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Sonochemically synthesis of pyrazolones using reusable catalyst CuI nanoparticles that was prepared by sonication

Abolfazl Ziarati, Javad Safaei-Ghomi *, Sahar Rohani

Department of Organic Chemistry, Faculty of Chemistry, University of Kashan, Kashan 51167, Iran

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ABSTRACT

A simple and green process to prepare copper iodide in nano scale via sonication was carried out. Subsequently, this nanoparticles was used as an efficient catalyst for the synthesis of 2-aryl-5-methyl-2,3-dihydro-1H-3-pyrazolones via four-component reaction of hydrazine, ethyl acetoacetate, aldehyde and β-naphthol in water under ultrasound irradiation. The combinatorial synthesis was attained for this procedure with applying ultrasound irradiation while making use of water as green ambient. Simple work-up, excellent yield of products and short reaction times are some of the important features of this protocol. Notably, this catalyst could be recycled and reused for five times without noticeably decreasing the catalytic activity.

1. Introduction

Ultrasound irradiation has progressively been considered as a simple, clean and convenient method in chemical synthesis in the last 30 years [1]. Ultrasonic activation, found on cavitation effects leading to mass transfer development, is extensively used nowadays to promote nano structure synthesis and also organic reactions [2]. An investigation of literature shows that the synthesis of nano crystalline and organic compounds has been improved by sonochemistry [3,4].

During the last decades, nano crystalline compounds has interested significant attention as efficient catalysts in many organic reactions due to their high surface-to-volume ratio and coordination parts which provides a large number of active sites per unit area compared to their heterogeneous counter parts [5,6]. In recent years, copper iodide has concerned much interest because of the uncommon characters such as negative spin–orbit splitting, unusually large temperature dependency, abnormal diamagnetism behavior, large direct band gap [7,8]. Also it has potential applications in solid-state solar cells, super ionic conductor and catalysis for synthesis of organic compounds [9,10]. CuI nanoparticles has indicated a significant level of performance as catalysts in terms of reactivity, selectivity, and better yields of products particularly in multi-component reactions [11,12].

The research in multi-component reactions (MCRs) is a hot topic of organic chemistry because of their advantageous in the preparation of different heterocyclic molecules and in drug discovery procedures [13]. Although MCRs are efficient, environmentally friendly, fast, atom economic and time saving style. They supply an effective tool for the preparation of various compounds with pharmaceutical and biological properties [14]. One type of these reactions is the synthesis of pyrazolones which display biological and pharmacological properties. The pyrazolone skeleton is exist in many antimicrobial [15], antifungal [16,17], antibacterial [18,19], anti-inflammatory [20,21] and antitumor [22] agents. They are also function as gastric secretion stimulatory [23], as antifilarial activities [24] and are important in depressant disease [25]. Among pyrazolones, there are also examples of drug-resistance antipyretic, analgesic [26] and a drug for the treating brain [26,27]. For example some of known drugs that have pyrazolone skeleton were shown in Fig. 1.

In continuous to progress the synthetic approach for the production of various medicinally compounds using reusable nano catalysts [28–31], herein we combined the advantages of ultrasonic irradiation and nanotechnology to design a new and efficient method for synthesis of pyrazolone derivatives using CuI nanoparticles under ultrasonic irradiation (Scheme 1).

2. Experimental

2.1. Materials and apparatus

All the chemicals reagents used in our experiments were analytical grade and were used as received without further purification. A multiwave ultrasonic generator (Sonicator 3200; Bandelin,

* Corresponding author. Tel.: +98 361 5912385; fax: +98 361 5552935.
E-mail address: safaei@kashanu.ac.ir (J. Safaei-Ghomi).

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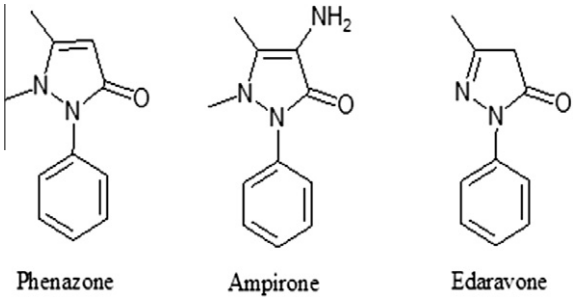


Fig. 1. Examples of drugs contain pyrazolone skeleton.

MS 73, Germany), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 200 W, was used for the ultrasonic irradiation. The ultrasonic generator automatically adjusted the power level. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance-400 MHz spectrometers in the presence of tetramethylsilane as internal standard. The IR spectra were recorded on FT-IR Magna 550 apparatus using with KBr plates. The elemental analyses (C, H, N) were obtained from a Carlo ERBA Model EA 1108 analyzer. Melting points were determined on Electro thermal 9200, and are not corrected. Microscopic morphology of products was visualized by SEM (LEO 1455VP). The N_2 adsorption/desorption analysis (BET) was performed at −196 °C using an automated gas adsorption analyzer (Tristar 3000, Micromeritics). Powder X-ray diffraction (XRD) was carried out on a Philips diffractometer of X'pert company with mono chromatized Cu Kα radiation (λ = 1.5406 Å). Transmission electron microscopy (TEM) images were obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 100 kV.

2.2. Preparation of copper iodide nanoparticles under ultrasound irradiation

The catalyst was prepared via sonochemical method (worked at 20 kHz frequency and 90 W power). $CuSO_4$ was used as the Cu source. Firstly the copper substrate (1 mmol) is ultrasonically cleaned for 20 s in acetone, followed by repeated rinsing with distilled water. After drying, the substrate is dipped slowly into a solution of KI (1 mmol) in 40 mL of distilled water and sonicated to react for 30 min. When the reaction was completed, disperse gray precipitate was obtained. The solid was filtered and washed with distilled water and ethanol several times and dried in vacuum in less than 40 °C.

2.2.1. Reusability of catalyst

The recovered catalyst from the experiment was washed by acetone and hot ethanol (3 × 5 mL). Then, it was dried and used in the synthesis of pyrazolones. Then the catalyst was recycled for five times.

2.3. General procedure for the synthesis of 2-aryl-5-methyl-2,3-dihydro-1H-3-pyrazolones

2.3.1. Typical heating method (method A)

A solution of hydrazine (1 mmol) and ethyl acetoacetate (1 mmol) in water (3 ml) was stirred at room temperature for 60 min. Then aromatic aldehyde (1 mmol), β-naphthol (1 mmol) and CuI nanoparticles (3 mol%) were added and heated to reflux for the appropriate times (monitored by TLC). After completed reaction the solid was filtered off and washed with chloroform. The residue was dissolved in hot ethanol and then filtered until heterogeneous catalyst was recovered. The filtrate was evaporated to afford the pure product in 67–74% yield.

2.3.2. Ultrasound irradiation method (method B)

In a two-necked flask, a solution of hydrazine (1 mmol) and ethyl acetoacetate (1 mmol) in water (3 ml) was sonicated at 20 kHz frequency and 50 W power, for 10 min in room temperature. Then aromatic aldehyde (1 mmol), β-naphthol (1 mmol) and CuI nanoparticles (3 mol%) were added and sonicated for appropriate times (monitored by TLC). After completed reaction the solid was filtered off and washed with chloroform. The residue was dissolved in hot ethanol and then filtered until heterogeneous catalyst was recovered. The filtrate was evaporated to afford the pure product in 86–93% yield. The spectral data for some selected compounds were given below.

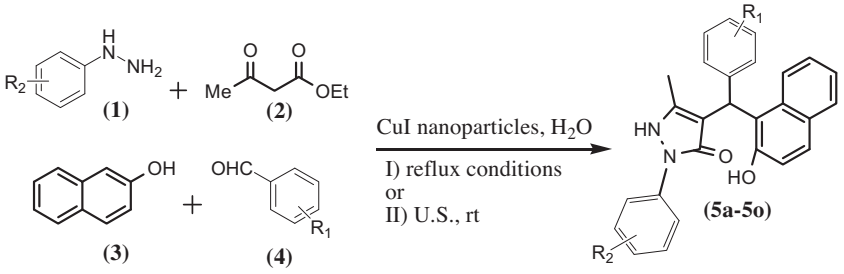
2.4. Representative spectral data

2.4.1. 4-[(2-Hydroxy-1-naphthyl)(phenyl)methyl]-5-methyl-2-phenyl-2,3-dihydro-1H-3-pyrazolone (5a)

White solid; m.p = 205–206 °C; FT-IR (KBr): 3418, 3161, 3084, 2911, 1613, 1593, 1492, 1412, 1279, 1211, 730 and 694 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) 2.11 (s, 3H, CH_3), 6.21 (s, 1H, CH), 7.08 (m, 4H, ArH), 7.13 (m, 2H, ArH), 7.18 (m, 3H, ArH), 7.29 (m, 3H, ArH), 7.31 (s, 1H, NH), 7.71 (m, 3H, ArH), 8.23 (s, 1H, ArH), 10.83 (brs, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 16.6, 40.9, 124.6, 125.3, 126.1, 127.4, 128.2, 130.5, 130.9, 131.6, 132.2, 133.0, 133.8, 133.9, 134.2, 138.9, 141.6, 146.8, 153.4, 159.1; Anal. Calcd. for $C_{27}H_{22}N_2O_2$: C, 79.77%; H, 5.46%; N, 6.90%; Found: C, 79.73%; H, 5.49%; N, 6.87%.

2.4.2. 4-[(2-Hydroxy-1-naphthyl)(4-methoxyphenyl)methyl]-5-methyl-2-phenyl-2,3-dihydro-1H-3-pyrazolone (5d)

White solid; m.p = 180–181 °C; FT-IR (KBr): 3421, 3151, 3091, 2942, 1618, 1591, 1486, 1416, 1292, 814, 731, 688 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) 2.13 (s, 3H, CH_3), 3.59 (s, 3H, OCH_3), 6.12 (s, 1H, CH), 6.77 (m, 2H, ArH), 6.95 (m, 2H, ArH), 7.08 (m, 1H, ArH), 7.23 (m, 2H, ArH),7.35 (s, 1H, NH), 7.46 (m,



Scheme 1. Synthesis of pyrazolones in the presence of CuI nanoparticles under reflux and sonication conditions.

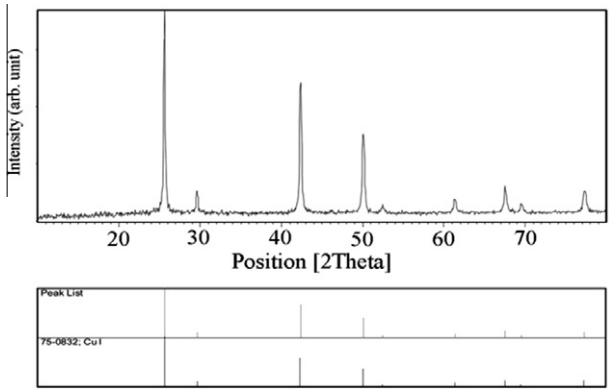


Fig. 2. The XRD pattern of CuI nanoparticles.

3H, ArH), 7.68 (m, 3H, ArH), 7.79 (m, 1H, ArH), 8.19 (s, 1H, ArH), 10.86 (brs, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 14.7, 34.4, 54.8, 106.6, 112.8, 119.1, 120.6, 121.8, 122.4, 124.9, 125.7, 128.2, 128.4, 128.5, 128.6, 132.6, 133.4, 136.1, 147.5, 148.6, 153.2, 156.7; Anal. Calcd. for $C_{28}H_{24}N_2O_3$: C, 77.04%; H, 5.54%; N, 6.42%; Found: C, 76.95%; H, 5.49%; N, 6.47%.

2.4.3. (2-(4-Clorophenyl)-4-[(2-hydroxy-1-naphthyl) (4-nitrophenyl)methyl]-5-methyl-2,3-dihydro-1H-3-pyrazolone (5l)

White solid; m.p = 183–184 °C; FT-IR (KBr): 3431, 3087, 2916, 1616, 1595, 1493, 1342, 812,758, 735, 692, 598 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) 2.19 (s, 3H, CH_3), 6.31 (s,1H, CH), 7.14 (m, 1H, ArH), 7.29 (s, 1H, NH), 7.33 (m, 3H, ArH), 7.46 (m, 1H, ArH),7.56 (m, 2H, ArH), 7.71 (m, 5H, ArH), 8.14 (m, 1H, ArH), 8.26 (m, 1H, ArH), 10.73 (brs, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 16.9, 40.8, 120.7, 121.4, 124.6, 125.9, 127.0, 127.2, 127.7, 128.3, 131.6, 133.5, 133.8, 134.2, 134.8, 138.2, 139.9, 149.6, 152.5, 153.7, 158.5, 163.1, 159.2; Anal. Calcd. for $C_{27}H_{20}ClN_3O_4$: C, 66.74%; H, 4.15%; N, 8.65%; Found: C, 67.01%; H, 4.13%; N, 8.78%.

2.4.4. (2-(4-Clorophenyl)-4-[(4-Bromophenyl)(2-hydroxy-1-naphthyl)methyl]-5-methyl-2,3dihydro-1H-3-pyrazolone (5o)

Yellowish solid; m.p = 157–158 °C; FT-IR (KBr): 3419, 3146, 3086, 2959, 1626, 1588, 1471, 1412, 1275, 816, 807, 736, 694 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.14 (s, 3H, CH_3), 6.12 (s, 1H, CH), 7.04 (m, 5H, ArH), 7.09 (s, 1H, NH),7.21 (m, 2H, ArH), 7.29 (m, 2H, ArH), 7.36 (t, 1H, ArH), 7.56 (t, 1H, ArH), 7.71 (d, 1H, ArH), 7.83 (d, 1H, ArH), 8.03 (d, 1H, ArH), 10.78 (brs, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 14.7, 36.4, 106.4, 120.2, 121.5, 122.2, 123.4, 126.7, 127.2, 127.6,128.4, 128.7, 128.9, 129.1, 129.2, 129.6, 131.4, 131.9, 133.5, 134.9,138.6, 146.2, 153.9; Anal. Calcd. for $C_{27}H_{20}BrClN_2O_2$: C, 62.39%; H, 3.88%; N, 5.39%; Found: C, 62.37%; H, 3.69%; N, 5.46%.

3. Results and discussion

3.1. Structural analysis of CuI nanoparticles

The XRD pattern of the CuI nanoparticles was shown in Fig. 2. All reflection peaks can be readily indexed to pure cubic crystal phase of nano crystalline copper iodide. Also no specific peaks due to any impurities were observed. The pattern agrees well with the reported pattern for copper iodide (JCPDS No. 75-0832). The crystallite size diameter (D) of the CuI nanoparticles has been calculated by Debye–Scherrer equation ($D = K\lambda/\beta\cos\theta$), where FWHM (full-width at half-maximum or half-width) is in radians and θ is the position of the maximum of diffraction peak ($\beta = 0.4723$ [°2θ]), K is the so-called shape factor, which usually takes a value about 0.9, and λ is the X-ray wavelength. Crystallite size of CuI has been found to be 20 nm.

The chemical purity of the sample as well as their stoichiometry was tested by EDAX studies. The EDAX spectrum given in Fig. 3 was shown the presence of copper and iodine as the only elementary components.

In order to investigate the morphology and particle size of CuI nanoparticles, SEM image of copper iodide nanoparticles was presented in Fig. 4. By SEM image some data about the morphology and size of catalyst particles were obtained. Particle size of the nano CuI was found to be small size till 20 nm.

The specific surface area was measured by nitrogen physisorption (the BET method), the specific surface area was approximately 1.94 m^2/g.

For more investigation of the influence of ultrasound irradiation in this reaction, the synthesis of nano copper iodide was compared with previously method such as pulse laser deposition technique,

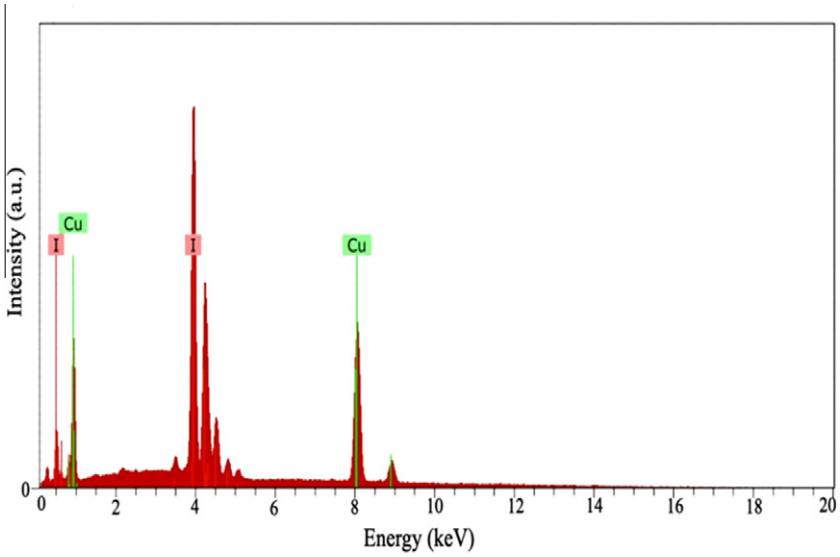


Fig. 3. The EDAX pattern of CuI nanoparticles.

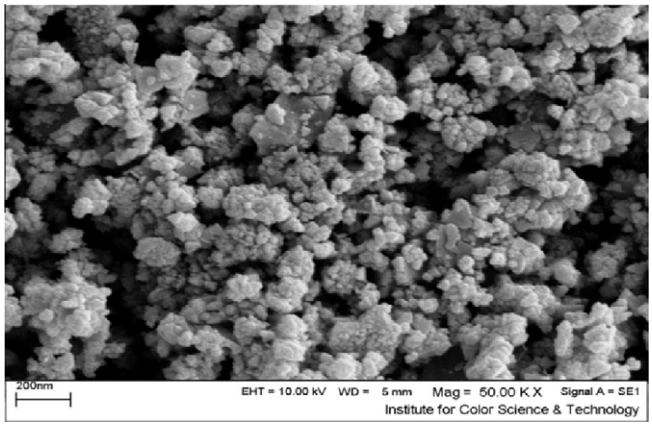


Fig. 4. SEM image of the CuI nanoparticles.

Surface-Etching Route, hydrothermal treatment, and coprecipitation [32–35] (Table 1).

As shown in Table 1, particle sizes of nano CuI prepared in the absence of ultrasound were ranging from 70 nm to 1 μm, and specific surface area was 2.08 $m^2 g^{-1}$ [36]. However, size of CuI nanoparticles prepared in the presence of ultrasound was reduced until 20 nm, and specific surface area was increased about 2.96 $m^2 g^{-1}$.

This observation is described by the effect of sonication. It is known that size control must be done within a very short nucleation period and the final particle number does not change during the particle growth. When the solution contain precursor is exposed to ultrasound irradiation, extremely-high pressures and temperatures are produced during acoustic cavitation, providing energy to generate CuI nuclei. Also, the produced high temperature and the adsorbed bubbling gasses on nuclei surface reduce the interfacial free energy between nuclei and solution, consequently inhibiting the growth of particles. Thus, a much more rapid nucleation followed with a slower grain growth leads to smaller particle sizes with high specific surface area in the process [37,38]. The increased surface area due to small particle size added benefit for its reactivity. This factor is responsible for the upward accessibility of the substrate molecules on the catalyst surface.

Table 2
Optimization of the model reaction using various solvents.

Entry	Solvent	Time (min)	Yield[a] (%)
1	CH_3CN	80	72
2	Toluene	80	70
3	H_2O	50	91
4	EtOH	60	85
5	$EtOH/H_2O$	60	87
6	Solvent-free	200	14

[a] Isolated yield.

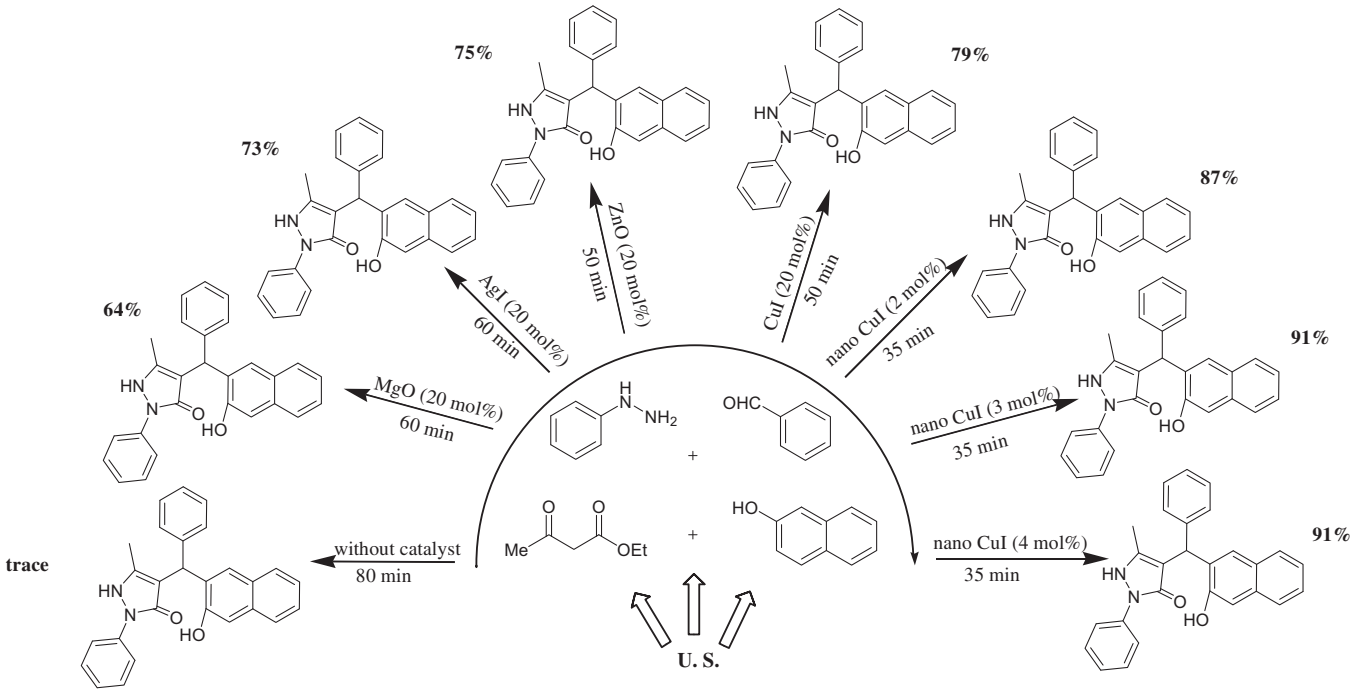
3.2. Catalytic behaviors of CuI nanoparticles

In order to consider the effects of this nano catalyst under ultrasound irradiation; catalytic behaviors of same types of catalyst such as MgO, ZnO, AgI, CuI were compared in the reaction of phenyl hydrazine, ethyl acetoacetate, β-naphthol and benzaldehyde

Table 1
Comparison of ultrasonic method with other methods.

Method	Ultrasonic[a]	Pulse laser deposition	Surface-Etching	Hydrothermal	Coprecipitation
Particle size	20–40 nm	about 1 μm	about 500 nm	70–110 nm	300–600 nm

[a] Reaction condition: reaction of $CuSO_4$ and KI at room temperature under ultrasonic irradiation.

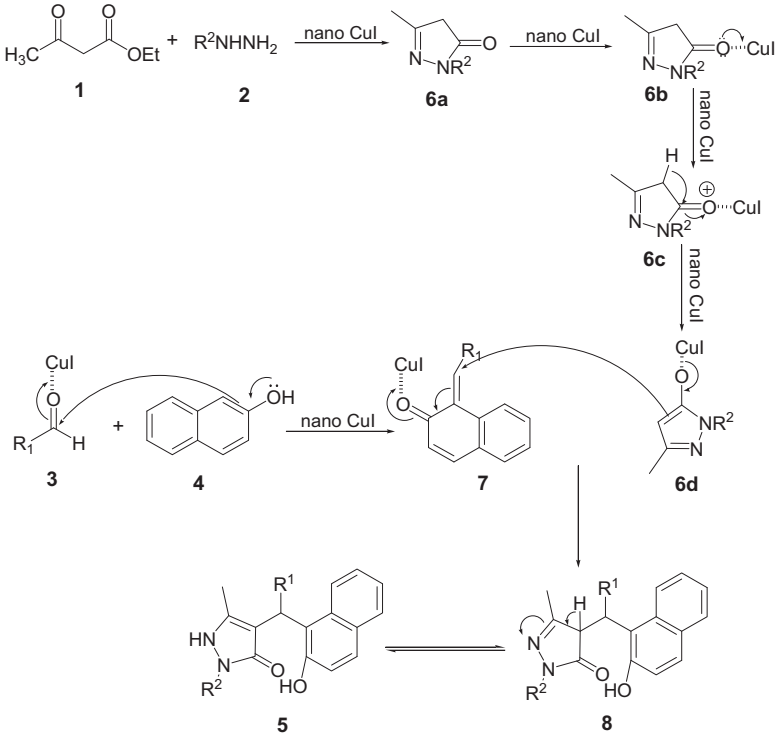


Scheme 2. Optimization of the model reaction using various catalysts under ultrasonic irradiation.

Table 3
Synthesis of pyrazolone derivatives under reflux conditions and sonication (method A and B).

Entry	R_1	R_2	Product	Method A[a]		Method B[b]		M.P. (°C)	
				Time (min)	Yield[c] (%)	Time (min)	Yield[c] (%)	Found	Reported
1	H	H	5a	360	72	35	91	205–206	205 [32]
2	4-Cl	H	5b	330	73	30	93	176–177	176 [32]
3	4-NO_2	H	5c	330	74	30	93	209–210	207 [32]
4	4-Me	H	5d	420	69	40	88	180–181	179 [32]
5	2-Me	H	5e	420	67	45	86	141–142	–
6	2-Cl	H	5f	360	71	35	90	133–134	–
7	4-Br	H	5g	360	73	35	92	179–180	–
8	2-NO_2	H	5h	360	72	35	91	156–157	157 [32]
9	4-OMe	H	5i	390	70	40	89	184–185	184 [32]
10	H	4-Cl	5j	330	71	40	92	161–162	–
11	4-Cl	4-Cl	5k	330	70	40	91	153–154	153 [32]
12	4-NO_2	4-Cl	5l	360	70	40	92	183–184	–
13	2-Cl	4-Cl	5m	390	71	40	90	122–123	–
14	4-Me	4-Cl	5n	420	68	45	87	173–174	–
15	4-Br	4-Cl	5o	330	70	40	92	157–158	–

[a] Reaction condition: reaction of hydrazine, ethylacetoacetate, β-naphthol and aldehyde in water at reflux.
[b] Reaction condition: reaction of hydrazine, ethyl acetoacetate, β-naphthol and aldehyde at room temperature under ultrasonic irradiation.
[c] Isolated yields.



Scheme 3. Possible mechanism for the formation of pyrazolones in the presence of CuI nanoparticles.

(Scheme 2). Obtain results were indicated that in absence of catalyst, trace amount of product was generated but in presence of CuI nanoparticles the reaction proceeds in high yield. Also the resulting of Scheme 2 shows the optimum amount of the catalyst was (3 mol%) of CuI nanoparticles which increasing of this amount did not show any significant change in yield and time of reaction.

Expectedly, the catalytic system should be influenced by various reaction factors, such as solvent system. To establish the optimal reaction conditions, we have screened the effect of different solvents with varying polarity and protic nature. It was observed that water proved to be the best choice for this reaction over any solvents such as toluene, acetonitrile and ethanol. Also the considerable results were not observed in solvent free conditions (Table 2).

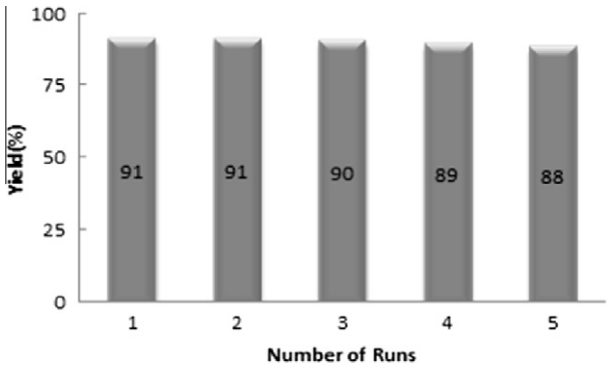


Fig. 5. Reusability study of nano CuI for model reaction.

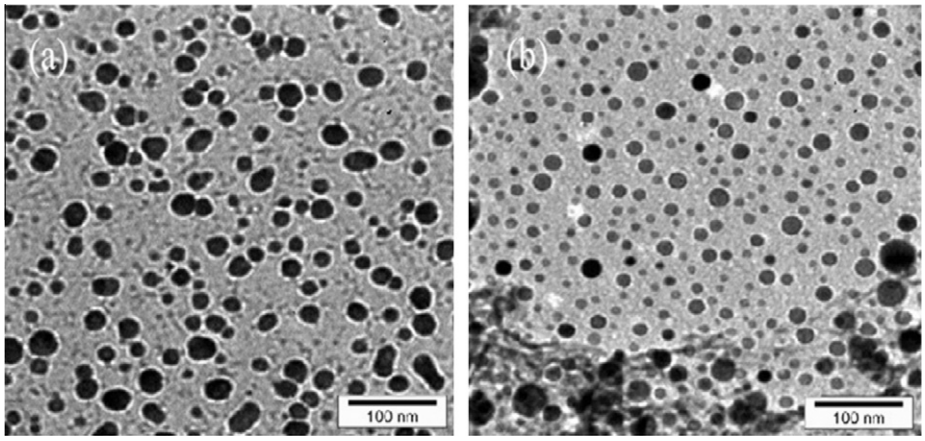


Fig. 6. TEM images of nano CuI before use (a) and after five times reuse (b).

The study was extended to prepare various 2-aryl-5-methyl-2,3-dihydro-1H-3-pyrazolones using CuI nanoparticles. For explain the efficiency and scope of the present process and to delineate the role of ultrasound, reactions were compared at reflux conditions (method A) and ultrasonic irradiation (method B) in water in the presence of nano copper iodide 3 mol% (Table 3). When the reaction was carried out under reflux conditions it gave comparatively low yields of products and took longer reaction times, while the same reaction was carried under ultrasonic irradiation gave excellent yields of products in short reaction times. Also, compared with conventional approach [39], this method is more environmentally friendly, particularly when considering the basic green chemistry concepts.

The reason may be the phenomenon of cavitation formed by ultrasound. Cavitation is the origin of sonochemistry, a physical process that builds, enlarges, and collapses gaseous and vaporous cavities in an irradiated liquid, hence enhancing the mass transfer and allowing chemical reactions to occur. Applying ultrasound, compression of the liquid is followed by rarefaction, in which a sudden pressure drop forms small, oscillating bubbles of gaseous substances. These bubbles are small and rapidly collapse, they can be seen as microreactors that offer the opportunity of speeding up certain reactions and also allow mechanistically novel reactions to take place in an absolutely safe manner [40–42].

A proposed mechanism for this four-component reaction was outlined in Scheme 3. The first step of this reaction can be visualized by activation of ethyl acetoacetate **1** with nano CuI, following by nucleophilic attack of hydrazine **2** to give **6a**. On the other hand, nano CuI allowing compound **6a** was adsorbed on its surface to provide **6d**. In another reaction, β-naphthol **4** undergoes condensation with aldehyde **3** in presence of nano CuI to afford α, β-unsaturated carbonyl compound **7**. Michael addition reaction between compounds **7** and **6d** gives intermediate **8** following by tautomerization to afford products **5**. The reaction mechanism involves a polar transition state starting from a neutral ground state, that under ultrasonic irradiation ionic reactions are accelerated by physical effects. Typically, in a heterogeneous solid/liquid system, the collapse of the cavitation bubble results in significant structural and mechanical defects. Collapse near the surface produces an asymmetrical inrush of the fluid to fill the void forming a liquid jet targeted at the surface. This effect is equal to high-pressure/high-velocity liquid jets. These jets activate the nano catalyst and increase the mass transfer to the surface by the disruption of the interfacial boundary layers as well as dislodging the material occupying the inactive positions. Collapse on the surface, produces an adequate amount of energy to cause fragmentation. Thus, in this situation, ultrasound can increase the surface area for a reaction and supply additional activation through efficient mixing and enhanced mass transport [43–46]. Furthermore, ultrasound irradiation activates the reaction mixture by inducing high local pressure and temperature generated inside the cavitation bubble and its interfaces when it collapses and accelerates the reaction rate and shortens the reaction time [41]. Therefore, it is reasonable to assume that these effects should accelerate this four-component reaction.

Consequently,the same reaction was carried out many times to check the reusability of catalyst. The catalyst could be reused for five times with a minimal loss of activity (Fig. 5).

The characterization of the nano CuI before use and after five times reuse showed the same particle size by TEM (Fig. 6). Interestingly, the shape and size of the nanoparticles remained unchanged before and after reaction. We believe that, this isalso the possible reason for the extreme stability of the CuI nanoparticles presented herein.

4. Conclusions

To summary, we offer an efficient method to prepare copper iodide in nano scale via sonication and report this nanoparticles as a highly efficient catalyst for the synthesis of 2-aryl-5-methyl-2,3-dihydro-1H-3-pyrazolones by means of a multi-component condensation of hydrazine, ethyl acetoacetate, aldehyde and β-naphthol in water under ultrasound irradiation. This method is applicable to a wide range of substrates, including aromatic aldehydes, and hydrazines to provide the corresponding pyrazolones in good to excellent yields. The present method indicates some advantages of sonication such as using green procedure, reducing reaction times, high yields, operational simplicity, and assist to prepare the lowest size and highest surface of CuI nanoparticles as catalyst.

Acknowledgement

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