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

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

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

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

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

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

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Abstract

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

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

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

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

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

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

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

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

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

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

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

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

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

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Metal- based drugs have been used in therapeutic medicine for several hundreds of years and are used in contemporary society for the treatment of a large variety of human ailments, e.g., cancer, diabetes, and rheumatoid arthritis, as well as in diagnostic medicine.
Dithiocarbamates have also been investigated for anti-cancer potential, must notably platinum and palladium dithiocarbamates. Based on cytotoxicity assays, often the metal-containing dithiocarbamate compounds show greater potency than cisplatin but, are not as cytotoxic as other standard drugs.
Thus the interaction of a new palladium(II) antitumor complex of [μ-buthylen bis(dithiocarbamato)-bis(bipyridine) Palladium(II)] Nitrate with Calf Thymus DNA was studied by isothermal titration method in 30mM Tris_HCl buffer solution (pH=7.0) at 300 and 310K.
There is a set of 23 binding sits(g) for the complex on the DNA with positive cooperativity in binding. n,the Hill coefficient (as a criterion of cooperativity) find out to be 4.9 at 300 K and 6.8 at 310K respectively. K_{app} the apparent equilibrium constant are 21.0 mM^{-1} and 39.2 mM^{-1} at 300K and 310K respectively.
The above compound can denature the DNA and the concentration of this ligand in the midpoint of transition ($[L]_{1/2}$), is decreased by improving temperature, from 0.21 mmol/L at 300K to 0.18 mmol/L at 310K. the conformational stability of DNA in the interaction with ligand (ΔG^0_{H2O}) determined to be 24.3 kJ/mol and 26.2 kJ/mol at 300K and 310K respectively.
Presence of ligand led to less stability of the DNA . values for m, (a measure of ligand strength for DNA denaturation) are 0.55 and 0.72 (kJ/mol).$(mol/L)^{-1}$ at 300K and 310K respectively.
Enthalpy of DNA denaturation by the complex ($\Delta H^0_{coformation}$ or $\Delta H^0_{denaturation}$) in the range of 300K and 310K is find out to be 5.6 kJ/mol. In addition, the calculated entropy (ΔS^0_{H2O}) of DNA denaturation by complex is -0.16 kJ/mol at 300K. the negative value of entropy change is related to the more disorder of denatured DNA with respect to the native DNA.

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

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ABSTRACT

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

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

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

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

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Phytochemical analysis of *Pterocarya fraxinifolia* L. from Guilan

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

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

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

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

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

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

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((Organic chemistry/ phytochemistry))

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

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

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

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

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

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

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7-9 March 2012

((Organic chemistry/ phytochemistry))

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

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

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

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

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

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

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

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

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

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

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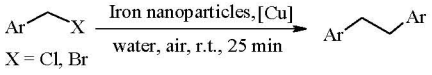
The development of useful reagents and efficient catalysts which enable carbon-carbon bond formation, is a key part of contemporary organic synthesis. The reductive coupling of organic halides is an important method for C–C bond formation where Wurtz and Ullmann reactions are classical methods for the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

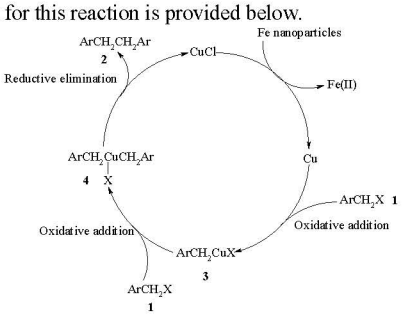
Recently transition-metal nanoparticles have attracted a great deal of attention; their preparation, structure determination, and applications are topics of current interest.[2] One of these applications is their use in reactions generating C–C bonds.[3]

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



1 **2**

A mechanistic rationalization for this reaction is provided below.



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N-Heterocyclic carbenes related to quinazoline at DFT

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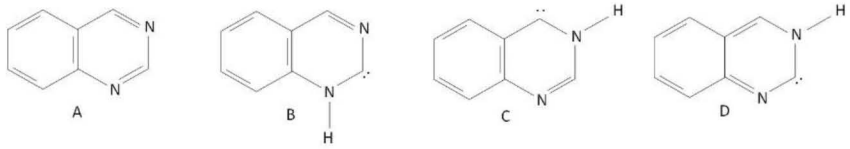
There is some scattered information about pyridine derived N-heterocyclic carbenes (NHCs) first proposed as a reaction intermediate 70 years ago by Hammick [1, 2]. Close to pyridine the quinazoline ring as an unstable compound, **A** (Scheme1), along with many alkaloids, is a widely recognized moiety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

Scheme 1. Three carbenic tautomers of quinazoline



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

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

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

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

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

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

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

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

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

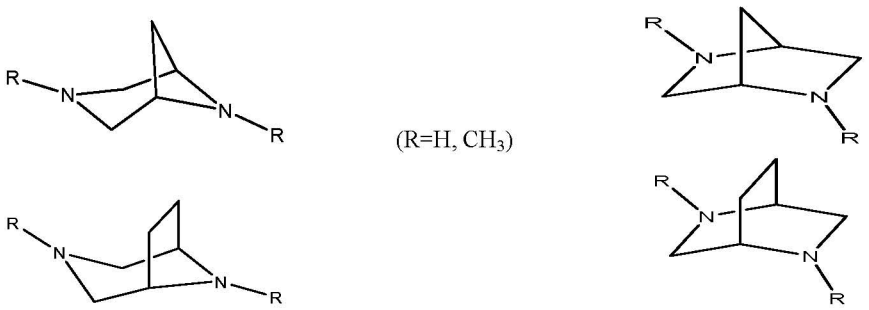

Figure 1

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

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Abstract:

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

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

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

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

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

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

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

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

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

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

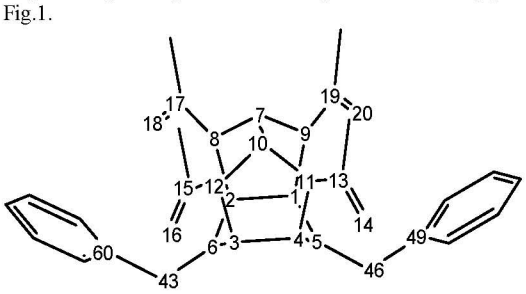

Figure 1. The atom numeration for tadbiw molecule used for calculations.

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

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

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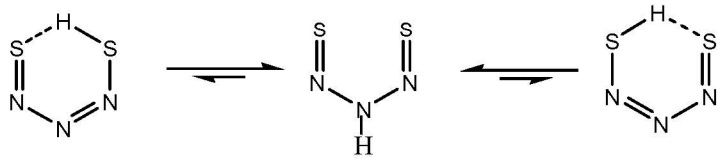
The nitrosamines constitute a family of potent carcinogens, which are formed readily from a diverse set of nitrogen compounds and nitrite or its derivatives [1, 2]. Similarly, N-thionitrosoamines, which are organic compounds that contain a new functional group, the thionitroso unit (-N=S), have been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



DTA MTD DTA

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

Reference

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

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

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

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

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

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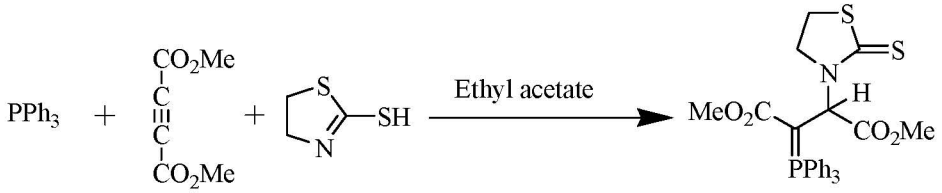
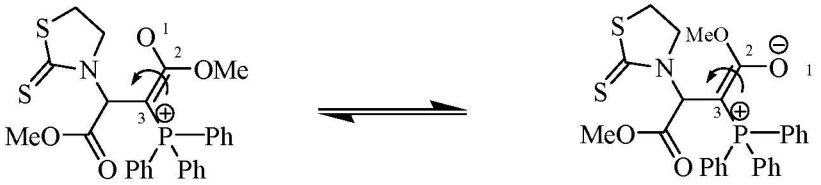
Phosphorus ylides are reactive systems which take part in many valuable reactions of organic synthesis [1]. Stable crystalline phosphorus ylides were obtained in excellent yields from the 1:1:1 addition reaction between triphenylphosphine **1** and dimethyl acetylenedicarboxylate 2 in the presence of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



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

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



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

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

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

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

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

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

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

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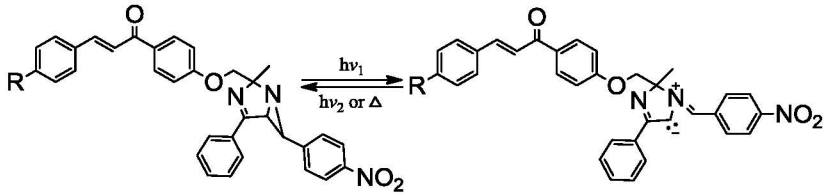
Study of photochromic materials has drawn great attention to their significant application in optical data storage, holographic storage, solar cells and as sensitizers [1-4]. Chalcone derivatives are known to exhibit excellent cytotoxic, antioxidant, antibiotic, and anticancer, activities [5]. In this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



Scheme 1

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

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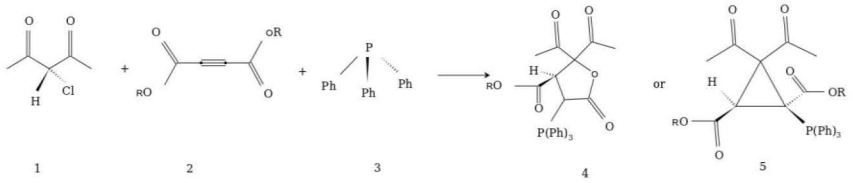
In the recent work, quantum mechanical calculations have been performed for proposed mechanism of the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of C-H acids such as 3-chloroacetylacetone in the gas phase (following Figure). All calculations were carried out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



R	product
Me	4
T-Bu	5

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

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

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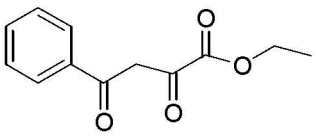
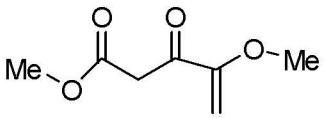
Abstract:
β-Dicarbonyls are capable of enol-keto tautomerism. The position of the enol-keto equilibrium for this class of compounds differs according to electronic characteristics of the substituents. Comparision stability of enol-keto forms and the hydrogen bond strength were investigated by electron-withdrawing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



EDPB



DMOA

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

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

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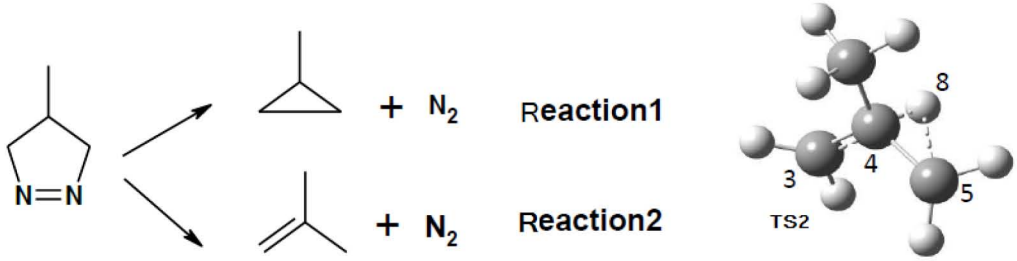
kinetic and mechanisms of nitrogene elimination from 4-methyl-1-pyrazoline (4M-1-PZ) and it's deuterated derivatives have been investigated in the gas phase with the B3LYP, B3PW91, MP2 and PBEPBE methods, using the 6-311++G(d,p) basis sets[1-3]. According to the type of products and their percentages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



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

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

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

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Ab initio calculation of absolute pK_b value in aqueous solution for nicotine.

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Abstract

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

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

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

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

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

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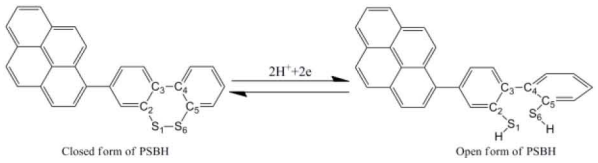
Organic compounds containing redox centers are attractive materials for molecular electronics because the current can be influenced either by electrochemical gating or by the presence of oxidizing or reducing agents [1]. Biphenyl unit is a good example of bistable molecular systems to switch because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



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

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

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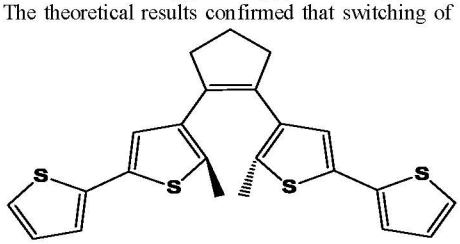
In this work, the effect of external electric field on the switching of 1,2-bis(5-methyl-2,2-bithiophen-4-yl)cyclopent-1-ene is considered. All calculation were performed using Gaussian 03 [1] software and the B3LYP/6-31G* method. The quantities of external electric fields on open and closed molecules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



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

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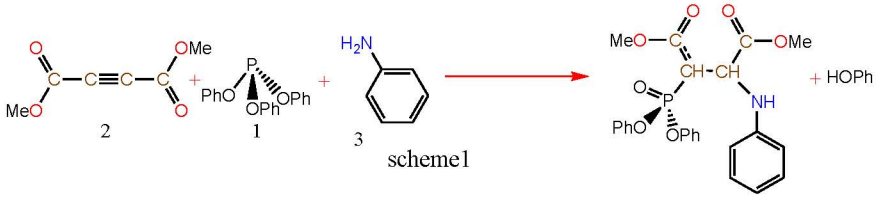
In the recent work, the variable mechanism were investigated for the reaction between triphenylphosphite, dialkyl acetylenedicarboxylates in the presence of N-H acids such as aniline in the gas phase (see scheme 1). Suitable mechanism was determined with respect to the potential energy surface. All calculation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



scheme1

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

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Abstract

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

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

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

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

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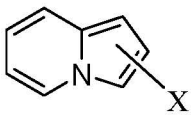
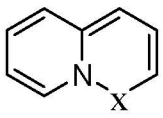
Aromaticity is one of the most important concepts in chemistry, but there is still a lot of debate about the extent to which reactivity, energetic, magnetic, and geometric criteria can evaluate this single, unifying property of molecules [1]. In this study, the aromaticity of a series of heterocycles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



1) X=N, O



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

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

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

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

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

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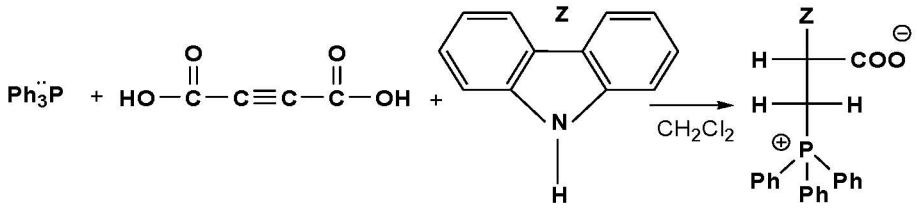
The kinetics of reaction between triphenylphosphine, acetylenedicarboxylic acid in the presence of carbazole has been spectrophotometrically studied in dry organic solvents at different temperatures. The observed overall second rate constant (k_2) for reaction decreases with decreasing solvents dielectric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



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

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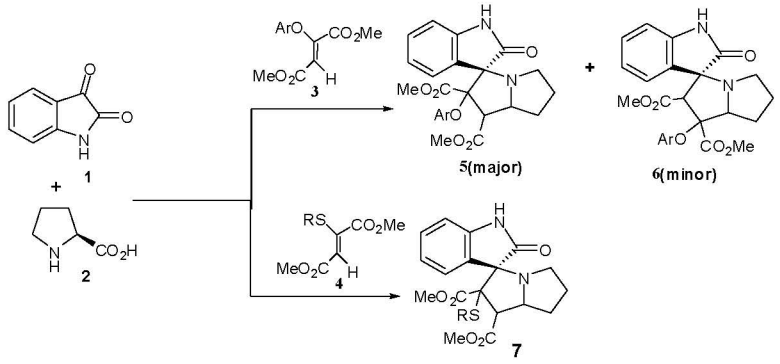
In principle, the regioselectivity could be rationalized in terms of the more favorable FMO interactions between the coefficient centers. The large–large and small–small interactions are more favored than the large–small and small–large ones [1,2]. Regioselectivity also can be analyzed in terms of the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



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

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

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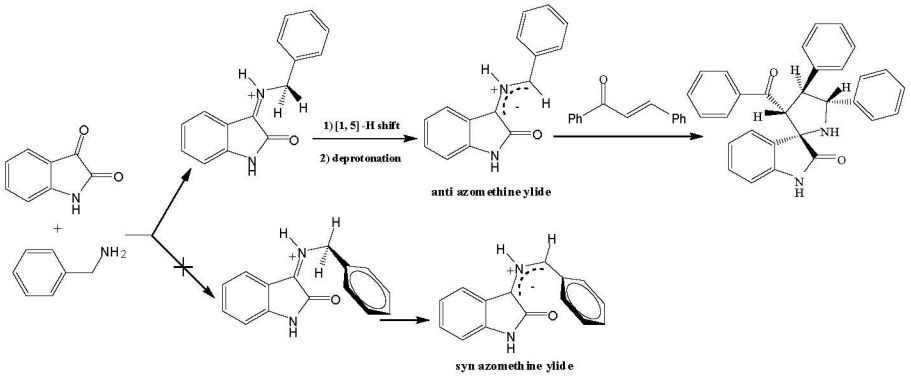
Azomethine ylides are a class of powerful reagents, which react readily with various dipolarophiles to afford pyrrolidines and pyrrolizidines [1]. A particularly mild method for the generation of nonstabilized azomethine ylides involves the [1,5] prototropic shift. The concept of the [1,5]-H shift in the iminium ion to form an azomethine ylide was proposed by Grigg [2]. However no theoretical studies on the mechanism aspects have been reported [3].
Herein, the molecular mechanism of the cycloaddition reaction between an azomethine ylide, generated from isatin and benzylamin, with chalcone as a dipolarophil has been investigated by means of a density functional theory (DFT) method. The energy path in preparing the azomethine ylide via a [1,5]-H shift in the iminium ion was evaluated. The regio- and stereoselectivity were explained on the basis of transition states stabilities and global and local reactivity indices of the reactants.



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

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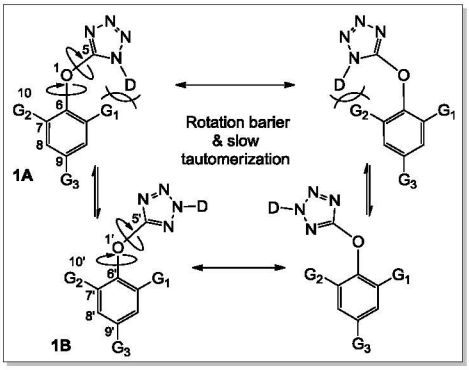
Deuterium isotope effects on carbon-13 chemical shifts are of great potential use for spectral assignments and structure determination. These effects unambiguously reveal the chemical shifts of the carbons in the neighborhood of the deuterium atom [1]. Deuterium isotope effects have also been reported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



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

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

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Abstract:

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

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

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

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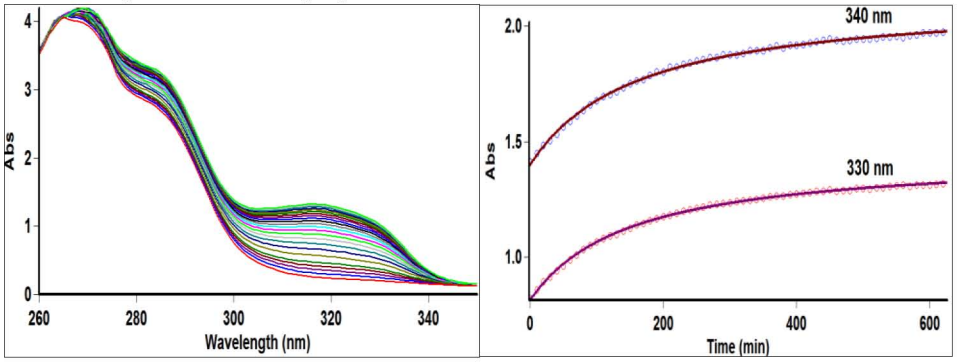
Kinetic studies were made of the reactions between triphenylphosphite and dialkylacetylenedicarboxylates in the presence of chloro-and fluoro-Aniline. To determine the kinetic parameters of the reactions, the reaction progress was monitored by UV spectrophotometry. The second-order fits were automatically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



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

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

1 2 3

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

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

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

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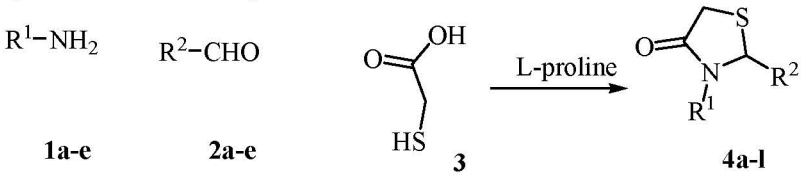
The thiazolidin-4-one ring system is a core structure in various synthetic pharmaceutical compounds, displaying a broad spectrum of biological activities. Several synthetic methods have been developed for the synthesis of 4-thiazolidinones [1]. The main synthetic routes to thiazolidin-4-ones involve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



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

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

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

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Abstract

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

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

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

Keywords: epoxy resin, thermal curing, polyamine, polyamide

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

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

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

The total reaction enthalpy (the maximum produced heat of reaction during curing) and glass Transition (Tg) was measured by DSC scans from 25 to 200 °C at rate of 10°C/min. All results were compared to those of bare epoxy resin and a decrease in ΔH and slight increase in Tg were observed.

In curing process, the reaction occurs between amine active hydrogen and epoxy groups. Reduction in total reaction enthalpy in presence of nano silica indicates lower degree of cure. Therefore, some of epoxy rings residue in the matrix and FT-IR spectra shows epoxy ring peak (the band at 914 cm^{-1}). These results indicate that some amine active hydrogen covered with nano particles [5,6].

As a matter of fact Tg depends on crosslinking and increases with higher crosslinking. DSC curves show slight increase of Tg upon addition of nano silica. This increase happens because of large surface area that enhances the crosslinking.

Nano composites with a 1 wt% in SiO2 and a good dispersion of silica nano particles, within fully cured DGEBA matrix were easily produced through the proposed synthesis route. Silica addition reduces cure kinetics. Cure activation energy is not influenced by the silica presence.

The nano composite glass transformation temperature depends on the heating rate of cure process, at higher silica content there is no difference in Tg values between plain polymer and nano composite.

It is known that properties of nano composites depend on both interfacial interactions and nano composites structure, that is on the nano particle size, size distribution, and surface chemistry. Therefore, the new route may allow projecting the nano composite.

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A New Strategy for the Chemoselective Sulfonamide N-Alkylation of Sulfonyl Ureas under Neutral conditions

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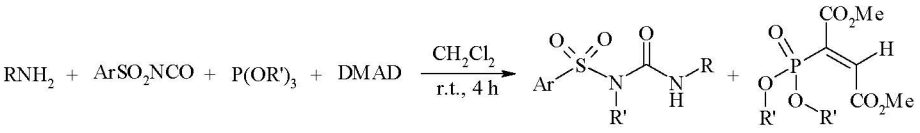
N-Alkylation is an important reaction in synthetic organic chemistry. The N-alkylation reaction with alkyl halides is well known,[1] but the use of alkyl halides is undesirable from an environmental point of view. Other alkylating reagents and conditions for N-alkylation include: alcohols/metal catalysts,[2] alcohols/Ph_3P/DDQ,[3] highly active methylating reagents such as Me_2SO_4, Me_3PO_4, and Me_2CO_3,[4] and also reductive amination of carbonyl compounds.[5] However, most of these methods have disadvantages such as high reaction temperatures, long reaction times, use of strong reducing reagents or hydrogen gas, and in some cases, use of very hazardous reagents.

The sulfonyl urea unit is an important structural motif found in biologically active organic compounds. These compounds, first discovered by Janbon et al.,[6] have been shown to be highly active herbicides, antidiabetics, and antitumor agents.[7]

Chemoselectively alkylated sulfonyl ureas are important compounds in medicinal studies. An important procedure for acquiring these compounds was reported by Roth et al. in 1995 in which sulfonyl ureas were alkylated with alkyl halides in the presence of DBU in acetonitrile.[8]

Herein, we report a new reagent for the chemoselective sulfonamide N-alkylation of sulfonyl ureas under neutral and mild conditions. Thus, a mixture of an amine **1** and an aryl sulfonyl isocyanate **2** was converted into the corresponding sulfonyl urea in dry CH_2Cl_2 at ambient temperature. The reactions reached completion within a few minutes, which was indicated by TLC monitoring. After addition of a trialkyl phosphite **3**, a solution of dimethyl acetylenedicarboxylate **4** in dry CH_2Cl_2 was slowly added to the reaction mixture and stirring was continued at ambient temperature for further two hours to afford the alkylated sulfonyl ureas **5** in excellent yields.



1 **2** **3** **4** **5** **6**

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New heterogeneous oxidant based on permanganate supported on aminated silica-gel for oxidation of alcohols

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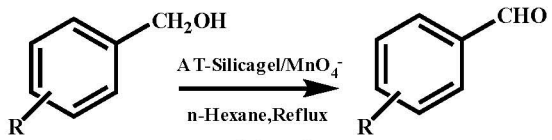
Abstract

Oxidation of alcohols to the corresponding aldehydes and ketones remains one of the most important reactions both from fundamental research as well as synthetic point of view [1]. Oxidation by homogeneous systems has many problems; such as tedious work-up, acidic media, and safety problems [the presence of toxic transition metal cations, e.g., Co(II), Pb(IV), Hg(II), Mn(IV and VII), Ag(I), Zr(IV)] [2]. Thus, developing an environmentally friendly and efficient heterogeneous oxidant is of paramount importance. In this work amino functionalized triazine supported on silica-gel was prepared by reaction of silicagel with cyanoric chloride in dry tetrahydrofurane in the presence of triethylamine followed by ethylene diamine treatment. This amino functionalized silicagel was reacted with CH_3I in dioxane. Subsequent reaction of this material with $KMnO_4$ gives AT-silicagel/MnO_4^-. This novel reagent was applied as an effective heterogeneous reagent for the oxidation of alcohols to the corresponding carbonyl compounds in the presence of n-hexane as a solvent and reflux conditions in high yield and excellent selectivity (Scheme 1). Our goals in undertaking this work were: (a) to overcomethe reported limitations and drawbacks such as tedious work-up, acidic media, e.g., (b) to devise a heterogeneous system, especially useful for industry, with many advantages such as reduced pollution, lower costs and simplicity in processing and handling. (c) to develop a high-yielding synthesis of benzaldehyde and its substituted homologues using a recyclable reagent. Different parameter such as type of solvent, reaction temperature, reaction time and amount of reagent were examined and it was found that the best results were obtained in the presence of n-hexane as a solvent in its reflux temperature. In conclusion, our studies showed that potassium permanganate heterogeneous reagent supported on aminated triazine rings linked on silica gel serve as highly active heterogeneous oxidant reagent for the oxidation of benzyl alcohol and its substituted homologues. This reagent exhibited excellent activity and selectivity under mild conditions and can be recyclable.



Scheme 1.

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Room–Temperature Synthesis of Monoarylidenes of Piperidin-4-one under Solvent-Free Conditions

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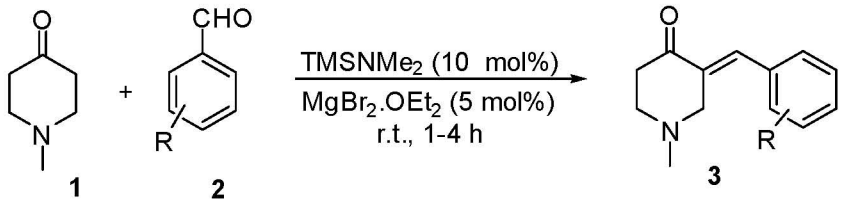
α,-β unsaturated ketones are of great importance in synthetic organic chemistry since they are key component of many natural and biologically active structure [1]. The chemistry of piperidin-4-one is of current interest due to potential medical and biological applications of its derivatives [2].

In addition, they could serve as convenient precursors for other nucleophylic synthetic transformations[3]. Several strategies are offered so far for the preparation of these compounds[4]. However, many of them usually incorporate more than one step reaction or need the use of commercially unavailable starting materials.

In the present work, an efficient synthesis of monoarylidenes of piperidin-4-one **3** was achieved by the reaction of 1-methyl 4-piperoidone **1** and aromartic aldehyde **2** in the presens of $MgBr_2.OEt_2$ under solvent free condition [5]. High yields of products are obtained at room-temperature and the procedure is applicable to the reactions with aromatic and aliphatic aldehydes.



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Synthesis of Poly N-isopropyl acrylamide as Thermosensitive Polymer

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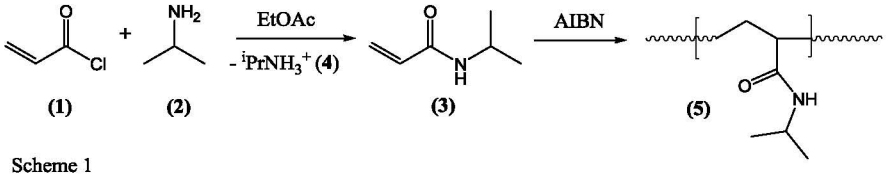
The linear poly (*N*-isopropylacrylamide) (PNIPAAm) is a thermoresponsive polymer whose aqueous solutions exhibit at reversible transition with a lower critical solution temperature LCST [1]. In this project we try to report a facial method to synthesize monomer and polymers of *N*-isopropyl acrylamide.

The reaction of acroleyl chloride (0.2 mol) (**1**), and isopropyl amine (0.4 mol) (**2**) in ethyl acetate led to the formation of N-isopropyl acrylamide (**3**) and isopropylammonium chloride (**4**). Precipitated salt **4** was filtered, the solvent of filtrate was evaporated at reduced pressure, and the residual was solidified after staying for 24 h at 0 °C after which monomer **5** obtained as white precipitate (Scheme 1). Monomer **3** polymerized in THF at 70 °C in the presence of AIBN, as free radical initiator, during which PNIPAAm formed as colloid, solvent was evaporated at reduced pressure, and polymer (**5**) obtained as colorless crystals.

The structure of monomer and polymer elucidated by IR spectroscopy. Thermosensitivity of polymer was studied at 25-40 °C. Measured LCST (32 °C) of synthesized polymer was in good agreement with reported one [2, 3]. This method may be a facile method for the synthesis of acrylamide thermosensitive polymer as well related monomers.



(1) (2) (3) (5)

Scheme 1

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Facile Method for the Synthesis of 2-substituted Quinazolin-4(1*H*)-one Derivatives Catalyzed by SiO_2-$H_3PW_{12}O_{40}$

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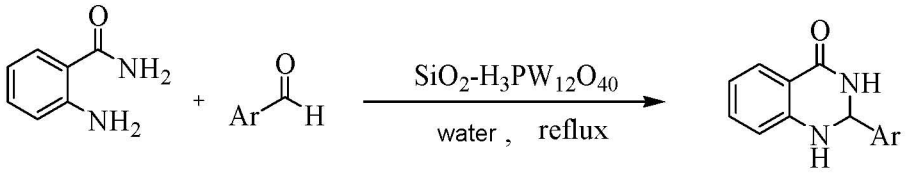
Among the various classes of heterocyclic compounds, quinazolin-4(1*H*)-ones form important component of pharmacologically active compounds, as they are associated with a wide spectrum of biological activities such as antiinflammatory, antihypertensive, anticancer, antitumor and antibacterial [1]. Various methods for the synthesis of 2-arylquinazoline were based on the reaction of 2-aminobenzamide with aromatic aldehyde catalyzed by some catalysts such as NH_4Cl, $AlCl_3/ZnCl_2$, *p*-TSA, and asymmetric Bronsted acids or one-pot condensation of isatoic anhydride, amines and aldehydes in organic solvent [2]. These reported methods involve various disadvantages, such as low yields, prolonged reaction times, and the use of toxic organic reagents and catalysts. Silica-supported 12-tungstophosphoric acid (PW/SiO_2) is a cheap, noncorrosive, easily available and reusable catalyst [3].
Herein, we report an efficient, mild, high yield and simple workup synthesis of quinazolin-4(1H)-one derivatives by cyclocondensation of *o*-aminobenzamide with different aldehydes or ketones in the presence of PW/SiO_2 in wather (Scheme 1).



Scheme 1

References:

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7-9 March 2012

Aldol Condensation of 2*H*-Thiopyran-4(3*H*)-one Using DMAP as Organocatalyst in Aqueous Media

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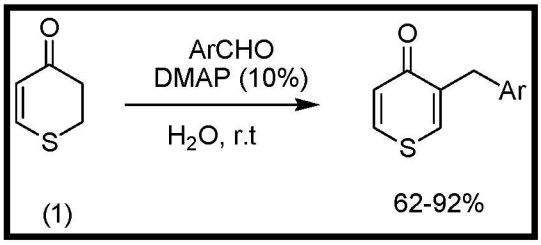
Thiopyran structures are one of the most important classes of sulfur containing heterocycles [1-3] with many applications in the preparation of natural and unnatural products such as the synthesis of polypropionates by aldol reactions [4]. Based on our previous related investigations [5], we were encouraged to study aldol condensation of dihydrothiopyran-4-one (1) in aqueous media. In this work we successfully achieved the expected products by using catalytic amounts of DMAP (4-Dimethylaminopyridine) as an organocatalyst, under very mild conditions. Reactions proceeded in good to high yields at room temperature with a very straightforward and easy workup procedure. The structure of the products is assigned based on their spectroscopic data. As a result of this work, reactions products were obtained rapidly and under relatively environmentally benign conditions.



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Preparation of semi-aromatic polyamides and investigation of structural parameters on their UV absorption

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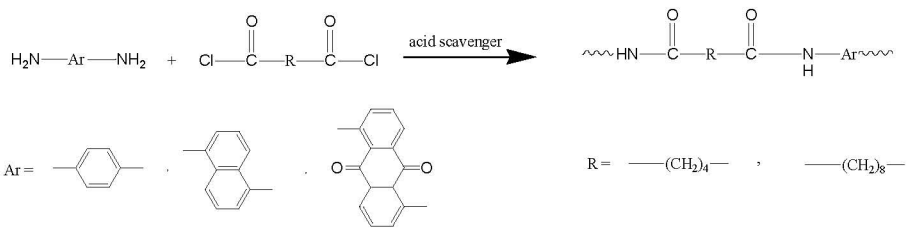
Polyamides have attracted many attentions since they were synthesized, characterized, and applied as commercial development of synthetic fibers, known commonly as nylons. It is known that aromatic polyamides are a class of high temperature resistance polymers with good chemical resistance, thermal stability, low flammability, and very good mechanical properties [1,2]. Polyamides are widely used in different products and industries including textile, automobile, aerospace, military, electronic, and other industries. So, their colors and their ability to absorb UV radiation strongly affect their applications in the mentioned industries [3,4].
In the present research, semi-aromatic polyamides with different aromatic groups (bulkiness) and different aliphatic units (methylene chains) were prepared through solution polycondensation method in the presence of an acid scavenger.



All the six polymers were characterized by conventional methods including FT-IR, NMR, and elemental analysis. Physical and thermal properties of the polymers including inherent viscosity, solubility, thermal stability and behavior, flame-retardancy and crystallinity of the polymers were studied. were studied. Also, UV absorption of polyamides was investigated and the effects of structure on it were studied. Incorporation of phenyl, naphthyl, and anthraquinoyl groups from one side, and size of aliphatic chain from another side (significant structural modifications that affected UV absorption) were studied.

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Heterogeneous palladium porphyrin as an efficient catalyst for the Heck reactions

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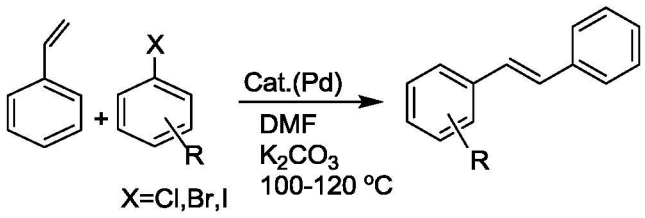
Palladium-catalyzed coupling of aryl halides with alkenes, Heck cross-coupling reaction, is an extremely valuable method for carbon-carbon bond formation [1-4]. It is now widely used in the special chemical and pharmaceutical manufacturing industries, because it is simple, versatile, and relatively mild. It is interesting to note that in the absence of catalyst, the reaction did not proceed. Heterogeneous palladium complexes having high activity and selectivity, offer several significant practical advantages in synthetic and industrial chemistry; among those, the ease of separation of the catalyst from the desired reaction products is most important [5-8].

In the present work, we report the preparation of heterogeneous *tetrakis*(4-pyridyl)porphyrinato-palladium(II) and its application in the Heck reaction of aryl halides in the presence of inorganic or organic bases. The effects of the various reaction parameters on the catalytic activity were studied [9]. Due to insolubility of this Pd(II) complex in all common organic solvents, its structural investigations were limited only to its physicochemical properties such as SEM, TGA, IR and UV-vis spectral data.



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Poly(ester imide)s as a New Kinds of Heat-resistant Polymers with Enhanced Solubility

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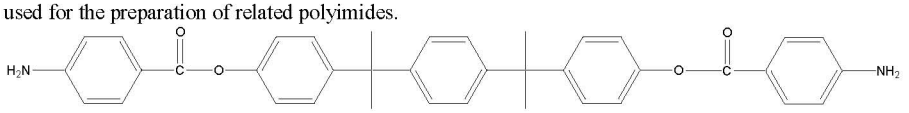
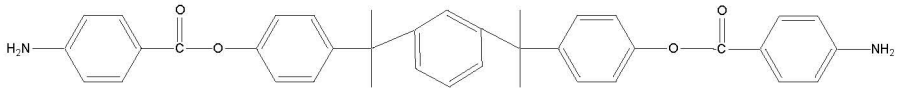
Among various polymers, polyimides received more attention due to their favorable balance of physical and chemical properties. Wholly aromatic polyimides are engineering plastics and are gaining wide acceptance by different industries because they contain a number of unique features. These include excellent physical properties, retention at elevated temperature and in wet environments, almost constant electrical properties over a wide range of temperatures, good chemical resistance and non flammability properties [1]. However, one of the drawbacks to the employment of these high performance polymers is the difficulty in processing due to their high melting temperatures or high glass transition temperatures [2]. Strong interaction between polyimide chains and their rigid structure are the main reasons for these behaviors. Copolycondensation is one of the possible ways for modification of polymer properties. Thus, for the processing of polyimides many copolyimides, such as poly(amide-imide)s, poly(sulfone-imide)s, poly(ether-imide)s, poly(ester-imide)s and other copolymers have been prepared [3, 4].
In this research, two new diamines were prepared via reaction of bis-phenol-p and bis-phenol-m with 4-nitrobenzoyl chloride and subsequent reduction of nitro groups. Monomers were fully characterized and used for the preparation of related polyimides.





Two-step polycondensation reaction of this monomer with different aromatic dianhydrides resulted in preparation of poly(ester imide)s. Polymers were characterized by FT-IR, H-NMR, and elemental analysis methods. Thermal and physical properties of the polyamides including thermal stability, thermal behavior, solution viscosity, and solubility behavior in addition to crystallinity, and molecular weights were studied. Polymers prepared from bis-phenol-p showed higher thermal stability and lower solubility in comparison to the similar polymers prepared from bis-phenol-m. It was related to the para-oreintation of bis-phenol-p polymers and better close packing and dipole-dipole interaction of the polymeric chains.

References:

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New types of poly (amide-imide)s: synthesis, characterization, and properties

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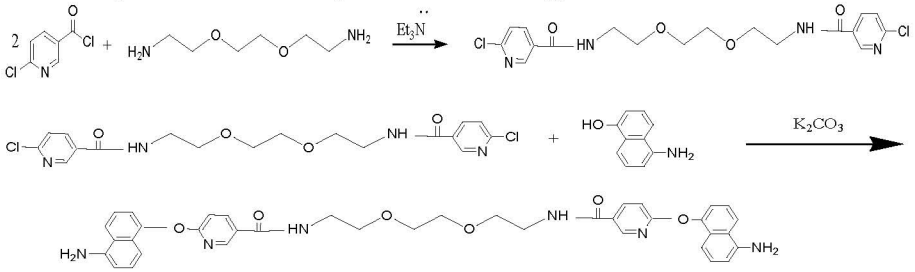
Aromatic diamines are valuable building monomers for the preparation of different types of high-performance polymers including polyamides, polyimides, and their copolymers. Copolycondensation is one of the possible ways for modification of polymer properties. Modification of the properties of polyamides by incorporation of imide groups and more hydrogen-bonded amide groups has been investigated and poly(amide imide amide)s have been studied extensively [1–3]. The incorporation of rigid segments in the polymer chain is an effective method to enhance the thermal stability. Thermal resistance of polyimides is higher than that of polyamides, but polyamides have better solubility and processability than polyimides. Poly(amide imide)s are known as valuable polymers among high-performance polymers due to the fact that they combine and inherit desirable features from both polyamides and polyimides [4].

In this research, a new diamine monomer containing pyridine, ether, amide, and aliphatic units was prepared via two step reactions. Nucleophilic chloro displacement reaction of 6-chloronicotinoyl chloride with two moles of 1,8-diamino-3,6-dioxaoctane afforded a dichloro compound. Subsequent reaction of dichloro compound with 5-amino-1-naphthol resulted in a new pyridine-based diamine.



The diamine containing preformed amide group was polycondensed with different dianhydrides to produce related poly(amide imide)s. The prepared monomer and all the polymers were characterized by conventional methods. Different physical and thermal properties of the polymers were studied. According to the obtained results, these polymers showed nice balance of properties including high thermal stability and improved solubility. Incorporation of aromatic and imide units was the main factor for enhancing thermal stability. Introduction of ether, aliphatic, pyridine, and bulky groups were significant structural modifications for improving solubility of the poly(amide imide)s.

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The Synthesis of Arylquinoxalines and Arylnaphthodiazepine Derivatives

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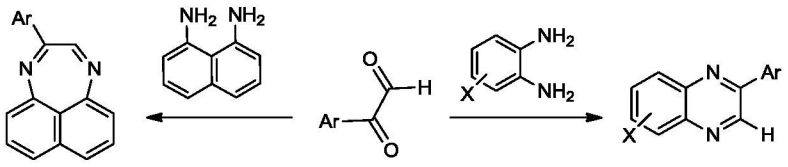
Quinoxaline and its derivatives are important nitrogen containing heterocyclic compounds of various biologically interesting properties with several pharmaceutical applications. Substituted quinoxalines are an important class of benzoheterocycles, which constitute the building blocks of wide range of pharmacologically active compounds having antibacterial, antifungal, anticancer, antitubercular, antileishmanial, and antidepressant activities activities [1-3].

Diazepines are interesting from the point of view of their chemical structure [4]. The diazepines constitute an important group of psychotherapeutic drugs and have been extensively studied because of their sedative-hypnotic, muscle relaxant, anxiolytic, and anticonvulsant properties [5]. The discovery of specific receptors in mammalian brain tissue for diazepines has led to a useful screening procedure to evaluate the interaction of various diazepines with the binding site. Due to their success and safety, diazepines have been amongst the most widely prescribed drugs during the last two decades.

Here, we report the synthesis a series of arylquinoxalines (**2**) and arylnaphthodiazepines (**3**) in good to excellent yields by reaction of 1,2-diaminobenzene derivatives and 1,8-diaminonaphthalene with arylglyoxals (**1**) respectively.



3 **1** **2**

Ar = ph, 3-BrC_6H_4, 4-BrC_6H_4, 3-OMeC_6H_4, 4-OMeC_6H_4
X = H, CH_3, NO_2

References:

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The Synthesis of Quinoxalinophenazine Derivatives

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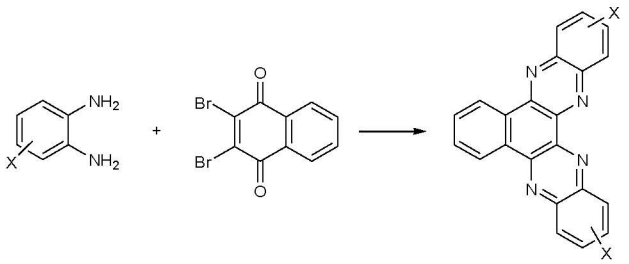
Phenazine derivatives are generally water-soluble and coloured compounds that often have antibiotic activity [1]. These compounds are produced by bacteria from diverse general including Streptomyces, Pseudomonas, Pelagiobacter and Vibrio [1-3]. Some bacterial isolates produce more than one type of phenazine, each composed of a heterocyclic, nitrogen-containing phenazine nucleus. The diversity of phenazines arises from the varied type and number of functional groups attached to this nucleus.
Here, we report the synthesis of a series of quinoxalinophenazine (**3**) by reaction of 1,2-diaminobenzene derivative (**1**) with 2,3-dibromo-1,4-naphtaquinone (**2**) in DMF/EtOH under reflux conditions, with high yield. These compounds were confirmed by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy determinate.



1 **2** **3**

X =H, Me, NO_2

References:

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Solvent-free Diastereoselective Synthesis of Dicyanotetrahydropyrrolo Phenanthrolines

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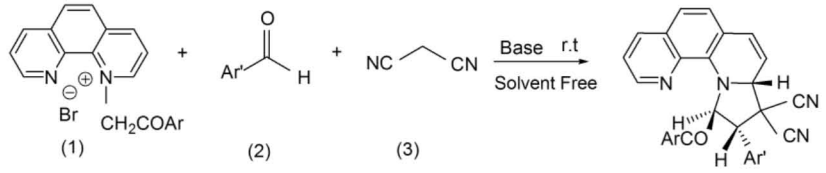
The solvent-free approach to the synthesis of molecules is an attractive one, since the majority of solvents are either toxic or flammable and add considerably to the cost of an overall synthesis. In many instances, the solvent-free approach allows shorter reaction times, improved selectivity and easier separations and purifications than conventional solvents [1].

Grindstone chemistry is a branch of green chemistry for solvent-free chemical reactions which can be probably conducted in high yield by just grinding solid/solid, solid/liquid, or even liquid/liquid together .There are several advantages to performing synthesis in dry media: (i) short reaction times, (ii) increased safety, (iii) economic advantages due to the absence of solvent[2]. In the last decade, interest in substituted [1,10]phenanthrolines has been increased and, as result, chemistry, synthetic methods and properties of these *N*-heterocycles have been studied by several group[3]. Owing to the increasing importance of these N-heterocycles in the field of biology and technology we now report an efficient and clean synthetic route for pyrrolo phenanthrolines in good yield.

We observed that three-component reaction of 1-***phenacyl***-1,10-phenanthrolinium bromide **1**, aromatic aldehydes **2** and malonitrile **3** in the presence of triethylamine as base, in green methodology, afforded chiefly a single diastereoisomer of tetrahydropyrrolo[1,2-*a*][1,10] phenanthroline derivatives **4** as new macromolecules in excellent yields .

It's clear that Lewis base such as triethyl amine and DABCO are good basic catalyst. Also NaOH is good basic catalyst but the reaction took about one hours to complete.

The isolated product was completely characterized by IR and ^{1}H NMR . The melting point of the compound was in agreement with those of literature reported[4].



Ar=4-Methylphenyl

Ar'=Phenyl, 3-Chlorophenyl,1-Naphthyl

Base: Et_3N , DABCO, NaOH

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$Fe(ClO_4)_3/SiO_2$-catalyzed synthesis of ß-amido carbonyl compounds through Dakin-west reaction

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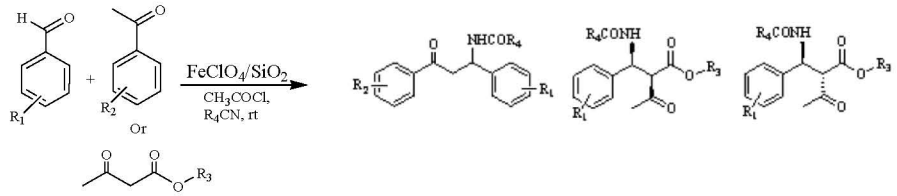
β-Acetamido ketone skeletons exist in a number of biological and pharmaceutical compounds makes them valuable building blocks [1,2] and there have been intensive attempts to synthesize β-amido ketones. The best-known route for the synthesis of these compounds is the Dakin–West reaction,[3] which involves the condensation of an α-amino acid with acetic anhydride in the presence of a base to afford the β-acetamido ketones.[4]Another procedure for the formation of these compounds from condensation of enolizable ketones, an aryl aldehyde, and acetyl chloride in nitriles in the presence of heterogeneous and homogeneous acid catalysts have been reported. Iron catalysts in organic reactions have recently received much attention in view of their cheapness and environmental friendliness. Amoung them ferric perchlorate and ferric perchlorate adsorbed on silica gel are ranked as powerful Lewis acids for affecting various organic transformations.[5]

In this communication we wish to report synthesis of β-amido ketones with enolizable ketones, acetonitrile, benzonitrile and acetyl chloride in the presence of $Fe(ClO_4)_3/SiO_2$ at room temperature (Scheme 1).



Scheme 1

References
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The Synthesis of (3-(2, 5-dimethoxyphenyl)isoxazol-5-yl)methanol

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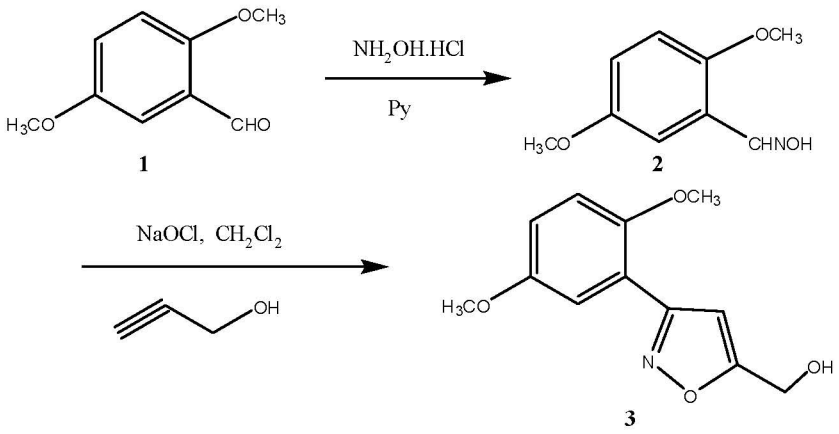
Compounds with isoxazole moiety have pharmacological, biological and industrial applications; specifically these compounds show antiviral activity [1]. Recently, the synthesis of isoxazole 4- and 5-carbaldehydes and their conversion to isoxazolyl-1, 4-dihydropyridines were studied [2].
In this research work, first, 2, 5-dimethoxybenzaldehyde (**1**) was transformed to 2, 5-dimethoxybenzaldoxime (**2**) by using NH_2OH in pyridine. The in-situ generated nitriloxide from reaction between **2** and NaOCl, was reacted with propargylalcohol to produce (3-(2, 5-dimethoxyphenyl) isoxazol-5-yl) methanol (**3**) in a cycloaddition procedure.
The structure of all the synthesized compounds was characterized and confirmed by FT-IR and NMR spectroscopy techniques.



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

Glutamic Acid: A New Catalyst for One-Pot Synthesis of 7-aryl-11,12 dihydrobenzo[h] pyrimido-[4,5-b]quinolone-8,10(7H,9H)-diones

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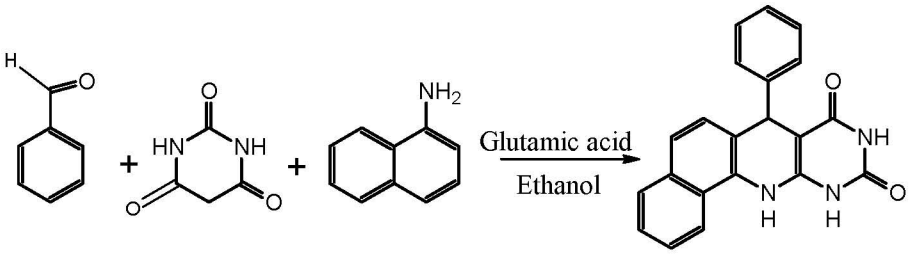
Abstract
Aseries of new 7-aryl-11,12-dihydrobenzo[*h*]pyrimido-[4,5-*b*]quinoline-8,10(7*H*,9*H*)-diones were synthesized via three component reaction of aldehydes, 1-naphthylamine and barbituric acid in Glutamic Acid Catalyst. The method provided several advantages such as easy work-up, high yields and environmentally benign procedure.7-Aryl-11,12-dihydrobenzo[*h*]pyrimido-[4,5-*b*]quinoline-8,10(7*H*,9*H*)-diones, a novel class of fused heterocyclic compounds, are incorporated by pyrimido-[4,5-*b*]quinoline-2,4(1*H*, 3*H*, 5*H*, 10*H*)-dione and [4,7]-phenantroline motifs, both of which possess various important bioactivities. For example, not only are pyrimido-[4,5-*b*]quinoline-2,4(1*H*, 3*H*, 5*H*, 10*H*)-dione derivatives antitumor, anticancer, antihypertensive, and antibacterial, they are also inhibitors of Kaposi's sarcoma-associated herpesvirus (KSHV) and topoisomerase, useful for the treatment of topoisomerase associated disease sand disorders[1–2].At the sametime,[4,7]-phenantroline derivatives exhibit antitumor,anticancer,antiviral, antimalarial, antiinfective, cytotoxic activities, as well as being triple-helix DNA stabilizing agents [3–4]. Hence, it is promising that the fused scaffolds of pyrimido-[4,5-*b*]quinoline-2,4(1*H*,3*H*,5*H*,10*H*)dionewith[4,7]phenanthroline,7-aryl-11,12-dihydrobenzo[*h*]pyrimido-[4,5-*b*]quinoline-8,10(7*H*, 9*H*)-diones, may display novel or enhanced significant bioactivities.



A typical rocedure for the preparation of 4a_4l: Aldehyde (1.2 mmol), 1-naphthylamine (2.2 mmol), barbituric acid (3.2 mmol) were added to a 20 mL round bottom flask containing 20%mol Glutamic Acid. The mixture was then stirred at 90 ˚C for appropriate time (monitored by TLC).
After completion of the reaction, the reaction mixture was added with 5 mL water. The precipitate was collected by suction and purified by recrystallization from EtOH to give products 4. The filtrate was concentrated under reduced pressure and dried at 100˚C to recover the ionicliquid for subsequent use. Some selected data:

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Synthesis of spiro[pyrazolo[3,4-*b*]pyridine-4′,3-oxindoles]*via* one-pot three component condensation reaction in water

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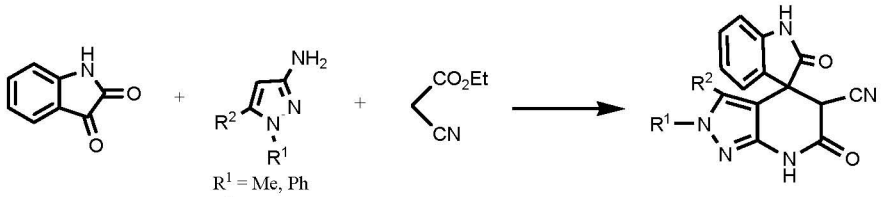
Multi-component reactions (MCRs) are special types of synthetically organic reactions in which three or more starting materials react to give a final product in a one-pot procedure. Such reactions are one of the best tools in modern organic synthesis to generate compounds libraries for screening purpous because of their productivity, simple procedure and facile execution [1]. Pyrazolo[3,4-b]pyridines are attractive compounds for drug discovery since many of such scaffolds exhibit a wide range of biological and pharmaceutical activities. These include HIV reverse transcriptase [2], anti-tumor and anti-proliferative [3], as well as compounds for treatment of Alzheimer's disease [4].

The other important structural fragment presents in our final products includes oxindole substructure, exists in many alkaloids (e.g., spirotryprostatin B, alantrypinone, and citrinadin A) [5]. In general compounds carring the indole moiety exhibit antibacterial and antifungal activities [6].

Aqueous media is an important advantage of this reaction. As water (green solvent) is the most environmentally acceptable, safest, and most abundant solvent [7]. In addition, water enable facile work-up protocols, as most organic compounds, being lipophilic, are readily segregated from aqueous media. Furthermore, water, as our reaction medium, processes conferring uniqe selectivity and reactivity [8].

Therefore, this work is devoted to the synthesis of new spiro-oxindoles by one-pot three component reaction of derivatives of isatin in aqueous media. The product which is gained has oxindole, pyridinone and pyrazole rings.



R^1 = Me, Ph
R^2 = H, Ph

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Effect of different diol and diamine chain extenders on aqueous anionic polyurethane dispersion properties

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A series of aqueous polyurethane dispersions were synthesized based on prepolymer mixing process by reaction of polytetramethylene glycol (PTMG) and isophorone diisocyanate (IPDI) which were extended with different diol and diamine chain extenders [1]. Anionic waterborne polyurethanes were obtained based on hydrophilic dimethylol propionic acid (DMPA) monomer in this research [2]. Aqueous polyurethane dispersion samples were prepared by placing polytetramethylene glycol into the reactor under N_2 atmosphere and mechanical stirring. The prepolymer with NCO terminated groups was obtained by addition of IPDI to polyol and increasing the temperature to 90°C [3]. This prepolymer was extended by proper amounts of DMPA solution in N-Methylpyrrolidone. Then the required amounts of different diol or diamine chain extenders were added to the reactor in chain extension step. In order to neutralize of the carboxylic acid groups of DMPA, triethyleneamine was added into the mentioned system. Finally stable emulsion of polyurethane samples were synthesized by adding the required amount of deionized water into the reactor to obtain aqueous dispersions PUs with 30 wt % solid content. Characterization of chemical structure and thermal-mechanical properties of these polymers were performed by FTIR and DMTA respectively. Chemical structure of polyurethanes extended by different chain extenders were proved with the disappearance of the NCO band at 2270 cm^{-1}. It was observed that with changing of the chain extender from diol to diamine, melting temperature of soft segment increases to upper temperatures significantly. The hydrophilicity of the prepared samples was measured by contact angle test and observed that diamine chain extenders afford lower contact angles.

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Preparation and characterization of novel chiral poly(amide-imide)/organoclay/TiO_2 bionanocomposites

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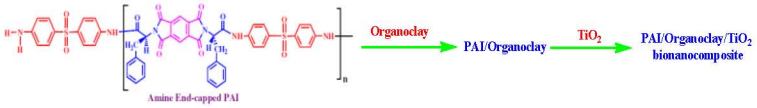
Composite materials represent one of the most active fields in the polymer industry. Many different types of fillers and nanoparticle have been added to polymers to provide an improvement of the final products. In recent years, it has been observed that the addition of just a small quantity of nano-sized layered silicates greatly improved the properties of virgin polymers without affecting their processability [1,2]. Also among many nanocomposite precursors, TiO_2 nanopowder is increasingly being investigated because it is non-toxic, chemically inert and has a high refractive index, UV filtration capacity and high hardness. Such materials on the nanoscale level show significant improvements in mechanical properties, heat distortion temperatures, thermal stability and enhanced barrier properties [3]. In the present investigation, novel series of poly(amide-imide)(PAI)/organoclay/TiO_2 bionanocomposites (BNC)s has been synthesis. At first, Cloisite Na^+ and protonated form of *L*-phenylalanine amino acid were used for the preparation of the novel chiral organoclay via ion-exchange reaction. Then, PAI containing phenylalanine amino acid was synthesized via solution polycondensation of *N,N'*-(pyromellitoyl)-bis-phenylalanine diacid with 4,4'-diaminodiphenylsulfone in the presence of tetrabutylammonium bromide as a green solvent. Then, this polymer was end-capped with amine end groups of diamine in the final polymerization process. In the next step, PAI/organoclay BNC films containing 5% of organoclay was prepared via solution intercalation method through blending of organoclay with the PAI solution. Then, different percentages of modified TiO_2 were added to PAI/organoclay for study the synergetic effect of both nanoparticles. The nanostructures and properties of the PAI/organoclay/TiO_2 BNCs were investigated using fourier transform infrared spectroscopy, X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and thermogravimetry analysis (TGA) techniques. XRD, FE-SEM and TEM results revealed the formation of exfoliated and intercalated organoclay platelets in the PAI matrix. TGA results indicated that the addition of organoclay and TiO_2 into the PAI matrix increases in the thermal decomposition temperatures of the resulted BNCs.



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Synthesis and Characterization of Chitosan-Agar Full-Polysaccharide Biodegradable Films by Reductive Amination

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During the last two decades, significant advances have been made in the development of the biocompatible and biodegradable materials for various applications such as drug delivery systems and tissue engineering [1,2]. Polysaccharides are the main part of the natural based biodegradable materials, because of their biocompatibility, biodegradability, and nontoxicity. Chitosan, a natural polymer obtained by alkaline deacetylation of chitin, is biocompatible and can be completely digested by the colonic bacteria [3]. Agar consists of a mixture of agarose and agaropectin. The predominant component of agarose is a linear polymer, made up of the repeating monomeric unit of agarobiose [4].

This work focuses on the synthesis of the chitosan-agar full-polysaccharide hydrogel by crosslinking of chitosan with periodate activated agar and subsequent reductive alkylation. Agar activated molecule prepared by periodate oxidation of the agar and then applied as a crosslinking agent to form a new hydrogel network. The effect of chitosan/agar weight ratio on the swelling behavior of the hydrogel at various pH solutions was investigated. The swelling of the hydrogel decreases with decreasing the acidity of the solution. A preliminary study was conducted on the hydrogel swelling and deswelling kinetics. The equilibrium swelling was achieved after 25 min. The data may be well fitted with a Voigt-based equation. The structure of the hydrogel was confirmed by FT-IR spectroscopy, scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and solubility test. Swelling measurements of the synthesized hydrogel showed good swelling capacity especially in acidic solutions. The polymers may have potential application in tissue engineering and drug delivery systems.

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Silzic-catalyzed synthesis bisamides

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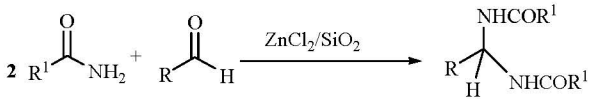
Multicomponent reactions (MCR) are chemical processes where three or more reagents combined to give the final product retain significant portions of all starting materials. Therefore, they lead to the connection of the starting materials in a single synthetic operation with high atom economy and bond-forming efficiency, thereby increasing molecular diversity and complexity in a fast and often experimentally simple fashion. For this reason, MCR are particularly well suited for oriented synthesis of pharmaceuticals and agrochemicals.

Gem-bisamides can be easily transformed into other useful materials such as gem-diaminoalkyl and aminoalkyl compounds and are of considerable interest in the synthesis of pharmacological materials such as peptidomimetic compounds. They could be synthesized via direct condensation of two moles of amides with aldehydes in the presence of acidic catalysts [1-4].

In this work, we have reported their synthesis in the presence of $ZnCl_2/SiO_2$ (silzic) under solvent-free conditions (Scheme 1).



Scheme 1.

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A convenient method for synthesis of new formyl coumarines derivatives

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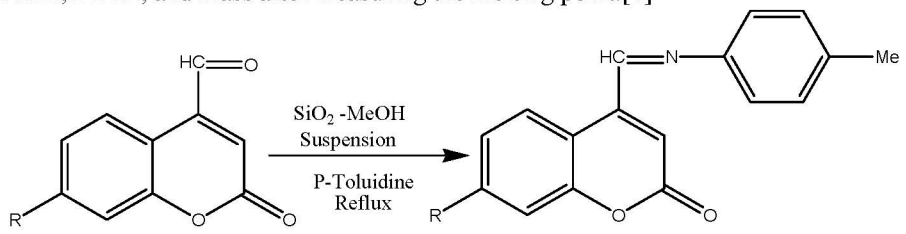
Abstract

In our efforts some substituted coumarine 4-carbaldehydes were prepared in moderate to good yield using dioxin as appropriate solvent .[1] for these important transformations 4-methyl coumarines were used as starting materials and SeO_2 was used as oxidizing agent of choice.[2,3] The molecular structure of the so-called composition was verified through some techniques of spectroscopy such as ^1H NMR, FT-IR, and mass after measuring the melting point.[4]



Keywords: coumarine -aldehyde –SeO_2-Synthesis-Oxidation.

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Study of Integral Skin PUFs Degradation Using Green Solvents

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Abstract

Since the last 40 years, polyurethanes have been used in an ever increasing range of application. For example Polyurethane integral skin foams are widely used in the automotive industry.with polyurethane production volumes increase, The amount of PU waste is also on the rise. For decrease the amount of waste disposal of these foams, chemical recycling is preferred as a useful method to achieve both targets: 1) making the industry more compatible with the environment, 2) defining an economic progress. Many scientists reported the glycolysis of PUF [1-3]. In this work, the one of the main goals was using the green solvent for glycolysis (DEG and EG / Sorbitol/water) and to reduce the energy and material losses. The materials used for the glycolysis were integral skin foam prepared with the formulation of Polyol/MDI in the ratio of 100:41 respectively. Two necked round bottom flasks were used for all reactions. The flasks were equipped with a condenser, a thermometer and an agitator. The scraps of Integral skin foam (15 g), NaOH (1 % w/w) and various systems (DEG and EG/Sorbitol/water) in which glycolysis reactions were running, were placed in the flaks. The reactor was heated up to 195±5°C with the difference of 5 °C and rpm 1000 at atm. The reaction extends to complete dissolution of foams. The reaction mixture transferred to a decanted funnel and was left to be cooled in room temperature. After several minutes, it was separated into clear upper and dark brown lower phases. The separated phases were analyzed by classical and instrumental methods. We have investigated that with the increasing sorbitol content, reaction time increased. This was possibly due to increasing viscosity of the reaction media as well as difficulties in nucleophilic attack of destroying agent to the polyurethane bonds (Figure1). The different catalysts were employed in the solvent system in order to decrease the dissolution time .NaOH had the greatest decreasing effect on the dissolution times. The ^{1}H_NMR ,^{13}C_NMR and FT_IR spectra showed that the processing of the chemical recycling of PU integral skin by solvent (DEG and EG / Sorbitol/water) and catalyst NaOH resulted good yield.

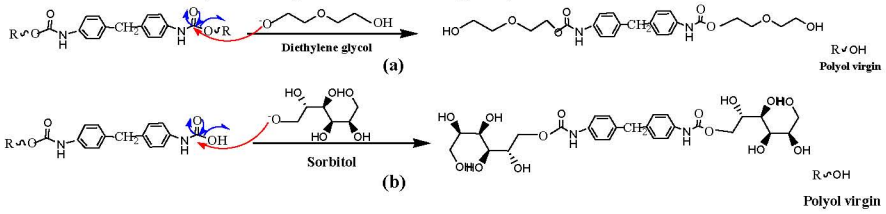

Fig.1. Mechanism reaction PUF by destroying solvent DEG(**a**),sorbitol(**b**)

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Ionic metal adsorption by hydrogels containing citric acid and imino diacetic acid

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The contamination of water resources by industrial effluents is a serious issue [1]. The determination of trace toxic metal ions and their removal with chelating polymers have gained great importance in environmental applications because of their high degree of selectivity, high loading capacity, versatility, durability, and enhanced hydrophilicity [2-4]. The necessity of reducing the concentration of heavy metals to acceptable levels in wastewater and the need for more highly specific metal-recovery processes in both hydrometallurgical and environmental applications have led to increasing interest in polymer-based adsorbents. In this work poly(styrene-alt-maleic anhydride) was grafted by citric acid or iminodiacetic acid in different molar ratios. The prepared polymers characterized by FT-IR and NMR spectroscopy. The prepared graft polymers have a pH sensitive properties and their pH of cloudy point in aqueous solution were determined. The graft copolymers was examined in ionic metal adsorption such as Pb^{2+}, Cr^{2+}, Ni^{2+}. The adsorption results of aforementioned metallic ion were high, so the prepared polymers show good ability in adsorption of metallic ion from aqueous solutions.

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$SbCl_5/SiO_2$: an efficient and facile heterogeneous catalyst for preparation of azo dyes based on β-naphthol at room temperature under solvent-free conditions

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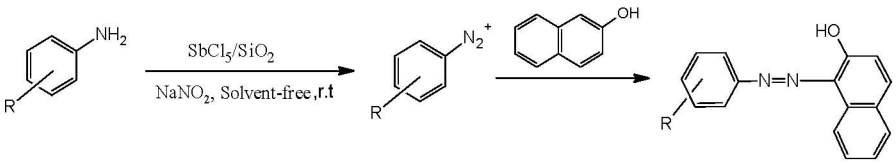
Supported-metal catalysts are widely used in the chemical industry and environmental protection. It is well known that the support has a great influence on the catalytic performance of catalysts [1]. Antimony pentachloride ($SbCl_5$), a thin, colored and fuming liquid, is used in industry and organic synthesis. This catalyst can be easily separated from the reaction products by simple filtration and quantitatively recovered in the active form [2]. Almost 10^6 tons of dyes are produced annually around the world, of which azo dyes, characterized by one or more azo groups linking substituted aromatic structures, represent more than 50% by weight. These dyes are widely used in a number of industries such as textile, food, cosmetics and paper printing. Approximately 10–15% of dyes are released into the environment during manufacturing and usage [3]. Diazonium salts are useful synthetic building blocks in organic synthesis because these compounds can be linked to methine or aromatic sp^2-hybridized C-atoms [4]. Herein, we wish to report a convenient and rapid one-pot method for diazotization and diazo coupling reactions using $SbCl_5/SiO_2$ under solvent-free conditions at room temperature. The reaction is clean and the purification of product is straightforward with excellent yield, especially solid anilines. These are azo dyes based on coupling of the β-naphthol and diazonium salts. $SbCl_5/SiO_2$ is friendly with respect to corrosiveness, safety, reduced waste and ease of separation and recovery. Spectroscopic methods such as ^{1}H- and ^{13}C-NMR, FT-IR, UV-Vis were used for identification of azo dyes.



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Highly efficient one-pot synthesis of trisubstituted imidazoles in the ionic liquids(ILs)

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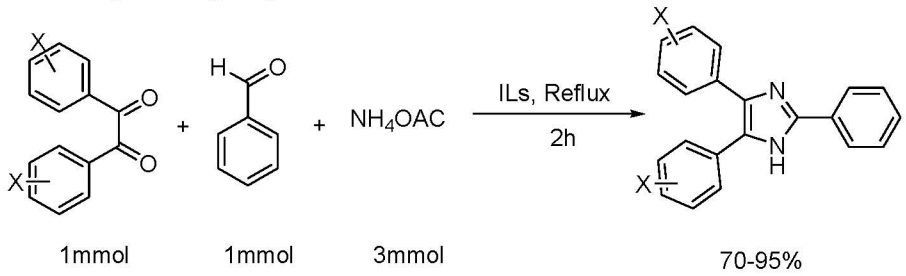
Operationally simple, atom economical, and scalable synthesis of 2,4,5-trisubstituted imidazoles from benzil, aldehydes, and ammonium acetate is shown to proceed readily in the ionic liquids with high yield. The scope of the reaction is quite broad; a variety of aromatic and aliphatic activated and unactivated aldehydes have all been shown to be viable substrates for this reaction. Excellent yields and purity were obtained by washing the products with hot ethanol.



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Catalyst-free synthesis of dihydropyridine from *Barbituric acid in water*

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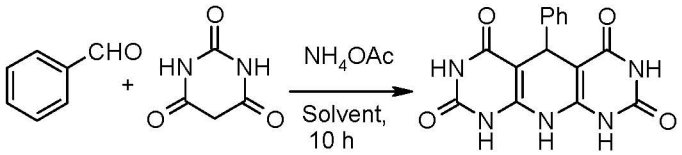
Operationally simple, atom economical, and green procedure has been developed for the synthesis of dihydropyridine derivatives by a simple condensation of barbituric acid, aldehyde and ammonium acetate in water under catalyst free conditions. Excellent yields and purity were obtained with only filtration and washing with hot water and ethanol.



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An efficient procedure for the one-pot synthesis of dihydropyrimidinones and 1,4-dihydropyridines catalyzed by $FeCl_3.SiO_2$ nano particle

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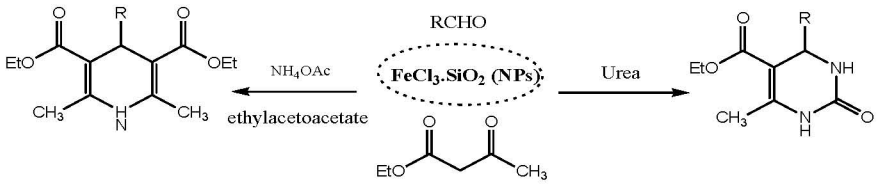
Multicomponent reactions, have become very popular in the discovery of biologically active novel compounds due to its simple experimentation, atom economy and high yields of the products [1]. Recently, a number of modified methods have been developed [2-4]. Solid acids and especially those based on micelle-templated silicas and other mesoporous high surface area support materials are beginning to play a significant role in the greening of fine and speciality chemicals manufacturing processes [5]. An economical and recyclable nano silica supported ferric chloride was prepared as heterogeneous catalyst for the synthesis of various substituted such as 1,4-dihydropyridines (DHP) and dihydropyrimidin-2(1H)-one (DHPM) via condensation of aldehydes with ethyl acetoacetate and ammonium acetate urea in ethanol. All the synthesized compounds have attracted large interest due to pharmacological and biological activities[6]. The products could be separated from the catalyst simply by filtration and the catalyst could be recycled and reused for several times without noticeably decreasing the catalytic



activity. The structure of products are confirmed by IR and1H NMR spectroscopic methods.

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

Efficient Synthesis of Functionalized Thiazolidines Containing Highly Polarized Carbon-Carbon Double bonds

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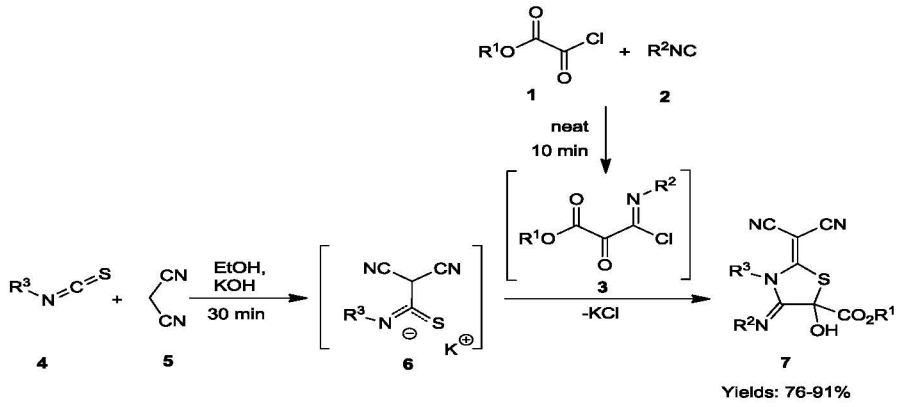
Thiazolidines and their derivatives are an important class of five-memberd heterocycles, which have found applications as analgesics, anti-inflammatory, antimicrobial, and antioxidant drugs.[1] We report on the reaction of Nef-isocyanide adducts **3**, obtained from alkyl chlorooxalates **1** with alkyl isocyanides **2** at room temperature, with potassium (2,2-dicyano-1-mercaptovinyl)(alkyl)amides **6**. This reaction leads to the formation of the thiazolidine derivatives **7**, in good yields.



The structures of compounds **7** were deduced from their IR, ^{1}H NMR and ^{13}C NMR spectral data. Various features of these transformations will be presented and discussed.

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One-pot three Component Synthesis of Benzo[b]pyran-3-carbonitrile Derivatives in Aqueous Glucose Solution as Medium and Promoter

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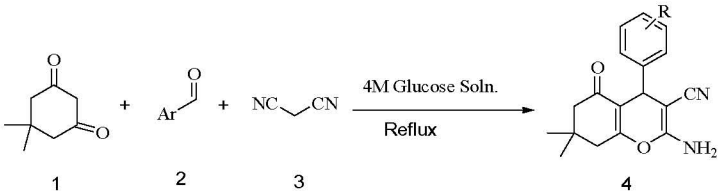
Benzo[b]pyran derivatives have been found as structural motif in the structure of some drugs which show various pharmacological properties such as peroxisome proliferator-activated receptor r and -γ (PPARr and γ) antagonists [1], and novel anti-ischemic agents [2]. So, the search for more environmentally benign and versatile synthetic methods is still an active area of research in organic chemistry. The well-known process for the synthesis of benzo[b]pyran derivatives includes a three-component reaction of cyclic 1,3-diketones, aryl aldehydes, and malononitrile which is carried out under various reaction conditions. Conditions such as microwave and electrogeneration of base were also employed in this process [3,4]. Because the idea of green chemistry has shifted somehow toward employing biobased materials with diverse structures, such as sugars, for the purposes of synthesis and catalysis, we have already reported the synthesis of 2-arylbenzimidazoles in aqueous glucose solution [5]. So, we herein wish to report a novel methodology for the synthesis of benzo[b]pyran-3-carbonitrile derivatives via a one-pot three-component reaction of dimedone (1), aromatic aldehydes (2) and malononitrile (3) in 4M aqueous glucose solution (Scheme 1).



1 2 3 4

Scheme 1

All of the products were obtained in less than a half an hour with excellent to quantitative yields. The products were precipitated completely after formation and can be isolated easily and washed by sitirring in water for half an hour. This reaction did not proceed well in pure water inferring to the role of glucose in the process. In summary, this methodology seems to be a good alternative to the present methodologies because of using an ecofriendly carbohydrate aqueous solution as a medium and catalyst.

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

Synthesis of New Polyether-Diester Podands Containing A 4*H*-pyran-4-one Unit

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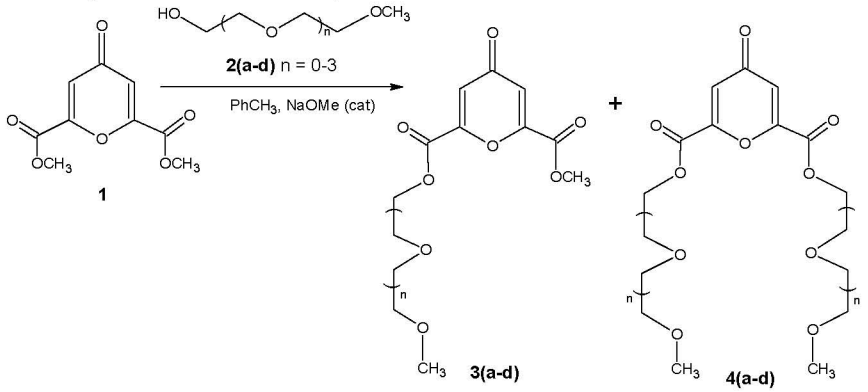
The synthesis and cation complexing characterization of noncyclic polyethers were reported in past decades. Until now a large variety and number of podands have been prepared and their properties have been studied extensively. Some of the properties of the synthetic noncyclic polyethers are similar to those of certain macrocyclic polyethers, however the synthesis of these are very simpler than them [1]. Heteroaromatic components can assume donor position in podands. 4*H*-pyran-4-one derivatives constitute a useful class of heterocyclic compounds which are widely distributed in nature. 4*H*-pyran-4-one and corresponding derivatives have been the subject of much research due to their importance in various applications and their widespread biological significance.

In continuation of our studies in the chemistry of 4*H*-pyran-4-ones [2-4], we have investigated the synthesis of new noncyclic polyether-diester ligands containing the 4*H*-pyran-4-one derivatives subcyclic unit. These compounds have been prepared by treating various glycols monomethylether (2) with dimethyl chelidonate (1) *via* transesterification reaction in toluene using sodium methoxide as catalyst. The reaction was driven to completion by the removal of methanol through its absorption onto molecular sieves. The proposed structures for the noncyclic polyethers-diesters (3-4) are consistent with data obtained from Mass, IR, ^{1}H and ^{13}CNMR spectra and elemental analyses.



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Highly efficient, solvent-free, one-pot synthesis of trisubstituted imidazoles using $SbCl_5/SiO_2$ as a novel catalyst

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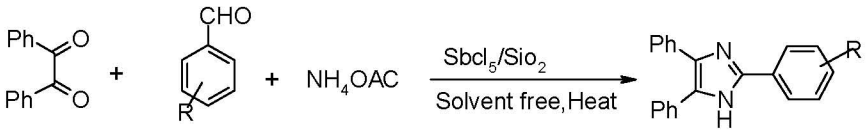
Multicomponent reactions enjoy an outstanding status in organic and medicinal chemistry for their high degree of atom economy and application in the diversity-oriented convergent synthesis of complex organic molecules from simple and readily available substrates in a single vessel [1]. One such reaction is the synthesis of imidazoles. Imidazole and their derivatives, which usually possess diverse biological activities, play important roles as versatile building blocks for the synthesis of natural products and as therapeutic agents [2]. Nowadays, solid-supported reagents have improved the activity and selectivity more than can individual reagents, because the surface area of the reagent is increased manifold. Antimony pentachloride ($SbCl_5$), a thin, colored and fuming liquid, is used in industry and organic synthesis. Since antimony pentachloride is a liquid with a high specific gravity that fumes in air and reacts with the moisture to form HCl, and since its handling and usability in the liquid form is laborious, the supported form is indeed preferable. It has been claimed that the supported $SbCl_5$ is a solid super acid. $SbCl_5$ is used extensively in organic synthesis as a Lewis acid for enhancing a variety of organic reactions [3]. Herein, we wish to report a mild and efficient methodology for the synthesis of tri-substituted imidazoles via direct tri-component condensation reaction between benzil, various aldehydes and ammonium acetate using catalytic amounts of $SbCl_5/SiO_2$. The key advantages of this process are short reaction times, high yields, reusability of catalyst, easy work-up and purification of products. Final products were fully characterized by IR, ^{1}H- and ^{13}C-NMR spectroscopic methods.



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The Synthesis of 5-(bromo methyl)-3-(3, 4, 5-trimethoxy phenyl) isoxazole as a new compound

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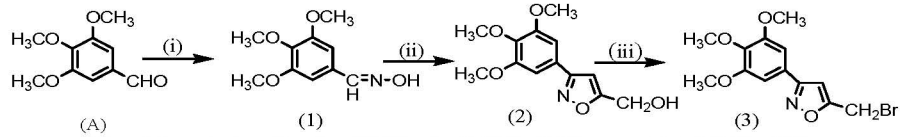
Isoxazole derivatives have been used as key intermediates in synthesis and have been investigated intensively for the last several years. Isoxazoles attract great interest because of their wide reaching application in the medicinal chemistry and material science [1]. For example in year 2010, A series of novel 2, 5–bis (3-indolyl) isoxazoles were synthesized as antitumor agent [2], In 2010 year, a seriese of isoxazole-based histon deacetylase (HDAC) inhibitors structurally related to SAHA were designed and synthesized [3] and in 2007 year, a set of new enantiopure isoxazoles derivatives were prepared and tested for their affinity and efficacy at human β_1-, β_2-, β_3-adernergic receptor subtype [4]. This research work describes the synthesis of new compound of isoxazole family. First, 3, 4, 5-trimethoxybenzaldehyde (A) was transformed to 3, 4, 5-trimethoxybenzaldehyde oxime (1) by using NH_2OH in pyridine. The in situ generated nitriloxide from reaction between (1) and NaOCl, in a cycloaddition procedure then was reacted with propargylalcohol and [2+3] cycloaddition to produce (3-(3,4,5-trimethoxyphenyl)isoxazol-5-yl) methanol (2), in final 3-(3,4,5-trimethoxy phenyl)-5-bromomethyl isoxazole (compound 3) prepared by reaction of PBr_3 and compound 2 in $CHCl_3$ (**scheme 1**).The structure of all the synthesized compounds was characterized and confirmed by FT-IR, ^{1}HNMR and ^{13}CNMR spectroscopy techniques.



Scheme1. Reagent and conditions: i) py, NH_2OH, reflux, ii) CH_2Cl_2, NaOCl, propargylalcohol, iii) PBr_3, $CHCl_3$.

In conclution, a series of isoxazole synthesized. We have successfully developed an other method for synthesis of disubstituted isoxazole from benzaldehyd with propargylalcohol that synthesis compound is useful as key intermediates for the synthesis of other compounds.

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7-9 March 2012

Synthesis of 14-alkyl- or aryl-14H-dibenzo [a,j]xanthenes using $SbCl_5/SiO_2$ as an facile catalyst in conventional and solvent-free conditions

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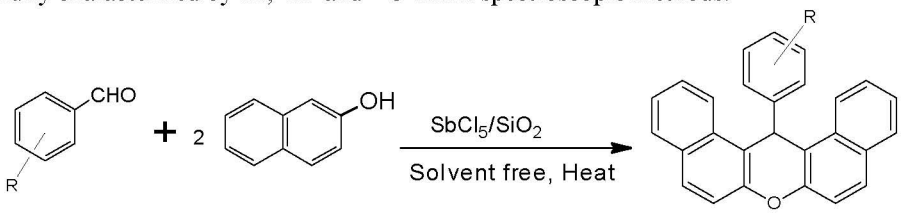
Organic syntheses involving greener process and under solvent free conditions have been investigated worldwide due to stringent environment and economic regulations[1]. Antimony pentachloride ($SbCl_5$), is used in industry and organic synthesis and since its handling and usability in the liquid form is laborious, the supported form is indeed preferable. It has been claimed that the supported $SbCl_5$ is a solid super acid. $SbCl_5$ is used extensively in organic synthesis as a lewis acid for enhancing a variety of organic reactions [2]. In recent years, much attention has been directed towards the synthesis of 14-substituted-14-H-dibenzo [a,j] xanthene derivatives[3]. Xanthene's heterocycles and derivatives are interest because they are an important class of natural compounds such as Bikaverin and Guayin which exhibiting a wide range of pharmaceutical and biological properties such as antiinflamatory, antitumor, and applied in photodynamic therapy[4].In continuation of our research program directed toward the synthesis of xanthenes, we wish to describe the synthesis of xanthenes, from β-naphthol and various aldehydes in the presence of a heterogeneous solid acid catalyst in high yields. Final products were fully characterized by IR, ^{1}H- and ^{13}C-NMR spectroscopic methods.



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An efficient three-component tandem reaction for the synthesis of pyrazolo[3,4-*b*]pyridine

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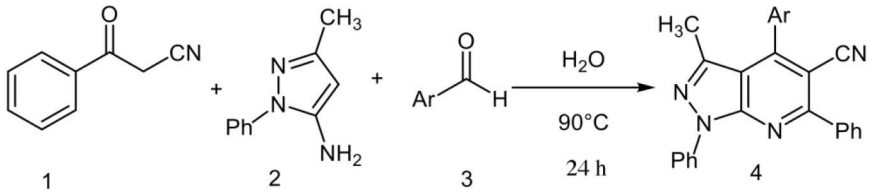
One-pot multi-component reaction (MCR's) strategies offer significant advantages over conventional linear-type syntheses by virtue of their convergence, productivity, facile execution and high yield [1]. In addition, the use of water as the reaction media has several benefits; water is a cheap, plentiful, nontoxic, nonflammable, green, neutral and natural solvent [2]. Also, by carrying out of the tandem MCRs in water and/or without any harmful organic solvents have increased importances [3]. The pyrazolo[3,4-b]pyridines in general, represent a unique class of compounds due to a wide range of medicinal uses reported in the literature [4]. In this work, we have reported the one-pot three-component condensation reaction as tandem of benzoyl acetonitrile (**1**), 3-methyl-1-phenyl-1*H*-pyrazol-5-amine (**2**) and aldehyde (**3**) in water in the absence of any organic solvent and catalyst at 24 hours that lead to pyrazolo[3,4-b]pyridine derivatives in good yield.



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Synthesis of 2-((4-chloro-2-oxo-2H-chromen-3-yl)methylen) amino)carboxylicacid

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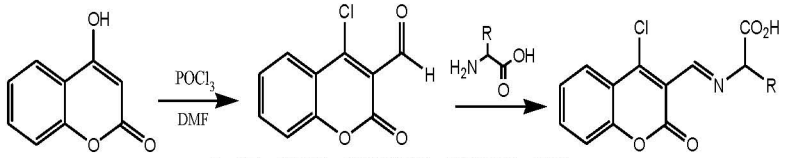
There are number of reports that natural and synthetic coumarin derivatives possess antimicrobial activity [1-2].Amino acids have found extensive application in the life sciences as components of biologically active peptides and small molecule pharmaceuticals[3].Schiff bases are the important compound owning to their wide range of biological activities industrial application[4].They have been found to possess the pharmacological activities such as anticancer, antibacterial, antifungal and antimicrobial[5-9].In the present work, we report the synthesis of Schiff'sbases of 4-chloro-3- coumarinaldehyde.

A number of novel 2-((4-chloro-2-oxo-2H-chromen-3-yl)methylen) amino)carboxylic acid in situ of reaction of amino acid with 4-chloro-2-oxo-2H-chromen-3-carbaldehyde were synthesized.



R = -CH3 , -CH(CH3)2 , -CH(CH3)(C2H5) , -CH2CH(CH3)2 , -CH2Ph

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Synthesis of N,N′-bis benzamido thiocarbonyl phenylenediamine derivatives

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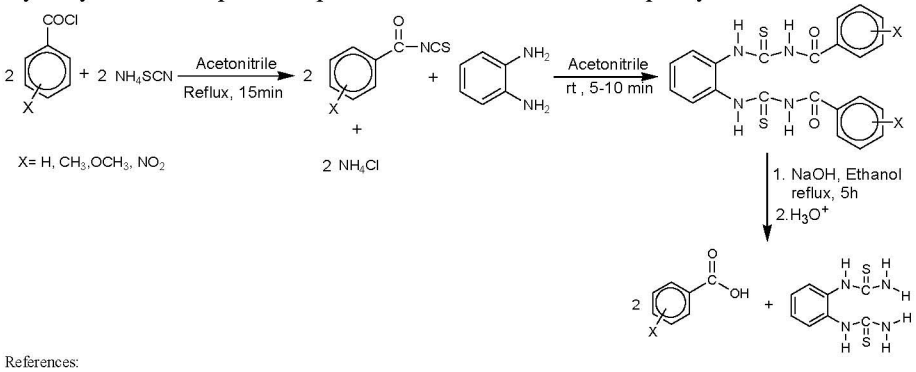
Tel: 0098-541-2447010, Fax: 0098-541-2431067;
E-mail: heydari@chem.usb.ac.ir

It is well known that thiourea derivatives exhibit potent antibacterial [1], fungicidal, antitubercular,
antitumor, antiviral, analgesic bioactivities and are also useful as insecticides, fungicides, herbicides [2], and plant-growth regulators [3]. The compounds containing thiourea as structural fragment in their molecules are suitable candidates for chemical modeling as precursors in the synthesis of heterocyclic active derivatives. The thioureides compounds are useful ligands in coordination chemistry, being studied their complexation behavior, general characterization and biological activity, especially as cancerostatic agents [4].
In this research, reaction of benzoyl isothiocyanates with *o*-phenylenediamine was studied. The results show products of the reaction are derivatives of N,N′-bis benzamido thiocarbonyl phenylenediamine in high yields and short reaction times. Hydrolysis of these products produce thiourea derivative of phenylenediamine.



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Polymeric nano-structures based on carbon nanotubes

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Polyethylenimine and their derivatives,especially poly(2 -oxazoline),are known as key compounds, opening up new aspects of polymerization chemistry of cyclic iminoethers and materials science. In this study, polyoxazoline bease on carbon-nanotube synthesized. functionalization nanotubes reaction as a macro-initiator in the polymerization cationic 2 - methyl -2 - oxazoline to be applied. Carbon nanotubes (CNTs) are ideal fillers for polymer composites due to their high Young's modulus combined with good electrical and thermal conductivity. The very high aspect ratio makes it likely that the addition of a small amount of CNTs strongly improves the electrical [1], thermal [2] and mechanical [3] properties of the polymer matrix. Thus, CNT/polymer composites combine the good processability of the polymers with the excellent mechanical and other functional properties of the CNTs. Polyoxazoline polymers with methyl (PMOZ), ethyl (PEOZ), and propyl (PPOZ) side chains were prepared by the living cationic polymerization method. In this contribution, we report a novel functionalization that follows the approach of the diazonium salts [4,5]. we have employed 4-(bromomethyl)aniline as the regentfor the generation of the diazonium salt . The resulting composite was characterized by TGA and DSC. The TGA were conducted in a Shimadzu TGA-50, under air at a heating rateof 5 °C/min, from room temperature to 800 °C. Nanostructured poly oxazoline were studied with the various methods, such as IR, TEM, SEM, HNMR, RAMAN. The PMOZ-modified nanotubes show a markedly increased suspendibility in chloroform due to the high solubility of PMOZ in this solvent. The impact of PMOZ as a biodegradable and biocompatible polymer, and its applications in tissue engineering give significance to these results, which could lead to the incorporation of nanotube-based advanced materials for biomedical purposes. At the same time, these results can be generalized to other monomers that polymerize via the same mechanism as PMOZ as well as to the generation of copolymers by using appropriate combinations of monomers.

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Synthesis and characterization of two tridentate imine compounds with diketone base as initial reactant

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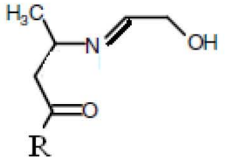
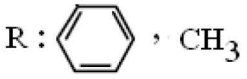
In recent years, some important potential applications, such as catalysis, magnetism, gas storage of the functional coordination complexes have been drawn considerable attention [1-3].
Some of the organic compounds consist of imine groups act as coordinated ligands. The Schiff bases ligands with the imine group derived from the condensation of primary amines and carbonyl compounds [4-5]. Herein, we report the synthesis of two distinct Schiff base organic compounds; L_1: 3-(2-hydroxyethylimine)-1-phenylbutane-1-one and L_2: 4-(2-hydroxyethylimine)pentane-2-one.
These two synthesized organic compounds; Schiff base ligand; with three sites for coordination are connecting as a chelate to the metal centers as nodes. So, these organic structures have best potential for some biological applications. Also, these structures are characterized by IR, ^{1}HNMR and ^{13}CNMR spectroscopies.





L_1 L_2

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Synthesis of some new tetrazolo pyrimidine derivatives

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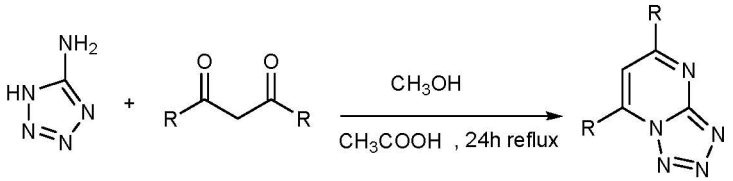
Pyrimidine is a heterocyclic aromatic compound containing two nitrogen atoms at positions 1 and 3 of the six-member ring. Pyrimidine nucleotides are of fundamental importance as precursors of DNA and RNA biosynthesis in all living organisms[1]. The regulation of pyrimidine biosynthesis in plants is poorly understood, relative to what is known in other organisms[2-4]. The fused derivatives by heterocyclic compounds display good antifungal
activity[5]. Tetrazoles have important applications in major areas, such as medicine, agriculture and food chemistry[6]. Tetrazoles have also important uses in organic synthesis[7]. In The present study reaction of 5- amino tetrazole with β- di- ketone derivatives produce some new tetrazolo pyrimidine derivatives.



R: CH_3 , Ph

Scheme 1

Structural characterization of these new compounds was carried out using IR, NMR, and MASS spectroscopy.

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Development of heterogeneous catalyst based on modified triazine ring supported on silica-gel for the Knoevenagel condensation

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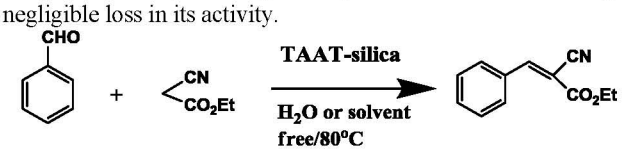
Heterogenization of homogeneous catalysts is an important topic in organic chemistry [1]. While some advantages of the homogeneous catalysts such as catalytic activities and selectivity are retained, other properties like easier work-up, recyclability and stability of the heterogeneous systems will be obtained. Knoevenagel condensation is a well-known organic reaction largely employed for C–C bonds formation [2]. The Knoevenagel adducts, in fact, are useful intermediates for further transformations, such as Diels–Alder and Michael additions. The classical Knoevenagel condensation has been carried out by reacting of a methylene active compound with an aldehyde or a ketone in the presence of a base. Methylene active compounds carrying two electron with drawing groups, such as malononitrile, cyanoacetates, malonates, and β-ketoesters, are generally used in the known condensations [3]. In this work, silica gel surfaces were modified with diethylenetriamine (DETA) via two step chemical reaction. Cyanuric chloride was chemically bound to the surface hydroxyl groups of silica-gel to give cc-silica. In the second step cc-silica was reacted with DETA to give diethylenetriamine on triazine ring bounded to silica-gel (TAAT-silica). This heterogeneous catalyst was used as a basic catalyst for the Knoevenagel condensation reaction of aromatic aldehydes and ethyl cyanoacetate in water as a solvent (Scheme1). The green and mild reaction conditions, medium to short reaction times, simple work-up, low cost and easy preparation of catalyst are the obvious advantages of the present catalyst. Finally, this catalyst can be recovered by washing with aqueous solution and used again at least three times without negligible loss in its activity.



Scheme 1. Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate using TAAT-silica as a heterogeneous catalyst.

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Radiation crosslinking of poly (butylene terephthalate) and its effects on thermal properties and flame properties

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Engineering plastics like polybutylene terephthalate due to its desirable properties as have various industrial applications such as in automotive, electric and electronic component industries. One of the ways to improve more these properties for special applications is crosslinking.[1] There are different methods to crosslink polymers, among which radiation cross linking method has more advantages than that of chemical methods. Major advantages are: process takes place at room temperature and under normal pressure; also irradiation takes place after the moulding process without presence any chemicals, substantial time and cost savings.[2,3] In this work the effect of radiation crosslinking on the thermal and flammability properties of polybutylene terephthalate (PBT) has been investigated. For this aim ROHDOTRON TT200 accelerator has been used. PBT/additives samples were prepared by using internal mixer 350-E made by Brabender Company. The mixing was carried out at 80 rpm and 240 °C. Rang dose of crosslinking the polymer was between 200 - 400 kGy. Thermal and fire tests such as heat distortion temperature, Thermogravimetric analysis and UL-94 test in vertical and horizontal position have been carried out on irradiated and non-irradiated samples. Result of TGA revealed that radiation crosslinking has effective role on the enhancement of thermal stability and increased char formation. According to the results of UL 94, irradiated samples burned with lower speed and less dripping.

Key words: radiation crosslinking, electron beam, polybutylene terephthalate, flammability, thermal properties

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

Fast and Efficient Method for Reduction of Carbonyl Compounds with $NaBH_4/Fe_3O_4$ Nanoparticles System

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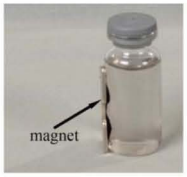
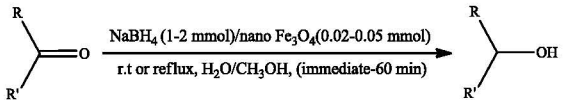
Increasing attention to the environmental concerns and the requirement for efficient and green catalysts have attracted chemists to use new and environmentally benign catalysts. Recently, nano- particles have been used in organic synthesis. Fe_3O_4 nano-particles are one kind of the most important nano-particles. Because excluding the normal nano behavior, they impact a characteristic magnetism which is helpful for its recycle. The catalyst can be recovered by the use of an external magnet and reused (Scheme 1)[1].

Reduction of carbonyl groups to the corresponding alcohols is one of the most important functional group inter-conversions in organic synthesis. On the other hand, metal hydrides are valuable reagents in modern organic chemistry. The most frequently used hydride is the $NaBH_4$ reagent. It is a mild, inexpensive and invaluable reagent for applications in a wide range of reduction processes. The reducing capability of $NaBH_4$ greatly could be accelerated by using many of additives [2,3]. In this investigation, we introduce a new combination system of $NaBH_4$ with catalytic amounts of magnetic Fe_3O_4 nano-particles (16.81 nm)[4]. as reusable and green catalyst for reduction of variety of carbonyl compounds such as aldehydes, ketones, acyloins, α-diketones and conjugated enones to their corresponding alcohols in high to excellent yields (Scheme 2).



Scheme 1



R, R': H, Alkyl, Aryl

Scheme 2

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Synthesis of optically active 1,2,4-triazolo-[3,4-b]-1,3,4-thiadiazole derivatives containing L-amino acid moieties

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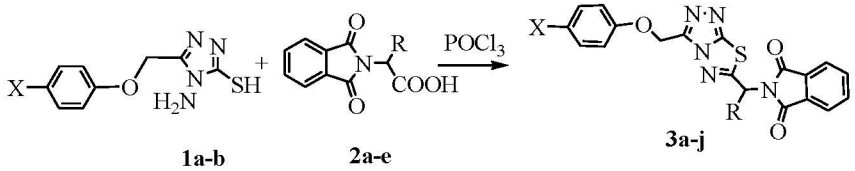
The recent literature is enriched with progressive findings about the synthesis and pharmacological activity of fused heterocycles. The [1,2,4]-triazolo-[3,4-b]-[1,3,4]-thiadiazole derivatives obtained by fusing the biolibale [1,2,4]-triazole and [1,3,4]-thiadiazole ring together, are reported to possess antimicrobial and antitubercular agents.[1] A literature search revealed which the preparation of these compounds have been extensively studied in the recent years, as followed from data of the most convenient procedure for the synthesis of [1,2,4]-triazolo-[3,4-b]-[1,3,4]-thiadiazole derivatives is based on the reaction of 5-substituted 4-amino-(4H)-1,2,4-triazole-3-thioles with carboxylic acids.[2]



1a-b **2a-e** **3a-j**

Scheme 1. Synthesis of compounds **3a-j**

In continuation of our effort to develop the synthesis of new optically compound derivatives,[3-5] we report herein, a simple and efficient method for the synthesis of substituted triazolothiadiazole 3a-j **via reaction between of amino triazole with N-aroyl L-amino acid. 5-substituted 4-amino-(4H)-1,2,4-triazole-3-thiole** 1a-b **was prepared by heating substituted 4-substitueted phenoxy acetic acid with one equivalents of carbonothioic dihydrazide in an oil bath at 170 °C. The resultant triazole** 1a-b **was further converted to 1,2,4-triazolo-[3,4-b]-1,3,4-thiadiazoles** 3a-j **through one pot reaction by condensation with N-phethaloyl L-amino acids** 2a-e **in the presence of $POCl_3$ respectively. Our synthetic approaches are depicted in Scheme 1. In Conclusion we have been able to synthesize some N-aroyl-L-amino acids having a free terminal carboxyl function, which can react with amino triazole. This reaction may be useful for combinational synthesis of type** 3 **compounds having various R substitutions with a view to test for biological activities**.

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Using 1-(1-buthyl sulfonic)-3-methylimidazolium nitrate and phosphorouspentoxide as a green solvent for the oxidation of benzylic alcohols to the corresponding carbonyl compound.

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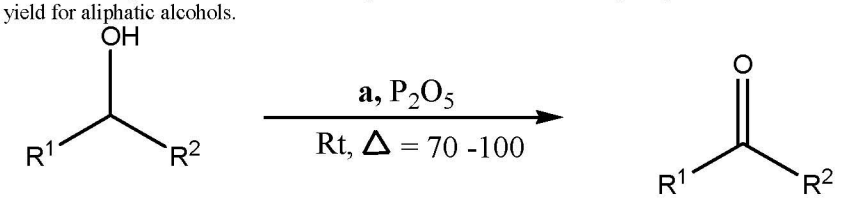
Ionic liquids, nowadays, have been using as green solvents in reaction media. Their safety, recyclability and ease of handling and etc are some of the outstanding characteristics of them [1]. Using ionic liquids having dual effects as solvent and reagent or catalyst have received considerable attention in recent years [2]. These applications eliminate the use of some toxic reagents such as transition metals, strong acids and especially high temperatures. On the other hand oxidation of benzylic alcohols to corresponding carbonyl compounds has been extensively studied and lots of catalysts and reagents have been envisioned for this procedure [3]. Ionic liquids, also, have been applied as green solvents and reagents for this transformation. Here in, we wish to report a green and versatile procedure for the oxidation of benzylic alcohols to carbonyl compounds via new nitrate – base ionic liquid in the presence of P_2O_5. Some of the benefits of the process are: the reagent is cheap and easy to handle in comparison with previous procedures. The ionic liquid is stable for long time. The byproducts are harmless to environment and the extraction is straightforward and the ionic liquid could be recovered completely. The reaction results in no yield for aliphatic alcohols.

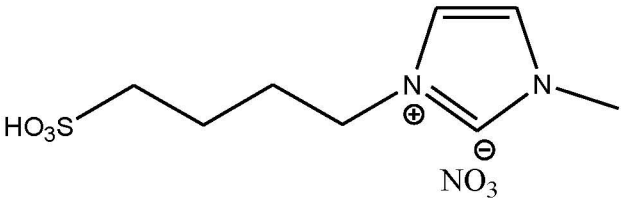


yield = 76-95 %

R^1= H, Ar, Alk

R^2= Ar, Alk

a =



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Solvent free azo dyes synthesis via coupling of α-naphthol in the presence of $SbCl_5/SiO_2$ at room temperature

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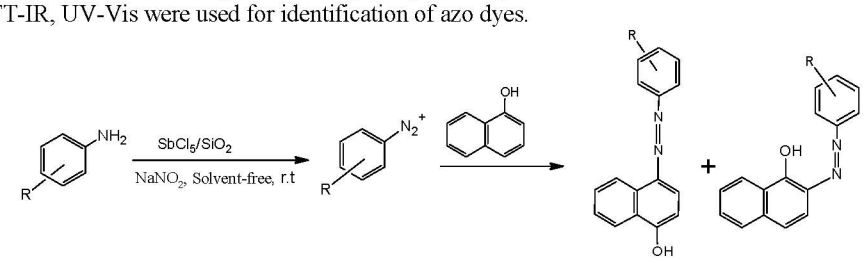
In recent years, the use of solid acids as heterogeneous catalysts has received significant interest in different areas of organic synthesis. Heterogeneous solid acids are advantageous over conventional homogeneous acid catalysts as they can be easily recovered from the reaction mixture by simple filtration and can be reused after activation or without activation, thereby making the process of N-donor solvents have been reported [1]. Diazonium salts are precursors of azo compounds which are very useful in the fields of dyes, pigments and advanced materials. Azo dye compounds are widely used as colorants in the textile industries but they have several other applications, for example, colorants for digital printing and photography; dyes for drug, food and cosmetic applications. Azo dyes are compounds that contain azo groups linked to methine or aromatic sp^2-hybridized C-atoms [2]. These azo dyes have two different products that separated with column chromatography. It is noted that lewis acid sites on silica-supported antimony (V) chloride ($SbCl_5$:SiO_2) act as highly efficient catalyst, even for low activity substrates, in the preparation of azo dyes in solvent free condition. The fact that $SbCl_5$ did not leach makes $SbCl_5/SiO_2$ as alternative heterogeneous acid catalyst to the conventional homogeneous acids at room temperature [3]. The formation of the diazotizing reagent starts with protonation of nitrous acid under strongly acidic conditions, and azo coupling occurs at room temperature in the presence of nucleophilic components and heterogeneous catalyst. Spectroscopic methods such as ^{1}H- and ^{13}C-NMR, FT-IR, UV-Vis were used for identification of azo dyes.



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7-9 March 2012

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

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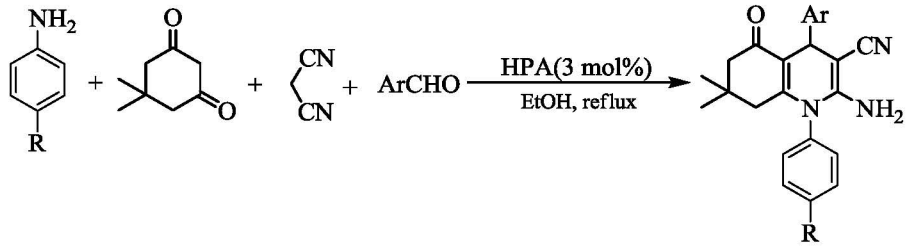
In recent years, an increasing interest has been focused on the synthesis of 1,4-dihydropyridine (DHP) compounds owing to their significant biological activities.[1] Quinolines having a 1,4-dihydropyridine nucleus are very important compounds because of their pharmacological properties such as antitumalarial, anti-inflamatory, antiasthamatic, antibacterial and antihypertensive.[2] Alternative strategies for their synthesis involving different catalysts and conditions have been developed.[3,4] However, some method suffer from drawbacks like some longer reaction times, unsatisfactory yields, harsh reaction conditions.

In continuation of our investigations on the synthesis of 1,4-dihydropyridine,[5] herein we describe a novel and efficient one-pot method for the preparation of 2-amino-7,7-dimethyl-5-oxo-1,4-diaryl-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile derivatives from cyclo-condensation of aldehydes, malononitrile, anilines and dimedone in reflux of ethanol as solvent and $HPA(AlPW_{12}O_{40}.XH_2O)$ as catalyst. This new one pot method has the advantages to give high yields, to be completed in short reaction times, with simple product isolation procedure.



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

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Peptides are known as natural drugs. Peptide Chemistry has reached a considerable level of maturity, and apparently almost with complex structure. Designing and synthesis of novel peptides as biologically active compounds is a central goal in drug discovery. [1]

In continuation of our recent research about the synthesis of novel peptides;[2-5] in this lecture designing, synthesis, and investigation of biological activities of some novel peptides will be presented. Since addition of hydrophobic moiety to a peptide sequence increase the peptide's ability to penetrate plasma membrane, in this way some peptides were synthesized with adding a hydrophobic moiety in the end of N- or C-terminus of peptides. Meanwhile, recently unusual amino acids are increasingly becoming important substrates in modern drug synthesis and discovery research. With these points in mind, some novel peptides were designed and synthesized using combination of known SPPS and SIS approaches.

In this lecture, the three main sections are as follows:

a) Synthesis of LH-RH analogues via Ugi-4CR and investigation of their anti-cancer activities.

b) Synthesis of novel analgesic and opioid peptides and comparison of their activities.

c) Combination of unusual amino acids with di- or tri-peptides, and investigation of their structure.

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Synthesis and characterization of a new bidentate Schiff base ligand

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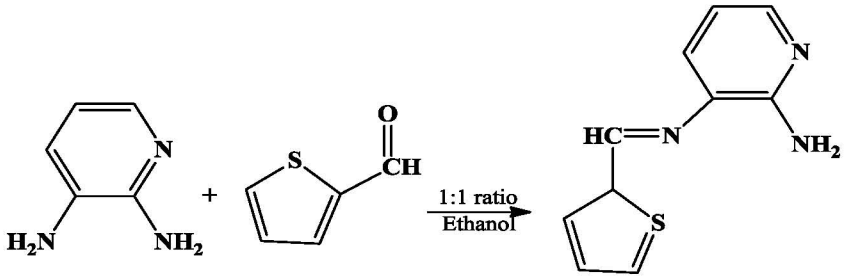
Abstract

Compounds with C=N functional group are known as Schiff base, which are usually synthesized from the condensation of a primary amines and active carbonyl groups. A large number of Schiff base compounds are often used as ligand in coordination chemistry by considering their metal binding ability [1]. These compounds may serve as models of relevance for biologically important species or as catalysts for various organic transformations, and are promising materials for optoelectronic applications and the design of biosensors [2-4].

The new unsymmetrical Schiff base ligand (*E*)-N^3–(thiophen-2-yl-methylene)pyridine-2,3-diamine (L_1H), was prepared by condensation of 2,3-diaminopyridine and thiophen-2-carbaldehyde in ethanol at -4 °C. The synthesized Schiff base ligand has been characterized with common physical methods such as elemental analysis (CHN), FT-IR, ^1H, and ^{13}C NMR.



The FT-IR spectrum of the ligand shows a sharp band at 1600 cm^{-1}, attributable to the imine group, but no bands due to m(C=O) vibrations. Observed bands at 3452 and 3286 cm^{-1} are assigned to NH_2 group. The ^1H NMR spectrum of Schiff base displayed nine resonances in the downfield region of the spectrum that can be assigned to protons of L_1H. One singlet at 5.41 ppm is assigned to NH_2 of the ligand. All aromatic protons and $-CH_{imine}$ resonate in 6.68-8.66 ppm. The ^{13}C NMR spectrum of the ligand display 10 distinct resonances assigned to the aromatic and imine carbons. All of obtained data confirms the formation of tridentate Schiff base ligand.

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Gewald and Ugi One-pot Multicomponent Reactions to Synthesis of Polysubstituted 2-Aminothiophens and Isocoumarins respectively Catalyzed by [HMIM]Br Ionic liquid

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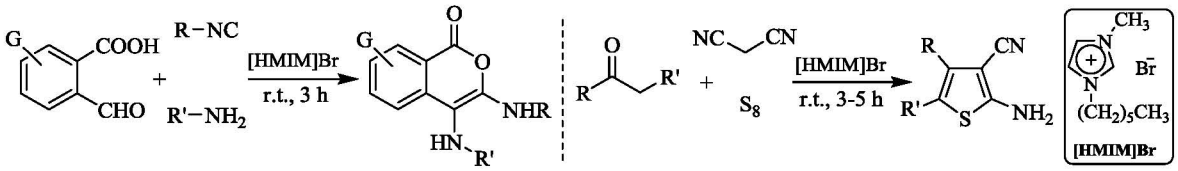
Substituted 2-aminothiophenes are important intermediates in the synthesis of a variety of agrochemicals, dyes and pharmacologically active compounds.[1] The most convergent and well-established classical approach for the preparation of 2-aminothiophenes is Gewald's method, which involves multicomponent condensation of a ketone with an activated nitrile and elemental sulfur in the presence of morpholine as a catalyst.[2]

Ugi four-component condensation (Ugi-4CC) usually refers to the reaction between amines, carbonyl compounds, carboxylic acids, and isocyanides. Really, there are many kinds of Ugi reactions since large variations of the nature of the components are possible.[3]

Ionic liquids, as environmentally benign solvents, offer an attractive alternative to conventional organic solvents because they are non-volatile, non-flammable, non-explosive, and can be recycled.[4]

The high yields, and ease of product isolation prompted us to investigate the Gewald and Ugi reaction but replacing the organic base with ionic liquid 1-hexyl-3-methylimidazolium bromide [HMIM]Br and using room temperature for heating.



In conclusion, we have introduced an efficient and environmentally friendly approach for the synthesis of polysubstituted 2-aminothiophenes via Gewald reaction and isocoumarins via Ugi-4CC using [HMIM]Br in good to excellent yields at room temperature. Also, the reaction workup is simple and the ionic liquid can be easily separated from the product.

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Theoretical Study on the Mechanism of Ugi Reaction

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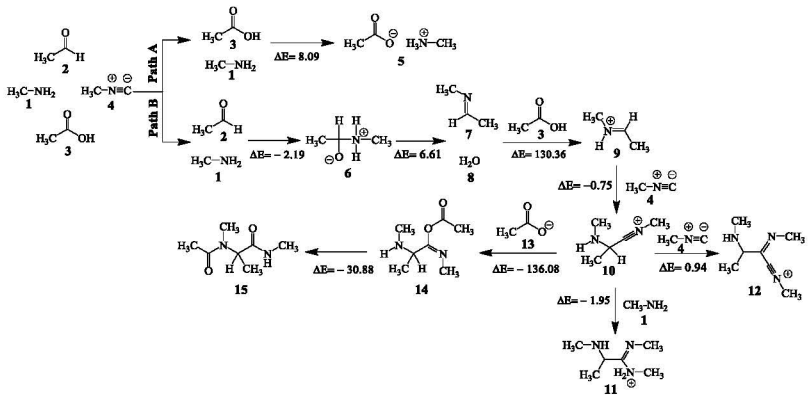
The Ugi reaction is a multi-component reaction in organic chemistry involving a ketone or aldehyde, an amine, an isocyanide and a carboxylic acid to form a bis-amide[1,2]. In this paper we try to report on the mechanism of Ugi reaction from theoretical point of view. Reagents, products and possible intermediates of Ugi reaction were designed and optimized at HF/6-31G* level of theory without any constrains. Heats of formation (HF, in Hartree) and relative stabilities (ΔE, in kcal/mol) were calculated and summarized in Table 1 and Scheme 1. The results were in agreement with experimental findings so that as well in experimental considerations, formation of **15** was kinetically the best choice to reaction proceeding.

Compound	HF	Compound	HF	Compound	HF
1	-95.140929	6	-248.000453	11	-399.356145
2	-152.856033	7	-172.002152	12	-436.005625
3	-227.743781	8	-75.987772	13	-227.172921
4	-131.845649	9	-172.365261	14	-531.601888
5	-322.871823	10	-304.212105	15	-531.651108

Table 1.



Scheme 1.

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Computational study of some 1, 3-dipolar cycloadition reactions

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Introduction: The chemistry of 1,3-dipoles has attracted great interest more than a century [1]. This kind of cycloaddition reaction is one of the most useful reactions for the synthesis of heterocyclic compounds [2].In the present work, we investigated reacting ethyl diazoacetate (4) with various alkynes (1-3) in gas phase (Fig.1).These reactions gave the 3- and 4-isomers [3].

Computational details: All calculations were performed with the Gaussian98 program [4]. For DFT calculations, the B3LYP/6-31G* level of theory was employed. The optimizations of equilibrium geometries of all products were obtained by full optimization at the ground states of products. Thermodynamic calculations are performed with the same method. Also we calculated the chemical hardness, η , and the global electrophilicity index, ω, that μ is the electronic chemical potential and are given by: $\eta \approx \varepsilon_L - \varepsilon_H$, $\omega = \left(\mu^2 / 2\eta\right)$, $\mu \approx (\varepsilon_H - \varepsilon_L)/2$

Results and discussions: In this work, at first, the maximum hardness principle (MHP) which was introduced by pearson [5] were used to predict the stability sequence of regioisomeres products in selected reactions(Fig.1). Our results reveal that MHP principal correctly predict the 3-isomer (5) is more stable than 4-isomer (6). Then the electronic chemical potential, μ, of reactants are used to indicate direction of charge transfer (CT) at these 1,3DC reactions. The results revealed that the three dipolarophiles with the electronic chemical potential values, μ, between -0.0947 a.u. and -0.1033 a.u., are lower than of their common dipole with value -0.1568 a.u. .Therefore CT at these reactions will be from the dipolarophile to dipole. Also, electrophilicity,ω, for reactants were calculated. Three dipolarophiles (1, 2, 3) presented electrophilicity,ω, with values 0.918 eV, 0.774 eV and 0.802 eV respectively. With the absolute of scale of electrophilicity based on the ω index these compounds can be classified as marginal(2,3) or may be moderate(1) electrophilies. On the other hand, electerophilicity,ω, of dipole (4) has values 3.82 eV, So, dipole classified as a strong electrophile. Results show that dipole has a lower chemical potential (-0.1568), which is the index that determines the direction of the electronic flux along the cycloadition. Furthermore, along this series of 13DC reactions the more favorable interaction will take place between the less electrophilic specie 2, namely the dipolarophiles in the present case, and the electrophilic dipole (4).At the end, thermodynamic results show that all pathways are exothermic. Computed reactions energies for 2 pairs of reactions (Gibbs free energy difference, ΔG) suggest that the pathway with 3-isomer product is thermodynamically the most favorable.

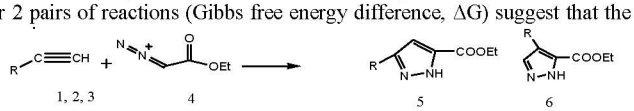

Fig.1. The considered reactions [3] (3 pairs reactions)
R= **1)** –CH2CH2OH **2)**-CH2CH2CH2OH
3) –CH2-CH2-C H(CH3) –OH

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A recyclable protocol for aza-Michael addition of amines to α,β-unsaturated carbonyl compounds using Hydroxy sodalite

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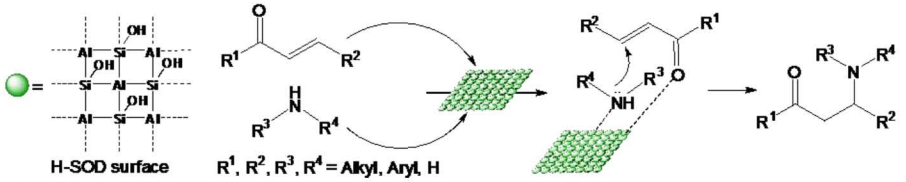
The aza-Michael addition is one of the widely used reactions for carbon-nitrogen bond formation in modern organic synthetic chemistry. Conjugate reaction of various amines with α,β-unsaturated carbonyl compounds provides β-amino carbonyl ingredients, which have attracted great attention for their use as key intermediates of anticancer agents, antibiotics and other drugs [1]. Generally, aza-Michael additions have been catalyzed by strong bases and acids [2]. However, many of these methods suffered from some drawbacks, for example, the requirement for a large excess of reagents, substrate selective for some catalysts, often involvement of some toxic solvents and occurrence some side reactions. Therefore, chemical researchers have paid more attentions to the development of more mild catalytic systems for the aza-conjugate reaction. Hydroxy sodalite (H-SOD) is a compact and stable kind of alumino silicate (zeolite) that have active surface of alumina and silica with ability of hydrogen bonding in dehydrated form. In this work, we have used hydroxy sodalite as a new catalysts for aza-Michael addition of amines to α,β-unsaturated carbonyl compounds. In this reaction Lewis acid site of H-SOD can active the carbonyl group of unsaturated ketone and hydroxyl group of its surface will adsorbed the amine on through hydrogen bonding. This protocol also has some advantages, such as readily work-up of the reactions, good to excellent yields, excellent reaction selectivity and good recyclability of the hydroxy sodalite.



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