



18th Iranian Seminar Of Organic
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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

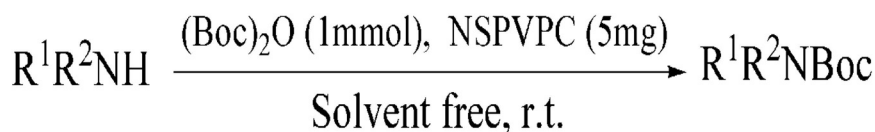
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Protection of organic functional groups is an important process during multi-step organic synthesis.[1] Among the many protecting groups for amines (Boc)₂O is used with high frequency. Activation is commonly achieved by the use of nucleophilic agents [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).



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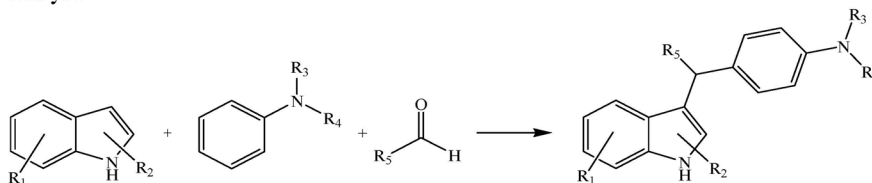
**One-pot synthesis of indol-3-yl(alkanes)benzenamine
in the presence of iron oxide nanoparticles**

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



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

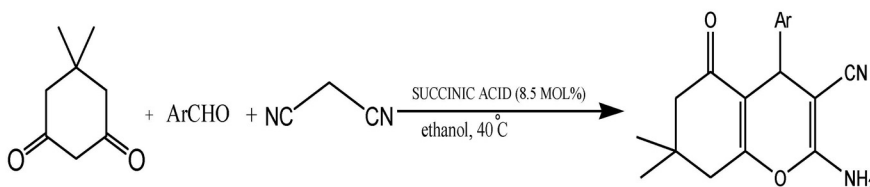
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Tetrahydrobenzo[b]pyrans derivatives have attracted strong interest due to their useful biological and pharmacological properties. Several methods have been reported for the synthesis of tetrahydrobenzo[b]pyrans.¹

In continuation of our research on green chemistry method by succinic acid catalyst and ethanol, an efficient, one-pot three –component tandem Knoevenagel-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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18th Iranian Seminar Of Organic
Chemistry
7-9 March 2012



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 aryldiazenyl 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 arenesulfonates in the presence of some stable aryldiazonium salts (arenediazonium o-benzenedisulfonimides, aryldiazonium silica sulfates and arenediazonium arylsulfonates). 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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18th Iranian Seminar Of Organic
Chemistry
7-9 March 2012



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



Photocatalytic degradation of organic dyes by mixed oxide ZnO-Fe₂O₃

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A mixed semiconductor ZnO-Fe₂O₃ was synthesised using inorganic salts as precursors by sol-gel method. The catalyst ZnO-Fe₂O₃ was synthesized at pH 7 turned out to be superior than sol-gel and commercial 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-Fe₂O₃ nanoparticles. 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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18th Iranian Seminar Of Organic
Chemistry
7-9 March 2012



**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 comparison 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 recrystallized 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 $\pi \dots \pi$ interactions.

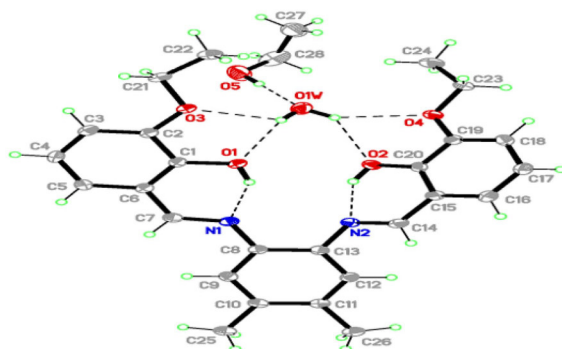


Fig. 1. ORTEP diagram of the ligand with atom numbering and 50% of ellipsoid probability.

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18th Iranian Seminar Of Organic
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7-9 March 2012



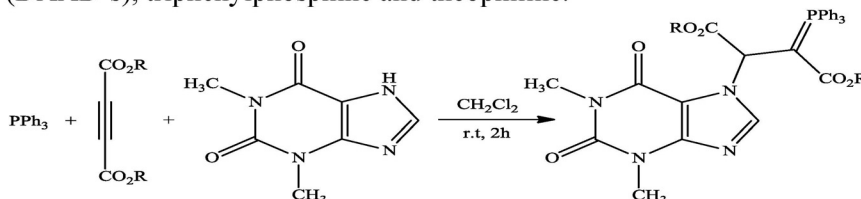
Three-component reaction between triphenylphosphine, dialkyl acetylenedicarboxylates and theophiline

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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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18th Iranian Seminar Of Organic
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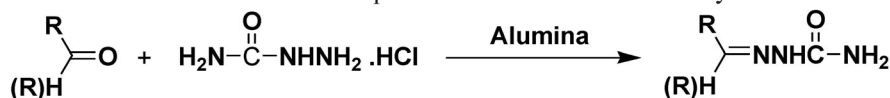


**The Study of Effect of Nano Basic Alumina as a Catalyst in Preparation of
Semicarbazones in Solvent Free Condition**

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Alumina (Al₂O₃) 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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18th Iranian Seminar Of Organic
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7-9 March 2012



Efficient Solvent-Free Synthesis of Bete Bromo Acetates by $\text{MgBr}_2 \cdot \text{OEt}_2$ -Catalyzed Ring-Opening Reaction of Epoxieds with Acetic Anhydride

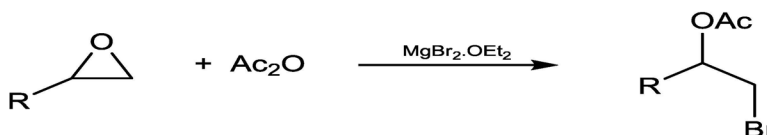
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Introduction and Objective: Epoxides have been recognized among the most versatile intermediates in organic synthesis. They can be easily prepared and due to their ring strain, they react with different nucleophiles with high regioselectively, which 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 ($\text{MgBr}_2 \cdot \text{OEt}_2$) has found many applications as a mild Lewis acid to ease up various synthetic organic transformations [3]. The MgBr_2 reagent, already successfully employed in the opening of epoxy- and aziridinoalcohols and derivatives [4]. In the present article, we introduce a $\text{MgBr}_2 \cdot \text{OEt}_2$ -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 $\text{MgBr}_2 \cdot \text{OEt}_2$ 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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18th Iranian Seminar Of Organic
Chemistry
7-9 March 2012



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

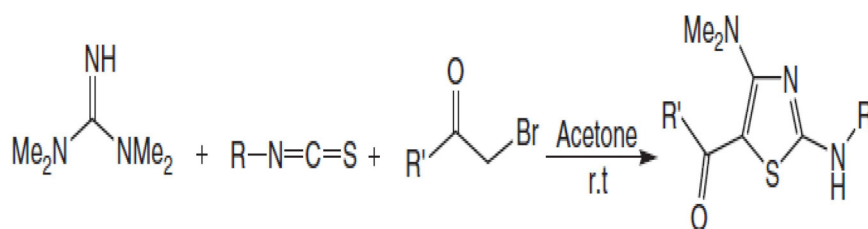
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The thiazole ring system is commonly found in many pharmaceutically important molecules. Numerous natural products containing this heterocycle have been isolated and exhibit significant biological activities [1]. Among aromatic heterocycles, thiazoles 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

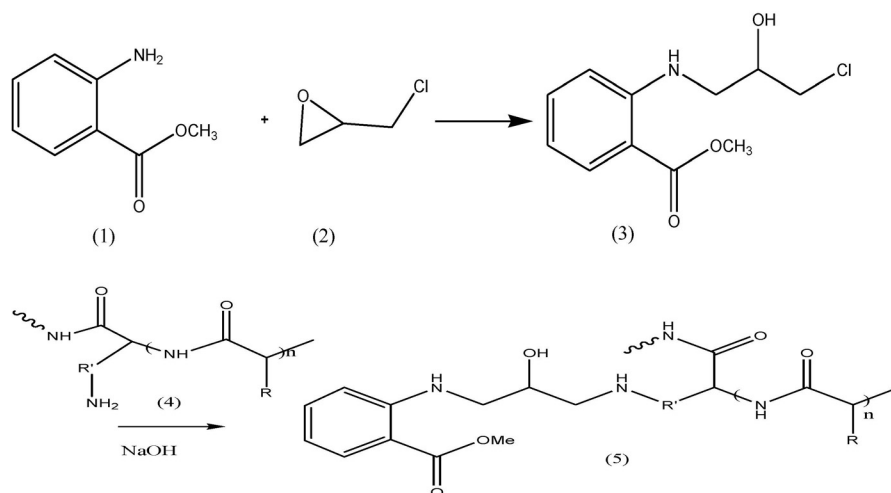
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The reaction of methylanthranilate (1), and epichlorohydrin (2) led to the synthesis of methyl 2-(3-chloro-2-hydroxypropylamino)benzoate (3). Reaction continued with collagen (4) and collagen possessing anthranilate moiety (5) was obtained in good 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)

References:

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

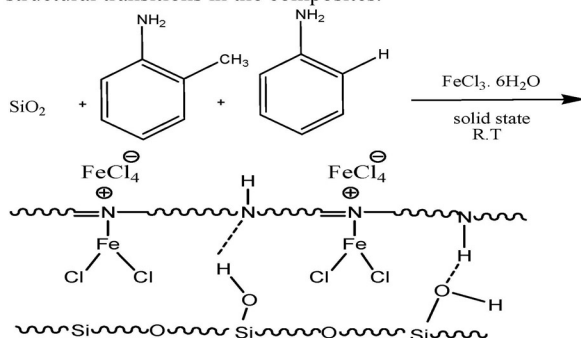
Ali Reza Modarresi-Alam^{a*}, Babak Abbaspour^a, Ali Reza Miri^a

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*modaresi@chem.usb.ac.ir

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. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was used as oxidant and with different ratios. We illustrated doping 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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18th Iranian Seminar Of Organic
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7-9 March 2012



PEG-SO₃H 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 development of heterogeneous methods with an active acid species can result in improvement in the overall 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 Brønsted acid catalyst for different organic functional group transformations either as reagent or as catalyst under heterogeneous and homogeneous [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-SO₃H 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, isatin 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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7-9 March 2012



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 O₂ 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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18th Iranian Seminar Of Organic
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7-9 March 2012



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

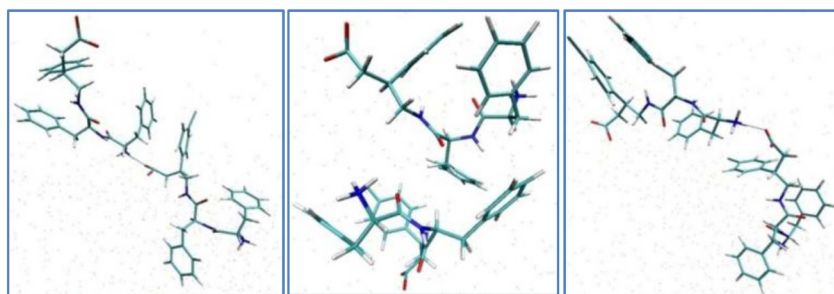
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The diphenylalanine dipeptide is a suitable building block for molecular self-assembly. It is well reported that misfolding of the peptidic chain may produce unwanted processes that provoke fatal diseases. One of these problematic processes could be 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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7-9 March 2012



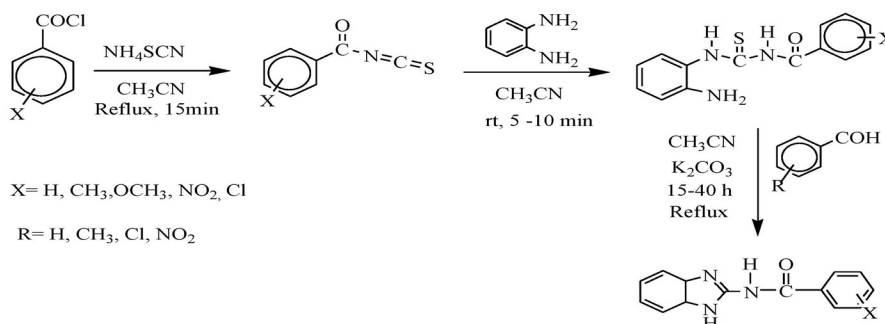
**Reaction of substituted N - (benzamido thiocarbonyl)
phenylenediamine with benzaldehyde derivatives**

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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 derivatives 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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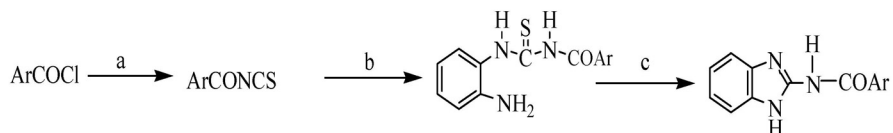


**Conversion of mono (2-substituted benzamido thiocarbonyl)
phenylenediamines to
benzimidazoles in the presence of ethyl bromoacetate**

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Chahooei

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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-NO₂-Ph, 4-Me-Ph

- a) NH₄SCN, CH₃CN, Reflux, 15 min b) o-phenylenediamine, CH₃CN, rt, 5-10 min
c) Ethyl bromoacetate, CH₃CN, K₂CO₃, Reflux, 10-15 h

References:

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18th Iranian Seminar Of Organic
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7-9 March 2012



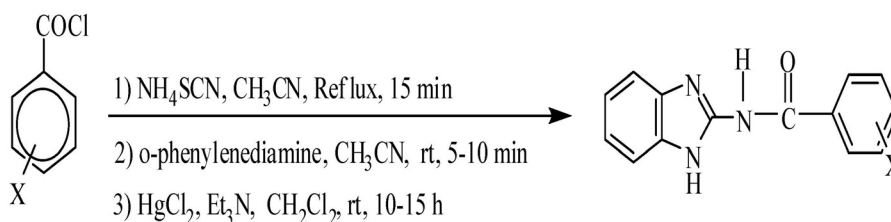
Synthesis of 2-substituted benzimidazoles in the presence of HgCl₂

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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 HgCl₂ led to the formation of corresponding 2-benzamido benzimidazoles in high yields at short reaction times.



X=H, CH₃OCH₃, NO₂, Cl

References:

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18th Iranian Seminar Of Organic
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Synthesis and Characterization of Polymerizable Urethane Acrylic Photoinitiator for UV-Curable Coatings

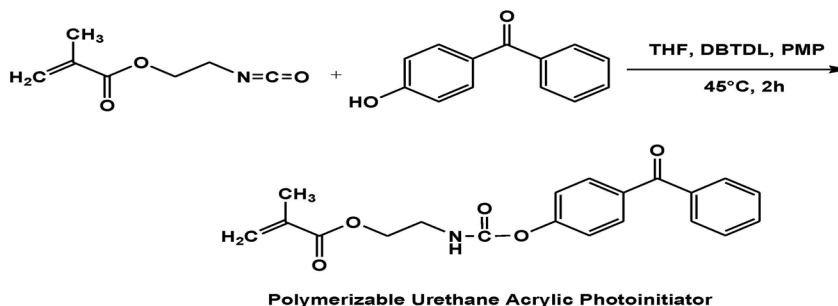
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Polymerizable urethane acrylic photoinitiator (PUAP) was synthesized by 2-isocyanato ethylmetacrylate and p-hydroxy benzophenone in present of dibutyltin dilaurate (DBTDL) as catalyst, p-methoxy phenol (PMP) as radical scavenger and tetrahydrofuran (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.



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18th Iranian Seminar Of Organic
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One-pot synthesis of pyrimidine-2-thiols in the presence of variety catalysts

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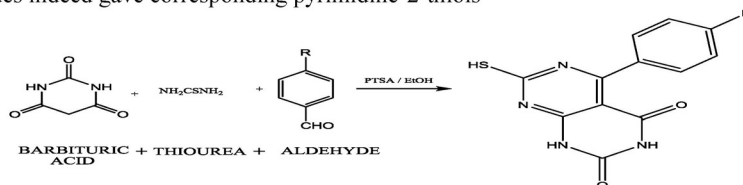
Bahman Sharifzadeh (PhD student of Organic Chemistry); Email: Shimibahman@yahoo.com

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 ¹H NMR spectrum of these compounds showed signals at 2.51 (CH₃) 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 synthesize pyrimidine-2-thiols in very pure condition and excellent yields.

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18th Iranian Seminar Of Organic
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7-9 March 2012



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

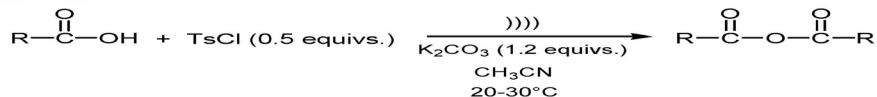
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Carboxylic acid anhydrides are well recognized as important class of reagents frequently used for a wide range of organic synthesis. In addition, they act as acylating agent and active intermediate in preparation of other functional groups such as 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.



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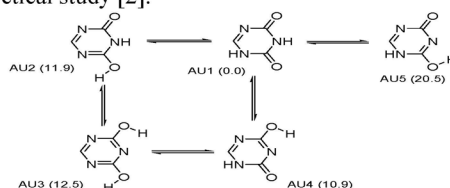
Water-assisted catalysis mechanism on tautomerism of 5-azauracil: A theoretical investigation

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(mzakarianejad@yahoo.com)

Tautomeric equilibrium in heterocyclic systems has been a significant interest and importance and has been studied theoretically using from semiempirical 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. results indicate that the tautomerization processes between isolated species cannot occur 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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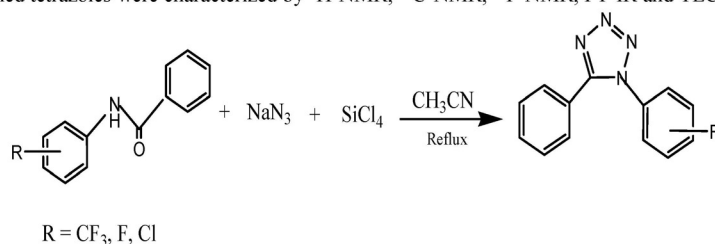
Synthesis of Hindered 1,5-Disubstituted Tetrazoles from Secondary Amides in One-Step

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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 $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, $^{19}\text{F-NMR}$, FT-IR and TLC.



Scheme

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

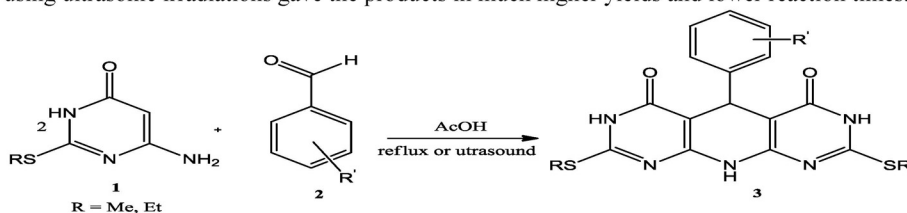
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Dihydropyridine derivatives possess a variety of biological activities and drugs such as nifedipine, nicardipine and amlodipine are effective cardiovascular agents for the treatment of hypertension [1-3]. Several fused heterocyclic system incorporating a pyrimidine ring in their structure, play important roles as antihypertensive, antiviral, anti-inflammatory 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 products (**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 products were established by spectroscopic (IR, ¹H NMR, ¹³C NMR) analysis.

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

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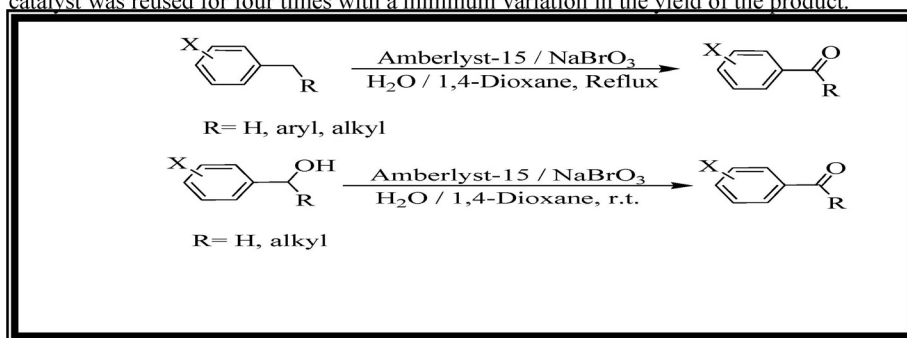
Amberlyst-15: an efficient and reusable catalyst for the oxidation of alkyl benzenes and alcohols with NaBrO₃

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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 NaBrO₃ 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

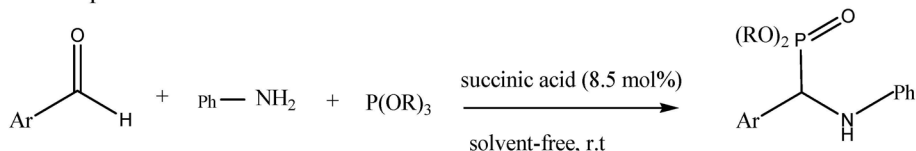
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α -Amino phosphonates are of growing importance in biological processes, because they are considered to be structural analogues of the corresponding α -amino acids and transition state mimics of peptide hydrolysis[1]. In these connection, the utilities 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 ^1H 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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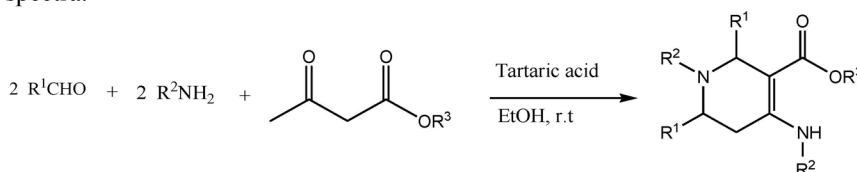
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The piperidine ring is common in a number of biologically important natural products[1]. There are thousands of literature references, including patents, which utilize such compounds in medicinal research[2]. Of these, 1,4 disubstituted piperidine 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 ¹H NMR spectra.



R¹, R²: ph, 4-Me-C₆H₄, 4-NO₂-C₆H₄, 4-F-C₆H₄, 4-OMe-C₆H₄

R³: 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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Halogenated compounds are widely used in chemistry synthesis, therefore synthesis of this compound 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 multipurpose reagent is very easy to prepare and can be used at room temperature. The proposed mechanism for this new method of α -bromo ketones is depicted in figure 1.

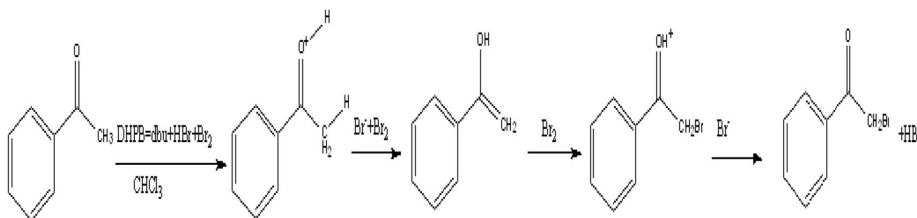
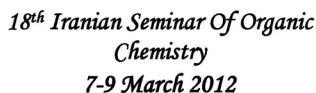


Figure 1

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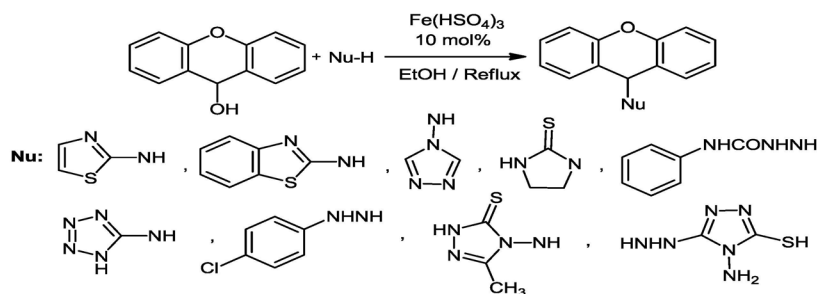


Efficient synthesis of novel 9H-xanthen-9-yl derivatives by $\text{Fe}(\text{HSO}_4)_3$ as a heterogeneous acid catalyst

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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 $\text{BF}_3 \cdot \text{Et}_2\text{O}$ have been reported [2-5]. We have previously reported that $\text{Fe}(\text{HSO}_4)_3$ 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-naphthol 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 $\text{S}_{\text{N}}1$ 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 regioselectivity. 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

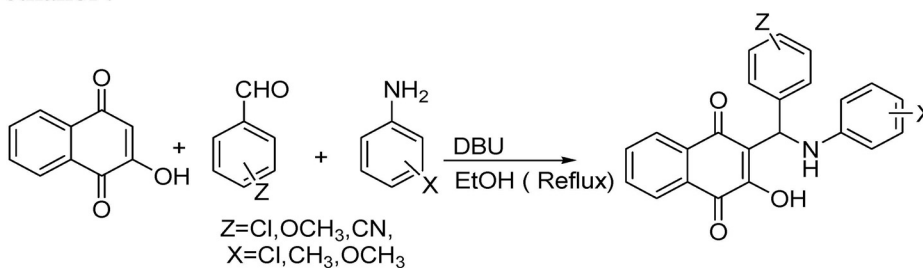
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ABSTRACT

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, leishmanicidal, 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- diones. 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 .



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7-9 March 2012



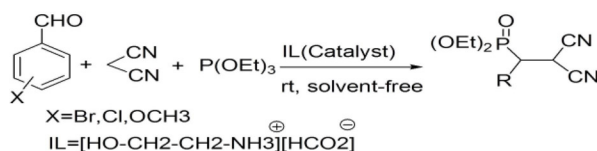
2-Hydroxy ethyl ammonium format as an efficient ionic liquid for as an efficient ionic liquid for efficient one-pot synthesis of β -hydroxyphosphonates

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Amongst 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, Brønsted 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 Brønsted 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].



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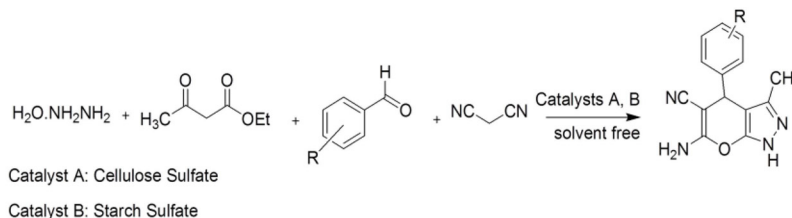
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Four-component synthesis of 1, 4-dihydropyrano [2, 3-c]pyrazoles using cellulose and starch sulfate as biodegradable and reusable catalysts

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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, 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 N₂ 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, ¹HNMR, and ¹³CNMR 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 ¹HNMR 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. ¹³C 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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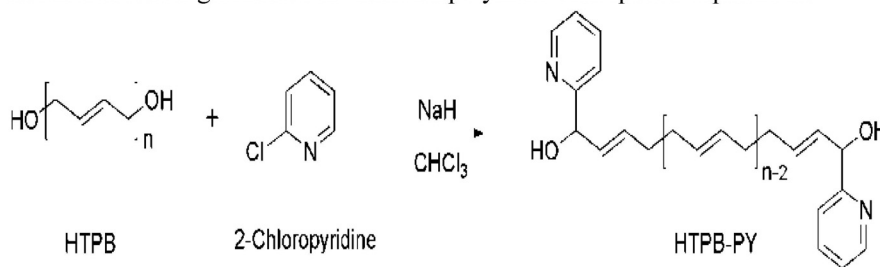
**Synthesis and characterization of terminally functionalized and epoxidized
hydroxyl-terminated polybutadiene**

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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[®] (2KHSO₅, KHSO₄, K₂SO₄) in buffered conditions [3]. The data from characterizing the products by ¹HNMR, ¹³CNMR, ¹⁴N-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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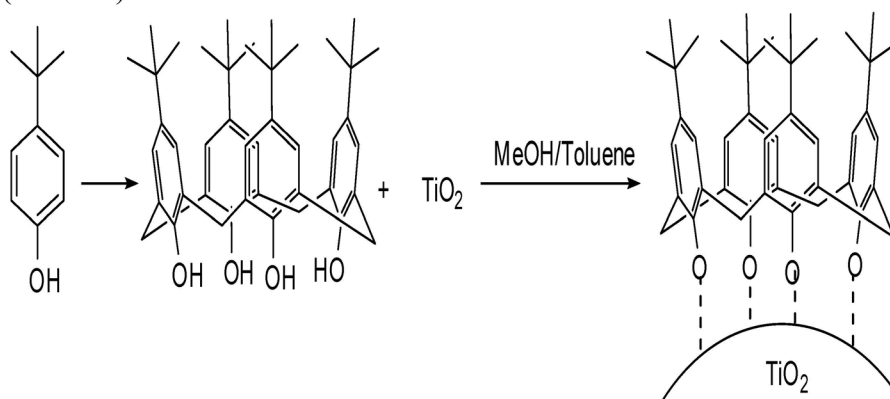
Synthesis of New Additive for Polymeric membranes based on Nanosupramolecule particles

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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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Tabatabayi seyed hossein

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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7-9 March 2012



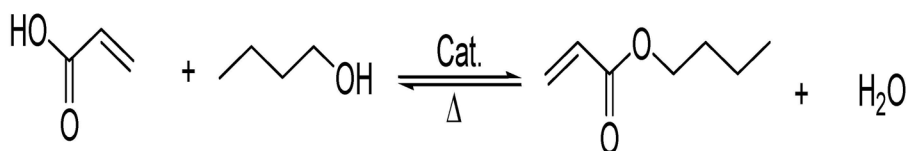
Design and Control of n-Butyl Acrylate Reactive Distillation Column System in Pilot Plant Scale

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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 types 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 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 Refractometry Spectroscopy and set at its optimal value.



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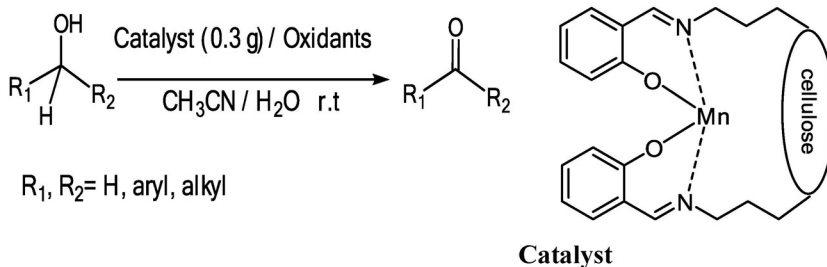
Green and efficient oxidation of alcohols catalyzed by Mn(II) salen complexes immobilized on cellulose in ambient condition

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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 complex catalyzed 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.



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18th Iranian Seminar Of Organic
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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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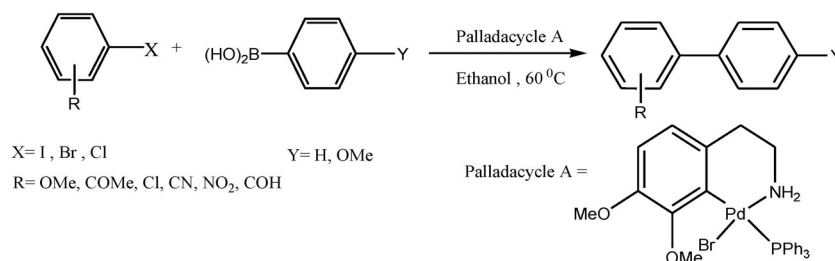
Transition metal-catalyzed cross-coupling reactions are one of the most important processes in modern organic synthesis for the formation of carbon-carbon and carbon-heteroatom bond [1]. Organopalladium compounds play an important role in homogeneous catalysis due to their versatility and nontoxicity.

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 $[\text{Pd}\{\text{C}_6\text{H}_2(\text{CH}_2\text{CH}_2\text{NH}_2)(\text{OMe})_2,3,4\}\text{Br}(\text{PPh}_3)]$. The activity of this complex was investigated in the Suzuki–Miyaura C–C cross-coupling and compared with a dimeric $[\text{Pd}\{\text{C}_6\text{H}_2(\text{CH}_2\text{CH}_2\text{NH}_2)(\text{OMe})_2,3,4\}(\text{I}-\text{Br})_2]$ 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

References:

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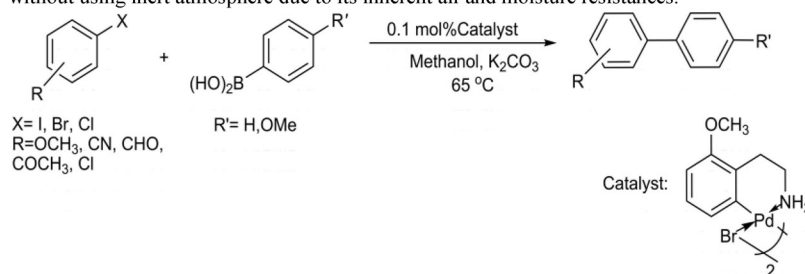
An Efficient Dimeric Ortho-Palladated Complex of 2-Methoxyphenethylamine for Suzuki-Miyaura Cross-Coupling Reaction under Microwave Irradiation and Conventional Heating

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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 $[\text{Pd}\{\text{C}_6\text{H}_3(\text{CH}_2\text{CH}_2\text{NH}_2)\text{-4-OMe-5-}\kappa^2\text{-C,N}\}(\mu\text{-Br})]_2$ 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 coupling 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

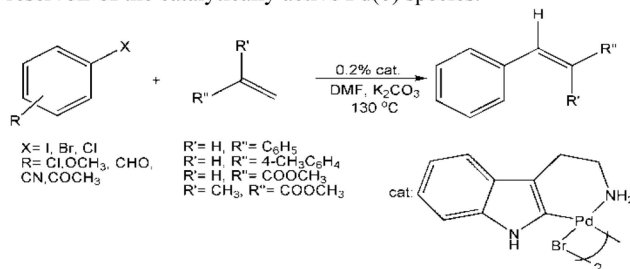
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The Heck coupling reaction is one of the most powerful tools in synthetic chemistry for constructing aromatic carbon-carbon bonds between complex organic molecules with potential industrial or pharmaceutical applications [1,2]. Various forms of palladium 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 $[\text{Pd}_2\{(\kappa^2\text{-}C,N\text{-}C_8H_5NCH_2CH_2NH_2)_2\}(\mu\text{-}Br)_2]$ 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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7-9 March 2012



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

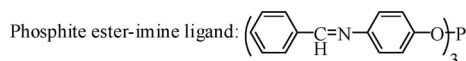
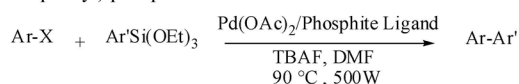
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Palladium catalyzed-transformations are among the most potent and convenient tools of modern organic synthesis for C-C bond formation [1]. There are various cross coupling reactions and among them the Hiyama coupling reactions using organosilicon reagents 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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7-9 March 2012

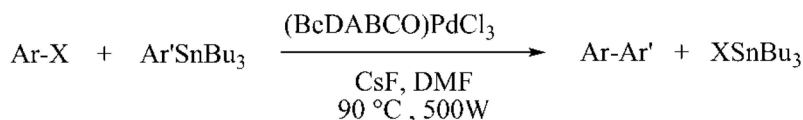


(BeDABCO)PdCl₃ as a highly active catalyst for the microwave-assisted Stille cross coupling reaction

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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)PdCl₃ homogeneous complex for the cross-coupling reaction of various aryl halides with phenyltributyltin under microwave irradiation. An efficient catalytic system using (BeDABCO)PdCl₃ 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).



Scheme 1. The Stille cross coupling reaction by (BeDABCO)PdCl₃

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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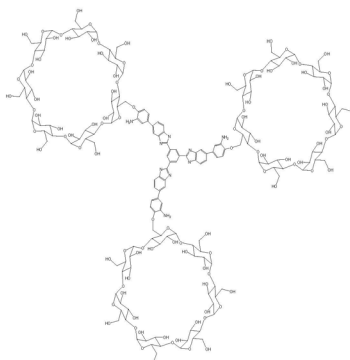
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7-9 March 2012



**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'-diaminobenzidine (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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$\text{BF}_3 \cdot \text{Et}_2\text{O}$, 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- $\text{BF}_3 \cdot \text{SiO}_2$ [1,2], $\text{BF}_3 \cdot \text{SiO}_2$ [3-5], $\text{SnCl}_4 \cdot \text{SiO}_2$ [6], nano- $\text{SnCl}_4 \cdot \text{SiO}_2$ [7], nano- $\text{TiCl}_4 \cdot \text{SiO}_2$ [8], and nano- $\text{SbCl}_5 \cdot \text{SiO}_2$ [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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18th Iranian Seminar Of Organic
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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 field 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 CaCl₂ 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 Ca²⁺ 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 (Ca²⁺ 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 Ca²⁺ 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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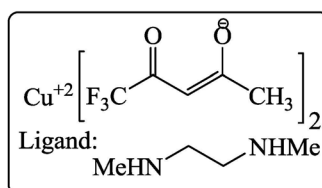
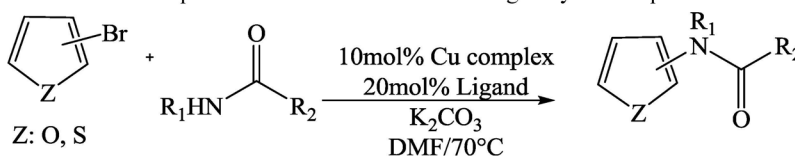


**C-N formation of Buchwald-Hartwig amidation type for substituted
thiophenes and furans**

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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 K₂CO₃ as base in presence of DMEDA as ligand, amidation of 2 and 3 Bromo thiophenes and furan rings has been completed. In 70°C temperature and DMF as the solvent good yields of products obtained.



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

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7-9 March 2012

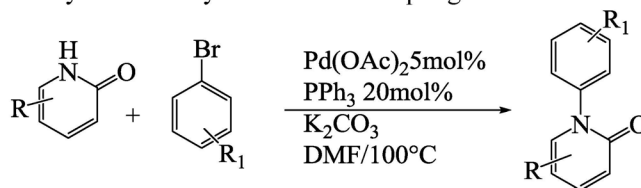


A New Methodology approach for coupling of pyridin-2-ones with aryl bromides Catalyzed by Palladium(II)

Zahra Yasaei*; Mehdi Soheilzad; Marjan Azimzadeh Arani and Mehdi Adib*
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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 conclusion, we have developed an efficient, general, catalytic system for C-N coupling of aryl bromides with pyridin-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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Chemistry
7-9 March 2012

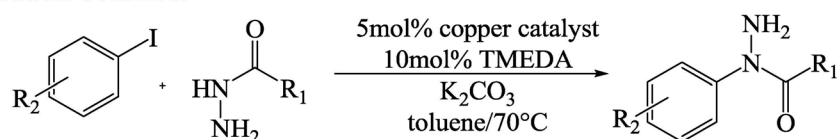


Regioselective synthesis of N-Aryl Hydrazide with copper(II) catalyst

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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*- substituted aryl iodides and N-protected hydrazine is reported. In presence of catalytic amounts of copper(II) trifluoroacetylacetonate and Tetramethylethylenediamine as ligand and K₂CO₃ as base good yields of products obtained.



In conclusion, we have developed an efficient, inexpensive, general, catalytic system for regioselective coupling of aryl iodides and benzoic hydrazide 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.

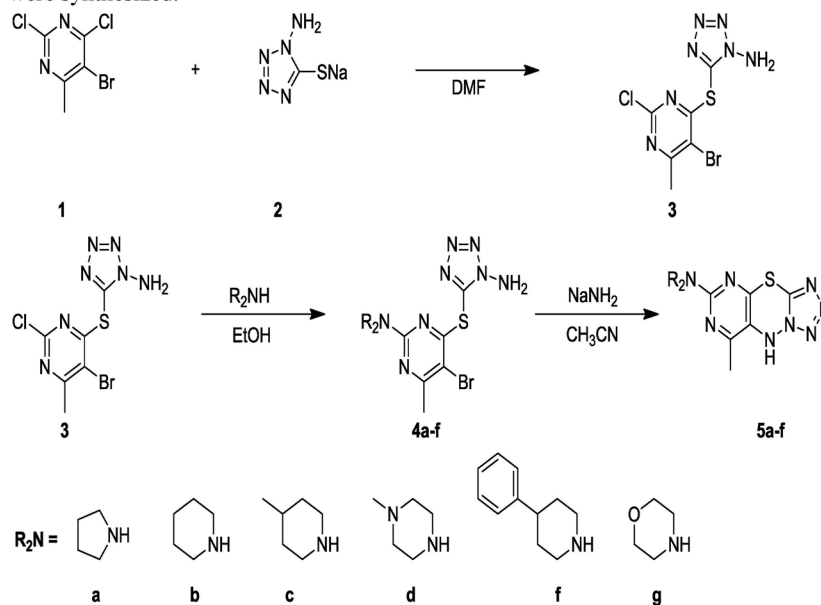
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Pyrimido thiazines are interesting compounds because of their biological activities[1]. Significant lipooxygenase inhibition activity are observed for certain 2-substituted pyrimido[4,5-b][1,4]benzothiazines, e.g. 4-methyl-2-(4-methylpiperazin-1-yl)-5H-benzo[b]pyrimido[5,4-e][1,4]thiazine, 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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18th Iranian Seminar Of Organic
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7-9 March 2012



**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.

Acknowledgments: S. B. thanks Ministry of Science, Research and Technology for financial support.

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



**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. clinopodioides* 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 apparatus from the aerial parts of three populations of *Z. clinopodioides* 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, referring 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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18th Iranian Seminar Of Organic
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7-9 March 2012



**Tandem bis-aza-Michael addition reaction of amines in aqueous
Medium catalyzed by Poly(ethylene glycol)-bound Sulfonic acid (PEG-SO₃H)**

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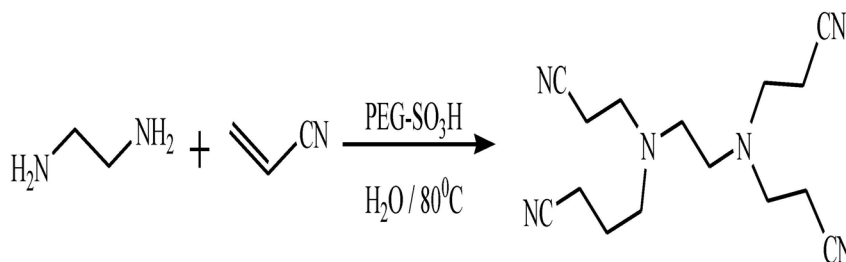
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The development of new methodologies aimed at improving synthetic efficiency is an important goal in contemporary organic synthesis. A domino process, which involves several bond-forming reactions in a single manipulation, represents an attractive 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-SO₃H, 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-SO₃H 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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18th Iranian Seminar Of Organic
Chemistry
7-9 March 2012



**PEG-SO₃H-catalyzed three-component coupling of naphthol, alkyne
and aldehyde: a novel synthesis of 1,3-disubstituted-3H-benzo[f]
chromenes**

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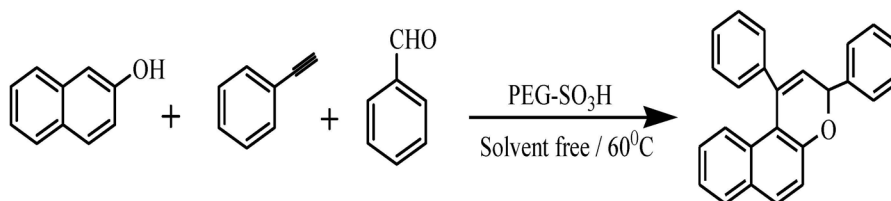
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Multicomponent reactions (MCRs) are special types of synthetically useful organic reactions in which three or more different starting materials react to give a final product in a one-pot procedure [1,2].

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-SO₃H. Accordingly, we first attempted a three-component coupling of 2-naphthol, phenyl acetylene and benzaldehyde using PEG-SO₃H 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-SO₃H 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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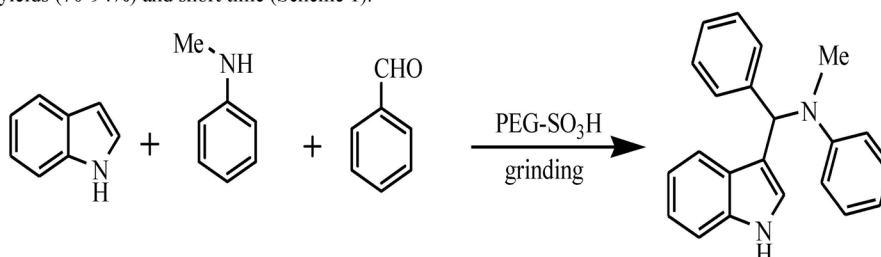
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7-9 March 2012



One-step, three-component synthesis of novel 3-substituted indoles using Poly(ethylene glycol)-bound Sulfonic acid (PEG-SO₃H) 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-SO₃H) works efficiently for organic transformations. In continuation of our efforts for exploring PEG-SO₃H 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-SO₃H as a reusable catalyst at room temperature, with high yields (70-94%) and short time (Scheme 1).



Scheme 1

Reference:

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



**One-step, three-component synthesis of highly substituted pyridines using
PEG-SO₃H as reusable catalyst**

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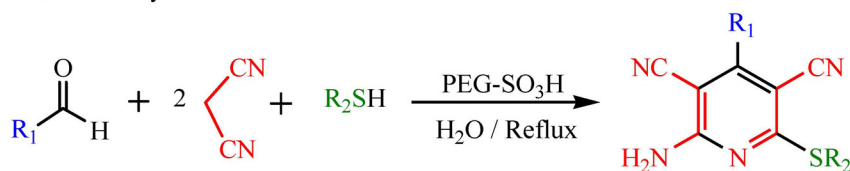
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The synthesis of 'privileged medicinal scaffolds' is highly important as these compounds often act as ligands for a number of functionally and structurally diverse biological receptors, and consequently, serve as a platform for developing pharmaceutical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

Among them, 2-amino-3,5-dicarbonitrile-6-sulfanylpiperidines 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 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-sulfanylpiperidines via multicomponent reaction of aldehydes, malononitrile, and thiols using PEG-SO₃H as a very mild, effective, environmentally benign, and reusable catalyst.



References:

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



One pot synthesis of β -amino ketones via direct Mannich-type reaction catalyzed with Poly(ethylene glycol)-bound Sulfonic acid (PEG-SO₃H)

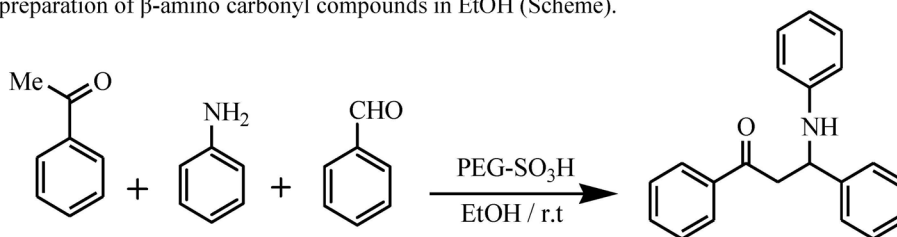
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Mannich reactions are among the most important carbon– carbon bond forming reactions in organic synthesis [1]. They provide β -amino carbonyl compounds, which are important synthetic intermediates for various pharmaceuticals and natural products [2]. 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-SO₃H) 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-SO₃H, for the preparation of β -amino carbonyl compounds in EtOH (Scheme).



References:

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18th Iranian Seminar Of Organic
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7-9 March 2012



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

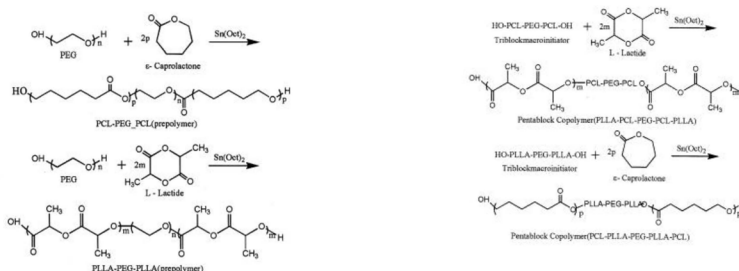
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Biodegradable polymers have been in use for many applications like surgical sutures, encapsulates, scaffolds, and other advanced bio- medical and pharmaceutical devices [1]. The properties of Polylactide (PLA) and poly(ϵ -caprolactone) (PCL), such 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 $\text{Sn}(\text{Oct})_2$ 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 ¹H-NMR and ¹³C-NMR analyses. Thermal behavior and thermal stability of these copolymers were evaluated by DSC and TGA thermograms, respectively.

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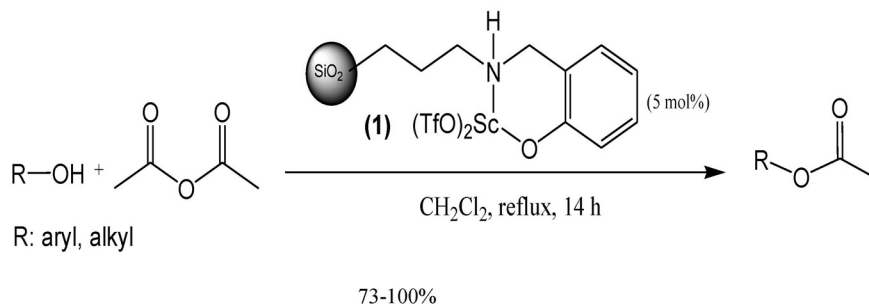
Silica-based scandium (III) as an efficient and recyclable interphase catalyst for acetylation of alcohols and phenols

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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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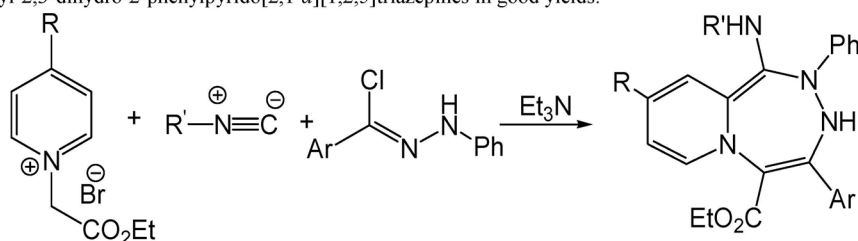
New Applications of Imidoyl Chlorides in Heterocyclic Synthesis

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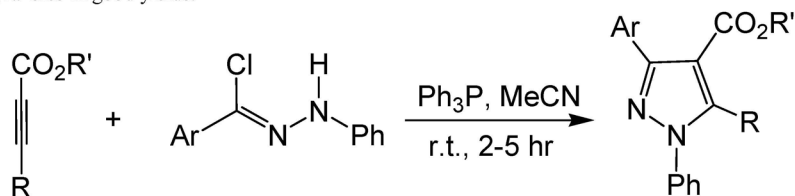
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Imidoyl chlorides (prepared *in situ* from the corresponding amides, Ph_3P and CCl_4), are employed in multi-component condensation reactions with nucleophiles and electron-deficient acetylenic esters to give new heterocyclic compounds. Thus, a sequential 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.



Yield: 72-81%

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.



Yield: 83-93%

Various features of these transformations will be presented and discussed.

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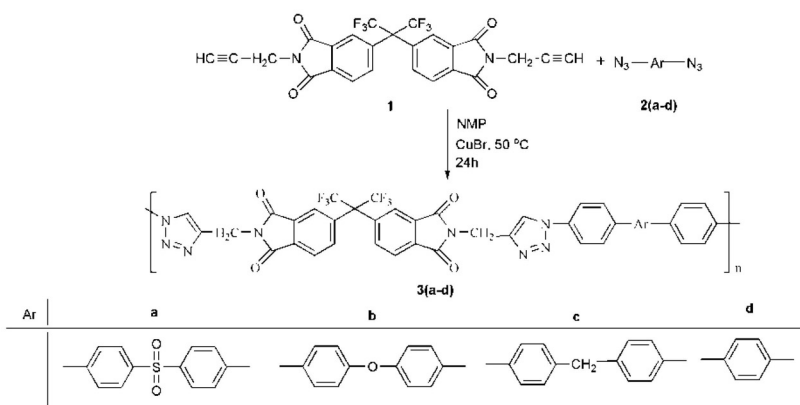
Preparation and Properties of Novel Polyimides Bearing Triazole Units in Backbone by Click reaction

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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) bisphthalimide (1). The polymerization of dialkyne (1) and diazides 2(a-d) was easily 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, ¹H 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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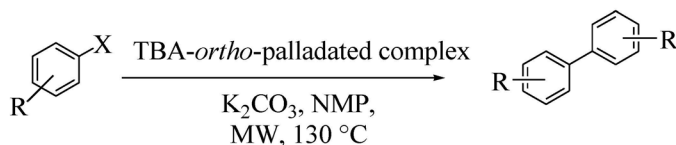
Microwave-promoted homo-coupling reaction of aryl halides using TBA-ortho-palladated complex

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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 $[\text{Pd}\{\text{C}_6\text{H}_4(\text{CH}_2\text{N}(\text{CH}_2\text{Ph})_2)\}(\mu\text{-Br})_2]$ 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: $[\text{Pd}\{\text{C}_6\text{H}_4(\text{CH}_2\text{N}(\text{CH}_2\text{Ph})_2)\}(\mu\text{-Br})_2]$

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

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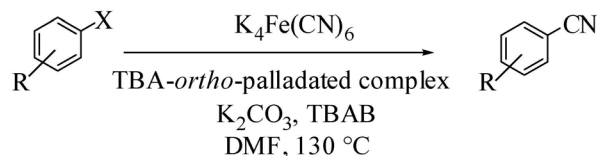
Microwave-assisted cyanation of aryl halides using TBA-ortho-palladated complex

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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: $[Pd\{C_6H_4(CH_2N(CH_2Ph)_2)(\mu-Br)\}_2]$

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

References

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18th Iranian Seminar Of Organic
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7-9 March 2012



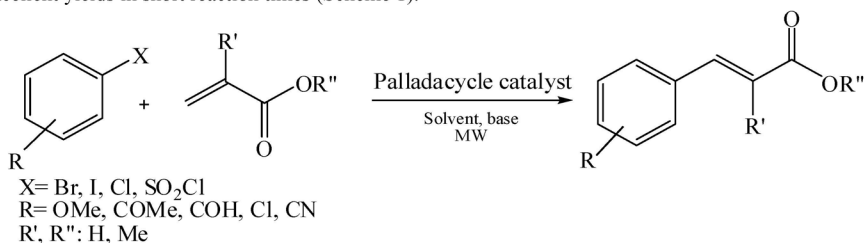
CN-dimeric and monomeric ortho-palladated complexes catalyzed microwave-promoted Heck coupling reaction

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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]. These 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 $[\text{Pd}\{\text{C}_6\text{H}_2(\text{CH}_2\text{CH}_2\text{NH}_2)(\text{OMe})_{2,2,3}\}(\mu\text{-Br})_2]$ and monomeric $[\text{Pd}\{\text{C}_6\text{H}_2(\text{CH}_2\text{CH}_2\text{NH}_2)(\text{OMe})_{2,2,3}\}\text{Br}(\text{PPh}_3)]$ complexes as efficient, stable and non-sensitive to air and moisture catalysts was investigated in the Heck coupling reaction. Vinylation of various aryl halides 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).



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

References

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18th Iranian Seminar Of Organic
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7-9 March 2012



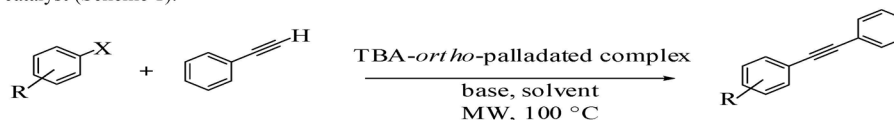
TBA-ortho-palladated complex catalyzed microwave-enhanced copper-free Sonogashira cross coupling reaction

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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 hindered 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 diphenylethyne were produced in excellent yields in short reaction times using catalytic amount of this catalyst (Scheme 1).



TBA-*ortho*-palladated: $[\text{Pd}\{\text{C}_6\text{H}_4(\text{CH}_2\text{N}(\text{CH}_2\text{Ph})_2)(\mu\text{-Br})\}_2]$

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

References

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7-9 March 2012



**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, has 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 swollen 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 Dailaman specimen these components were found with small amount.

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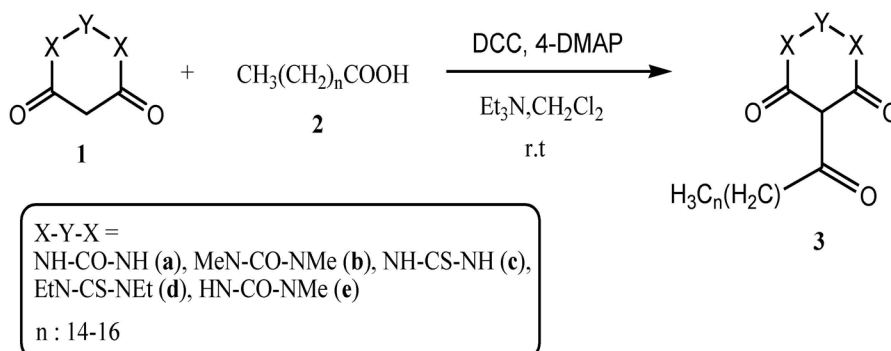
Investigation of the acylation reaction of (thio)barbituric acid derivatives for the synthesis of new type of micelle

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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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7-9 March 2012



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

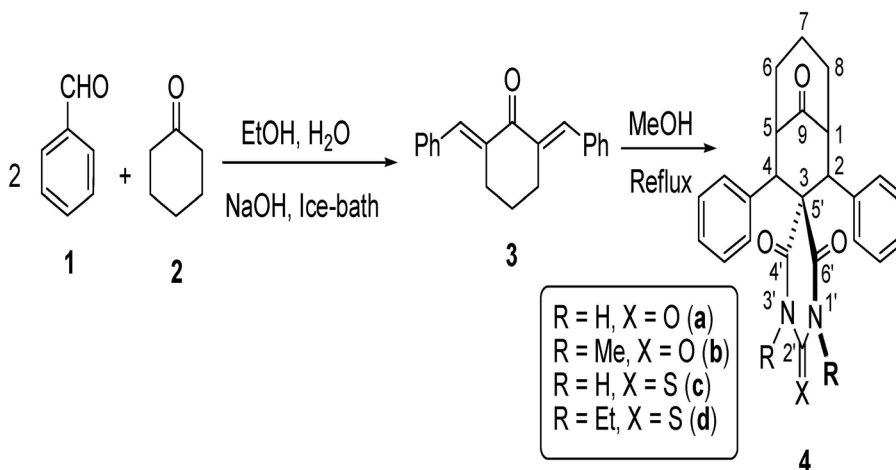
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Spiro [bicyclo] barbiturates are well-known as biological and pharmaceutical effects [1]. Several works have been reported for the synthesis of other spiro barbiturates (except spiro[bicyclo] barbiturates based on cyclohexanone) [2-4]. As we searched 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 ^1H NMR, ^{13}C NMR, FT-IR, UV-visible and mass spectroscopy techniques (Scheme 1).



Scheme 1

References

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7-9 March 2012

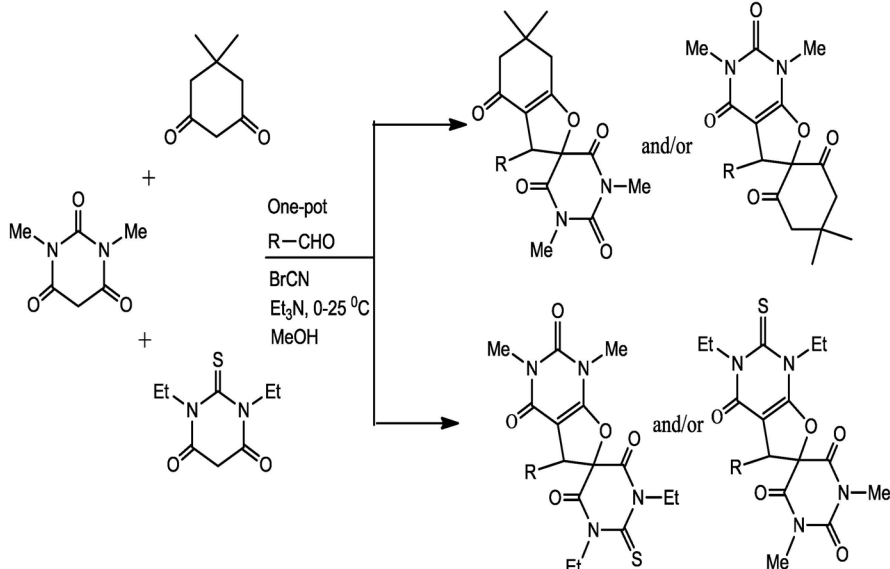


One-pot, crossed multi component reaction for selective formation of spiro dihydrofuranes and spiro furo[2,3-d]pyrimidines in the reaction of dimedone, barbituric acids, BrCN and aldehydes

Alireza Shokr, Nader Noroozi Pesya*, Marziyeh Bagheri* and Mohammad Behrui
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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, ¹H-NMR, ¹³C-NMR and Mass analysis.



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Chemistry
7-9 March 2012



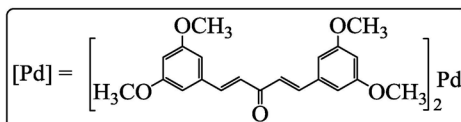
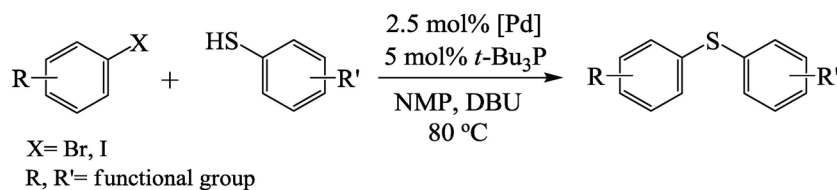
A New Methodology Approach for Synthesis of Aryl Sulfides Catalyzed by Palladium

Mehdi Soheilizad*, Marjan Azimzadeh Arani, Zahra Yasaei, Sadegh Shabani, Mehdi Adib
School of Chemistry, University College of Science, University of Tehran, Tehran

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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18th Iranian Seminar Of Organic
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7-9 March 2012



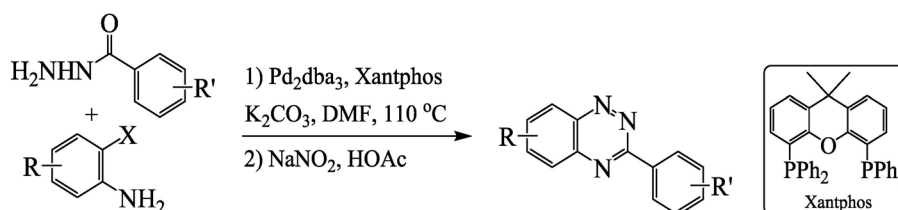
A Mild and Efficient Palladium-Catalyzed of benzo[e]-1,2,4-triazines by Reaction of 2-Haloanilines and Benzohydrazides

Mehdi Soheilizad* and Mehdi Adib

School of Chemistry, University College of Science, University of Tehran, Tehran

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 Pd₂dba₃/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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Chemistry
7-9 March 2012

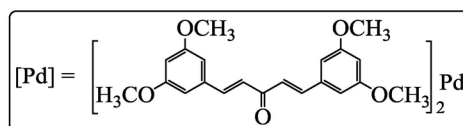
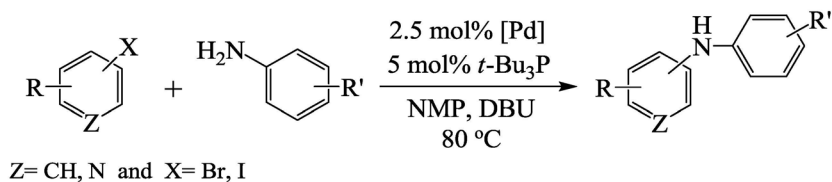


A New Strategy for Buchwald-Hartwig Coupling of Aryl and Hetroarylhalides with Primary Amines Catalyzed by Palladium(0) Complex

Mehdi Soheilizad*, Zahra Yasaei, Marjan Azimzadeh Arani, Sadegh Shabani, Mehdi Adib
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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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18th Iranian Seminar Of Organic
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7-9 March 2012



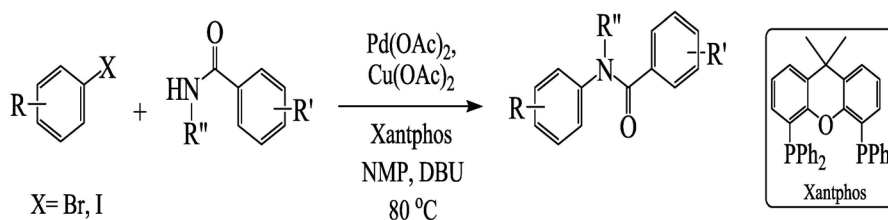
A New Methodology for Synthesis of *N*-arylamides: Palladium-/Copper Catalyzed *N*-Arylation of Amides and Aryl Halides

Mehdi Soheilizad*, Sadegh Shabani, Mehdi Adib

School of Chemistry, University College of Science, University of Tehran, Tehran

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



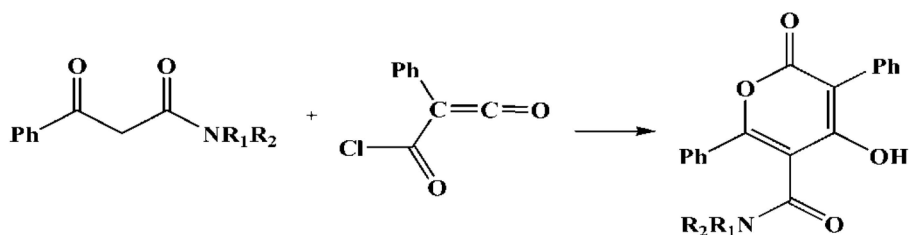
Synthesis of 2-Pyrone derivatives from (chlorocarbonyl)phenyl ketene with β -ketoamids and 4-hydroxy-2H-thiochromen-2-one

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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-diketones[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-dione derivatives using the reaction of 4-hydroxy-2H-thiochromen-2-one derivatives with (chlorocarbonyl)phenyl ketene in good yields.

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



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

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Iran.

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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18th Iranian Seminar Of Organic
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7-9 March 2012



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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18th Iranian Seminar Of Organic
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7-9 March 2012



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

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

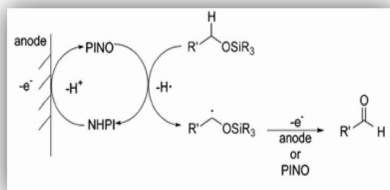
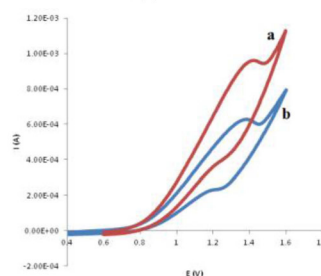


Fig 2-electrocatalytic oxidation of silylether



electrochemical cell was used for the analytical experiments. An Ag/AgNO₃ 0.01 M+0.1Mm Ethoxytrimethylsilane+CH₃CN+tetra-butylammonium bromide 0.1 M electrode was used as a reference. A glassy carbon disk (diameter 5 mm) was used as working electrode.

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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7-9 March 2012



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

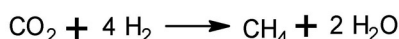
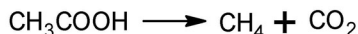
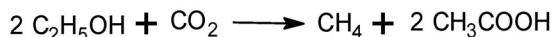
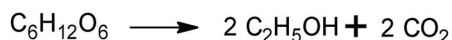
J. Abedini-Torghabeh*, A. Najafi, A. Adinehnia, M. Alizadeh, A. Oghaziyan

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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 acidogenesis 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]:



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 m³ 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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18th Iranian Seminar Of Organic
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7-9 March 2012



**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 ¹HNMR 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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18th Iranian Seminar Of Organic
Chemistry
7-9 March 2012



**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 CO₂ 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 supercapacitor 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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Chemistry
7-9 March 2012



**A Green Protocol for Reduction of Aromatic Nitro Compounds to
Amines with NaBH₄/Cu(dmgl)₂ System in Water**

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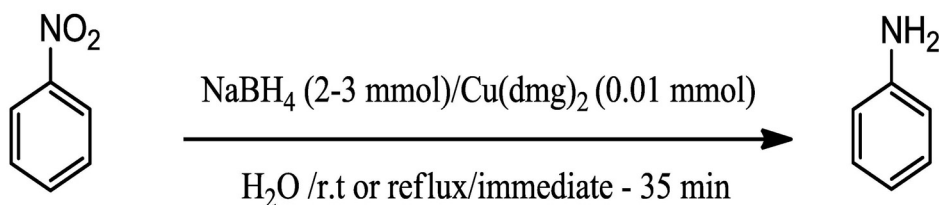
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Aromatic amines are important starting materials and intermediates for manufacturing a great variety of chemicals, such as dyestuffs, pharmaceutical products, agricultural chemicals, photographic chemicals, surfactants, textile auxiliaries, chelating 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 NaBH₄/Cu(dmgl)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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18th Iranian Seminar Of Organic
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7-9 March 2012



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

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



**Synthesis 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 H₂ 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 CO₂[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 (TGA/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 Cu-Cr-O nanocomposites can be produced by using a temperature as low as 600 °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; Sol-gel chemistry; Citric acid; Nanomaterials; Catalysts;

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18th Iranian Seminar Of Organic
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7-9 March 2012



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

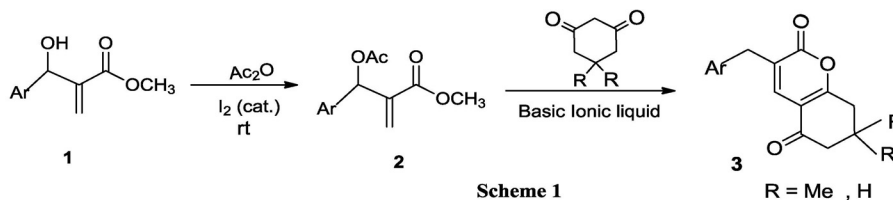
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Various derivatives of α -pyrone, have been synthesized and evaluated for their biological activities in recent years. Some of these products have exhibited a broad range of activities such as anti-HIV, antimicrobial, antifungal, anti-alzheimer and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

Based on our continued interests in the development of benign methods in the synthesis of heterocycles of medicinal importance [6], we studied the synthesis 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 excellent 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 excellent yields (80-91%) (Scheme1).



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



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



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

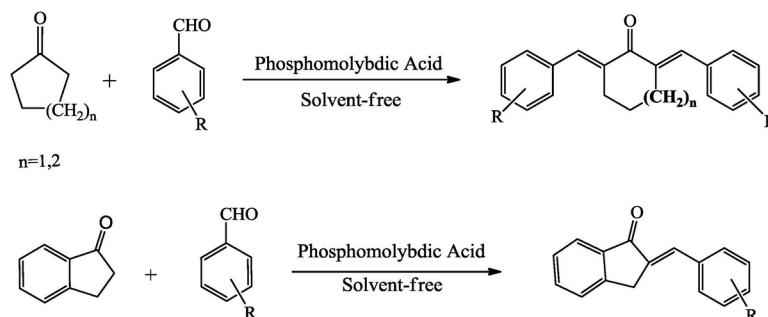
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The aldol condensation of cycloalkanones and aromatic aldehydes is one of the most important methods for the preparation of α,α' -bis(substituted benzylidene) cycloalkanones. Although this method has been introduced over than 100 year ago, however, 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 phosphomolybdic 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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18th Iranian Seminar Of Organic
Chemistry
7-9 March 2012



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 : $\text{mg/ml Hb} = 1.55 \text{ OD}_{280} - 0.76 \text{ OD}_{260}$. 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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18th Iranian Seminar Of Organic
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7-9 March 2012



One-pot, water-medium green synthesis of the Hantzsch product by PEG-SO₃H

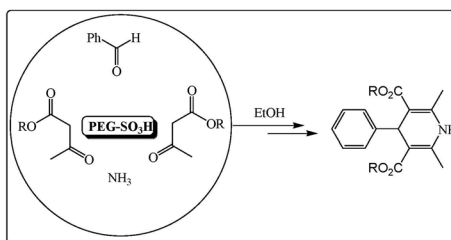
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Recently, due to the vast medicinal utility of 1,4-dihydropyrimidine (Hantzsch product) and its derivatives, various methods to prepare these compounds have been reported. [1] Based on recent efforts to use eco-friendly reagents in chemistry, we choose 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-friendly 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-SO₃H reduced after 3 cycles.

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



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

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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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18th Iranian Seminar Of Organic
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7-9 March 2012



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



Microsynthesis and gas chromatography electron ionization mass spectrometry 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.

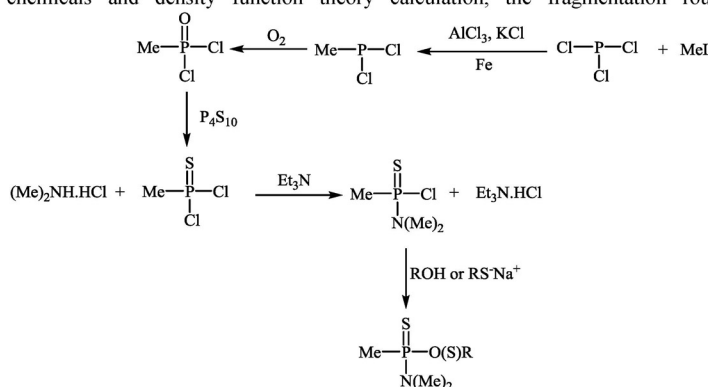


Fig. 1. Microsynthesis route of *O(S)*-alkyl *N,N*-dimethylamino methylthiophosphonates (methylthiophosphonothiolates)

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



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



Al(DS)₃ efficiently catalyzed condensation of 1,4-dicarbonyl compounds and amines in water at room temperature: a green Paal-Knorr pyrroles synthesis

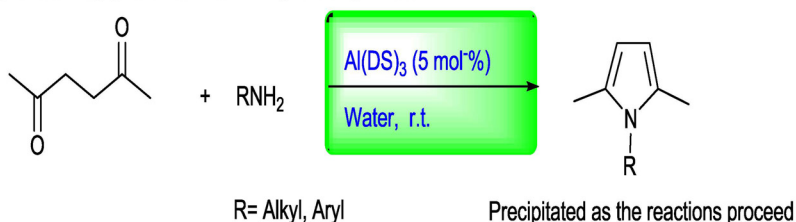
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‘Click chemistry’, a term recently coined by Sharpless and co-workers,¹ denotes a growing family of powerful chemical reactions that are based on ‘spring-loaded’ energy-intensive substrates that can, under the right conditions, unload their energy 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

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



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 flavonoids: 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-hexane, 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 was established by ¹H NMR, ¹³C NMR, ²D NMR (C-H-Cosy, HMQC), DEPT and Mass spectroscopy and confirmed in accordance with bibliographic data and computational chemistry results.

The three components were evaluated against 7 microorganisms including gram(+) bacteria by measurement 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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18th Iranian Seminar Of Organic
Chemistry
7-9 March 2012



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 (IC₅₀ 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, Antimicrobial activity, Total phenolic

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



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



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 period 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%), *Artemisia* 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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18th Iranian Seminar Of Organic
Chemistry
7-9 March 2012



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-benzoquinones. 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 pharmacological 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 addition 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, aceto 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, ¹³CNMR, ¹HNMR, MS study.

The presence of poor leaving groups or bulky groups on the reactive positions of chemically generated o-benzoquinone, 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 addition 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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18th Iranian Seminar Of Organic
Chemistry
7-9 March 2012



Study of Hydrophobic Mismatch Alleviation Mechanism By Molecular Dynamics Simulation of
KALP₁₅ 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 KALP₁₅ peptide (Aminoacid sequence: Ac-GKK (LA)₄L KKA-NH₂) 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 KALP₁₅ 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 Å° for DPPC bilayer and the length of hydrophobic stretch of 13.5 Å° for KALP₁₅ peptide, gives rise to negative hydrophobic mismatch of -14.5 Å°. 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. KALP₁₅ 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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