a facile method for the synthesis of a novel class of 4H-furo[3,4-c]chromen-4-one derivatives from 3-acetyl-2H-chromen-2-one and cyclohexylisocyanide. The structures of compounds were deduced from their mass, IR, ^{1}H and ^{13}C NMR spectroscopic data.



R^2=H, Br
R1=Me, Ph

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A simple method for the synthesis of functionalized 6H-Benzo[c]chromen-6-ones by reaction of 2-oxo-2H-chromenes-3-carbonitrile and phenylethylidene malononitrile

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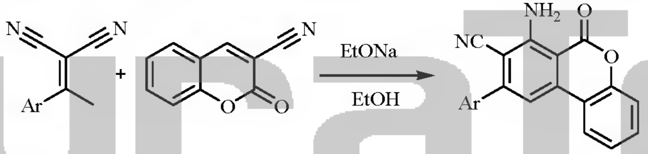
Benzo[c]chromen-6-ones (biaryl lactones) are of considerable pharmacological relevance and occur in various natural products, such as autumnariol, autumnariniol, alternariol, altenuisol, ellagic acid, or coruleoellagic acid.[1,2] 6H-Benzo[c]chromen-6-one is a common core structure existing in various natural products, as well as many pharmaceutical compounds, such as families of graphislactones and chrysomycins.[3] Polysubstituted chromene derivatives are very important heterocyclic compounds that frequently exhibit a variety of biological activities.[4] These activities include anticancer,[5] anticoagulant,[6] and fungicidal activities.[7] They are also find applications as pigments and potential biodegradable agrochemicals. Because of their usefulness, the synthesis of these compounds has attracted a lot of interests.[8] 6H-Benzo[c]chromen-6-ones have been prepared by cyclization reactions of 1,3-bis (silyloxy)-1,3-butadienes.[9] Because of their usefulness, continuous efforts have been devoted to the development of versatile synthetic methodologies for this class of compounds. Herein, we report an efficient method for the construction of 6H-Benzo[c]chromen-6-one derivatives using 2-oxo-2H chromenes-3-carbonitrile and phenylethylidene malononitrile in the presence of EtONa in Ethanol as a solvent. The structures of the products were deduced from their IR, mass, ^{1}H NMR, and ^{13}C NMR spectra.



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Preparation of a Novel Chiral Composite by Doping of Poly[(±)-2-sec-butylaniline] Base with Silica Sulfuric Acid under Solid-State Condition

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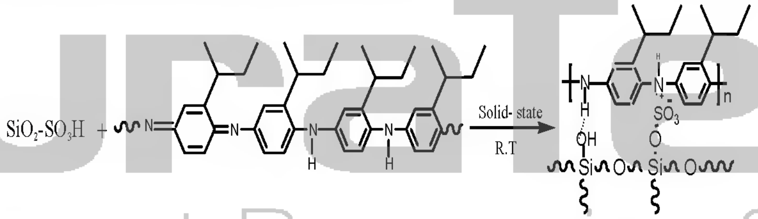
Polyaniline (PANI) is one of the important conducting polymers. The stability of polyaniline is a key factor in most of its applications and can be assessed from various viewpoints. Major limitations of using polyaniline are insolublity of polyaniline in the most organic solvents. Solubility of polyaniline in the organic solvents increase by substituents such as alkyl chain, alkoxy group and polar substituted. Thus, the substituted polyaniline has attracted attention of many of the researcher [1]. Doped PANI by polymeric acids such as poly(acrylic acid) and poly(styrene sulphonic acid) greatly increases chemical stability and preserves the electrical conductivity of a material and showing improved solubility and process ability [2]. In recent years, there has been increased interest in synthesizing chiral conducting polymers mainly because of their potential applications in chiral separations, surface-modified electrodes, as well as chemical and biological sensors. Chiral PANI and its derivatives were synthesized usually by either codissolving PANI and a chiral acid in common solvents or by polymerizing aniline in the presence of a chiral acid [3].
Herein we wish to report a new application for solid acids such as silica sulfuric acid (SSA) [2-4]. In this work poly[(±)-2-sec-butylaniline] base was doped with SSA in solid-state to preparation of the composite. SSA acts as primary (solid acid) and secondary dopant. The composite was characterized by FT-IR, UV-Vis and conductivity measurements. SEM was done to study the morphology of composite.



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$FeNH_4(SO_4)_2.12H_2O$ A Reusable Catalyst for Synthesis of some New 2-Amino-4H-pyrans derivatives

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Several improved procedures for the preparation of 4*H*-pyrans have been reported. Various catalysts such as acetic acid, Basic quaternary ammonium salt, $RE(PFO)_3$, and s-proline have been used for this reaction.[1]

In view of our general interest in the multi-component condensations (MCCs),[2] we report herein, a simple, facile, rapid and efficient MCRs for the preparation of some new 2-Amino-4*H*-pyrans derivatives with $FeNH_4(SO_4)_2.12H_2O$(alum), as a nontoxic, inexpensive, and easily available reagent.

When a mixture of dimedone 1, aldehyde 2, active hydrogen compounds 3 (malononitryle, ethyl and methyl cyanoacetate), 5 mL ethanol 96% and $NH_4Al(SO_4)_2.12H_2O$ was heated with stirring at 80 °C. After completion of the reaction (TLC, ethyl acetate / n-hexane, 1/1), the crude product was recrystallized from ethanol.All products were characterized by ^1H, ^{13}C NMR, IR, M.S. and elemental analyses.

Scheme 1

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Multicomponent reactions of ammonium acetate, triphenylphosphine, acetylene esters and arylglyoxals for the synthesis of pyrrole derivatives

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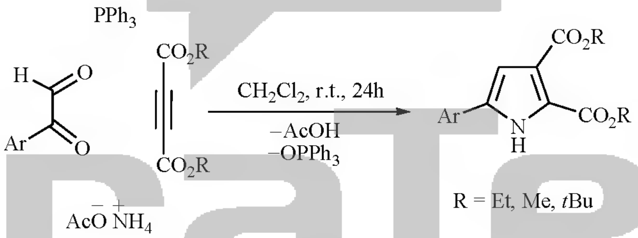
Pyrrole is one of the most important simple heterocycles, which is found in a broad range of natural products and drug molecules, and is also of growing relevance in materials science. The pyrrole nucleus is widespread in nature, and, as previously mentioned, is the key structural fragment of heme and chlorophyll, two pigments essential for life [1-3].

Recently, significant attention has been paid to the multi component reactions for the synthesis of nitrogen-containing heterocycles. Multicomponent reactions lead to the connection of three or more starting materials in a single synthetic operation with high atom economy and bond-forming efficiency, thereby increasing molecular diversity and complexity in a fast and often experimentally simple fashion. For this reason, multicomponent reactions are particularly well suited for diversity-oriented synthesis, and the exploratory power arising from their conciseness makes them also very powerful for library synthesis aimed at carrying out structure–activity relationship (SAR) studies of drug-like compounds, which are an essential part of the research performed in pharmaceutical and agrochemical companies [4-6].

In this work, we study the reaction between triphenylphosphine, dialkyl acetylenedicarboxylate, ammonium acetate and arylglyoxals, which leads to N-unsubstituted pyrroles (Scheme 1).



Scheme 1.

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Microwave-assisted deprotection of sulfonamides under heterogeneous conditions

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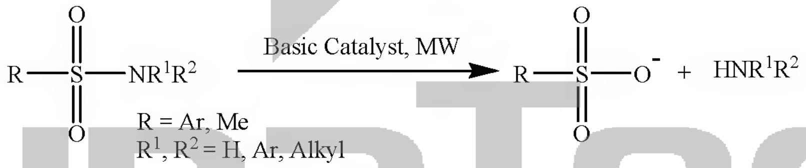
Sulfonamides are important pharmaceutical compounds and many drugs containing these functionality are in clinical use as antibacterials, diuretics, anticonvulsants, hypoglycemics and HIV protease inhibitors [1]. Sulfonamides are also stable derivatives of amines which frequently used as versatile intermediates in organic synthesis. Due to the stability of sulfonamide bond, its removal needs to the harsh basic reaction conditions which is problematic for the other present functional groups in the molecule and often results in the formation of undesired side products.

Recently, a number of modified procedures have been developed for desulfonylation of sulfonamide using sodamide, Bu_3SnH, SmI_2, $TiCl_4/Zn$, $Sc(OTf)_3$, BCl_3 and Mg/MeOH. Available methods are limited and often require harsh conditions such as a strong acid or more commonly TFA, long reaction times, and occasionally reflux conditions. However, some limitations restrict the applicability of these procedures and hence searching a new method that serves the selective and efficient deprotection of sulfonamides should is of interest. [3-5].

In this work, we report a new efficient protocol for the deprotection of sulfonamides using microwave irradiation and a heterogeneous catalyst under solvent-free conditions (Scheme 1). Carrying out of this reaction with heterogeneous supported catalyst led to the advantages such as cleaner reaction, easy work-up, high yields and high selectivity.



Scheme 1.

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Preparation, Characterization and First Application of Silica Supported Acidic Ionic Liquid as a Reusable Catalyst for the Synthesis of 2-aryl-2,3-dihydroquinazolin-4(1H)-ones under solvent-free conditions

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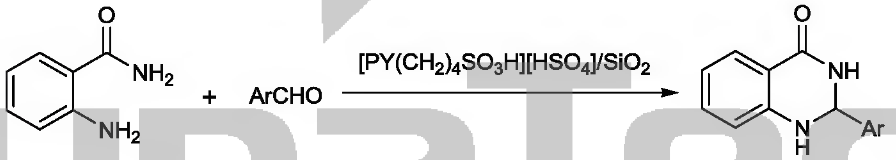
Quinazolin-4-ones are an important class of heterocycles with a wide range of pharmacological and biological activities.[1,2] Various methods have already been proposed for the synthesis of these compounds[3] and the most general ones involves cyclocondensation of anthranilamides with aldehydes in the presence of various promoting agents, such as $Sc(OTf)_3$,[4]p-toluenesulfonic acid/DDQ,[5] I_2/KI in water,[6] $CuCl_2$ in ethanol[7] and $KMnO_4$ under microwave irradiation.[8] Many of these methodologies, however, suffer from disadvantages such as unsatisfactory yields, expensive catalysts, long reaction times, toxic organic solvents, and harsh reaction conditions.

In this work, a new route to the synthesis of 2-aryl-2,3-dihydroquinazolin-4(1H)-ones has been developed through heterocyclization of 2-aminobenzamide with aromatic aldehydes in the presence of $[PY(CH_2)_4SO_3H][HSO_4]/SiO_2$ as a new solid acid supported catalyst. The present methodology offers several advantages, such as a simple procedure with ease of handling, short reaction time, high yields, and the absence of any volatile and hazardous organic solvents.



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Piperazinium Triflate (PT): a novel and efficient catalyst for the synthesis of benzimidazoles

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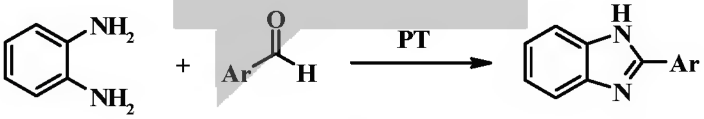
Benzimidazoles are important natural and non-natural heterocyclic compounds, due to their wide range of pharmacological activity, industrial and synthetic applications. Many strategies are available for benzimidazole synthesis [1,2]. Several methods have been reported in the literature for the synthesis of benzimidazole and its derivatives. While many published methods are effective, some of these methods suffer from one or more disadvantages. We thought that there is scope for further innovation towards milder reaction conditions, short reaction time, and better yields. In view of the emerging importance of PT as novel and recyclable reaction media, we wish to report the use of PT as an efficient promoter for the mild and facile synthesis of benzimidazole derivatives (Scheme 1).



Scheme 1.

In this study, 2-substituted benzimidazoles are selectively synthesized by reacting aryl-1,2-diamines with aromatic aldehydes using catalytic amount of PT under optimized conditions. The reaction of o-phenylendiamine with benzaldehyde was used as a model reaction. To study the scope of this method, a series of aldehydes and phenylendiamine derivatives were applied. All the products were characterized by ^{1}H and ^{13}C NMR spectra, melting point and comparison with authentic samples.

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Synthesis and characterization of new polyimides containing tetraaryl imidazole pendent groups

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A new polymerization in the anhydride acid has developed for the one- step synthesis of polyimides from various diamines and dianhydrides. Aromaeic polyimides containing side tetraaryl imidazole pendent groups have been synthesized by low temperature solution polycondensation of certain aromatic dianhydrides with aromatic diamins containing preformed side tetraaryl imidazole pendent groups followed by chemical imidizatin at room temperature in the presence of pyridine and acetic anhydride.

The preliminary studies on some of the polymerization variables (e.g., concentration and time) suggest that the Imidization is very fast and the chain growth is likely to proceed via the addition of the growing imide segments.

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One-Pot Synthesis of 2-Arylbenzimidazole, 2-Arylbenzothiazole and 2-Arylbenzoxazole Derivatives Using Cobalt(II)-Salen Complex

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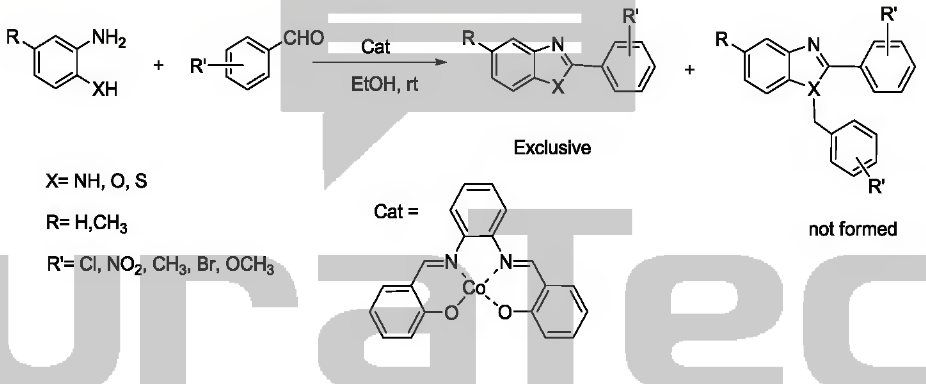
The efficient synthesis of 2-arylbenzimidazole, 2-arylbenzothiazole and 2-arylbenzoxazole derivatives are described by condensation of aryl aldehydes and o-phenylenediamines, 2-aminothiophenol and 2-aminophenol in a single pot using a catalytic amount of cobalt(II)-salen complex (5.0 mol%) in excellent isolated yields. Benzo-fused heterocyclic systems such as benzimidazole, benzothiazole, and benzoxazole derivatives are present in natural products and in synthetic pharmaceutical and agrochemical compounds [1-3]. These compounds have been extensively studied due to their wide ranges of application, e.g., biological and therapeutic activities (such as an anticancer agent [4], an orexin-1 receptor antagonist [5], a HIV reverse transcriptase inhibitor [6], to name just a few). In this study, we report a practical synthesis of 2-arylbenzimidazoles starting from o-phenylenediamines and aldehydes under an air atmosphere in the presence of a catalytic amount of salen cobalt (II) at room temperature .The method is simple, the condition is mild and the yields are high and regioselective.



Scheme 1

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Synthesis of Some New Imidazoles Derivatives Via Amidine Intermediate

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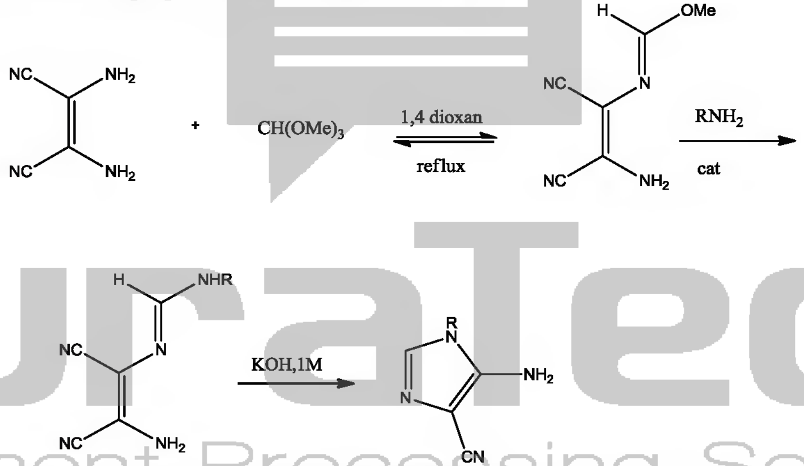
As an important member of the five-membered ring heterocycles,imidazole moiety is present in a wide range of naturally occurring molecule.Compounds with imidazole moiety have many pharmaceutical activities.The biological importance of the imidazole ring system has made it a common structure in numerous synthetic compounds,such as fungicides,herbicides,plant growth regulators and therapeutic agents.[1]

In this project we want to synthesized imidazole by means of amidine and different amines.

Imidazole derivatives can obtain by three steps reactions.First, we synthesized imidate from reaction of DAMN and trimethyl orthoformate.Then the reaction of imidate with appropriate amine afforded to amidine.Finally, cyclization amidine in presence of base prepared imidazole derivatives. [2]



The structures of all compounds were confirmed by FT-IR, ^{1}H-NMR and ^{13}C-NMR.

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Copper(I)-catalyzed synthesis of 1,3-enynes via coupling between vinyl halides and alkynes under ligand-free conditions

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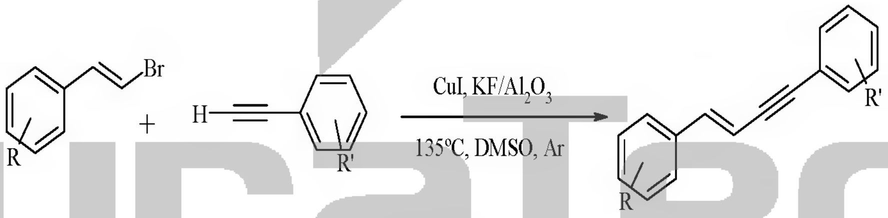
The 1,3-enyne is a core structure of various natural products or designed pharmaceutical molecules[1]. A variety of methods reported for the synthesis of 1.3-enyne including, Pd/Cu, Cu, Fe catalyzed Sonogashira coupling between terminal alkyne and vinyl halide[2], metal-catalyzed couplings between a terminal alkyne and an organometallic alkene (B, Sn, Te, Al, Cu, Zr) and coupling reaction between an alkene and an alkynylmetal (Mg, Cu, Zn, Si, Sb, Sn)[3]. Although most of these methods are useful for the synthesis of 1,3-enynes, a convenient and efficient method is required to overcome the problems in them, which involve the long reaction times, use of toxic and expensive ligands or metals and difficulty to prepare of this reagents [4].

Herein we report a mild procedure for the synthesis of different 1,3-enyne in high yields using KF/Al2O3 as base, CuI as catalyst in DMSO as solvent at 135°C and under ligand free conditions. All products were characterized well with 1H and 13C NMR spectra and melting points by comparison with authentic samples (Schem 1.).



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Synthesis of 3,4-dihydropyrimidine-2(1H)-ones and thiones catalyzed by nano-structured Fe_2O_3 in solvent-free conditions at room temperature and microwave irradiation: a green protocol

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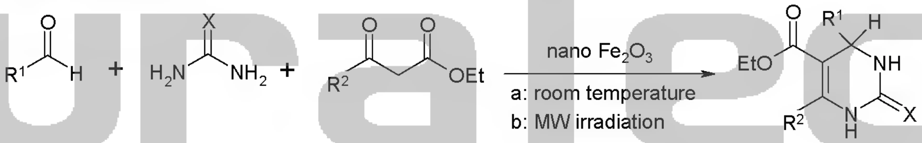
Dihydropyrimidinones and their derivatives are well known heterocyclic units in the realm of natural and synthetic organic chemistry due to their wide spectrum of biological and therapeutic properties such as antibacterial, antiviral, antitumor and anti-inflammatory activities [1, 2].

In recent years several methods for the synthesis of DHPMs have been developed to improve and modify this reaction [3-5]. However, in spite of their potential utility, many of these reported one-pot protocols suffer from drawbacks such as the use of expensive reagents, strong acidic conditions and long reaction times. Therefore, to avoid these limitations, the introduction of a milder and more efficiently methods accompanied with higher yields are needed.

Nanoscale heterogeneous catalysts are highly preferred as they offer high surface area and low-coordinated sites, which are responsible for the higher catalytic activity, having the advantage of easy product purification and reusability of the catalyst [6, 7].

There are no reports on the use of Fe_2O_3 nanoparticles for a three-component synthesis of 3, 4-Dihydropyrimidine-2(1H)-ones and thiones. The present study can be considered as the green protocol for synthesis of 3, 4-Dihydropyrimidine-2(1H)-ones and thiones at room temperature.

The magnetically recoverable iron oxide nanoparticles are found to be more efficient for the synthesis of 3, 4-Dihydropyrimidine-2(1H)-ones by means of a three component coupling (3CC) of aldehyde, β-ketoester, urea or thiourea. The salient features are short reaction times, high conversions, solvent-free reaction conditions, and the use of easily recyclable catalyst without loss of considerable catalytic activity. This method is applicable for a wide range of substrates. Various reaction parameters are optimized for this reaction, for example: Recycling of nano-Fe_2O_3, influence of solvent and catalyst concentration. This reaction was done in two conditions: 1: at room temperature; 2: with using microwave irradiation.



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Reaction of isocynides with actived acetylenes in the presence of n-formyluea

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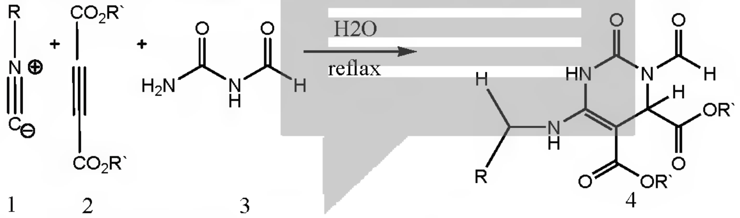
Introduction

Isocynides are only class of stable organic compounds with a formally divalent carbon. Owing to its reactivity the isocynide group differs fundamentally from other functional groups[1]. One of the classic themes in the chemistry of isocyanides is heterocyclic synthesis. Multi-component reactions (MCRs), by virtue of their convergence,facile execution, and generally high yielde of products,have attracted much attention from the point of combinatorial chemistry.of pivotal importance in this area are the isocyanide based MCRs such as the versatile Ugi and Passerini reactions [2].

Result and discussion

Cyclohexyl isocyanide (1) and dimithylacetylene dicarboxylate (2) undergo a smooth reaction in the presence of n-formylurea (3) , in water at reflax to produce dimethyl 6-(cyclohexylamino)-3-formyl-1,2,3,4-tetrahydro-2- oxopyrimidine-4,5-dicarboxylate (4) in 82%yield (scheme1).



1 2 3 4

Materials and methods

All of chemical materials used in this work were purchased from Merck and used without further purification. Melting points were measured on an Electrothermal 9100 apparatus. NMR spectra were recorded with a Bruker DRX – 300 AVANCE instrument (300.1 MHz for ^{1}H and 75.4 MHz for ^{13}C) with $CDCl_3$ as solvent . Chemical shifts are given in ppm relative to internal TMS , and coupling constant (J) are reported in Hertz (Hz) . The IR spectra were recorded in KBr on a Bruker – Tensor – 27 spectrometer. Mass spectra were recorded with a Finnigan – Matt 8430 mass spectrometer operating at an ionization potention of 70 eV.

General procedure

To a stirred solution of n-formylurea (1mmol) in water reflax in 90° C was added dialkylacetylene dicerboxylate (1mmol) and isocyanide(1mmol) . The reaction mixture was then stirred for 24 h in reflax condition. After one day organic phase created in water phase which it separated with decantor.

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Molybdate sulfuric Acid (MSA) catalyzed of 2-Aryl-3- amino benzofuran Derivatives by a Three-component Reaction of Arylglyoxal monohydrates , Banzamide and β- Naphtol

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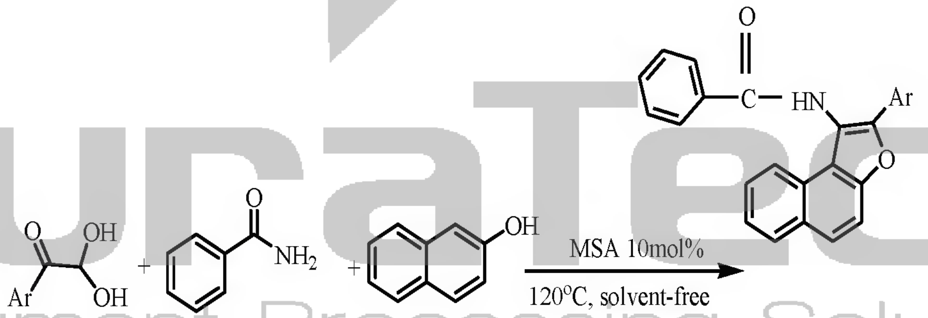
Benzofuran derivatives are a major group of biologically active heterocycles, which are usually important constituents of plant extracts used in medicinal chemistry for their various biological activities [1].For examples, they are active as inhibitors of 5- lipoxygenase, antagonists of the angiotensin II receptor, blood coagulation factor xa inhibitors, ligands of adenosine A_1 receptor, and potent platelet aggregation inhibitors [2].

A solvent-free or solid state reaction obviously reduce pollution, and help to decrease costs due to the simplification of experimental procedure, work up technique and saving in labour. Interest in the environmental control of chemical processes has increased remarkably during three decades ago (over the past three decades) as a response to public concern about the use of hazardous chemical materials. Therefore, to improve the effectiveness of this method in preventing chemical waste, it is important to investigate optimal reaction conditions [3].

In continuation of our recently studies [3] on the application of inorganic solid acid, in these works we present molybdate sulfuric acid (MSA) as a new solid acid to catalytic synthesis of 2-Aryl-3-amino benzofurans in good to excellent yields, using the starting materials arylglyoxal monohydrats , β-Naphtol and benzamide.



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Synthesis of Fluorescein Aromatic Esters and Their Hydrolysis Studies in the Presence of Lipase

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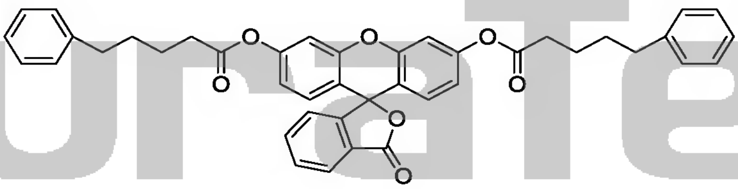
The synthesis of xanthenes has attracted the attention of organic chemists due to their wide range of biological and therapeutic properties [1]. Due to their importance, the discovery and introduction of new methods for the synthesis of novel xanthene derivatives have been under attention. fluorescein esters can to use for examination activity of lipase. First time Guilbault successfully established the fluorometric method for the estimation and detection of lipase using a series of fluorescein esters with 2-18 carbon chains [2-4]. Recently, we synthesdize a series of aromatic esters of fluorescein, and also studied their spontaneous and enzymatic hydrolysis [5].
Considering the above reports, we wish to report the synthesis of a series of aromatic esters of fluorescein, and also study their spontaneous and enzymatic hydrolysis.

A series of fluorescein aryl esters were synthesized by the esterification of fluorescein with carboxylic acids in the presence of DCC and their hydrolytic properties were investigated. The rate of hydrolysis in the presence or absence of lipase, due to the increase of fluorescein concentration, was measured by monitoring of fluorescence of the solution and correlated with enzyme activity. In addition, the chain length effect of aralkyl fluorescein esters was studied. Fluorescein bis(5-phenylvalerate) was found to be better substrate than their homologs for the fluorometric assay of lipase with the higher rate of hydrolysis and better K_m value.



Fluorescein bis(5-phenylvalerate)

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New Sequential Ugi/Click Reaction for the Synthesis of Functionalized Pseudopeptides

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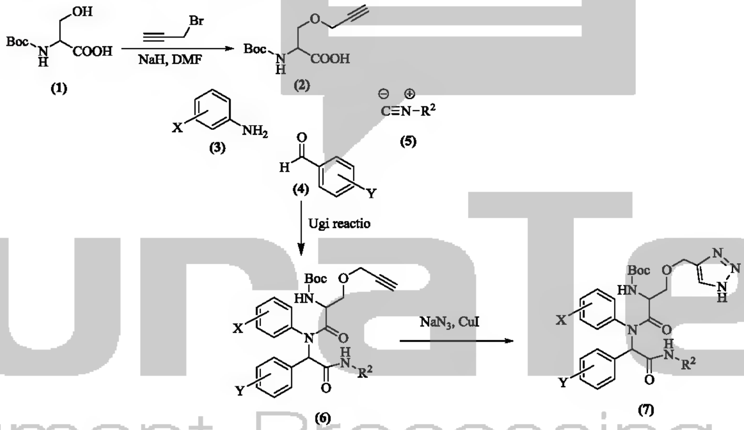
Multi-component reactions have huge potential for the rapid generation of small molecules libraries. However, there is a continuous need for designing and carrying out the reactions with novel starting materials in organic synthesis [1]. Ugi-4CR based on isocyanide is an efficient approach for the synthesis of structurally functionalized diverse complex molecules and they could supply the feedstock for advanced research in chemical biology [2].
In this approach, we would like to introduce protected *N-tert*-butoxy carbonyl *O*-propargylated -*L*-serine **(2)** as a starting material in Ugi-4CR.
Reaction of *N*-tert- butoxy carbonyl *O*-propargyl -*L*-serine **(2)**, aromatic aldehyde **(4)**, primary amines **(3)**, and isocyanides **(5)** leads to synthesis of pseudopeptide **(6)** which could be used for click reaction with Natrium azide in the presence of cuprous iodide. The existence of acetylenic moiety in the structure of product could add the huge potential for the synthesis of new small library.



Scheme1: Synthesis of functionalized pseudopeptide

Key word: pseudopeptide, Ugi/click reaction, *N-tert*- butoxy carbonyl *O*-propargyl -*L*-serine.

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Characteristics of nano-crystalline zeolites beta synthesized with various organic templates

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The aim of this work was to study the effect of organic templates on the size, shape and physicochemical properties of zeolite beta. Nano-crystalline zeolites beta were synthesized in the presence of alkali media with similar Si/Al ratio using various organic templates (Tetra-Ethyl Ammonium Hydroxide (TEAOH),Tetra-Propyl Ammonium Bromide (TPAB),Tetra-Methyl Ammonium Bromide (TMAB), Di-ethylenetriamine (DETA), ethanol (ETL), and with no template (NT) present) under hydrothermal conditions at 150 °C. The precursor gels had the molar compositions: $1SiO_2$: $0.02Al_2O_3$: 0.35 Template: 0.154 Na_2O: $3H_2O$. Colloidal Silica was added to a mixture of comprising aqueous solution of template and NaOH pellets with vigorous stirring for 30 minute to form a clear gel. Then an aqueous solution containing $Al_2(SO_4)_3$ were added to the mixture. Ethanol formed during hydrolysis was evaporated resulting in a viscous gel, which was aged under stirring at room temperature for 24 h. Hydrothermal treatment of nucleated gel was carried out in a stainless steel autoclave with Teflon cup (75 mL) for 48 h at 150 °C under autogenous pressure. The resulting solid product was filtered and washed with deionized water until the pH of filtrate was less than 9, obtained. The solid was dried at 110 °C for 10 h. The samples were characterized by XRD, SEM, and BET surface area measurements. The SEM results revealed that the synthesized zeolites with different templates had different morphology and particle size. Powder X-ray diffraction showed sharp and broad reflections corresponding to those for zeolite beta synthesized with TEAOH and DETA. XRD patterns indicated the amorphous nature of samples synthesized with TPAB, TMAB, ETL, and NT. The results of XRD and BET are shown in the Table1.

Table 1 Surface area and Crystal Size by XRD for synthesized samples

Type of template	Crystal Size by XRD (nm)	BET surface area (m^2/g)
TEAOH	36.16	57.82
TPAB	77.26	—
TMAB	81.42	—
DETA	31.16	1.92
ETL	97.79	5.45
NT	69.81	—

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Palladium-catalyzed Mizoroki–Heck coupling reaction using arylphosphite ligand contain imino functional groups

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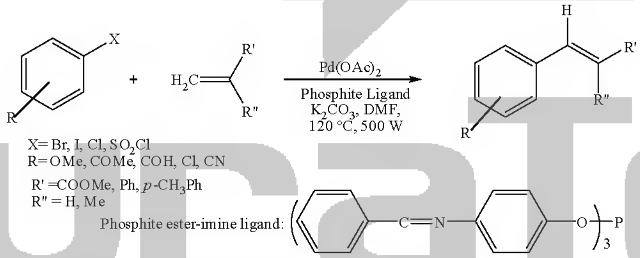
Pharmaceutical Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan 84156, IR Iran

Among the palladium catalyzed transformations, Mizoroki–Heck reaction is one of the most powerful cross coupling reactions for the synthesis of functionalized aryl-alkenes [1]. Mizoroki–Heck reaction's activity is highly dependent on the nature, electronic and steric effect of the ligand. Therefore, most studies have focused on the development of efficient ligands to obtain high catalytic activity. Sterically bulky and electron-rich mono and diphosphines [2], cyclometalated phosphines [3] and phosphine-free ligands such as *N*-heterocyclic carbenes [4] showed high activities in the cross-coupling reactions. Phosphine ligands suffer some drawbacks such as sensitivity to air or moisture and requirement for an inert environment for carrying out the reaction [5], and most of the *N*-heterocyclic carbene ligands must be synthesized through multi-steps [6]. Sterically hindered phosphite ligands are less expensive and more stable to air and moisture than phosphine ligands [7]. All phosphites, which were employed in transition metal-catalyzed transformations, have been more widely used as anti-oxidants.
In this report, an efficient, stable and non-sensitive to air and moisture catalytic system based on palladium- Schiff base tri-ester phosphite [8] for the Mizoroki–Heck reaction of various aryl halides and also arenesulfonyl chlorides with different coupling partner alkenes is described under microwave irradiation (Scheme 1). The products were produced in excellent yields and short reaction times using palladium acetate and tris (parabenzylidine amino phenyl) phosphite with 1:2 ratios in DMF at 120 °C and 500 W.



Scheme 1. The Heck cross-coupling reaction of aryl halides with different olefines

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Suzuki–Miyaura coupling reaction using Pd(OAc)$_2$/arylphosphite ligand contain imino functional groups

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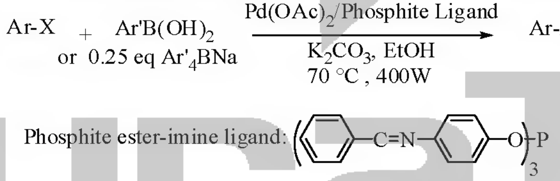
Among the palladium catalyzed-transformations, the Suzuki-Miyaura coupling is one of the most utilized synthetic methods for the production of biaryl compounds. The key benefits of the Suzuki-Miyaura coupling are the mild reaction conditions, commercial availability of organoboron reagents, and removal of the nontoxic boron-containing byproducts [1-2]. The Suzuki–Miyaura reaction usually is mediated by a palladium–phosphine complex as a catalyst. Most research has developed to obtain high catalytic activity with efficient ligands. Generally, sterically bulky and electron-rich phosphine ligands showed high activities in the cross-coupling reactions [3]. Moreover, a number of important studies have focused on the development of phosphine-free ligands such as N-heterocyclic carbenes [4]. Phosphine ligands suffer some drawbacks such as sensitivity to air or moisture and requirement for an inert environment for carrying out the reaction [5]. Although carbene-type ligands are more stable than alkyl phosphines, they must be synthesized through multi-steps [6] In contrast to the phosphines, phosphite ligands are less expensive and more stable to air and moisture [7]

In this report, an efficient, stable and non-sensitive to air and moisture catalytic system based on palladium- Schiff base tri-ester phosphite for the Suzuki-Miyaura reaction of various aryl halides with aryl boronic acids and sodium tetraphenylborate is described under microwave irradiation (Scheme 1). Schiff base tris(parabenzylidine amino phenyl) phosphite as an efficient and stable ligand [8] exhibits good activity in this palladium catalyzed cross-coupling reaction. This catalytic system in ethanol as microwave-active polar solvent at 70 °C and 400 W, led to C-C bond formation in short reaction times and corresponding products were produced in good to excellent yields.



Scheme 1. The Suzuki cross-coupling reaction of aryl halides

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Preparation of lactones via Wittg reaction

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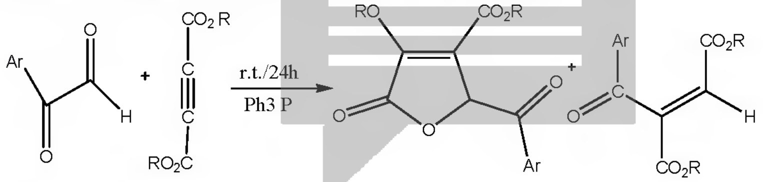
ABSTRACT

The reaction between dimethylacetylenedicarboxylate and various arylglyoxals in the presence of triphenylphosphine leads to unsaturated γ-butyrolactone derivatives and highly substituted enones in fairly good yields at room temperature.

Intrudoctin

Among the methods available for heterocyclic synthesis , the generation of 1,3-dipolar species and their trapping by suitable π systems leading to five – membered heterocycles occupies a prime position[1]. Zewitterionic species often result from addition of nucleophiles to activated alkynes. Triphenylphosphine (Ph_3P) has been the most studied nucleophilic species. Unsaturated γ-butyrolactones or butenolides are important structural units in natural products [2]. There has been considerable effort on the synthesis of these compounds due to discovery of many naturally occurring cytotoxic or antitumour agents containing this structural unit .

The one-pot three-component reactions of arylgltoxals **1** with dialkyl acetylenedicarboxylates **2** in the presence of Ph_3P proceeded spontaneously at room temperature in CH_2Cl_2 and were complete with in 24h. The ^1H and ^{13}C NMR and IR and mass spectra of the reaction mixtures clearly indicated the presence of two products,namely,the unsaturated γ-butyrolactone **3** and highly substituted enone **4** (scheme**1**).



1 2 3 4

Scheme1

Result and discussion

The reaction of DMAD with arylglyoxal in the presence of Ph_3P at room temperature in CH_2Cl_2 was complete with in 24 houres and products accept in the good yields.

Typical procedure for the preparation of methyl 2,5-dihydro-4-methoxy-2-(benzoyl)-5-oxofuran-3-carboxylate (3) and dimethyl 2-(benzoyl)-butenedioate (4): To a stirred solution of arylglyoxal(1mmol) and triphenylphosphine(1mmol) in CH_2Cl_2 (10ml) was added dimethyl acetylendicarboxylate(1mmol) in CH_2Cl_2 ,at room temperature, over 10 min via a syringe. The reaction mixture was stirred at room temperature for 24h.The solvent was removed under reduced pressure and the residue was purified by column chromatography (Merck silica gel 60,70-230 mesh) using hexane/EtOAC (8:2) as eluent.

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Preparation of 12-Aryl 8-9-10-12-tetrahydro benzo[a]xanthen-11-one catalyzed using L-Proline

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Xanthenes and benzoxanthenes are a key structural element of many biologically active compounds such as antibacterials [1], antivirals [2], antiinflammatoryagents [3] and in photodynamic therapy.[4] Thus, the synthesis of benzoxanthenes currently is of great interest. Various methods have been reported for the synthesis of xanthene derivatives including the reaction of 2-naphthol with aldehyde derivatives and dimedone.[5] Over, these methods have many disadvantages such as low yields, the need for a prolonged reaction time, the use of toxic organic solvents, excess reagents and harsh reaction conditions. [6] Thus, development of a new procedure for the synthesis of dibenzoxanthene derivatives would be highly desirable.

In summary, we have described an efficient and mild method for the preparation of 12-Aryl-8-9-10-12-tetrahydrobenzo[a]xanthen-11-one using 2-naphthol, aryl aldehydes and dimedone using L-Proline catalyst and in EtOH at room temperature condition (Scheme 1).

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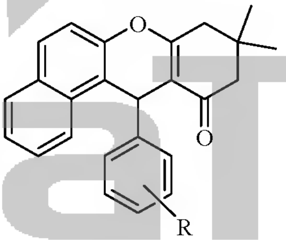

Scheme 1

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Solvent-free multicomponent reaction of methyl propiolate and malonyl dichloride in the presence of primary amins: Synthesis of 2-pyridones

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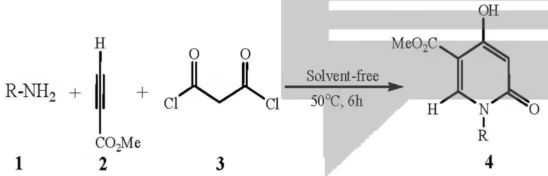
Abstract: The 2-pyridone core structure is an important heterocyclic framework that can be found in numerous biologically active compounds. It is also a versatile synthon that can be further transformed to pyridine, piperidine, quinolizidine, and indolizidine alkaloids [1]. N-Alkylated 2-pyridones are important intermediates in the synthesis of polycyclic compounds because of their biological significance [2]. The broad range of applications of the 2-pyridone structural motif has resulted in several synthetic methods [3]. Here, we describe an efficient synthesis of functionalized 2-pyridones via the reaction of alkyl amines **1** with methyl propiolate **2** in the presence of malonyl dichloride **3** under solvent-free conditions at 50°C (see the following Scheme).



1, 2, 4	R	Yield (%) of 4
a	Bn	92
b	4-Me-C_6H_4-CH_2	90
c	4-MeO-C_6H_4-CH_2	87
d	4-Cl-C_6H_4-CH_2	89

The structures of compounds were apparent from the ^{1}H NMR, ^{13}C NMR and IR spectra which are in agreement with the proposed structures. In conclusion, we have described a convenient route to 2-pyridones, from malonyl dichloride and methyl propiolate in the presence of primary amines. The advantage of the present procedure is performing the reaction under solvent-free conditions by simple mixing of the starting materials.

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Synthesis of Benzoxazines, Benzothiazines and Quinoxalines in Ionic Liquids

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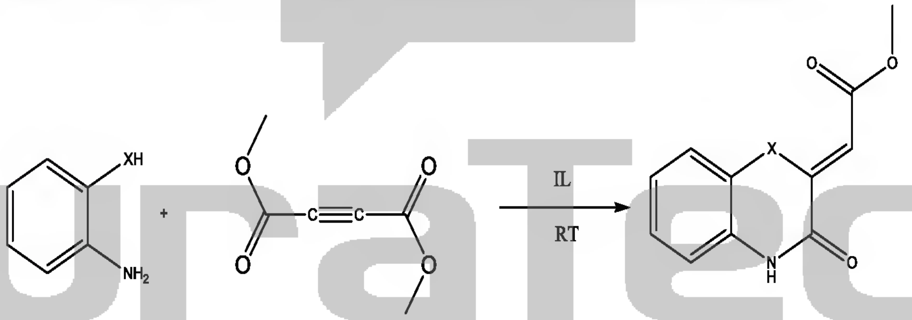
Ionic liquids have emerged as a new class of alternatives to conventional solvents since they have many fascinating properties which make them of fundamental interest to all chemists [1].

1,4-Benzoxazin-3(4H)-one and 1,4-benzothiazin-3(4H)-one derivatives are also interesting group of heterocyclic compounds from pharmacological and agricultural points of application. The 1,4-benzoxazin-3(4H)-one moiety can be found in molecules that exhibit plant resistance factors against microbial diseases and insects and analgesic, antimicrobial and potassium-channel modulating properties, whereas 1,4-benzothiazin-3(4H)-ones, like semotiadil, are antihypertensive drugs, calcium antagonists, and highly potent inhibitors of low density lipoprotein (LDL) oxidation.

Quinoxaline not only has application as dyes and building blocks in the synthesis of organic semiconductors but also serves as useful rigid subunits in macrocyclic receptor for molecular recognition and chemically controllable switches [2]. Quinoxalines also play an important role as a basic skeleton for the design of a number of antibiotics such as echinomycin, actinomycin, and leromycin. It has been reported that these compounds inhibit the growth of gram-positive bacteria, and are active against various transplantable tumors [3].

In this work, 1,4 benzoxazines, benzothiazine, quinoxaline are prepared by mixing commercially available 2-aminophenols, o-aminothiophenol, o-phenylenediaminewith dimethyl but-2-ynedioate in [omim]Br ionic liquid. After 1 min at room temperature products precipitate spontaneously.



X=NH,O,S

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Anhydrous FePO4 Catalyzed One Pot Synthesis of 2-Substituted Benzimidazoles

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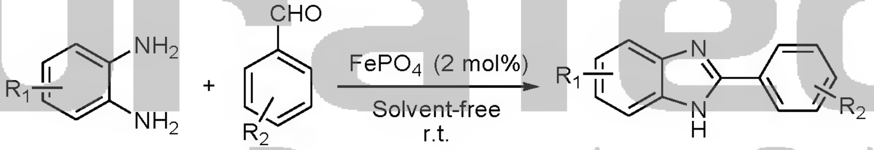
Benzimidazoles are highly biologically active compounds and exhibit antiviral, antinulcer, antihypertension, and anticancer properties [1]. Because of wide biological significance, the synthesis of these compounds has received a great deal of attention. Consequently, a variety of methods have been developed for the preparation of substituted benzimidazoles [2-3]. Many of these processes suffer from one or more limitations, such as long reaction times, occurrence of several side reactions, drastic reaction conditions, low yields, and tedious work-up procedure. Therefore, the search continues for a better catalyst for the synthesis of benzimidazoles in terms of mild reaction conditions.

One the other hand, Iron(III) phosphate is very relatively cheap and safe catalyst that is prepared using $Fe_2(SO_4)_3$ and disodium phosphate and purchased as commercially.

In this study, 2-substituted benzimidazoles are selectively synthesized in high yields under extremely mild conditions via the condensation of aryl-1,2-diamines with aromatic aldehydes using catalytic amount of Iron(III) phosphate under solvent free conditions (Scheme 1). The use of readily available Iron(III) phosphate as a reusable and recyclable catalyst makes this process quite simple, convenient, and environment-friendly.



Scheme 1

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Preparation of 5-Substituted 1-H-Tetrazole Using Heterogeneous Catalyst

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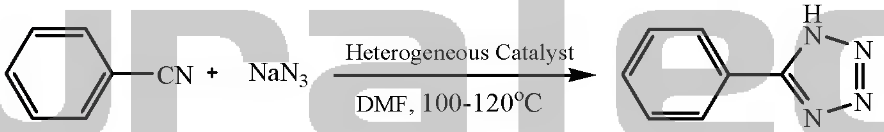
Tetrazoles are a class of heterocycles that have received attention due to their wide range of applications in medicinal chemistry and material sciences [1]. Several methods for the synthesis of 5-substituted tetrazoles have been reported through the [2+3] cycloaddition of nitriles using NaN_3 or $TMSN_3$ in the presence of catalysts such as $BF_3.OEt_2$, $Pd(OAc)_2/ZnBr_2$, $Zn(OTf)_3$, $AlCl_3$, and $Pd(PPh_3)_4$. However, a drawback of these homogeneous catalytic processes is difficulty in separation and recovery of the catalysts [2]. Heterogeneous catalysts have successfully been utilized in several organic transformations to minimize undesirable waste causing environmental pollution. Several heterogeneous catalytic systems using nanocrystalline ZnO, Zn/Al HT, Zn hydroxyapatite, Cu_2O, Sb_2O_3, $FeCl_3$-SiO_2, $CdCl_2$, γ-Fe_2O_3, ZnS, and natural natrolite zeolite were reported [3,4]. These methods require a large excess of sodium azide, longer reaction time, and toxic and expensive metals. Therefore, the development of heterogeneous catalyst system without transition metals that are cheap, available and non-toxic is desirable. In this study we have used different heterogeneous catalyst such as K-10, amberlyst 15, KSF, silicagel, phosphomolybdic acid and tungesto phosphoric acid for the synthesis of 5-substituted 1-H-tetrazole. To compare the catalytic activity of catalysts, the reaction of benzonitrile and sodium azide in DMF was chosen as standard reaction (Scheme 1). KSF as an environmentally friendly catalyst shows better catalytic performance than other catalyst for the synthesis of 5-substituted 1-H-tetrazole.



Scheme 1

Reference

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Photochromism of new bicyclic aziridine containing pyrazole ring

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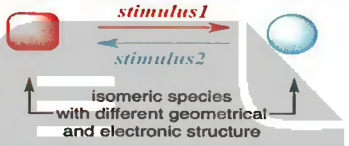
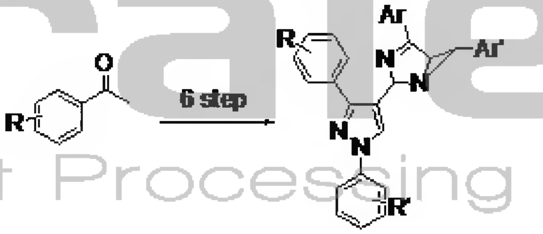
Chromism is defined as a transformation of a chemical species between two forms by application of a stimulus, where the two forms have different absorption spectra, and the process is often reversible [1-2].



There are many ways in which colour can be caused to arise by both chemical and physical means, all of which are used or have potential in technological applications. Functionalized aziridines are an extremely important class of compounds; as they are precursors of new biologically active componds, they are very useful synthethic intermediates. Examination of new methods of the synthesis of aziridine derivatives has therefore attracted considerable attention [3-5]. Synthetic way for preparation of this photochromic compounds involving multicomponent reaction of aziridines with pyrazole derivatives. At first ketoaziridine prepared in three steps by reaction between an aromatic ketone with benzaldehyde substituted, and then were brominated α,β-unsaturated ketones, followed by aziridination with solution of ammonia in absolute ethanol at room temperature [5]. Pyrazole derivatives were prepared of vilsmier-Haack reaction in two steps. Desired compounds were synthesized via three component reaction of pyrazole derivatives and aziridines in good yields. All compounds were characterized by spectroscopic methods. We find that target compounds show photochromic and solvatochromic properties. These compounds exhibit behavior photochromic in crystalline state and solution. With the intention of study photochromic properties of these compounds, UV–Visible absorption spectra and they spectral changes were recorded in various solvents.



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A facile one-pot green synthesis of 2-amino-4H-pyrans

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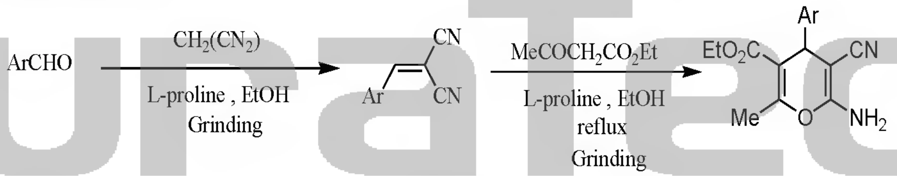
Multicomponent reactions, on the other hand, have become very popular in the discovery of biologically active novel compounds due to its simple experimentation, atom economy and high yields of the products [1].

2-Amino-4H-pyran derivatives represent an important class of compounds. They are often used in cosmetics and pigments, and utilized as potentially biodegradable agrochemicals [2]. Polyfunctionalized 4H-pyrans also constitute a structural unit of many natural products [3] and biologically interesting compounds which possess various pharmacological activities, such as antiallergic, antitumor ,antibacterial [4]. 4H-Pyran derivatives are also potential calcium channel antagonists [5] which are structurally similar to biologically active 1,4-dihydropyridines.

The development of environmentally benign, efficient and economical methods for the synthesis of biologically interesting compounds remains a significant challenge in synthetic chemistry. Herein, we wish to report an efficient synthesis of 2-amino-4H-pyrans using of aromatic aldehydes, malononitrile and ethylacetoacetate by L-Proline in EtOH under reflux conditions (Scheme 1). The advantages of this method are higher reaction yields, short reaction times and use of EtOH as an environment friendly solvent.



Scheme 1

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Mono- and bis- isatin phenolic arylation with variety linkages via $AlCl_3 - CH_3CO_2H$

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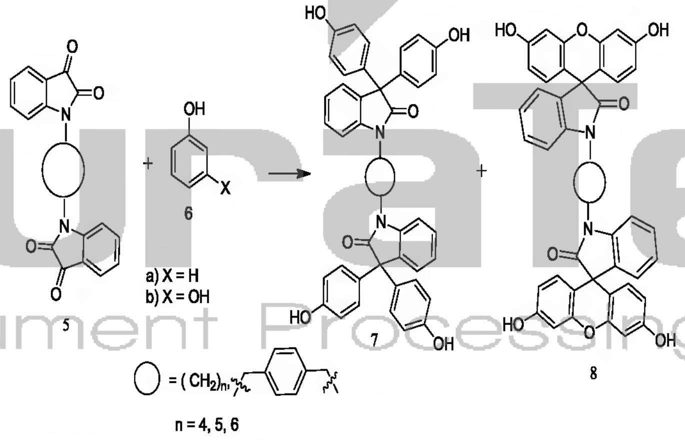
Abstract:

Friedel-Crafts type reactions of phenol derivatives with some cyclic ketones such as ninhydrin and isatin, in the presence of variety catalyst was previously examined. Friedel- Crafts type reaction of isatin derivatives have been studied by Olah et al., which generates 3,3-diaryloxindole derivatives in good yields in CF_3S0_3H. However, CF_3S0_3H is very strong acid, very expensive and also is not easy to handle. In contribution to this work here we report a one-pot solvent free phenolic arylation of mono- and bis- isatin in the presence of different catalysts. For this propose one-pot solvent free reaction of isatin and 2eq of phenols in the presence of varieties of catalyst (activated KSF, $AlCl_3$- glacial AcOH, and H_2SO_4-glacial AcOH) is reported. All synthesized compounds were separated purified and characterized by their TLC, mp ^1H NMR, ^{13} C NMR and IR.



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An Efficient One-Pot Diels-Alder Reaction of Styrylcyclohexenones Using $LiClO_4$ as the Catalyst

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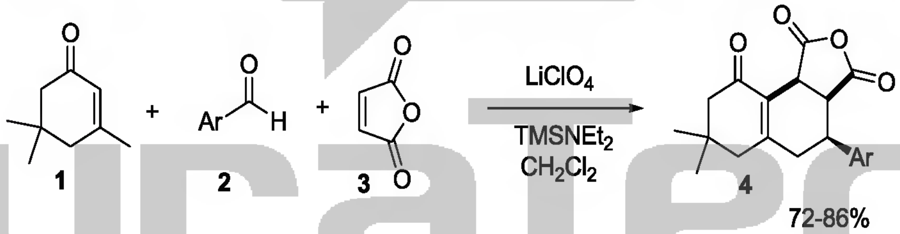
Diels-Alder (DA) cycloadition is one of the most important reactions in organic chemistry due to producing up to four stereogenic centers in a single step reaction with a relatively convenient synthetic procedure [1]. In continuation of our previous work on the synthesis of a series of new dienes [2] and their DA reactions [3], we were encouraged to study the one-pot version of the whole process starting from components **1**, **2**, and **3**. In the presence of $LiClO_4$ and in dichloromethane solution, exclusively endo stereoisomers of substituted dehydrodecaline derivatives **4** were obtained in high yields. Products were characterized by spectroscopic methods and their stereochemistry was confirmed by X-ray crystallography analysis. In summary, this method provides rapid access to endo diastereomers of **4** under mild condition.



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Synthesis of Benzothiazepines in Ionic Liquids

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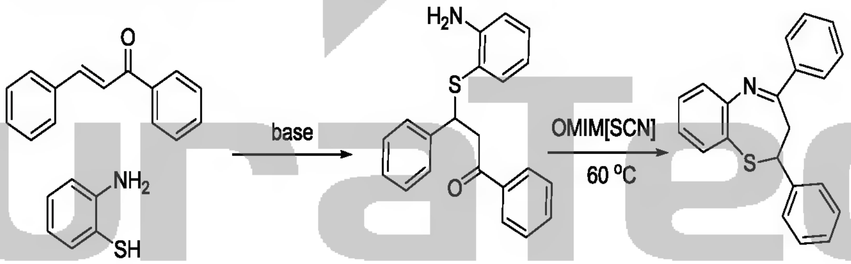
Benzothiazepines are widely used in a number of different therapeutic areas and therefore represent an interesting scaffold for de novo exploration. The well-recognized pharmacological properties of [1,5]-Benzothiazepines include anti-anginal and anti-hypertensive properties. Successful introduction of diltiazem and clentiazem for angina pectoris, hypertension, arrhythmias and other related cardiac disorders proved potential of [1,5]-benzothiazepine moiety[1].

Green Synthesis is defined as environmentally benign chemical synthesis. The various approaches of green chemistry include use of green reagent in synthesis, green catalyst, microwave induced green synthesis and ultrasound assisted green synthesis. All these approaches help in reducing the atmospheric pollution. Recently, a new class of solvent has emerged—ionic liquids. They have many fascinating properties which make them of fundamental interest to all chemists, since both the thermodynamics and kinetics of reactions carried out in ionic liquids are different to those in conventional molecular solvents, then the chemistry is different and unpredictable at our current state of knowledge.

However, in addition to the scope for exciting new discoveries with which they tease us, ionic liquids have no measurable vapor pressure, and hence can emit no volatile organic compounds. They have attracted, quite justifiably, enormous attention as media for green synthesis[2].

In the present work we have investigated eco-friendly synthesis of [1,5]-benzothiazepine derivatives by the use of IL, Octylmethylimidazolium thiocyanate, as solvent, using 3-(2-aminophenylthio)-1,3-diphenilpropan-1-one at 60 °C and room temperature in 5 hours.



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Silica supported perchloric acid as a highly efficient and reusable catalyst for the preparation of 3,4-dihydropyrimidinones/thiones

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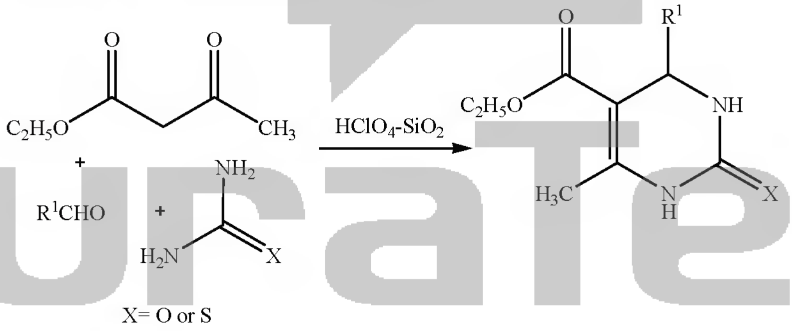
Dihydropyrimidinones (DHPMs) exhibit various types of pharmacological activities such as antibacterial and antifungal, antiviral, antioxidative, as well as anti-inflammatory. In addition, being potent calcium channel modulators, they display coronary dilation and antihypertensive effects [1-3].
We have demonstrated that silica supported perchloric acid [4] is a new efficient catalyst for preparation of 3,4-dihydropyrimidinones/thiones using ethyl acetoacetate, substituted aromatic aldehydes, and urea/thiourea (Scheme). This method is important from an environmental point of view and economic considerations, because it produces little waste. The work has been carried out under thermal solvent-free conditions. In this method excellent yield of 3,4-dihydropyrimidinones/thiones is reported.



Scheme

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A simple synthesis of stable phosphorus ylides containing cyano groups, from the reaction between triphenylphosphine and acetylenic esters in the presence of CH acid compounds

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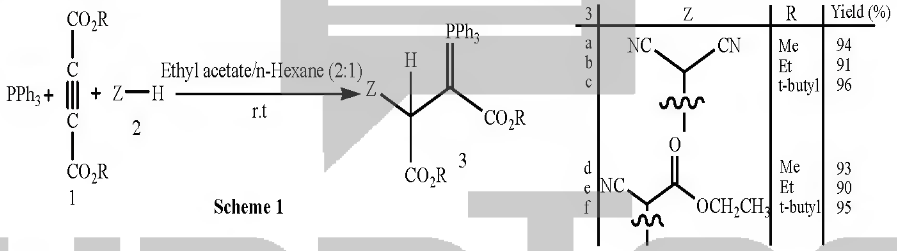
The synthesis of phosphorus ylides is important in organic chemistry because of their applications in the synthesis of organic products [1], especially the synthesis of naturally-occurring products with potentially useful biological and pharmacological properties [2]. Phosphorus ylides are reactive intermediates, which take part in many valuable reactions in organic synthesis [3-5], and several methods have been developed for their preparation. We have prepared novel stable cyano-functional phosphorus ylides using a one-pot reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of strong CH-acids such as malononitrile or ethyl cyanoacetate. The present method has the advantage that not only is the reaction performed under neutral conditions, but also that the reagents can be mixed without any activation (Scheme 1).



Scheme 1

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A facile synthesis of Furo[2,3-d]pyrimidines in aqueous media

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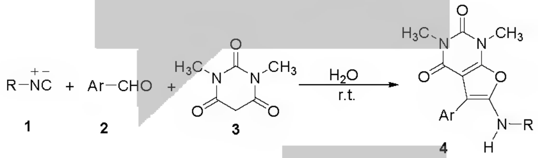
Abstract

Some reactants such as isocyanides are strategic reagents for synthesis of organic structures [1, 2]. There are many diverse cycloaddition reactions in which isocyanides play a key role for synthesis of different types of heterocycles [3,4]. Because of the environmental concerns, safety consideration and for cost containment reasons the reduction of organic solvents for reaction, with phasing out of certain solvents such as some of chlorinated hydrocarbons, has become of pressing interest. In continuation of our investigations on development of synthesis of five and six membered rings [5,6], we now describe the synthesis of furo[2,3-d]pyrimidine derivatives **4** by means of a mild one-pot reaction between isocyanides **1** and aldehydes **2** in the presence of 1,3-dimethylbarbituric acid **3** in aqueous media. All Compounds are stable solids whose structures are fully characterized and supported by IR, ^{1}H and ^{13}C NMR and Mass spectroscopy.



R: *t*-butyl, cyclohexyl

Ar: 2-chlorophenyl, 3-chlorophenyl, 4-chlorophenyl,4- methylphenyl, 2,4-dichlorophenyl

Scheme 1.

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Synthesis of pyridine substituted cyano-2,3-dihydropyrrolo[1,2-f]phenanthridine derivatives

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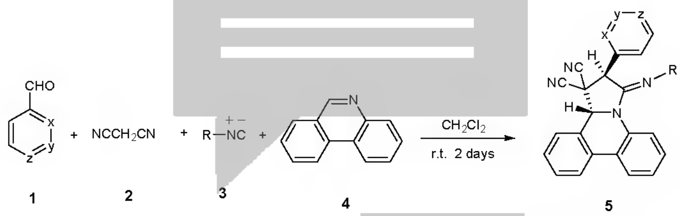
Abstract
Multicomponent reactions (MCRs) have been appeared as a powerful tool for the synthesis of many diverse organic compounds [1,2]. Hence, the novel MCRs designation for synthesis of valuable compounds with highly applications remains the interest of synthetic organic chemist [3,4]. Deploying such an approach for the preparation of heterocyclic phenanthridine derivatives is of importance to medicinal chemistry and material science [5]. In continuation to our synthetic investigations [6], we now describe a new four-component reaction in which 2-aryl-3-(alkyl)-2,3-dihydropyrrolo[1,2-f]phenanthridine-1,1(12bH)-dicarbonitrile derivatives **5a**–**f** in 83–95% yields can be synthesized by reacting pyridinecarboxaldehydes **1**, isocyanides **3**, and phenanthridine **4** in the presence of malonitrile **2** at room temperature (Scheme 1). Compounds **5a**–**f** are stable solids whose structures are fully characterized and supported by IR, ^{1}H and ^{13}C NMR and Mass spectroscopy.



5	R	x	y	z	% yield
a	cyclohexyl	N	CH	CH	95
b	cyclohexyl	CH	N	CH	90
c	cyclohexyl	CH	CH	N	92
d	*t*-butyl	N	CH	CH	83
e	*t*-butyl	CH	N	CH	87
f	*t*-butyl	CH	CH	N	89

Scheme 1.

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The Synthesis Of Polyamidoamine (PAMAM-CHO)Dendrimer Aldehyde End Groups

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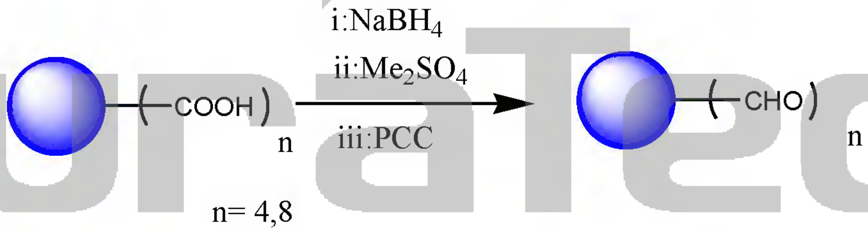
Abstract

Dendrimers are spherical, hyperbranched macromolecules with a large number of terminal groups [1,2]. Dendrimers are spheroid or globular nanostructures that are precisely engineered to carry molecules encapsulated in their interior void spaces or attached to the surface . Size, shape, and reactivity are determined by generation (shells) and chemical composition of the core, interior branching, and surface functionalities. Dendrimers are constructed through a set of repeating chemical synthesis procedures that build up from the molecular level to the nanoscale region under conditions that are easily performed in a standard organic chemistry laboratory. The dendrimer diameter increases linearly whereas the number of surface groups increases geometrically [3,4].

PAMAM-CHO dendrimer was synthesised by divergent method. It was characterized by FTIR , ^1H NMR and ^{13}C NMR spectrums.

Key words Polyamidoamine , PAMAM-CHO, Dendrimer



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A catalyst-Free and rapid Qinoxalines synthesis using an ultrasound tip.

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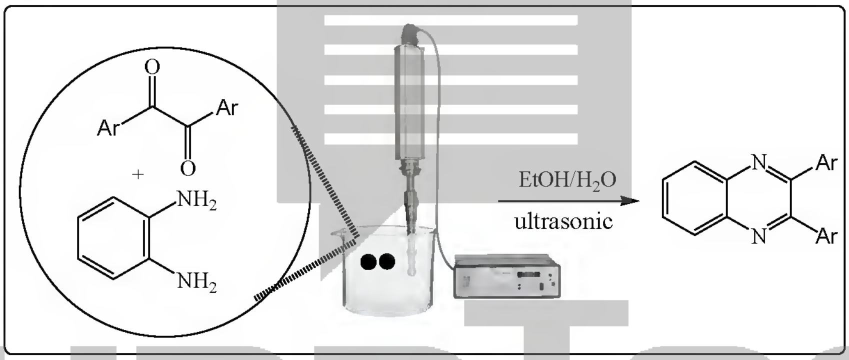
Quinoxaline and its derivatives are an important heterocycle compounds in chemistry and pharmacy that exhibit biological activities. [1] In other hand, because of shorter time and mild conditions of ultrasonic assisted synthetic method, in recent years, ultrasound (US) has been used in organic synthesis with increasingly attention. [2] Based on US interest in organic synthesis, we investigated a rapid and highly efficient method in synthesis of quinoxaline derivatives using ultrasonic irradiation.



In a general experimental procedure, benzyl and 1,2-diamine were mixed and irradiated in catalyst-free condition and the mixture of EtOH/H_2O used as solvent. The mixture of product monitored by TLC, after completion of the reaction, the crude product was filtered, washed with water and then recrystallized from ethanol to afford pure quinoxaline.

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Synthesis of 4[H]-benzo[b] pyran derivatives using Molybdate sulfuric acid (MSA) as catalyst

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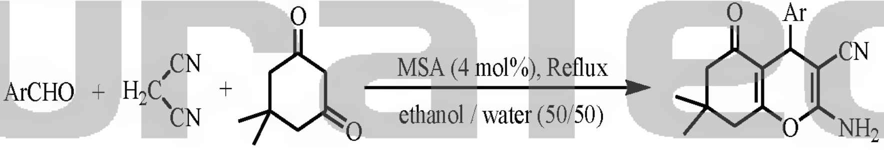
Many important heterocycle synthesis are multicomponent reactions. Recently the synthesis of 4H-Benzo(b)pyran derivatives have attracted great interest due to biological and pharmacological activities the 4H-Benzo(b)pyran derivatives show various pharmacological properties such as spasmolytic, diuretic, anticoagulant, anticancer and anti anaphylactic activities[1]. Interest in the environmental control of chemical processes has increased remarkably during three decades ago (over the past three decades) as a response to public concern about the use of hazardous chemical materials. Therefore, to improve the effectiveness of this method in preventing chemical waste, it is important to investigate optimal reaction conditions [2].

To determine the simple and suitable conditions for synthesis of 4[H]-benzo[b] pyran derivatives using Molybdate sulfuric acid(MSA) as a solid acid catalyst, the treatment of aromatic aldehyde, malonononitril and dimedone were chosen as general reaction. At first, we found that in the absence of the catalyst, the reaction did not proceed even at a high temperature. After examining the various amounts of MSA and a wide range of temperatures and using of different solvents, it was found that this condensation reaction can be efficiently carried out by adding 4 mol% (0.012 gr) of catalyst at refluxing ethanol/ water of 50/50 conditions in a short time span of 10-30 minutes. The use of excess amounts of the catalyst did not have a marked influence on the product yield or reaction rate.

This is of special interest for this reaction because Molybdate sulfuric acid(MSA) is environmental friendly and it is soluble in water.



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Brønsted acidic ionic liquid as a metal free catalyst for the one-pot synthesis of α-aminonitriles under mild and solvent-free conditions

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The Strecker reaction [1] is one of the most important multicomponent reactions in organic chemistry for the direct one-pot synthesis of α-aminonitriles. In this reaction three components including a carbonyl compound (generally an aldehyde), an amine and either alkaline metal cyanide or hydrogen cyanide couple together and produce α-amino nitriles, which are highly useful synthons for the synthesis of α-amino acids [2] nitrogen-containing heterocycles such as imidazoles and thiadiazoles [3] and other biologically useful molecules [4]. Many catalysts have been used to promote the Strecker reaction using TMSCN. Recently, the use of ionic liquids (ILs) has been increasing with a very fast rate because of their beneficial properties. A subdivision of ILs is protic ionic liquids (PILs), which are produced through the combination of a Brönsted acid and a Brönsted base [5].Methyl imidazolium hydrogen sulfate ([Hmim][HSO_4]) has easily been synthesized and used as an efficient, inexpensive and reusable catalyst in organic synthesis [6].Moreover, the present ionic liquid is halogen free and because of less carbon numbers, this ionic liquid has less toxicity. Therefore, [Hmim][HSO_4] can be introduced as a green ionic liquid.

In this work we report an efficient method for one-pot three-component synthesis of α-amino nitriles from various carbonyl compounds, anilines and TMSCN in the presence of catalytic amount of [Hmim][HSO_4] under solvent-free conditions at room temperature.

Using this procedure, different kinds of aromatic, aliphatic and heterocyclic aldehydes were treated with aniline and TMSCN to produce the corresponding α-amino nitriles under solvent-free conditions in high to excellent yields.

Using inexpensive and non-toxic catalyst, mild reaction conditions, short reaction times, high yields, the simplicity of the reaction procedure and easy work-up were the notable advantages of this method.

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A Convergent Synthesis of Fused Spiro[1,4-dihydropyridine-oxindole] Compounds under Ionic Liquid Catalysis

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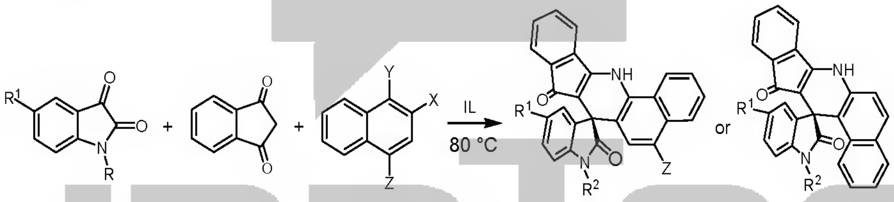
The heterocyclic spiro-oxindole ring system is a widely distributed structural framework present in a number of pharmaceuticals and natural products.[1] Spiro[pyrrolidine-oxindole] ring systems, for example, are found in a number of alkaloids such as horsifiline, spirotryprostatine A and B and elacomine.[2] This prevalence has led to interests in development of new methods for construction of various diversely functionalized spirocylic oxindoles.[3] Ionic liquids, by virtue of their organic and ionic nature, are potent solvents, exerting nearly all kinds of interactions on reacting species, including transition states, whereupon sometimes give rise to improved yields and rate enhancements.[4] Structural variation of ionic liquids gives more flexibility to their applications, as provides fine tunning of their miscibility to merit phase-separation from products.[5] Moreover, functionalized ionic liquids offer the task-specific elements for designed catalysis applications.[6] In this view and in line with our interest in performing reactions with the aid of ionic liquids,[7] and also in continuation of our studies on synthesis of spiro-oxindole heterocycles,[8] herein we report an expedient synthesis of some fused spiro[1,4-dihydropyridine-oxindole] compounds under catalysis of a task-specific ionic liquid. Good functional group tolerance and broad scope of usable substrates are other prominent features of the present methodology.



R^1 = H, OCH_3, Br, NO_2, I, Cl R^2 = H, Bn   X = H, NH_2 Y = H, NH_2 Z = H, Br

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Tetramethylguanidinium triflate: An efficient catalyst solvent for henry reaction

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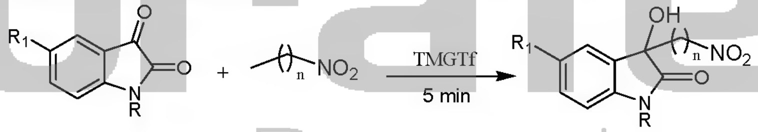
Several carbon-carbon bond forming reactions have been discovered and well reported in the literature.[1] The most prominent ones are aldol reaction, Gringnard reaction, … and Henry reaction.[2] Henry reaction is a classic-carbon-carbon bond-forming reaction and has been applied extensively in organic synthesis of β-nitroalkanols which are versatile intermediates for the preparation of nitro alkenes, 2-amino-alchohols, 2-nitro-ketones and biological compounds including fungicides, insecticides, natural prouducts and certain antibiotics.[3] Isatin is an active carbonyl compound, which like aldehydes can take part in henry reaction. Being prompted by recent interests in the synthesis of indolin-2-ones from isatin derivatives, we planned to investigate the possible improvement of henry reaction of isatin and nitro alkane for synthesis of 3-hydroxy-3-nitromethyl-oxindole. Based on our literature survey, there are only two reports on the henry reactions of isatin derivatives.[4,5] Thus, the development of simple and efficient reaction condition is an active area of research and there is a scope for further improvement towards milder reaction conditions, short reaction time and higher product yields. Ionic liquids, by virtue of their organic and ionic nature, are potent solvents, exerting nearly all kinds of interactions on reacting species, including transition states, whereupon sometimes give rise to improved yields and rate enhancements.[6] Structural variation of ionic liquids gives more flexibility to their applications, as provides fine tunning of their miscibility to merit phase-separation from products. In conclusion an efficient and convenient route to the synthesis of the title compounds was introduced here. Tetramethylguanidinium triflate ionic liquid plays as a catalyst solvent and can be recovered for reuse several times. Another advantages of the present method may be; requiring no metal catalysts or additional solvent.



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One-pot synthesis of substituted ethyl 2-amino-6-(hydroxymethyl)-8-oxo-4-phenyl-4,8-dihydropyrano[3,2-b]pyran-3-carboxylate

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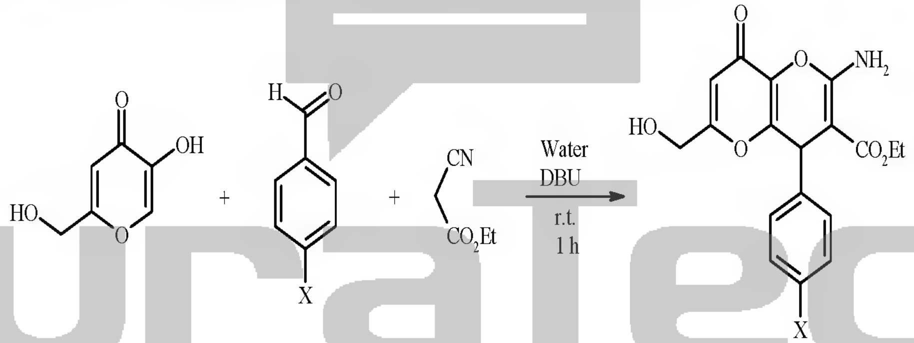
Green and sustainable chemistry has now attained the status of a major scientific discipline and the studies in this area have led to the development of cleaner and relatively benign chemical processes with many new technologies being developed each year [1]. Another window of green chemistry to take into consideration is the development of the one-pot multicomponent reactions (MCRs) which are one of the best tools in the synthesis of organic compounds [2-3]. Herein, we describe a very simple, green and efficient route for the synthesis of ethyl 2-amino-6-(hydroxymethyl)-8-oxo-4-phenyl-4,8-dihydropyrano[3,2-b]pyran-3-carboxylate via a three-component reaction of kojic acid **1**, aromatic aldehydes **2** and ethyl cyanoacetate **3** in water at room temperature by vigorous stirring.



1 2 3 4

X = H, CN, NO$_2$

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(Al_2O_3/H_3PO_4): an efficient and recyclable heterogeneous catalyst for A three-component synthesis of 1-carbamato-alkyl-2-naphthol derivatives

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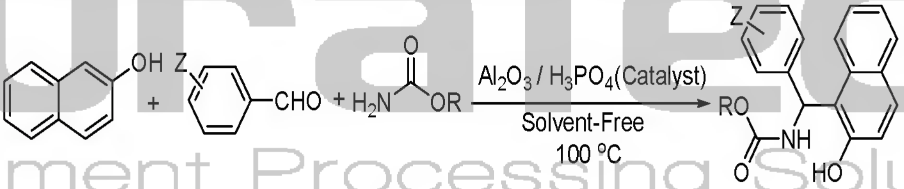
Multi-component reactions have attracted considerable attention in organic syntheses as they can produce the target products in a single operation without isolating the intermediates and thus reducing the reaction times and energy [1,2]. Heterogeneous catalysts have gained much importance in recent years due to economic and environmental considerations. These catalysts are generally less expensive, highly reactive, eco-friendly, and convenient to handle, with enhanced reaction times, greater selectivity, simple workup, and recoverability of catalysts [3].
A new one-pot, efficient three-component condensation of benzaldehydes, 2-naphthol, and carbamates in the presence of alumina-supported phosphoric acid, Al_2O_3/H_3PO_4, as an effective heterogeneous catalyst for the synthesis of 1-carbamato-alkyl-2-naphthol derivatives under solvent-free conditions is described (Scheme 1). The yields are excellent and the reactions go to completion within 10–15 min. The present methodology offers several advantages, such as high yields, short reaction times, and very easy workup.



Scheme 1

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Synthesis of New 1,3,4-Oxadiazole-2(3H)-thione Derivatives

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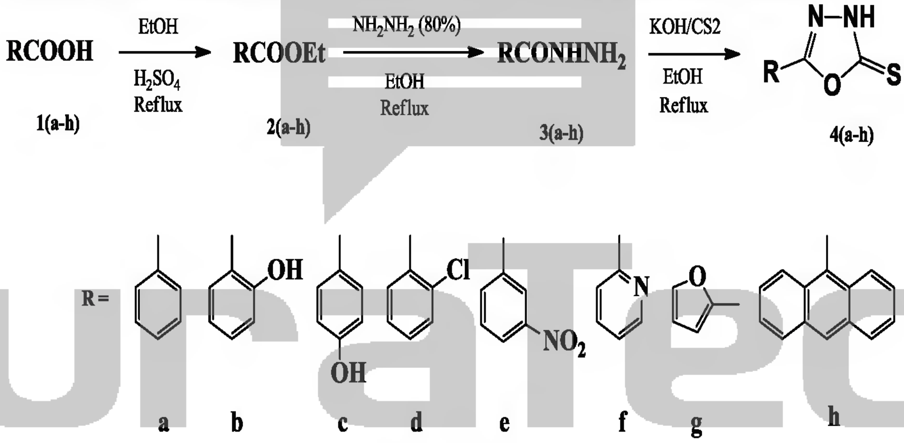
Nitrogen containing heterocycles with an oxygen atom are considered as an important class of compounds in medicinal chemistry because of their interesting diversified biological applications [1]. During the past years considerable evidences have also accumulated to demonstrate the efficacy of 1,3,4-oxadiazoles including antibacterial, fungitoxic, insecticidal, herbicidal, anticancer, anti-inflammatory [2,3]. For this reason our aim was to synthesize various 1,3,4-oxadiazole-2(3)-thione derivatives to make notable contributions to this class of heterocyclic compounds. We report the synthesis and characterization of some 5-substituted-1,3,4-oxadiazole-2(3H)-thiones **4(a-h)** using the synthetic procedure based on the ring closure reactions of appropriate acid hydrazides with carbon disulphide. The newly synthesized compounds were characterized by IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy Scheme 1.



Scheme 1

References

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Alkylation of 1,3-dicarbonyl compounds with benzylic and allylic alcohols using $Al(OTf)_3$ as catalyst

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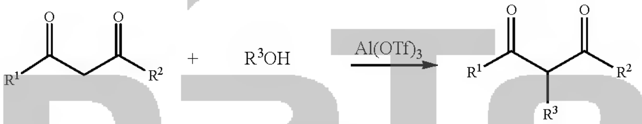
Construction of C-C bonds is always one of the central themes in organic synthesis. The direct reaction of alcohols (ROH) and active methylenes (R′-CH_2-R″) has attracted much attention in recent years. Because only H_2O is generated as the side product and the preparation of the active intermediates, such as organometallic compounds and halides or a related species is not required. Although the advantages of enhancing atom efficiency and avoiding waste are realized, the successful examples of such "green" transformation are limited due to the low reactivity of alcohols toward the nucleophiles [1]. Recently, some Lewis acidic metal catalysts such as $InCl_3$ [2], $InBr_3$ [3], $Bi(OTf)_3$ [4] and $Ln(OTf)_3$ (Ln=La, Yb, Sc, Hf) [5], have been described as effective catalysts for the addition of β-dicarbonyl compounds to allylic and benzylic alcohols. Besides, Brønsted acids, such as H-montmorillonite, dodecylbenzenesulfonic acid [6], p-toluenesulfonic acid [7] and 12-phosphotungstic acid [8] have been found to be the effective catalysts for the addition of β-diketones to secondary alcohols. Although remarkable progress has been made in the Lewis or Brønsted acid catalyzed addition of β-dicarbonyl compounds to alcohols, few examples of the reaction of β-dicarbonyl compounds to aliphatic, primary or terminal allylic alcohols has been established.

In this paper, we were able to demonstrate that aluminum triflate [$Al(OTf)_3$] is a highly efficient catalyst for this transformation (Scheme). The reactivity of $Al(OTf)_3$ to mediate this useful carbon–carbon bond formation was exemplified by short reaction times and high product yields obtained for reactions with primary, terminal allylic, aliphatic and primary benzylic alcohols.



Scheme

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Regioselective brominations of aromatic compounds using 1,4-bis(triphenyl phosphonium) butane peroxodisulfate (BTPPBPODS)

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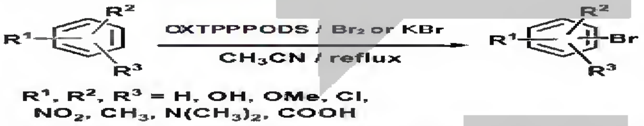
The manufacture of many bulk and fine chemicals involves bromination of aromatics.Various methods have been developed and reported for the bromination of aromatic systems using a variety of brominating agents under various reaction conditions.Some of these methods involve the use of Br_2/Lewisacids,NBS/PTSA,HBr/H_2O_2,HBr/DMSO,$NH_4Br/H_2O_2/CH_3COOH$,pyridinium hydrobromide perbromide,KBr/H_2O_2/Oxone, $CuBr_2$/t-BuO-NO. However, these methods suffer from one or more disadvantages such as a long reaction time, low yield, use of toxic solvents, requirement of excess of reagents/catalysts, laborious workup procedures, and hash reaction conditions. [1-3]

In continuation with the search for simple non-hazardous methods for the transformations in organic synthesis,[4,5] herein we wish,direct bromination of wide range of aromatic compounds substituted with electron donating groups such as methoxy,hydroxy,or amino groups have been achieved with high regioselectivity by the reaction with BTPPBPODS under mild conditions in acetonitrile in excellent yields.



In conclusion, we have developed a complete regioselective bromination of activated aromatic compounds under the mild conditions using as an oxidant. The stable BTPPBPODS can be readily prepared, which can be handled easily and safely.In addition, the catalyst, BTPPBPODS is inexpensive, not moisture sensitive, sub-molar amounts of BTPPBPODS are required. Longer reaction times are required when lesser amounts of BTPPBPODS are employed. It is important to note that no bromation aromatics derivatives were afforded when the reactions were carried out without using any BTPPBPODS in the reaction.

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A rapid, one-pot, four-component route to 1H-pyrazolo[1,2-b]phthalazine-5,10-diones

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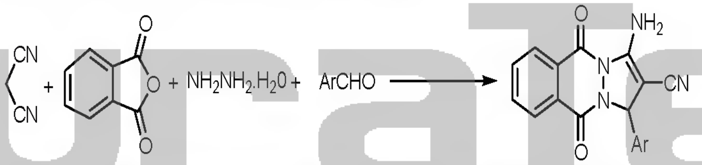
Multi-step reactions usually produce significant amount of waste, principally due to a series of complex isolation procedures which often involves toxic, hazardous and expensive solvents after each step. Thus, multi-component reactions (MCRs) constitute an efficient synthetic strategy for the rapid and effective libratory organic transformations. Because, products are prepared in a one-pot and single step and the diversity can be obtained directly by changing the reacting components [1,2]. On the other hand, polyfunctionalized heterocycles play considerable roles in the drug discovery process, and analysis of drugs shows that most of them are polyfunctionalized heterocycles. Therefore, research on the multi-components synthesis of polyfunctionalized heterocyclic compounds is an interesting challenge. Nitrogen-containing heterocyclic compounds are widespread in nature, and their applications to biologically active pharmaceuticals, agrochemicals, and functional materials are becoming more and more important . Among a large variety of nitrogen-containing heterocyclic compounds, heterocycles containing bridgehead hydrazine have received considerable attention because of their pharmacological properties and clinical applications. Similarly, pyrazoles are important compounds that have many derivatives with a wide range of interesting properties, such as anti-hyperglycemic, analgesic, anti-inflammatory, anti-pyretic, anti-bacterial, and anti-viral activities. Considering the important biological properties of heterocycles containing bridgehead hydrazine, a number of methods have been reported for the synthesis of these heterocycles .[3]



Accordingly, we herein report a rapid and efficient method for the preparation of 1H-pyrazolo[1,2-b]phthalazine-5,10-dione in high yield and short reaction time by a cyclo-condensation reaction of aldehyde, malononitrile, hydrazinium hydroxide and phthalic anhydride in ethanol using solid acid as an inexpensive and readily available catalyst .

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Synthesis and antibacterial activity of some novel thiosemicarbazieds and 1,2,4-triazol derivatives

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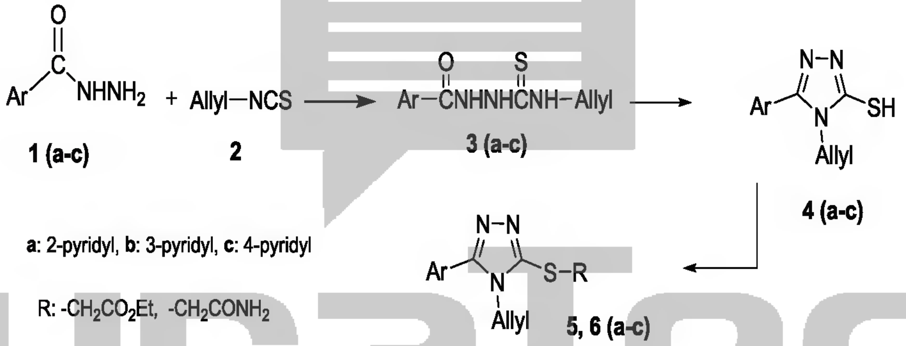
It is well known that thiosemicarbazide derivatives exhibit interesting biological properties [1]. These compounds are not only a segment of biologically important but also a versatile intermediate for the synthesis of heterocyclic compounds. In addition, the chemistry of 1,2,4-trriazol-3-thiols and their S-substitution derivatives have attracted the attention of chemists due to attractive biological activities [2]. On the other hand, incorporating the pyridine ring into active compounds may improve their biological or physiological activities [3].
In view of this report, our attention was directed to synthesize of new compounds **3-6 (a-c)** and consideration of their antibacterial effects. Therefore, synthesis of some novel 1,2,4-triazoles bearing a pyridyl unit using 4-allyl-1-(x-picolinoyl)-thiosemicarbazide (x = 2,3,4) in an alkaline solution, respectively, is reported. The S-alkylation of triazole derivatives is also reported (Scheme 1). All synthesized compounds were characterized by elemental analyses, the IR and NMR spectroscopic data.



Scheme 1.

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Catalyst free and green synthesis of chromenes derivatives under ultrasound irradiation

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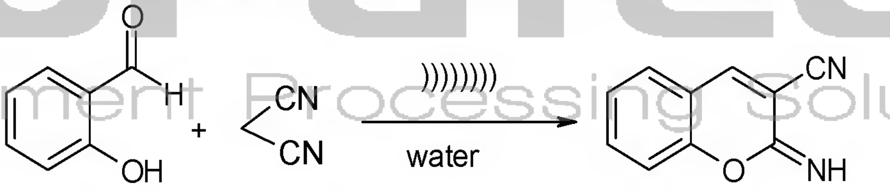
Sonochemistry shares with sustainable chemistry such aims as the use of less hazardous chemicals and solvents, a reduced energy consumption and an increased product selectivity. In this regard, ultrasound and microwave heating are in many instances complementary techniques for driving chemical reactions. Our first aim is to introduce readers to ultrasound and its effects, and to make them aware that sonochemistry is in fact a unique and distinctive chemistry, in which the physical properties of the medium may have a decisive effect on chemical reactivity. Although the extreme conditions inside an acoustic bubble have been a matter of controversy, recent findings have provided an accurate estimate of local tempera tures and clarified the chemical events to be expected. In addition, it has become possible to rationalize sonochemical reactions following an analysis of experiments [1].
The 2-amino-chromenes are widely employed as pigments, cosmetics, potential agrochemicals, and represent an important class of chemical entities being the main constituents of many natural products. Furthermore, chromenesrepresent an important class of compounds being the chain components of many naturally occurring products, and have been of interest in recent years due to their useful biological properties such as anticoagulant, anticancer, spasmolytic, and antianaphylaction activity. 2-Amino-4H-chromenesare generally prepared by refluxing malononitrile, aldehyde, in the presence of hazardous organic bases such as piperidine in organic solutions, such asethanol and acetonitrile for several hours [2]. During the course of our study aimed for improving the ecocompatibility of certain organic processes, we have been particularly interested in the synthesis of 2-amino-chromenes in water and solvent free conditions to develop environmentally benign reactions. Herein, we wish to report an efficient preparation of 2-amino-chromenes derivatives from the simple reaction of salicylic aldehydes with malononitrilein waterunder ultrasound irradiation.



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Iodination of terminal alkynes using Hexamethylene bis(N-methyl imidazolium dichloroiodate) as an ionic liquid reagent

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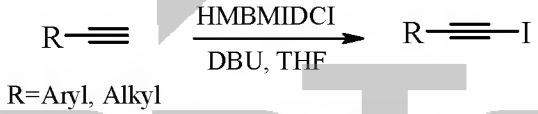
Iodoalkynes are important intermediates in organic synthesis [1]. They are found to possess anti-HIV, antimicrobial and fungicidal activity [2].

Some methods for the preparation of iodoalkynes include iodination of phenylacetylenes using I_2/NH_3 [3a], KI/TBHP [3b], I_2/DMAP, CuI/TBAB/Et_3N, KI/CuI/Et_3N/$PhI(OAc)_2$, n-BuLi/ZnI_2/BTMSPO, $I(Py)_2BF_4/CH_3ONa$ [3c], BTMSPO/CuI or ZnI_2 [3d].

Although some of this reported procedures are effective, some of them have certain drawbacks, for example formation of diyne as by-product, use of transition metal catalyst, use of moisture sensitive bases and intermediates and long reaction time. Herein, we report an efficient method for iodination of terminal alkynes to prepare iodoalkynes using HMBMIDCI and DBU in THF at room temperature (Scheme 1). A wide variety of terminal alkynes was examined under this condition for 10-75 minutes and the results showed the yields of desired products are excellent (80-90%) for aromatic alkynes containing both of electron-donating and electron-deficient groups in meta, para and ortho positions.



Scheme 1. Iodination of terminal alkynes

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Solvent-free synthesis of penta-substituted pyrroles: one-pot reaction of amine, alkyl acetoacetate, and fumaryl chloride

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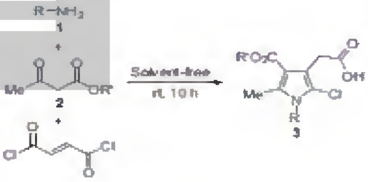
Abstract

A novel, convenient, and efficient approach to the synthesis of penta-substituted pyrroles has been reported based on the multicomponent reaction. Solvent-free condition for the formation of enaminones from primary amines and alkyl acetoacetates and it's reaction with fumaryl chloride lead to the formation of pyrroles that have halide, CH_2CO_2H, ester functional groups, and two alkyl substitutions.

Five-membered, nitrogen-containing heterocycles, such as pyrroles, indoles, and carbazoles, are important building blocks in an extensive number of biologically active compounds.[1] Among them, pyrroles are heterocycles of great importance because of their presence in numerous natural products like heme, chlorophyll. Consequently, a large number of methods have been developed for their synthesis, which include: Knorr, Paal–Knorr, Hantzsch syntheses,.

we become interested in the application of fumaryl chloride in multicomponentreaction for first time (which display electrophilic property at the two site of its structure) to synthesize highly functionalized. pyrroles. Our strategy to reach this goal is outlined in Scheme 1. The reaction between primary amines 1, alkyl acetoacetate 2, and fumaryl chloride under solvent-free conditions at room temperature (the amine and alkyl acetoacetate are mixed first and then fumaryl chloride is added) leads to the formation of pentasubstituted pyrroles 3 in 70–85% yields (Scheme 1). The data obtained from elemental analysis, IR, 1H and ^{13}C NMR, and mass spectra confirmed all of the proposed products.



Product	R	R'	Yield % of 3
3a	^{t}Bu	Me	70
3b	^{t}Bu	Et	78
3c	n-Pr	Me	85
3d	n-Pr	Et	85
3e	allyl	Me	73
3f	allyl	Et	70
3g	^{i}Pr	Me	80
3h	^{i}Pr	Et	80

Scheme 1.

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Simple and Efficient Method for Formylation of Alcohols Catalyzed with $MoCl_5$

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O-Formylation could be the method of choice for protection of alcohls in a complex synthetic sequence, because deformylation can be affected selectively in the presence of acetate or other other ester protecting groups. Further, if the alcoholic group is planned to be oxidized later in the synthetic sequence, the formylated alcoholic group need not be deprotected and direct oxidation under Oppenauer conditions can be realized. Although various formylating agents have been reported previously, there are still serious limitations for the preparation of formates due to the drastic reaction conditions, the use of uncommon reagents, formation of undesirable or toxic by-products, the application of expensive catalysts for preparation of formylating agents, and thermal instability of the reagents. To the best of our knowledge, one of the most common formylating agents is formic acid which is corrosive and toxic. Meanwhile, acid-sensitive functional groups may be affected and side reactions may be increased in the formylation reaction by using formic acid. Among formylating agents ethyl formate offers several advantages such as easy work-up, availability of the reagent, and relatively low cost. Some of the recently reported methods include formylation with ethyl formate in the presence of different reagents or catalysts, namely metal triflates such as $Ce(OTf)_4$, $In(OTf)_3$, Bi(III) salts, heteropoly acids, silphos $[PCl_3\text{-}n(SiO_2)_n]$, silica sulfuric acid and $Al(HSO_4)_3$, cerium poly-oxometalate, silica triflate, and $TiCl_3(OTf)$. In this project, we wish to introduce $MoCl_5$ as an efficient catalyst to perform formylation of alcohols under mild conditions. The product formates were obtained in high to excellent yilds by this protocol (scheme) .[1,2,3,4]

$$\mathrm{ROH} + \mathrm{H\overset{\overset{O}{\|}}{C}OC_2H_5} \xrightarrow{MoCl_5} \mathrm{RO\overset{\overset{O}{\|}}{C}H} + \mathrm{C_2H_5OH}$$

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Synthesis of benzylamine by new catalysts in mild condition

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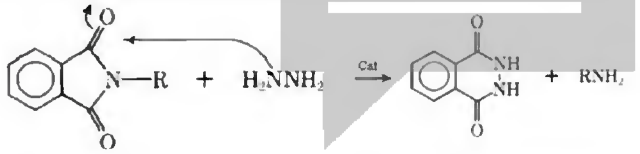
One of the most interesting energetic molecules developed in recent years is the polycyclic nitramine 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW or CL-20).CL-20 is a new explosive that is 14-20 % more powerful than tetranitrotetraazacyclooctane(HMX)[1].

The synthesis of hexaazaisowurtzitanes was considered to be limited solely to the condensation of certain benzylamines with glyoxal. However, is that the synthesis described by Nielsen and co-workers despite several attempts, seems limited to benzylamines [2-3]. we persent here synthesis of benzylamine that was not produced in our country. One method for synthesis of amine is reaction of potassium phthalimide with alkylating agents leads to the N-alkylphthalimide. N-Substituted phthalimides may be converted into the corresponding primary amine by hydrolysis or hydrazinolysis[4-5] . It is well known that alkylphthalimides are often difficult to hydrolyse. It has now been found that this can easily be achieved indirectly, the condensation product with hydrazine hydrate being readily hydrolysed. In addition, lewis acids can also be improved reaction conditions.



We prepared N-benzylphthalimide by heating benzyl chloride with a mixture of phthalimide and potassium carbonate, a method which avoids the troublesome preparation of potassium phthalimide. An excess of the halide is used and is recovered by steam-distillation. N-benzylphthalimide hydrazinolysis into benzylamine in present of different lewis acids such as $AlCl_3$, $Bi(NO_3)_3$, $ZnCl_2$, $FeCl_3$, … , and optimized condition and by used new lewis acids , yield was increased .

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Multicomponent reactions of dimethyl choloromalonate and dialkyl acetylenedicarboxylate in the presence of N-Nucleophiles

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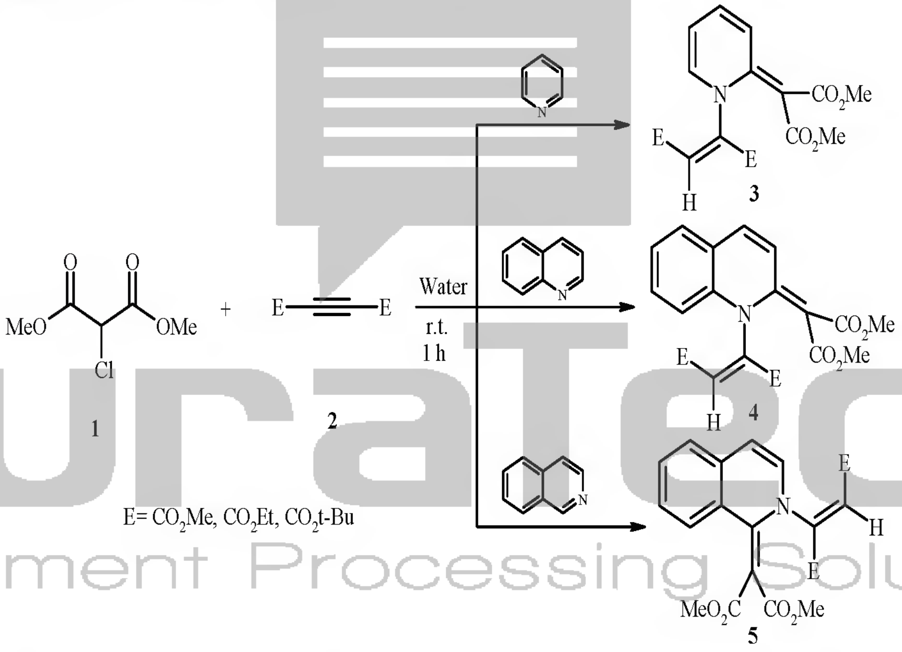
Multicomponent reactions (MCRs), with three or more reactants combined in a one-pot procedure to give a single product, have become increasingly popular during the last decade [1]. Consequently, domino reactions including multicomponent reactions (MCRs) have been used as a powerful tool to achieve this goal [2]. A broad range of biological activities has been reported for compounds containing the pyridine, quinoline and isoquinoline system and a number of these compounds are patented as potential therapeutic agents [3-4]. Herein, we describe a three-component condensation in which N-Nucleophiles react with dimethyl choloromalonate **1** in the presence of acetylenic esters **2** in water at room temperature by vigorous stirring to afford **3**, **4** and **5**.



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An efficient organocatalytic method for tandem synthesis of functionalized 2-pyridones

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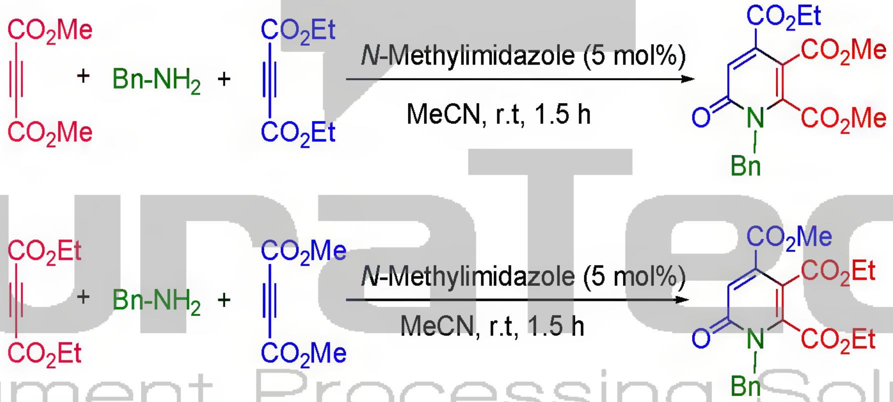
The last decade has witnessed significant advances in the use of small organic molecules to catalyze chemical transformations [1-3], and organocatalytic methods have emerged as a powerful approach for the preparation of important building blocks or compounds.[4-7] In this Letter, we report a novel three-component reaction for the synthesis of highly functionalized 2-pyridones using N-methylimidazole as an organocatalyst. The 2-pyridone moiety is found in a large number of pharmaceuticals, agrochemicals, and functional materials. It is also a versatile synthon that can act as a common intermediate for the preparation of a wide variety of alkaloids [8,9].

In this reaction organoatalysts such as1,4-Diazabicyclo[2.2.2]octane (DABCO), pyridine, isoquinoline and N-methylimidazole was used and N-methylimidazole was found the best results than others under identical reaction conditions. Other catalysts, such as DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), Ph_3P, and K_2CO_3 (an inorganic base), were unsuccessful.

A variety of different reaction conditions were employed in an attempt to optimize the yields and improve the purity of the products. First, the reaction was carried out using various amounts of the catalyst; 5 mol% of N-methylimidazole in MeCN was found to give the best result. Subsequently, the solvent effects were examined, and the best results were obtained in MeCN. The generality of this transformation was demonstrated by applying various primary amines and acetylenic esters under optimized conditions [N-methylimidazole (5 mol%), MeCN, 1.5 h] The structures of product were deduced from their IR, ^1H NMR and ^{13}C NMR. The mass spectra of these compounds displayed, in each case, the molecular ion peak at the appropriate m/z values.



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A Novel Method for the Synthesis of α-Carbamoyloxyphosphonates and Studying of Their Anti-Cholinesterases Activities

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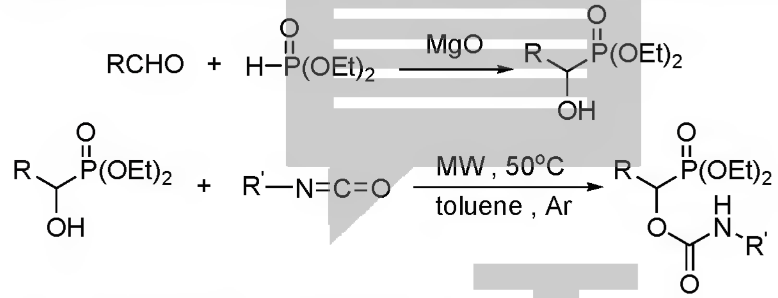
Organophosphorus compounds have found a wide range of application in the areas of industrial, agricultural and medicinal chemistry owing to their biological and physical properties, as well as their utility as synthetic intermediates [1]. α-Functionalized phosphonic acids are valuable intermediates for the preparation of medicinal compounds and synthetic intermediates [2]. In spite of widely studied α-functionalized phosphonates, relatively few papers have been reported on the chemistry of α-carbamoyloxyphosphonates [3]. Herein, we report novel method for the synthesis of α-carbamoyloxyphosphonates from the reaction of α-hydroxyphosphonates, prepared by previously reported method [4], with isocyanates under microwave irradiation. (Scheme1).



Scheme1. Two-step synthesis of α-carbamoyloxyphosphonates

Acetylcholinesterase (AChE) is an enzyme that degrades the neurotransmitter acetylcholine, producing choline and an acetate group [5]. α-Carbamoyloxyphosphonates act as acetylcholinesterase (AChE) inhibitors and hence prevent the termination of a nerve impulse in the postsynaptic membrane.

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A facile, one-pot synthesis of functionalized dihydropyrano[3,2-c]chromenes

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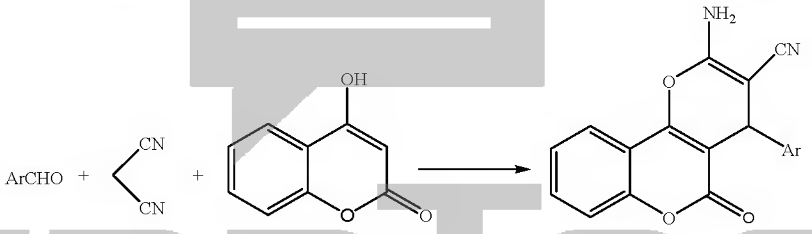
Multi-component reactions (MCRs) have attracted the attention of synthetic organic chemists for building highly functionalized organic molecules and pharmacologically important heterocyclic compounds [1]. Dihydropyrano[c]chromenes are of considerable interest as they possess a wide range of biological properties [2]. These compounds are widely used as anticoagulant, spasmolytic, anticancer, diuretic and antianaphylactin agents in the field of drugs and pharmaceuticals [3].

A number of methods have been reported for the synthesis of 3,4-dihydropyrano[c]chromene [4]. Some of these procedures require the use of toxic organic solvents, expensive catalysts and tedious workup. During the course of our systematic studies directed towards the development of environmentally friendly procedures for several important organic transformations [5], we considered it necessary to develop a general rapid, high yielding, environmentally benign and easy synthetic protocol for a variety of chromene derivatives.



1 2 3 4

Accordingly, we herein report the synthesis of 3,4-dihydropyrano[c]chromenes (4) by the reaction of aromatic aldehydes (1), malononitrile (2) and 4-hydroxycoumarin (3) in the presence of catalyst in 5 ml aqueous ethanol (1:1, H_2O–EtOH). The structures of all products were confirmed using physical and spectral (NMR and IR) data.

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7-9 March 2012

A simple and efficient procedure for the synthesis of α,α′-benzylidene bis(4-hydroxycoumarin)

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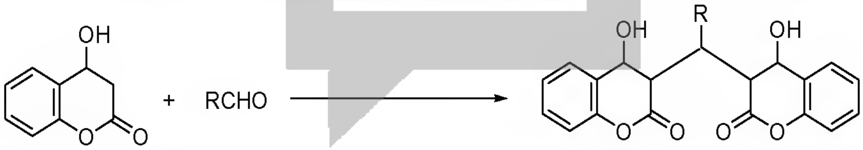
Due to special reactivity of 4-hydroxycoumarin, the synthesis of new coumarin derivatives of dimer and tetramer type has been carried out. Coumarins and their derivatives are characterized by excellent different bioactivity such as antibacterial, antifungal, pharmacological, anti-cancer and anticoagulant activity.[1,2] Biscoumarins derivatives are efective urease inhibitors Also, a number of coumarin derivatives of dimer and tetramer type were shown HIV inhibitory activity. α,α′-benzylidene bis(4-hydroxycoumarin) is prepared with hazardous catalysts, such as glacial acetic acid and acetic anhydride, ethylenediammonium diacetate, and piperidine. However, some of these protocols require long reaction times and they are effectiveness and ecofriendliness. Thus, the introduction of milder faster and more eco-friendly methods is still in great demand. From the environmental acceptability, recently inorganic acidic salts have widely used in organic synthesis because of minimized wastes, simplicity in handling and decreased reactor corrosion problems.[3,4]



In continuation of our studies on the synthesis of heterocyclic compounds,we wish to report the results that led to an extremely convenient method for the preparation α,α′-benzylidene bis(4-hydroxycoumarin) from aromatic aldehydes and 4-hydroxycoumarin in the presence of a solid acid in excellent yield.

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Vinyl triphenylphosphonium salt mediated synthesis of 2-(4,5-Dihydro-3H-pyrrol-2-yl)-but-2-enedionic acid dialkyl ester

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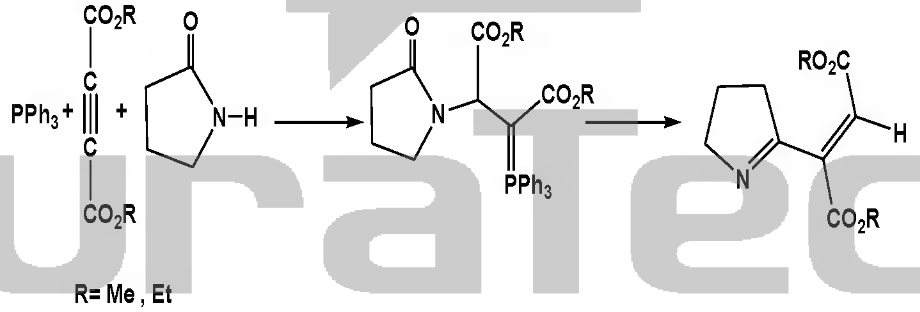
The Wittig reaction is one of the important methods for the synthesis of carbon–carbon double bond [1–3]. phosphorus ylides, are useful in reacting with a carbonyl compound to form an olefin and a phosphine oxide so as to be termed as Wittig reagents. Stabilized phosphoranes, obtained from the three-component reaction between dialkyl acetylenedicarboxylates and 2-pyrrolidin in the presence of triphenylphosphine, undergo a smooth intramolecular Wittig reaction in boiling toluene to produce functionalized 2-(4,5-Dihydro-3H-pyrrol-2-yl)-but-2-enedionic acid dialkyl ester in good yields[4].



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MgO nanoparticles catalyzed one-pot synthesis of 1H-Indole-4(5H)-ones via multi component reactions

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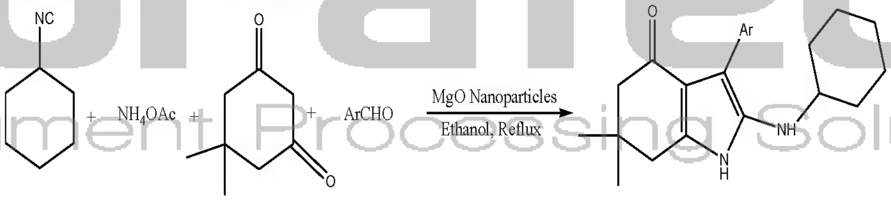
Last decade has witnessed tremendous growth in the field of nanoscience and nanotechnology. Several reports showed an amazing level of the performance of nanoparticles as catalysts in terms of selectivity, reactivity, and improved yields of products. In addition, the high surface-to-volume ratio of nanoparticles provides a larger number of active sites per unit area compared to their heterogeneous counter parts. [1].

Multi-component reactions (MCRs) have emerged as an efficient and powerful tool in modern synthetic organic chemistry allowing the facile creation of several new bonds in a one-pot reaction. The strategy of MCR is particularly for the preparation of heterocyclic compounds is a particularly attractive field in light of the paramount role of these targets in pharmaceutical chemistry [2].

The indole nucleus is an important substructure found in numerous natural alkaloids. The diversity of the structures encountered, as well as their biological and pharmaceutical relevance,

has motivated research aimed at the development of new, economical, efficient, and selective synthetic strategies, particularly for the synthesis of substituted indole rings [3].

Herein, we used MgO nanoparticles as an efficient catalyst for the synthesis indoles derivatives via multi component reactions of isocyanides, aldehydes, 1,3-dicarbonyl compounds and ammonium acetate under reflux conditions. In Conclusion an efficient and facile method for the preparation of 1H-Indole-4(5H)-ones derivatives has been developed using MgO nanoparticles. This method has some advantages such as mild reaction conditions, high yields and shorter reaction times.



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Magnetic Fe_3O_4 nanoparticles as novel, effective, and reusable catalysts for the preparation of 3,4-dihydroquinoxalin-2-amine derivatives

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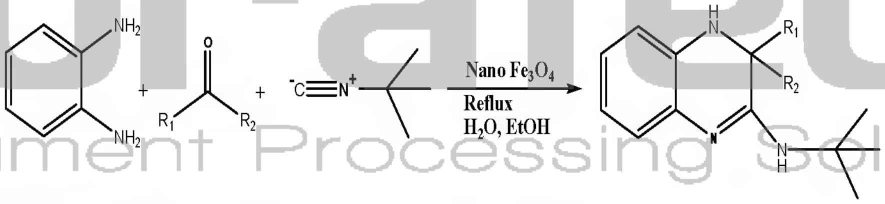
Transition metal salts play an important role as efficient catalysts in organic reactions. In the last decade, transition metal-catalyzed organic reactions have grown into an essential and highly important class of reactions in modern organic chemistry. Magnetic nanoparticles are a class of nanostructured materials of current interest, due largely to their advanced technological and medical applications, envisioned or realized [1], and also superparamagnetic nanoparticles of Fe_3O_4 have been extensively developed and studied for basic scientific considerations and also for manifold technological purposes [2].
Isocyanide-based multicomponent reactions (IMCRs) are particularly interesting as they are more versatile and diverse than other MCRs. MCRs involving isocyanides have emerged as valuable tools for the preparation of structurally diverse chemical libraries of drug-like heterocyclic compounds. Among the various classes of nitrogen-containing heterocyclic compounds, quinoxalines display a broad spectrum of biological activity. Quinoxalines play an important role as a basic skeleton for the design of a number of antibiotics, such as echinomycin, actinomycin, and leromycin [3].
In accordance with the significance of application these compounds, and the role of nanoparticles in catalysis, we wish to report a mild and efficient route to the synthesis of quinoxaline derivatives in aquoes ethanol media. The reactions were conducted in the prescence of Fe_3O_4 nanoparticles via three component reaction of o-phenylenediamine, ketones and isocyanides under reflux conditions. This method has some advantages such as high yield, mild conditions and simple procedure in shorter reaction times.



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New one-pot quick synthesis of tricyclic dispiro structures: 1,2-Bispyrimidine 3-Aryl Cyclpropanes

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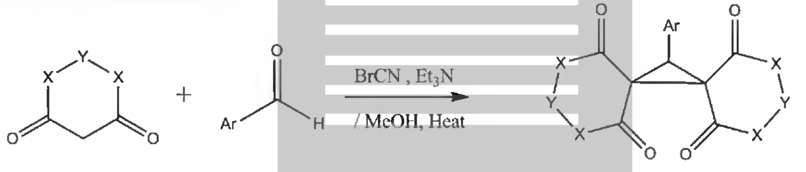
Abstract:

The cyclopropyl group is an important structure in many herbal compounds, displaying antibacterial, antiviral and some enzyme inhibition activities [1]. The methods of cyclopropanes synthesis has divided to two main groups: intramolecular cyclization and interaction of alkenes and a carbenes [1,2]. Reaction of halogenated acid anion with the activated alkene followed by cyclization with elimination of halogen has generated substituted cyclopropanes [2]. On the other hand Michael Initiated Ring Closer (MIRC) is an important synthesis method for cyclization [3]. Cyanogen bromide is useful brominating and cyanating agent as; the bromination and cyanation of imidazoles[4] and α-bromination of β-aminoenones [5]. This Paper describes the Reaction of barbituric acid (BA), 1,3-dimethyl barbituric acid (DMBA), Dimedone and Meldrum's acid with cyanogen bromide and various aldehydes in presence of triethylamine afforded a new class of heterocyclic stable 1,2-Bispyrimidine 3-aryl cyclpropanes which are dimeric forms of barbiturate (uracil and thiouracil derivatives) at 50 °C.

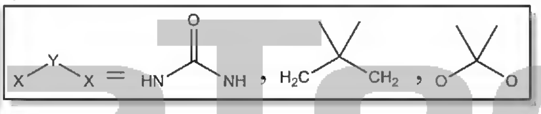


1

2a-l

3a-l

2a = bezaldehyde
2b = 2-nitro benzaldehyde
2c = 3-nitro benzaldehyde
2d = 3-methoxy benzaldehyde
2e = 4-methoxy benzaldehyde
2f = 4-bromo benzaldehyde
2g = 4-cyano benzaldehyde
2h = 2-pyridocarbaldehyde
2i = 3,4,5-trimethoxy benzaldehyde
2j = 2-pyrole carbaldehyde
2k = furfuraldehyde



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A new method for quick one-pot preparation of cyclopropane structure: Direct transformation of aldehyde to 3-aryl-1,1,2,2-tetracyanocyclopropanes

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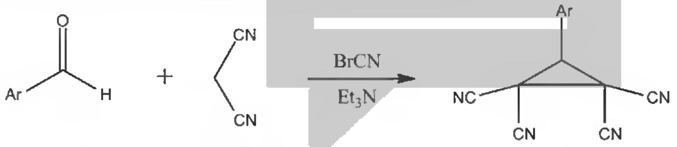
Keyword: Malononitrile, one-pot reaction, 3-aryl-1,1,2,2-tetracyanocyclopropane

Abstract:

In multicomponent reactions(MCRs),three or more reactants come together in a single reaction vessel to form new products that contain structural unit so fall the components .This type of reaction becomes increasingly important inorganic and medicinal chemistry because it allows to obtain highly sophisticated polyfunctional molecules through simple one-pot procedures. Over the past decade, industrial and academic research has made powerful MCR strategies into one of the most efficient and cost-effective tools for combinatorial synthesis[1]. On the other hand the cyclopropyl group is an important structure in many herbal compounds, displaying antibacterial, antiviral and some enzyme inhibition activities [2]. Cyanogen bromide is useful brominating and cyanating agent as; the bromination and cyanation of imidazoles[3] and α-bromination of β-aminoenones [4]. This paper describes a new direct, one-pot chemical transformation of aldehydes **1a-k** and malononitrile **2** into 3-aryl-1,1,2,2-tetracyanopropanes **3a-k**. the reaction of 1 with cyanogen bromide in the presence of triethylamine in ethanol afforded the bromodicyanomethanide as we have described recently in the case of barbituric acid, thio barbituric acid [5]



1 a-k 2 3 a-k

1a = bezaldehyde
1b = 2-nitro benzaldehyde
1c = 3-nitro benzaldehyde
1d = 3-methoxy benzaldehyde
1e = 4-methoxy benzaldehyde
1f = 4-bromo benzaldehyde
1g = 4-cyano benzaldehyde
1h = 2-pyridocarbaldehyde
1i = 3,4,5-trimethoxy benzaldehyde
1j = 2-pyrole carbaldehyde
1k = furfuraldehyde

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One-pot synthesis of aryl-14H-dibenzo[a,j]xanthene derivatives catalyzed by $FeNH_4(SO_4)_2.12H_2O$

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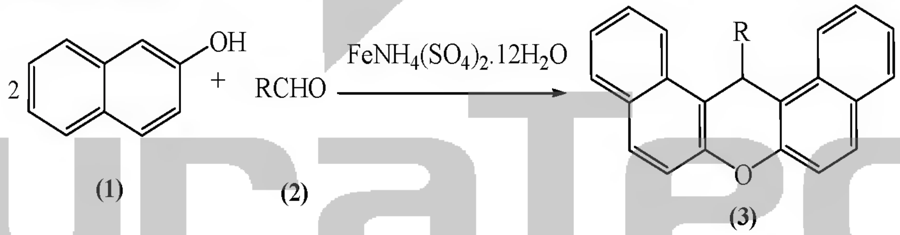
Xanthene derivatives are an important class of heterocyclic compounds. Xanthenes possess broad spectrum of biological and pharmaceutical activities, such as analgesic, antitumor, anticancer, diuretic and herbicide activities.[1]

The heterocyclic xanthene ring system is a widely distributed structural framework that is present in a number of pharmaceuticals and natural products.[2]

We have concentrated most of our recent studies on the preparation of bioactive heterocycles, and have already described simple, efficient procedures, and MCRs for preparation of cis-isoquinolonic acid.[2] We have designed the three-component, ne-pot synthesis of aryl-14H-dibenzo[a,j]xanthene **3** from ß-naphthol **1**, aldehyde **2** , using the non-toxic and easily available $FeNH_4(SO_4)_2.12H_2O$ as a heterogeneous catalyst. (Scheme 1)



Scheme 1

References:

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An efficient one pot synthesis of highly functionalized dispiropyrrolidine thiophenone via [3+2] cycloaddition

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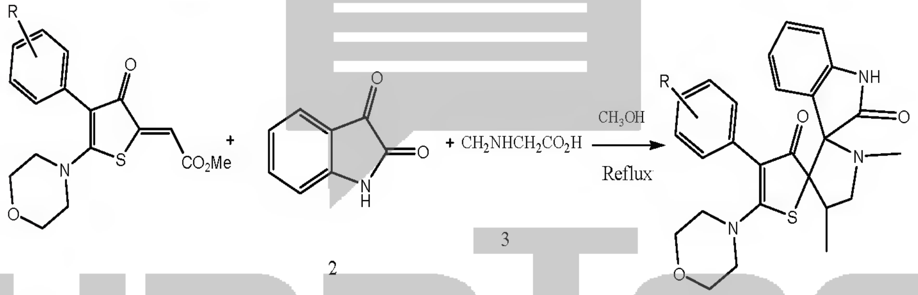
1,3-Dipolar cycloaddition of azomethine ylides with olefins is one of the important reactions in organic synthesis since it produces a variety of five-membered heterocycles, such as pyrrolizidines. Because of their structural and stereochemical complexity as well as their diverse and potent biological activities, pyrrolizidines are very attractive synthetic targets. These compounds are also present in a wide variety of natural products [1].

Gelesmine, pseudotabersonine, formosanine, isoformosanine, morroniside and mitraphylline are some of the alkaloids containing spirooxindole ring systems [2]. Of particular interest, spiropyrrolidinyloxindole ring systems are also found in a number of alkaloids such as horsifiline, spirotryprostatine A and B, and elacomine etc. Derivatives of spirooxindole find very wide biolo-gical applications as anti-microbials, anti-inflammatory, antitumourals, antibiotic agents and inhibitors of human NK-1 receptors [3].

In this report we used (E)- Arylidenethiophenone as unusual dipolarophiles for dispiropyrrolidine thiophenones with potential biological significance. We observed that when the dipolarophiles 1a–j, were subjected to 1,3-dipolar cycloaddition with the azomethine ylide generated by decarboxylation condensation of isatin (2) and sarcosin (3) in methanol, a mixture of cycloadducts 4a–j was obtained .



2

3

1a-j
R1: Me,Et,Ph
R2:Me, OH ,Br, OMe

4a-j
R1: Me,Et,Ph
R2:Me, OH ,Br, OMe

1a–e
R^1: Me,Et,Ph
R^2:Me, OH ,Br, OMe

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Synthesis of β-Amino ketones via direct Mannich-Type reactions, catalyzed with Zr-SD under environmentally friendly conditions

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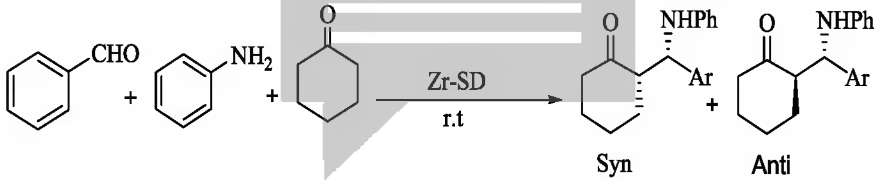
Three-component reactions have emerged as a useful method, since the combination of three-components to generate new products in a single step is extremely economical, among the multi-component reaction.[1-3]

This reaction provides direct access to β-amino carbonyl compounds which are key component of many natural products and possess a wide range of biological activities. In addition, they are key versatile intermediates in synthetic organic chemistry.

In conclusion, we have developed a novel and efficient catalytic method for Mannich reaction of aldehydes, amines and ketones. We have shown that the reaction proceeds much faster when Zr-SD is employed as a catalyst compare to uncatalyzed reaction.



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Magnesium oxide nanoparticles cayalyzed one-pot synthesis of 1H-Indole-4(5H)-ones via multi component reactions

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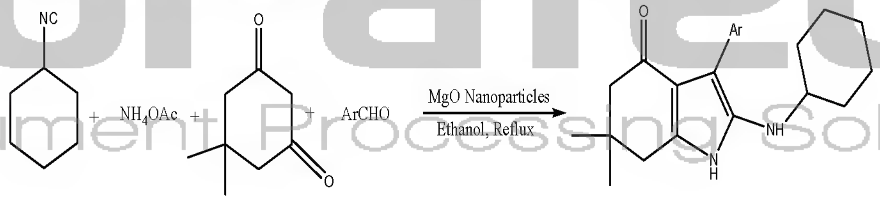
Last decade has witnessed tremendous growth in the field of nanoscience and nanotechnology. Several reports showed an amazing level of the performance of nanoparticles as catalysts in terms of selectivity, reactivity, and improved yields of products. In addition, the high surface-to-volume ratio of nanoparticles provides a larger number of active sites per unit area compared to their heterogeneous counter parts. [1].

Multi-component reactions (MCRs) have emerged as an efficient and powerful tool in modern synthetic organic chemistry allowing the facile creation of several new bonds in a one-pot reaction. The strategy of MCR is particularly for the preparation of heterocyclic compounds is a particularly attractive field in light of the paramount role of these targets in pharmaceutical chemistry [2].

The indole nucleus is an important substructure found in numerous natural alkaloids. The diversity of the structures encountered, as well as their biological and pharmaceutical relevance,

has motivated research aimed at the development of new, economical, efficient, and selective synthetic strategies, particularly for the synthesis of substituted indole rings [3].

Herein, we used MgO nanoparticles as an efficient catalyst for the synthesis indoles derivatives via multi component reactions of isocyanides, aldehydes, 1,3-dicarbonyl compounds and ammonium acetate under reflux conditions. In Conclusion an efficient and facile method for the preparation of 1H-Indole-4(5H)-ones derivatives has been developed using MgO nanoparticles. This method has some advantages such as mild reaction conditions, high yields and shorter reaction times.



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Nanocrystalline Silver Iodide-Mediated Three Component Coupling of Aldehydes, Ketones and Alkyl Halides in Aqueous Media

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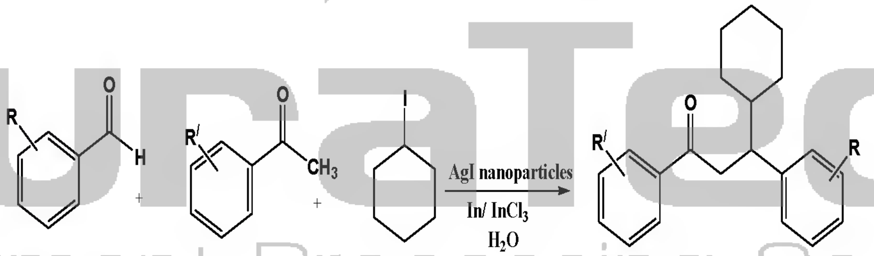
One-pot multicomponent coupling reactions (MCRs) have received much attention in recent years. Especially, multicomponent reactions that can be run under solvent-free conditions or in water for achieving atom economy and the identification of catalytic procedures are ideal protocols for the development of environmentally friendly and economical advantageous chemical processes[1]. An efficient method has been developed for the Barbier–Grignard-type alkylation reaction of aldehydes and ketones using unactivated alkyl halides in water, in the presence of an In/CuI/I_2 or In/AgI/I_2 system [2]. The reactions proceeded more efficiently in water than in organic solvent. Nanocrystalline metal oxides find excellent applications as active adsorbents for gases and destruction of hazardous chemicals. They are also gaining tremendous importance due to their distinct catalytic activities for various organic transformations.

The present work describes conjugate addition of alkyl iodides to various α,β-unsaturated carbonyl compounds which prepared with aldol condensation between aldehydes and ketones in the presence of silver iodide nanoparticles.

The high reactivity of AgI-nanoparticles is due to the high surface area of nanoparticles combined with unusual reactive morphologies. Moreover, heterogeneous catalysts are easy to separate and can be recycled. This is very beneficial for industrial process in the green chemistry domain. In conclusion we have developed an efficient and practical method for the Barbier–Grignard-type alkylation reaction. Our new method has some advantages such as mild reaction conditions, high yields and shorter reaction times.



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An Effiecient One-Pot Synthesis of 2-Amino-4H-Chromenes by using Magnesium Oxide Nanoparticles as a Mild and Green Catalyst

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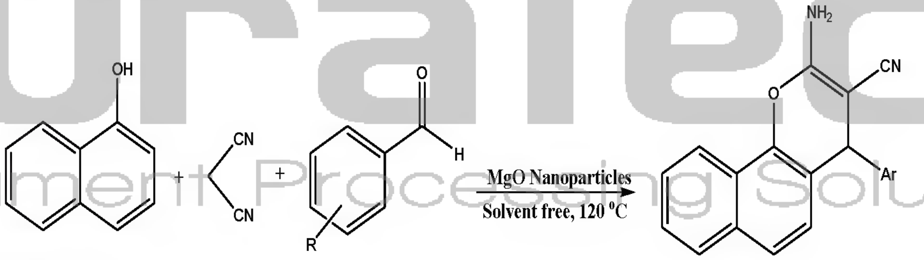
2-Amino-4H-chromenes are important heterocycles that are known to possess multiple biological activities. The synthesis of 2-Amino-4H-chromene derivatives has been received special attention to chemists because of their wide range of therapeutic properties, such as antibacterial, antiviral, and anti-inflammatory activities [1].

One-pot multicomponent coupling reactions (MCRs), where several organic moieties are coupled in one step, for carbon-carbon and carbon–heteroatom bond formation is an attractive synthetic strategy for the synthesis of compound libraries of small molecules for potential applications in medicinal and pharmaceutical chemistry [2].

Nanotechnology has been one of the most active research areas in recent years. The reactivity of a catalytic nanoparticle is largely determined by the energy of surface atoms, which can be easily gauged by the number of neighboring atoms by the bonding modes and accompanying energies of small molecules to be transformed on the nanoparticle surface [3].

In this research we have explored for A^3 coupling of aldhyde, 1-naphthol and malononitrile in the presence of MgO nanoparticles to the synthesis of 2-amino-4H-chromenes derivatives under solvent free conditions. In the view of recent interest in the use of heterogeneous catalysis we have developed magnesium ozide nanoparticles as an inexpensive, non-volatile, recyclable, non-explosive, easy to handle, and eco-friendly catalyst can be used in many organic synthesis.



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Synthesis and Characterization of siloxane surfactants in water and their surface energy characteristics.

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Abstract:

A simple but efficient method has been followed for the synthesis of water soluble siloxane amphiphile by grafting poly(ethylene glycol) (PEG) onto the hydrophobic poly(hydromethyl siloxane) backbone. Systematic variations in the amount of PEG incorporations were carried out to get water soluble oligomers.

Keywords: Siloxane surfactant; Surface properties; Sessile drop method

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Synthesis of new derivatives of pyridazino[4,3-e][1,2,4]triazolo[3,4-b][1,3,4]thiadiazine

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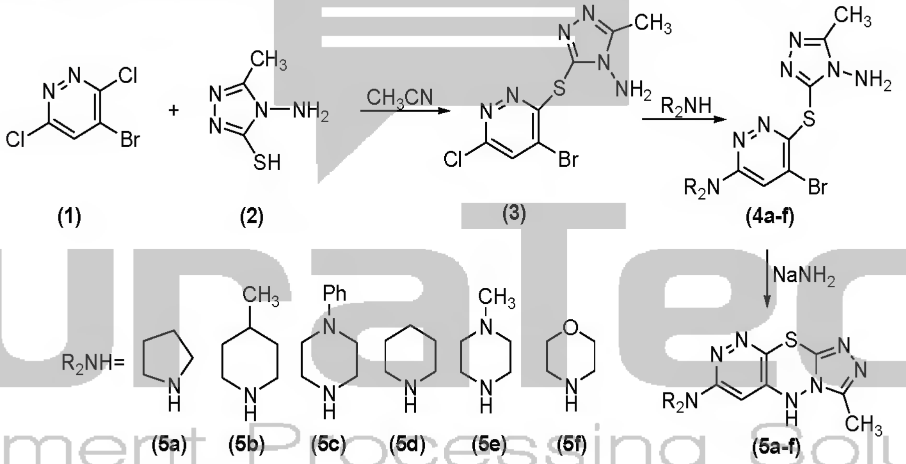
Triazoles and especially fused triazoles are also an important class of heterocyclic compounds with antifungal, anticonvulsant, herbicidal and antidepressant activities [1]. Pyridazinothiadiazines are also of interest as potential inhibitors of cyclic nucleotide phosphodiesterase[2], dyestuff [3], and precursors of herbicides [4]. In continuation of our interest in chemistry of fused heterocycles of pharmacological importance and exploration of their synthetic pathways, we decided to synthesize the new heterocyclic systems of pyridazino[4,3-e][1,2,4]triazolo[3,4-b][1,3,4]thiadiazine. In this study, the prepared ٤-bromo-٣،٦-dichloropyridazine was reacted with 1-amino-2-mercapto-5-methyl-1,2,3-triazole in acetonitrile which was subsequently treated with secondary amines and cyclized in the presence of sodium amide.



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Synthesis of new derivatives of pyrimido[4,5-e][1,2,4]triazolo[3,4-b][1,3,4]thiadiazine

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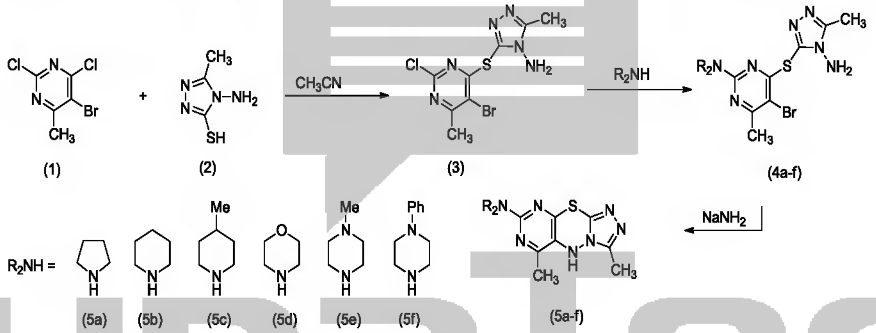
Pyrimidine derivatives and heterocyclic annulated pyrimidines continue to attract great interest because of the wide variety of interesting biological activities observed for these compounds[1]. Moreover, triazoles and especially fused triazoles are also an important class of heterocyclic compounds with antifungal [2], anticonvulsant [3], herbicidal [4], and antidepressant activities [5].

In continuation of our studies towards the synthesis of fused heterocycles of biological importance containing pyrimidine [6] moieties, we describe here the synthesis of some new derivatives of tricyclic 3,6-dimethyl-5H-pyrimido[4,5-e][1,2,4]triazolo[3,4b][1,3,4] thiadiazines **(5a-f)**.



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Synthesis of pyrrolobenzothiazole derivatives via a three-component reaction

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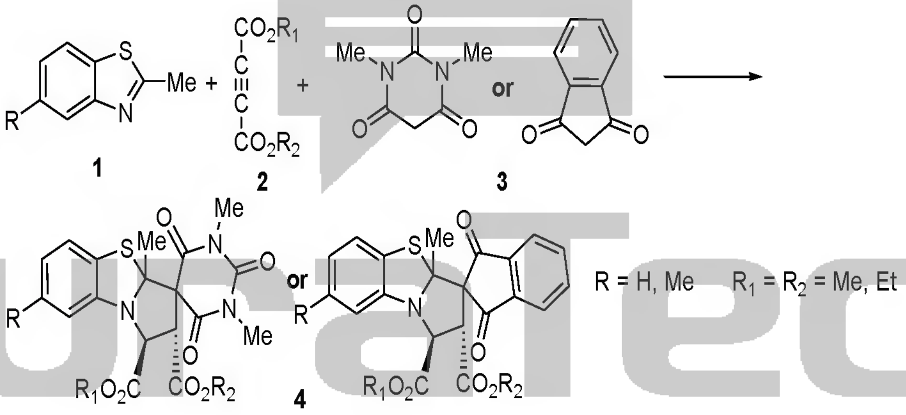
The reaction of nucleophilic species with acetylenic esters leading to the formation of zwitterions has been known for a long time [1]. These reactive intermediates, however, have only recently received attention from the vantage point of their use in carbon-carbon and carbon-heteroatom bond forming reactions [2]. The benzothiazole–moiety can be found as a common substructure in a large number of compounds with a wide range of biological activities [3]. Numerous papers have shown that the benzothiazole nucleus possesses a potent anticancer activity against human cancer [4]. The benzothiazole constitutes an important scaffold of drugs, possessing several pharmacological functions, rendering this molecule and its derivatives powerful antitumour agents [5]. In recent years, several attempts were made for modifying the benzothiazole nucleus to improve their antitumor activities [6]. In this letter, I report the results of my studies involving the reaction of zwitterions derived from 2-methylbenzothiazole or 2,5-dimethylbenzothiazole **1** and acetylenic esters **2** in the presence of 1,3-dicarbonyl compounds **3**, which constitutes a synthesis of pyrrolobenzothiazole derivatives.



R = H, Me $R_1 = R_2$ = Me, Et

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One-pot three-component synthesis of 1-amidoalkyl-2-naphthol using acetic acid

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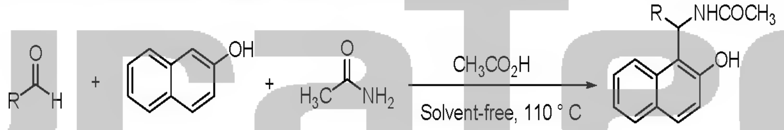
Amidoalkyl naphthols are important compounds because of their useful biological and pharmacological activities. Furthermore, 1-amidoalkyl-2-naphthol can be converted to useful and important biological building blocks and their hydrolysis leads to 1-amino methyl 2-naphthols, compounds that exhibit hypotensive and bradycardia effects in humans. Thus, the synthesis of amidoalkyl naphthols is an important useful task in organic Chemistry [1-3].

In this paper we report a simple and environmentally benign methodology for synthesis of amidoalkyl naphthols via one-pot three-component condensation reaction between aldehydes, 2-naphthol and acetamide using catalytic amounts of CH_3COOH as a safe, environmental, non-toxic and expensiveness catalyst under solvent-free conditions.



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Efficient one-pot synthesis of 14-substituted-14H-dibenzo[a,j]xanthenes using 1-methyl-3-butylimidazolium hydroxide [bmIm]OH under solvent-free conditions

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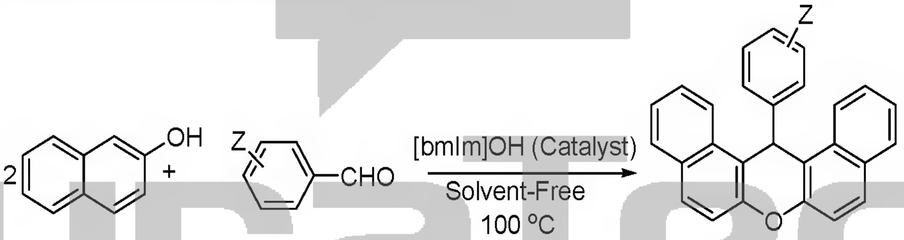
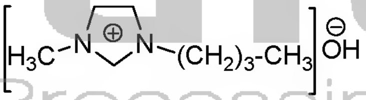
Ionic liquids have been the subject of considerable interest in the context of green synthesis because of their wide acceptability as alternative green reaction media [1]. 1-Methyl-3-butylimidazolium hydroxide, [bmIm]OH, [2] as catalyst has been in Michael addition of active methylene compounds to conjugated ketones, carboxylic esters, and nitriles [3] and dechlorination of poly(vinyl chloride) [4].

In this research, a Brønsted-basic task-specific ionic liquid, 1-methyl-3-butylimidazolium hydroxide was employed as a catalyst for the synthesis of 14-alkyl- or aryl-14H-dibenzo[a,j]xanthenes via the one-pot condensation of β-naphthol with aliphatic or aromatic aldehydes under solvent-free conditions. The yields are excellent and the reactions go to completion within 25–30 min. The novel synthesis method offers the advantages of high yields, short reaction times, simplicity and easy workup. The catalyst could be recycled and reused without a noticeably decrease in its activity.



[bmIm]OH (Catalyst):



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Synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-ones using catalytic amount of phosphoric acid supported on alumina

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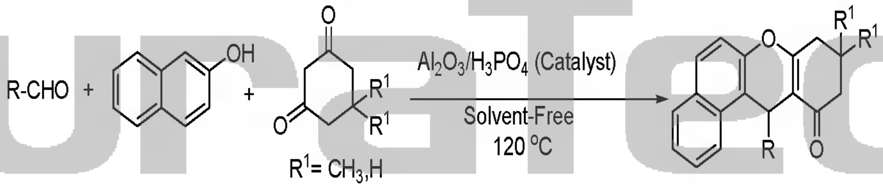
Heterogeneous catalysts have gained significant attraction due to economic and environmental considerations. The catalysts used are generally inexpensive and readily available. They can be handled conveniently and removed from the reaction mixture, thus making experimental procedures simple [1].

In continuation of our work on the development of useful synthetic methodologies [2], We have extended our studies to the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a] xanthen-11-ones by three component condensation of β-naphthol, aromatic aldehydes, and dimedone in the presence of phosphoric acid supported on alumina (H_3PO_4/Al_2O_3) as recyclable heterogeneous catalyst under solvent free conditions (Scheme 1). This synthetic methodology offers the advantages of high yields, short reaction times, simplicity and easy workup. The catalyst could be recycled and reused without a noticeably decrease in its activity.



Scheme 1

References:

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Preparation of 1-(α-aminoalkyl)-2-naphthols by a three-component reaction catalyzed by DABCO under mild and green conditions

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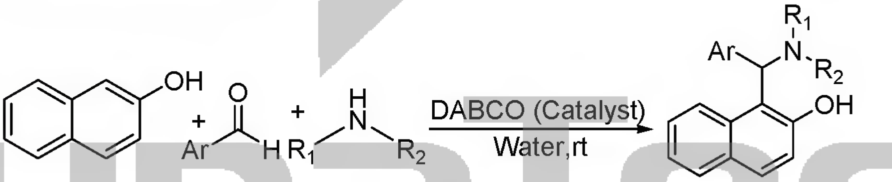
Multi-component reactions (MCRs) have attracted considerable attention since an increasing number of organic chemical compounds are formed by MCRs that convert more than two educts directly into their products by one-pot reactions [1].

One of these MCRs is the preparation of 1-(α-aminoalkyl)-2-naphthols (the Betti bases). In this research, we represent an advance in the context of synthetic methodology towards mentioned class of biologically important molecules. The preparation of 1-(α-aminoalkyl)-2-naphthols can be carried out by three component condensations of 2-naphthol, arylaldehyde and amines in the presence of DABCO as catalyst in aqueous media at room temperature (Scheme).



Scheme

The method has been applied for the synthesis of a range of compounds with variable functionalities in excellent yield. Green reaction conditions, short reaction time, excellent yields of the products make this methodology highly significant.

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A New Synthesis of 1,5-Diionic Organophosphorus Compounds from the Reaction between Triphenylphosphine and Propiolic Acid in the Presence of N-H Heterocyclic Compounds

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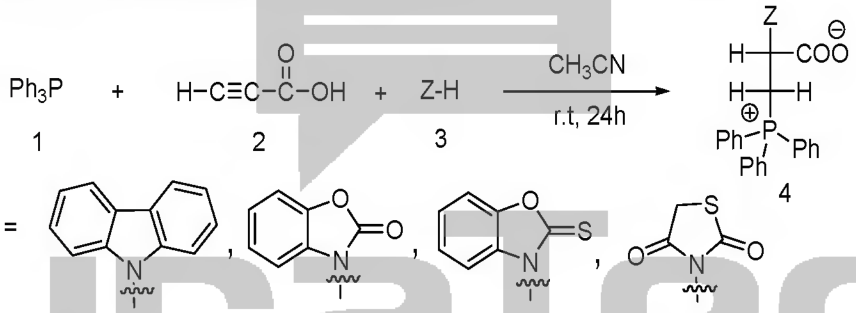
Organophosphorus compounds, i.e. those bearing a carbon atom directly bound to a phosphorus atom, are synthetic targets of interest, not least because of their value for a variety of industrial, biological, and chemical synthetic uses [1a]. The successful attack by nucleophilic trivalent phosphorus on a carbon atom **is** facilitated when the latter is part of, or conjugated with, a carbonyl group, or when it is part of an unsaturated bond otherwise activated [1]. There are many studies on the reaction between trivalent phosphorus nucleophiles and α,β-unsaturated carbonyl compounds in the presence of a proton source such as NH or CH-acids [2]. Here wish to report for the first time the addition of triphenylphosphine **1** to propiolic acid **2** in the presence of N-H heterocyclic compounds **3** such as carbazole, 2-benzoxazolinone, 2-mercaptobenzoxazol and 2,4-thiazolidinedione for preparation of 1,5-diionic organophosphorus compounds **4** in excellent yields at ambient temperature.



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A Novel and Efficient Synthesis of Stable 1,5-Diionic Organophosphorus Compounds from the Reaction between Triphenylphosphine and Acetylenedicarboxylic acid (ADA) in the Presence of C-H Acids

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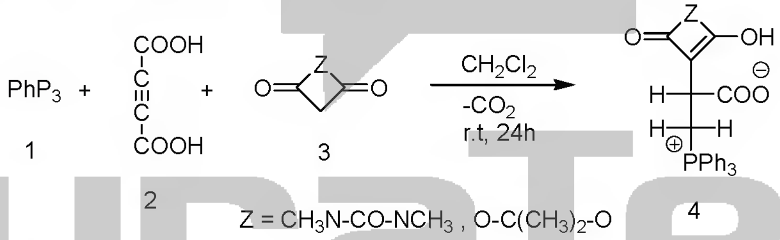
Organophosphorus compounds are synthetic targets of interest because of their applications in a variety of industrial, biological, and pharmacological activities and in chemical synthetic uses [1]. In continuation of our investigation on the reaction between trivalent phosphorus nucleophiles and acetylenic esters in the presences of acidic organic compounds [2-4] we wish to report for the first time the addition of triphenylphosphine **1** to acetylenedicarboxylic acid (ADA) **2** in presence of C-H acids **3** such as 5,5-dimethylcyclohexane-1,3-dione (dimedone), N,N′-dimethyl barbituric acid, acetylacetone and acetoacetanilide leads to stable 1,5-diionic organophosphorus compounds **4** in excellent yields at ambient temperature.



Z = $CH_3N\text{-}CO\text{-}NCH_3$, O-C$(CH_3)_2$-O

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Hexamethyl Phosphorous Triamide (HMPT) as a Reagent for the Synthesis of New Stable Phosphorus Ylides

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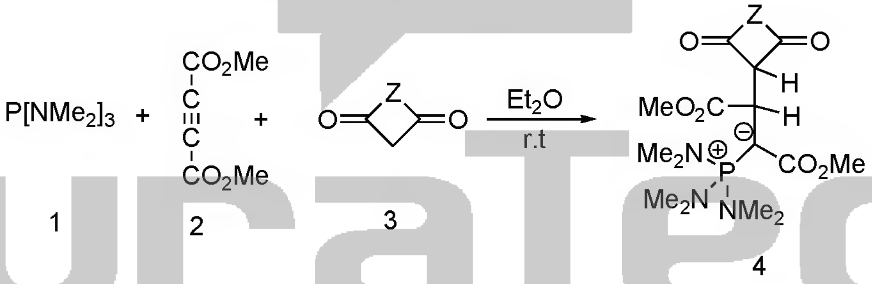
In recent years there has been increasing interest in the synthesis of organophosphorus compounds having a carbon atom bonded directly to the phosphorus atom [1−4]. This interest has resulted from the recognition of the value of such compounds in a variety of biological, industrial, and chemical synthetic uses. A large number of methods have appeared describing novel syntheses of organophosphorus compounds. In continuation of our investigation on the reaction between trivalent phosphorus nucleophiles and acetylenic esters in the presences of acidic organic compounds [2-4] we wish to report a convenient and facial one pot, three component reaction between hexamethyl phosphorous triamide (HMPT) **1** and dimethyl acetylenedicarboxylate (DMAD) **2** in the presence of C-H acids **3** such as acetylacetone, 1,3-indandione, dibenzoylmethane and anthrone for preparation of new and stable phosphorous ylides **4** in excellent yields at ambient temperature.



References:

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$Fe(DS)_3$ catalyzed One-pot synthesis of 2-amino-3-cyanopyridines

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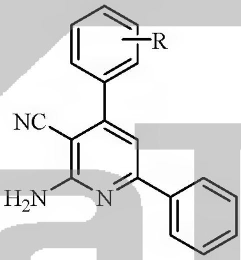
Many natural occurring and synthetic compounds containing the pyridine scaffold possess interesting pharmacological properties. [1] Among them, 2-amino-3-cyanopyridines have been identified as IKK-β-inhibitors. [2] Besides, they are important and useful intermediates in preparing variety of heterocyclic compounds. [3] Therefore, the synthesis of 2-amino-3-cyanopyridines continues to attract much interest in organic chemistry. It has also been reported that the 2-amino-6-aryl-3-cyano-4-piperidinylpyridine core structure can be constructed using a one-pot coupling reaction of acetophenone, piperidine, malononitrile and ammonium acetate in conventional heating mode.[4] Nevertheless, the protocol gives comparatively lower yields and longer reaction time. In this article a series of 2-amino-3-cyanopyridine derivatives have been prepared by one-pot condensation from malononitrile, aromatic aldehyde, methyl ketone and ammonium acetate using $Fe(DS)_3$ (Scheme 1). On basis of our knowledge, 2-amino-3-cyanopyridine derivatives have not been prepared by $Fe(DS)_3$ yet. This method has the advantage of high yields and being environmentally-friendly.



Scheme 1

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[Bmim]OH-mediated cascade reaction: Green one-pot synthesis of benzofurans

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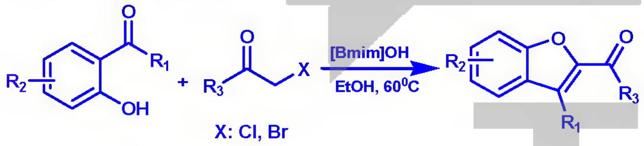
Benzofuran derivatives are important components of those clinically used plant extracts due to their excellent properties, such as antibacterial, antimicrobial, antitumor, and the ability to control calcium level. Thus many research efforts have been focused on the efficient synthesis of these molecules [1-3].

Design a catalyst with high activity and selectivity, which is benign to the environment and easily recovered, is an interesting and rapidly growing area of synthetic chemistry. Owing to their green credentials, ionic liquids (ILs) have attracted considerable interest as environmentally benign reaction media, catalysts and reagents [4]. They are also easy to recycle[5].

This one-pot synthetic protocol involves the utilization of halogenated ketone with salicylaldehyde or o-acylphenols in the presence of ionic liquid [Bmim]OH in ethanol as a solvent. For optimizing the reaction condition, we tried the reaction at the different solvents, ethanol was found to be the best solvent. The Products were characterized by IR, ^{1}HNMR, ^{13}CNMR spectroscopy and mass spectrometry.



In conclusion, we report a new one-pot method of an ionic liquid-promoted RapeStoermer reaction for the efficient preparation of a series of 2,3 substituted benzofurans in excellent yields. This reaction contains certain value from a green-chemistry viewpoint using ionic liquid [Bmim]OH as a green reaction promoter. The method is highly atom efficient as there is no by-product formation. This reaction features with mild reaction condition and wide access of the starting materials. This mild annulation strategy developed here may find application in the synthesis of other hetero-containing aromatic compounds.

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Microwave-Assisted One-Pot Synthesis of Substituted 4,7-Phenanthroline and Pyranoquinoline Derivatives Catalyzed by lewis Acid Ionic liquids

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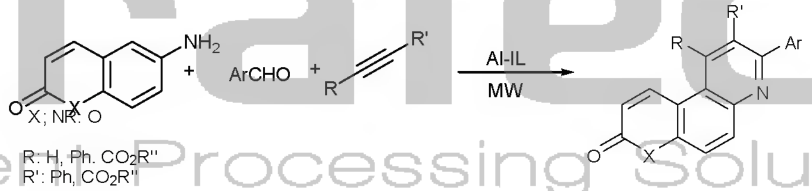
Quinolines and their derivatives are important scaffolds not only for their wide spectrum of biological activities[1]. like anti HIV,antituberculosis, antimicrobial, antifungal,and anticancer, but also for their formation of conjugated molecules and polymers that combine enhanced electronic, optoelectronic, or nonlinear optical properties with excellent mechanical properties[2.Moreover, it is expected that pyranoquinoline, which contain both a quinoline ring and pyran moieties, afford unique biological activities, such as psychotropic activity, antiallergic activity, anti-inflammatory activity, estrogenic activity, and are used as potential pharmaceuticals[4].

In view of the importance of these compounds, there has been growing interest in development of synthetic methods for pyrano quinoline by aza-Diels–Alder reaction[5]. However, many of these synthetic protocols suffer from disadvantages, such as harsh reaction conditions, multistep reaction, expensive reagents and longer reaction time, large amount of catalyst and lower yields.

Combination of Lewis acids with microwave irradiation has become a powerful synthetic tool for the rapid synthesis of a variety of biologically active compounds. Ionic liquids show Lewis acidity when a Lewis acid, which forms the counterion, is used in excess. In this work we used 1,3-Dialkyl-imidazolium chloride as IL and aluminum trichloride($AlCl_3$) to prepare lewis acid ionic liquid (Al-IL) to catalyze multicomponent aza-Diels–Alder reaction of various heterocyclic amines, aldehydes and alkynes under microwave irradiation. The methodology is novel, simple, rapid, inexpensive and an environment friendly affording good to high yield.



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Efficient one-pot synthesis of 1,2,4-benzothiadiazine-1,1-dioxides catalyzed by Palladium(0) complex

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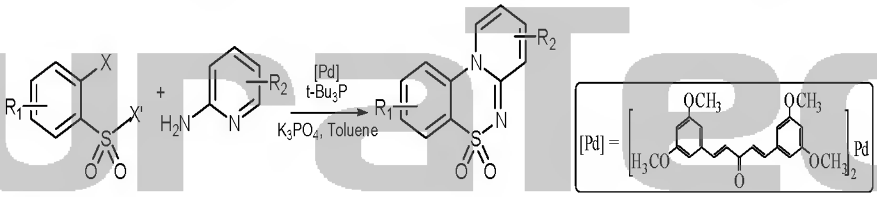
Benzothiadiazine-1,1-dioxides are important targets in synthetic and medicinal chemistry because of their broad range of biological activities, such as antihypertensive, antimicrobial, and antiviral[1]ones. So far several synthetic routs have been reported for the preparation of these heterocycles. Most of these non-catalytic approaches suffered from considerably harsh reaction conditions causing the formation of byproducts and a somewhat limited availability of starting materials narrowing the chemical space for drug design[2]. Recent advances in this area have allowed for this type of reaction by using catalytic amounts of metal under milder conditions[3].

Herein, we developed a straightforward approach to synthesis of 1,2,4-benzothiadiazine-1,1-dioxides through a palladium-mediated sequence involving the sulfonylation of the 2-aminopyridine derivatives and the interamolecular aromatic nucleophilic substitution of the ortho-halogen atom respectively. In this reaction, we used of Bis (3,5,3',5'dimethoxydibenzylideneacetone) palaladium(o) as a new catalyst and tritert-butylphosphine as a ligand and K_3PO_4 as base. Various functional groups are well tolerated in this mild reaction condition and desired products were obtained in high yield. The investigation revealed that the nature of the o-halogen and the electronic character of the benzene ring substituent have a significant effect on the rate of the reaction. The products were characterized by IR, ^{1}HNMR, ^{13}CNMR spectroscopy and mass spectrometry.



X:Cl, Br,I
R_1, R_2: functional group

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A novel three-component Synthesis of 1,2-dihydroisoquinolines containing 2-thiohydantoins in water

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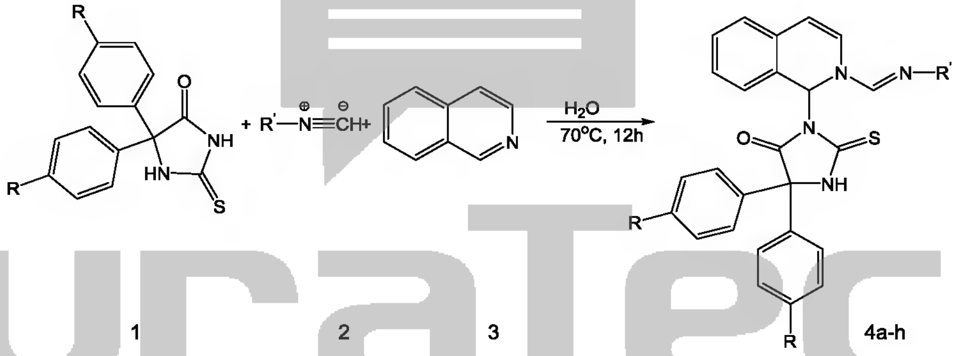
Multi-component reactions (MCRs) have attracted much attention for combinatorial chemistry. Of pivotal importance in this area are the isocyanide based MCRs such as the versatile Ugi and Passerini reactions [1]. Isocyanides are compounds with an extraordinary functional group; its unusual valence structure and reactivity have been discussed for over one and a half centuries [2]. Isocyanides are the only class of stable organic compounds with a formally divalent carbon. Owing to its reactivity the isocyanide group differs fundamentally from other functional groups [3]. We design multi-component reactions in water, without the employ of any harmful organic solvents. Herein we describe an efficient reaction of thiohyantoins **1** with isocyanide **2** and isoquinoline **3**, which constitutes a synthesis of 1,2-dihydroisoquinolines **4** in good yields.



R=H, Me, Cl R'=Cy, tBu

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Alumina sulfonic acid: An Efficient Catalyst for the Synthesis of Coumarin via Pechmann Condensation under Solvent Free Condition

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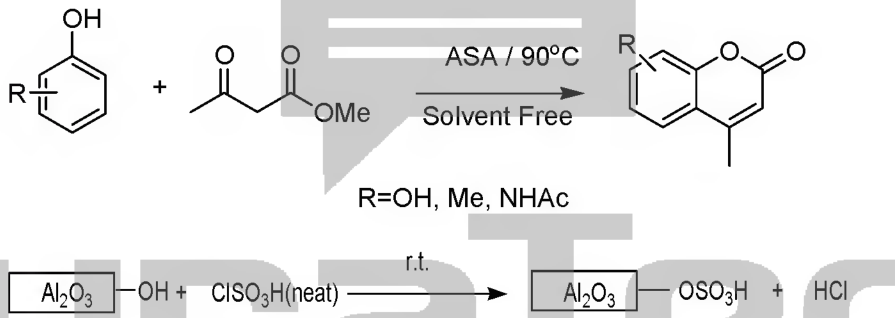
Coumarins, the most important classes of fluorescent molecules, constitute important structural features present in a number of bioactive naturalproducts. They exhibit a wide range of physiological activities, such as anti inflammatory[1], antibacterial [2], anticancer [3], anticlotting [4] and anti-HIV [5] activities. Naturally, there have been continuous efforts to develop new convenient and practical syntheses of coumarin and its derivatives the Pechmann reaction is an important approach. 4-Substituted coumarins can be synthesized simply by the condensation of substituted phenols with methyl acetoacetate .



Scheme 1

In conclusion, we have developed an efficient and environmentally benign methodologies for the synthesis of coumarin the advantages of these methods are reduced reaction time, higher yield, mild reaction condition, easy work up and economic viability of the catalyst.

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A Simple method for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones using nano silica supported perchloric acid under solvent-free conditions

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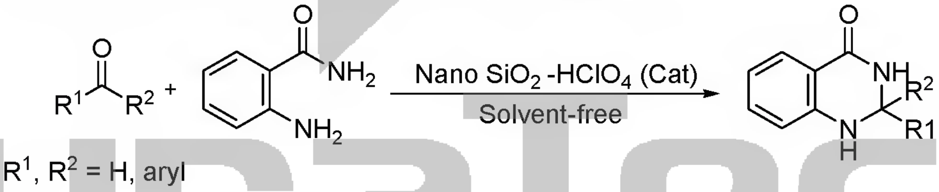
2,3-Dihydroquinazolin-4(1H)-ones are a class of heterocycles that has attracted much attention because they possess potential pharmaceutical activities [1]. They can be easily oxidized, using $KMnO_4$, to quinazolin-4(3H)-ones that are useful as growth inhibitor against leukemia cells [2]. There are several advantages in the use of $HClO_4$–SiO_2 [3] as catalyst for this transformation, which include high yields of products, simplicity in operation, cleaner reaction profiles and short reaction times [4] In continuation of our ongoing research toward the synthesis of heterocyclic compounds by greener and environmentally benign approaches [4], we reported the synthesis of 2,3-dihydroquinazolin-4(1H)-ones by the condensation of anthranilamide and aldehydes or ketones under solvent-free in the presence of nano silica supported perchloric acid as low cost, non toxic, environmental compatible, reusable, more economic and easy to handle catalysts (Scheme 1).



Scheme 1: Synthesis of 2,3-dihydroquinazolin-4(1H)-ones

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Rapid Solvent-Free Procedure for the Efficient Synthesis of 3,4-Dihydropyrimidin-2(1H)-Ones (Thiones)

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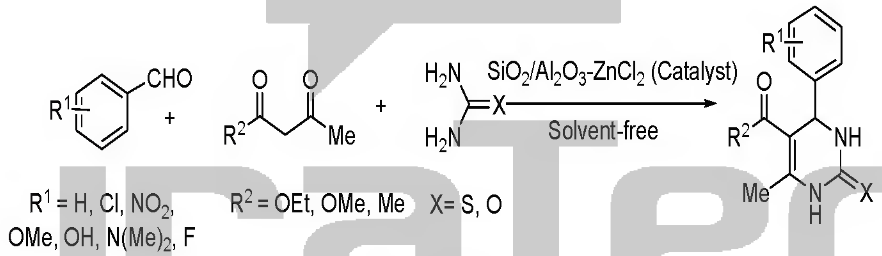
Multi-component reactions have gained increasing attention for the synthesis of new heterocycles of medicinal importance [1]. Biginelli reaction is one of the most versatile reactions for the selective construction of heterocycles. The simple and straightforward procedure reported by Biginelli [2] in 1893 involves a three component condensation reaction of β-ketoesters, arylaldehyde, and urea to give 3,4-dihydropyrimidin-2-(1H)one (DHPMs) in one-pot. The DHPMs derivatives have received considerable attention in recent years essentially because of their importance in medicinal chemistry [3]. Herein, we developed a safe alternate method for the synthesis of 3,4-dihydropyrimidin-2(1H)-one/thione derivatives in presence of silica/alumina supported zinc chloride as a solid acid catalyst. The cayalyst is safe, easy to handle, environmentally benign and presents fewer disposal problems (Scheme1).



Scheme 1

References:

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Three-component Preparation of 2-Amino-4H-1,3-oxazines Using Phosphomolybdic Acid Supported on Silica Gel (PMA-SiO_2) as an Efficient Catalyst

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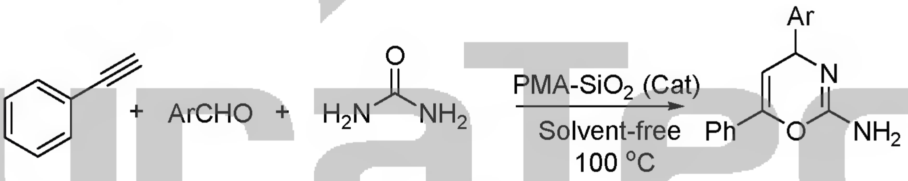
2-Amino-4H-1,3-oxazines are important synthetic intermediates in organic synthesis [1] and these skeletons have been shown biological activities [2]. Phosphomolybdic acid (PMA) belongs to the class of heteropoly acids (HPA). Catalysis with HPAs is a field of growing importance. HPAs are commercially available, cheap and environmentally friendly catalysts. They exhibit high activities and selectivities and allow cleaner processing over conventional catalysts. HPAs have a very strong Bronsted acidity. In fact, it is reported that HPA has much higher activity than H_2SO_4, TsOH and $BF_3{\cdot}OEt_2$ [3]. For the reusability of the catalyst it has been supported on silica gel. A comparison in the yield and time of the reactions shows that supporting of PMA on SiO_2 presents the better catalytic activity than PMA alone [4].
The aim of the present protocol was to summarize the data on the one-pot preparation of 2-amino-4H-1,3-oxazine derivatives in high yield using a three-component condensation of phenyl acetylene, aromatic aldehyde and urea in the presence of phosphomolybdic acid supported on silica gel (PMA-SiO_2)as catalyst under thermal solvent-free conditions (Scheme1).



Scheme 1

References:

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Synthesis of mono-, and bis-substituted 3-aminoalkylated indoles via $ZnCl_2$-KSF

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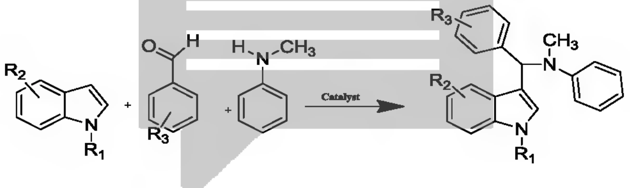
The indole derivatives serve as a scaffold in a number of antibacterial, antiviral, and protein kinase inhibitors. Indole-based derivatives have been investigated for anticancer activities. The 3-substituted indoles are structural units of many natural and biologically interesting compounds, which possess various pharmacological activities. Multicomponent reactions (MCRs) are of increasing importance in organic and medicinal chemistry, as high degrees of molecular diversity can be introduced by these reactions in a very fast, efficient, and time saving manner without the isolation of any intermediates. Recently the 3-indole derivatives were synthesized by one-pot condensation reaction of indole or N-methylindole, substituted or unsubstituted benzaldehyde, and N-methylaniline. The reaction condition were optimized in various solvents, such as DCM, DMSO, DMF, THF, CH_3CN and also using different catalysts such as $Yb(OTf)_3$–SiO_2 and bromodimethylsulfonium bromide (BDMS), PMA-SiO_2 and etc.[1-3].



R_1= H, CH_3 R_2= H, Br, OMe R_3= H, CH_3, OH, OMe, Cl, NO_2

Scheme 1. Synthesis of 3-substituted indoles.

In contribution to this one-pot component reactions and compare with other catalysts reported in the literature, here we utilizing several Lewis acids either as activated on silica gel and KSF or using directly aprotic Lewis acids such as $FeCl_3$ and $ZnCl_2$. In summary, different variation of catalyst, such as $FeCl_3$-KSF, $ZnCl_2$-KSF, HCl-KSF, $Na_2S_2O_8$-SiO_2, H_2SO_4-SiO_2, Iodine… was used, among these catalyst so far $ZnCl_2$-KSF were found to give a better yield. In other efforts several bis-indoles with variety linkages are in progress.

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Cytotoxic activity of Varthemia persica DC. from Kashan

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Asteraceae or Compositae (commonly referred to as the aster, daisy, or sunflower family), is an exceedingly large and widespread family of vascular plants [2]. The genus Varthemia (from Asteraceae family) has one species, V. persica DC, in Iran with having three varieties including var. persica, squarrosula and stenocephalas [3,4]. Artemia salina was first described (as Cancer salinus) by Carl Linnaeus in his Systema Naturae in 1758. The resilience of these creatures makes them ideal test samples in experiments. Artemia is one of the standard organisms for testing toxicity of chemicals [5]. The brine shrimp lethality assay is considered a useful tool for preliminary assessment of toxicity [6,7,8].

At this research we have evaluated cytotoxic activity of methanolic extract of this plant. Results exhibit that this plant has significant toxicity and may be a good resource for extracting anticancer compounds.

Keywords: Varthemia persica DC., Cytotoxic activity, Asteraceae, Artemia salina

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Synthesis of Polythiophene/ Titanium Dioxide Nanocomposites through "In Situ" Polymerization Method

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Considering the recent needs of modern society and improvements in nanotechnology fields especially in this case nanocomposit extensive applications in which they are regarded as new materials made with fillers which have nano size. These materials have a big potential for applications in automotive and aerospace industry as well as in construction properties. Polymer and metal oxide have been studied for many years for independent electrical, optical and mechanical properties. One widely studied metal oxide is titanium dioxide due to its unique optical, electrical, chemical and photocatalytic properties. Similarly polythiophene (PT) as a conducting polymer have been investigated extensively because of their interesting semiconducting electronic and optical qualities, combined with processing advantage and good mechanical characteristics [1-3].

This research study explains an efficient method for synthesis of polythiophene/titanium dioxide (PT/TiO_2) nanocomposites with various TiO_2 ratios. These nanocomposites were provided through one step "In-Situ" deposition oxidative polymerization of PT by $FeCl_3$ applied as an oxidant with fine grade powder of anatase TiO_2 nanoparticles cooled in an ice bath. Then, the properties, structural, crystallographic, morphological and thermal characteristics of nanocomposites were investigated by using SEM (scanning electron microscope), FT-IR (Fourier transform infrared), XRD (x-ray diffraction), and TGA (thermogravimetric analysis) techniques. The synthesized PT/TiO_2 nanocomposites have higher thermal stability than that of pure PT. Also, study of electrical conducting of nanocomposites by a specific instrument (four-point probe) clarified that with introducing TiO_2 nanoparticles, the conductivity of polymer changes.

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Simple and efficient method for the synthesis of highly substituted imidazoles using supported ionic liquid-like phase (SILLP)

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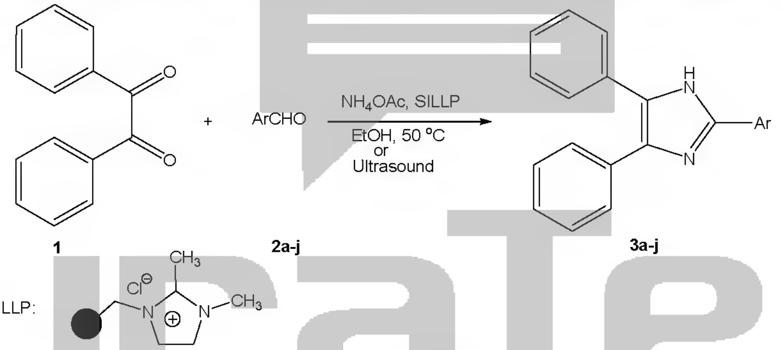
Multi-substituted imidazoles, an important class of pharmaceutical compounds [1], exhibit a wide spectrum of biological activities such as nitric-oxide synthase inhibition, anti-inflammatory, antiparasitic, antifungal, antidepressant, antitubercular, anticancer and antiviral activities, as well as antileishmanial activity against Leshmania donovani [2]. Therefore, preparation of substituted imidazoles has been attracted considerable attention in recent years.

In the course of our search for the development of efficient and environmentally friendly protocols for the synthesis of biologically important heterocyclic products [3], we studied the synthesis of highly substituted imidazole derivatives as potential drug candidates, over supported ionic liquid-like phase (SILLP) catalyst using ultrasonic irradiation. Initially the SILLP was prepared by using Merrifield resin and the condensation of benzyl (1 mmol), 4-chlorobenzaldehyde (1 mmol) and ammonium acetate (4 mmol) were done in the presence of SILLP under ultrasonic irradiation. This reaction furnished the desired products (**3a-j**) in short reaction times (5- 6 min) and high yields (85-95%) (Scheme1).



Scheme1

The structures of the all products were confirmed by spectroscopic (IR, ^{1}H NMR, ^{13}C NMR) and elemental analyses.

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The synthesis of (Z)-2-(4-chloro-3,3,7-trimethylindolin-2-ylidene)-2-cyanoacetamide and 4-chloro-3,3,7-trimethyl-2-(2-methylpyrimidin-5-yl)-3H-indole

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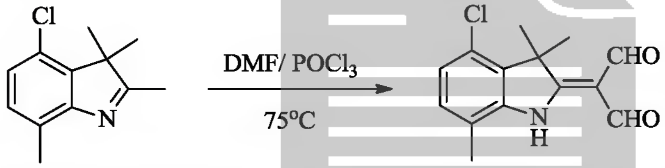
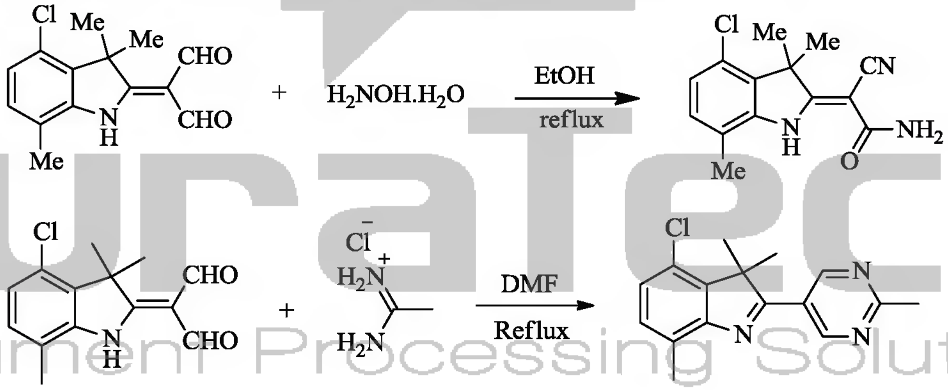
In 1959, Fritz[1] reported the N-formylation of the 3,3-disubstituted 3H-indole(indolenine) with using the Vilsmeier reagent DMF and $POCl_3$. No further studies of the formylation of these types of compound have been reported since.

In this research, we synthesized the novel diformyl compounds from 4-chloro-2,3,3,7-tetramethyl-3H-indole by the action with Vilsmeier reagent at 75°C in excellent yield[2].



Condensation of corresponding diformyl with hydroxylamine hydrate and 1-aminoethaniminium chloride produced (Z)-2-(4-chloro-3,3,7-trimethylindolin-2-ylidene)-2-cyanoacetamide[3] and 4-chloro-3,3,7-trimethyl-2-(2-methylpyrimidin-5-yl)-3H-indole, respectively, in excellent yields.



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Microwave-Assisted Synthesis of Diverse (E)-Ethyl 3-(Phenylamino)-2-(phenylcarbamoyl)acrylates Catalyzed by Bi(OTf)$_3$-[bmim]OTf

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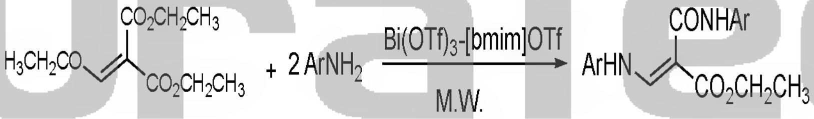
Enamines based on dialkylacetylendicarboxylates are important intermediates in the synthesis of heterocycles and multicomponent reactions, also with potential medicinal application[1].The synthesis and stereochemistry of enamines is well investigated. A common method for their synthesis is the reaction between dialkylacetylendicarboxylates and alkylpropiolates with amines in MeOH[2]. Recently Stolle et al. discovered that the solvent has a strong influence on the E/Z ratio of the product[3]. However, one of the challenging problems in such processes is the introduction of appropriate substituents because in some cases the presence of functional substituents often hinders the desired synthesis. Accordingly, development of synthetic routes to produce these compounds has received considerable attention.

Now, in continuation of our recent investigation on organic transformation catalyzed by bismuth(III) salts in ionic liquids[4], we have demonstrated a practical and concise synthesis of structurally diverse (E)-ethyl 3-(phenylamino)-2-(phenylcarbamoyl)acrylates via microwave-assisted reaction catalyzed by Bi(OTf)$_3$-[bmim]OTf from anilines/amines and diethyl 2-(methoxymethylene)malonate as substrates. In this flexible and straightforward synthetic route, Bi(OTf)$_3$-[bmim]OTf was illustrated as a powerful catalyst which was susceptible for further reuse without loss of efficiency for at least five runs. Notable features of our approach are the use of simple precursors and consequently potential ability of this procedure to the wide spectrum of these enamine derivatives, scale-up synthesis of the derivatives, the recycling of the catalyst and the high reactivity towards the reaction. We also believe that the protocol described herein represents a new and efficient way for the large-scale synthesis of (E)-ethyl 3-(phenylamino)-2-(phenylcarbamoyl)acrylates.



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A simple approach to the synthesis of highly functionalized pyrrole derivatives

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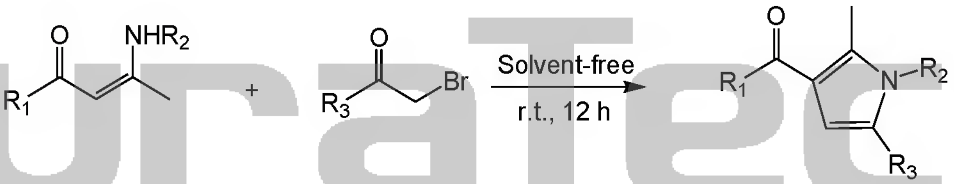
Abstract: Simple N-heterocycles receive considerable attention in the literature as a consequence of their exciting biological properties and their role as pharmacophores. Of these heterocycles, the synthesis, reactions, and biological activities of pyrroles stand as an area of research in heteroaromatic chemistry, and this structural motif appears in a large number of pharmaceutical agents and natural products. Accordingly, many strategies have been developed for the preparation of pyrroles. Despite these new developments, the classical Paal-Knorr reaction remains one of the most attractive mathods for the synthesis of pyrroles, also enaminones are employed in several new preparations of the pyrrole derivatives. As a part of our current studies on the development of new routes in pyrrole synthesis, we wish to report a convenient and facile synthesis of functionalized ethyl 1-alkyl-5-(4-alkyl)-2-methyl-1H-pyrrole-3-carboxylate, ethyl 4-acetyl-1-alkyl-5-methyl-1H-pyrrole-2-carboxylate, diethyl 1-alkyl-5-methyl-1H-pyrrole-2,4-dicarboxylate and 1-(1-alkyl-5-(4-alkyl)-2-methyl-1H-pyrrol-3-yl)ethanone from the reaction of enaminone derivatives and α-haloketones, at room temperature in good yields. The presented reactions of enaminones with α-haloketones provide a simple entry into the synthesis of polyfunctionalized pyrrole derivatives of potential synthetic interest. This catalyst-free and synthetic method seems facile; work up procedure is easy.



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$Cu(NO_3)_2.3H_2O$ as an efficient catalyst for deprotection of acylals under solvent-free conditions

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The protection and deprotection of aldehyde functionalities is important in synthetic organic chemistry. In recent years, acylals have been introduced as suitable protection groups for this purpose [1], because of their stability in mildly acidic and basic medium and ease of chemoselective preparation in the presence of ketones [2]. In addition, they can be used as carbonyl surrogates for asymmetric synthesis [3]. However, the final stages of chemical manipulation require their cleavage to regenerate the parent aldehydes. A variety of reagents for the removal of acylals have been developed. Many of these methods suffer one or more drawbacks, such as the strong acidic and basic conditions, the use of harmful volatile organic solvents, unsatisfactory yields, expensive reagents, longer reaction times and tedious work-up procedure. Also very few reports are applicable to both the synthesis as well as deprotection of acylals. Synthesis of 1,1-diacetates by $Cu(NO_3)_2.3H_2O$ has been reported in the literature [4]. In this article, we report an efficient method for solvent-free conversion of acylals to their corresponding aldehydes using $Cu(NO_3)_2.3H_2O$ in the presence of wet SiO_2 (Scheme 1).

$$RCH(OAc)_2 \xrightarrow[\substack{\text{wet } SiO_2 \text{ (0.3 g , 50 \% w/w)} \\ \text{Solvent-free , 90 °C}}]{Cu(NO_3)_2.3H_2O \text{ (0.2 mmol)}} RCHO$$

Scheme 1.

Experimental

A mixture of acylal (1 mmol) , $Cu(NO_3)_2.3H_2O$ (0.2 mmol, 0.048 g) and wet SiO_2(0.3g, 50% w/w) was heated in an oil bath (90°C). The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was triturated with CH_2Cl_2 (5 mL) and filtered. The solid residue was washed with water (5 mL). Then the product was extracted with CH_2Cl_2 (3×5 mL).The organic layer was washed with saturated $NaHCO_3$ and dried over $MgSO_4$. Evaporation of the solvent gave the corresponding carbonyl compounds in good to high yields.

Conclusion

In conclusion, we report a simple and efficient method for rapid transformation acylals to the parent aldehydes using $Cu(NO_3)_2.3H_2O$ in the presence of wet SiO_2 (50% w/w) under solvent-free conditions. This deprotection methodology appears to be general. Not only 1,1-diacetates of aromatic aldehydes but also 1,1-diacetates of dialdehydes and aliphatic, heterocyclic and α,β-unsaturated aldehydes undergo smooth deprotection under these reaction conditions. This procedure has valuable advantages, for example short reaction times, simple work-up, high yields of products, absence of solvent, and use of commercially available reagents.

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Fe(DS)$_3$-Catalyzed Synthesis of 2-Substituted Benzoxazoles

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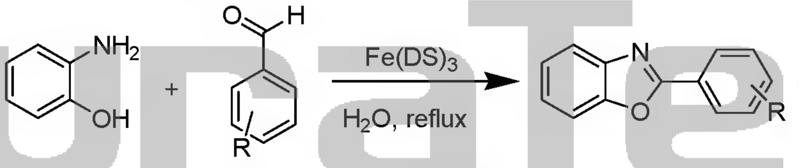
Synthesis of 2-substituted benzoxazoles has attracted interest in diverse areas of chemistry.[1] These heterocycles have shown different pharmacological activities such as antiviral, antimicrobial, anti-Parkinson, anticancer, and antibiotic properties.[2] The benzoxazole scaffold is also found in many biologically active compounds such as elastase inhibitors[3] and H_2 antagonists.[4] There are different methods for the synthesis of 2-arylbenzoxazoles based on substituted 2-aminophenols as starting materials.[5] Many of the procedures produce toxic or environmentally problematic by-products, often involve laborious workup procedures, or suffer from poor yields. Therefore, development of more convenient, environmentally friendly, and practical synthetic methods for benzoxazoles still remains an active area of research.

Therefore, we wish to report an efficient synthesis of 2-substituted benzoxazoles using of 2-aminophenol and various substituted arylaldehydes by Fe(DS)$_3$ in H_2O at reflux temperature (Scheme 1). The advantages of this method are higher reaction yields, short reaction times and use of H_2O as an environment friendly solvent(Scheme 1).



Scheme 1

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Synthesis of new trimeric calix[4]arene derivatives

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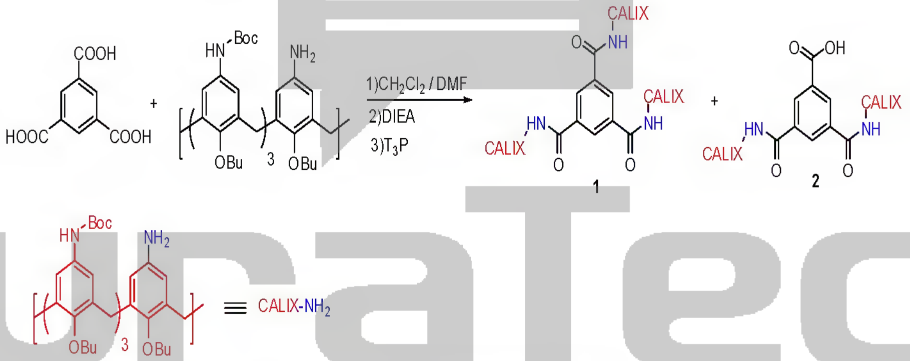
Macrocyclic compounds are of great importance in supramolecular chemistry whenever selective molecular recognition is desired [1]. Calixarenes have attracted attention because of their potential for forming host–guest complexes and serving as useful building blocks in supramolecular chemistry [2]. The covalent assembly of two or more calixarene subunits is a useful approach to tailor multicavity supramolecular receptors displaying intriguing geometries and molecular recognition abilities that are absent in the single-cavity molecular frameworks of their precursors [1].
Reaction between protected calix[4]arene with di-tert-Butyl dicarbonate and 1,3,5-benzenetricarboxylic acid leads to Dimeric and Trimeric calix[4]arene derivatives (scheme1). According to our previous work, we hope that the new synthesized molecules can bind protein surface specifically [3].



scheme1: synthesis route of **1** and **2**

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A Simple and Effective Approach to the Synthesis of Alkynyl Selenides from Terminal Alkynes

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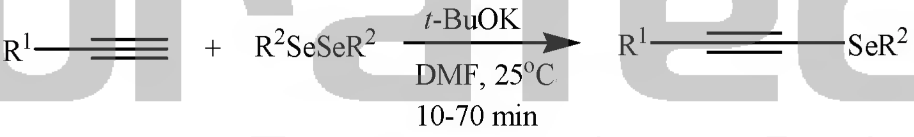
Organoselenium compounds have pivotal role in biology and pharmacology. Among them, alkynyl selenides are considered as crucial synthons in the transformations of a wide range of functional groups with a high degree of selectivity [1].

Generally, the methods for the preparation of alkynyl selenides include: (a) metal-assisted cross-coupling with either Mg or Cu salts;(b) reaction of alkynyl organometallics with organoselenenyl halides (RSeX) or diorgano diselenides (RSeSeR)[2]; (c) Intramolecular Wittig reaction of α-acyl-α-seleno phosphoranes; (d) seleno functionalization of alkynes; (e) reaction of (potentially explosive) bromoalkynes with selenolates or diselenides; and (f) coupling of terminal acetylenes to phenylselenenyl bromide in the presence of $CsOH.H_2O$.

Most of the available synthetic protocols suffer from various disadvantages such as long reaction times, low temperatures, use of air and moisture sensitive and expensive reagents, and the use of hazardous organic solvents. Taking into account these constraints, we present herein a simple, mild and efficient procedure for the synthesis of alkynyl selenides by reacting terminal alkynes with respective diorganic diselenides in the presence of potassium t-butoxide (Scheme 1).



(Scheme 1)

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Pyridinium Salts – Versatile Reagents for the Regioselective Synthesis of Functionalized Thiazocino[2,3-b]indoles by Tandem Dinucleophilic Reaction of Thiooxindoles

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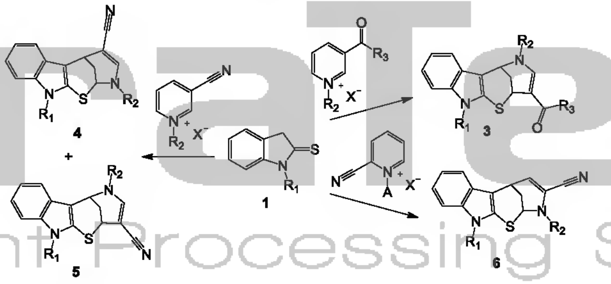
Pyridinium salts represent important synthetic building blocks for the synthesis of various pharmacologically relevant bridged and non-bridged di- and tetrahydropyridine derivatives. These products occur in various natural products and synthetic pharmaceuticals.[1] At the same time, heterocyclic systems containing an annulated pyridinium core, such as quinolinium and isoquinolinium salts, are of considerable importance as building blocks for the synthesis of various alkaloid frameworks [2].
In recent years, Langer et al. studied various cyclization reactions of dinucleophiles with pyridinium, e.g. the cyclization of 1,3-bis(silyl enol ethers), masked 1,3-dicarbonyl dianions, with quinolinium, isoquinolinium, quinazolinium,1 and quinoxalinium salts. Moghaddam and coworkers studied various cyclization reactions of quinolinium and isoquinolinium salts with various heterocycles [3]. Herein, we report the synthesis of functionalised 2,5,6,11-tetrahydro-2,6-methano[1,5]thiazocino-[2,3-b]indoles by what are, to the best of our knowledge, the first cyclizations of thiooxindoles with 3-acylpyridinium salts.



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Pyridinium salts as substrate for tandem dinucleophilic cyclization with cyclohexan-1,3-diones

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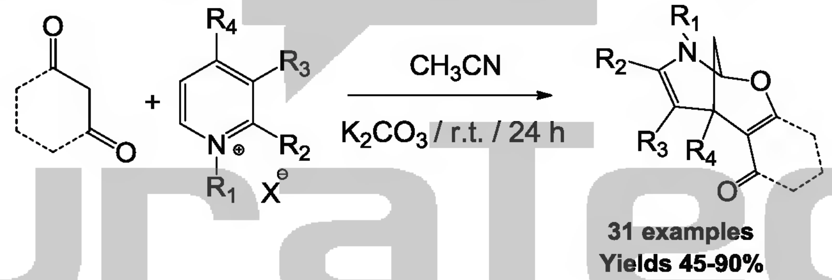
The nucleophilic addition to pyridinium salts has recently proven to be a powerful method for the construction of dihydropyridines variety [1], which are not only valuable intermediates in organic synthesis but also interesting compounds in medicinal and bioorganic chemistry. Nevertheless tetrahydropyridine ring is an essential building block for numerous natural products, synthetic pharmaceuticals, and a wide variety of biologically active compounds [2].
During the last decade the reaction of dinucleophiles with dielectrophiles was a major research subject in both our laboratories. For example, we have studied reactions of quinolinium, isoquinolinium, quinazolinium, and quinoxalinium salts with 1,3-bis(silyl enol ethers), masked 1,3-dicarbonyl compounds, which provided a facile access to a number of bicyclic systems [3].
In this paper, we discovered an interesting reaction which represents an external dinucleophilic addition of the dimedone molecule on the pyridinium salt, delivering 10-aza-tricyclo[7.3.1.0*2,7*]trideca-2(7),11-dienes in modest yield. This efficient cycloaddition encouraged us to investigate this process, to improve the reaction conditions, and to extend the reaction to other pyridinium salts and diketones.



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Fast, easy, solvent-free Knoevenagel condensation with a variety of substituted benzaldehydes and ethyl cyanoacetates to Synthesis of Ethyl α-cyanocinnamates catalyzed by KF–Al_2O_3

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Abstract:
The Knoevenagel condensation is one of the most important, useful and widely employed methods for the formation of carbon-carbon bonds, It has been used for the preparation of a range of substituted alkenes and bioactive molecules, and as a key step in natural product synthesis [1-4]. we wish to report the condensation catalyzed by KF–Al_2O_3, which gives excellent yields of high purity, milder reaction condition, shorter reaction time, and the catalyst can be recycled by re-treated simply. We report a comparative study of the Knoevenagel condensation with a variety of substituted benzaldehydes and active methylene compound such as ethyl cyanoacetates, using three different methodologies: (a) acetic acid reflux; (b) acetonitril reflux; and (c) solvent free conditions. Almost without exception these reactions proceeded faster, more cleanly and in higher yields when the reactions were conducted in a solvent-free fashion. Products are obtained in high yields after short reaction times (table1).

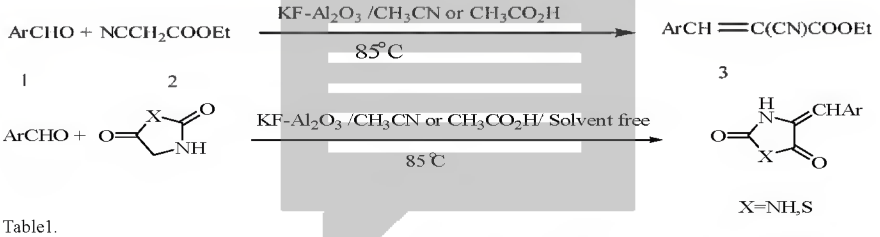
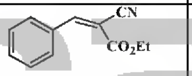
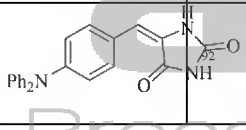


Table1.

Entry	Ar	Product	CH_3CN		CH_3CO_2H		Solvent-free	
			Yield %	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)
1	C_6H_5		66	3.5	78	3	84	2.5
2	4-$(Ph)_2NC_6H_4$		92	4	98	4	100	3.5

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Solvent-free Synthesis of Bis(arylmethylidene)dioxan-5-ones under ultrasonic conditions

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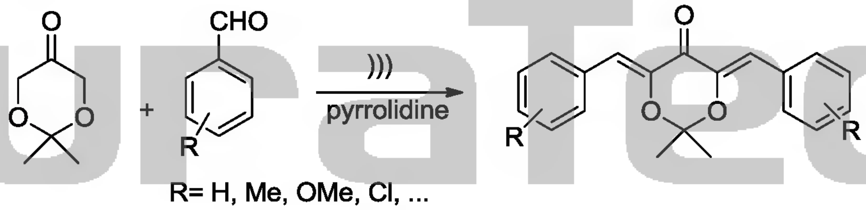
Crossed aldol condensation of cyclic ketones with aromatic aldehydes is extensively studied for the synthesis of bis(arylmethylidene)cycloalkanones [1]. In recent years, various methods are introduced for the synthesis of these compounds by using microwave radiation, ultrasound waves, and Lewis acid catalysts.

We recently reported the first synthesis of 4,6-bis(arylmethylidene) dioxan-5-ones by double crossed-aldol condensation of a variety of aromatic aldehydes with 1,3-dioxan-5-one in the presence of magnesium bromide diethyl etherate and diethylamine at room temperature [2].

In the framework of our studies on the development of environmentally green synthetic methods [3], we now report a double crossed-aldol condensation of a variety of aromatic aldehydes with 1,3-dioxan-5-one in the presence pyrrolidine as an organocatalyst and under ultrasonic irradiation. Reactions take place at room temperature and no solvent is required. Good yields of 4,6-bis(arylmethylidene) dioxan-5-ones are achieved in a facile procedure.



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The Effect of Catalysts on The Rate of Amidine

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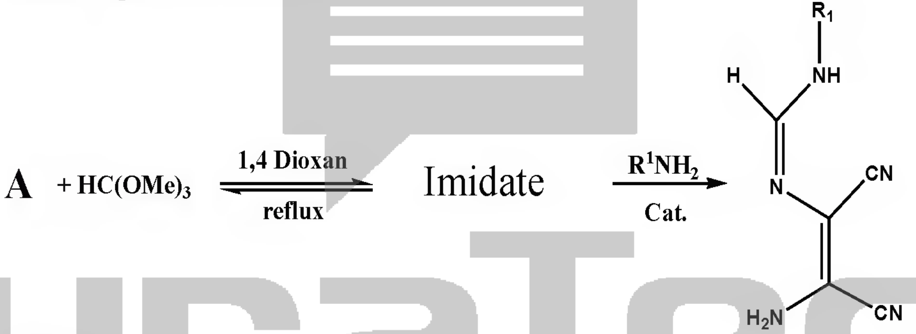
Introduction:

Amidines form a class of compounds possessing a wide range of biological activities. Amidines derivatives possessing anti-inflammatory, analgestic activity, anticancer, antiplatelet and antimicrobial activities have been reported in the literature. Amidines are versatile nitrogen ligands which the steric and electronic properties can easily be modified by the introduction of different substituents. [1-3]

Method:

In this project we have used for Amidine of Imidaite as raw material. Compound " A " is a appropriate di amine, Then we considered the effect of different catalysts on the rate a special amidine [1 -3].



Result:

After conducting studies on the reaction time, the use of catalysts, for example; silica sulfuric acid, it can be very effective [1-3].

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Synthesis of Some Novel 2-Methylthio Pyrimidine Derivatives in the Presence of Copper Oxide

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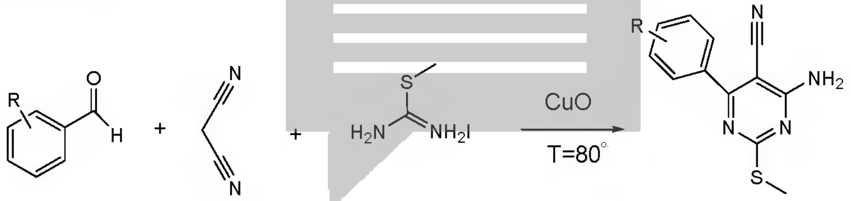
One of the most widespread areas of research in organic chemistry is represented by looking for new efficient synthetic procedures toward heterocyclic compounds. 2-Methylthio pyrimidine derivatives constitute a group of heterocyclic building blocks which are found in the structure of many biologically active molecules and also are appropriate precursors for a vast number of compounds with important biological and pharmacological properties [1,2]. Therefore, both the growing significance of 2-methylthio pyrimidine derivatives as intermediates for the synthesis of biologically valuable compounds and the few number of reports found in the literature about their synthesis prompted us to find a new efficient and ecofriendly procedure for the direct synthesis of novel 2-methylthio pyrimidine-5-carbonitrile derivatives. Enhancement of the reaction efficiency from both economic and ecological viewpoints through solvent-free reaction conditions has given these kinds of procedures an outstanding synthetic value [3].
Herein, we have introduced a rapid, efficient, and environmentally benign solvent-free multicomponent reaction for the synthesis of some novel 2-methylthio pyrimidine derivatives **4** in the presence of CuO (Scheme 1).



1 2 3 4

Scheme 1

Bulk CuO used in this process showed two different roles first as a base to release amidine from its salt, then as an acidic catalyst to activate the alkene intermediate toward Michael addition of amidine derivative. Short reaction times, excellent yields of products, simple work-up and performing the reaction under solvent-free conditions are the advantages of the present study.

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An efficient synthesis of 1,4-dihydroquinoline using nano- NiO as a catalyst

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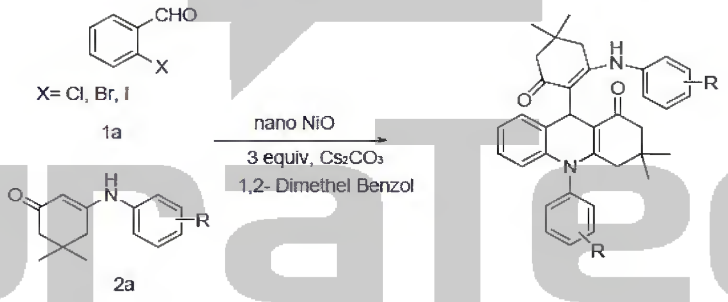
INTRODUCTION:

1,4-dihydroquinoline is a particularly interesting core and it structure appears increasingly in compounds of therapeutic importance. Compounds of such structure have shown various pharmaceutical activities such as hypotensive agents or inhibitors of potassium ion channels [1]. The transition metal-catalyzed C-N cross-coupling process is considered as an important methodology, which has been widely applied in pharmaceutical and medicinal chemistry. Although remarkable success in both palladium. and copper, catalyzed versions of this strategy has been achieved, the development of alternative catalysts involving more cheap, nontoxic, and environmentally friendly metals is still highly desired [2]. Ultra-fine NiO nano-ceramic particles with a uniform size and well dispersion characteristics are strongly desirable for many applications, e.g. synthesis of composite materials, magnetic, electro chromic, heterogeneous catalytic materials, etc [3]. We herein report an efficente and high yield method for the synthesis of 1,4- dihydroquinoline compounds with 2- halo banzaldhydes and β-enaminones in the presence of nano- NiO as stable and rusebale catalyst



(Scheme 1).

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Simple and efficient method for synthesis of 2-methylene imidazo[1,2-a]pyridine derivatives

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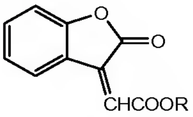
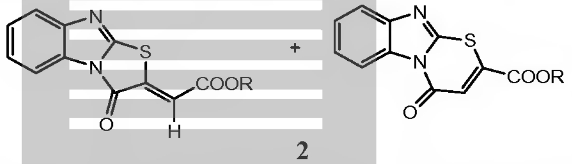
Synthesis of 2-methyleneimidazo[1,2-a]pyridin-3(2H)-ones and their derivatives are interest because they constitute an important class of naturally occurring compounds. Many of them exhibit useful and diverse biological activity such as antifungal, anticoagulant, antispasmotic, anticholerostatic, and molluscacide activity[1]. In addition, other similar compounds such as coumarins are interest as a result of their toxicity, carcinogenicity and diverse pharmacological properties. Recently Yavari reported a new method for Synthesis of fused α-methylene-γ-butyrolactone derivatives through pyridine-induced addition of phenols to dimethyl acetylenedicarboxylate **1**[2] and Heravi also Synthesis of thiazinobenzimidazole Derivatives in hot methanol or microwave condition **2** [3].

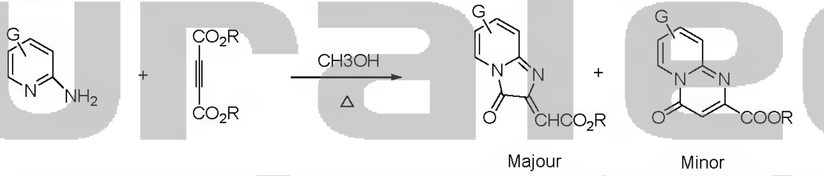


1



2

Although this ring system has been the objective of synthetic projects in several laboratories, the number of different approaches is not large. As part of a research program on the synthesis of a heterocyclic system containing nitrogen, we report a synthesis of fused 2- methyleneimidazo[1,2-a]pyridine one derivatives through the reaction of dialkylacetylenedicarboxylates such as DMAD or DEAD with 2-amino pyridine derivatives in the absence of any catalyst in greater than 70% overall yield.



In summary, a new and reliable procedure for synthesis of 2-methyleneimidazo[1,2-a]pyridin-3(2H)-ones and their derivatives, is described. The synthesis starts from commercially available or readily prepared starting materials and furnishes a complex heterocyclic scaffold in essentially one step. Biological results regarding the newly obtained class of inhibitors will be reported elsewhere.

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Brone sulfonic acid; effective catalyst for synthesis of tricyclobenzenes

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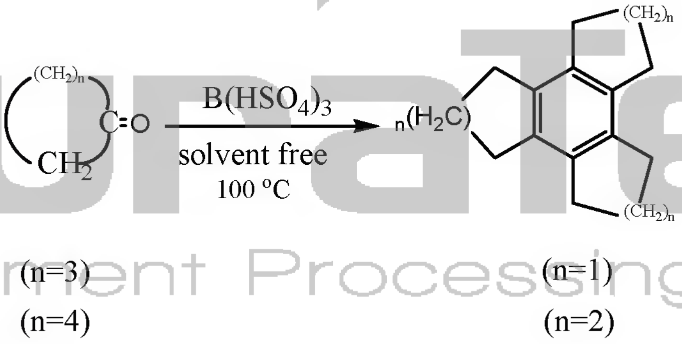
Polyarylated benzene propellers have attracted a great deal of enthusiasm toward leading edge carbon nanotechnology for developing new efficient molecular rotors and new electroluminescent materials for flat-panel displays. Owing to their unique chemical, photophysical, and optical properties, these aromatic scaffolds are not only useful as building blocks for materialand biological sciences, but also important for understanding the concept of aromaticity, chemical reactivity, and reaction kinetics. Recently polyaromatic hydrocarbons such as p-conjugated polyaromatics, dendrimers and their derivatives find several applications in liquid crystals,laser dyes,electronic and opto-electronic devices, and molecular wires.

Numerous synthetic methodologies to highly functionalized aromatic π -systems have been reported in the literature. However, the literature methods involve the use of amount of solvent, prolonged reaction time , high pressures , the use of toxic reagents often result in low yields of the desired products and incompatibility with the green chemistry protocols.

In this research an efficient, green and simple solvent-free method for the synthesis of tricyclolbenzenes from cyclopentanone and Cyclohexanone in the presence of catalytic amount of Borone sulfonic acid is described. The reactions proceed offer advantages such as shorter reaction times, simple work-up and excellent yield.This catalyst is safe and easy to handle. Boron sulfonic acid as a solid acid catalyst was easily prepared by addition of chlorosulfonic acid to boric acid under N_2 atmosphere at room temperature [1]. This reaction was easy and clean, because HCl gas was evolved from the reaction vessel immediately.



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Diformylation of 2,3,3,6,7-pentamethyl-3H-indole by Vilsmeier-Haack reagent and synthesis of 2-(1-(2,4-dimethylphenyl)-1H-pyrazol-4-yl)-3,3,6,7-tetramethyl-3H-indoly.

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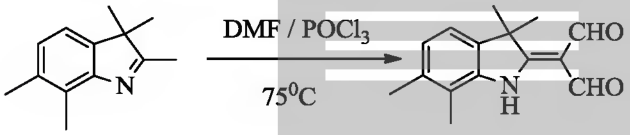
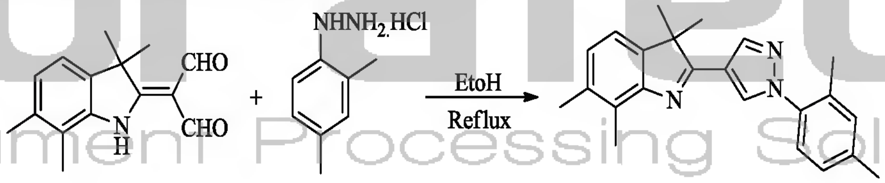
The recognition of the power of the species produced by the combination of phosphoryl chloride with the amide of a secondary amine has its origins in a paper in 1896later work by Fischer, Muller and Vilsmeier, and then by Vilsmeier and Haackand later by the groups of Arnold and Meth-Cohnclarified the process and made it into a widely used regimen for the acylation, especially formylation of reactive aromatic and hetero-aromatic compounds, and indeed, non-aromatic compounds[1].In 1959, Fritz[2] reported the N-formylation of the 3,3-disubstituted 3H-indole(indolenine) with using the Vilsmeier reagent DMF and $POCl_3$. No further studies of the formylation of these types of compound have been reported since.

In this research, we synthesized the novel diformyl compounds from 2, 3, 3,6,7 -pentamethyl-3H-indole by the action with Vilsmeier reagent at 75°Cin excellent yield.



Scheme1

In this reaction, we synthesized.,2-(1-(2,4-dimethylphenyl)1H-pyrazol-4-yl)-3,3,6,7-tetramethyl-3H-indole From the reaction of the resulted diformyl with (2,4-dimethylphenyl) hydrazine hydrochloride in EtOH/reflux for 6 hours, after cooling, the combined organic lyers evaporated to dryness, the residual material was basified by NaOH, and the resulted precipitate was washed well with H2O, and then was purified by recrystallization from absolute EtOH. [3,4]



Scheme2

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Superparamagnetic iron oxide as an efficient and recyclable catalyst for chemoselective thioacetalization of aldehydes under solvent-free conditions

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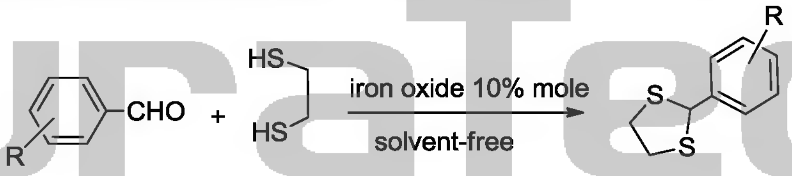
We recently presented an efficient protocol for the room-temperature protection of alcohols and phenols with HMDS and also Strecker reactions using superparamagnetic Fe_3O_4 particles [1]. In these investigations, after separation of the catalyst using an external magnet, the silyl ether products were easily obtained in good purity by evaporation of the volatiles. No additive or co-catalyst, and no solvent during the reaction or work-up were required. The ease of accessibility of the catalyst at low cost along with its full recovery upon completion of the reactions and the chemoselectivity of the process are advantages of this method. This has encouraged us to study other organic functional group transformations.

In the present work, a simple and efficient chemoselective thioacetalization of carbonyl compounds has been achieved using superparamagnetic iron oxide (Fe_3O_4) (10 mole%) as the catalyst under solvent-free conditions. The catalyst could be readily recovered and reused for several runs without loss of catalytic efficiency. In addition, the relatively low reaction rate of ketones allows the chemoselective protection of aldehydes in the presence of the ketone functionality. The present protocol offers an alternative method for thioacetalization under solvent-free conditions in terms of efficiency, operational simplicity, reusability of the catalyst, and environmental friendliness.



R=4-OMe, 4-Cl, 4-NO_2, 4-Me, ...

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A Straightforward Synthesis of 3-arylquinolinones Catalyzed by Palladium

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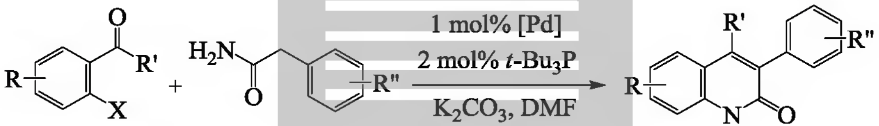
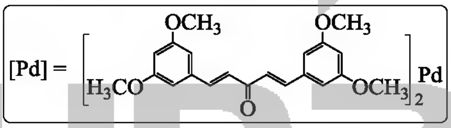
In organic and medicinal chemistry, 3-arylquinolinones are key intermediates. A number of routes for synthesis of these important organic compounds described in the literature.[1] But most of them reported that final products have required to relatively harsh conditions to preparations and the yields of products often is low.[2]

Herein, in continuing with our research on palladium-catalyzed coupling reactions on different nucleophiles, we envisaged a straightforward approach to synthesis of 3-arylquinolinones through a sequence of palladium-mediated N-arylation and aldol condensation reactions in intermolecular and intramolecular, respectively. In this methodology, we use of Bis(3,5,3',5'-dimethoxydibenzylideneacetone)palladium(0) as a new catalyst and tri-tert-butylphosphine as ligand. We observed that this catalyst reagent system is a very convenient and efficient tool for N-arylation reaction.



X= Cl, Br, I
R, R', R"= functional group



In conclusion, we have developed an alternative strategy for the synthesis of 3-arylquinolinones using a palladium-catalyzed cross-coupling reaction between enolizable amides and o-carbonyl substituted aryl halides. It has the advantage of being a convergent one-pot cascade sequence rather than one which often requires multiple steps. Another attractive feature of this methodology is the broader availability of o-carbonylcontaining aryl halides versus their amino or nitro counterparts.

Acknowledgment. We thank "National Elite Foundation" for financial support of this work.

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Synthesis, characterization and herbicidal activities of new 1,3,4-oxadiazoles, 1,3,4-thiadiazoles and 1,2,4-triazoles derivatives bearing (R)-5-chloro-3-fluoro-2-phenoxypyridine

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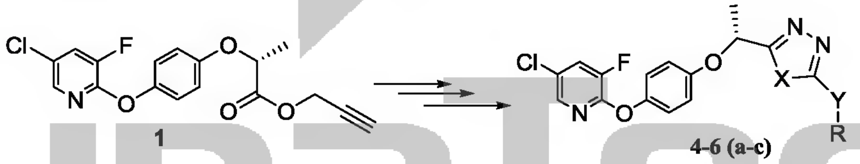
A variety of 1,2,4-triazole derivatives have been described for their biological activities including anti-depressive, anti-inflammatory, antibacterial, antifungal, insecticidal and herbicidal properties [1]. Also, the biological activities of 1,3,4-oxa and thiadiazoles such as anti-tumor, antiviral, antimicrobial, anti-inflammatory, antifungal and herbicide have been the subject of many literature reports [2,3] in recent years.

On the other hand, Aryloxyphenoxypropionate herbicides (APPH) are known as interesting and highly effective class of herbicides in the international market over the past decade [4]. They are used effectively in a number of crops including soybeans and cereal grains, such as wheat and Barley, to control grass weeds. It is well known that if an active nucleus is linked by another nucleus, the resulting molecule may possess greater potential for biological activities.

In view of these highlights and due to the biological importance of 5-heterocyclic rings in hand, our attention was directed to the synthesis of these heterocycles linked with the Clodinafop herbicide framework as a screening target, to create some novel bioactive compounds (**Scheme 1**). The herbicidal activities of these synthesized rings are also reported.



X = NH, NMe, NPh, O, S **Y = H, NH, O, S** **R = H, Me, Ph**

Scheme 1.

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Synthesis of new substituted Tetrathiofulvalene

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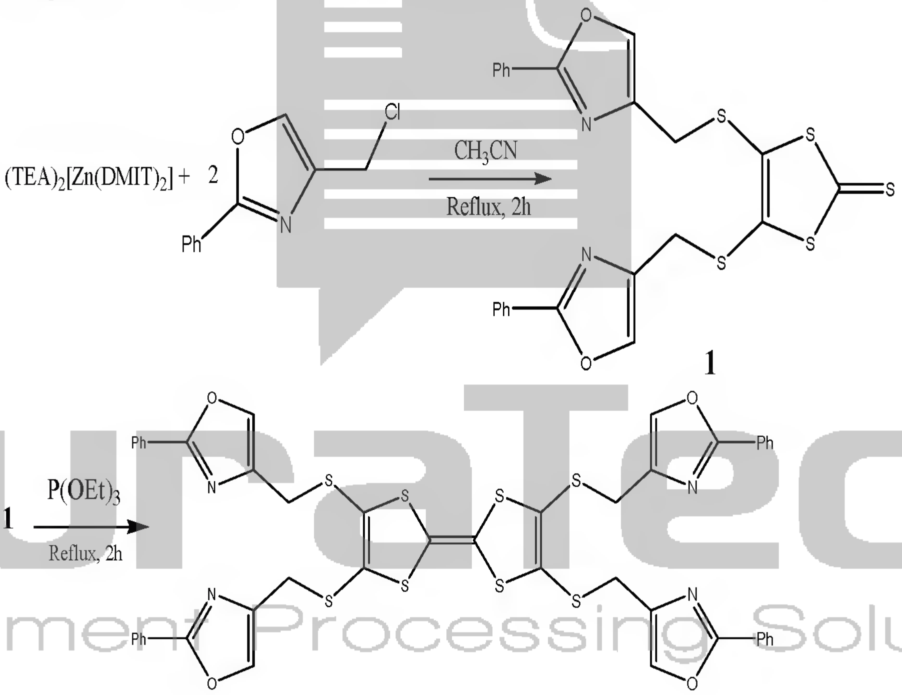
Substituted Tetrathiofulvalenes (TTF) and their selenium and tellurium analogues have been attracted much interest in the field of organic metals and superconductors. [1] The thiolate and TTF ligands containing N-coordination atoms present two coordination poles which can selectively bind different metals and act as bridging unit in variety of coordination architectures. [2] Reaction of 2-phenyl-4-chloromethyl-1,3-oxazole with DMIT [3] gave the thione **1**. The coupling reaction of thione **1** in neat triethyl phosphite afforded new π-donor **2**. Electrochemical redox properties were investigated by cyclic voltametric measurement. The charge transfer complex of **2** with p-chloranil was prepared and its physical properties were investigated. The complexation of product **2** with some transition metal salts was under investigation.



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A Convenient One- pot Three-component Synthesis of Pyridopyrimidinone Derivatives

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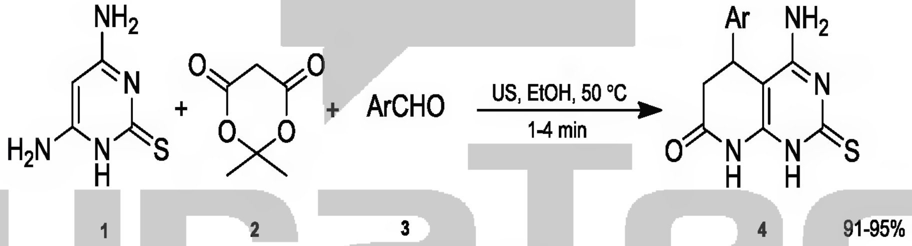
The importance of fused pyrimidines, common source for the development of new potential therapeutic agents, is well known. Among them, the pyridopyrimidine scaffold and their oxo and thioxo derivatives is a well known pharmacophore in drug design and it is associated with a wide range of biological properties [1]. Pyridopyrimidines ring system is present in a number of biologically active compounds which includes antitumor, antipyretic, analgesic, antihistaminic, PDE4 inhibitor, adenosine kinase inhibitor, tyrosine kinase inhibitor, and diuretic activities [2]. As a part of our continued interests in employing multi-component reactions in the synthesis of biologically important products [3], we report herein a very simple and highly efficient method for the synthesis of several pyrido[2,3-d]pyrimidinone derivatives (**4**) based on a three-component condensation reaction between, 4,6-diaminopyrimidine-2(1H)-thione (**1**), meldrum`s acid (**2**) and arylaldehydes (**3**) under ultrasound conditions (Scheme 1). This method benifits the advantages of higher yields, lower cost, easy workup and short reaction times (1-4 min).



Scheme 1

References:
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Synthesis of pyrazolotriazoles using ionic liquid, 2-hydroxyethylammonium formate, as a recoverable catalyst

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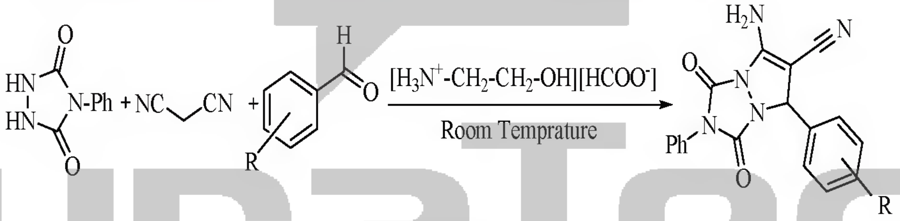
Ionic liquids (ILs) technology offers a new and environmentally benign approach toward modern synthetic chemistry. Ionic liquids have interesting advantages such as extremely low vapor pressure, excellent thermal stability, reusability, and talent to dissolve many organic and inorganic substrates [1]. Ionic liquids have been successfully employed as solvents and catalyst for a variety of reactions [2-5], which promise widespread applications in industry and organic synthesis.

In this research, we report preparation of pyrazolo[1,2-a][1,2,4]triazole derivatives by a three-component reaction of arylaldehydes, 4-phenyl-1,2,4-triazolidine-3,5-dione, and malononitrile in the presence of a catalytic amount of 2-hydroxyethylammonium formate $[H_3N^+–CH_2–CH_2–OH][HCOO^-]$ as an inexpensive and available ionic liquid under solvent-free and ambient conditions.(Scheme 1).



Scheme

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DBU AS AN EFFICIENT CATALYST FOR ONE-POT, THREE COMPONENT SYNTHESIS OF HYDROXYL NAPHTHALENE-1,4-DIONE DERIVATIVES

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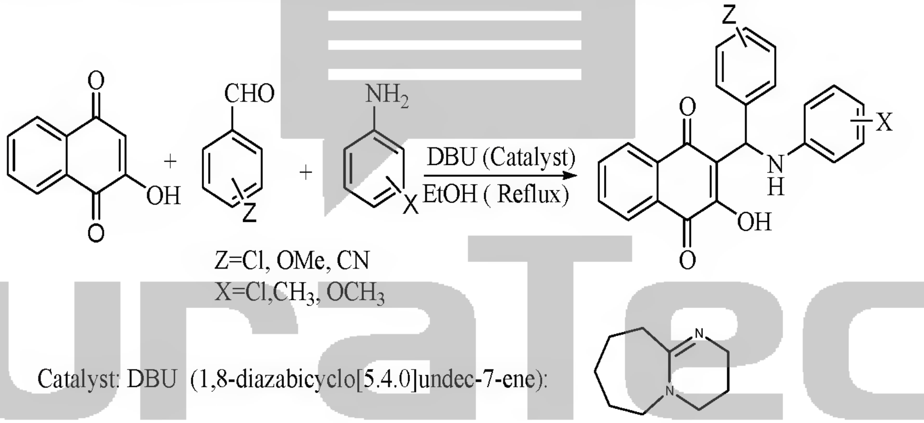
Multi-component reactions (MCRs), in which multiple reactions are combined into the synthetic operation have been used extensively to form carbon-carbon bonds in synthetic chemistry [1]. Molecules with the quinone structure constitute one of the most interesting classes of compounds in organic chemistry, due to their biological properties such as antitumor, molluscicidal, leischmanicidal, anti-inflammatory, and antifungal activities and also their industrial applications [2]. In continuation of our research on application of catalysts in organic synthesis [3], We are currently investigating the synthesis of hydroxyl naphthalene-1,4-dione derivatives via a facile, atom economical, and three-component condensation reaction of 2-hydroxynaphthalene-1,4-dione, aromatic aldehydes and anilines derivatives in the presence of a catalytic amount of DBU in refluxing ethanol (Scheme 1).



Scheme 1

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Three component synthesis of functionalized 2-amino-4-aryl-5,10-dioxo-5,10-dihydro-4H-benzo[g]chromene-3-carbonitrile Derivatives

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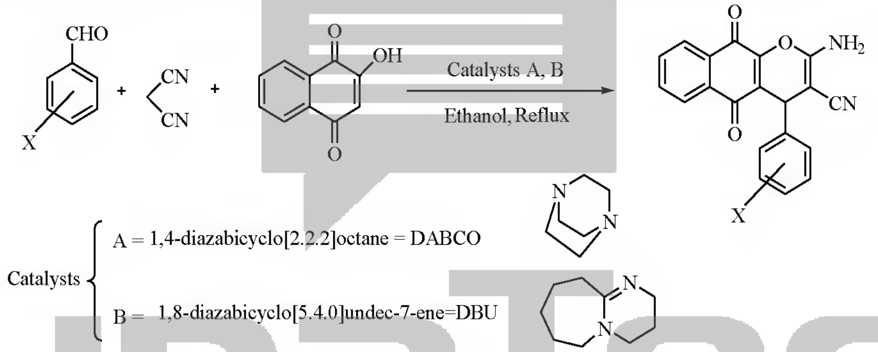
Benzo[g]chromenes show a variety of biological activities, including anticancer [1,2] , anti-inflammatory [3], antimalarial [4,5] and pesticides activities [6] .
Herein, we wish to report a new method for the synthesis of 2-amino-4-aryl-5,10-dioxo-5,10-dihydro-4H-benzo[g]chromene-3-carbonitriless from reaction between an aryl aldehyde, malononitrile, and 2-hydroxynaphthalene-1,4-dione in the presence of a catalytic amount of 1,4-diazabicyclo[2.2.2]octane(DABCO) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as inexpensive and available basic catalysts in ethanol under reflux conditions (Scheme1).



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Cellulose sulfuric acid catalyzed multicomponent reactions for synthesis of spirooxindoles in aqueous medium

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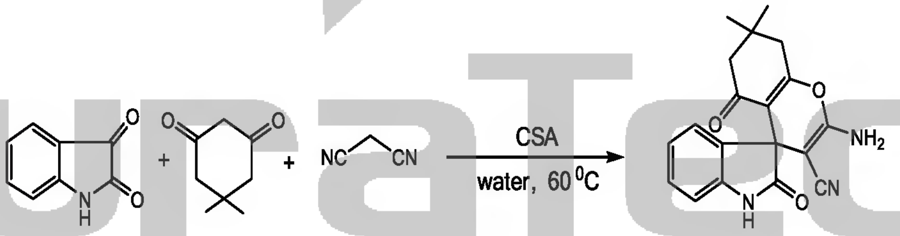
The heterocyclic spiro oxindol ring is a core structure presenting in a number of pharmaceuticals and natural products, including cytostatic alkaloids such as spirotryprostatins A, B, and strychnophylline[1]. Among them, functionally substituted 4H-chromenes have received considerable attention due to their wide of useful biological properties, including spasmolitic, diuretic, anticancer and antianaphylactic activities [2]. In recent years, the synthesis of spiro compound via multicomponent condensation reactions has been developed and several methods for the synthesis of 4H-chromene have also been reported [3].

On the other hand cellulose and its derivatives have some unique properties which make them potent as conventional organic supports for catalytic applications [4].

In this research we report a simple and efficient method for the synthesis of spiro oxindoles with fused chromenes, through the three-component one-pot reaction between isatin, dimedone and malononitrile in the presence of catalytic amount of celloluse sulfonic acid in water as green solvent. Mild reaction condition, readily prepared catalyst, using environmentally friendly processes, easy work up procedure and good to excellent yields (83-95%) are the merits of our method.



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L-Proline-catalyzed synthesis of fused dihydropyridines through Hantzsch reaction.

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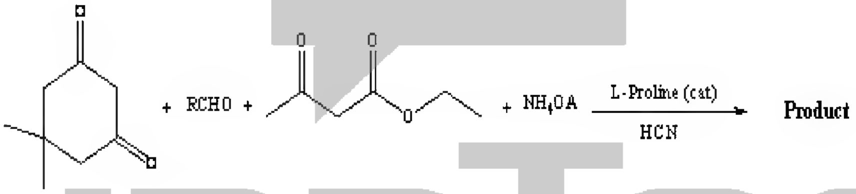
Compounds containing the 4-substituted 1,4-dihydropyridine (DHP) nucleus comprise a large family of medicinally important compounds. At the first synthesis of substituted 1,4-dihydropyridines was carried out by condensation of ethylacetoacetate, aromatic aldehydes and ammonia. The reaction was conducted in acetic acid or atreflux in ethanol [1] for long periods resulting low to moderate yields. To modify, several methods have been reported comprising the use of microwave, [2] iodotrimethylsilane (TMSI), [3] ionic liquids, [4,5] metal triflates, [6] HYzeolite, [7] HClO4–SiO2, [8] organo catalysts and polymers for the synthesis of 1,4-DHPs. However, in this paper we wish to disclose a facile and an efficient route to synthesize dihydropyridines via four-component condensation reactions of aldehydes, dimedone, and ethyl acetoacetate and ammonium acetate in the presence of L-Proline catalyst in HCN at ambient temperature through Hantzsch reaction (Scheme 1). High yields, shorter reaction time, simple work up procedure and operational simplicity are the key features of this protocol.



Scheme 1

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Photochromism of several new quinone aldehydes

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Photochromic quinones are a class of organic photochromic compounds that have become known as photochromic substances quite recently compared with other compounds. It turned out those anthraquinone derivatives with an aryloxy group at the peri-position relative to the carbonyl group change colour reversibly in the presence of UV light. At present, the photochromism of quinones is described by the interconversion photoinduced para-ana-quinoid transformations owing to photochemical movement of different aryl, and acyl groups [1-4]. Synthetic way for preparation of these compounds involving aromatic substitution reaction of 1-chloro-9,10-anthraquinone with commercially available hydroxy benzaldehydes or preparation hydroxy benzaldehydes in the presence of potassium carbonate in N,N-dimethylformamide gave desired compounds in good yields. All compounds were characterized by spectroscopic methods. Photochromic reaction consists in the migration of the p-formyl phenoxy group to the carbonyl oxygen accompanied by the reorganization of the π-bond system of the molecule and is usually photochemically reversible (Scheme 1). In order to study photochromic properties of target p-formyl phenoxyanthraquinones, UV–Visible absorption spectra and they spectral changes were recorded in various solvents. One of them electronic spectral changes presented in figure 1. This figure shows Overlaid absorption spectra of p-formyl phenoxyanthraquinone at different interval times in dichloromethane at room temperature upon irradiation at 365 nm for 0, 6, 12, 18, 24, 30, 36 and 42 seconds. Appearance of the long-wavelength absorption of the "ana"-quinone form at 470 nm that point to ana form is produced, and increases in intensity with increasing total time of irradiation, indicating the progress of the forward photochromic reaction. The other compounds gave similar spectra.

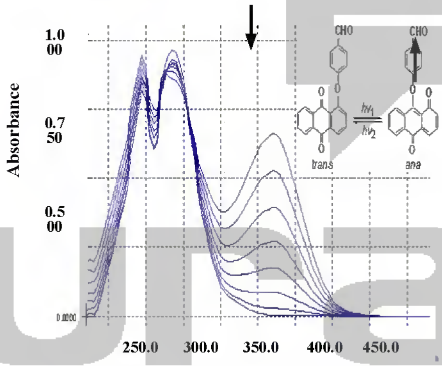
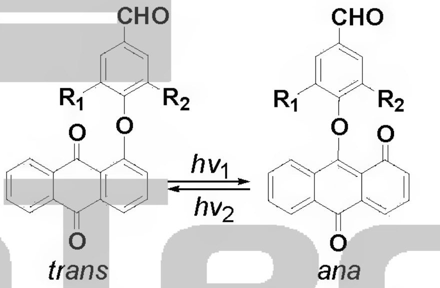


Figure 1. Absorption spectral changes of *p*-formyl phenoxy-anthraquinone in DCM at room



Scheme 1. Photochromism of quinone aldehydes between "*trans*"-quinone, and "*ana*"-quinone, forms.

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Evaluation of various parameters on the synthesis of Pd supported on carbon activated and the effect of Pd/C catalyst in the second step of synthesis of HNIW

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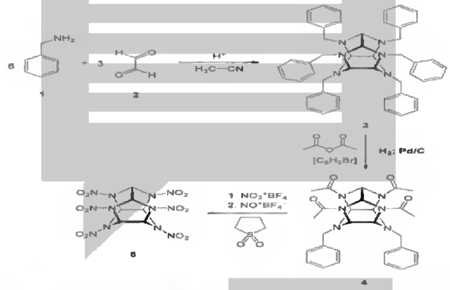
The synthesis and properties of the polycyclic, nitramine explosive 2,4,6,8,10, 12-hexanitro-2,4,6,8,10, 12-hexaazatetracyclo [5,5,0,$0^{5,9}$,$0^{3,11}$]dodecane (HNIW) has attracted considerable interest in the area of explosives chemistry. It is generally known that HNIW is made by a three steps process, consisting of (i) creation of the basic cage structure in the form of the hexabenzyl derivative **3** 2,4,6,8, 10,12 -hexabenzyl-2,4,6,8,10, 12-hexaazatetracyclo [5,5,0,$0^{5,9}$,$0^{3,11}$] dodecane (HBIW) (ii) debenzylation of HBIW and forms TADBIW **4**, and (iii) nitration TADBIW to give HNIW **5**. [1]



In order to produce TADBIW from HBIW, the researcher, has to use proper hydrogenation catalysts.

In the present study, the palladium supported on activated carbon has been successfully synthesis and then applied for selective hydrogenation of HBIW to TADBIW [2, 3]. Pd deposition on the activated carbon was carried out via the incipient wetness impregnation technique using Pd (II) chloride. Reaction conditions for synthesis of Pd/C catalyst was optimized several factors, such as; PH, adsorption temperature, precipitation temperature, the time of adsorption and various concentration of Pd solution on the product yield was investigated in the converted of HBIW to TADBIW. Reactions were designed by Fractional Design software in 30 levels with 5 parameters. The morphology of the Pd/C catalyst was characterized by a SEM (Scanning electron microscope).

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One-pot, multicomponent synthesis of highly substituted pyridines by using task-specific ionic liquid

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The pyridine scaffold is a key constituent of a wide range of naturally occurring and synthetic bioactive compounds, pharmaceuticals, and functional materials [1]. 2-Amino-3,5-dicarbonitrile-6- sulfanylpyridines exhibit various pharmacological activities and are useful as antihepatitis B virus, antiprion, antibacterial, and anticancer agents [2]. Thus, the synthesis of these compounds has attracted much attention, and a number of procedures have been developed to prepare these compounds using a variety of protocols. One of the most attractive routes for the synthesis of these compounds involves the cyclocondensation of aldehyde, malononitrile and thiol [3].

This condensation has been carried out under various conditions [4]. However, some of these protocols have significant drawbacks e.g. formation of inevitable side products, prolonged reaction times, low yields, harsh reaction conditions, tedious workup and use of expensive and environmentally toxic catalysts as well as solvents.

In recent years, room temperature ionic liquids have received considerable attention as an alternative green reaction medium for numerous organic reactions due to their favorable properties, such as good solvating capability, wide liquid range, negligible vapor pressure, tunable polarity, high thermal stability and ease of recyclability. They are also played a significant role in controlling the reactions as catalysts [5].

Herein, we wish to report an efficient method for the synthesis of corresponding 2-amino-3,5-dicarbonitrile-6-thio-pyridines by using task-specific ionic liquid, in short reaction time and high yields.

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The structure study of 1,3-diaryl-3H-benzo[f]chromenes

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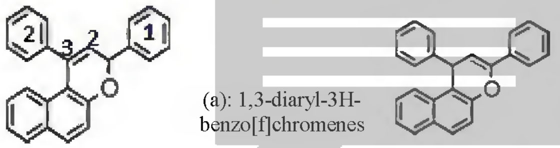
There has been considerable interest in chromenes and their benzo-derivatives, not least because of their value for a variety of industrial, biological and chemical synthetic uses. In particular benzo[f]chromenes (naphthopyrans) are of special interest as photochromic compounds, electronic display system, optical switches and temporary or permanent memories [1]. Our aim in this paper, we investigate the stability and the isomer structure of diaryl-benzo[f]chromenes(I).

From the theoretical point of view, by considering the position of double bond (C2=C3) with respect to the plane of the heterocyclic ring and with respect to Ph groups, two isomers can be drawn for I (Fig. 1). The calculations of geometrical parameters and electronic energies for the isomers were performed using the Gaussian 09 program package. In this work, we applied the B3LYP level using different basis sets and MP2/6-31g** level of theory.



(a): 1,3-diaryl-3H-benzo[f]chromenes

(b):1,3-diaryl-1H-benzo[f]chromenes

Figure 1: Two possible isomer diaryl-benzo[f]chromenes.

The energy differences between two a and b isomers, calculated at the B3LYP level using different basis sets and MP2/6-31g** level of theory is at almost 5kcal/mol. But a closer look at the structure and energy value shows that isomer b is more stable than isomer a, because heterocyclic ring of the b isomer is more planar than that isomer a. According to our calculations, the dihedral angle between phenyl (1) and heterocyclic ring, on average, are 10.88 and is more than that of phenyl (2), which is in good agreement with the experimental results. The full optimized geometrical parameters of 1,3-diaryl-3H-benzo[f]chromenes isomers are in excellent agreement with the results of the experimental structures [3] nearly in the experimental error range.

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A novel and efficient one step synthesis of benzo[4,5]imidazo [1,2-a] pyrimidine

Introduction

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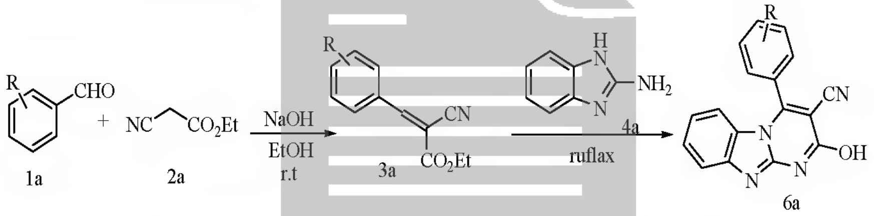
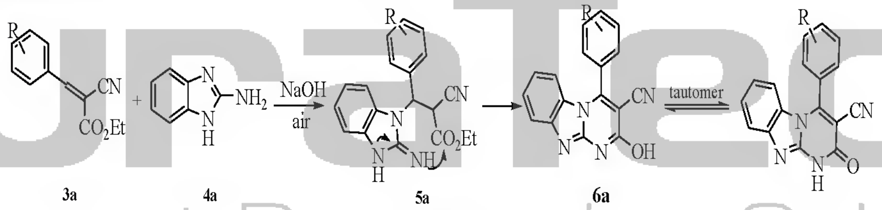
The applications of multi-component condensation reactions (MCRs) involving starting materials with different functional groups is very important in the organic chemistry. Purification of products resulting from MCRs is also simple since all the organic reagents employed are consumed and are incorporated into the target compound [1, 2]. In the present investigation, we have demonstrated that the MCRs between, aromatic aldehydes **1a**, ethyl cyanoacetate **2a** and 2-amino benzoimidazole **4a** and permitted air-oxidation of the initial MCR products into 2-hydoxy-4-benzo[4,5]imidazo [1,2-a] pyrimidine-3-carbonitrile **6a** (scheme 1).



scheme 1

The formation of the products **6a** is assumed to take place via an initial addition of the more nucleophilic endocyclic nitrogen in 2-amino benzoimidazole **2a** to the intermediate **5a** with subsequent intramolecular cyclization and aromatization to give the final product (scheme 2). The structures of all the new synthesized compounds were established on the basis of their spectral IR, ^{1}H-NMR and ^{13}C- NMR spectroscopy.



scheme 2

References

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Synthesis of some perfluoro heterocyclic compounds by pentafluoropyridine

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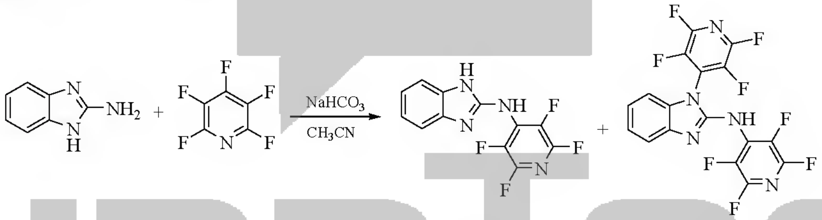
Fluorinated heterocyclic compounds are used as building blocks in the pharmaceutical industry and the majority of commercially important life-science products [1]. Nucleophilic displacement of fluorine in pentafluoropyridine occurs very readily because the heterocyclic ring is activated strongly both by the presence of the nitrogen heteroatom and by the activating influence of the fluorine substituents themselves. The site reactivity order of pentafluoropyridine toward nucleophilic attack follows the sequence 4-fluorine > 2-fluorine > 3-fluorine [2,3]. In this paper, we describe our initial investigations which demonstrate nucleophilic substitution of pentafluoropyridine with a wide range of nucleophiles and highlight how the resulting products 2,3,5,6-tetrafluoro-4-pyridine derivatives in second step no cyclised in the 3-position of fluoropyridine. Reaction of pentafluoropyridine with 2-amino benzoimidazole under basic conditions in acetonitrile at reflux gave a product **1a** and **2a** (scheme 1).



1a **2a**

Scheme 1

In this case, the first more nucleophilec nitrogen atom install attack from cyclic in 4-position of pentafluoropyridine and give **1a** , in letter step free nitrogen addition to an other molecule of pentafluoropyridine. In this case no cyclised in second step. The structure of compounds **1a** and **2a** inferred from their ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data.

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Synthesis and characterization of some novel N-substitution thiourea and imidazole 2-thiols

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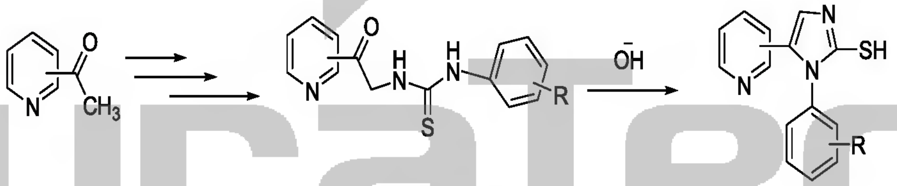
N-substitution thioureas are important organic compounds because of their pharmacological activities. Specially, some of their derivatives have been used in the anti-histamine drugs [1]. These compounds are not only a segment of biologically important but also a versatile intermediate for the synthesis of heterocyclic compounds.

On the other hand, imidazoles are widely distributed in nature, and known as biocatalyst and biological ligand. They play a vital role in life activities [2]. Furthermore, imidazole-2-thioles have been used as rubber antioxidants, as accelerators of rubber vulcanization in industry and are light-sensitive photographic materials [3]. Some these derivatives, such as 1-methylimidazole-2-thiol (Methimazole), have been clinically used for the treatment of several diseases [4]. Consequently, the synthesis of imidazole-2-thioles containing two aryl rings still remains an active research area.

In view of these reports, we wish to report the synthesis of some novel N-substitution thiourea and imidazole-2-thiol derivatives. The synthetic pathway of the title compounds is presented in Scheme **1**. IR, ^{1}H and ^{13}C-NMR spectroscopy as well as elemental analysis data were used for identification of these compounds.



Scheme 1.

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Synthesis, lipophilicity studies and antibacterial properties of some novel indolecontaining pseudopeptides

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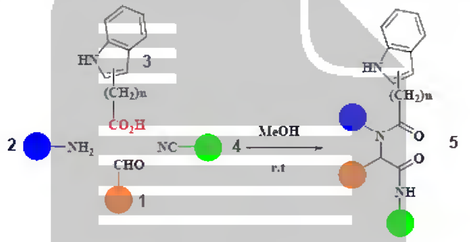

Indole nucleus is a substructure found in numerous natural products and pharmaceuticals possessing anti-inflammatory, antimalarial, antidepressant, antitumor and various other activities. Among the large family of indoles, indole carboxamides have recently attracted a great deal of attention of chemists and biologists due largely to their various pharmacological activities such as antioxidant, hypocholestrolemic, antihistaminic and Immunosuppressive.

Furthermore, in recent years, peptides and pseudopeptides especially those containing tryptophan have gained popularity as promising building blocks for design and development of novel materials with potential application areas ranging from drug design to biotechnology [1].

Considering all above, we`ve been greatly encouraged to synthesis novel indole-containing pseudopeptides via Ugi-4CR by the importance of indole carboxamides and the fact that although functionalized indole ring systems have been found frequently in biologically active compounds, indole derivatives as MCR partners are rather under-represented[2]. The compounds have been screened for their antimicrobial activity and they are found to exhibit moderate antimicrobial activities. The lipophilicity studies showed that most of the compounds possess optimum range for oral absorption and cell membrane permeation, as well as blood brain barrier permeation.

Keywords : Indole-containing pseudopptides, Antimicrobial activity, Lipophilicity

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Preparation and application of SiO_2/1-methylpiperidinium chloride /Barium sulphate composite nano-particles in the synthesis of 1,5-diaryl-3-(arylamino)-1H-pyrrol-2(5H)-ones

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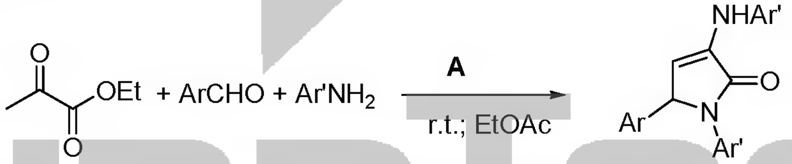
Multi-component composites have been interested in a wide range of possessions and properties because these materials have complex structures and multiphase morphology, which escort these materials to a huge multiplicity of properties [1]. Due to new and high demands of organic synthesis to multi-functionalized catalysts, the preparation of organic–inorganic nano-composites is a special category of nano-materials [2]. In the useful conditions, the organic–inorganic nano-composites are servers of both phases, such as solidity, stability, and reusability of the composite [2]. With the advent of nano-science and nanotechnology, the aim of scientists has been closer to reality to design new functional materials combining the best specific properties of organic and inorganic materials. Thus, development of multi-component nano-materials has received a great deal of attention in basic and applied research in recent times.

This article gives an overview of the controlled synthesis of silica gel / 1-methylpiperidinium chloride / barium sulphate composite nano-particles (**A**) through acidic hydrolysis of tetraethoxyorthosilicate (TEOS) in the presence of 1-methylpiperidinium hydrogensulfate and barium chloride. In continue the prepared composite has been applied for the catalytic preparation of a variety of 1,5-diaryl-3-(arylamino)-1H-pyrrol-2(5H)-ones from the reaction of amines, aldehyde and ethyl pyruvate under ambient conditions [3 (Scheme 1).



Scheme 1: preparation of 1,5-diaryl-3-(arylamino)-1H-pyrrol-2(5H)-ones using **A** nano-composite as catalyst

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LiOH as a bifunctional reusable catalyst for the synthesis of bis(pyrazolyl)methanes

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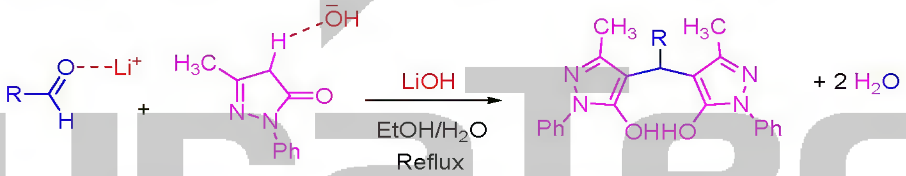
Among the heterocyclic ring systems, pyrazolone derivatives have a wide range of unique biological activities. Some of the pyrazolone derivatives are now included in many of commercialized drugs for brain ischemia [1], and myocardial ischemia [2]. Among them, bis(pyrazolyl)methanes (BPMs) such as 4,4′-(arylmethylene)-bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)s have a broad spectrum of approved biological activity [3]. In spite of extensive application of 4,4′-(arylmethylene)-bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)s, a few methods have been reported for the preparation of these interesting compounds. Nevertheless, most of these methods suffer from limitations such as moderate yields, long reaction times, harsh reaction conditions, application of hazardous solvents and/or tedious workup procedures. Therefore, finding an efficient and a capable protocol for the preparation of 4,4′-(arylmethylene)-bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)s is of obvious importance. Considering above facts and as a part of our researches to develop efficient and environmentally benign synthetic methods in organic chemistry, we report here the application of LiOH as an efficient, inexpensive, water-tolerant and bifunctional catalyst for the synthesis of 4,4′-(arylmethylene)-bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)s in aqueous medium.(Scheme 1)



Scheme 1. Bifunctionality of LiOH in the synthesis of bis(pyrazolyl)methanes

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Synthesis of Novel Derivatives of pyrazolo [4, 3-e] pyridines using nano-particle Fe_3O_4

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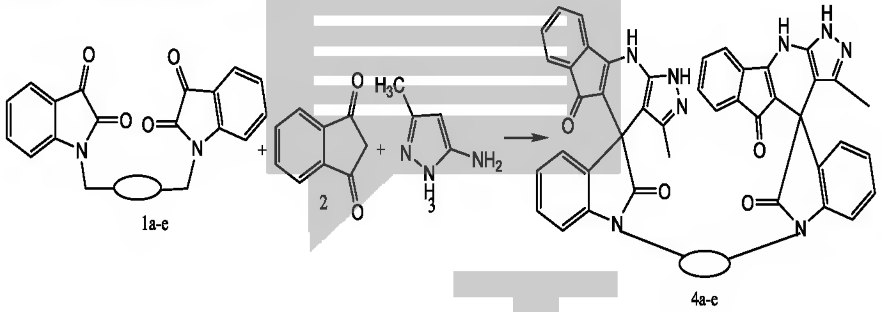
Pyrazolo[3,4-b]pyridines have shown several interesting biological and pharmacological applications such as antitubercular action [1], activity against Gram-positive and Gram-negative bacteria [2], and adrenocortropic hormone (ACTH)-releasing factor and corticotrophin-releasing factor (CRF) antagonist activity [3]. As many of which have been assessed as anti-HIV, anti-viral, anti-tumor, anti-fungal, and anti-consultants agents [4] also showed interesting biological activity.

Recent development in the pyrazolopyridines chemistry and our continued interest in the development of efficient and environmentally friendly procedure for the synthesis of pharmaceutical compound [5-7] triggered us to describe here an efficient method for the regioselective synthesis of new derivatives of pyrazolopyridines through multicomponent reactions of 3-amino-5-methylpyrazole, synthesized bis isatin and active indandione (Scheme 1).



Scheme 1

All of synthesized compounds were characterized by IR, NMR and elemental analysis.

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1,3-Dibromo-5,5-dimethyl hydantoin (DBH)-catalyzed efficient and highly rapid synthesis of bis(indolyl)methanes under mild condition

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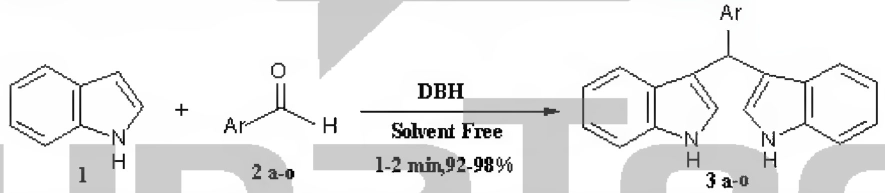
Indoles and their derivatives are used in the field of pharmaceuticals, material sciences and agrochemicals. Therefore, significant efforts have been directed towards the synthesis of these molecules. Different reagents have been applied for the synthesis of bis(indolyl)methanes such as AcOH ,InF_3,$AlPW_{12}O_{40}$,$ZrOCl_2.8H_2O$, $LiClO_4$, PPh_3HClO_4,P_2O_5/SiO_2,$ZrCl_4$, $La(PFO)_3$,$Dy(OTf)_3$, CAN ,$NaHSO_4.SiO_2$,$Sb_2(SO_4)_3$, $Zr(DS)_4$,Zeokarb-225, trichloro-1,3,5-triazine, silica sulfuric acid , H_2NSO_3H , Zeolite, I_2 , PCL_5 , $CuBr_2$,VCl_3 ,ZnO , $Bi(NO_3)_3\cdot 5H_2O$ and TiO_2. However, these methods suffer from one or more disadvantages such as low yield, a long reaction time, use of an excess of reagent/catalyst and toxic solvents, expensive reagents, difficult work-up and formation of hazardous by products.[1-3]

In continuation with the search for simple non-hazardous methods for the transformations in organic synthesis using halogenating agents[4,5], herein we wish report on the use of DBH as a more robust and efficient catalyst in the one-pot synthesis of Bis(indolyl)methanes **3a–o** by reaction of indole **1** and various aldehydes **2a-o** under solvent free conditions.



In conclusion, the advantages of this method in comparison with other previously reported are the following: The yields of products are better than the previous reported yields. In addition, the catalyst DBH is inexpensive, not moisture sensitive, sub-molar amounts of DBH are required. Longer reaction times are required when lesser amounts of DBH are employed. It is important to note that no bis (indolyl) methanes derivatives were afforded when the reactions were carried out without using any DBH in the reaction.

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Synthesis of Novel Derivatives of Coumarins using nano-particle Fe_3O_4

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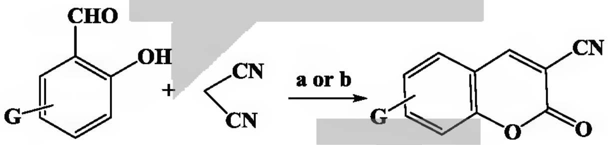
Coumarins are well known natural products for their diverse biological activity [1]. Coumarin derivatives display a broad range of applications to the pharmaceutical, perfume and cosmetic industries [2]. They are also exploited as intermediates and building blocks in organic synthesis [3] 3-Carboxycoumarins are important initial compounds for the synthesis of coumarins, they are traditionally prepared by Knoenenagel condensation of 2-hydroxybenzaldehydes with active methylene compounds [4]. But the reported methods always suffer from drawbacks such as long reaction time, high temperature, or necessary catalyst [1].
In continuation of our ongoing studies to synthesize of heterocyclic and pharmaceutical compounds at mild and practical protocols [5-7], we wish to report our preliminary results on the preparation of nano-Fe_3O_4 and their application as a green catalyst for the synthesis of azo-linked coumarin (Scheme 1).



a) Nano Fe_3O_4(aq) / Reflux
b) Ultrasound irradiation (U. S.)

Scheme 1

All of synthesized compounds were characterized by spectroscopic methods (IR, ^{1}HNMR and ^{13}CNMR) and elemental analysis.

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[7] Nikpassand M, Zare L, Shafaati T, Chin. J. Chem. (in press)

An efficient HS zeolite catalyzed one-pot protocol for the synthesis of coumarin derivatives

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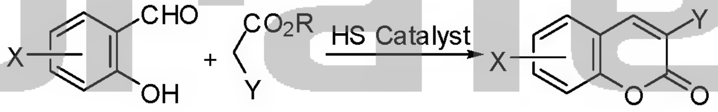
Coumarin and its derivatives occur widely in nature, and have been exploited in biological, chemical and physical fields. These compounds are also used in perfumes and cosmetics [1] and they are found to possess several biological activities [2]. Conventional routes for the synthesis of coumarin-containing compounds involve the Pechmann, Perkin, Reformatsky, Wittig and Knoevenagel reaction. Coumarin derivatives are readily synthesized by the above mentioned reactions; however, all reported methods have disadvantages (harsh and long reaction conditions, non-environmentally friendly solvents, low yields, difficult purification or expensive catalysts, complicated procedure for the preparation of catalysts and producing by products), making the development of a new reliable high-yielding method for the synthesis of coumarins desirable.

In this present article, we demonstrate the Knoevenagel reaction for the synthesis of coumarin derivatives by the condensation of an o-hydroxyaryl aldehyde with an activated β-dicarbonyl C-H acids under classical heating conditions in the presence of hydroxy sodalite as a new, efficient, excellent, readily available, very inexpensive and recyclable catalyst.



X= Alkyl, Aryl, H, Halid
Y= CO_2R, CN, $COCH_3$

References:
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A novel and efficient one step synthesis of 2-amino-pyrimidines using amino-functionalized SBA-15 catalyst

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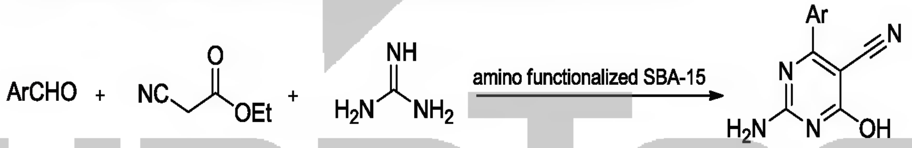
N-Containing heterocycles are ubiquitous to among pharmaceutical compounds [1]. Pyrimidine exhibits a wide spectrum of pharmacophore as it acts as bactericidal, analgesic, fungicidal, anti-tumor agents, anti-hypertensive [2]. Thus alternative strategies for their synthesis involving different catalysts and conditions have been developed.

It is of a great practical importance to synthesize pyrimidine derivatives using easily separable and reusable solid catalysts. SBA-15 mesoporous silica with well ordered hexagonal arrays of cylindrical channels, narrow pore size distributions, remarkable thermal stability, large uniform pore size, high surface area [3] is important heterogeneous catalysts.

In continuation of our interest in the synthesis of heterocyclic compounds, we report in this work the synthesis of substituted 2-amino-5-cyano-4-hydroxy-6-aryl pyrimidines derivatives by three component condensations of aromatic aldehydes, ethyl cyanoacetate and guanidine using a catalytic amount of amino-functionalized SBA-15 as reusable and eco-friendly catalyst under mild conditions. This efficient technique has the advantages to give 2-amino-pyrimidines derivatives using a reusable catalyst in good to high yields, to be completed in short reaction times and to offer a simple product isolation procedure.



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Ultrasound-assisted synthesis of substituted 3-amino-4H-chromenes using NH_2-SBA-15 catalyst

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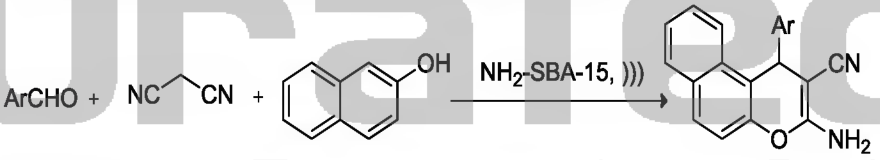
3-Amino-4H-chromenes and their derivatives are of considerable interest as they possess a wide range of biological properties [1], such as spasmolytic, diuretic, anticoagulant, anticancer and antianaphylactic activity [2]. In addition, they can be used as cognitive enhancers for the treatment of neurodegenerative diseases, including Alzheimer's disease, amyotrophic lateral sclerosis, Huntington's disease, Parkinson's disease, AIDS associated dementia and Down's syndrome as well as for the treatment of schizophrenia and myoclonus [3]. Thus the synthesis of 3-amino-4H-chromenes is of much importance to organic chemists [4]

In continuation of our investigations in the synthesis of heterocyclic compounds [5], herein we describe an efficient and convenient synthesis of 3-amino-chromenes using functionalized SBA-15 catalyst under ultrasonic irradiation. In this work we introduce a three-component reaction of aldehyde, malononitril, and 2-naphthol in the presence of a catalytic amount of NH_2-functionalized SBA-15 catalyst for synthesis of 3-amino-1-phenyl-1H-benzo[f]chromene-2-carbonitrile derivatives. These derivatives are obtained in excellent yields by proceeding through a simple, mild, and efficient procedure utilizing ultrasonic irradiation.



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(BeDABCO)PdCl$_3$ as an active catalyst for the Hiyama cross coupling reaction

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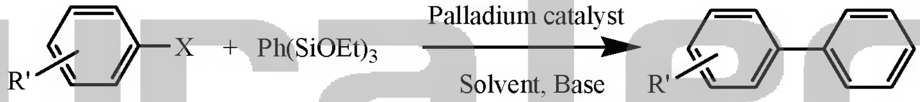
Palladium-catalyzed C–C coupling reactions to produce symmetrical and unsymmetrical biaryls are among the most potent and convenient tools of modern organic synthesis [1]. Biaryls are applied as the building block of a wide range of herbicides, pharmaceuticals; natural and bioactive products [2]. Hiyama coupling reactions using organosilicon reagents have been intensively developed and utilized as an important and useful method for producing carbon-carbon bonds. Silicon compounds are more stable toward air and moisture than organomagnesium and organozinc reagents. The organosilicon reagents are available at low cost or are very easily prepared, nontoxic, and are very stable to other functionalities and to the reaction conditions [3-5]. The many efforts have been focused on the development of efficient and selective catalytic systems for this transformation using various palladium catalysts.

In continuation of our recent investigations on the synthesis of the palladium catalysts and application of these complexes in the cross coupling reactions [6-7], we now wish to report the extension of (BeDABCO)PdCl$_3$ homogeneous complex for the cross-coupling reaction of various aryl halides with triethoxy(phenyl)silane.

An efficient catalytic system using (BeDABCO)PdCl$_3$ was developed for the Hiyama cross-coupling reaction. The substituted biaryls were produced in excellent yields using catalytic amount of this catalyst in NMP at 100 °C (Scheme 1). Benzyl dabco as an efficient ligand and also a quaternary ammonium salt had efficient stabilizing effect on the Pd(0) species.



Scheme 1. The Hiyama cross coupling reaction by (BeDABCO)PdCl$_3$

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Multicomponent reactions of kojic acid and acetylenic esters in the presence of isoquinoline

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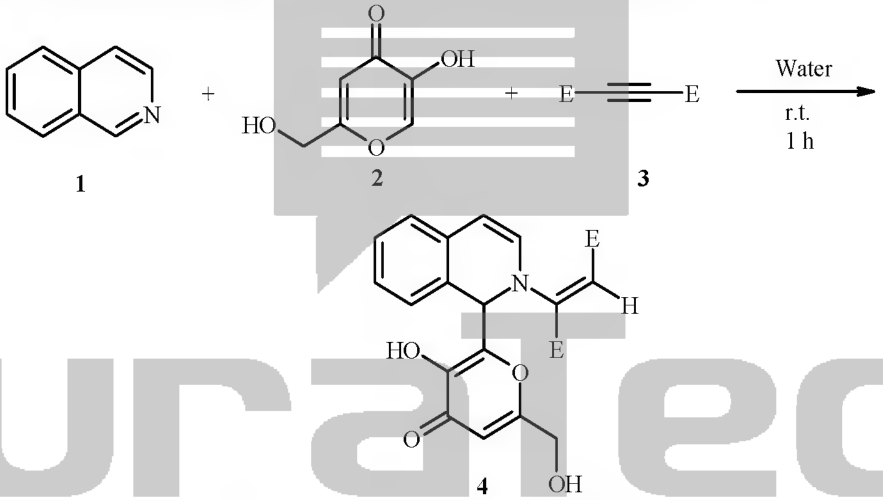
Multi-component reactions (MCRs) are useful organic reactions in which three or more starting materials react to give a product [1]. 1,2-Dihydroisoquinolines, as basic scaffolds in many natural products and pharmaceuticals that show significant biological activities [2-3], have promoted considerable efforts toward their synthesis. Herein, we describe a three-component condensation in which isoquinoline **1** react with kojic acid **2** in the presence of acetylenic esters **3** in water at room temperature by vigorous stirring to afford 1,2-Dihydroisoquinoline derivatives **4** as sole product in good to high yields.



4,5	E	Yield of **4** (%)
a	CO_2Me	85
b	CO_2Et	81
c	CO_2t-Bu	76

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A simple and efficient one-pot synthesis of 2-substituted benzimidazoles

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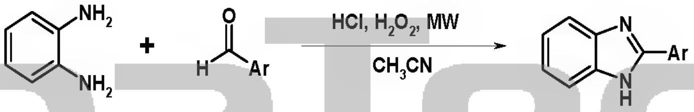
Benzimidazole structures are classified under several classes of drugs [1], based on the possible substitution at different positions of the benzimidazole nucleus. Introduction of a small substituent into the 2- and 5-position is characteristic for benzimidazole anti-helmentics; alternatively, bulky 2-substituents characterizing drugs used in the treatment of peptic ulcer and are sometimes referred as proton pump inhibitors; bulky 1- and 2-substituents are found in H1-anti-histaminics. All these compounds contain the benzimidazole skeleton and hence it has been assumed that this skeleton is necessary for the therapeutic effect. Methods of benzimidazole synthesis include the condensation of o-aryldiamines and aldehyde in refluxing nitrobenzene [2,3]. The condensation of o-aryldiamines with carboxylic acids or their derivatives in the presence of strong acids such as polyphosphoric acid [4] or mineral acids [5].

In connection with our research program directed toward the synthesis of benzimidazole, we hope to describe the synthesis of benzimidazoles from several kinds of aromatic aldehydes and o-phenylenediamine in the presence of H_2O_2/HCl under microwave irradiation in high yields. The structure of products has been assigned by physical and spectroscopic data.



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Nano Fe_2O_3 as magnetically recyclable catalyst for the solvent-free synthesis of 5(4H)-isoxazolone under microwave conditions

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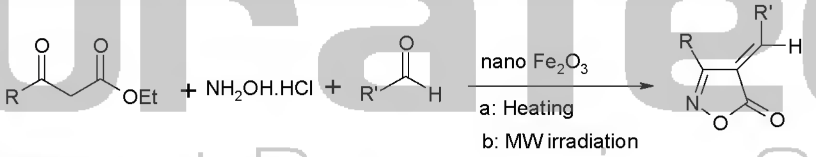
Oxazoles play very important role in the manufacturing of various biologically active drugs as analgesic, anti-inflammatory, anti-depressant, anti-cancer, anti-microbial, anti-diabetic and antiobesity[1-3]. 5-isoxazolone derivatives have been associated with diverse pharmacological activities and they have been used in the dye chemistry [4].

Multicomponent reactions offer convenient procedures for the introduction of many points of structural diversity into heterocyclic compounds prepared in a straight forward manner in a single synthetic step. Combining these features with the extremely fast reaction kinetics of microwave-assisted organic synthesis provides new methods for the rapid and efficient synthesis of heterocyclic libraries suitable for biological evaluation [5].

Magnetic nanoparticles have emerged as one of the most useful heterogeneous catalysts due to their numerous applications in nano catalysis, biotechnology, and medicine. Of these, Fe_2O_3 nanoparticles are the most promising catalysts because of their ease of handling, ease of recovery with external magnetic field, high catalytic activities, and reactivities in various organic transformations. However, there are no reports on the use of Fe_2O_3 nanoparticles for a three-component synthesis of 5(4H) isoxazolone [6,7].

In this article, we report that nano-Fe_2O_3 is a highly efficient and economically viable catalyst for the one-pot synthesis of 5(4H) isoxazolone from hydroxyl amine hydrochlorid, sodium acetate, acetoacetic ester or benzoyl acetic ester and appropriate aldehyds in two conditions thermal heating and microwave irradiation.

Various reaction parameters are optimized for this reaction, recycling of nano-Fe_2O_3, influence of solvent and catalyst concentration. In conclusion, this procedure offers several advantages including (i) the reaction is simple to execute; (ii) the yields are excellent; (iii) the procedure does not require specialized equipment; (iv) a very simple work-up; (v) solvent-free condition and short reaction time.



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Synthesis of new alkenes from the Wittig reaction of 4-pyrone phosphonium salt with various arylaldehydes

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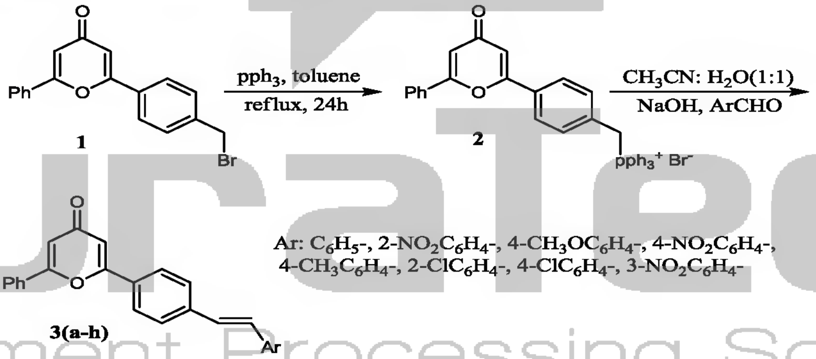
4-pyrones have been extensively studied due to a wide range of applications. They are biologically active and synthetically useful compounds [1-2]. Furthermore, the Wittig reaction is one of the powerful and versatile methods in organic synthesis for the formation of carbon-carbon double bonds [3]. Thus, we became interested in the synthesis and characterization of this category of compounds. In this work, phosphonium salt **2** was synthesized by treatment of 2-(4-bromomethylphenyl)-6-phenyl-4H-pyran-4-one **1** with triphenylphosphine in toluene in 83% yield. Treatment of **2** with various arylaldehydes such as (Ar= C_6H_5-, 2-$NO_2C_6H_4$-, 4-$CH_3OC_6H_4$-, 4-$NO_2C_6H_4$-, 4-$CH_3C_6H_4$-, 2-ClC_6H_4-, 4-ClC_6H_4- and 3-$NO_2C_6H_4$-) in the presence of sodium hydroxide in CH_3CN:H_2O (1:1) afforded E-alkenes **3(a-h)** in 20-82% yields. The chemical structures of products were stablished by spectral data and elemental analysis. In Conclusion, we have investigated the Wittig reaction of phosphonium salt with a number of aryl aldehyeds to afford derivatives in good yields. The Wittig reaction can be applied with confidence to many alkene syntheses.



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Synthesis and study of anthranilated sorbitol as sunscreen

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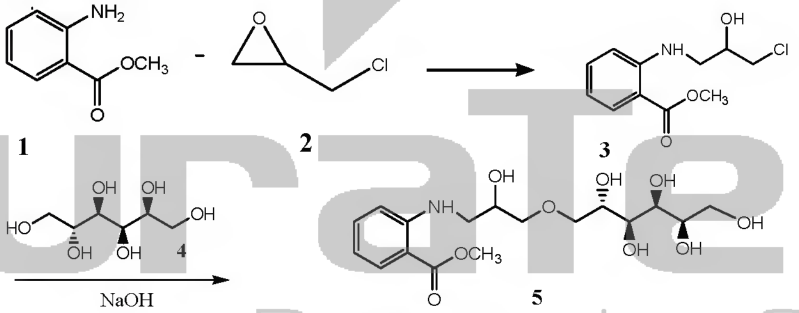
The reaction of methylanthranilate **(1)**, and epichlorohydrin **(2)** led to the synthesis of methyl 2-(3-chloro-2-hydroxypropylamino) benzoate **(3)**. Reaction continued with sorbitol **(4)** and methyl 2-(3-oxo (4R,5 S,6 S,7 S)-octane -2,4,5,6,7,8 -hexaol amino) benzoate **(5)** was obtained in good yield (Scheme 1). Structures of products were elucidated by IR and NMR spectroscopy.

The efficiency of products was studied by UV- spectroscopy as sunscreen. UV- spectrum of product showed strong and distinct absorbtion at 354 nm, which was proper evidence to sunscreen ability of product.



(Scheme 1)

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Nano $BF_3.SiO_2$: An efficient and eco-friendly catalyst for synthesis of azo dyes based on 1-naphthol

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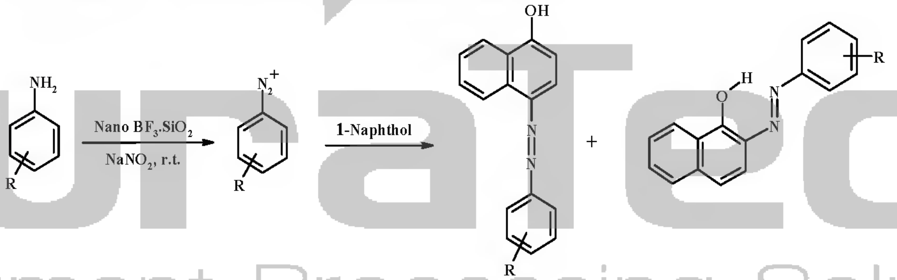
Diazonium salts are very important intermediates in the synthesis of aromatic compounds [1] and they are precursors of azo compounds. Aromatic azo compounds constitute a very important class of organic compounds because of their widespread applications in many areas of technology and medicine. They are well known for their use as analytical reagents, in dye industry or as chemotherapeutic drugs [2]. They are also used as chiral receptors, liquid crystals, new glassy materials and chiral switches in photochemistry [3]. Considering that the synthesis of some azo dyes based on 1-naphthol requires some special conditions such as low temperature and concentrated liquid acids, in addition to high costs it leads to corrosion of reactors and equipments. Nowadays, solid supported reagents have resolved these problems and improved activity and selectivity than individual reagents [4]. When $BF_3.OEt_2$ is added to a reaction mixture, particularly in a protic medium, it can also function as a Brönsted acid. The resulting surfaces possess surface species such as Si-OBF$_2$ or the ion pairs such as Si-OBF$_3^-$ H$^+$. It has been claimed that supported BF_3 is a solid super acid [5]. Therefore, nano $BF_3.SiO_2$ is a bench-top catalyst which is cheap, readily available, eco-friendly and efficient for promotion of many acid catalyzed organic reactions [6]. In this research, we have investigated the application of nano $BF_3.SiO_2$ for synthesis of azo dyes based on 1-naphthol under mild conditions. In this method, it is not require providing special cold conditions for stabilization of diazonium salt. The reaction easily takes place at room temperature and resulting diazonium salt can remain on the solid substrate for several weeks. Final products were identified by ^{1}H- and ^{13}C-NMR, FT-IR and UV-Vis spectroscopic methods.



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$NaBH_4/NiCl_2\cdot 6H_2O$: A Green Synthetic Method for Mild and Convenient Reduction of Nitroarenes in Water

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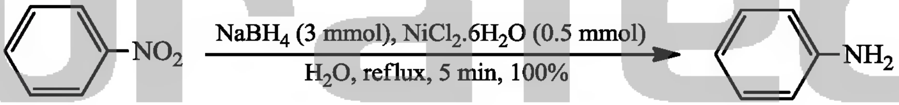
Arylamines are widely used as antioxidants and intermediates for dyes, photographic, pharmaceutical and agricultural chemicals. So, reduction of aromatic nitro compounds is one of the important methods for the preparation of arylamines. It is known that sodium borohydride alone does not reduce nitro compounds under ordinary conditions. However, the reducing capability of $NaBH_4$ could be increased towards the reduction of nitro compounds with Lewis acids, mixed solvent systems and some other additives. In this context, $NaBH_4$ in the presence of $NiCl_2\cdot 6H_2O$ reduces varieties of nitroarenes to their corresponding amines in high to excellent yields. Reduction reactions were carried out in H_2O as eco-friendly solvent at 60–80 °C.



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Selective, solventless and efficient N-Boc protection of amino acids using $MgBr_2$ recyclable catalyst in the presence of triethylamine

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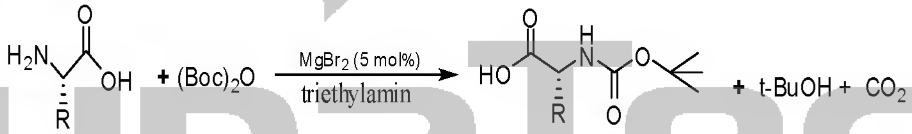
Amino acids are among important compounds in organic, pharmaceutical, agrochemical and polymer chemistry [1]. The development of mild and selective methods for masking amino groups, as well as deblocking of the protected derivatives continues to be a significant aspect in the synthetic chemistry [2,3].

A larg variety of protective groups have been formulated among which the commercially available di-tert butyl dicarbonate [$(Boc)_2O$] group is extensively used as an amino acid protecting group in organic synthesis, because this group is very stable to reaction conditions and is suitable for clean and rapid introduction[4].

Here we report an efficient, solventless, and chemoselective protection of amino acids using $MgBr_2$ (5 mol%) Catalyst in the presence of triethylamine. In this method, various amino acids were converted to their corresponding N-t-Boc derivatives at room temperature in good yield.

All products were characterizd by IR, ^1H-NMR, ^{13}C-NMR and mass spectra and their physical properties.



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An Efficient Green Methodology For The Boc Protection Of Alcohols and Phenols Using $MgBr_2$ Recyclable Catalyst

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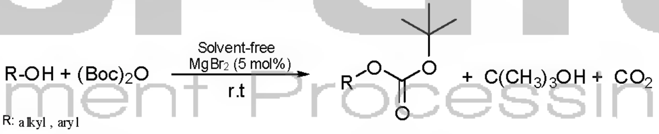
Protection and deprotection of organic functional groups play essential roles in accomplishing multi-step syntheses. In a multi-step organic synthesis, it usually becomes necessary to protect hydroxyl groups. Depending on the simplicity of the process, ease of operation and workup, yield of the desired product and its stability to the reaction conditions, and the overall expenses of the process, a suitable process will be chosen. On these grounds, diverse arrays of different methods are developed during the years for protection/deprotection of various functional groups[1,2]. Protection of the hydroxyl group(s) is necessary in order to maintain these activities and avoid expected side reactions [3]. The choice of protecting groups is often critical for synthesis success, specially for the total synthesis of complex natural products and analogs [4,5]. A larg variety of protective groups have been formulated among which the commercially available di-tert butyl dicarbonate [$(Boc)_2O$] group is extensively used as Alcohols protecting group in organic synthesis, because this group is very stable to reaction conditions and is suitable for clean and rapid introduction.

We report herein our results about protection of Alcohols and Phenols in the presence of catalytic amount of $MgBr_2$ (5 mol%). Solventless condition, easy work-up, short reaction time, excellent yields and reusability of the catalyst are the striking features of this methodology which can be considered to be one of the better methods for the protection of Alcohols and phenols. Primary and secondary alcohols are easily protected in good yield and Short time.



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One-pot procedure for the synthesis of 1,8-dioxo-octahydroxanthenes in the presence of $MgBr_2$ catalyst

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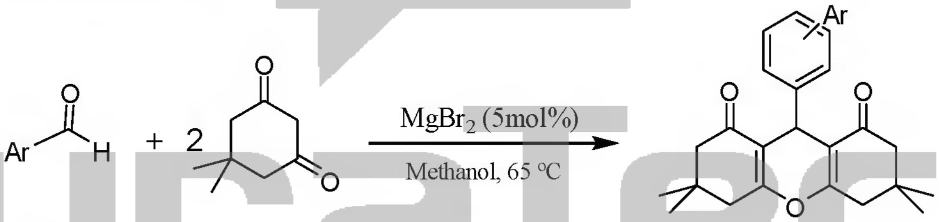
Xanthene's derivatives are parent compounds of a large number of naturally occurring and synthetic derivatives, and occupy a prominent position in medicinal chemistry[1]. The synthesis of xanthenes has attracted the attention of organic chemists due to their wide ranging biological and therapeutic properties including antibacterial[2a] and antiviral[2b], and because they are good candidates for use in photodynamic therapy (PDT) [2c]. There are several reports in the literature for the synthesis of 1,8-dioxo-octahydroxanthene derivatives employing aromatic aldehydes and 5,5-dimethyl-1,3-cyclohexanedione. Therefore the introduction of a mild and efficient method to synthesize 1,8-dioxo octahydroxanthene derivatives is still needed.

On other hand, $MgBr_2$ catalysts have gained interesting attraction in recent years due to economic and environmental considerations[3]. These catalysts are generally inexpensive and easily available. They can conveniently be handled and removed from the reaction mixture, thus making the experimental procedure simple and eco-friendly. Recently, we have utilized different heterogeneous catalysts successfully for various chemical transformations[4].

Herein, we report a very simple procedure for the preparation of 1,8-dioxo-octahydroxanthene derivatives via the condensation reaction of various aromatic aldehydes with dimedone using $MgBr_2$ as a reusable and inexpensive catalyst.



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Synthesis of a New composite of Poly(anilinum hydrochloride) by $FeCl_3.6H_2O$ as Oxidant in the Presence of Silica Under Solid-State Condition

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Polyaniline (PANI) was first discovered in 1835 and used as dye known as aniline black for cotton. It is probably the most common conducting polymer, good environmental stability and the ease of preparation increased commercial applications of PANI [1].

PANI is most commonly prepared through the chemical or electrochemical oxidative polymerization of aniline monomer in acidic solution. The first conducting polymers (CPs) were insoluble, intractable, non-melting and thus not processable.

Adding inorganic particles such as silica (SiO_2) to the polymers provide a new class of materials with novel properties is named composites. Organic–inorganic composites with different combinations of the two components have attracted significant attention as they have interesting physical properties and potential applications. Composites of CPs prepared by the incorporation of metal (e.g., Au, Pd or Cu) or semiconductor (CdS or CdTe) or metal oxide (Fe_3O_4 or SiO_2) particles into CPs attract substantial research efforts, as these hybrid materials possess new catalytic, electronic, or optoelectronic functionalities.

Among them the use of silica particles is continuously growing because of its high specific area, large porous volume, and large mechanical and thermal stability. Silica is an important technical material since it is widely used in pharmaceutical, electronic packaging and other applications and also in the preparation of silica glass, chromatographic columns.

In this investigation, it was demonstrated that a new composite of poly(anilinum hydrochlorid)/silica was successfully synthesized under solid-state condition. $FeCl_3.6H_2O$ is used as oxidant. Using the silica can improve the properties of poly(anilinum hydrochlorid) and vice versa. Moreover, the procedure is very simple, convenient and under solvent-free condition [2].

The doping, synthesis and characterization processes of this composite were confirmed using UV-vis and FT-IR spectroscopy, and by means of comparison with polyaniline emeraldine base and salt synthesized in solution. The morphology and particles size of composite were determined using SEM.

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Use of $FeCl_3.6H_2O$ as Oxidant in Synthesis of a New Nanocomposite of Poly(anilinum hydrochloride) in the presence of Nanasilica Under Solvent-Free Condition

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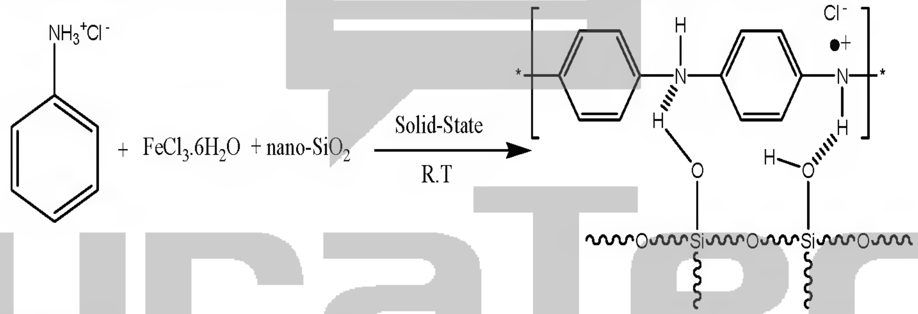
High Electrical Conductivity, good environmental stability and the ease of preparation increased applications polyaniline (PANI). It has gained much commercial applications.

Adding inorganic particles such as silica (SiO_2) to the polymers provide a new class of materials with novel properties is named composites. These particles improve electrical, thermal and mechnical properties of polymers [1-6].

The in situ oxidative polymerization of monomer, anilinum hydrochloride, was used to synthesize a new nanocomposite of polyaniline and nanosilica in the presence of $FeCl_3.6H_2O$ as oxidant under solid-state (solvent-free) condition for the first time. The doping, synthesis and characterization processes of this nanocomposite were confirmed using UV-visible and FT-IR spectroscopy, and by means of comparison with polyaniline emeraldine base and salt synthesized in solution. The morphology and particles size of nanocomposite were determined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). TEM image of the samples clearly indicate that the materials have uniform solid nanospheres (no hollow spheres or fibers) and their average diameters are in the range of 30 nm.



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Silica Sulfuric Acid/HNO_3 as a Novel Heterogeneous System

for the Nitrolysis of DADN to HMX under Mild Conditions

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Tehran Iran

1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (HMX), also referred to as octogen or cyclotetramethylenetetramine, is a highly energetic material that is useful in variouse explosives and propellants for military and non-military applications[1–3].

Some procedures are described for preparing HMX from hexamine. The first know process for the manufacture of HMX was developed in 1940's as Bachmann process [4]. This process typically provides yields of 80-84% which only about 10-40% is HMX. There are several drawback in this process and a great amount of another explosive, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) is produced. For improving of these problems another synthetic routs involving various intermediates for making HMX have been proposed. Some intermediates that have been use to produced HMX are 3,7-dinitro-1,3,5,7-tetraazabicyclo [3,3,1] nonane (DPT), 1,3,5,7-tetraacetyl 1,3,5,7-tetraazacyclooctane (TAT) , etc. One of these intermediate involving 1,5-diacetyl-3,'7-dinitro-l,3,5,7-tetraazacyclooctane (DADN) gives a better yield of HMX than the established Bachmann process.

3 **4**

The present investigation focuses on a new method for nitrolysis of DADN to HMX by developing a new nitrolysis process involving the use of nitric acid catalyzed by Silica Sulfuric Acid (SSA). In order to optimize the process parameters for synthesis of HMX to obtain higher yield and purity, a study was carried out with variation of some parametric conditions like time, mole ratio of SSA and nitric acid. This method gave us a green and mild conditions for nitration reaction.

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PEG-SO_3H as Eco-friendly Polymeric Catalyst for Efficient Oxidation f Aryl Alcohols and Alkyl Arenes Using Potassium Bromate in H_2O/CH_3CN and Room Temperature

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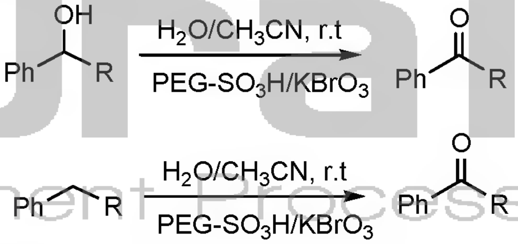
Oxidation reactions are among the most important transformations in synthetic chemistry and offer important methodology for the introduction and modification of functional groups [1,2]. The oxidation of alcohols into aldehydes and ketones is a ubiquitous transformation in synthetic chemistry as well as in chemical industry for the preparation of many drugs, vitamins and fragrances. During the last two decades, there has been a spectacular development in this field and a large number of novel and useful oxidation reactions have been developed [3,4].

On the other hand, Poly (ethylene glycol)-bond Sulfonic acid (PEG-SO_3H) is a solid acid which can be used for different organic functional group transformations as catalyst under heterogeneous and homogenous conditions.

In this research, we report a new, simple, mild, and effective procedure for the oxidation of aryl alcohols and alkyl arenes into aldehydes and ketones via a mild reaction in the presence of potassium bromate as oxidant and PEG-SO_3H as catalyst with high yields (77-96%). In conclusion we have developed a facile, convenient and environment-friendly protocol for the oxidation of organic compounds under green conditions.



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Na mediated synthesis of β-hydroxyselenides through ring opening of epoxides

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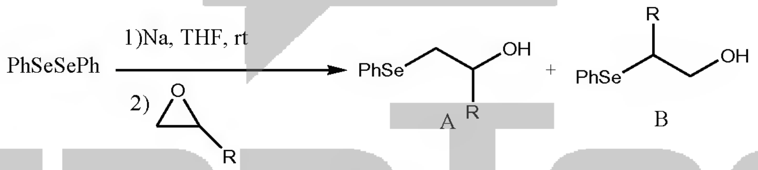
Introduction

Epoxides represent one of the functional groups most widely used in synthesis because, in addition to the easy introduction of the oxirane functionality into a molecule, they are susceptible to react with a vast number of nucleophiles to yield valuable bifunctional compounds in a rather simple procedure [1]. Recently, several reagents have been reported in the literature that can promote ring opening of epoxides [2-3]. However, the reported methods have some limitations such as: use of strong and non-selective catalysts, toxic and expensive reagents, low yield and long reaction times.

According to the above mentioned considerations, we were encouraged to seek a novel mild and efficient methodology for the ring opening of epoxides lacking some of the mentioned limitations. So, we wish to report a novel catalyst-free procedure for the synthesis of β-hydroxyselenides including Na mediated breaking of Se-Se bonds and the nucleophilic epoxides ring opening with of the arylselenolate ions (Scheme 1).



Scheme1

In summary, an efficient one-pot protocol was developed for synthesizing β -hydroxy selenides by using sodium metal.A series of epoxides was converted into the corresponding β -hydroxy selenides on treatment with diphenyldiselenide .In this work, we have developed efficient, mild, and selective methods for synthesis of β-hydroxy selenide using small solvent at room temperature.

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Na-Promoted Cleavage of Diorganyl disulfides:A novel and mild protocol for the synthesis of β-hydroxy sulfides through ring opening of 1,2-epoxides

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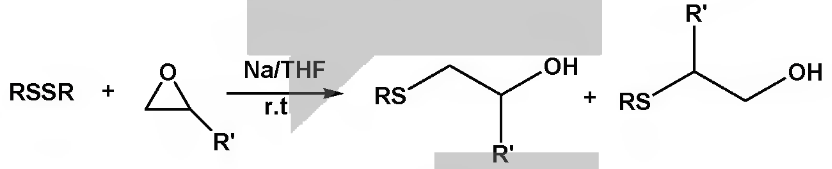
β-Hydroxysulfides are important class of organic compounds, which have been found to be useful in medicinal chemistry and organic synthesis.[1] Many methods have been reported for the synthesis of β-hydroxysulfides,[2], but many of these methods involve the use of toxic and expensive reagents, drastic reaction conditions, poor regioselectivity, extended reaction times, unsatisfactory yields and entail undesirable side reactions due to oxidation of thiols or rearrangement of oxiranes[3]. During the last few decades, cleavage of symmetrical diorganyl-disulfides have received much effort for preparation of sulfide (RS^-) anions and subsequently formation of C-S bonds. In this work, we have explored an one-pot method for subsequent synthesis of organic sulfides by sodium-promoted cleavage of diphenyldisulfides and subsequently synthesis of β-hydroxysulfides with sulfide anions (Scheme 1).



1 2 3 4

Scheme 1

To conclude, an efficient one-pot protocol was developed for the synthesis of β-hydroxysulfides by using sodium metal in THF. The notable advantages of the present procedure include: (a) good yield, (b) mild reactions conditions, (c) use of relatively non-toxic reagents and solvents and (d) general applicability accommodating a variety of substitution patterns.

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A facile synthesis of β-Nitro alcohol using Amberlite IRA-400 as a Heterogeneous catalyst

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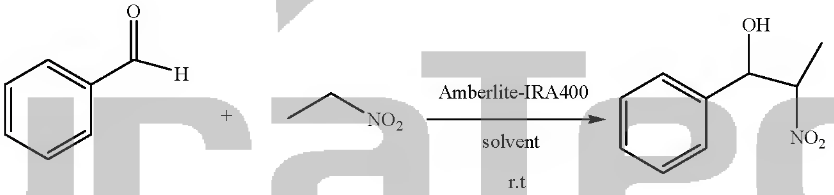
The Henry reaction, the reaction of a nitroalkane with an electrophilic carbonyl derivative (aldehyde or ketone), discovered in 1895[1] is an efficient method for C–C bond construction. This reaction became very popular because the resulting β-nitroalcohols are highly valuable synthons for the preparation of useful intermediates in synthetic organic chemistry[2].

Large variety of catalysts were used in this reaction such as alkali metal bases and alkaline alkoxides in alcoholic solution [3], simple amines [4], ammonium salts [5] and guanidine derivatives [6]. Due to the high cost of the catalyst or low turnover, some type of recyclable catalyst would be desirable for the practical application of this reaction. Amberlite IRA-400, is a strong base of a quaternary ammonium hydroxide type that it is stable, environmental and recyclable catalyst.

Herein we report the Henry reaction of nitroethane that give β-nitroalcohols using Amberlite IRA-400 as a heterogeneous catalyst in high yields (Scheme 1).



Scheme 1

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A simple and efficient method for N-formylation of amines using $NbCl_5$ catalyst under solvent-free conditions

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Formamides are a class of important intermediates in organic synthesis. They are Lewis bases, which are known to catalyze reactions such as allylation[1] and hydrosilylation[2] of carbonyl compounds. More recently, asymmetric allylation of aldehydes has been achieved with chiral formamides.[3] Furthermore, formamides are very useful reagents in Vilsmeier formylation reactions and they have been used in the synthesis of formamidines and isocyanides. [4] More over, the formyl group is a useful amino-protecting group in peptide synthesis and N-formylamino acid esters can, for example, serve as starting materials for peptide synthesis.[5]

More recently, $NbCl_5$ has become a research focus as a Lewis acid catalyst in promoting various organic transformations. Compared with other Lewis acids, niobium penta chloride has some advantages, such as ease of handling, moisture stability, and low catalyst loading. Herein, $NbCl_5$ was employed as a green, inexpensive and environmentally friendly catalyst for the synthesis of formamides via one-pot condensation of amines and formic acid at 70 ◦C under solvent-free conditions. In our experimental procedure no isolable side product has been observed. All the aromatic and aliphatic amines reacted well to give the N-formylated product in good to excellent yield (85-98%). Compared with conventional methods, the main advantages of the present procedure are milder conditions, shorter reaction time, simplicity, easy work up and higher yields.

$$\text{RNHR'} + \text{HCOOH} \xrightarrow[\text{Solvent- free; } 70\ ^{0}\text{C}]{\text{NbCl}_5\ 10\ \text{mol\%}} \text{RR'NCHO}$$

R= aryl, alkyl
R'= aryl, alkyl, H

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Niobium pentachloride catalyzed efficient and simple synthesis of 3,3-diindolyl-2-oxindole derivatives under ambient conditions

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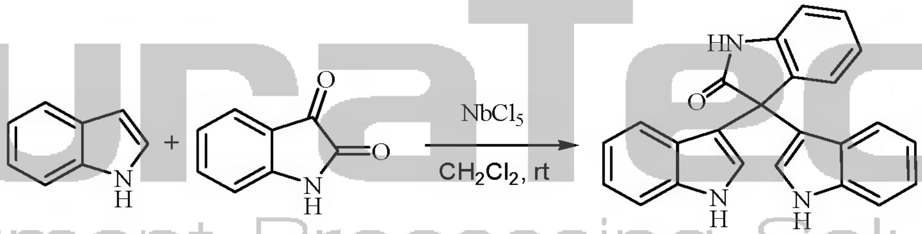
Catalysis lies at the heart of countless chemical protocols, from academic research laboratories to the chemical industry acid catalysts are essential for various chemical reactions in chemistry. Among them, $NbCl_5$ has emerged as an efficient Lewis acid in promoting various organic transformation, such as Diels–Alder reaction, ring-opening of epoxides, Mukaiyama aldol reaction, Biginelli reaction, dealkylation of alkyl aryl ethers and C–H insertion reaction [1,2] .

oxindole derivatives have attracted considerable interest due to their diverse biological properties and therapeutical applications, namely as antibacterial, antiprotozoal and anti-inflammatory agents and are also patented as PR (progesterone receptors) agonists[3,4]. Therefore, in this article, we report a novel and efficient protocol for the synthesis of 3,3-diindolyl-2-oxindole derivatives from the 2:1 coupling of indole and isatine derivatives using niobium pentachloride as an inexpensive solid acid catalyst under ambient condition. $NbCl_5$ exhibited remarkable catalytic activity with respect to the reaction time (50–120 min), the product yield (75–98%), and amount of catalyst(10 mol%).



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Preparation of an energetic plasticizer N,N′dimethyl methylen bisnitramine (DNDA5)

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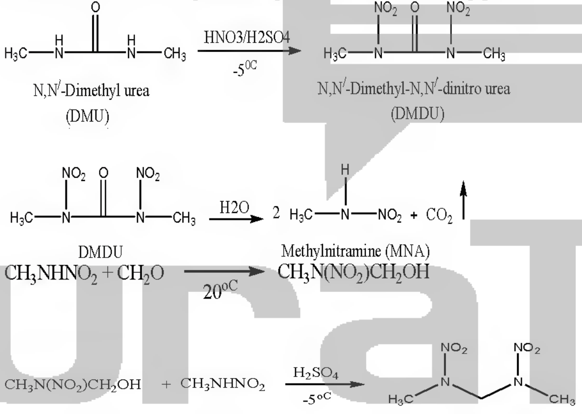
Energetic plasticizers of solid propulsion have been used to improve the mechanical properties of the polymer matrix in propellants [1]. One important part to achieve such a behavior is the use of special plasticizer (DNDA), which is mixed into the propellant dough. Furthermore the auto ignition temperatures have been raised and the adiabatic flame temperatures reduced at comparable force values resulting in less barrel erosion [2]. The DNDA plasticizers are three grade: DNDA5, DNDA6 and DNDA7 [3].

In this research work preparation of energetic plasticizer N,N′dimethyl methylen bisnitramine (commonly called 2,4-dinitro-2,4-diazapentane or DNDA5) in 4 step, starting from dimethylurea will be reported. At first the dimethylurea was nitrated with nitric acid and then dinitro-dimethylurea was hydrolyzed to prepare the methyl nitramine. The reaction of formaldehyde with methylnitramine gave the 2-nitro-2aza propanole as a desired product. At the end, this compound with extra methylnitramine gave the target molecule, i.e. N,N′dimethyl methylen bisnitramine. The products were assigned with ^{1}H-NMR, ^{13}C-NMR, IR spectroscopic method and melting point.



N,N′-Dimethyl urea (DMU)

N,N′-Dimethyl-N,N′-dinitro urea (DMDU)

DMDU

Methylnitramine (MNA)

$$CH_3NHNO_2 + CH_2O \xrightarrow[20^{oC}]{} CH_3N(NO_2)CH_2OH$$

2,4-Dinitro-2,4-diaza-pentane
(N,N′-dimethyl methylene bisnitramine)

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Plant-Mediated Synthesis of Metallic Nanoparticles: A Green and Cost-Effective Avenue to Nanomaterials

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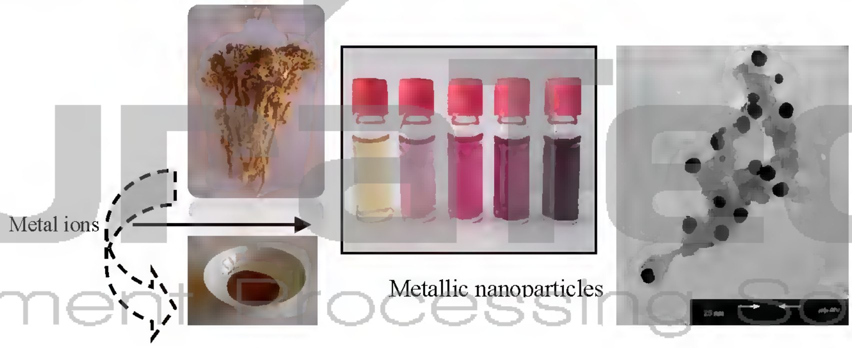
Nanoscale materiales have attracted great interest due to their unique physical, chemical, and thermodynamic properties that have made them useful in such diverse fields as catalysis, electronics, optics, and even in biological and medical science. A lot of techniques have been developed for the synthesis of nanoparticles. However, it is inevitable that the interventions of environmentally harmful and toxic chemicals interfere in the synthesis procedures of nanoparticles. Recently, the green synthesis or fabrication of nanoparticles have been considerably studied by using harmless alternative biocompatible molecules such as proteins, peptides, cellulose, soybeans, gellan gum, vitamin B_2, starch, D-glucose and etc. as stabilizing or reducing agents. From these studies, biosynthetic method employing live plant or plant extract has emerged a simple and viable alternative to traditional chemical procedures and physical methods only in recent years [1]. Recently, our research interests have been turned to this field and our group demonstrated that the extract of several plants could be used to synthesize different metallic nanoparticles in aqueous solutions. The natural antioxidant components and the hetrocyclic components are believed to be responsible for the reduction and the stabilization of nanoparticles, respectively. In this presentation, our latest results will be shown in some details.



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Enhancement of Physical Stability of Caffeine via Cocrystalization; Theoretical Study

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Caffeine (**CAF**) as a pharmaceutical model compound generally forms cocrystals with carboxylic acids via O–H(acid)···N(**CAF**) and C–H(**CAF**)···O(acid) hydrogen bonds. The cocrystal formation leads to improve drug substance physicochemical properties [1]. In the present work, four cocrystals of caffeine with oxalic, malonic, maleic and glutaric acids [2] were considered by the quantum mechanical calculations.

All structures were optimized at the B3LYP/6-311++G(d,p) level of theory [3]; the electron charge density calculated by the atoms in molecules (AIM) [4] method and donor acceptor interactions (E^2) obtained from natural bond orbital (NBO) [5] analysis. The results demonstrate that the stability of cocrystal **CAF**:oxalic acid is higher than other cocrystals on aqueous solution (see Fig 1). This is in agreement with the experimental results.

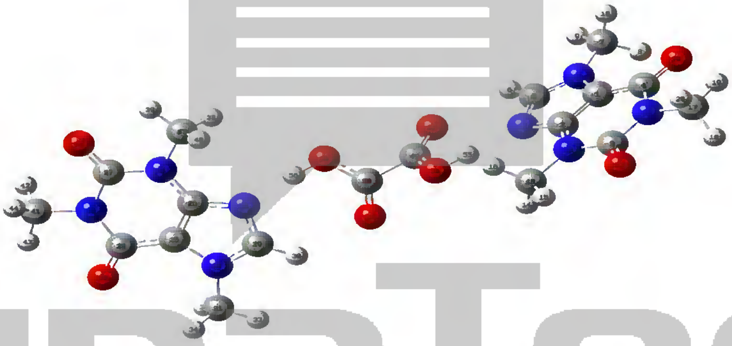

Figure 1. The structure of 2:1 **CAF**: oxalic acid cocrystal.

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Effect of substituents on rotational barrier in thioacetamides and selenoacetamides : DFTcalculations

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The carbonyl group is probably the most important functional group in organic chemistry, and its properties are strongly affected by substituents .According to importance of C-N bond rotation in amide's chalcogenides we have studied some derivatives of R_2NCYCH_3 (R=H , CH_3 ,CH_3CH_2 , Br, Cl , COH, $COCH_3$,Cyclopropyl and Y =S , Se) .In some of these compounds the barrier energies are so small that not attainable from NMR experimental methods.So computational methods can covered this disadvantage. In this work we used quantum chemistry methods all of calculations were performed by Gaussian 09 program with B3LYP level of theory in combination of 6-311G (d , p) Basis set .The barrier energies for thioacetamides are nearly 15 Kcal/mol and for seleno acetamides are 18 Kcal/mol. The data obtained from calculations shows that seleno amides have more barrier energy and substituents have very effect an this energy so that for halogene as substituent barrier energy is very low (nearly 7 kcal/mol).

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18th Iranian Seminar Of Organic Chemistry
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Synthesis, Characterization and Theoretical Study with Combined X-Ray Structure of 2-((E)-(p-tolylimino) methyl)-6-methoxyphenol

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Abstract

In our Laboratory we prepared and characterized of **2-((E)-(p-tolylimino)methyl)-6-methoxyphenol. This bidentate ligand is widely used for** the synthesis of metal complexes. In this paper, we want to show its X-ray structure and calculated structure. Crystal structure of **2-((E)-(p-tolylimino) methyl)-6-methoxyphenol** is Orthorhombic, space group P2(1)2(1)2(1) with a=5.89850(10), b = 9.2333(2), c = 23.2771(5) Å, alpha = 90 deg, beta = 90 deg, gamma = 90 deg and Z=4 [1]. The crystal structure [Fig. 1] was solved by direct methods and refined by Full matrix least squares to final values R1 = 0.0409 and wR2 = 0.0964 with 2376 reflections ($I>2\sigma(I)$). In the other hand the geometry of this compound was optimized using B3LYP/6-31G* level [12] treatment, the optimal geometry and electronic structure have been obtained by using the Gaussian-03 program package [2]. Geometry optimizations of the crystal structure of the Schiff base compound were made on the isolated molecule or gas phase, and in all calculations it was found that the most stable conformer is the X-ray crystallographic structure. The optimized structure is shown in Fig. 3. X-ray data with ab-initio calculations data, the agreement between the experimentally observed (X-ray) and quantum-chemically (B3LYP/6-31*) computed structural parameters is reasonably good.

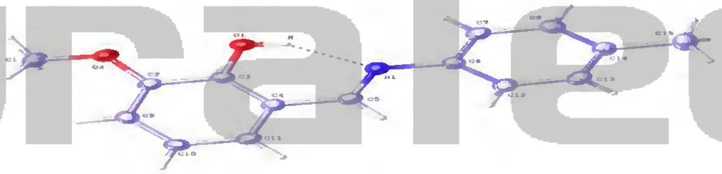

Fig. 1. The Crystal structure of 2-((E)-(p-tolylimino)methyl)-6-methoxyphenol compound

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Efficient Synthesis of Stable Cyano-Ethoxy Carbonyl Tetrahydropyrrolo Phenanthrolines with Four Diastereoisomeric Centers

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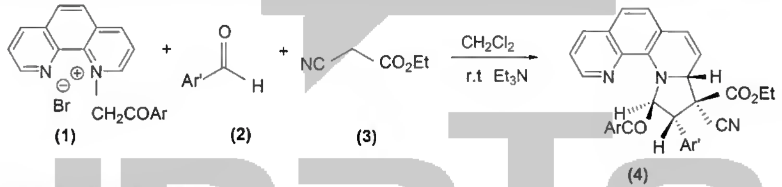
Cycloimmonium ylides, obtained from various synthetic methods, form a well-known class of zwitterionic compounds that display interesting chemical behaviors .[6]The chemistry of cycloimmonium ylides has been widely studied by several groups .[7] In the last decade, interest in [1,10]phenanthrolinium N-ylides has been increased and, as result, the synthesis of new heterocyclic systems of phenanthroline have been reported . These polycyclic compounds are very interesting molecules not only from chemical viewpoint (synthesis, reactivity, stereochemistry, etc.) but also for their industrial applications. [8]

Here we succeed in contribution of 1,10-phenanthrolinium ylide , in a multi-component one-pot Knoevenagel condensation. We observed that 1-(phenacyl)-1,10-phenanthrolinium bromide **1**, can react with aromatic aldehyde derivatives **2** and ethyl cyanoacetate **3** in the presence of triethylamine as base, to give 9-cyano-9- ethoxy carbonyl -8a,9,10,11 tetrahydropyrrolo [1,2-a][1,10] phenanthrolines **4** as novel stable helical macromolecules.

Herein, 1,10-phenanthrolinium N-ylide , which generated in situ in the presence of base, attacks the Knoevenagel's intermediate , that generated simultaneously. Then cyclization will occur to give desired product. This product, against similar compound [9], is so stable that could not remove any by-product by the action of triethylamine, or in the presence of air.

The structure of compounds was determined on the basis of its elemental analyses, IR, ^{1}H, ^{13}C NMR spectroscopy, mass spectra. Explicit structural elucidation of compounds was accomplished by single crystal X-ray diffraction. Analysing the X-ray ORTEP , showing a distortion from planarity and confirm helical chirality of these molecules.



Ar=phenyl, 4- Methylphenyl

Ar'=Phenyl, 3-Methylphenyl, 1- Naphthyl

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A periodic DFT study of tetrazole adsorption on anatase TiO_2 (001), (101) and (100)surfaces

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Abstract:

Titanium dioxide (TiO_2) has been extensively studied for many years as a model metaloxide with a wide range of applications in catalysis, photochemistry, and electrochemistry [1]. The most stable polymorph is rutile [2], but anatase and brookite are also common, especially in nanoscale natural and synthetic samples. Tetrazoles [3] (CN_4H_2) are exceedingly important compounds due to their practical role in different industrial and medical applications. In medicine, the tetrazole ring is present in a wide range of drugs [4,5]. The objective of the present study is to theoretically investigate adsorption of tetrazol on TiO_2-anatase (001), (101) and (100) surfaces (Fig.1) by means of a periodic slab model and density functional theory (DFT) approach. Adsorption energies were computed and reported in the Table 1.

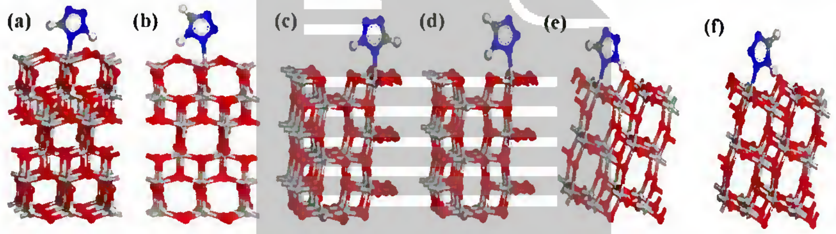

Fig. 1: (a) 2H (001), (b) 1H (001), (c) 2H (100), (d) 1H (100), (e) 2H (101), (f) 1H (101).

Total energy TiO_2	Total energy tetrazol	Total energy complex	Adsorption energy,
-24006.3055605(001)	-258.2840589(2H)	-24264.6501471	-37.98
-24006.3055605(001)	-258.2793892(1H)	-24264.6675463	-51.83
-24006.4135743(101)	-258.2840589(2H)	-24264.7402240	-26.73
-24006.4135743(101)	-258.2793892(1H)	-24264.7366276	-27.39
-24006.3904374(100)	-258.2840589(2H)	-24264.7112562	-23.07
-24006.3904374(100)	-258.2793892(1H)	-24264.7108474	-25.74

Table 1

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Three *N*-heterocyclic carbenes from quinoline at DFT

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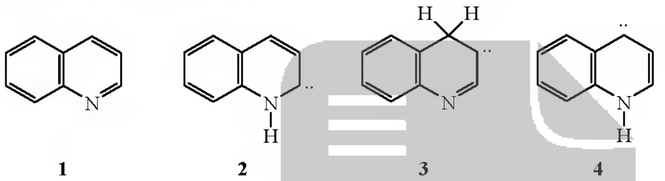
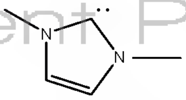
Pyridine - derived N-hetrocyclic carbens (NHCs) have been stimulated many chemists, in the recent years, both experimentally and computationally [1, 2]. Similarly, for quinoline **1** as a heavier counterpart, there are three possible carbene tautomers, **2-4** (Scheme1).



Scheme1. Three carbene tautomer of quinoline.

We carried out a DFT study (B3LYP/6-311++G** and B3LYP/AUG-cc-pvtz) on the stability, geometry and multiplicity of these carbene structures. Structures **2** and **4** appear planar (C_s), while **3** is nonplaner (C_1). The ground states of **2** and **4** are singlets, yet that of **3** is triplet. Table 1 shows the principal thermodynamic data. Accordingly, the tautomer **2** is the most stable one with the lowest heat of hydrogenation as well as the highest $\Delta E_{HOMO-LUMO}$ [3]. Comparing these findings with those of synthesized Arduengo NHC confirmed less stability and/or viability for **2-4**.

Table 1. Calculated thermodynamic data (kcal/mol) for **2-4** and Arduengo NHCs at B3LYP/6-311++G** and B3LYP/AUG-cc-pvtz (in *italics*).

Structure	E_S	E_T	ΔE_{S-T}	E_R	ΔE_H	$\Delta E_{HOMO-LUMO}$
2	-252148.3, *-252172.5*	-252117.8, *-252142.9*	30.4, *29.6*	40.1, *41.4*	-39.6, *-39.9*	77.7, *77.3*
3	-252102.1, *-252126.5*	-252112.1, *-252136.2*	-10.1, *-9.7*	87.2, *87.4*	-88.2, *-87.7*	51.9, *52.4*
4	-252133.7, *-252158.8*	-252119.6, *-252144.4,*	14.1, *14.4*	55.6, *55.06*	-56.5, *-56.1*	62.1, *61.9*
	-141921.9, *-141935.4*	-141839, *-141852.6*	82.9, *82.8*	-	-17.9, *-12.4*	132.4, *130.3*

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Tautomery Scheme in 4-acyl Pyrazolone

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Over the past centuries, the chemistry of heterocycles has been an absorbing issue for scientists. Among all heterocyclic compounds, pyrazolones and their derivatives [1,2] have been mostly studied because they belong to a wide area of compounds which serve as products and intermediates in chemical, analytical, agricultural, biological and pharmaceutical chemistry [3]. Especially, pyrazolone derivatives have been used as an inhibitor of TNF-α to prevent cancer [4]. The most interesting aspect of 4-acyl pyrazolone (especially for us) is its diversity in tautomerism. Therefore, to continue the interest in theoretical study of tautomerism in organic compounds [5,6] and because of the effect of tautomerism in 4-acyl pyrazolone on its chemical and biological activities, especially their complexation and inhibitory properties, it is very important to learn about the complete scheme of tautomerism in 4-acyl-pyrazolone. In this line, the effects of solvent should be also clearly revealed.

In the present work, employed DFT calculations were conducted to obtain optimized structures of 4-acyl pyrazolone tautomers (19 tautomers) using B3LYP/6-311++G** calculations [7]. Gaussian 98 [8] program package was employed for optimizing the structures and calculation of molecular properties. In addition, molecular parameters, IR frequencies and relative energies were obtained for all the tautomers. It was found that the existence of aromatic ring, keto tautomer (versus enol tautomer), N-H bond (versus C-H bond) and C=N double bond (versus N=N double bond) are stabilizing factors for determining the relative stabilities of tautomers. Calculation of vibrational modes showed that, in accordance with the reported experimental frequencies, intramolecular hydrogen bond (which exists in some tautomers) decreased the calculated value of OH frequency. Moreover, the solvent effects on relative stabilities of tautomers were calculated. The relative stabilities of all the tautomers in acetone, tetrahydrofurane and chloroform (in all solvents, except water) were relatively the same as the gas phase stabilities, with some small differences in tautomers with very low or very high ΔG_{solv}. Interestingly, a nearly good relationship was found between dipole moments of tautomers and its ΔG_{solv} in chloroform, which showed that, by increasing the dipole moment of each tautomer, the absolute amount of its ΔG_{solv} in chloroform increases.

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Aromaticity of Non-benzenoid systems with Odd Rings having Conjugated Circuits

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The importance of conjugated circuits within a polyclic aromatic hydrocarbon has been recognized by Randic [1]. In this research, several aromaticty indices including nucleus independent chemical shift (NICS), HOMO-LUMO gap, harmonic oscillator model of aromaticity (HOMA) and ^{1}H and ^{13}C NMR chemical shifts were used to evaluate in detail the conjugated circuits for a set of polycyclic aromatic hydrocarbons. The study shows that even for the compounds having similar skeleton (**1** and **2**, **Figure 1**), both with a [18] annulene perimeter, the local aromaticty of individual rings are quite different.

For example, the NICS(1) values for five and seven-membered rings in **1** are -15.9 and -5.2, respectively. In comparison, the values for **2** are -11.0 and 7.5, respectively. This can be due to the compensatory effects of the diatropic and paratropic ring currents of different moieties within the main framework. All the structures were optimized at the B3LYP/6-311+G** level, and the magnetic susceptibility (χ, CSGT-B3LYP/6-311+G**), ^{1}H and ^{13}C chemical shifts, NICS values (GIAO-B3LYP/6-311+G**) and HOMA were evaluated for the B3LYP optimized geometries [2].

1

2

Figure 1. Only two examples of the non-benzoid systems having odd rings.

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The mutual relationship between cation-π and anion-π interactions

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Noncovalent interactions, such as cation-π and anion-π interactions are shown to play key roles in chemical and biological systems [i]. Cation-π interactions are among the strongest nonbonded interactions that their strength depends on the nature of aromatic system and the charge of the cation [ii]. The current study is aimed to understand how the cation-π and anion-π interactions mutually influence each other by using a complex involving three aromatic rings (Benzen (BEN), Trifluorobenzene (TFB) and Hexafluorobenzene (HFB)) with face-to-face arrangements ; alkali metal cations were face to BEN and TFB and fluorine atom were face to TFB and HFB (see Fig. 1). The geometry optimization were carried out at the M06-2x/6-31+G(d) level of theory using the GAUSSIAN09 program [iii].

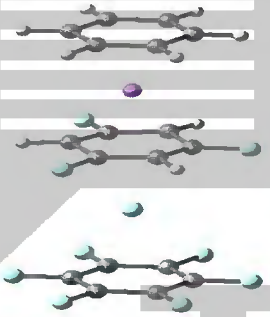

Figure 1.The structure of BEN···Y^+···TFB···F^-···HFB (Y^+= Li^+, Na^+ and K^+) complexes.

The results of quantum mechanical calculations, including binding energy, electron charge density calculated by atoms in molecules (AIM) method, donor acceptor interaction energies E^2 obtained from natural bond orbital (NBO) analysis show that the cation-π and anion-π interactions weaken each other, but the effect of cation-π on the anion-π interaction is stronger which increases by the decrease in the cation radius.

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Theoretical and experimental Comparison of NMR Shieldings and NBO analysis in 2-Trifluoroacetylphenol

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A numerically accurate implementation of the gauge-including atomic orbital (GIAO)[1] and individual gauges for atoms in molecule (IGAIM)[2] methods for the calculation of NMR shieldings in density functional theory (DFT) and Hartree-Fock theory (HF) is applied. Results calculated by these method are compared with experimental results for 2-Trifluoroacetylphenol (TFAP). HF level with large 6-311++G(2df,p) basis set rather than B3LYP level with 6-311++G(d ,p), 6-٣١1G(d ,p) and 6-31G(d ,p) basis sets was tested. To investigate the effect of CF3 group on the hydrogen bond strength, the charge distributions, steric effects, and electron delocalization in TFAP and salicylaldehyde (SA) were studied by the Natural Bond Orbital (NBO) method [3] for optimized compounds at B3LYP/6-311++G(d,p) level of theory.

Results of ^{1}HNMR chemical shifts show that GIAO approach in this study has transparency to the correlation treatment with experimental results and is less sensitive to basis set size rather than IGAIM. Also the comparison of theoretical and experimental results showed that basis sets as large as 6-311++G(d ,p) provide better agreement with experiment than is obtained with smaller basis set and there is no significant difference between results of HF/6-311++G(2df,p) and B3LYP/6-311++G(d ,p).

The comparison of charge distribution calculated by the NBO method for optimized geometries of TFAP and SA indicates that substitution of CF3 group for H in SA reduces the charge distribution over ring atoms, which indicates the strong electron withdrawing nature of the CF_3 group. And the natural charges over H of hydroxyl group and C and O in carbonyl group in TFAP are lower than those in the corresponding atoms in SA, respectively. According to pairwise steric exchange energies, ΔE(i,j), there are the steric exchange energy between π(O=C) and σ(C-F) of 1.27 kcal/mol and between σ(C-F) and electron lone pairs of oxygen atom (LP(2)O) of C=O in TFAP of 0.79 kcal/mol, also there are some steric effects between σ(C-C) of$C-CF_3$ and LP(2)O of C=O in TFAP of 18.38 kcal/mol and between σ(C-H) of aldehyde group and LP (2)O in SA of 16.13 kcal/mol. These results could be used to explain the shorter O···O distance in TFAP than that in SA.

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Intramolecular hydrogen bonding in 2-Trifluoroacetylphenol: Infrared spectrum and quantum chemical calculations

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A combination of experimental studies and density functional theory (DFT) calculations have been used to predict the IR and Raman and ^{1}HNMR spectra for 2-Trifluoroacetylphenol (TFAP) as a Schiff base compound and the results were compared with those of salicylaldehyde (SA)[1]. Calculations were performed at B3LYP [2, 3] and BLYP [2, 4] levels of the theory using the 6-31G**, 6-311G** and 6-311++G** basis sets. The stable molecular structure in the ground state of TFAP is an intramolecularly hydrogen-bonded closed conformer at all levels of theory. The vibrational frequencies of FT-IR for TFAP in CCl_4 solution has been assigned with the aid of theoretical ones. The scaled frequencies at B3LYP /6-311++G** is in good agreement with the corresponding experimental values by acceptable deviations. Comparison of the vibrational spectra and structural parameters of TFAP with those of SA reveals a slightly stronger H-bond in SA than that in TFAP. The calculated OH/OD stretching and OH/OD out-of-plane bending modes are in good agreement with the calculated O···O distances and ^{1}HNMR results. The results is also proves that substitution of H with the CF3 group reduces the strength of the hydrogen bond.

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Thermodynamic study of selected 1,3-dipolar cycloadition reactions: A DFT study

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Introduction:

Cycloaddition reactions are one of the most important processes with both synthetic and mechanistic interest in organic chemistry. The strochemistry and regioselectivity present in these processes are the most abundant and useful of all precyclic reactions [1]. Regioselectivity of some 1,3 dipolar cycloadition reactions are investigated with thermodynamic study and using DFT method.

Computational aspects:

The equilibrium geometries of all reactants and products are obtained by full optimization at the ground states of the molecules using the B3LYP/6-31G(d) level of theory. Thermodynamic calculations are performed with the same method. All calculations are carried out using the GAUSSIAN 98 program [2].

Results and discussions:

In this work, DFT calculations are carried out to investigate role of substituents in thermodynamic of favored product according to 3- and 4-isomers that are expected[3]. Thermodynamic results show that all pathways are exothermic by 70.80 -73.27 Kcal/mol. It is found that the reaction with the largest exothermicity is related to 3-isomer pathway (Fig1). Investigation of total energy (E_{tot}) of products show that 3-isomer products are more stable than 4-isomer products . Computed reactions energies for 2 pairs of reactions (Gibbs free energy difference, ΔG) suggest that the pathway with 3-isomer product is thermodynamically the most favorable by 56.41-59.26 Kcal/mol and show that all reactions are spontaneous process ($\Delta G<0$). Also, we calculated equilibrium constant for these reactions.

Fig.1. The considered reactions (3 pairs reactions) R= **1)** –CH2CH2OH **2)** -CH2CH2CH2OH

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Reinvestigation of O…H—O intramolecular hydrogen bond in malonaldehyde and its dirivatives: An comparison between the various models

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Hydrogen bond is one of the most important concepts in chemistry, biochemistry, and bio- physics. The intramolecular hydrogen bond (IHB) often plays a significant role in chemical reaction, conformational preference and crystal engineering[1,2]. The IHB energy is the authoritative criterion for evaluation the IHB strength. The different methods for estimation of IHB energy were proposed. All of the computations in the present study were performed by Gaussian 98 and series of program. The geometry optimizations were carried out at MP2/6-311++G(d,p) level of theory.

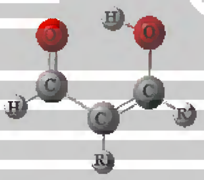

Fig.1. Molecular structures of malonaldehyde and its derivatives

In this work we have been used four of different methods for estimation of IHB energy that are as follows: related rotamers, Isodesmic reaction, Buemi and Jablonski methods. There are three different situations(R_1, R_2) for halogen substitution in RAHB ring of respective systems(fig. 1). We evaluated the O-H…O IHB energies by using the appropriate models and examined the relations between these outcomes and various descriptor of HB, such as geometrical parameters (O…O and H…O distances), O-H vibrational frequency, topological (ρ,$\nabla^2\rho$, H, V…) and NBO parameters. It was found that the most appropriate model, with minimal deviation, for various proton acceptors is different, but in general, the related rotamers model is the most suitable for estimation the IHB energies. For instance, the regression coefficients for linear dependence between the IHB energies and electron density at hydrogen bond critical point are given in Table I.

TableI. Correlation between energy (kJ/mol) and descriptor parameters of HB

Parameters	R^2_{RRM}	$R^2_{Jablonski}$	$R^2_{Isodesmic}$	R^2_{Buemi}
$d_{(O...O)}$	0.967	0.561	0.529	0.938
$d_{(O...H)}$	0.963	0.602	0.503	0.926
$d_{(O—H)}$	0.891	0.663	0.500	0.861
$_{(O...H)}\rho$	0.959	0.601	0.562	0.929
$H_{(O...H)}$	0.974	0.576	0.564	0.938
$L_{(O...H)}$	0.892	0.418	0.378	0.834

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Exploring and comparing the various aspects of potential energy surfaces of β-aminoacrolein and other chalcogen (S, Se) analogues

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β -Aminoacrolein is the simplest member of β- aminoketones, as one of the most important of organic compounds, which has two different functional groups, keto and imine, and can display three class of tautomer, such as ketoamine, ketoimine and enolimine, which interconvert by tautomeric equilibriums (Fig. 1). Moreover, some of the conformers of this molecule involved in asymmetric N-H...O and N…H-O intramolecular hydrogen bonds that strongly coupled with π-electron delocalization and belong to the resonance assisted hydrogen bonds systems (RAHB) [1-3]. In the present study, we investigated and compared the various aspects of potential energy surface of β -aminoacrolein with its thio and seleno analogoues, such as the local and global minimums, proton transfer process from thermodynamic and kinetic point of views.

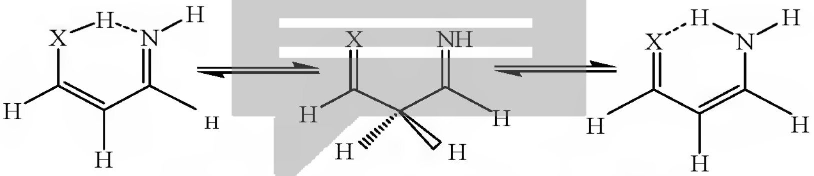

Fig.1. Tautomeric equilibriums of title compounds (X= O, S ,Se)

The geometrical optimization for all of the local minimums and transition structures were carried out by HF, B3LYP and MP2 methods with the most usually 6-311++G(d, p) and 6-311++G(3df,3pd) basis sets. Additionally, the most extended wave function used to perform the atoms in molecules (AIM) and natural bond orbital's (NBO) population analysis.

The results of our calculations clearly show that the numbers of local and global minimums of PESs under the insertion of S or Se remain constant but their natures were changed. These molecules have the similar conformational and tautomeric preferences. For instance, the ketoamine with its thio and seleno analogues are the most stable tautomer, which is related to the π-electron delocalization. Finally, for better understanding the nature of the hydrogen bonds, we evaluated and compared the different HB energies with their geometrical, topological, spectroscopic and molecular orbital descriptors. According to these HB descriptors, we found that with insertion of other chalcogen elements (S, Se), the strength of intramolecular hydrogen bonds are significantly decreased.

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Molecular modeling studies of some HIV-1 integrase inhibitors using Docking analysis

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Abstract

Human Immunodeficiency Virus 1 integrase (HIV-1 IN) is the enzyme responsible for integrating the viral DNA into the host genome, and is essential to the replication of the virus [1]. Recently, 1, 3, 4-oxadiazole substituted naphthyridine were reported as selective integrase inhibitors, which possess antiviral activity [2]. Computational methods have developed as useful tools in facilitating new drug discovery. By the use of these methods, the biological activity of the candidate molecules can be estimated before experimental trials [3] To further explore the structural requirements of 1, 3, 4-oxadiazole substituted naphthyridine as integrase inhibitors and their mechanism of action, docking analysis was performed . In docking study the two most active compounds and the two least active compounds were docked into the active site using the crystal structure of Integrase. The required factors to increasing the activity of compounds were investigated and the docking results indicate a good correlation between the inhibitory activity of these compounds and the free energy of bonding in active site.

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A QSAR study on some berberine analogues as a novel class of the Low Density Lipoprotein Receptor Up-Regulators

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Abstract

Berberine, a natural product extracted from a traditional Chinese herb Huanglian (Coptis chinensis), is a promising cholesterol lowering drug [1]. Quantitative structure-activity relationship (QSAR) has been applied to modeling and predicting the low density lipoprotein receptor (LDLR) up-regulatory activity of twenty berberine analogues. Structures of these compounds were optimized geometrically by Hyperchem7.0 and molecular descriptors were obtained by Dragon5.5 software. Multiple linear regression (MLR) based on stepwise variable selection was employed to find the most convenient quantitative models. The best linear model composed of four molecular descriptors which including; information indices, Burden eigenvalues and WHIM descriptors. The results of this QSAR model show that the predicted LDLR up-regulatory activity values have a good correlations with experimental ones ($R^2 = 0.83$, $F = 18.66$, Std. Error of the Estimate of 0.75). Cross validation to evaluate the reliability of model was performed by MATLAB software..The effect of number of descriptors on the correlation coefficient (R) and F-ratio were considered. It is observed that R and F are increased due to increasing the number of descriptors. Correlation between biological activity of compounds and some physicochemical descriptors resulted a benefit correlation with size, charge, aromaticity and resonance.

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DFT study of earth alkaline metals interactions with some Phthalocyanine anion derivatives, structure and stability constantand

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Abstract

Phthalocyanine compounds with the formula MPc (Pc.phthalocyaninato anion $C_{32}H_{16}A$, $A=H_2$ or divalent metals) have been widely used as organic dye stuff because of their intense absorption of light in the visible and ultraviolet regions, their excellent stability to chemical or thermal treatments, and their relatively low cost. The most stable structure of MPc has been shown to be square planar and to be classified into a D_{4h} point group. In the case of MH_2, the molecular symmetry is reduced to D_{2h} due to two hydrogen atoms in the middle of the Pc ring. In a recent book on metal phthalocyanines (MPcs) these compounds were called "a gift to molecular physics" because of their unique properties which found so many different remarkable applications. More than 70 different elemental ions, can be incorporated into the central cavity of Pc and an enormous number of derivatives can be synthesized. In spite of all this abundance of data, there are,however, only two papers published so far where structures of three MPcs were established in the gas phase. So we have been studied the structures of some MPcs ($M=Ca^{2+}$, Mg^{2+})(1)by quantum mechanics theoretically methods.and Structural analysis is assisted by ab initio/DFT calculations

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AB initio Study of The cornforth rearrangement of 4 -carbonyl substituted oxazoles in comparison whit compounds Thiazoles

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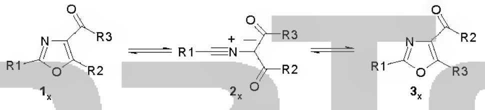
The cornforth rearrangement involves the thermal interconversion of 4-carbonyl substituted oxazoles, with "exchange between the C-C-O side chain and the C-C-O fragment of oxazole ring. These reactions generally involve compounds where a heteroatom(-OR,-SR, -F, -Cl, -Br and-I) is attached to the 5 -position (R_2) of the starting oxazole (1_x).[1] This rearrangement can be rationalized by postulating the dicarbonylnitrile ylide (2_x) as an intermediate. Supporting evidence for the interconversion was reported by Dewar and Turchi [3].

Geometry optimizations are carried out by HF and B_3LYB methods. This is using 6-31G* basis set of the GAUSSIAN 98 system of programs. Global minima are specified on corresponding energy surfaces through relax scan using Keyword 'FOPT (Z-matrix)' at HF/6-31G* level of theory. The optimized geometrical outputs of the latter are used as inputs for the UB_3LYB/6-311++G** calculations. In order to find energy minima keyword 'FOPT' and for transition states keyword 'FOPT (QST_3)' are used. To confirm the nature of the stationary species and evaluate the activation energy barriers for rearrangement, frequency calculations (keyword: FREQZNORAMAN) are carried out. The calculations show that, the rearrangement rate of oxazoles are more than thiazoles and it is done easier.



$R_2 = R_3$= H, F, Cl, Br and I
cornforth rearrangement oxazoles

Table 1: Changes of activation Gibbs free energies level of theory for conversion of oxazoles and Thiazoles to dicarbonylnitrile ylide.

Rearrangement	$\Delta G^{\#}$Oxazoles	$\Delta G^{\#}$ Thiazoles
1_H to 3_H	30/2۶	38/67
1_F to 3_F	21/9۵	32/58
1_{Cl} to 3_{Cl}	27/5۷	37/02
1_{Br} to 3_{Br}	27/8۸	38/85

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Theoretical study of S-N compounds as dithionitrosomethan and its tautomers

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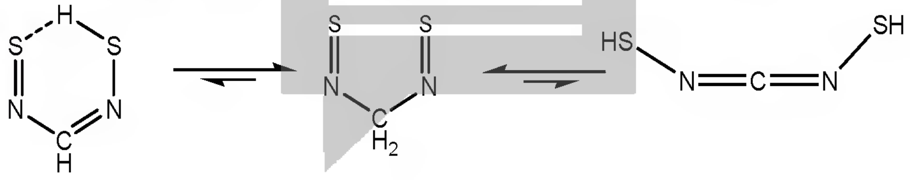
Sulfur-nitrogen containing compound have been the focus much research effort for over half a century [1,2].The study of S-N compounds, by experimental and theoretical chemists alike, remains and active research area in current in organic chemistry [3,4].Thionitrosomethane is the simplest member of aliphatic S-N compounds. By substitution a thionitroso group on the one of hydrogen atoms of thionitrosmethan, the new compound which called dithionitrosmethan, was introduced. This compound can be participating in the dithionitrosmethan(DTM) ↔ N-mercapto thionitroso methanimine(MTI) ↔ N,N- dimercapto methan diimine(DMD) tautomeric equilibrium (Fig. 1)



DTM MTI DMD

B3LYP and MP2 calculations have been carried out on the different tautomers of dithionitrosmethan(DTM) and the equilibrium conformations were determined. In general, the MTI tautomers are more stable than the other ones. The most stable (MTI-13, MTI-23) comformeric pairs are recognized as global minimum. Surprisingly, the chelated MTI form (MTI-11) with S-H···S intramolecular hydrogen bond (IHB) is unstable than the global minimum. The evaluation of hydrogen bond energy by different methods and also the geometrical parameters, results of AIM and NBO, clearly predict that the hydrogen bond strength in MTI-11 is lower than the malonaldehyde (MA).

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Evaluation the intramolecular hydrogen bond energy from the characteristic of potential energy surface of simple RAHB systems

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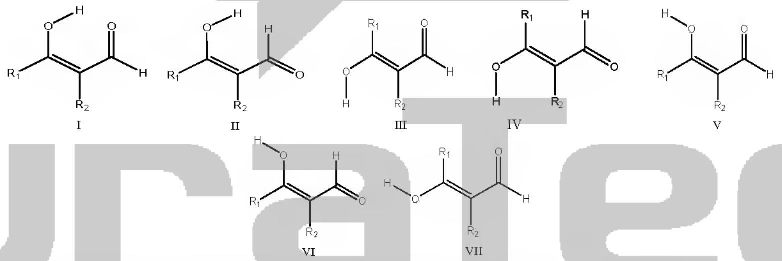
Hydrogen bond is one of the most important concepts in chemistry, biochemistry and biophysics. The intramolecular hydrogen bond (IHB) often plays a significant role in chemical reaction, conformational preference and crystal engineering of organic compounds [1, 2]. When the proton donor and acceptor are connected by a conjugated framework, a resonance assisted hydrogen bond (RAHB) is introduced. The O–H···O bridge in malonaldehyde derivatives (Fig. 1) are the simplest RAHB systems which has been extensively studied [3, 4]. The prediction of the RAHB energy is one of the most important problems in science due to the great role of this band in biological phenomenon. In the present context, we explored the potential energy surface of simple RAHB systems and presented the new paths for estimating their energies.

The geometrical optimization for all of the local minimums and transition structures were carried out by MP2 method with the standard 6-311++G(3df,3pd) basis sets. The optimized structures were used to obtain the appropriate wave function files for AIM and NBO analyses. Our computational results clearly show that, in simple RAHB systems with three rotational degree of freedom about the C-C, C=C and C-O bonds, three different paths (I, II, III) for estimation the RAHB energy are existing.



(Fig.1) $RRM_1 = (E_I - E_{II}) - (E_{III} - E_{IV})$ $RRM_2 = (E_I - E_{III}) - (E_V - E_{VII})$ $RRM3 = (E_I - E_V) - (E_{II} - E_{VI})$

For better understanding the precision of these hydrogen bond energies, we explored the correlation between the HB energies with geometrical, topological, spectroscopic and molecular orbital descriptors. According to these correlations, we found that the RAHB energies that obtained by latest method (III) is not satisfactory but the other (I, II) present the excellent linear correlation between the RAHB energies and all of descriptors.

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Molecular structure and intramolecular hydrogen bonding of o-hydroxypropiophenone. A DFT study

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Molecular structure, vibrational frequencies and ^{1}HNMR of o-hydroxypropiophenone (OHPP), a simple compound to study the intramolecular hydrogen bond, have been investigated by means of density functional theory (DFT) calculations, using Gaussian 03W software package. The geometrical parameters and Frequencies calculated at B3LYP [1, 2] level and BLYP [1, 3] level using 6-31G**, 6-311G** and 6-311++G** basis sets and compared with the analogous parameters of salicylaldehyde (SA). OHPP can exist in two tautomeric forms; the keto and the enol form. The relative stability of each form depends on the electronic state of the molecule. From geometry parameters, the main effect of ethyl group on carbon of carbonyl group in OHPP is shortening of the O···O distance and lengthening of the O—H bond length in comparison with the corresponding values for SA. The calculated O···O and O—H distances in OHPP are 0.072–0.066 Å and 0.003–0.004 Å, respectively, shorter and longer than those in SA. The calculated proton chemical shifts at B3LYP level with 6-311++G** and 6-31G** basis sets is 12.8 and 13.3 ppm, respectively.

The ratio νOH/νOD and γOH/γOD of OHPP appears at 3341/2436 and 829/610 cm^{-1}, respectively, at B3LYP/6-311++G**, which are consistent with the calculated geometry and chemical shift results.

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Kinetic Resolution of Fluorescein bis(2-phenylbutyrate) Catalyzed by Lipase

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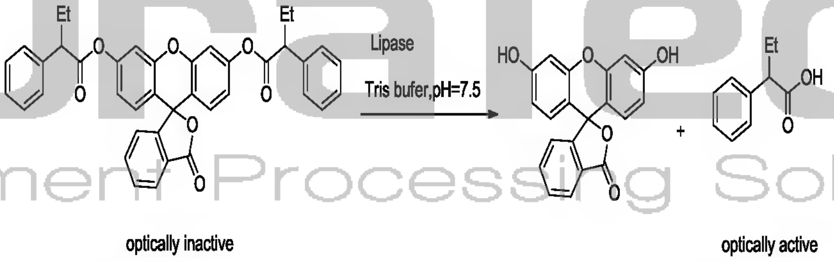
Enzymatic resolution of racemic compounds is widely used by organic chemists.Enzymes are nowadays widely recognized among the most active and selective catalysts for the preparation of optically active compounds. The outstanding properties of these catalysts in terms of substrate specificity, chemoselectivity, regioselectitivty and especially, enantioselectivity make them particularly attractive for the production of fine chemicals.Many hydrolytic enzymes, especially lipases, are commerciallyavailable and are used to resolve racemic acids andalcohols.Several empirical rules about faster reacting stereoisomers have been proposed [1–٤].

Considering the above reports, we wish to report the synthesis of fluorescein bis(2-phenylbutyrate) and with employing the lipase as a biocatalyst for the hydrolytic resolution of 2-phenylbutyric acid.Fluorescein bis(2-phenylbutyrate) synthesized by the esterification of fluorescein with racemic2-phenyl butyric acid in the presence of DCC. The enzymatic hydrolysis of racmate and mesofluorescein bis(2-phenylbutyrate) carry out in the presence of 0.01M Trisbufer in pH 7.5 and lipase.



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Theoretical investigation in β–aminophosphonato ester from the reaction between triaryl phosphite and dimethyl acetylenedicarboxylate in the presence of NH-containing heterocyclic.

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Quantum mechanical calculations were undertaken for determination of the stability of the two isomers of β-aminophosphonato esters **4**. The results showed that compounds **4** with gauch arrangment and [(2S*,3S*) or (2R*,3R*)] configurations are more stable than [(2S*,3R*) or(2R*,3S*)] geometries. Results (theoretical calculations) were consistent with the experimental data arised from NMR spectroscopy.

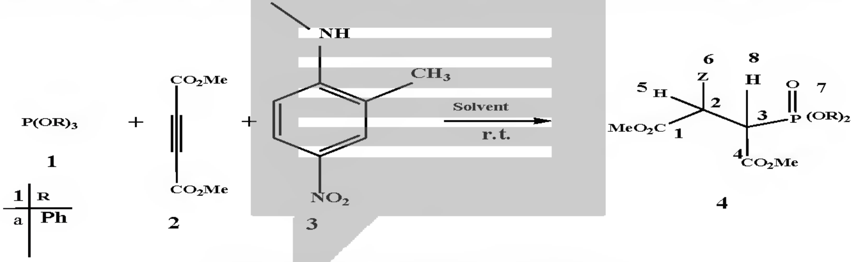

Figure. Synthesis of β-aminophosphonato esters **4**

For assignment of the two [(2S*,3S*)or (2R*,3R*)] and [(2S*,3R*) or (2R*,3S*)] isomers in β-aminophosphonato esters **4**, first their structures, were optimized at the HF/6-31G(d,p) level of theory by Gaussian 03 program. The relative stabilization energies for both isomers have been calculated at the HF/6-31G(d,p) and B3LYP/6-311G(d,p) levels. The number of critical points and intramolecular hydrogen bonds have been recognized as well as the charg of atoms that were constructed on the two isomers. In addition, J_{x-y}, the values of proton and carbon coupling constans, and also chemical shifts ($\delta^{H}_{iso,}$ δ^{C}_{iso}) have been calculated at the mentioned level using the SPINSPIN keyword.. The results, altogether, reveal the effective factors on the stability of the two[(2S*,3S*) or (2R*,3R*)] and [(2S*,3R*) or (2R*,3S*)] isomers.

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Dynamic ^{1}H NMR Studies Along With Mechanical Calculations for Determination of Rotational Energy Barrier in a Particular Stable Phosphorus Ylide.

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Theoretical studies was investigated on the basis of rotation around the carbon-carbon double bond in a particular phosphorus ylied namely dimethyl 2-(2-mercapto-2-thiazolin-3-yl)-3-(triphenylphosphanylidene) butanedioate[1] using ab intio method at HF/6-31G level of theory. Theoretical activation parameters at 298 K involving $\Delta S^{\neq}$ (-11.04, J/mol K), $\Delta H^{\neq}$ (35.88 kJ/mol), $\Delta G^{\neq}$ (69.16 kJ/mol) and with kinetic parameter E_a (68.36 KJ/mol) were determined .

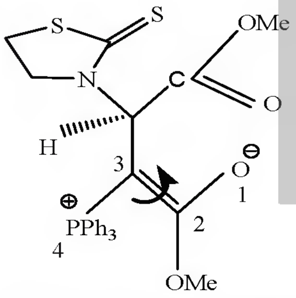

Figure 1. The performance of $O_1C_2C_3P_4$ dihedral angel in a synthesized phosphorus ylide.

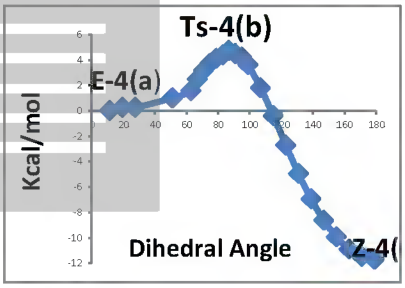

Figure 2. Relative energy in phosphorus ylide (see Fig. 1) versus dihedral angels O1C2C3P4

In order to determine theoretical rotational energy barrier in the rotational interchangeable process of the two Z- and E-isomers in mentioned ylide, first their structures were optimized at HF/6-31G level of theory by Gaussian 03 program package. Then, relative energy versus dihedral angle (O1C2C3P4, see Figure 1) was plotted for determination of activation parameters which shown in Figure **2**. In briefly, mechanical calculations for compound **1** confirmed a restricted rotation around the carbon-carbon double bond. Herein, the theoretical results obtained from ab intio method at HF/6-31G level of theory were in consistent with the ^{1}H NMR experimental data.

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A comparison between experimental and theoretical results about some functionalized azo compounds

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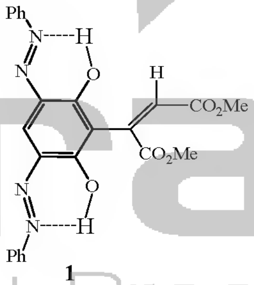
Azoaromatic compounds have been widely used as dyes and pigments in a variety of industrial and chemical synthetic products [1-2].

The molecule of azo pigments have one or some azo chromophore –N=N- that form a bridge between two organic part [3].

Also, they play an important role in other practical applications such as biological reactions [4], optical storage technology and photo electronic effects [5].

We have reported a simple and efficient reaction for the synthesis of the multifunctionalized azo structures (1 and 2) and the characterization of the synthesized azo pigments has been described by different spectroscopic techniques. The influence of the substituents on the data of them has been described. Also, theoretical calculations are expected in principle to produce many properties and structural features can be obtained with an accuracy that is competitive with experiment. Ab initio calculations at the HF/6-311G* level of theory provide a picture of the cis and trans configurations of several azo derivatives from both structural and energetic points of view. Twenty six forms were studied by computational methods and we found that the possibility of hydrogen bonding in these molecules is the most important factor for the stability of them.



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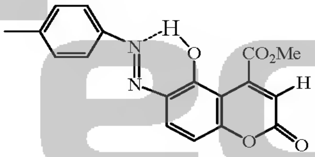

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Dynamic ^{1}H NMR Study around the Carbon-Carbon Single Bond in a Particular Phosphorous Ylide

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In the present work, dynamic ^{1}H NMR effects are investigated at different temperatures within a particular phosphorous ylide around the carbon-carbon single bond for the two **Z**-and-**E** isomers (Following Figure). Activation parameters were successfully calculated for the two (Z) and (**E**) isomer. On the basis of dynamic ^{1}H NMR data, activation parametrs containing $\Delta H^{\#}$,$\Delta G^{\#}$,$\Delta S^{\#}$ along with kinitics parameters involving k_c and E_a were recognized for the following reaction.

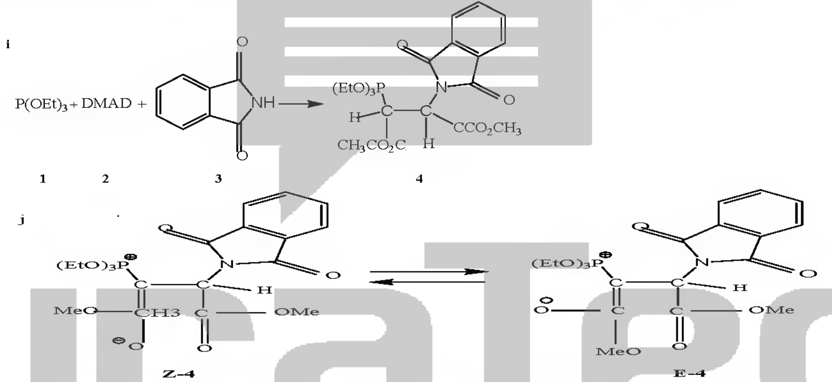

Figure: i) Synthesis of reaction between trithyl phosphite, dimethyL acetylendicarboxylate N-H hetrocycle compound 3 for generation of ylide**4**.
j) Interchangeable process for the two **Z-4** and **E-4** rotational isomers.

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A theoretical investigation on the electronic structural properties and some important activity of a group of organic compounds

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Abstract

Imines or Schiff base are some of the most widely used organic compounds. They are used as pigments and dyes, catalysts, intermediates in organic synthesis, and as polymer stabilizers [1]. Schiff bases have also been shown to exhibit a broad range of biological activities, including antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral, and antipyretic properties [2]. Corrosion is an electrochemical process by which the metallic structures are destroyed gradually through anodic dissolution [3]. So, various attempts must be employed to prevent this destructive process. Some of inhibitors are chemical compounds containing some coordination sites like O, N and S atoms. The corrosion inhibition efficiency of these compounds is connected with their adsorption properties. The structural properties of corrosion inhibition compound are important. In this study the effect of structural properties on chemical activity for four compounds has been studied by some quantum chemical calculations [4,5]. The correlation between the molecular structures and some calculated electronic properties has been investigated by using some quantum chemical calculations, All structures of these compounds have been optimized, highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), energy level and energy gap, surface and dipolmoment have been computed, and then the relations between the inhibition efficiency and all quantum chemical parameters have been discussed.

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A DFT study of molecular structure and intramolecular hydrogen bonding of N-salicylideneaniline

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Molecular structure and vibrational frequencies of N-salicylidenaniline (SAn) have been investigated by means of density functional theory (DFT) calculations. The geometrical parameters and Frequencies calculated at B3LYP [1, 2] and BLYP [1, 3] levels using 6-31G**, 6-311G** and 6-311++G** basis sets and compared with the analogous parameters of 2-iminomethyl-phenol (2IMP). The assignments of the observed fundamental bands have been proposed on the basis of peak positions and relative intensities.

After fully optimization, it has been shown two tautomers of intramolecular hydrogen bond, O—H···N in enol form and O···H—N in cis-keto form, have a comparable stability. Both of them have a non-planar structure with the dihedral angel between the rings of 38.5° and 16.3°, respectively, at B3LYP/6-311++G**. Energy difference between them is obtained as 4.6 kcal mol^{-1} at this level of theory. From geometry parameters, the main effect of phenyl substitution on nitrogen of imine group in SAn is shortening of the O···N distance and lengthening of the O—H bond length in comparison with the corresponding values for 2IMP. The calculated O···N and O—H distances in SAn are 0.018–0.032 Å and 0.002–0.011 Å, respectively, shorter and longer than those in 2IMP. The ratio νOH/νOD and γOH/γOD of SAn that appears at 3221/2349 and 848/622 cm^{-1}, respectively, are consistent with the calculated geometry results. Theoretical calculations show that the hydrogen bond strength of SAn is slightly stronger than that of 2IMP.

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Substitution effect on intramolecular hydrogen bond in 3-aminoacrylaldehyd and its derivatives: A theoretical study

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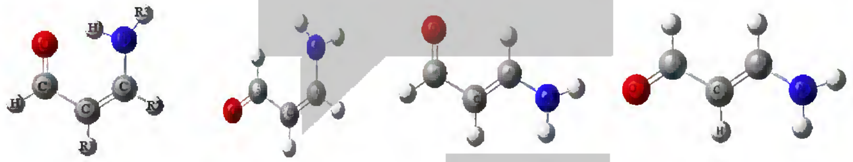
The molecule 3-aminoacrylaldehyde ($H_2NCH=CHCHO$, hereafter 3AA) can exist in sevsral heavy-atom conformations that are distinguished by cis or trans arrangements of the substituents at the C=C double bond combined with different rotations of the CHO group about the C-C single bond. In the crystal and in polar solvents the configuration about the C=C bond is trans, but in non-polar solvents evidence of a cis form is seen[1,2]. The CSC form is capable of forming an internal N-H…O hydrogen bond which ispresumably responsible in large part for its predominance(Fig.1). All of the computations in the present study were performed by Gaussian 98 and series of program. The geometry optimizations were carried out at MP2/6-311++G(d,p) level of theory. The optimized Structures were used to obtain the appropriate wave function files for AIM and NBO analyses.



CSC CST TSC TST

Fig. 1. Diagrams of planar conformers of 3-aminoacrylaldehyde

Various methods for estimation of intramolecular hydrogen bond energy have been proposed. It was found that most appropriate model, with minimal deviation for 3-aminoacrylaldehyde and its derivatives, but in general, the related rotamers model is the most suitable for estimation the IHB energy. There are three different situations (R_1,R_2 and R_3) for halogen substitution in respective system(Fig. 1. CSC form). The results obtained by various descriptor of HB (such as geometrical parameters, N-H vibrational frequency, topological and NBO parameters) and RRM energy shows that R_1, (F in R_3 situation) and R_2, (Br, Cl in R_3 situation) respectively reduce and increase IHB strength.

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Theoretical Study of Tautomerism , and Geometrical Isomerism of 2-amino-1-methyl-1H-imidazol-4-ol in Water Solvent

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The purpose of this study is the determination of the solvent effects on the stability of tautomeric forms of 2-amino-1-methyl-1H-imidazol-4-ol molecule the author uses B3LYP/6-311++G** level of theory.[1]
2-amino-1-methyl-1H-imidazol-4-ol is an amino acid that occurs in vertebrate tissues and in urine . Creatinine ($C4H7N3O$) is produced from creatine, a
molecule of major importance for energy production in muscles. Creatinine (creat) is transported through the bloodstream to the kidneys. The kidneys filter out most of the creatinine and dispose of it in the urine An abnormal level of creatinine in biological fluids is an indicator of various disease states [2,3]
The present study reports the results of a systematic theoretical examination of tautomeric forms using DFT model chemistry of particular interest are the molecular geometries , tautomeric equilibria, geometrical isomerism. The geometries of all compounds investigated were completely optimized with the gaussian 03 program employing the B3LYP/6-311++G** level of theory [4]
The kinetic and thermodynamic Data in water solvent are nearly similar to those in the gas phase but their rate constant are slightly less than those in the gas phase.

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DFT Study on Tautomerism of Creatinine in The Chloroform Solvent

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In The present study the density functional theory (DFT) and Gibbs free energy calculations were performed to investigate the stability and tautomerism of creatinine.

Five different forms are possible for the creatinine . forms that the most stable forms is 2-imino-1-methyl imidazolidin-4-one (Keto-Form). The obtained data showed that 2-imino-1-methyl imidazolidin-4-one is stable form.[1]

The quantum chemical calculations were performed with Gaussian 03 suite of programs full geometry optimizations were carried out using the density functional theory (DFT) calculations with the B3LYP/6-311++G** level.[2,3] Relative Gibbs free energies can be used to obtain ΔG and K_{eq} between tautomers and $\Delta G^{\#}$ and rate constants for tautomerism interconversions of each molecule.،The structure of transition state between each pair of tautomers was optimized by appling Schlegels synchronous transit-guided quasi-newton (QST3) method started from the fully optimized structure of one tautomer and finished on the fully optimized structure of another tautomer.The transition states were verified with frequency calculations to ensure they were first order saddle points with only one negative eigenvalue. Additionally intrinsic reaction coordinate (IRC) calculations proved that each reaction linked the correct products with reactants.Rate constant were calculated by canonical transition state theory using eyring equation.free energy of salvation for each molecule was calculated using SCRF keyword with Tomasis polarized continuum(PCM) model.[4]

The DATA from calculations show that in different solvent, small variations can be observed in ΔG values but the direction of those changes are not identical for all moleculs.

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Configuration Changes and Contributions to Entropy for 1,2-Dichloroethane and Hexane Moleculs By HF/6-31G* Method

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Entropy is the most influential concept to arise from ststistical mechanics.The free rotation of a rigid molecule is also quantized (the angular momentum and its projection are integer multiples of h/2π), so the rotational energy is restricted to certain discrete levels. Rotational spectra are characterized by the constants A, B, and C, where $A \equiv h/(8\pi^2 I_A)$ and likewise for B and C. The quantities $I_{A,B,C}$ are the principal moments of inertia of the molecule, with the convention $I_A \leq I_B \leq I_C$ (or $A \geq B \geq C$). Many computer programs, including ab initio packages, report the rotational constants when provided with a molecular geometry. The rotational contribution to the entropy depends on the product of the moments of inertia [1] How much does this contribution change as the configuration of a molecule changes?
In the present study the author uses Gaussian program Version 03
The author, examine two molecules here: **1,2-dichloroethane** (CH_2ClCH_2Cl) and **hexane** (C_6H_{14}). The author uses energies and rotational constants from HF/6-31G* calculations.
1,2-dichloroethane (CH_2ClCH_2Cl) can be in a gauche form (Cl-C-C-Cl dihedral angle of +- 60 degrees) or a trans form (Cl-C-C-Cl dihedral angle of 180 degrees). The trans form has the Chlorine and Carbon atoms closer to collinear which results in the larger rotational constant and smaller product of the moments of inertia.
hexane (C_6H_{14}) can be in an extended form or various forms which are more curled up. There are three C-C-C-C dihedral angles in hexane. In the extended form all three dihedral angles are 180 degrees. In the curled (helical) form all three angles are 60 degrees. In the very curled form the dihedral angles are +60, +60, -90. The last angle is different from -60 due to steric repulsion.[2]
As you can see from results, gauche form has the highest S_{rot} for 1,2Dichloroethane molecule,While verycurled form has the highest S_{rot} for Hexane molecule.

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Calculation of the vibrational frequencies for C_4H_8S (Thiophene, tetrahydro-) by mPW1PW91/6-311G** Method

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The purpose of this study is the calculation of vibrational frequencies of Thiophene , tetrahydro by DFT method
A molecule composed of n- atoms has 3n degrees of freedom. This leaves 3n-6 degrees of vibrational freedom (3n-5 if the molecule is linear). Vibrational modes are often given descriptive names, such as stretching, bending, scissoring, Rocking, and Twisting. [1]
The vibrational frequencies produced by ab initio programs are often multiplied by a scale factor (in the range of 0.8 to 1) to better match experimental vibrational frequencies.
This scaling compensates for two problems:
1) The electronic structure calculation is approximate. Usually less than a relativistic full configuration interaction is performed.
2) The potential energy surface is not harmonic. For bond stretches a better description of the potential energy surface is given by the Morse potential $E(x) = D(1-\exp(-\beta(x-x_0)))^2$ illustrated below. In this equation E is the potential energy, D, β, and x_0 are constants, and x is the interatomic distance
The programs that predict vibrational frequencies do so by calculating the second derivative of the potential energy surface with respect to the atomic coordinates. This provides the curvature at the bottom (minimum) of the well. For a harmonic potential $E(x) = k x^2$ this is directly related to the vibrational energy level spacing. For a Morse potential (with the same second derivative at the minimum) the anharmonicity causes the vibrational energy levels to be more closely spaced as illustrated in the figure.[2]
In the present study, the vibrational frequencies obtained for C_4H_8Swere scaled by 0.8978 (Thiophene, tetrahydro-) With mPW1PW91 method using the 6-311G** basis sets.

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Halogen effects on the various cycloaddition reactions of 1,3-cyclopentadiene with ketene

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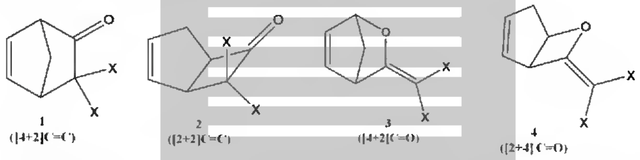
The Diels-Alder [4+2] and [2+2] cycloadditions have been one of the most useful reactions in the field of organic synthesis [1, 2]. The cycloadditions of cyclopentadiene and ketenes are studied by a combination of kinetic, product studies and trajectory calculations. In this work, we carried out a DFT (B3LYP/6-31+G*) study on the cycloaddition reactions of 1,3-cyclopentadiene with different dihaloketenes. Different pathways leading to the following structures are presented in Scheme 1.



Scheme 1. Four products obtained through [4+2] and [2+2] cycloaddition reactions.

Ketenes can react with the cyclopentadiene both across C=C or C=O bond, but reactions across the C=C bonds of ketenes yield the more stable cycloadducts (Table 1). The calculated enthalpy changes for all reactions in different pathways are negative and the order of corresponding ΔHs as a function of substituted halogens X is F > Br > Cl > H. This trend indicates the more thermodynamic favorability for dihaloketene compared to unsubstituted ketene in the cycloaddition reactions. Also, our investigation shows that for [4+2] and [2+2] cycloadditions across the C=O, the order of stability of the products is as follows: Cl > H > Br > F (Fig. 1).

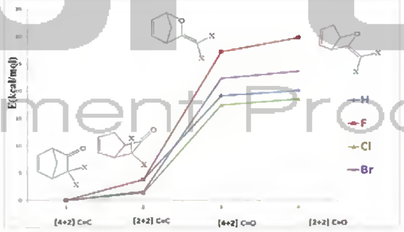


Figure 1. Relative energies of the products.

Table 1. The B3LYP/6-31+G* calculated relative energies for different dihaloketene-cyclopentadiene cycloaddition pathways yielding **1-4**, along with the calculated ΔHs in parentheses (in kcal/mol).

X	1	2	3	4
H	0 (-17.2)	3.8 (-13.4)	19.1 (-1.8)	20.1 (-2.8)
F	0 (-48.8)	3.8 (-45.0)	27.1 (-21.6)	29.7 (-19.1)
Cl	0 (-29.8)	1.4 (-28.4)	17.4 (-12.3)	18.5 (-11.2)

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An Ab Initio Study on the ability of N,N'-bis(4-phenylazo) (salicylaldimine) 3-chloro-1,2-phenylenediamine for extraction of some bivalent cations

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ABSTRACT

Schiff bases compounds are known as effective hosts for absorption and determination of trace amounts of M^{2+} ions. Recently the host-guest interactions between Schiff bases and various metal cations have received considerable attention from both experimental and theoretical standpoints. In the present research, quantum chemical calculations at B3LYP/LANL2MB level of theory are performed to estimate the extraction power of the title Schiff base for some bivalent cations. The theoretical results are compared with the experimental data in which the M^{2+} ions are adsorbed quantitatively during the passage of aqueous samples through an octadecyl (C_{18}) silica membrane disk modified by the Schiff base ligand and subsequent determination of cations by flame atomic absorption spectrometry. The extraction power of an extractant for metal ions is closely related to the binding energy of the ion to the ligand. The pairwise interaction energy, ΔE, between host molecule (L^{2-}) and guest (M^{2+}) is estimated as the difference between the energy of the complex [ML] and the energies of isolated partners: $\Delta E = E_{ML} - (E_L^{2-} + E_M^{2+})$
The geometries of all species including the uncomplexed ligand and its complexes with the metal cations were optimized at the B3LYP/LANL2MB level of theory. To explicitly display the hydration of different metal cations, all metallic cations were considered as six-coordination $[M(H_2O)_6]$ complexes and the following reaction was used to calculate the relative binding energies:
$M^{2+}(H_2O)_6 + L^{-2} \rightarrow ML + 6H_2O$
The calculated binding energies for Cu^{2+}, Zn^{2+}, Cd^{2+}, Ca^{2+}, and Cd^{2+} are -1460.4, -1186.1, -1168.2, -1133.1, -1111.3 kJ mol^{-1}, respectively. The computed values are in accordance with the selectivity trend observed in the solid-phase extraction.

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Alumina Supported Acidic Ionic Liquid: Preparation, Characterization and Its Application as Catalyst in the Synthesis of 1,8-Dioxooctahydroxanthenes

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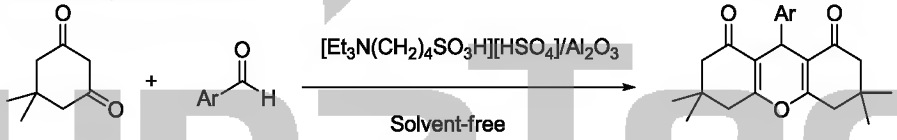
Xanthenes are important class of organic compounds with a large number of naturally occurring, as well as synthetic derivatives, and occupy a prominent position in medicinal chemistry.[1]A number of these compounds have been considered as dyes and fluorescent visualization materials for biomolecules and laser technologies.[2] Furthermore, these compounds have been investigated for their agricultural bactericide activity,[3] anti-inflammatory effect,[4] and antiviral activity.[5]

Recently, many synthetic methods for preparing xanthenediones have been reported by the condensation of aromatic aldehydes and active methylene carbonyl compounds in the presence of various acid catalysts.[6-9] Many of these procedures suffer from lack of selectivity, unsatisfactory yields, being costly, toxicity of the reagents, or required special conditions.

Thus,we report herein an efficient synthesis of 1,8-dioxooctahydroxanthenes by the reaction of dimedone with aryl aldehydes using $[Et_3N(CH_2)_4SO_3H][HSO4]/Al_2O_3$ as a new solid acid supported catalyst. Reusability, easy work up, inexpensive, ready availability of the catalyst makes the procedure an attractive alternative to the existing methods for the synthesis of 1,8-dioxooctahydroxanthenes.



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A Convenient Method for the Synthesis of 2-{2,6-Bis-[2-(4-dialkylaminophenyl)vinyl]-pyran-4-ylidene} malononitrile Derivatives as Red-Light Emitting Compounds

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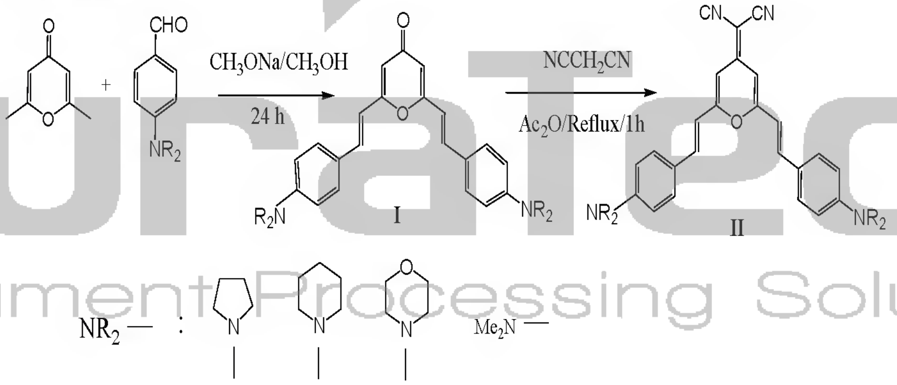
Dicyanomethylene is a strong electron acceptor. Its typical derivative, 4-(dicyanomethylene)-2-methyl-6-(p-(dimethylamino)styryl)-4H-pyran (DCM), has been applied on fabricating of organic light-emitting diodes (OLED) for its excellent light-emitting properties. In addition, DCM dye also has strong nonlinear optical properties. It is a favorable functional chromophore being highly expected on exploring of organic nonlinear optical materials. The DCM analogues have the typical donor- π -acceptor (D-π -A) structure and their emissions arise from intramolecular charge transfers. These types of compounds are usually synthesized by condensation reactions between donor containing aldehydes and acceptor containing, dicyanomethylidenepyrans.

In this work, we found a convenient new method for synthesis of d-DCM derivatives and were synthesized series of new bis condensated compounds by condensation of 2,6-dimethyl-4H-pyran-4-one with appropriate aminoaldehydes. In the next step from reaction of bis-styryl substituted derivatives of 4H-pyran-4-one with malononitrile, d-DCM derivatives were obtained as red-light emitting compounds. The advantage of this method was formation of bis compounds without presence of mono condensated compounds as by product under mild condition.



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Synthesis of Propacene as a Novel Burning Rate Catalyst

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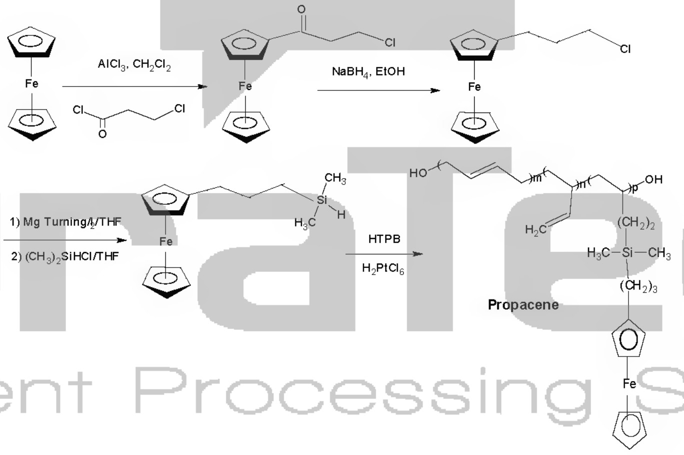
Burning rate catalysts such as ferrocene and its derivatives have been widely used as combustion catalysts for solid composite propellants. They are added to enhance the burn rate of ammonium perchlorate based composite propellants. Although ferrocene and many of its derivatives are known to be good high burning rate catalyst, they have one big disadvantage. These compounds have a tendency to migrate through the solid polymeric matrial of the cured propellant into the liner and onto the surface of the propellant grain during storage. This can lead to localised high burn rates in the motor and instability in motors ballistic performance. We synthesized suitable ferrocene containing compound for preventation of migration of the ferrocene moiety in the composite propellant. New functional prepolymer was synthesized which contain ferrocenyl groups grafted by hyrosilylation reaction of organosilicon ferrocene derivative (3) to carbon-carbon double bonds of hydroxy terminated polybutadiene (HTPB). This new prepolymer was named "Propacene".

At the begining of this work, we reacted ferrocene with 3-chloropropenoyl chloride in the presence of aluminium chloride in dichloromethane and synthesized 3-chloropropenoyl ferrocene (1). Compound 1 under influence of $NaBH_4$ solution in ethanol was transformed to 3-chloropropylferrocene (2). In next step, the Grignard reagent formed from reaction of compound 2 with magnesium turning was treated with dimethylchlorosilane solution in THF and 3-(dimethylsilyl)propylferrocene (3) obtained as brown oil. Finally, from hydrosilylation reaction of compound 3 with HTPB prepolymer [catalysed by a solution of chloroplatinic acid hexahydrate ($H_2PtCl_6.6H_2O$) in 2-propanol], Propacene as a novel burning rate catalyst was obtained. Some important properties of this compound e.g. viscosity, glass transition temperature, iron percentage and density are consistent with characteristics which were need in preparation of composite propellant.



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Click Chemistry for Preparation of Miscellaneous Heterocyclic Scaffolds

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Since the vast majority of natural products, drug-like compounds and intelligent materials such as photochromic compounds possess heterocyclic scaffolds, the ability to synthesize efficiently diverse heterocyclic compounds is critical. In this seminar synthesis of several photochromic intelligent compounds based on heterocyclic scaffold 1,3- diazabicyclo [3.1.0] hex-3-enes derivatives and in some cases preparation of their AgNPs will be discussed in detail. In other efforts application of MCRs in synthesis of several useful medicinal compounds such as clopidogrel, bis-pyrazolines, pyrimidine-2-thiols, pyridazinones, phthalazinones, mono-, bis-and tetrakis-hydantoins and thiohydantoins are discussed. In most cases the reactions have simple reaction conditions, use readily available starting materials and reagents, use benign or easily removable solvents, simple product isolation by non-chromatographic methods (crystallization), high atom economy and generate only inoffensive byproducts with very high chemical yields were considered.

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Early Realization of Scientific Goals in Iran Twenty Years Plan oportuninity weakness and new horizons in chemistry of I.R.Iran will be also discussed

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In this paper, performance of Iranian researchers as shown by the latest information gathered from the scientific data base published by Scopus during the recent years, is examined and compared with those of several neighboring countries in particular with Turkey and some of the advanced countries. The results of this investigation indicates that in 2011, Iran with 34055 scientific docu- ments ranked eighteen world wise while Turkey with 31,150 scientific documents ranked nineteen behind Iran. In 2011, Iran held the first rank in the region in production of scientific documents in accordance with Scopus data base.

In addition, when we consider total number of published scientific documents world wise in 2011 in which the ratio of population of each country to the total world population is also taken into consideration, Iran with a ratio of 1 /42 as compared with 1/29 for Turkey, ranked higher and as such is considered to be in a superior scientific position in the region. This position has continued to be maintained in 2012 and has even reached a higher standing.

Keywords: Realization of scientific goals as set within the projected twenty years plan of country progression, Scopus scientific data base, scientific documents.

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Synthesis and Characterization of Novel UV-Curable Epoxy Rosinate

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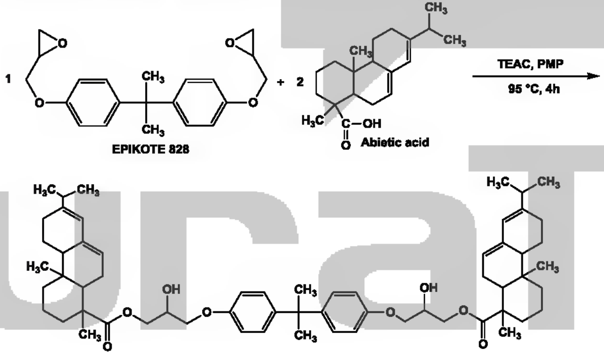
The rosin is a solid form of natural acidic resin which is obtained from pine wood. It is semi transparent and varies in color from yellow to black. It chiefly consists of different resin acids, especially abietic acid. The resin acid molecule possesses two chemically reactive centers, the double bonds and the carboxyl group [1-4]. Rosin has a comprehensive application in adhesives, printing inks, protective coatings, rubbers and pharmaceutical [5]. In this work, novel UV-curable epoxy rosinate was synthesized by epoxy resin (EPIKOTE 828) and purified rosin. The reaction was achieved in presence of triethyl ammonium chroride (TEAC) as catalyst and p-methoxy phenol (PMP) as inhibitor in 95 °C for 4 hours (End Acid value=0.5). UV curable resin was formulated by benzophenone, dimethyl-p-toluidine (DMPT) and trimethylol triacrylate (TMPTA) as reactive diluents. The film properties such as hardness, gloss, impact and adhesion have been evaluated after UV radiation curing.



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Reaction between ortho-amino AromaticAcid Chlorides and DialkylAcetylenedicarboxylates By triphenyl phosphin

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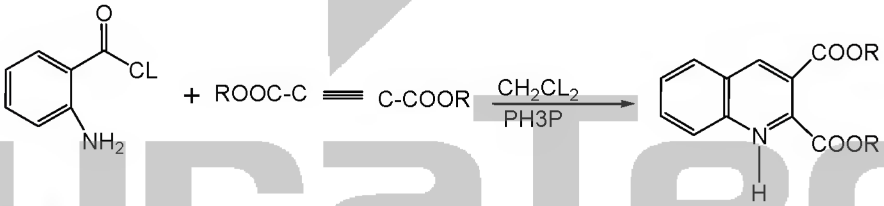
Abstract

Quinolines[1] are interesting synthetic targets because they act as building blocks for a large number of natural products. In recent years there has been an increase in interest in the synthesis of quinoline compounds. This interest has resulted from the use of such compounds in variety of biological and synthetic applications.[2] While a number of synthetic methodologies for the quinoline ring system have been developed,[3] the literature describing a novel one-pot cyclization method based onconsecutive processes in rather scarce. Here we describe a two-component condensation reaction between an ortho-amino aromatic acid chloride and an electron-poor acetylenic ester efficiently provides fully substituted electron-poor and quinoline in a one-pot reaction.



4a R"= Me
4bR"=Et
4c R"=tBu

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NMR Study,Theoretical Calculations for $4'$-Chloro-$2,2':6',2''$-Terpyridine and $4'$-Phenyl-$2,2':6',2''$-Terpyridine Ligands

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Applications is the result of a great advance in the design of terpyridine derivative in the last decade. The well-known characteristics of terpyridine metal complexes, such as their special redox and photophysical properties, depend on the electronic influence of the substituents. Therefore, terpyridine complexes may be used in photochemistry for the design of luminescent devices[1] or as sensitizers for light-to-electricity conversion[2] .The many interesting applications of functional metalcoordinating $2,2':6',2''$-terpyridine compounds in the fields of supramolecular and macromolecular chemistry as well as electrochemistry has resulted in an impressive growth in the number of novel synthetic procedures. The tridentate ligand$2,2':6',2''$-terpyridine and its derivatives bonded to a metal have been well studied in the area of supramolecular chemistry. Recently, as an extension in the exploration of this type of metal-binding domains, symmetric divergent and $4'$-functionalized terpyridine have been used in the formation of coordination architectures. Indeed, the scarcely reported examples on this subject include only the $4'$-chloro-$2,2':6',2''$-terpyridine and $4'$-phenyl- $2,2':6',2''$-terpyridine ligand.

In the present work the NMR spectra of the $4'$-Chloro-$2,2':6',2''$-terpyridine and $4'$-phenyl-$2,2':6',2''$-terpyridine ligand based on theoretical calculations. TheNMR data of these ylides are consistent with results obtained from theoretical calculation. In addition useful information was obtained from studies of chemical shift and coupling constant.Hertz is a unit representing the chemical shift of a proton resonance frequency of the spectrometer in terms of parts per million from tetra methyl silane is used. TMS porotons resonate is exactly zero. The proposed this present work was effect of substituted Color and Phenyl in the $4'$ position of the $2,2':6',2''$-terpyridine Ligand on the NMR data is studied.Slot spin-spin for a chemist it is important that contain valuable information about the structure of the molecule provides. Coupling constant shows how a nuclear are effected by spin states of its neighbors.

Calculation methods: The primary structure are designed by soft ware Gauss view. The combination of structural optimization, frequency calculations and NMR were done using soft ware Gaussian03.The quantities of carbon and hydrogen atoms isotropic latency have been studied. Chemical shift at # hf/6-31g (d,p) level has been studied. Coupling constant in # hf/6-31g(d,p) using the keyword in the spin-spin are obtained.Latency isotropic chemical shift to calculate the quantity of hydrogen atoms relative to tetra methyl silane.

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Ecofriendly and facile Nano ZnO and Nanocrystalline aluminium oxide catalyzed synthesis of 3-aryl-2H-benzo[1,4]thiazine Derivatives and Ab initio and DFT Calculation

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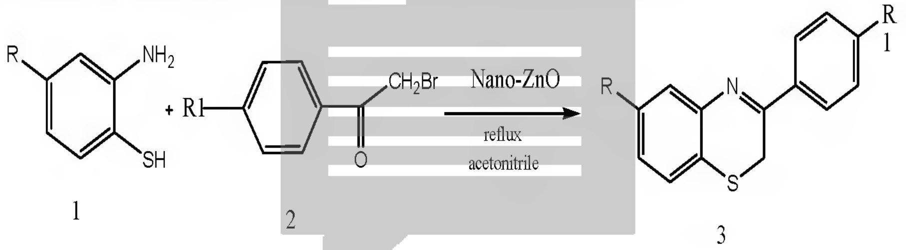
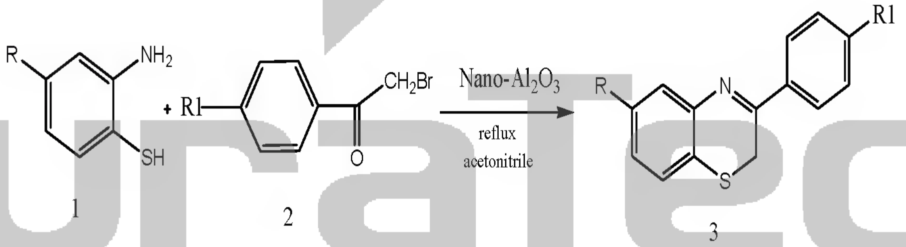
Abstract: Nano zinc oxide (Nano-ZnO) and Nanocrystalline aluminium oxide were explored as a heterogeneous and reusable catalysts for the synthesis of 3-aryl-2H-benzo[1,4]thiazine derivatives. The spectroscopic studies and synthesis of 3-aryl-2H-benzo[1,4]thiazine derivatives via the condensation of o-aminothiophenols and 2-bromo-1-aryl-ethanones has been very considerable . In this investigation we report the synthesis of these derivatives at one step reaction in high yields by ^{1}HNMR, FT-IR. The B_3LYP/HF calculations for computation of FT-IR spectra have been carried out for the title compounds at the 6-31G* and 6-311++G** basis set levels. Predicted vibrational frequencies have been assigned and compared with experimental FT-IR spectra and they are supported each other.





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Identification and measurement of the phenolic compounds in cigarette smoke and using of perlite filtration for their absorption

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Abstratc:

Perlite is an amorphous volcanic glass that has a relatively high water content, and typically formed by the hydration of obsidian. It occurs naturally and has the unusual property of greatly expanding when heated sufficiently. It is an industrial mineral and a commercial product useful for its light weight after processing. One of the properties of this kind of perlite formation of glass form for the temperatur around of 850–900 °C. The trapped water in the structure of perlite material and followed by vaporizing causes the expansion of the material to 7–16 times biger than to originals. Hereby this materials widly have an enough surufaces and cavity to absorption some of chemical compounds such as phenolic derivatives. In this research a kind of perlite that extracted from Kerem Boghlar mine (in Miyaneh city) was used. The composition of the perlite by X-rar analysis contains inorganic compounds such as Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, SO_3, K_2O, TiO_2, MnO and Fe_2O_3. in it. Herein the phenolic compound from smoke of Farvardin cigarette before and after filtration were indentified. The analysis was showed that majority of the trapped phenolic compounds such as : Phenol, Hydroquinone, Resorcinol, Pyrocatechol, m-Cresol, p-Cresol and o-Cresol. The employment technique for indentify of the absorbed materials on the perlite was GC-MS spectroscopy. The mainstream smoke that was trapped by the perlites, Cambridge filter and cigarette filter was extracted by pure methanol as eluent and then analyzed by coupled GC/MS. Eventually the results from GC/MS analysis was showed that a wide range of the phenolic compounds of Farvardin cigarette absorbed by perlite filtration. The structure of perlite after absorbing was also studied by XRD and XRF analysis.

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CuO nanoparticles catalyzed one pot synthesis of 14-aryl-14*H*-dibenzo[a,j]xanthenes

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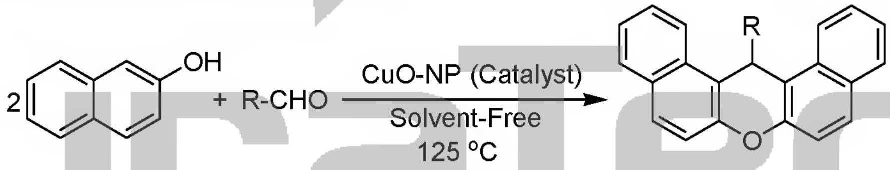
The synthesis of xanthenes, especially benzoxanthenes, has emerged as a powerful tool in organic synthesis due to their wide range of biological and therapeutic properties such as antibacterial, antiviral and anti inflammatory activities, as well as in photodynamic therapy and for antagonism of the paralyzing action of zoxazolamine [1].

Metal nanoparticles have high surface to volume ratio and unresidual energy which are mainly responsible for their catalytic activity in various different organic transformations [2]. Nanosize catalysts can act as a bridge between homogeneous and heterogeneous catalysis. It offers the advantage of homogeneous and heterogeneous catalysis disciplines and provides unique activity with high selectivity in catalysis [3]. Application of free nanoparticles as a catalyst is an important vital route to understand the basics in catalysis. However less attention has been paid towards free nanoparticle catalysis. Hence, the development of free nanoparticles with versatile catalytic activity is still an attractive and challenging task from the point of view of academia and industry.

In this research, we report a simple and convenient procedure for the synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a,j*]xanthene derivatives is described through a one-pot condensation of β-naphthol with aryl aldehydes in the presence of CuO nanoprticles as heterogeneous catalyst under solvent free conditions (Scheme).



Scheme

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A green one-pot multicomponent synthesis of functionalized 4*H*-chromenes using well-ordered mesoporous silica nanoparticles as a reusable nanocatalyst

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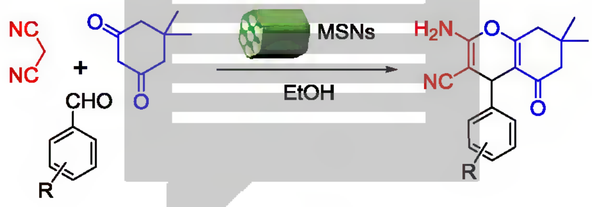
Functionalized 4*H*-chromenes are the most common and important feature of a variety of natural products. These derivatives have meaningful biological activities such as antimicrobial and antifungal, antitumor, antioxidant, hypotensive, antileishmanial, antiproliferation, local anesthetic, antiallergenic and central nervous system (CNS) activities as well as treatment of Alzheimer's disease and Schizophrenia disorder. [1]

Mesoporous silica nanoparticles (MSNs) have attracted considerable interest in life and materials science. Their unique properties, such as tunable monodisperse diameter (50–200 nm), tunable pore size (2 to 4 nm) and high specific surface area (800–1000 $m^2 g^{-1}$), offer a large range of applications such as drug delivery, MRI, cancer cells targeting, photodynamic therapy or antireflective coatings and catalysis. [2]



Scheme 1

As part of our program aimed at developing new and environmentally benign synthetic methodologies, Herein, we report for the first time a simple and efficient method for the synthesis of functionalized 4*H*-chromenes through the three-component one-pot condensation of aryl aldehydes, malononitrile, and cyclic 1,3-diketones using well-ordered mesoporous silica nanoparticles as a green and reusable nanocatalyst (Scheme 1).

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MgO nano particle as a recyclable catalyst for the multi-component synthesis of pyranopyrazole derivatives in aqueous medium

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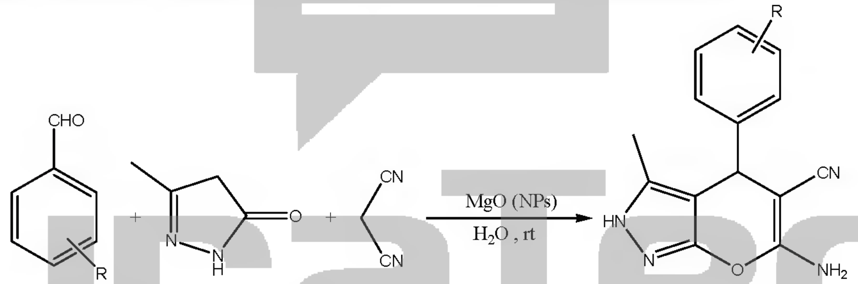
Multi-component reactions (MCRs) have emerged as an efficient and useful tool in modern synthetic organic chemistry due to their valued features, such as atom economy, straight forward reaction design and the opportunity to construct target compounds by the introduction of several variety elements in a single chemical event [1]. One type of these reactions is the synthesis of Pyranopyrazoles. These compounds constitute one of the privileged heterocyclic scaffolds known to exhibit important biological activities, such as analgesic [2], anti-tumor, anti-cancer [3], anti-inflammatory properties [4] and also serve as potential inhibitors of human Chk1 kinase [5]. Nowadays the nano catalysts have very advantages because the surface area of the reagent is increased manifold. Among the nanoheterogeneous basic catalysts, magnesium oxide is a versatile material used as catalyst for several base-catalyzed organic transformations [6]. Herein we describe a one-pot multicomponent synthesis of pyranopyrazoles from aryl aldehydes, malononitrile and 3-methyl-2-pyrazolin-5-one in the presence of MgO nano particle in water as medium. This procedure offers several advantages including mild reaction condition, cleaner reaction, reusability of catalyst, high yield of products as well as a simple experimental procedure, which makes it an attractive process for the synthesis of pyranopyrazoles and their derivatives.



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New and Nonexpensive poly (ethylene terephthalate) (PET)/clay nanocomposites: Study on synthesis and characterization

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In recent decades, nanotechnology has been widely applied to polymeric materials, with the ultimate goal of dramatically enhanced performance [1]. Montmorillonite (MMT) is the most studied mineral because of its favorable characteristics, such as swelling ability and cationic exchange capacity [2]. In the synthesis of polymer clay nanocomposites, the clay is treated with an organic modifier before it is mixed with the polymer [3].Several technologically important polycondensations have been used in nanocomposites preparation with layered silicate such as polyimides [4]. General refluxing, Microwave irradiation and Ultrasonic irradiation have been used here to distribute the nano sized particles in a polymer matrix in order to prepare the corresponding nanocomposites in different ratios.

The organo-modified montmorillonite (MMT) was prepared by a cation-exchange method, which is a displacement of the sodium cations of cloisite Na^+ with the tetrabutyl ammonium bromide in DMAc/H_2O (50%). The montmorillonite (1.0 g, 0.95 meq) was dispersed in 200 mL of DMAc/deionized water (50%). The amount of tetrabutyl ammonium bromide added was about 1 CEC, based on the cation exchange capacity (CEC = 0.95 meq/100 g) of the MMT. This dispersion was mixed and stirred vigorously at 70 °C for 5 h, followed by filtration and continuous washing at 70 °C with deionized. The solvent was removed by evaporation under vacuum. The first method: Different amounts of prepared tetrabutyl ammonium-MMT (5, 10, 20 wt %) were first swollen in DMAc. Then the layered silicate dispersion mixed with the solution of PET and the mixture was stirred at 70 °C for 5 h and then irradiated under ultrasound for 5 h and precipitated in deionized water. The second method include irradiation under ultrasound for 1 h and then irradiation under MW for 70 s. The third method include usual refluxing over night.

The best method was the first one. there are not much difference between FT-IR spectra of resulting nonocomposites with that of pure PET except for the Si-O, Al-O and Mg-O bands which proves the presence of MMT in the PET matrix. The XRD experiments were used for measuring the interlayer distance of MMT after modification with the ammonium salt and in nanocomposites. The XRD data of PET/ tetrabutyl ammonium-MMT nanocomposites indicated a degree of exfoliation. PET/ tetrabutyl ammonium-MMT (5%) showed a degree of exfoliation, PET/ tetrabutyl ammonium-MMT (10%) shows a degree of flocculated and PET/ tetrabutyl ammonium-MMT (20%) shows some intercalated structure. The level and degree of dispersion was investigated by TEM. Well-dispersed organo-modified MMT in PET matrix are observed obviously.

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Amphiphilic Diblock Copolymers Based on Poly(2-ethyl-2-oxazoline) and Poly(caprolactone): Synthesis and Characteristics

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Previous studies demonstrated that biodegradable polymeric materials can form useful drug delivery system. The powerful potential of polymeric micelles as drug carriers lie in their unique characteristics, such as nano-size and thermodynamic stability [1–3]. Amphiphilic block copolymers can self-assemble into polymeric micelles in aqueous solution. These polymeric micelles are composed of hydrophobic segments as the internal core and hydrophilic segments as the surrounding corona. The hydrophobic core may serve as a nano-reservoir for hydrophobic agent, while the hydrophilic shell provides a protective coating between the core and the external medium [4].

Amphiphilic block copolymers, poly(2-ethyl-2-oxazoline)-b-poly(caprolactone), (PEOz-b-PCL) were synthesized via ring opening polymerization of caprolactone in the presence of poly(2-ethyl-2-oxazoline), (PEOz). The copolymers form micelle-like nanoparticles by their amphiphilic characteristics. Molecular weight distributions of PEOz-b-PCL were determined using a gel permeation chromatography (GPC) and their structures were examined by Nuclear Magnetic Resonance (NMR). Fourier transform infrared (FT-IR) spectroscopy was used to confirm the structure of copolymer. The sizes of nanoparticles ranged from 60 to 120 nm as measured by dynamic light scattering detection, and were larger with higher molecular weight of the copolymers. The Critical Micelle Concentration (CMC) of these nanoparticles in water decreased with increasing molecular weight of hydrophobic segment. copolymers were able to load the organic and inorganic guest molecules. Application of host-guest systems such as nanocatalyst for Heck chemical reaction was also investigated.

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Silica supported perchloric acid ($HClO_4$-SiO_2) catalyzed four-component synthesis of 2*H*-indazolo[2,1-b]phthalazine-triones

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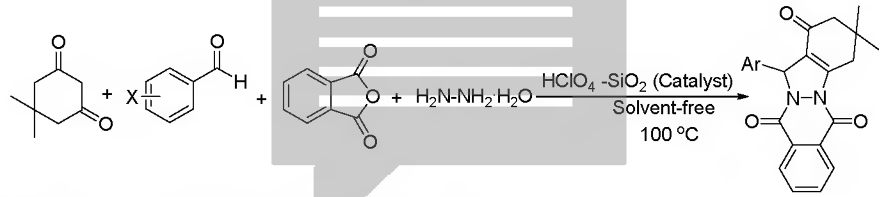
Heterocyclic compounds occur very widely in nature and are essential to life [1]. Nitrogen-containing heterocyclic molecules constitute the largest portion of chemical entities, which are part of many natural products, fine chemicals and biologically active pharmaceuticals vital for enhancing the quality of life [2]. In this research, we wish report an efficient method for the preparation of 2*H*-indazolo[2,1-b]phthalazine-trione derivatives using $HClO_4$–SiO_2 [3] as recyclable solid acid catalyst under solvent-free conditions (Scheme 1).



Scheme 1

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Nano silica supported perchloric acid catalyzed three-component Synthesis of triazolo[1,2-a]indazole-trione derivatives

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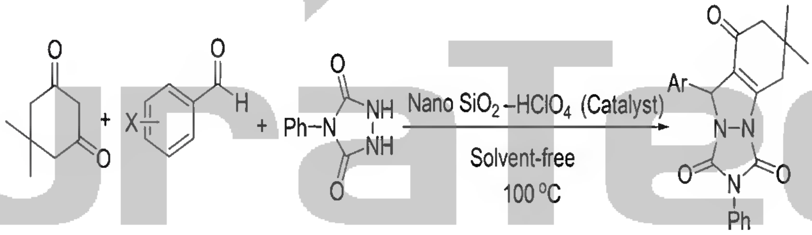
Among large variety of nitrogen-containing heterocyclic compounds, heterocycles containing an urazole moiety are of interest because they constitute an important class of natural and non-natural products, many of which exhibit useful biological activities and clinical applications [1-2]. In this research, we report that nano silica supported perchloric acid [3] has been utilized as an efficient heterogeneous recyclable catalyst for the one-pot three component coupling (3CC) synthesis of triazolo[1,2-a]indazole-trione derivatives from aryl aldehydes, dimedone, 4-phenyl-1,2,4-triazolidine-3,5-dione (Scheme).

Scheme



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Nano-ZnO: An eco-friendly catalyst for preparation of pyranopyrazoles

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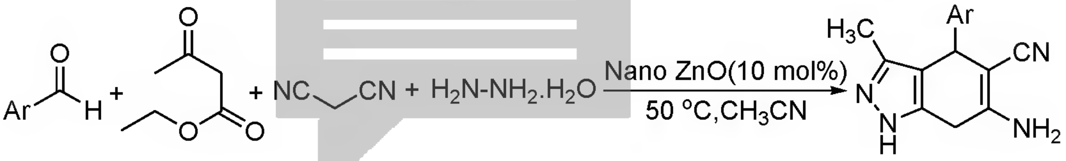
Pyranopyrazoles are fused heterocyclic compounds that possess many pharmaceutical ingredients and biological properties such as analgesic, anti-tumor, anti-cancer, and anti-inflammatory properties [1].Nanoparticle research is currently an area of intense scientific interest due to a wide variety of potential applications in biomedical, optical and electronic fields [2]. In this research, we report that nano-ZnO (10 mol%) is a highly efficient catalyst for the one-pot four component coupling (4CC) synthesis of 6-amino-2*H*,4*H*-pyrano[2,3-c]pyrazole-5-carbonitriles from aryl aldehydes, ethyl acetoacetate, malononitrile and hydrazine hydrate (Scheme)· The method presented is environment friendly, inexpensive and functionality tolerable to give the products in good to excellent yields.



Scheme

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Nano silicon dioxide as a highly effective heterogeneous catalyst for the rapid synthesis of pyranopyrazoles via a tandem four-component reaction

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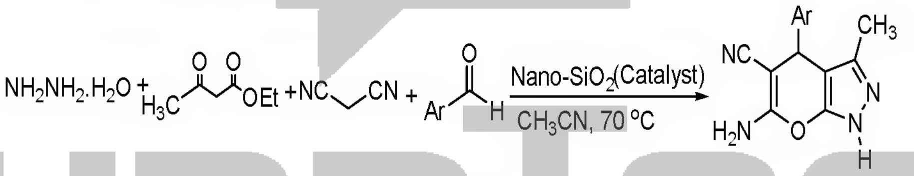
Pyranopyrazoles are fused heterocyclic compounds that possess many biological properties such as fungicidal, bactericidal [1], vasodilatory activities [2] and act as anticancer agents [3]. They also find application as pharmaceutical ingredients and biodegradable agrochemicals [4]. Apart from this, pyrano[2,3-c]pyrazoles have been shown to act as potential insecticidal and molluscicidal agents. As a result, considerable attention has been focused on the development of new methodologies for the synthesis of these heterocycles.

A four-component reaction of hydrazine hydrate, ethyl 3-alkyl-3-oxo propanoate, aldehydes and malononitrile has been achieved in the presence of nano sized silicon dioxide as a highly effective heterogeneous catalyst to produce of 6-amino-3-alkyl-4-aryl-5-cyano-1,4 dihydropyrano[2,3-c]pyrazole derivatives in excellent yields and in a short reaction time (Scheme 1).



Scheme 1

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Large Scale Synthesis of Graphene Oxide

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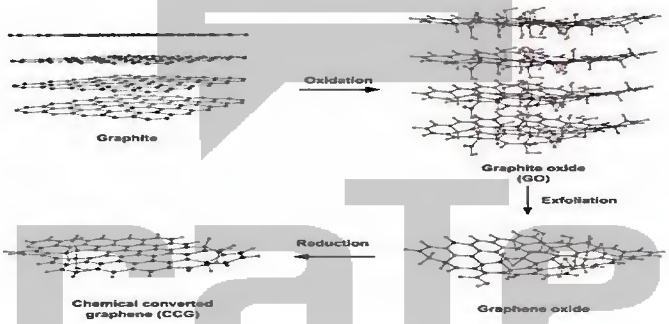
Graphene is a wonder material with many superlatives to its name. It is the thinnest material in the universe and the strongest ever measured. Graphene is a two-dimensional material with layers of carbon atoms that the 6 pieces of the rings are that together have been. Graphene easily be obtained from graphene oxide. In recent years this material has become the most exciting topics. Graphene has attracted much attention from researchers due to its interesting mechanical, electrochemical, and electronic properties. It has many potential applications such as polymer filter, sensor, energy conversion, energy storage devices and the medical field. There is in graphene in fields such as physics, chemistry, and materials science and among others. Interest in graphene's exceptional physical properties, chemical tuneability, and potential for applications has generated thousands of publications and an accelerating pace of research, making review of such research timely. Graphene oxide is a very soft material and in fact is a polymer of carbon, oxygen and hydrogen. In colloidal form in various shapes that can occur. Despite of these benefits and working, the production efficiency is very low. The present work introduce a revolutionary modification of Hummers method for large scale synthesis of graphene oxide (Scheme).



(Scheme)

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Ruthenium Nanoparticles Supported on the Periodic Mesoporous Organosilica as Highly Effective and Recyclable Catalyst for the Aerobic Oxidation of Alcohols

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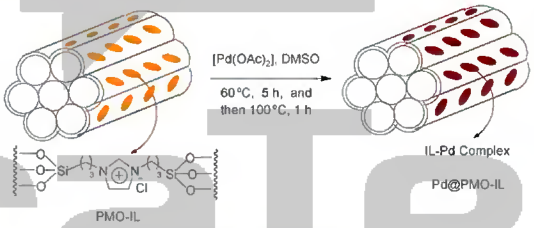
Abstract

The periodic mesoporous organosilica is built from bridge organosilanes of type $(R'O)_3Si\text{-}R\text{-}Si(OR')_3$ wherein organic groups R, are homogeneously distributed throughout the stable inorganic framework [1-2]. Very recently, we have demonstrated for the first time that an ionic liquid based periodic mesoporous organosilica (PMO-IL, scheme 1) is an effective and powerful support for the immobilization and stabilization of Pd nanoparticles on the Suzuki-coupling reaction in water [3], and the aerobic oxidation of alcohols [4]. We have also investigated the use these materials in order to immobilize $Yb(OTf)_3$-pypox catalyst system in the enantioselective Strecker reaction of imines with trimethylsilyl cyanide (TMSCN) to afford the corresponding chiral α-aminonitriles [5]. In continuation of this study, herein, we wish to disclose that a novel ruthenium-supported catalyst comprising PMO-IL material (Ru@PMO-IL) is a highly efficient catalyst for the selective oxidation of a wide variety of alcohols, including not only benzylic and allylic, but also alicyclic and aliphatic alcohols in the presence of molecular oxygen/ or air as the oxidant .



Scheme 1. Preparation of the Pd@PMO-IL catalyst.

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Synthesis and characterization of hybridized nanoparticles of Co-Mn immobilized on bone by osmosis method and its application for oxidation of diphenylmethane to benzophenone.

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In this paper Co/Mn nanocatalyst was prepared by using osmosis method. The nanocatalyst was characterized by XRD, TEM, SEM, BET, and UV-vis techniques and were tested for oxidation of diphenylmethane to benzophenone. Selective oxidation of diphenylmethane to benzophenone is an industrially important synthetic process, as the product benzophenone is known as a component of many consumer products and is used as a fixative for heavy perfumes and in the manufacture of antihistamines and insecticides [1-3]. The synthesized nanocatalyst exhibited high catalytic activitiy for the oxidation of diphenylmethane under heterogeneous conditions. In order to obtain maximum conversion, the reaction parameters such as reaction temperature, time, amount of catalyst and pressure of oxygen gas were optimized. Under the optimized conditions, a maximum of 87% conversion and 90% selectivity was achieved with heterogeneous hybrid Co/Mn nanocatalyst over calcined bone. The reaction did not proceed in the absence of catalyst. Benzophenone was the major product and the other products were found to be benzoic acid and a little amount of other products . The catalyst can be recovered and recycled by a simple decantation.

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Efficient oxidation of sulfides catalyzed by multi-wall carbon nanotubes supported manganese(III) porphyrin

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Metalloporphyrins were designed to mimic the function of cytochrome P-450 and these studies led to finding a number of synthetically useful catalysts for the selective oxidation of hydrocarbons [1]. The main goal in this area is designing selective, stable, and high turnover catalytic systems [2]. Several simple oxidants such as iodosylbenzene, hypochlorite, *m*-chloroperbenzoic acid, hydrogen peroxide and periodates have been extensively studied in the oxygenation reactions catalyzed by metal complexes in order to understanding the mechanism of cytochrome P-450 monooxygenation enzyme [3-7]. The main disadvantage of homogeneous metalloporphyrins is their instability toward oxidative degradation and difficulty in recovery of these expensive catalysts, which limit the practical applications of metalloporphyrin catalysts in both synthetic chemistry and industrial processes. Therefore, immobilization of metalloporphyrins on solid supports can provide catalysts, which are easier to handle, and may exhibit improved selectivities and activities because of the support environment.

Here, efficient oxidation of sulfides with sodium periodate catalyzed by manganese (III) tetrapyridylporphyrin supported on multi-wall carbon nanotubes is reported. This catalyst shows high activity in the oxidation of various sulfides to their corresponding sulfoxides and sulfones at room temperature. The effect of oxidants, solvents, and catalyst amount was also investigated in this catalytic system. This heterogeneous catalyst can be reused several times without significant loss of its activity.

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A convenient and efficient protocol for the preparation of 1,1'-(arylmethylene) diurea derivatives by sulfonic-acic functionalized nano-silica

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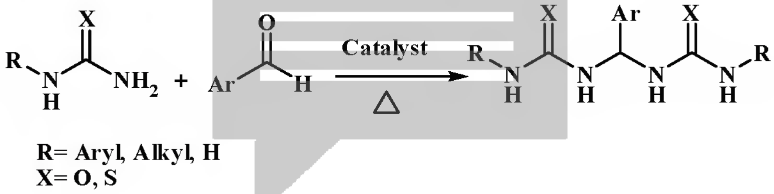
Compounds bearing amide and bisamide groups is important intermediates in organic synthesis since these groups can be easily transformed into other functionalities (such as *gem*-diaminoalkyl and aminoalkyl group) and are of considerable interest in the synthesis of pharmacological materials such as peptidomimetic compounds [1,2]. Therefore, preparation of amides has been attracted considerable attention from the past and in recent years.

The aim of the present protocol is to summarize the data on the one-pot preparation of 1,1'-(arylmethylene) diurea derivatives in good yield using a three-component condensation of an aromatic aldehydes and urea derivatives in the presence of sulfonic acid functionalized nano-silica as catalyst under thermal conditions (Scheme 1).



Scheme 1.

To study the scope of this method, a series of aldehydes and urea derivatives were applied. In all cases, aromatic aldehydes substituted with electron-donating or electron-withdrawing groups underwent the reaction smoothly and gave the products in good yields. All the products were characterized by ^{1}H and ^{13}C NMR spectra, melting point and comparison with authentic samples.

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Application of sulfonic acid functionalized nanoporous silica (SBA-Pr-SO_3H) in the solvent free synthesis of isoindigo derivatives

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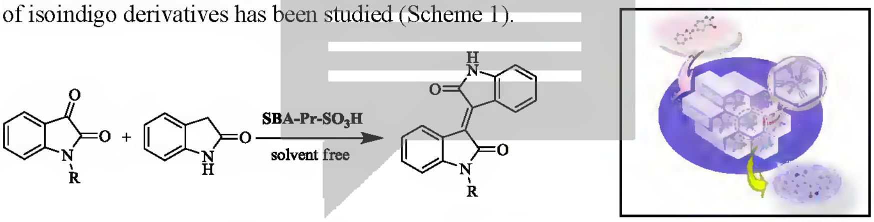
Traditional heterogeneous catalysts e.g. $AlCl_3$ and BF_3 have serious drawbacks in the nature and industries because of their active sites [1]. Mesoporous silica materials have attracted considerable attention for their application as catalyst support [2] and catalyst [3]. SBA-15 was first synthesized by Zhao et al. in 1998 [4, 5] and then sulfonic acid functionalized nanoporous silica (SBA-Pr-SO_3H) was synthesized from SBA-15 as a green solid acid catalyst [6, 7]. Induribin is an active ingredient of a traditional Chinese medicine recipe which used for treatment of leukemias [8]. Isoindigo (3,3′-bisindole) and induribin (3,2′-bisindole) are regioisomer of themselves. In this paper, the condensation of isatin derivatives with oxindole in the presence of nanoporous solid acid catalyst (SBA-Pr-SO_3H) for the preparation of isoindigo derivatives has been studied (Scheme 1).



Scheme 1: synthesis of isoindigo derivatives

A novel and highly efficient method for the synthesis of isoindigo derivatives has been developed in the solvent free reaction of isatin derivatives and oxindole by using recyclable and environmentally benign SBA-Pr-SO_3H as a nano and green solid acid catalyst and nano reactor.

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Palladium supported on periodic mesoporous ionic liquid (Pd@PMO-IL): as efficient and reusable nanocatalyst for the Heck reaction

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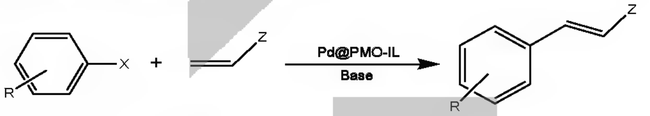
The Mizoroki-Heck carbon-carbon cross-coupling is one of the most important transformations which is very attractive between chemists due to its key role in organic chemistry and drug synthesis.[1-3] The Heck reaction has been traditionally performed in the presence of palladium catalyst under homogeneous conditions using phosphine ligands,[4] more recently *N*-heterocyclic carbenes (NHCs) have been used as wonderful alternative ligands in this regard.[5] However, homogeneous systems suffer from problems including catalyst recovery and product separation.[6] A significant strategy to overcome aforementioned problems is the use of palladium supported on surfaces such as polymers, modified silicas and aluminas,[5] which among them silica supported ionic liquid is very efficient. Although several studies have been developed in this area,[7] however, leaching of palladium catalyst from support surface and formation of Pd-black during reaction progress are still drawbacks of these systems. More recently, we found that a novel ionic liquid based periodic mesoporous organosilica is an efficient and reusable support for the immobilization and stabilization of Pd-catalyst (Pd@PMO-IL) in the Suzuki reaction and aerobic oxidation of alcohols.[8, 9] Herein, we have studied the efficiently of this palladium nanocatalyst in the Heck cross-coupling reaction. The Pd@PMO-IL catalyst was first prepared by treatment of palladium acetate with PMO-IL nanostructure in DMSO solvent under argon atmosphere. Then the application of the catalyst was investigated in the Heck coupling of variety of different activated and deactivated aryl halides with alkenes (Scheme1). The results showed that the catalyst can be recovered and reused several times without any decrease in activity and selectivity.



R: Activated and deactivated groups
Z: CO_2CH_3 or $CO_2CH_2CH_3$

Scheme 1: Heck cross-coupling reaction of aryl halides with alkenes in the presence of **Pd@PMO-IL**

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Hydroxyl-Terminated Polybutadiene Epoxidation Using *In Situ*-Generated Dimethyl Dioxirane and Nano TiO_2

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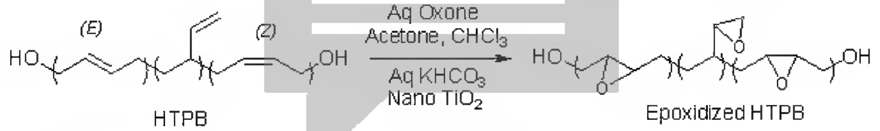
The introduction of one or more epoxy functional groups in non-polar polymer chains that contain non-conjugated carbon–carbon double bonds can increase the polarity of the final polymers and lead to the production of new special polymer products [1]. There are some experimental methods for the epoxidation of C=C bonds in the polymer structure such as, thermal oxidation [2], oxidation with $Vo(acac)_2$ complex [3] and epoxidation using peroxide [4] and peracids [5] but all of them have some advantages and disadvantages, for example the epoxidation process was accompanied by several side reactions and higher temperatures were needed in order to obtain higher conversion degrees. These drawbacks can be solved by using in situ-generated dimethyl dioxirane (DMD) in epoxidation of double bonds. In situ generated DMDs are cyclic peroxides known as powerful, reactive and efficient oxidizing agents and DMD usually prepared from the reaction of acetone and aqueous "Oxone®" ($2KHSO_5$, $KHSO_4$, K_2SO_4) in buffered conditions. In this report, the results indicate that using nano TiO_2 as a catalyst increases the epoxidation yield, especially of cis double bonds.



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The first chemical synthesis Polythiophene/Ag Nanocomposites by use of $AgNO_3$

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The interest in the development of inorganic/organic composite has grown rapidly due to the wide range of high potential application of these materials. Among the organic part is conducting polymers, such as polyaniline(PANi), polypyyrole(PPy) or polythiophene(PTh)[1]. Among electrically conducting polymers, PTh is the most important material because of their distinctive electrochemical, magnetic, and optical properties as well as their wide range of applications. Current important application areas include solar cells, supercapacitors, support materials, sensors, field effect transistors and other electronics devices[2]. Conducting polymers have redox properties and have been shown to be excellent hosts for trapping nobel metal such as silver and gold. Among nobel metals, silver nanopaticles have gained much interest due to its applications in catalysis, in conducting ink, as a substra in surface enhance Raman spectroscopy, in anticancer activity[3], optical sensor and as a potential antibacterial agent[4]. In this novel approache, no additional reducing/oxidizing agent, or surfactant was employed. $AgNO_3$ was completely dissolved in H_2SO_4(as a dopant), Then thiophene was dropwise added under vigorous stirring. The molar ratio $AgNO_3$/thiophene was taken 1:2. Thiophene, $AgNO_3$ and H_2SO_4 were mixed and this reaction was carried out under N_2 atmosphere for 3h.

Results: Ag/PTh nanocomposites have been prepared by reducing $AgNO_3$. The resulting products were characterized by analysis FT-IR, UV-vis, XRD, SEM, TEM. we observed a strong interaction between the Ag^+ ion and sulfur atom of thiophene ring. Therefore Ag^+ ion was reduced to Ag nanoparticles and thiophene was oxidized to polythiophen. This work provides a simple route for the synthesis of Ag/PTh nanocomposites.

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Synthesis Polythiophene/Ag Nanocomposites by use of Ag presynthesized

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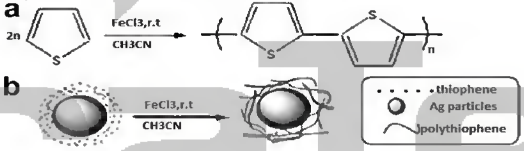
The inorganic-organic hybrids are a promising class of new materials, owing to the advantageous properties of the polymer matrix and the embedded inorganic particles. The combinations often lead to synergistic effects, resulting enhanced properties, making these materials applicable in various fields. conjugated polymers such as polypyrrole(PPy), polyaniline(PANi), have been succssesfully combined with different inorganic materials including metal nano particles (Ag, Au, Cu, and pd), leading to nanocomposites with high conductivity, catalytic activity, thermoelectric properties[1], etc. Polythiophene(PTh) as conducting polymer has attracted considerable attention over the past years due to numerous solid states potential applications in many fields, such as microelectronic devices, catalysts, organic field effect transistors and chemical sensors and biosensors[2]. Among nanoprticles, silver nanopaticles have gained much interest due to its applications in catalysis, in conducting ink, as a substra in surface enhance Raman spectroscopy, in anticancer activity, optical sensor and as a potential antibacterial agent[3]. In present work, Ag nanoparticle were synthesized by reaction of silver nitrate($AgNO_3$) with sodium borhyride($NaBH_4$). A Known mass of Ag prepared was finely dispersed in a conical flask containing acetonitrile(CH_3CN), after which a known quantity of thiophene was injected. A particular amount of solution $FeCl_3$ in CH_3CN was then added to the solution in one go. The reaction mixture was magnetically stirred at room temperature(r.t).

Results: PThs are often considered to be useful matrices for the immobilization of the dispersed nobel metal nanoparticles. The porous structure of conducting polymer allows dispersing the metal particles into the polymer matrix and generates additional electrocatalytic sites. more over, incorporation of metal nanoparticles into conducting polymers provides enhanced performance for both the "host" and "guest". The resulting Pth/Ag composites characterized by FT-IR, UV-vis; SEM, TEM and XRD.



Scheme 1. Schematic representation of the process for a) polymerization of thiophene and b)formation of PTh/Ag composites.

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Nanocrystalline Silver Iodide Catalyzed Three Component Coupling of Aldehydes, Amines and Alkynes under Solvent Free Conditions

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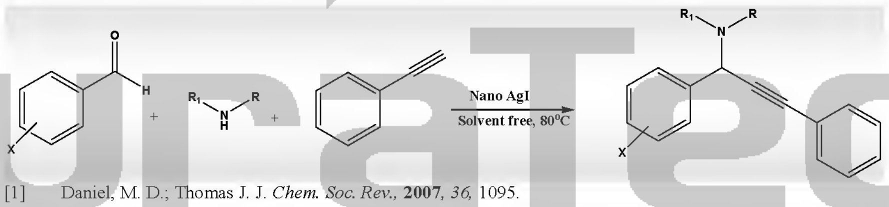
Multicomponent reactions (MCRs) are special types of synthetically useful organic reactions in which three or more different starting materials react to give a final product in a one-pot procedure. MCRs are powerful tools in the modern drug discovery process and allow the fast, automated, and high-throughput generation of organic compounds [1]. Propargylic amines product of the A^3-coupling between aldehydes, amines and alkynes, are useful building blocks as well as important skeletons of biologically active compounds. The synthesis of propargylic amines derivatives has been received special attention to chemists because of their wide range of therapeutic and biological properties, such as antibacterial, antiviral, and anti-inflammatory activities [2,3]. In this work we used AgI nanoparticles as an efficient catalyst for the multicomponent reactions for the synthesis of propargylic amines which could be successfully carried out under mild conditions in the absence of both the ligands and strong bases. In conclusion, we have developed an efficient, inexpensive, and environmentally benign catalyst system for the efficient carbon-carbon and carbon-heteroatom coupling to the synthesis of propargylic amines derivatives in the presence of silver iodide nanoparticles under solvent conditions. Silver iodide nanoparticles as an efficient, non-volatile, recyclable, non-explosive, catalyst can be used in catalysis many organic reactions.



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Sulfonic Acid Supported on Magnetic Nanoparticles as Magnetically Recyclable Heterogeneous Catalyst for the Efficient Synthesis of Bis(pyrazolyl)methanes

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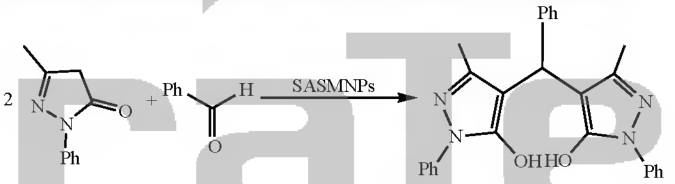
nanoparticles (NPs) have been used as alternative matrix for supporting homogeneous catalysts. As a consequence, NPs could have a higher catalyst loading capacity and a higher dispersion than many conventional support matrices, leading to an improved catalytic activity of the supported catalysts. However, conventional separation methods may become inefficient for support particle sizes below 100 nm. The incorporation of magnetic NPs (MNPs) such as iron oxide into supports offers a solution to this problem [1,2].

Pyrazoles are an important class of bio-active drug targets in pharmaceutical industry [3,4]. For example, they exhibit anti-anxiety, antipyretic, analgesic and anti-inflammatory properties. 2,4-Dihydro-3*H*-pyrazol-3-one derivatives including 4,4′-(arylmethylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ols) which have a broad spectrum of approved biological activity, are being used as anti-inflammatory, antipyretic, gastric secretion stimulatory antidepressant, antibacterial and antifilarial agents [5,6].

Here, we report an efficient method for the synthesis of a variety of bis(pyrazolyl)methanes by sulfonic acid supported on magnetic nanoparticles (SASMNPs) as an efficient catalyst. Good to high yields, short reaction times, simple work-up, ease of catalyst recovery, no by-product formation and re-usability of the catalyst without appreciable loss of activity make this method attractive and a useful contribution to the present methodologies.



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A novel polyamidoamino dendrimer based on carbon nanotube as nanocarrier

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Abstract

Dendrimers are a novel macromolecule with highly branched dendritic molecules which possess unique properties including relatively large molecular size, narrow size distribution, welldefined globular structure, and ease of derivatization via the peripheral functional groups. These properties have attracted a great interest in exploring their potential applications such as macromolecular catalysis [1], drug delivery [2], gene transfection, and imaging [3], magnetic resonance imaging (MRI) contrast agents [4], and metal ion extraction [5]. Dendrimer polyamidoamine (PAMAM) as one of commercial ones due to the controllable mass, the water solubility, and the possibility of surface functionality, has been widely used in the biomedical and genetics [6].

In this work we describe the synthesis, characterization and properties of polyamidoamino (PAMAM) dendrimer based on carbon nanotube. Polyamidoamino dendron were synthesized from triazine as core through divergent method and t repetitive Michael addition and amidation reactions. In the first step, synthesis was initiated divergently from a functionalized Triazine containing ethylenediamine and aromatic molecules.. Then carbon nanotubes were functionalized by Polyamidoamino dendron. In these cases, non-covalent functionalization is accomplished by the interaction of delocalized π-bonds on the CNTs wall due to sp^2 hybridization with π-bonds of aromatic rings on functionalized.

Loaded palladium nanoparticles by ddendrimer were used as the nanocatalyst for the Heck reaction between iodobenzene and ethyl acrylate. The majority of reaction occurred in the first hour, and the rate of reaction in the presence of nanocatalyst was very high. These results show that the rate of the Heck reaction is very high in the presence of catalyst and that (PAMAM) dendrimer can be used to transport and support catalysts. Structure, characteristics and catalytic activity of synthesized systems was investigated using spectroscopy and microscopy methods.

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The Silica(acac) Supported Pd(0) Nanoparticles As An Efficient And Reusable Heterogeneous Catalyst In The Suzuki-Miyaura Cross-Coupling Reaction

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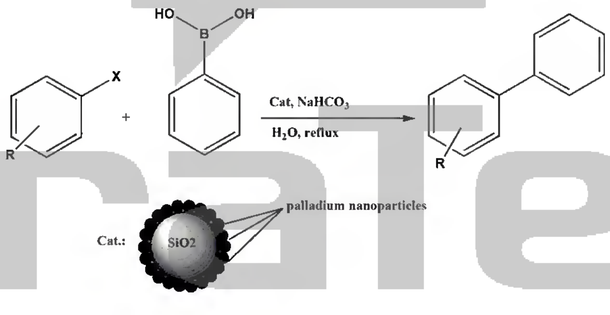
The Suzuki–Miyaura coupling reaction is one of the most straightforward and powerful palladium-catalyzed methods for selective C–C bond formation [1,2] and due to its importance in synthesis of natural products and functional materials, huge number of studies have been devoted to the development of this cross-coupling reaction [3].

Herein we wish to report the preparation of silica(acac) supported Pd(0) nanoparticles as an efficient and novel heterogeneous catalyst that efficiently can be applied for the Suzuki–Miyaura, coupling reaction. This catalyst was synthesized and its application was investigated in Suzuki–Miyaura coupling reaction. The products were produced in good to excellent yields using a catalytic amounts of Pd(0) nanoparticles. The reaction was carried out in H_2O as a solvent under green conditions in the presence of $NaHCO_3$ as the friendly base.

There are several advantages in this work over reported methods, including easy separation of the product and recovery of the catalyst as a heterogeneous catalyst, the catalyst is not sensitive to oxygen, and the reactions were carried out under ambident atmosphere.



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Synthesis of Polythiophene-SnO_2 Nanocomposites and Studying their Physical Properties

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Polymer and metal oxides have been studied for many years for their independent electrical, optical, and mechanical properties. Recently, the combination of semiconducting and mechanical properties of conjugated polymers with the properties of metals or semiconducting inorganic particles has brought new prospects for applications. Encapsulation of inorganic nanoparticles inside the shell of conducting polymers is the most popular and interesting aspect of nanocomposites synthesis and they have unique microstructure, outstanding physiochemical Synthesis of polythiopheneconstructing nanoscopic assemblies in sensors and microelectronic [1-4].

This research work describes an efficient method to synthesize and characterization of polythiophen/tin dioxide (PT/SnO_2) nanocomposites by one-step *in situ* polymerization of thiophene. Using $FeCl_3$ as an oxidant in the presence of different amount of SnO_2 nanoparticles. The obtained Fourier-transform infrared (FTIR) spectra of PT/SnO_2 nanocomposites showed that the FTIR spectra of nanocomposites are similar of the PT spectrum, which shows that PT chains have been formed in the nanocomposites. Also, the resulted X-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscope (SEM) data confirmed that SnO_2 nanoparticles are encapsulated by PT polymer. Electrical conductivity measurements indicate that the conductivity of nanocomposites decreases with increasing SnO_2 content.

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Synthessis Nano-copper chromite catalysts ($CuCr_2O_4$) for employe in the several organic reaction

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The copper chromite ($CuCr_2O_4$) is one of the most efficient materials, has wide commercial application as catalysts being used in the unit processes of organic synthesis such as hydrogenation, dehydrogenation, hydrogenolysis, oxidation, alkylation, cyclization, etc. It can be used in the pollution abatement as the catalyst to remove aqueous organic wastes, volatile organic compound (VOC) and vehicular primary emissions such as CO, unburned hydrocarbon, NO x and soot[1]. In addition it has been used in various composite solid propellants as one of the efficient combustion supporting catalysts in the domain of space vehicles (rockets) and weapon industries (high explosives, ballistic missiles). Furthermore, copper chromite has been proved as promising catalyst for the production of H_2 a clean energy carrier, by photo-catalytic phenomena, conversion of alcohols, water gas shift reaction, through sulphur based thermo-chemical water splitting cycles, etc. The next application of $CuCr_2O_4$ is catalyst for alternative fuels preparations[2], synthesizing methanol, an important hydrogen carrier; high alcohol synthesis (HAS) by hydrogenation of CO or CO_2[3] , and fast pyrolysis of biomass to bio-oil products[4]. The catalyst is also helpful in the production of drugs and agro chemicals. In fine chemicals industry for perfumery and synthesis of fragrances[5] . In this article we present the synthesis of Cu-Cr-O nanocomposites via a citric acid (CA) complexing approach. Techniques of thermo-gravimetric/differential thermal analyzer (TGe DTA), X-ray diffraction (XRD), transmission electron microscopy (TEM) as well as scanning electron microscopy (SEM) have been employed to characterize the thermal decomposition procedure, crystal phase, microstructural morphologies and grain size of the as-synthesized materials, respectively. The results show that well-crystallized Cue Cr e O nanocomposites can be produced by using a temperature as low a s 600 ^{0}C. Phase structure of the as-obtained Cu-Cr -O nanocomposites depends on the Cu/Cr molar ratio in the starting reactants.

Keywords: Copper chromite composite oxide; Sole gel chemistry; Citric acid; Nanomaterials; Catalysts;

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Sulfonic acid-functionalized ordered nanoporous Na$^+$-montmorillonite (SANM) as a novel, efficient and recyclable catalyst for the one-pot synthesis of 1,8-dioxo-dodecahydroxanthene derivatives

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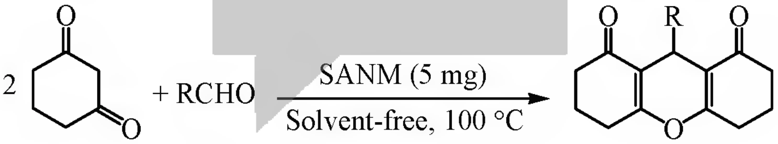
This article reports the anchoring of sulfonic acid moieties onto natural clay (sodium montmorillonite) for the synthesis of a novel and efficient catalyst [1]. Catalyst preparation included the reaction of sodium montmorillonite with chlorosulfonic acid to bond the internal and edge hydroxyl groups of the clay to sulfonic acid moieties. The synthesized catalyst was characterized by FT-IR, TEM, BET, XRD, TGA and Elemental analysis. We have found that the prepared reagent can be used as an efficient catalyst for the promotion of the synthesis of various 1,8-dioxo-dodecahydroxanthene derivatives by the reaction of aldehydes with 1,3-cyclohexanedione respectively (Scheme 1). This novel synthetic method has the advantages of high yields, short reaction times, low cast and recyclability of the catalyst, simplicity and easy work-up compared to the conventional methods reported in the literature.

Keywords: Xanthenes, aldehydes, 1,3-cyclohexanedione, Na$^+$-montmorillonite



Scheme 1

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Polypyrrole/Zinc Oxide Nanocomposite Films: Synthesis and Characterization

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During the past decade, nanotechnology has become an active field of research because of its tremendous potential for a variety of applications. Conducting polymer–inorganic oxide nanocomposites have recently attracted great attention owing to their unique microstructure, outstanding physiochemical and electro- optical properties, and wide range of potential uses as a battery cathode and also in constructing nanoscopic assemblies in sensors and microelectronics [1]. Polypyrrole (PPy) is a conductive polymer with a conjugated-electron backbone that displays unusual electronic properties and uses in batteries, supercapacitor, bio sensors, conductive textiles and fabrics, mechanical actuators, electromagnetic interference shielding, antistatic coating, and drug delivery systems [2]. ZnO is semiconducting in nature having unique properties like large exciton binding energy (60 meV) and relatively large direct band gap of ~ 3.3 eV at room temperature [3].

In this research work, PPy was synthesized by chemical oxidative polymerization method using ferric chloride ($FeCl_3$) as an oxidant in the HCl solution [4]. The known amount of PPy powder was dissolved in NMP solvent and ZnO nanoparticles in different amounts were dispersed in PPy solution and stirred continuosly. The films from these composites solutions were prepared on a glass substrate by the solution casting technique and dried at room temperature. PPy/ZnO nanocomposite films were characterized Fourier-transform infrared (FTIR), thermogravimetric analysis (TGA), X-ray diffraction (XRD), and scanning electron microscope (SEM) techniques for their structure and morphology. The synthesized PPy/ZnO nanocomposite films had higher thermal stability than that of pure PPy. Also, the electrical conductivity of the obtained nanocomposites was investigated by four-point probe instrument.

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Pd nanoparticles immobilized on Fe_3O_4@SiO_2–PAMAM as recoverable catalysts for Heck reaction

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Recently, nanosized Pd catalysts have attracted considerable interest in chemistry and material sciences, due to the potential value of their applications [1–3]. However, having small sizes and high surface areas, colloidal nanosized catalyst particles have some disadvantages in practical processes, such as serious aggregation and inefficient separation. To overcome these limitations, a great deal of attention has been paid to solidsupported heterogeneous nanosized catalyst particles [4–7].

This study reports the syntheses of Fe_3O_4@SiO_2–G_n–PAMAM–Pd(0) and their applications as magnetically recoverable catalysts for the Heck reaction. The PAMAM dendrimers were grown on the surface of Fe_3O_4@SiO_2 to obtain the Fe_3O_4@SiO_2–G_n–PAMAM employing a divergent route starting from the amine-functionalized Fe_3O_4@SiO_2. A Michaeltype addition reaction took place between the pre-existing amino groups and the methyl acrylates.The controlled growth of polyamidoamine (PAMAM) dendrimers with different generations on Fe_3O_4@SiO_2 surfaces was monitored by FT-IR spectra. Subsequently, Pd nanoparticles with diameters of about 2.5 nm were stabilized homogeneously on the surface of Fe_3O_4@SiO_2–G_n–PAMAM ($n = 1–3$), investigated by transmission electron microscopy (TEM) measurements. The Fe_3O_4@SiO_2–G_n–PAMAM magnetization behaviour obtained using the VSM. In particular, the composites made of superparamagnetic Fe_3O_4 nanocrystals with diameters of about 19 nm are very suitable as catalyst supports for catalyst separation under a relatively low external magnetic field and catalyst re-dispersion after removing the external magnetic field.

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Novel Types of Polyimide-Silica Nano-Hybrids: Synthesis and Investigation of Morphology and Thermal Properties

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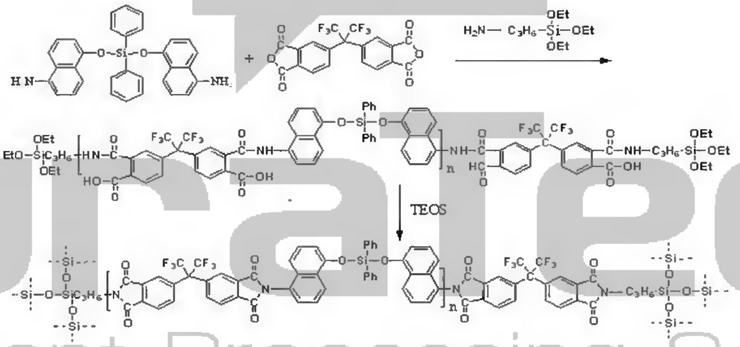
Numerous methods to obtain polyimides with chemically modified chain structures have been introduced for balancing of the thermal stability and the processability [1]. The main structural modifications to attain processable polyimides have been carried out by introducing flexible spacers and also bulky substitutes such as pendent aryl rings into their backbone. Nowadays, polyimide-inorganic hybrid materials have become a popular topic in material science because of their excellent properties [2,3]. A new bulky siloxane-based diamine was prepared and used for the synthesis of related polyimide via reaction with hexafluoroisopropylidene diphthalic anhydride (6FDA). Polyimide-silica (PI-SiO_2) hybrids with a nanostructure were successfully prepared using the sol-gel process of tetraethoxysilane in the presence of aminopropyl triethoxysilane-end capped poly(amic acid) solution. The chemical structure of the samples was characterized by FT-IR, EDAX, and elemental analysis. Morphology of the films was investigated by SEM, TEM, and XRD. TGA and DMTA were used to measure the thermal performance of the nano-hybrids. Si-mapping of samples indicated that SiO_2 particles were well distributed in PI matrix with particle size of about 60 nm. The results also indicated that T_g and decomposition temperatures of the nano-hybrids increased with increasing silica content up to 20% with respect to pure polyimide.



Scheme1. Preparation of the polyimide-silica nano hybrid

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MCM-41-nPrNH$_2$ as an efficient nano-catalyst for the synthesis of 2-phenyl-imidazo[1,2-a]pyridine derivatives

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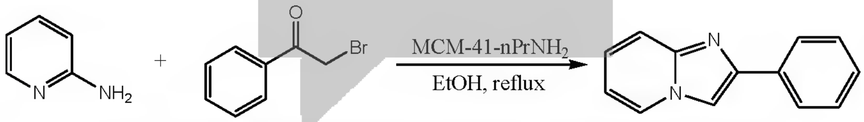
Amino propyl anchored on MCM-41 was used as a basic catalyst for the rapid and 'green' synthesis of 2-phenyl-imidazo[1,2-a]pyridine derivatives. This solid base catalyst is found to be very efficient with reusability for a number of times and consistent activity. Solid catalysts possess numerous advantages over soluble homogeneous catalysts as they can be easily recovered from the reaction mixture and reused. The imidazo[1,2-a] annulated nitrogen heterocycles bearing pyridine, pyrazine and pyrimidine moieties constitute a class of biologically active compounds that are potent anti-inflamatory and antibacterial agents[1], inhibitors of gastric acids secretion[2] and calcium channel blockers [3]. Also these compounds were identified as a novel class of MtGS inhibitors [4].

In connection with our interest in the preparation and use of solid catalysts for the production of fine chemicals, in the present work, aminopropyl was bonded onto MCM-41 mesoporous molecular sieves, which was found to be a highly active basic catalyst towards the synthesis of 2-phenyl-imidazo[1,2-a]pyridine from the reaction of phenacyl bromide and 2-aminopyridine in ethanol under reflux condition (Scheme 1).



Scheme 1 Synthesis of 2-phenyl-imidazo[1,2-a]pyridine derivatives *via* MCM-41-nPrNH$_2$

In summary, this new solid base catalyst has the following advantages: (a) short reaction times (b) high yields (c) high catalytic activity under mild reaction conditions, (c) easy separation of the catalyst after the reaction and (c) reusability of the catalyst for several times.

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$FeCl_3/SiO_2$ NPs; A Recyclable Heterogeneous Catalyst for the Synthesis of highly substituted functionalized oxazines

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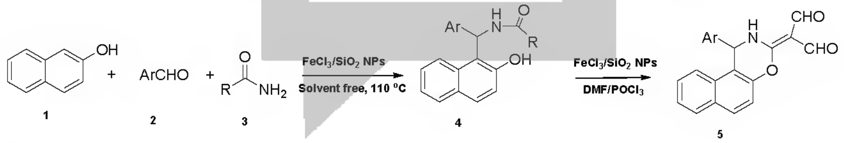
Solid supported reagents are unique acid catalysts that have become popular over the last two decades. The activity and selectivity of a reagent diffused on the surface of a support is amended as the effective surface area of the reagent is increased multifold, and thus they are expected to perform more effectively than the individual reagents [1]. Among various solid supports, nano silica is usually preferred since it displays many advantageous properties such as high surface area, excellent stability (thermal and chemical), good accessibility, and organic groups can be robustly anchored to the surface; to provide catalytic centres [2,3].

We herein describe a new, convenient synthesis of amidoalkyl naphthols by multicomponent reaction of 2-naphthol, aromatic aldehydes and acetamide catalyzed by $FeCl_3/SiO_2$ NPs under solvent free conditions. Then, the prepared amidoalkyl naphthols were treated with Vilsmeier reagent in the presence of $FeCl_3/SiO_2$ NPs at room temperature to give oxazine derivatives.



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Silver Iodide (AgI NPs) as a green and efficient catalyst for one pot synthesis of 1,2-dihydro-1-arylnaphtho[1,2-*e*][1,3]oxazine-3-ones

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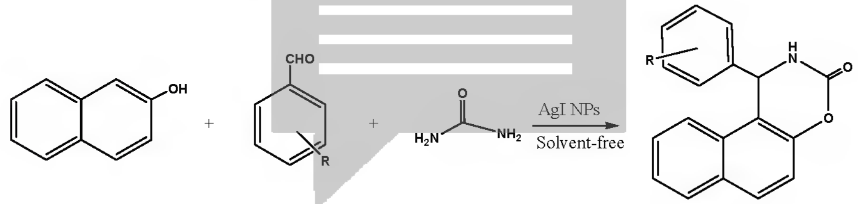
Multicomponent coupling reactions have become of growing relevance in the development of efficient new syntheses [1,2]. When coupled with the reactivity of metal catalysts, this approach can be particularly effective in the conversion of simple building blocks directly into important functional subunits [3]. Oxazinone, benzoxazinone and their derivatives are an important class of heterocyclic compounds, because many of these heterocyclic systems exhibit biological activities, such as HIV-1 reverse transcriptase inhibitors [4]. For example, naphthalene-condensed 1,3-oxazin-3-ones have been reported to act as antibacterial agents [5].

The reaction of 2-naphthol, benzaldehyde, and urea in the presence AgI NPs was carried out under thermal solvent-free conditions for 10 min. In conclusion, a reliable, rapid, and environmentally benign method for synthesizing 1-amidoalkyl-2-naphthols has been developed. In addition to the purity of the products, the short reaction times and ease of work-up make the method advantageous.



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Preparation of the novel chiral nanocomposite by doping of poly[(±)-2-*sec*-butylaniline] with nanosilica sulfuric acid as solid acid dopant under solid-state condition

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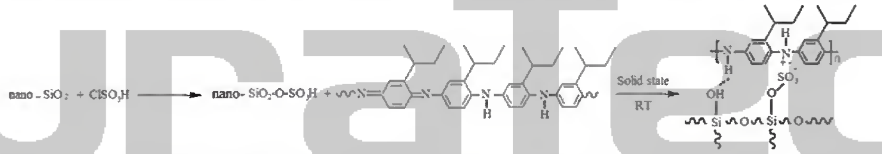
Polyaniline (PANI) is an organic conducting polymer that is well-known as an environmentally stable and highly tunable conducting polymer, which can be produced as bulk powder and films with the feasibility of low-cost and large-scale production. So it has great potential for commercial applications, such as antistatic coatings, corrosion-prevention coatings, chemical sensors, supercapacitors, batteries and energy storage [1]. However, it is difficult to process because of its insolubility in most of the common solvents. In the process of improving processability of PANI, many composites have also been prepared. In the case of polyaniline, the inorganic particles such as metal oxide (Fe_3O_4, TiO_2, SiO_2, WO_3) and metals (Au, Ni, Ag) were also used for the polyaniline based composites. Among them the use of silica particles is continuously growing because of its high specific area, large porous volume, and large mechanical and thermal stability [2].

Herein we wish to report a new application for solid acids such as nanosilica sulfuric acid (SSA) [3]. In this work poly [(±)-2-sec-butylaniline] base was synthesized from its salt form by the solution method, then base polymer was combined with nanosilica sulfuric acid without any solvent in mortar for first time. Doping process of nanocomposite was confirmed by FT-IR and UV-Vis. The morphology and size of nanocomposite particles determined by the scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The nanocomposite particle size was 25 nm before workup (bw) and 29 nm after workup (aw).



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Three-component synthesis of highly functionalized imidazoles via PEG-SO_3H as green and homogenous catalyst

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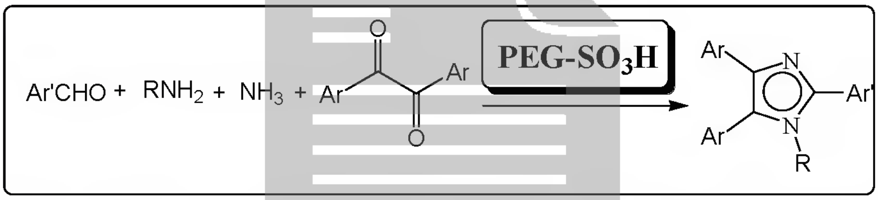
Compounds with moiety of imidazole have biological and pharmaceutical applications, such as being as an antagonist and inhibitor. [1-3] Acid-catalyzed one-pot, four-component condensation of aldehydes, amines and benzyl in presence of ammonia is an efficient method for preparation of the fully functionalized imidazoles derivatives. [2]



In this paper we have introduced a polyethyleneglycole supported sulfuric acid catalyst (PEG-SO_3H). PEG-SO_3H via high efficiency in homogenous media, and with high yield productivity used in preparation of the fully substitute imidazoles. Reusability of the catalyst is another advantage of the PEG-SO_3H that can be mentioned even in homogenous condition.

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Ionic Liquid / MWCNT-Composite, Application to Fabrication of Biosensor

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Carbon nanotubes (CNTs) are considered as an important group of carbon based nanomaterials with attractive electronic, chemical, and mechanical properties. Their unique properties and high surface area make them extremely attractive for adsorptions organic molecules based on π-π stacking. Due to the ability of carbon nanotubes to facilitate the electron-transfer reactions, the CNTs were used in catalytic and electrocatalytic process frequently [1,2]. Another important class of materials is ionic liquids (ILs). Because of their high stability, high electrical conductivity, and very low vapor pressure, ILs hold a great promise for green chemistry applications in general and for electrochemical applications in particular. Recently, a new composite has been fabricated using multiwall carbon nanotubes (MWCNT) and the ionic liquids. These composite shows very attractive properties compared to other conventional composites using graphite and mineral oil, such as carbon ceramic, carbon paste, sol-gels and polymers notably improved stability [3,4]. In this work, 1-buthyl-3-methylimidazolium hexafluorophosphates and carbon nanotube were used to fabrication of IL/CNTs-Composite. This composite frequently used to modification of electrode and construction of sensors and biosensors. The IL/CNTs-Composite used to loading of the palladium complex. The immobilization of Pd-Complex was done by simply immersing of glassy carbon modified IL/CNTs electrode into Pd-Complex acetonitrile solution. Evaluation of modified electrode by cyclic voltammetry and in different scans rates implied that this redox couple can be used as a shuttle of electron during the oxidation of NADH. Due to the production of NADH during the oxidation of alcohols by alcohol dehydrogenase in presence of NAD^+, the IL/CNTs/Pd-complex electrodes have exhibited strong and stable electrocatalytical response towards ethanol.

The used Pd-Complex was synthesized by refluxing homoveratrylamine and 2,6-dichlorobenzaldehyde in a 1:1 molar ratio in ethanol for 2h. The formed Schiffbase was reacted with $Pd(OAc)_2$ (1:1) in CH_2Cl_2 followed by treatment in situ with NaBr gave the insoluble dimeric complexe with bromine bridges [5].

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SCF-MO Ab-initio study of structure of hetero metaphanes

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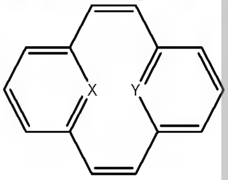
Hetro metaphanes are compounds possesing an aromatic and a hetro aromatic rings and an aliphatic units forming a bridge between at least two positions of the aromatic rings. They exhibit an interesting stereochemistry molecular parts are placed and sometimes fixed in unusual orientations toward each other, and often the molecules are not rigid but (conformationally) flexible. Ring strain and, as a consequence, deformation of the aromatic rings out of planarity are often encountered.[1, 2]
In this study we try to report the ab-initio calculations on metacyclophane structures with defferent hetro aromatic rings (Scheme 1) to have the effect of heteroatom on the conformation of meta hetrophanes.
Some meta heterophanes **1** optimized at HF/6-31+G* level of theory using Gaussian software.[3] Heats of formations (HF, in hartree) and optimized structures were summarized in Table1 (3rd raw for non planar and 6th raw for planar structures).



1	a	b	c	d	e	f
X	N	P	B	P	B	B
Y	N	P	B	N	N	P

Table 1

	a	b	c	d	e	f
C=C	1.33	1.34	1.33	1.37	1.38	1.36
X-X	2.39	3.07	1.71	1.81	1.82	1.47
HF	-644.8191577	-1217.2875661	-585.2261471	-931.0872104	-901.3335262	-615.1798292
C=C	1.38	1.37	1.35	1.41	1.38	1.36
X-X	1.45	1.88	1.64	1.64	1.74	1.46
HF	-644.7408868	-1217.105618	-585.2806471	-930.9098697	-901.3224948	-615.179830098
ΔE	49.11	114.17	-34.19	55.54	6.92	0.00

Comparison of distance between heteroatoms indicated that increasing the radius of heteroatoms (P-P>N-N>P-B>P-N>B-B>N-B) increased ΔE of planar and non-planar structures. Among compounds **1a** and **1d** are suitable to be proper nano switches.
In summary conformation of metacyclophanes were under control of several parameters such as the type and the radii of hetero atoms. If would be of course to have direct conformational data concerning all stable conformers of studied molecules for comparison with the results of the ab-initio calculations.

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Synthesis and Characterization of Emeraldine Base Polyaniline/Zinc Oxide Nanocomposite Films

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Inorganic nanoparticles of different nature and size can be combined with the conducting polymers, giving rise to a host of nanocomposites with interesting physical properties and important application potential [1]. Over the last three decades, conductive polymers have been investigated extensively. Among the conducting polymers, polyaniline (PANI) has been of great interest to many researchers because of its reasonably good conductivity, stability, easy preparation, affordability and redox properties [2]. Both insulating emeraldine base (EB) and conducting emerladine salt (ES) are the stable forms of polyaniline. Wide band gap and semiconductivity of zinc oxide makes it an attractive material for wide variety of applications such as solarcells, sensoring applications. Due to its excellent optical and electrical properties zinc oxide also found to be potentially applicable in lasers light emitting diodes nanoresonators and cantilevers [3].

In this research work, EB-PANI was synthesized by chemical oxidative polymerization of aniline in HCl solution using ammonium peroxidisulphate [4]. The obtained polymer was then reacted with ammonia solution to obtain turned blue EB-PANI. The known amount of EB powder was dissolved in NMP solvent and ZnO nanoparticles in different amounts were dispersed in EB solution and stirred continuosly. The films from these composites solutions were prepared on a glass substrate by the solution casting technique and dried at room temperature. The obtained films were characterized by Fourier-transform infrared (FTIR), thermogravimetric analysis (TGA), X-ray diffraction (XRD), and scanning electron microscope (SEM) techniques for their structure and morphology. The synthesized nanocomposites had higher thermal stability than that of pure EB-PANI.

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An Efficient and Facile Ultrasonic-Accelerated One-Pot Synthesis of of 3,4-dihydropyrano[c]chromenes with ɣ-Fe2O3 nanoparticles

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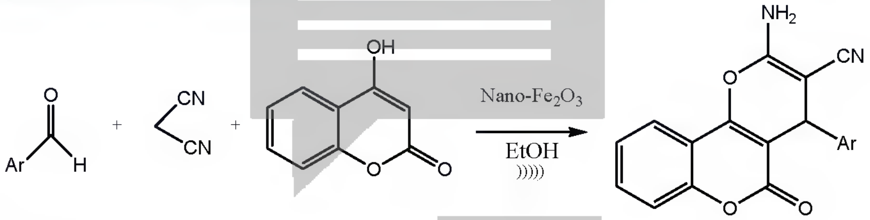
Nowadays, ultrasonic irradiation technique has been employed not only to decrease reaction times but also to improve yields in a large variety of organic synthesis. we were encouraged, in this paper, to study useful application of ultrasound in the highly efficient one-pot synthesis of a variety of 4H-chromenes derivatives via condensation reaction between aromatic aldehydes, malononitrile with 4-hydroxycoumarin in ethanol under the10 wt% of ɣ-Fe2O3 catalyst.The advantages of this protocol include a simple workup, high rates, use of inexpensive non-toxic catalyst, improved yields, and use of ethanol as a relatively environmentally benign solvent. Pyrano [3,2-c]chromene derivatives are a class of important heterocycles with a wide range of biological properties [1] such as spasmolytic, diuretic, anticoagulant, anti-cancer, and anti-anaphylactic activity[2] . Moreover they can be used as cognitive enhancers, for the treatment of neurodegenerative diseases,including Alzheimer's disease, amyotrophic lateral sclerosis, Parkinson's disease, Huntington's disease, AIDS associated dementia and Down's syndrome as well as for the treatment of schizophrenia and myoclonus[3] .



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The Synthesis Of Poly(propyleneimine) Dendrimer Aldehyde End Groups (PPI-CHO) In Two Generations

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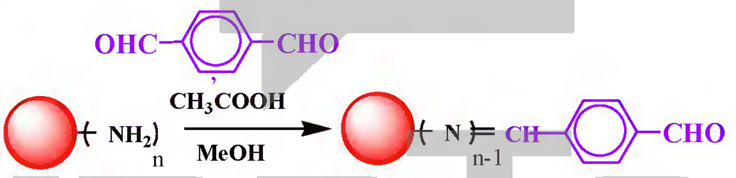
Poly(propyleneimine) dendrimer (PPI) is a nanostructure that is precisely engineered to carry molecules encapsulated in its interior void spaces or attached to the surface [1,2]. Terminal amine groups of PPI dendrimers can be substituted by various functional groups for applications[3,4] .In this study ,PPI derivatives with aldehyde end groups were synthesized from 1,4- butanediamine core with generations 1 and 2 primary amine terminal dendrimer [5,6].the synthesis of PPI-CHO dendrimers (G1& G2 generation numbers) were carried out by addition of terephthaldialdehyde in acetic acid and MeOH .

PPI-CHO dendrimer was characterized by FT IR,^{1}H NMR, ^{13}C NMR spectrums. The synthesized dendrimer derivatives are expected to have a wide variety of applications in many fields,e.g.,biological, Industrial and medical applications.



n=4,8 for G1 &G2

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CuO Nanoparticles: A Simple, Effective, and Reusable Heterogeneous Catalyst for preparation of 14-aryl-14*H*-dibenzo[a, i] xanthene-8 ,13-diones

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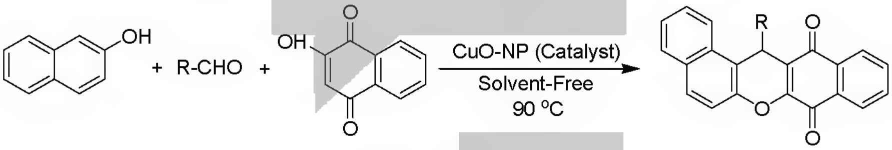
Xanthenes and benzoxanthenes have been reported to posses diverse biological and therapeutic properties such as antibacterial [1], antiviral [2], and anti-inflammatory activities [3], as well as photodynamic therapy [4] and for antagonism of the paralyzing action of zoxazolamine [5]. The other useful applications of this heterocycles are as dyes [6], fluorescent materials for visualization of biomolecules [7], and in laser technologies [8].

In continuation of our research on applications of heterogeneous catalysts in organic synthesis [9], and our interest in the synthesis of reactive dyes based on 2-hydroxy-1,4-naphthoquinone encouraged us to the synthesis of 14-aryl-14*H*-dibenzo[a,i]xanthene-8,13-diones from β-naphthol, aromatic aldehydes and 2-hydroxy-1,4-naphthoquinone under solvent- free conditions in the presence of catalytic amount of nanocrystalline CuO as a recyclable heterogeneous catalyst (Scheme). This method has the advantages of high yield, clean reaction, simple methodology and short reaction time.



Scheme

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SiO_2 nanoparticles catalyzed condensation of β-naphthol and aldehydes: One-pot synthesis of 14-substituted-14*H*-dibenzo[a,j]xanthenes

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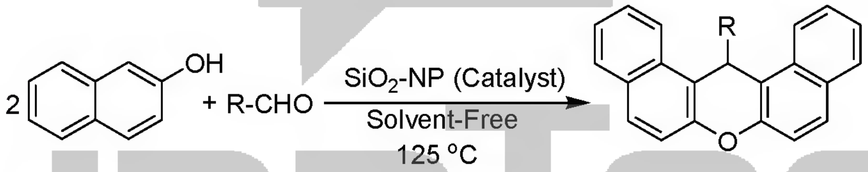
Heterogeneous catalysis is particularly attractive as it allows the production and ready separation of large quantities of products with the use of a small amount of catalyst [1]. In recent years, there has been growing interest in the catalytic properties of transition metal nanoparticles [2]. The high surface area-to-volume ratio of solid-supported metal nanoparticles (1–10 nm in size) is mainly responsible for their catalytic properties and this can be exploited in many industrially important reactions [3]. Recent literature shows that the application of nanoparticles as catalysts in organic synthesis has been little explored. SiO_2-Nanoparticles, in particular, being cheap, require catalytic amount for high yields of products in short reaction times as compared to traditional catalysts.

In this research, we report a simple and convenient procedure for the synthesis of 14-substituted -14*H*-dibenzo[a.j]xanthene derivatives through a one-pot condensation of β-naphthol with various aldehydes in the presence of SiO_2 nanoparticles as the catalyst under thermal and solvent-free conditions.



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Three component synthesis of 2-amino-4*H*-chromene derivatives

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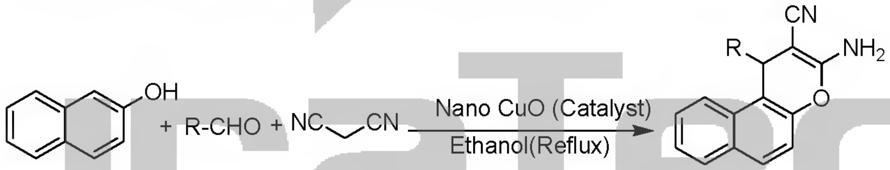
A multi-component reaction (MCR) is a one-pot reaction in which three or more reactants are combined together to generate a desired product without the isolation of any intermediate [1,2]. The MCR strategy has gained increasing attention in the past decade because of its capability to prepare compound libraries in the field of modern medicinal and combinatorial chemistry [3,4].

A particularly interesting group of chromenes are 2-amino-4*H*-chromenes (or 2-amino-4*H*-benzo[b]pyrans), since they are used as cosmetics and pigments [5], spasmolytic, diuretic, anticoagulant, anti anaphylactic [6, 7], antibacterial [8], anti canceragents, and as potent apoptosis inducers.

In this research, a simple, clean, and environmentally benign three-component process to the synthesis of 2-amino-4*H*-chromenes using nano-CuO, as an efficient catalyst is described. A wide range of aromatic aldehydes easily undergo condensations with β-naphthol and malononitrile in ethanol as solvent under reflux conditions to afford the desired products in good to excellent yields (Scheme1). The protocol presented here has the merits of environmentally benign, simple operation, and convenient work-up. Furthermore, the catalyst can be easily recovered and reused without losing its activities.



Scheme1

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Novel Polythiophene/Zinc Oxide Nanocomposites

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A nanocomposite is a multiphase material derived from the combination of two or more components, including a matrix (continuous phase) and a discontinuous nano-dimensional phase with at least one nano-sized dimension (i.e.,less than 100 nm). During the past decade a new branch of materials science, nano-structured materials, has been developed, leading to the discovery of the special characteristics of nano-sized solid materials [1]. Encapsulation of inorganic nanoparticles inside the shell of conducting polymers is the most popular and interesting aspect of nanocomposites synthesis [2]. Various derivatives of conducting polythiophene (PT) have been investigated extensively because of their interesting semiconducting, electronic and optical properties, combined with processing advantages, and good mechanical characteristics [3].

This research work describes an efficient method to synthesize of ZnO nanoparticles and PT/ZnO nanocomposites. ZnO nanoparticles were prepared by reacting zinc acetate and KOH in methanol solution [4]. Then, PT/ZnO nanocomposites were synthesized by one-step in situ deposition oxidative polymerization of thiophene using ferric chloride ($FeCl_3$) as an oxidant in the presence of different amount of the synthesized ZnO nanoparticles. The obtained nanocomposites were characterized by Fourier-transform infrared (FT-IR), thermogravimetric analysis (TGA), X-ray diffraction (XRD), and scanning electron microscope (SEM) techniques for confirming their structure and morphology. Electrical conductivity measurements showed that with the increasing contents of ZnO in nanocomposites, the conductivity decreases.

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Physical Properties Investigation of Conducting Polyaniline-titanium dioxide Nanocomposites Prepared by "In Situ" Polymerization Method

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The discovery of conducting polymers has opened up a new promising field in material science and engineering [1]. Among them, conducting polyaniline (PANI) is one of the most promising conducting polymers because of its unique electrical, optical, and optoelectrical properties, as well as its ease of preparation and excellent environmental stability. Nowadays, conducting PANI/inorganic nanocomposites have also attracted more and more attention [2]. The properties of these nanocomposites are quite different from PANI and the corresponding inorganic nanoparticles due to interfacial interactions between inorganic nanoparticles and PANI macromolecules [3]. Among those inorganic nanoparticles, titanium dioxide (TiO_2) nanoparticles are appealing because of their excellent physical and chemical properties, as well as extensive applications in diverse areas, such as coatings, solar cells, and photocatalysts [4].

In this research work, PANI/TiO_2 nanocomposites were prepared through in situ oxidative chemical polymerization of various concentrations of aniline on the surface TiO_2 nanoparticles by using $(NH_4)_2S_2O_4$ as oxidant agent. The obtained nanocomposites were characterized using scanning electron microscopy (SEM), thermogravimetric analysis (TGA), X-ray diffraction (XRD), Fourier-transform infrared spectra (FT-IR), and electrical conductivity measurements. The obtained results showed that the amount of PANI deposited on the TiO_2 nanoparticles increases with increasing the monomer concentration, while the electrical resistivity of the composites decreases due to the formation of a continuous layer that coats the nanoparticles surface. FT-IR spectra of the nanocomposites revealed strong interaction between PANI and TiO_2, as characterized by a shift band towards pure PANI with increasing aniline concentration. TGA results showed that the PANI/TiO_2 nanocomposites have higher thermal stability than pure PANI. The SEM images of the nanocomposites revealed that PANI consisted of particles that form a continuous coating that fully encapsulates the TiO_2 particles. The XRD pattern suggested that PANI did not modify the crystal structure of TiO_2, but TiO_2 affected the crystallization of PANI to some extent.

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Supported Palladium Nanoparticles as Catalyst For Carbon–Carbon Bond Construction (Heck Reaction) In Organic Synthesis.

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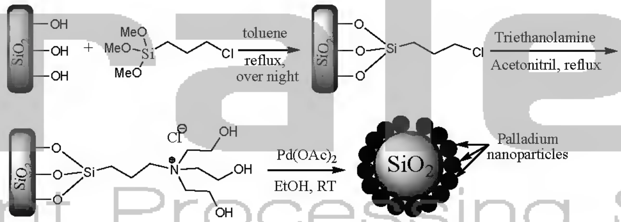
Abstract: Catalytic carbon–carbon coupling reactions are of substantial interest for the production of chemicals. Heck reaction, one of the most important C-C coupling reactions in organic synthesis [1], is mostly catalyzed by palladium complexes in homogeneous solution. Important advantages of this reaction are the broad availability of aryl bromides and chlorides, and the tolerance of the reaction for a wide variety of functional groups. Regarding industrial applications, however, these catalysts are expensive (Pd, phosphanes or special ligand systems) and only very few experiments are reported about the separation from the reaction mixture and their reuse [2]. In this work, the catalytic activity and selectivity of palladium nanoparticles supported on silica surface in carbon–carbon coupling reactions of aryl iodides and bromides with olefins (Heck reaction) are reported. The supported Pd nanoparticles exhibit high activity towards the Heck reaction for very small palladium concentrations (0.1 mol %). The electronic nature of the aryl halides and the olefins has a dominating effect on the reaction yield. The catalysts can be easily separated from the reaction mixture and reused after washing without loss in activity.



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One-pot, water-medium green synthesis of the Hantzsch product by PEG-SO_3H

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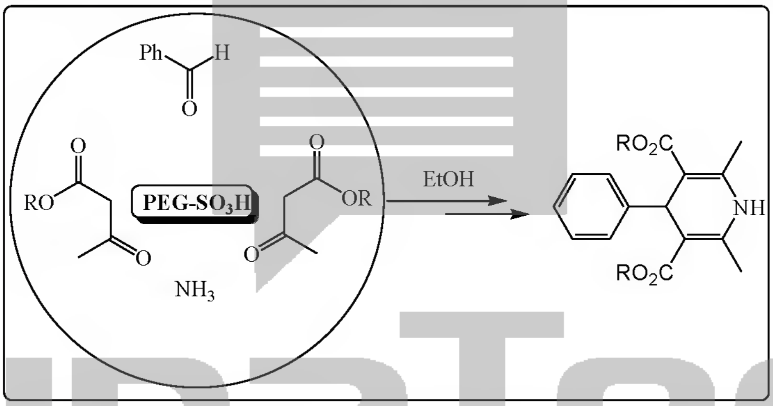
Recently, due to the vast medicinal utility of 1,4-dihydropyrimidine (Hantzsch product) and its derivatives, various methods to prepare these compounds have been reported. [1] Based on recent efforts to use eco-friendly reagents in chemistry, we choose the modified Polyethylene glycol (PEG) as the catalyst for synthesis of Hantzsch product. This product is obtained from a multi-component organic reaction between an aldehyde, 2 equivalent of a β-ketoester a nitrogen donor such as ammonium acetate.



In this project we prepare the sulfonic acid modified polyethyleneglycole as a recyclable and environmentally-friend catalyst, then we investigated the operation of this catalyst in Hantzsch reaction. The products were obtained in high yield, but the catalytic activity of PEG-SO_3H reduced after 3 cycles.

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Nanocrystalline TiO_2–$HClO_4$ as a new, efficient and recyclable catalyst for the chemoselective *N*-Boc protection of amines

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Protection and deprotection of organic functions are important processes during multi-step organic synthesis [1]. Between the several methods available for the protection of amines, *N*-*tert*-butylcarbonylation has attracted the attention of many organic chemists. This considerable attention can be attributed to the stability of *N*-*tert*-butylcarbamates againt bases, nucleophiles, catalytic hydrogenation and racemization [2,3], as well as easy removal of the Boc moiety by reagents such as CF_3CO_2H, formic acid, HCl in ethyl acetate or 10% H_2SO_4 in dioxane. Among different reagents which are available for the *N*-Boc protection of amines [4], the di-*tert*-butoxypyrocarbonate is the most popular because of its commercial availability, low cost and stability and efficiency. However, there are several drawbacks behind the classical *N*-Boc protection technique. The tedious work-up takes time and side products are generated. Moreover, the catalysts used to promote the reaction are most of the time very costly and non-recoverable [5]. In continuation of our ongoing research program on the protection of organic functional groups [6,7]. We have found that TiO_2–$HClO_4$, as a new solid acid [8], can be used as an efficient catalyst for the chemoselective *N*-Boc protection of amines. The synthesized catalyst was characterized by FT-IR, SEM, TEM, BET and XRD analyses. Our novel synthetic method has the advantages of high yields, short reaction times, low cost and recyclability of the catalyst, simplicity and easy work-up compared to the conventional methods reported in the literature.

$$R_1R_2NH_2 \xrightarrow[\text{Solvent free, r.t}]{(Boc)_2O\text{ (1mmol), }HClO_4\text{-}TiO_2\text{(5mg)}} R_1R_2NHBoc$$

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Nano TiO_2: An Efficient and Recyclable Heterogeneous Catalyst for the One-pot Synthesis of 1-(α-aminoalkyl) naphthols

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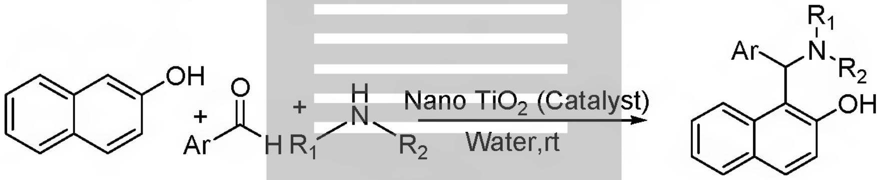
Nanocrystalline TiO_2 particles are of interest due to their unique properties and several potential technological applications such as photocatalysis, sensors, solar cells and memory devices [1].

Nanocrystalline powders were applied for several transformations in organic chemistry [2]. In this research, synthesis of 1-(α-aminoalkyl) naphthols, the Betti Bases, has been carried out over nanocrystalline TiO_2 as catalyst from three-component reactions of amines, benzaldehydes and 2-naphthol in aqueous media at room temperature (Scheme 1).



Scheme 1

From the context of green chemistry this reaction is highly significant as the reactions are extremely atom-efficient and have been performed in water avoiding the use of harmful organic
solvents.

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NanoTiO$_2$: Heterogeneous catalyst for the rapid synthesis of pyranopyrazoles

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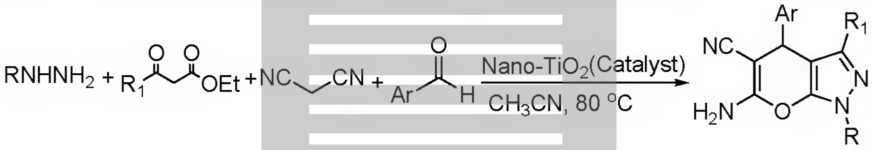
One of the main challenges in medicinal chemistry is the design and synthesis of biologically active molecules [1]. Pyranopyrazoles are fused heterocyclic compounds that possess many pharmaceutical ingredients and biological properties [2].

In this research, we report that nano-TiO$_2$ is a highly efficient catalyst for the one-pot four component coupling (4CC) synthesis of 6-amino-2*H*,4*H*-pyrano[2,3-c] pyrazole-5-carbonitriles from aryl aldehydes, ethyl acetoacetate, malononitrile and hydrazine hydrate (Scheme 1). This methodology offers significant improvements with regard to the scope of this transformation, simplicity in operation and avoiding expensive or corrosive catalysts.



Scheme 1

References:

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A convenient method for the preparation of 2,4,5-triarylimidazoles using $Sn_{0.986}Ni_{0.014}O$ nano-particles as heterogeneous reusable catalyst

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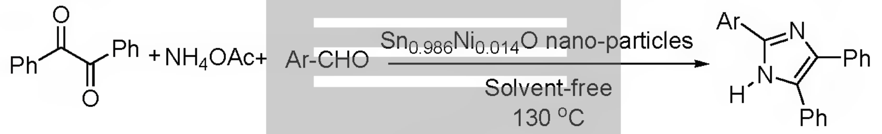
Compounds containing imidazole skeletons exhibit important biological activitiesand play important roles in biochemical process [1-3]. Also large classes of imidazole derivatives are used as ionic liquids [4-5]. Thus these properties have inst1ituted a diverse collection of synthetic approaches to these heterocycles. A number of routes have been developed for synthesis of substituted imidazoles.

Herein $Sn_{0.986}Ni_{0.014}O$ nano-particles was employed as useful and novel catalyst for the synthesis and easy purification of 2,4,5-triarylimidazole derivatives via one-pot three-component cyclocondensation of benzil, ammonium acetate, an amine source and aldehydes under thermal conditions in high yields (Scheme 1).



Scheme 1

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Preparation of methyl (2-hydroxynaphthalen-1-yl)(aryl)methyl/benzylcarbamate derivatives using $Sn_{0.986}Ni_{0.014}O$ nano-particles

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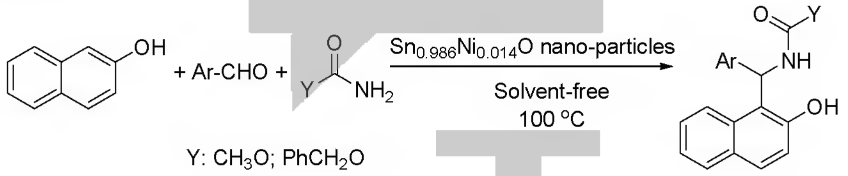
Carbamate skeletons are important components of natural products and versatile precursors for synthesis of pharmaceuticals such as mitomycin [1-2], saxitoxin [3] and bleomycin [4]. In addition, carbamates are intermediates of the Curtius degradation route to amines [5]. They abound as nitrogen or oxygen protecting groups [5]. Therefore, the preparation of carbamate derivatives has been attracting considerable attention in both the past and in recent years.

The present work concentrates on the multi-component condensation reaction of aldehydes, 2-naphthol and methyl/benzyl carbamate has been done by the using of $Sn_{0.986}Ni_{0.014}O$ nano-particles as an efficient catalyst. This methodology results in the synthesis of a variety of methyl (2-hydroxynaphthalen-1-yl)(aryl)methyl/benzylcarbamate derivatives in high yields. $Sn_{0.986}Ni_{0.014}O$ nano-particles has been prepared from the reaction of $SnCl_2$ and $NiCl_2$ (Scheme 1).



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Preparation and application of $Sn_{0.986}Ni_{0.014}O$ nano-particles in the synthesis of 1-amido alkyl-2-naphthole derivatives

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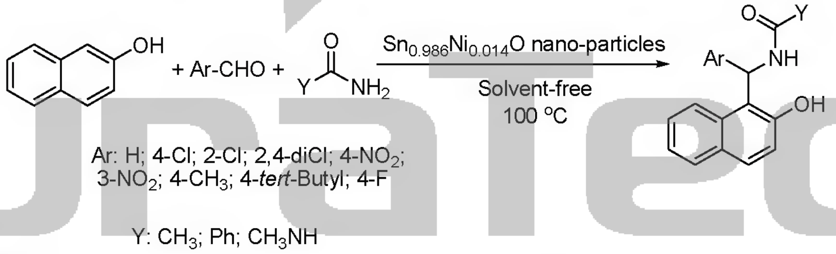
Multi-component condensation reactions of aldehydes, 2-naphthol and acetamide / benzamide have been done by using $Sn_{0.986}Ni_{0.014}O$ nano-particles as an efficient catalyst. This methodology results in the synthesis of a variety of methyl *N*-((2-hydroxynaphthalen-1-yl)(aryl)methyl)acetamide / benzamide derivatives in high yields. Despite their importance from pharmacological and synthetic points of view, comparatively few methods for the preparation of 1-amidoalkyl 2-naphthol derivatives have been reported via multi-component reactions of aldehydes, 2-naphthol and acetamide / benzamide using acidic catalysts [1-2]. $Sn_{0.986}Ni_{0.014}O$ nano-particles have been prepared from the reaction of $SnCl_2$ and $NiCl_2$. The prepared catalyst has been characterized through a powder X-ray diffraction pattern, TEM, FT-IR and UV. The average diameter of particles is evaluated to be approximately 25 nm.



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Use of atomic force microscopy and fractal analysis to characterize the surface of nanocomposite for potential application in membrane science

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The surface topology of filtration membranes plays an imperative role in determining their fouling tendency. Rough surfaces foul more easily because roughness increases surface area and affects other parameters that can also influence fouling rates. An increase in surface area increases the number of contact points between foulants and surface [1]. On the other hand, the presence of antimicrobial agents in the rough surface in contact points can be useful in eliminating the pathogens [2]. The bactericidal activity of photocatalytic anatase crystalline titanium dioxide (TiO_2) has drawn a great deal of attention. The bactericidal property, in combination with other properties such as high catalytic activity, chemical stability, low energy source and nontoxicity, make TiO_2 ideal as an alternative material for environmental purification systems for the treatment of water and air [3]. TiO_2 photoactivity is strongly influenced by the presence of noble metals [4]. Silver has received great attention due to the unique properties, which were introduced onto the TiO_2 system [5]. In this study, we synthesized the poly(vinyl alcohol)/Ag/TiO_2/iminolactone nanocomposites by solution casting method with different weight percentage. Characterization with fourier transform infrared spectroscopy, field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM) confirmed the success in synthesizing the nanocomposites. The obtained results from FE-SEM analysis showed that the average size of the nanoparticles in the nanocomposite structures were in the range of 35-46nm. Also in this study, we look for a better understanding of the effects of the nanoparticles on the antimicrobial properties with AFM by means of root-mean square roughness and fractal analysis as a tool for investigation of surface properties.

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Investigation on synthesis and morphology characteristic of novel chiral poly(amide-imide)/TiO_2/organoclay nanocomposites

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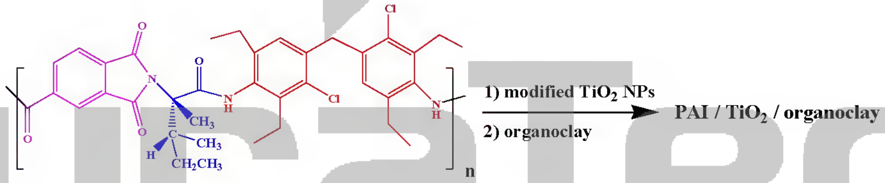
Nanocomposites (NCs) materials are two phase systems that consist of a polymeric matrix and dispersed inorganic particles of nanometer scale [1]. Nanoclays have several advantages over conventional microsized clays in polymer composites such as: good mechanical and gas barrier properties, thermal stability and conductivity properties without significant reduction in other relevant properties, including toughness [2-4]. In the present investigation, the goal is to build poly(amide-imide) (PAI)/TiO_2/oganoclay NCs. First, a new optically active PAI was synthesized from the polymerization reaction of *N*-trimellitylimido-L-isoleucine diacid with 4,4′-methylenebis(3-chloro-2,6-diethylaniline) using molten tetra-*n*-butylammonium bromide and triphenyl phosphite as a condensing agent and green media. Then the surface of TiO_2 nanoparticles (NPs) was modified with γ-aminopropyltriethoxyl silane as a coupling agent. The obtained polymer and inorganic metal oxide nanoparticles were used to prepare of PAI/TiO_2 NC through ultrasonic irradiation. Then several amount of organoclay [5] were added to the PAI/TiO_2 system to obtained PAI/TiO_2/oganoclay NCs (scheme 1). The resulting nanocomposites were characterized by FT-IR, powder X-ray diffraction, field emission scanning electron microscopy, transmission electron microscopy and thermogravimetric analysis techniques.



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SiO_2 nanoparticle as an efficient catalyst for one-pot synthesis of 2-amino-4*H*-chromenes

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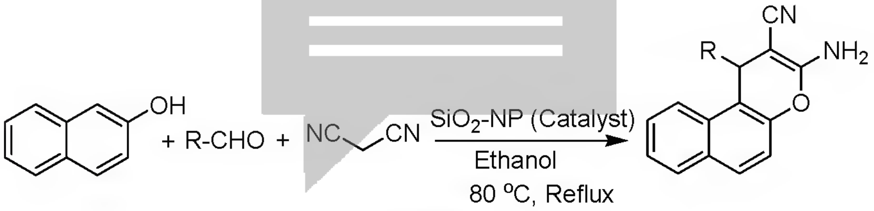
2-Amino-4*H*-chromenes and their derivatives are of considerable interest as they possess a wide range of biological properties [1], such as spasmolytic, diuretic, anticoagulant, anticancer and anti anaphylactic activity [2]. In addition, they can be used as cognitive enhancers, for the treatment of neurodegenerative diseases, including Alzheimer's disease, amyotrophic lateral sclerosis, Huntington's disease, Parkinson's disease, AIDS associated dementia and Down's syndrome as well as for the treatment of schizophrenia and myoclonus [3].

For these reasons and in our continuing interest in the development of environmental friendly protocols for one-pot solvent-free multi-component reactions [4], we report herein our results for the synthesis of 2-amino-4*H*chromene scaffold using nano silicon dioxide as an efficient catalyst for the three-component condensation of an aldehydes, malononitrile and *β*-naphthol with excellent yields in ethanol under reflux conditions (Scheme).



Scheme

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Silica nanoparticle-catalyzed synthesis of 14-aryl-14*H*-dibenzo[a,i]xanthene-8,13-diones under thermal solvent-free conditions

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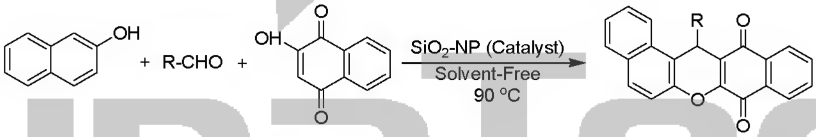
Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale size-dependent properties are often observed. Thus, the properties of materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant. For bulk materials larger than one micrometer (or micron), the percentage of atoms at the surface is insignificant in relation to the number of atoms in the bulk of the material. The interesting and sometimes unexpected properties of nanoparticles are therefore largely due to the large surface area of the material, which dominates the contributions made by the small bulk of the material [1].

In this paper, we report a simple and efficient synthesis of 14-aryl-14*H*-dibenzo[a,i]xanthene-8,13-dione derivatives using silica nanoparticle as heterogeneous catalyst. 14-Aryl-14H-dibenzo[a,i]xanthene-8,13-diones were prepared from the condensation reaction of β-naphthol, aromatic aldehydes and 2-hydroxy-1,4-naphthoquinone with excellent yields and short reaction time under solvent-free conditions. The reaction is very simple and the catalyst can be easily separated from the reaction mixture. The catalyst could be recycled and reused several times without significant loss of activity.



Scheme

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Synthesis and characterization of novel amino-functionalized periodic mesoporous ionic liquid

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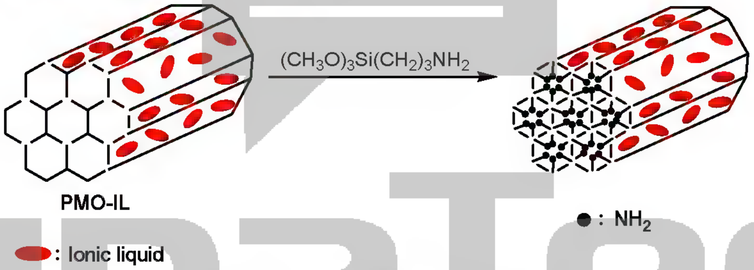
Since the discovery of the first family of mesoporous silica solids by Beck *et al.*, several studies have been developed in this field.[1a] To increase the applications of these materials in areas such as chromatography, adsorption, catalysis and sensor technology, the solids were then modified with several organic functional groups.[1b, 2] The last materials called hybrid organosilicas which among them the periodic mesoporous organosilicas (PMOs) are the best due to high loading and uniform distribution of organic groups in their frameworks.[2b, 3] More recently, bifunctional PMOs become an active area of catalytic research because the materials have large internal surface area, containing organic functional groups inside both the walls and pores of mesostructures.[2b, 3] Although several studies have been published in this area, however, there is not any report on the bifunctional ionic liquid and amino based organosilica materials.[3, 4] Herein, we have synthesized and characterized, for the first time, a new bifunctional PMO based on ionic liquid and aminopropyl functional groups (PMO-IL-NH_2). This material was prepared by grafting of 3-aminopropyltrimethoxysilane on a novel ionic liquid based PMO under argon atmosphere (Scheme 1).[5, 6] According to significant properties of ionic liquids, amino ligand and mesoporous solids, the obtained nanostructure is a novel material which has potential applications in several areas of chemistry and material sciences.



Scheme1: Preparation of PMO-IL-NH_2 nanostructure

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Modification of MWCNTs using amino-alkoxysilanes through amidic bond formation

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Carbon nanotubes (CNTs) apply so reinforce in polymer composites due to their excellent mechanical and thermal properties [1]. But two main challenges, (I) agglomeration of the carbon nanotubes in the polymer matrix; (II) weak interfacial adhesion between the CNTs and the matrix. Chemical functionalization of CNT improves disperse ability and interfacial adhesion. we chose silanization process by applying aminoalkoxysilanes. In past works, mostly silanization processes with functional alkoxysilanes have done by hydrolysis of alkoxy and reactivity of alcoholic groups [1,2]. In this work, aminoalkoxysilne molecules were bonded to MWCNTs from the side of amino termination through amidic bond formation, thus we have a hybrid consisting of CNT and alkoxysilane. Processing stages include oxidation, chloroacylation, and amination..Techniques used in purification are as follows: filter under vacuum, sonication in water bath, centrifugation with low power. FT-IR, RAMAN, SEM and EDX analysis were employed to characterize the changes in CNTs surface morphology and chemistry. For valuation of raw CNT, TGA (Thermal Gravimetric) under heating to 800^0 C in air was used. TGA represented initial sample have high purity and decomposed in one step about 480^0 C. FTIR results for the pristine MWCNTs, the bonds at 3447 and 1047 cm^{-1} attributed to presence of the hydroxyl groups (-OH) on the MWCNTs. For the oxidized MWCNTs, the bonds at 1698 and 1186 cm^{-1} are attributed to the C=O and C-O stretching vibrations of the carboxylic groups (-COOH), respectively. In amino-functionalized MWCNTs, peaks at 1650-1660 cm^{-1} associated with the stretching of the C=O amidic group. The main features CNTs in the Raman spectrum are the radial mode band (100-400 cm^{-1}), disorder-induced D-band which appears at about 1350 cm^{-1}, G-bond which represent the crystalline graphitic and in-plane vibrations of sp^2 carbon (1500-1600 cm^{-1}). The value of the intensity ratio of the D and G-bonds (I_D/I_G) changed along functionalization reactions. SEM exhibited that mid functionalization, MWCNTs unbraid. EDX analysis demonstrated presence of silane atoms in product.

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Synthesis and Characterization of Metal Nanoparticle Embedded Polymer-heteropolyanion Composites

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The desire to synthesize nanostructures that combine the mechanical flexibility, optical and electrical properties of conducting polymers with the high electrical conductivity and magnetic properties of metal nanoparticles has inspired the development of several techniques for the controlled fabrication of metal nanoparticle-conducting polymer composites. The incorporation of metal nanoparticles in the conducting polymer offers enhanced performance for both the host and guest [1]. Polyaniline (Pani) is a conductive polymer,is cheap and stable to heat and air atmosphere. It is also the first commercially available conducting polymer [2].The strong oxidizing potential and acidic character of Keggin type polyoxometalates, phosphotungstic acid (PW12) provides perfect environment for the polymerization of monomers such as aniline, pyrrol or thiophene to yield corresponding polymer-polyoxometalate composites.

In this research, we have synthesized and characterized a hybrid of conducting polymer-heteropolyanion (with the Keggin structure)-metal nanoparticle. Phosphotungstic acid has been employed as the oxidizing agent for the polymerization of aniline and the reduced polyoxometalate is used as reducing agent for the reduction of metal ions to form metal nanoparticle embedded Pani-PW12-Ag composites.

X-ray diffraction confirmed the presence of Ag nanoparticles in Ag-Pani-PW12 composite.The XRD pattern of composite showed four strong peaks with maximum intensity at 38.1, 44.3, 64.4 and 77.4 degrees representing Bragg`s reflections from (111) ,(200), (220), and (311) planes of the standard cubic phase of Ag. Also, other specteroscopic data confirmed synthesis of this composite.

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Surface modified nano Al_2O_3/MMA/AN nanocomposites: Sonochemical assisted emulsion polymerization

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Iorganic-norganic nano-composite materials have gained colossal interest in different applications [1]. The nano scale inorganic particles have a strong affinity for agglomeration because of their high surface energy [2]. Surface modification of inorganic nanoparticles (NP)s with an organic compounds is one of the ways to reduce the surface energy and also simultaneously increase the compatibility with the organic polymer matrixes [3]. Hexadecyltrimethoxysilane (HDTMS) is one of the silane coupling agents, which was developed for preparation of hydrophobic coatings. Sonochemistry is a technique which is used to prepare nanosized compounds. In polymer science ultrasonic cavities can be used for preparation of nanoscale polymers and nanocomposites [4]. In ultrasound assisted emulsion polymerization, very fine and stable homogeneous monomer droplets get formed because of cavitational activity at interface of immiscible organic liquid phase causing interruption the later by micro jets. In this study nano Al_2O_3 particles were modified with hydrophobic HDTMS segments by ultrasonic method. For preparation of nanocomposites (NC)s, the emulsion polymerization of methyl methacrylate and acrylonitrile (MMA/AN) was performed in the presence of this nano particles. The results of FE-SEM analysis confirmed the existence of spherical Al_2O_3nano particles with sizes between 20-45 nm and polymer particles with size less than 100 nm in NC structured.

Keywords: nanocomposite; sonochemicalsynthesis; emulsion polymerization; hydrophobic coatings

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Synthesis and characterization of transition metal substituted Keggin type polyoxometalate in SBA-15 nanostructure catalysts and investigation of its catalytic application in oxidation of alcohols

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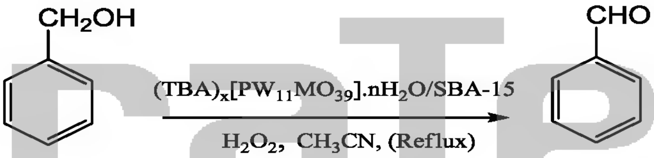
Polyoxometalates (POMs) as inorganic metal–oxygen cluster compounds [1], especially the familiar Keggin-type POMs, have been widely used as acid and oxidation catalysts as well as bifunctional catalysts [2-4]. Heterogeneous catalysis using POMs have also been realized generally by dispersing them on solid supports in order to combine the properties of both the polyoxometalates and a high surface area support. Some nanoporous silica-supported heteropoly acids and their salts, have shown high catalytic activity and shape selectivity especially for conversion and formation of large organic molecules [5-6]. nanoporous silica-supported POMs were usually prepared by impregnation or sol–gel inclusion. Since no strong chemical linkage existed between the supports and the POMs, the POMs were easily leached from the surface in polar solvents, or migrated to aggregate on the outer surface of the support when water was formed as a side-product in the reaction. A few efforts were made to immobilize POMs on nanoporous MCM-41, SBA-15, MCF, and SiO_2 xerogel by electrostatic interaction or on nanoporous, mesoporous and amorphous silica by dative bonding via a postsynthesis route [7]. Oxidation reactions with molecular oxygen and hydrogen peroxide as "green" methods for organic synthesis have gained significant impetus over the past decade [8]. In this work a polyoxometalates – composite was prepare by sol-gel technique and characterized by IR , TEM, SEM and XRD. The characterization results reveal that the $[TBA]_x[PW_{11}MO_{39}].nH_2O$/SBA-15 structure remained intact after formation of the composite. This composite was used as an efficient heterogeneous catalyst for oxidation of alcohol by H_2O_2. It has been shown high to excellent yields and high reusability in oxidations of various alcohols with hydrogen peroxide.



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Synthesis of hydroxyl terminated nano-PAMAM dendrimer and its pharmaceutical evaluations

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Nano dendrimers are a branch of nano particle group that are interested in variety of fields [1]. Because of their ability to confinement of molecules in their branches or ability to connection with the functional surface groups, these particles are able to use as a targeted delivery of many particles especially for drugs [2]. In this study, hydroxyl derivative of nano-PAMAM dendrimers were synthesized and evaluated to bind to the drugs containing carboxylic acid moiety. According to the reports, shelf life of the drug effect for dendrimers with hydroxyl terminal groups is very high [3]. Also in lower generation of dendrimers, in addition to their less toxicity [4], dramatic increase in the solubility of hydrophobic species was also observed [5]. Nano dendrimer compound with hydroxyl terminated groups were prepared from the reaction of synthesized PAMAM dendrimers with tris hydroxymethyl amino methane in DMSO. The structure of the desired product was confirmed by spectral and microanalytical data. Consequently, the resulted product was reacted with acyl chloride derivative of aspirin. The results of multiple tests were indicated that the successful conjugation was performed and the complexes of Nano dendrimer to drugs were obtained.

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A theoretical study on the [1,5]-prototropic generation of an azomethine ylide and regioselectivity of the 1,3-dipolar cycloaddition using DFT-based reactivity indices

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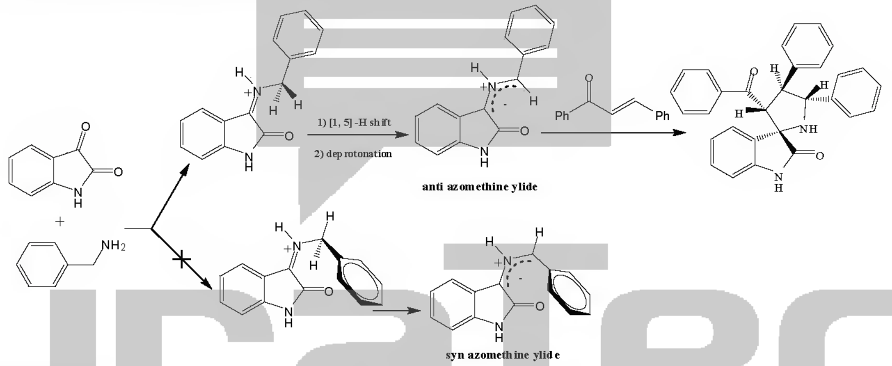
Azomethine ylides are a class of powerful reagents, which react readily with various dipolarophiles to afford pyrrolidines and pyrrolizidines [1]. A particularly mild method for the generation of nonstabilized azomethine ylides involves the [1,5] prototropic shift. The concept of the [1,5]-H shift in the iminium ion to form an azomethine ylide was proposed by Grigg [2]. However no theoretical studies on the mechanism aspects have been reported [3].

Herein, the molecular mechanism of the cycloaddition reaction between an azomethine ylide, generated from isatin and benzylamin, with chalcone as a dipolarophil has been investigated by means of a density functional theory (DFT) method. The energy path in preparing the azomethine ylide via a [1,5]-H shift in the iminium ion was evaluated. The regio- and stereoselectivity were explained on the basis of transition states stabilities and global and local reactivity indices of the reactants.



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Solvent free acetylation of alcohols and phenols with acetic anhydride in the presence of fine nanoparticle of nano-Ni as a green and heterogeneous catalyst

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The acetylation reaction of hydroxyl groups have been received considerable attention in organic synthesis for a variety of useful organic compound[1]. It also provides an efficient route for protecting OH groups during oxidation [2,3]. In This article OH group protection is achieved through with acetic anhydride. Nano-Ni is also potential green catalyst for acetylation of alcohols and phenols under solvent-free condition (Scheme 1). The acetylation of different types of alcohols including primary, allylic, benzylic, hindered and unhindered secondary and sterically hindered tertiary alcohols were investigated in the absence of solvent by Ac_2O in the presence of Nano-Ni as a green and heterogeneous catalyst. Very small amount of catalyst, mild reaction condition, room temperature, excellent yield and no undesirable side products, be recycled for further reaction are important features of this protocol. The solvent-free condition employed in the present method should make it environmentally friendly and useful for industrial application .These compounds are widely used as perfumes, cosmetics, flavors, food, additives, plasticizers and polymers[1].

$$\mathrm{ROH} \xrightarrow[\mathrm{Ac_2O\ \ r.t}]{\text{Nano Ni}} \mathrm{ROAC}$$

R: benzyl, allyl, propagyl, isoamyl, cinnamyl, tert-butyl, 2-butyl, phenyl, cyclohexyl

Scheme 1

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Synthesis, Characterization and Studying Physical Properties of Conducting Polyaniline/Silica Nanocomposites

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Nanocomposites are a special class of materials having unique physical properties and wide application potential in diverse areas [1]. Novel properties of nanocomposites can be obtained by the successful combination of the characteristics of parent constituents into a single material [2]. Encapsulation of inorganic nanoparticles inside the shell of conducting polymers is the most popular and interesting aspect of nanocomposites synthesis [3,4]. Among the conducting polymers, polyaniline (PANI) has drawn the attention of scientists because of its reasonably good conductivity, stability, easy preparation and affordability [5].

The present research work describes an efficient method for synthesis of a series of polyaniline/silica (PANI/SiO_2) nanocomposites with different SiO_2 ratios. These nanocomposites were prepared by one-step in-situ deposition oxidative polymerization of aniline hydrochloride using ammonium peroxysulfate (APS) as an oxidant in the presence of different amounts of ultra fine grade powder of SiO_2 nanoparticles cooled in an ice bath. The obtained dark green nanocomposites were characterized by Fourier-transform infrared (FT-IR), thermogravimetric analysis (TGA), X-ray diffraction (XRD) and scanning electron microscope (SEM) techniques. The obtained results showed that SiO_2 nanoparticles have been encapsulated by PANI with a strong effect on the morphology of PANI/SiO_2 nanocomposites. Investigation of the resulting TGA curves showed that the synthesized PANI/SiO_2 nanocomposites had higher thermal stability than that of pure PANI. Electrical conductivity measurements by four-point probe technique indicated that electrical conductivity of nanocomposite at low SiO_2 content is much higher than of neat PANI, while with the increasing contents of SiO_2, the conductivity decreases.

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Conducting Polypyrrole/SnO_2 Nanocomposites: Preparation, Characterization and Properties Investigation

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Conducting polymer-inorganic oxide nanocomposites have recently attracted great attention owing to their unique microstructure, outstanding physiochemical and electro- optical properties, and wide range of potential uses as a battery cathode and also in constructing nanoscopic assemblies in sensors and microelectronics [1]. Polypyrrole (PPy) is a promising intrinsically conducting polymer in electronics, optical, biological and medical areas due to its straightforward polymerization, cytocompatibility, environmental stability and electrical conductivity that can be controlled by changing the doping degree. Unfortunately, the poor processability and inadequate mechanical properties of PPy limit its commercial applications [2]. Tin dioxide (SnO_2) is an n-type semiconductor oxide material with wide band-gap energy of 3.54 eV at 300 K. SnO_2 has potential applications in dye-based solar cells, semiconductors, photoconductors and gas sensors [3].

In this research work, a serious of polypyrrole-SnO_2 nanocomposites was prepared by the polymerization of pyrrole using ferric chloride in the presence of various amounts of nano- SnO_2 particles. The obtained composites were characterized by Fourier-transform infrared spectra (FT-IR), thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM) techniques. Also, the electron conductivity of the products was measured at room temperature on compressed pellets of the powder by conventional four-point probe technique. The obtained FT-IR spectra showed that the polymerization of pyrrole has been successfully achieved on the surface of the SnO_2 nanoparticles. TGA results indicated that the synthesized nanocomposites have higher thermal stability than that of pure PPy. Study of XRD patterns showed that diffraction pattern of nanocomposites is the same as that of nano-SnO_2, indicating that PPy has no influence on the crystal structure of SnO_2. Investigation of electrical conductivity measurements showed that the electrical conductivity of nanocomposites is depends on the concentration of SnO_2 in PPy and reaction conditions

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Synthesis of A New Aromatic Diamine Containing Pyridine and 1,3,4-Oxadiazole Moieties, Modification of Sodium Montmorillonite Nanoparticles

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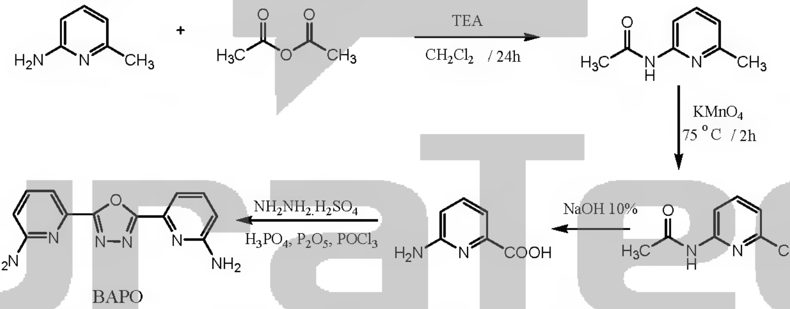
The commonly used organo-modification agents are long carbon-chain alkyl ammonium salts. The preparation and processing of some polymer/clay nanocomposites (PCNs) are carried out at high temperatures, and the thermal decomposition of the long carbon chain of quaternary ammonium salts is inevitable. Therefore, the thermal stability of organic swelling agents may have significant effects on the preparation, performance and application nanocomposites [1-2]. In this work, the new aromatic diamine (BAPO) containing pyridine and 1,3,4-oxadiazole rings has been designed and synthesized in 4 steps, Scheme 1. 2-Amino-6-methyl pyridine was acetylated, oxidized with KMnO4, and deprotected to give 2-amino-6-picolinic acid [3]. New diamine (BAPO) has been synthesized in good yields by reaction of 2-amino-6-picolinic acid with hydrazine sulfate in a mixture of phosphoric acid, P_2O_5 and with addition of $POCl_3$. The end product was fully characterized with conventional spectroscopy techniques.



Scheme 1

Sodium montmorillonite nanoparticles have been organically modified using the dihydrochloride salt of BAPO. Thermal property of the BAPO-MMT was studied using Thermo Gravimetric Analysis (TGA). The results confirmed the intercalation of BAPO within the clay galleries. The obtained organoclay exhibits improved thermal stability in compared with long carbon-chain alkyl ammonium modified organoclays.

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Knoevenagel Condensation of Isatins with Malononitrile/Ethyl Cyanoacetate in the Presence of Sulfonic Acid Functionalized Silica (SBA-Pr-SO_3H) as a New Nano-reactor

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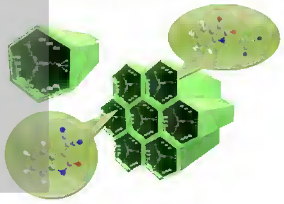
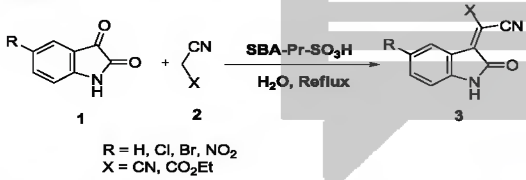
The Knoevenagel condensation [1] as an effective and general reaction for the formation of carbon-carbon bonds, has been widely used in organic synthesis [2]. There are various reports about the application of isatin in Knoevenagel condensation [3]. Many of these products present significant biological activities or they are used in the synthesis of natural products [4]. Condensation of malononitrile or ethyl cyanoacetate **2** with isatin and its derivatives **1** to prepare 2-oxoindolin-3-ylidene malononitrile/cyanoacetate **3** using different solvents such as ethanol, methanol, and DMSO has been studied [5]. Microwave irradiation [6] and grinding in the presence of water [7] are the other methods for the synthesis of these compounds. Here, we report our results on the condensation of isatin with malononitrile or ethyl cyanoacetate in the presence of sulfonic acid functionalized nanoporous silica (SBA-Pr-SO_3H) as a nano-reactor.





Considering solvent effects in this reaction, it was found that water is the solvent of choice which results in high product yields in shorter reaction times. Corresponding products were synthesized successfully in water and new compounds were characterized by IR, Gc-Mass, and ^{1}H NMR spectral data. SBA-Pr-SO_3H having highly ordered hexagonally arranged mesochannels, thick walls, high thermal stability, and high surface area was proved to be an efficient heterogeneous solid acid catalyst in this reaction. Short reaction times, excellent product yields, being environmentally benign, and simple workup procedure are the advantages of this methodology.

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And efficient synthesis of 1,4-dihydroquinoline using nano- NiO as a catalyst

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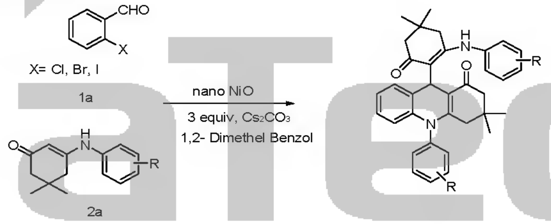
INTRODUCTION:

1,4-dihydroquinoline is a particularly interesting core and it structure appears increasingly in compounds of therapeutic importance. Compounds of such structure have shown various pharmaceutical activities such as hypotensive agents or inhibitors of potassium ion channels [1].

The transition metal-catalyzed C-N cross-coupling process is considered as an important methodology, which has been widely applied in pharmaceutical and medicinal chemistry. Although remarkable success in both palladium. and copper, catalyzed versions of this strategy has been achieved, the development of alternative catalysts involving more cheap, nontoxic, and environmentally friendly metals is still highly desired[2].

Ultra-fine NiO nano-ceramic particles with a uniform size and well dispersion characteristics are strongly desirable for many applications, e.g. synthesis of composite materials, magnetic, electro chromic, heterogeneous catalytic materials, etc [3].

We herein report an efficente and high yield method for the synthesis of 1,4- dihydroquinoline compounds with 2- halo banzaldhydes and β-enaminones in the presence of nano- NiO as stable and rusebale catalyst (Scheme 1).



scheme 1

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Preparation and Identification of a New chiral Nanocomposite of Poly[(+)-2-*sec*-butylaniline] with Nanosilica

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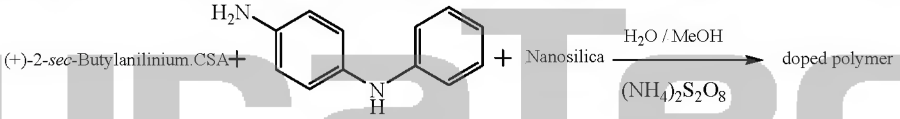
In recent years, there has been increased interest in synthesizing chiral conducting polymers mainly because of their potential applications in diverse areas, such as chemical and biological sensors, asymmetric electrochemical synthesis, chiral stationary phase for enantioselective liquid chromatography (HPLC) separation, electrodes for enantioselective recognition or capable of performing bio-electro-synthesis, membrane separation technology and microwave absorbents [1-5]. A series of chiral conducting polymers, such as polyaniline (PANI) [6], polyacetylene, polypyrrole, polythiophene, polytoluidine, polydiacetylene, polyisocyanide, and polyazulene, have been reported in the literature [1-5]. In the present investigation, a new chiral nanocomposite of poly[(+)-2-*sec*-butylaniline] doped with camphorsulfonic acid was synthesized and characterized in the presence of nanosilica for the first time in aqueous solution. This method uses *in situ* oxidative polymerization of [(+)-2-*sec*-butylanilinium] camphorsulfonate salt as a monomer in the presence of initiator and ammonium peroxodisulfate as oxidant. The resulting nanocomposite was characterized using FT-IR and UV-Vis spectroscopy. The morphology of nanocomposite was determined using TEM and SEM. TEM images of the samples clearly indicate that the nanomaterials have uniform solid nanospheres and their diameters are in the range of 20-30 nm.



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Synthesis and Characterization of a New Nanopolymer of Poly[(+)-2-*sec*-butylaniline]

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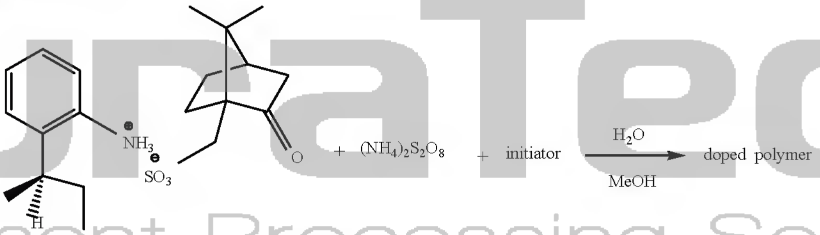
Conducting polymers continue to be the focus of active research in many areas and fields [1]. Polyaniline is unique among conducting polymers in its wide range of electrical, electrochemical, electroluminescence, optical and anticorrosion applications as well as good stability [2-3].

Chiral polyaniline (PANI) and its derivatives were synthesized usually by either codissolving PANI and a chiral acid in common solvents [4] or by polymerizing aniline in the presence of a chiral acid [5]. To achieve highly efficient chemical separations using chiral PANI as the chiral stationary phase, it is essential to have both high chirality and high surface area. The use of substituents such as alkyl or alkoxy chains or polar substituents is seen as a means of improving both the solubility of PANI in organic and aqueous media, and the process ability of these materials [6].

In this work, a new nanopolymer of poly[(+)-2-*sec*-butylaniline] doped with camphorsulfonic acid was synthesized and characterized for the first time in aqueous solution. This method uses oxidative polymerization of [(+)-2-*sec*-butylanilinium]camphorsulfonate salt as a monomer in the presence of initiator and ammonium peroxydisulfate as oxidant. The resulting nanopolymer was characterized using FT-IR and UV-Vis spectroscopy. The morphology of nanopolymer was determined using TEM and SEM. TEM images of the samples clearly indicate that the nanomaterials have uniform solid nanospheres and their diameters are in the range of 20-30 nm.



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urfactants: Chemistry, Properties and Their Industrial Applications

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Surface active agents (surfactants) are organic compounds that constitute one of the major parts of the chemical manufacturing products. Nowadays with rapid population growth and increasing needs of this population to use detergents, cleaners, personal care products etc and development of various industries and expand the use of surfactants in these industries increase the proportion of surfactant manufactures in chemical products [1].

Chemically, surfactant molecules are composed of a long hydrophobic hydrocarbon tail with a polar hydrophilic head that means they have two distinctly different characteristics, polar and non polar, in different parts of the same molecule. Surfactant molecules at low concentration in aqueous media tend to be located in the liquid surface and reduce surface tension of water. With increasing the concentration of surfactant, surfactant molecules form aggregates in aqueous solution that called micelles. In micelle structure ionic head-groups of surfactant molecules lie near the water, whereas the hydrocarbon tails project inwardly [1, 2].

The polar part of surfactant may be ionic or non-ionic. Surfactants are classified by the charge of the polar head group. It is divided into the four classes anionic, cationic, non-ionic and zwitterionic.

Surfactants use in many partial applications and products including detergents and cleaners, textile industry, personal care and cosmetics, pharmaceuticals, agrochemicals and food products, petroleum industry, biotechnology, paints and inks etc [1, 2].

Chemists have focused on changing of the surfactants chemical structures to improve their properties and develop their usages. This had led to the preparation of new generation surfactants such as Gemini (dimeric), cleavable, polymeric and polymerizable surfactants [2].

Gemini surfactants are the family of surfactant molecules possessing two hydrophobic tails and two hydrophilic head group connected by a spacer. Compared to their conventional analogs, Gemini surfactants considerably possess much lower critical micelle concentration (CMC) values, much lower C_{20} values and more soluble in water [3].

Many chemists are working on Gemini surfactants (synthesis, physic-chemical properties and applications) in their research laboratories over the world and it is anticipated that Gemini surfactants used in home and industrial applications.

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