Ultrasonics Sonochemistry 20 (2013) 1069–1075

Contents lists available at SciVerse ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

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

ARTICLE INFO

Article history:
Received 4 November 2012
Received in revised form 14 January 2013
Accepted 17 January 2013
Available online 26 January 2013

Keywords:
Ultrasonic irradiation
CuI nanoparticles
Pyrazolones
Four-component reactions
Green chemistry

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).

1350-4177/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ultsonch.2013.01.005

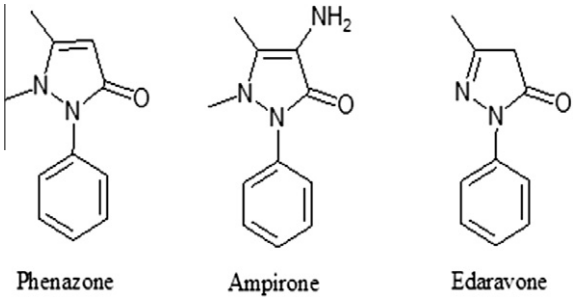


Fig. 1. Examples of drugs contain pyrazolone skeleton.

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.

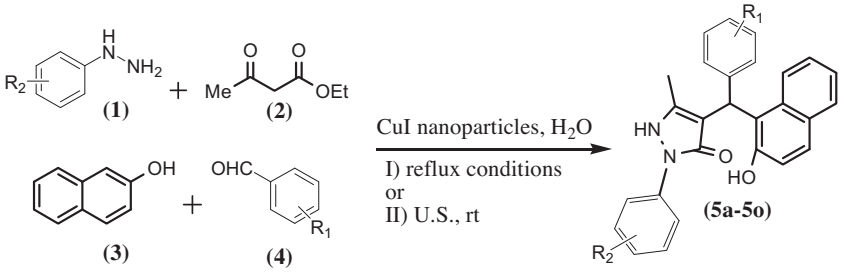
2.4. Representative spectral data

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.