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New pyrazolone derivatives synthesis: Comparison of the catalytic effect of three typically different Brønsted acid catalysts on the reaction progression

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Abstract

Via the one-pot condensation reaction of ethyl acetoacetate, aromatic aldehydes, 2,4-dinitrophenylhydrazine, and *β*-naphthol, new pyrazolone derivatives were synthesized in the presence of three Brønsted acid catalysts. These Brønsted acid catalysts are silica sulfuric acid (SSA), tetra-n-butyl ammonium hydrogen sulfate ($TBAHSO_4$) and [2,2′-Bipyridine]-1,1′-diium tricyanomethanide {$[2,2'\text{-BPyH}][C(CN)_3]_2$}. Each of the combinations has its own characteristics. SSA is a heterogeneous catalyst. $TBAHSO_4$ is a phase transfer catalyst and {$[2,2'\text{-BPyH}][C(CN)_3]_2$} is an ionic liquid. We compared the obtained results of the catalysts. In most cases, the results were comparable. But, sometimes $TBAHSO_4$ and {$[2,2'\text{-BPyH}][C(CN)_3]_2$} give the better results to the SSA in terms of reaction time and yields. Even though, isolation of SSA from products was easier than the separation of two other catalysts.

Keywords: Pyrazolone; silica sulfuric acid; tetra-n-butyl ammonium hydrogen sulfate; [2,2′-bipyridine]-1,1′-diium tri-cyanomethanide; solvent-free condition.

Introduction

The multicomponent reactions (MCRs) are the interesting methods that have high importance in the synthesis of various organic substances [1]. MCRs can reduce the number of synthetic steps and then provide easy and rapid access to form the target molecules [2]. Also, these techniques are the highly valuable routs for the drug synthesis such as functional chromophores, pharmaceutical compounds and marine alkaloids derivatives [3].

Among the various nitrogen-containing heterocyclic substances, pyrazolone derivatives are important molecular frameworks that widely occur in pharmaceutical agents and natural products [4]. Since the introduction of the first pyrazolone derivatives- as antipyrine- to relieve pain, fever, and inflammation in 1884, great attention has been focused on antipyrine and pyrazole derivatives as the powerful analgesic, anti-inflammatory, and antipyretic agents.

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As a result of such investigations, a large number of pyrazoles derivatives has been synthesized and applied on the clinical level. After that, many pyrazolone compounds have been prepared and introduced to the bazaar [5], for example, metamizole which is primarily used for perioperative pain, acute injury, colic, cancer pain, other acute/chronic forms of pain and high fever unresponsive to other drugs. Like paracetamol, it has minimal anti-inflammatory effects [6]. Phenazone – also known as phenazon – is an analgesic, nonsteroidal and anti-inflammatory drug and also an antipyreticone [7]. Moreover, propyphenazone is used for the treatment, control, prevention, and improvement of pain and fever [8]. Edaravone is a free radical scavenger for the treatment of amyotrophic lateral sclerosis (ALS) [9] and cardiovascular diseases [10]. Telin, [4,4-dichloro-1-(2,4-dichlorophenyl)-3-methyl-1H-pyrazole-5(4H)-one] acts as an anti-cancer agent *via* catalytic blocking of telomerase [11]. ARONIS023059-[2-Phenyl-5-(trifluoromethyl)-4H-pyrazol-3-one] was tested in the bioassay antiprion activity in F3 and AcN2a cellar lines evaluated as inhibition of protease-resistant prion protein accumulation [5].

There are many reagents such as CuInanoparticles [12], sodium dodecyl sulfate [13], and PEG-SO_3H[14] which have been catalyzed during the synthesis of pyrazolone derivatives.

Due to the pharmacological importance of pyrazolones, the synthesis of new pyrazolone derivatives is gaining attention.

Experimental

General

Chemicals including tetra-*n*-butyl ammonium hydrogen sulfate ($TBAHSO_4$) were purchased from Merck or Sigma-AldrichChemical Companies. Silica sulfuric acid (SSA) and [2,2′-Bipyridine]-1,1′-diium tricyanomethanide {[2,2′-BPyH][$C(CN)_3]_2$}were synthesized according to our previously reported papers[15,16].The products were characterized by their spectral (IR,^{1}H-NMR, and^{13}C-NMR) data. The ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) were runonaBrukerAvanceDPX-400FT-NMR spectrometer (δ in ppm). IR spectra were recorded on a Perkin Elmer Spectrometer (in cm^{-1}).

General procedure for the synthesis of 2-(2,4-dinitrophenyl)-4-((1-hydroxynaphthalen-2-yl)(Aryl)methyl)-5-methyl-1*H*-pyrazol-3(2*H*)-one derivatives

To a mixture of aromatic aldehyde (1 mmol), ethyl acetoacetate (0.130 g, 1 mmol), 2,4-dinitrophenylhydrazine (0.108 g, 1 mmol), and *β*-naphthol (0.144 g, 1 mmol) in a round-bottom flask equipped to a condenser, 1 mol% of Brønsted acid catalyst (SSA, $TBAHSO_4$ or {[2,2′-BPyH][$C(CN)_3]_2$}) was added, and the resulting mixture was magnetically stirred under solvent-free conditions at room temperature for the appropriated time (Table 3). The progress of the reaction was monitored by TLC (*n*-hexane–EtOAc = 5:2). At the end of the reaction, EtOAc (10 mL) was added and refluxed for 5 min, and the work-up was made in two ways; for $TBAHSO_4$ or {[2,2′-BPyH][$C(CN)_3]_2$}: the reaction mixture was washed with water (10 mL) and decanted in order to separate the catalyst from the product (the reaction product was soluble in the hot EtOAc while the catalyst was soluble in water). For SSA: the reaction mixture was filtered. In both cases, the organic layer was evaporated, and the crude product was purified by recrystallization from EtOH.

1-(2,4-Dinitrophenyl)-4-((2-hydroxynaphthalen-1-yl)(3-nitrophenyl)methyl)-5-methyl-1H-pyrazol-3(2H)-one(**2A**)
Chamomile color solid; m.p. 295-297ºC
IR (KBr): υ 3282, 3093, 1615, 1587, 1510, 1330 cm^{-1}.
^{1}H-NMR (400 MHz, DMSO-*d6*): δppm 11.88 (s, 1H), 8.96 (d, 1H), 8.91 (s, 2H), 8.53 (s, 2H), 8.40 (q, 2H), 8.38 (d, 2H), 8.34 (d, 2H), 7.88 (t, 2H), 3.42 (s, 3H).
^{13}C-NMR (100 MHz, DMSO-*d6*): δppm 148.34, 146.83, 135.6, 134.87, 133.37, 130.6, 129.84, 128.53, 124.61, 124.05, 122.89, 121.23, 116.9, 95.71.

1-(2,4-Dinitrophenyl)-4-((2-hydroxynaphthalen-1-yl)(4-nitrophenyl)methyl)-5-methyl-1H-pyrazol-3(2H)-one(**2A**)
Chamomile color solid; m.p. 300-302ºC
IR (KBr): υ 3279, 3091, 1615, 1593, 1575, 1509, 1329, 1137cm^{-1}.
^{1}H-NMR (400 MHz, DMSO-*d6*): δppm 11.93 (s, 1H), 8.96 (s, 1H), 8.89 (s, 2H), 8.52 (d, 2H), 8.49 (d, 4H), 8.42 (d, 2H), 8.26 (d, 4H), 3.41 (s, 3H).
^{13}C-NMR (100 MHz, DMSO-*d6*): δppm 147.96, 146.53, 144.19, 140.07, 132.8, 130.3, 129.7, 128.16, 124.16, 122.85, 120.99, 116.98, 116.13, 108.52.

4-((2-Chlorophenyl)(2-hydroxynaphthalen-1-yl)methyl)-1-(2,4-dinitrophenyl)-5-methyl-1H-pyrazol-3(2H)-one(**3A**)
Bright orange solid; m.p. 200-202 ºC
IR (KBr): υ 3286, 3090, 1616, 1581, 1508, 1334 cm^{-1}.
^{1}H-NMR (400 MHz, DMSO-*d6*): δppm 12.8 (s, 1H), 9.24-8.99 (d, 3H), 8.51-8.26 (d, 6H), 7.61-7.60 (b, 6H), 3.38 (s, 3H).
^{13}C-NMR (100 MHz, DMSO-*d6*): δppm 157.21, 156.95, 146.18, 154.06, 137.39, 137.0, 136.94, 131.77, 130.09, 129.67, 127.62, 127.22, 122.86, 117.01.

4-((4-Chlorophenyl)(2-hydroxynaphthalen-1-yl)methyl)-1-(2,4-dinitrophenyl)-5-methyl-1H-pyrazol-3(2H)-one (**4A**)
Orange solid; m.p. 273-274 ºC
IR (KBr): υ 3285, 3091, 1613, 1584, 1326, 1137, 1083 cm^{-1}.
^{1}H-NMR (400 MHz, DMSO-*d6*): δppm 11.756 (s, 1H), 8.91 (s, 1H), 8.76 (s, 2H), 8.45 (d, 2H), 8.42(d, 2H), 7.89 (d, 4H), 7.63(d, 4H), 3.38 (s, 3H).
^{13}C-NMR (100 MHz, DMSO-*d6*): δppm148, 144.38, 137.21, 134.97, 133.73, 132.74, 129.75, 129.65, 129.07, 128.94, 122.94, 116.8.

1-(2,4-Dinitrophenyl)-4-((2-hydroxynaphthalen-1-yl)(p-tolyl)methyl)-5-methyl-1H-pyrazol-3(2H)-one(**5A**)
Bright orange solid; m.p. 237-239 ºC
IR (KBr): υ 3453, 3285, 3089, 1613, 1584, 1518, 1326, 1134, 1079 cm^{-1}.
^{1}H-NMR (400 MHz, DMSO-*d6*): δppm 11.62 (s, 1H), 8.87 (s, 1H), 8.68 (s, 2H), 8.40 (q, 2H), 8.11 (d, 2H), 7.71 (d, 4H), 7.32 (d, 4H), 3.38 (s, 3H), 2.56 (s, 3H).
^{13}C-NMR (100 MHz, DMSO-*d6*): δppm 149.4, 144.4,140.5,136.8,131.0,129.6,129.5,129.2,127.3,122.9,116.69,21.07.

1-(2,4-Dinitrophenyl)-4-((2-hydroxynaphthalen-1-yl)(2-hydroxyphenyl)methyl)-5-methyl-1H-pyrazol-3(2H)-one(**6A**)
Red solid; m.p. 254-256 ºC
IR (KBr): υ 3269, 3101, 1618, 1588, 1513, 1419, 1315, 1135cm^{-1}.
^{1}H-NMR (400 MHz, DMSO-*d6*): δppm 11.79 (s, 1H), 10.27 (s, 1H), 9.03 (d, 3H), 8.44 (s, 1H), 8.12-7.92 (d, 3H), 7.92 (s, 1H), 7.0 (s, 4H), 3.41 (s, 3H).
^{13}C-NMR (100 MHz, DMSO-*d6*): δppm 160.0, 156.8, 146.4, 144.4, 144.3, 136.7, 131.9, 129.7, 129.2, 126.4, 123.0, 120.0, 119.4, 116.6, 116.2.

1-(2,4-Dinitrophenyl)-4-((2-hydroxynaphthalen-1-yl)(3-hydroxyphenyl)methyl)-5-methyl-1H-pyrazol-3(2H)-one(**7A**)
Red solid; m.p. 264-265 ºC
IR (KBr): υ 3480, 3289, 3113, 1615, 1588, 1512, 1328 cm^{-1}.
^{1}H-NMR (400 MHz, DMSO-*d6*): δppm 11.61 (s, 1H), 9.68 (s, 2H), 8.84 (s, 1H), 8.60 (s, 1H), 8.39 (d, 2H), 8.03 (d, 2H), 7.26 (t, 3H), 7.18 (m, 2H), 6.88 (d, 2H), 3.35 (s, 3H).
^{13}C-NMR (100 MHz, DMSO-*d6*): δppm 157.7, 149.6, 144.4, 136.9, 134.9, 129.9, 129.7, 129.3, 122.9, 118.7, 117.8, 116.5, 113.18, 113.

1-(2,4-Dinitrophenyl)-4-((2-hydroxynaphthalen-1-yl)(4-hydroxyphenyl)methyl)-5-methyl-1H-pyrazol-3(2H)-one(**8A**)
Dark red solid; m.p. 286-288 ºC
IR (KBr): υ 3464, 3272, 3110, 2926, 1737.8, 1587.7, 1513, 1331.6 cm^{-1}.
^{1}H-NMR (400 MHz, DMSO-*d6*): δppm 11.59 (s, 1H), 10.12 (s, 1H), 8.88 (s, 1H), 8.62 (s, 2H), 8.39 (d, 2H), 8.08 (d, 2H), 7.68 (d, 4H), 6.92 (d, 4H), 3.40 (s, 3H).
^{13}C-NMR (100 MHz, DMSO-*d6*): δppm 170.3, 159.97, 149.94, 144.4, 136.4, 129.26, 128.8, 124.68, 123.04, 116.56, 115.02.

1-(2,4-Dinitrophenyl)-4-((2-hydroxy-3-methoxyphenyl)(2-hydroxynaphthalen-1-yl)methyl)-5-methyl-1H-pyrazol-3(2H)-one(**9A**)
Yellow solid; m.p. 247-249 ºC
IR (KBr): υ 3430, 3297, 3124, 2937, 1621, 1610, 1591, 1521, 1326 cm^{-1}.
^{1}H-NMR (400 MHz, DMSO-*d6*): δppm 11.73 (s, 1H), 9.51 (s, 2H), 9.01 (s, 2H), 8.87 (s, 1H), 8.38 (d, 2H), 8.05 (d, 2H), 7.46 (s, 2H), 7.06 (s, 2H), 6.87 (s, 2H), 3.85 (s, 3H), 3.33 (s, 3H).

1-(2,4-Dinitrophenyl)-4-((3-ethoxy-4-hydroxyphenyl)(2-hydroxynaphthalen-1-yl)methyl)-5-methyl-1H-pyrazol-3(2H)-one(**10A**)
Red solid; m.p. 247-248 ºC
IR (KBr): υ 3424, 3287, 3115, 2943, 1611, 1588, 1514, 1277 cm^{-1}.
^{1}H-NMR (400 MHz, DMSO-*d6*): δppm 11.62 (s, 1H), 9.69 (s, 2H), 8.91 (s, 1H), 8.61 (s, 2H), 8.41 (d, 2H), 8.13 (d, 2H), 7.42 (s, 2H), 7.23 (d, 2H), 6.98 (d, 2H), 4.21 (q, 2H), 3.42 (s, 3H),1.48 (t, 3H).
^{13}C-NMR (100 MHz, DMSO-*d6*): δppm 150.1, 149.8, 147.2, 144.3, 136.4, 129.6, 128.8, 125.0, 123.0, 122.5, 116.6, 115.6, 110.8, 63.9, 14.6.

1-(2,4-Dinitrophenyl)-4-((2-hydroxynaphthalen-1-yl)(pyridin-3-yl)methyl)-5-methyl-1H-pyrazol-3(2H)-one(**11A**)
Chamomile color solid m.p. 252-254 ºC
IR (KBr): υ 3440, 3297, 3095, 1619, 1583, 1514, 1325, 1084 cm^{-1}.
^{1}H-NMR (400 MHz, DMSO-*d6*): δppm 11.86 (s, 1H), 9.03 (s, 2H), 8.96 (s, 2H), 8.84 (s, 2H), 8.73 (d, 2H), 8.48-8.45 (q, 2H), 8.32 (d, 2H), 8.26 (d, 2H), 7.60 (m, 3H), 3.41 (s, 3H).
^{13}C-NMR (100 MHz, DMSO-*d6*): δppm 150.93, 148.8, 146.4, 144.3, 137.3, 133.8, 130.1, 129.8, 129.7, 129.2, 124.0, 122.8, 118.2, 116.9, 116.7, 110.7.

1-(2,4-Dinitrophenyl)-4-((2-hydroxynaphthalen-1-yl)(thiophen-2-yl)methyl)-5-methyl-1H-pyrazol-3(2H)-one(**12A**)
Red solid; m.p. 237-238 ºC
IR (KBr): υ 3446, 3287, 3088, 1613, 1515, 1421, 1318, 1141cm^{-1}.
^{1}H-NMR (400 MHz, DMSO-*d6*): δppm 11.76 (s, 1H), 9.00 (s, 2H), 8.94 (s, 1H), 8.51-8.48 (d, 2H), 8.00-7.98 (d, 2H), 7.84-7.83 (d, 2H), 7.59 (d, 2H), 7.28-7.26 (q, 3H), 3.41 (s, 3H).
^{13}C-NMR (100 MHz, DMSO-*d6*): δppm 144.4, 144.1, 138.39, 138.3,

136.8, 136.0, 131.7, 129.9, 129.8, 129.4, 128.2, 123.0, 116.3.

1-(2,4-Dinitrophenyl)-4-(furan-2-yl(2-hydroxynaphthalen-1-yl)methyl)-5-methyl-1H-pyrazol-3(2H)-one(**13A**)
Dark red solid; m.p. 222-225 ºC
IR (KBr): υ 3443, 3278, 3118, 1616, 1531, 1508, 1415, 1301 cm^{-1}.
^{1}H-NMR (400 MHz, DMSO-*d6*): δppm 11.73 (s, 1H), 8.91 (s, 1H), 8.69 (s, 2H), 8.46 (d, 2H), 8.00 (t, 4H), 7.07 (s, 2H), 6.76(s, 3H), 3.40 (s, 3H).
^{13}C-NMR (100 MHz, DMSO-*d6*): δppm 148.9, 146.4, 145.8, 144.2, 138.8, 136.9, 131.7, 130.0, 129.8, 129.3, 122.9, 122.7, 117.9, 116.5, 116.0, 114.9, 112.7, 112.4.

4-((4-(Dimethylamino)phenyl)(2-hydroxynaphthalen-1-yl)methyl)-1-(2,4-dinitrophenyl)-5-methyl-1H-pyrazol-3(2H)-one(**14A**)
Black solid; m.p. 246-247 ºC
IR (KBr): υ 3443, 3275, 3090, 2805, 1602, 1511, 1325 cm^{-1}.
^{1}H-NMR (400 MHz, DMSO-*d6*): δppm 11.61 (s, 1H), 8.94 (d, 1H), 8.62 (s, 2H), 8.42 (q, 2H), 8.12 (d, 2H), 7.685(d, 4H), 6.85(d, 4H), 3.41 (s, 3H), 3.09 (s, 6H).
^{13}C-NMR (100 MHz, DMSO-*d6*): δppm 151.8, 150.6, 144.2, 136.1, 129.6, 128.9, 128.5, 123.19, 120.7, 116.5, 111.7, 98.0, 21.07.

4-((2,4-Dichlorophenyl)(2-hydroxynaphthalen-1-yl)methyl)-1-(2,4-dinitrophenyl)-5-methyl-1H-pyrazol-3(2H)-one(**15A**)
Chamomile color solid; m.p. 225-227 ºC
IR (KBr): υ 3523, 3280, 3101, 2923, 1614, 1587, 1517, 1499, 1326, 1092 cm^{-1}.
^{1}H-NMR (400 MHz, DMSO-*d6*): δppm 12.03 (s, 1H), 9.068 (s, 2H), 8.89 (d, 1H), 8.41 (m, 3H), 8.18 (q, 5H), 7.78 (s, 1H), 7.60 (q, 3H), 3.51 (s, 3H).
^{13}C-NMR (100 MHz, DMSO-*d6*): δppm144.54, 143.8, 137.1, 135.0, 134.0, 130.4, 129.4, 129.3, 128.2, 127.8, 123.4, 122.7, 118.1, 116.9, 116.6, 115.5, 110.76.

1-(2,4-Dinitrophenyl)-4-((2-hydroxynaphthalen-1-yl)(naphthalen-2-yl)methyl)-5-methyl-1H-pyrazol-3(2H)-one(16A)
Yellow solid; m.p. 263-264 ºC
IR (KBr): υ 3423, 3293, 3107, 1614, 1589, 1517, 1304, 1138 cm^{-1}.
^{1}H-NMR (400 MHz, DMSO-*d6*): δppm 11.86 (s, 1H), 9.56 (s, 1H), 8.90 (s, 1H), 8.68 (s, 1H), 8.42 (d, 1H), 8.17-8.04 (m, 7H), 7.75-7.64 (m, 7H), 3.33 (s, 3H).

1-(2,4-Dinitrophenyl)-4-((2-hydroxynaphthalen-1-yl)(2-methoxyphenyl)methyl)-5-methyl-1H-pyrazol-3(2H)-one(**17A**)
Red orange solid; m.p. 246-248 ºC
IR (KBr): υ 3434, 3289, 3113, 1622, 1599, 1585, 1330, 1253, 1136 cm^{-1}.
^{1}H-NMR (400 MHz, DMSO-*d6*): δppm 9.068 (s, 2H), 8.92 (d, 1H), 8.37-8.09 (m, 3H), 8.15-8.09 (m, 4H), 7.59-7.57 (m, 3H), 7.27 (d, 3H), 7.19-7.15 (t, 3H), 4.018 (s, 3H).
^{13}C-NMR (100 MHz, DMSO-*d6*): δppm 157.92, 151.33,145.0,131.6,129.98,129.8, 127.5,125.7,123.2,122.8,122.7,122.3,120.7, 116.7,112.1,111.9, 55.7.

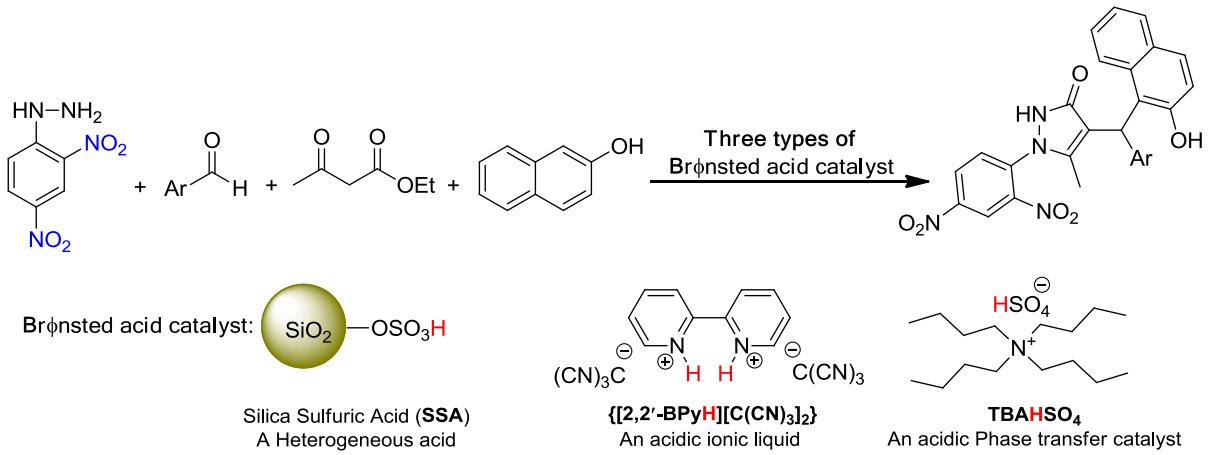
4-((3,4-Dimethoxyphenyl)(2-hydroxynaphthalen-1-yl)methyl)-1-(2,4-dinitrophenyl)-5-methyl-1H-pyrazol-3(2H)-one(**18A**)
pale yellow solid; m.p. 263-265 ºC
IR (KBr): υ 3450, 3281, 3113, 2923, 1611, 1515, 1319, 1139, 1017cm^{-1}.
^{1}H-NMR (400 MHz, DMSO-*d6*): δppm 11.69 (s, 1H), 8.95 (d, 1H), 8.70 (s, 2H), 8.46 (d, 2H), 8.21 (d, 2H)7.51 (s, 2H), 7.36 (d, 2H), 7.16 (d, 2H), 3.95 (s, 3H), 3.91 (s, 3H), 3.42 (s, 3H).

^{13}C-NMR (100 MHz, DMSO-*d6*): δppm151.2, 149.7, 149.1, 144.4, 136.6, 129.6, 129.1, 126.3, 123, 122.4, 116.7, 111.5, 108.5, 55.59, 55.53.

Results and discussion

In view of the above-mentioned facts, it was of interest to study the synthesis of some new pyrazolone derivatives *via* condensation of 2,4-dinitrophenylhydrazine (DNPH), aromatic aldehydes, ethyl acetoacetate, and *β*-naphthol in the presence of silica sulfuric acid (SSA), tetra-*n*-butyl ammonium hydrogen sulfate ($TBAHSO_4$) and [2,2′-Bipyridine]-1,1′-diium tricyanomethanide {[2,2′-BPyH][$C(CN)_3]_2$} as three Brønsted acid catalysts.

Previously, we have studied the synthesis of some heterocyclic compounds such as indolenines [17,18], quinoxalines [19], and also application of Brønsted acid catalysts [20,21] in organic transformations. Consequently, the purpose of this study was the synthesis of new pyrazolone derivatives containing the 2,4-dinitrophenyl group (**A**) (Scheme 1).



Scheme 1. Synthesis of the new 2,4-dinitrophenyl group containing pyrazolone derivatives

As we know, SSA is a heterogeneous catalyst [15], $TBAHSO_4$ is a phase transfer catalyst [22] and, recently, we reported {[2,2′-BPyH][$C(CN)_3]_2$} as an ionic liquid [16]. Both three catalysts are Brønsted acid. In this study, we report that these catalysts can promote the synthesis of new pyrazolone derivatives including the 2,4-dinitrophenyl group (**A**).

First, for optimizing the reaction conditions, control experiments were performed. As a model reaction, 2-Naphthaldehyde, ethyl acetoacetate, 2,4-dinitrophenylhydrazine, and *β*-naphthol were condensed in the presence of Brønsted acid catalyst (SSA, $TBAHSO_4$ or {[2,2′-BPyH][$C(CN)_3]_2$}) under solvent-free conditions at 25–100 °C (Table 1). As shown in Table 1, the best results were obtained when the reaction was carried out in the presence of 1 mol% of the catalyst at room temperature. In the absence of the catalyst, the reaction progress is sluggish.

Table 1. Condensation reaction of 2-Naphthaldehyde, ethyl acetoacetate, 2,4-dinitrophenylhydrazine, and *β*-naphthol (each one 1 mmol) with different amounts of catalysts

Catalyst	Mol% of catalyst	Temperature (°C)	Time (min)	Yield (%)
--	--	100	80	35
SSA	0.5	25	15	60
	0.5	100	15	78
	1	25	10	78
	1	100	10	83
	1.5	100	10	85
$TBAHSO_4$	0.5	25	10	81
	0.5	100	10	81
	1	25	7	91
	1	100	7	91
	1.5	100	7	91
{[2,2′-BPyH][$C(CN)_3]_2$}	0.5	25	7	88
	0.5	100	7	88
	1	25	5	93
	1	100	5	93
	1.5	100	5	91

Secondly, we applied a range of aromatic aldehydes in the condensation reaction with ethyl acetoacetate, 2,4-dinitrophenylhydrazine, and *β*-naphthol under the optimized reaction conditions to the synthesis of the new pyrazolone derivatives including the 2,4-dinitrophenyl group (**A**) (Table 2).

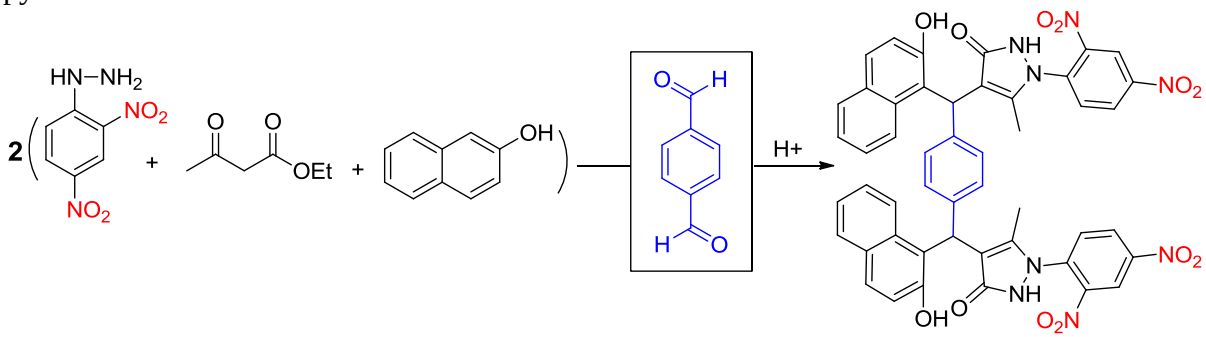
Table 2. Synthesis of the new pyrazolone derivatives includes the 2,4-dinitrophenyl group (**A**) *via* condensation of aldehyde, ethyl acetoacetate, 2,4-dinitrophenyl phenylhydrazine, and *β*-naphthol (each one 1 mmol) in the presence of1mol% of silica sulfuric acid (**1**), tetra-*n*-butyl ammonium hydrogen sulfate (**2**) or {[2,2′-BPyH][$C(CN)_3]_2$} (**3**) under solvent-free at room temperature

Entry	Aldehyde	Reaction time (min)			Isolated yield (%)		
		1	2	3	1	2	3
1	3-Nitrobenzaldehyde	10	7	5	80	86	88
2	4-Nitrobenzaldehyde	10	7	5	83	91	93
3	2-Chlorobenzaldehyde	10	7	5	83	90	93
4	4-Chlorobenzaldehyde	8	6	5	78	85	90
5	4-Methylbenzaldehyde	14	12	10	75	88	88
6	2-Hydroxybenzaldehyde	12	10	8	81	83	85
7	3-Hydroxybenzaldehyde	12	10	5	85	85	87
8	4-Hydroxybenzaldehyde	12	10	5	78	89	88
9	2-Hydroxy-3-	1	7	5	81	85	89

	methoxybenzaldehyde	0					
10	3-Ethoxy-4-hydroxybenzaldehyde	12	12	7	86	82	84
11	Nicotinaldehyde	20	20	15	87	85	95
12	Thiophene-2-carbaldehyde	20	15	10	90	84	89
13	Furan-2-carbaldehyde	20	15	12	78	82	82
14	4-(Dimethylamino)benzaldehyde	20	20	10	85	85	91
15	2,4-Dichlorobenzaldehyde	10	10	7	80	91	93
16	2-Naphthaldehyde	10	7	5	78	91	93
17	2-Methoxybenzaldehyde	15	12	10	82	83	88
18	3,4-Dimethoxybenzaldehyde	15	15	10	86	81	89

As shown in the Table 2, tetra-n-butyl ammonium hydrogen sulfate (2) or {[2,2′-BPyH][C(CN)$_3$]$_2$} has a slightly better performance than the two other catalysts, although the process of separating the product from acid is easier than the rest.

The synthesis of the bipodal pyrazolone *via* reaction between terphetahdehyde and two equivalents of other substrates in the presence of above-mentioned catalysts became of interest. Although we could synthesize a product, ^{1}H-NMR and ^{13}C-NMR could not confirm the structure of the product.



Scheme 2. Proposed route for the synthesis of the bipodal pyrazolone

Figure 1 shows ^{1}H-NMR spectrum of*4-((4-chlorophenyl)(2-hydroxynaphthalen-1-yl)methyl)-1-(2,4-dinitrophenyl)-5-methyl-1H-pyrazol-3(2H)-one* (**4A)** as a model compound. The peak at 3.38 corresponds to the methyl groups (-CH$_3$). Also, peak at 11.75ppm is related to the phenolic OH. This pattern is repeated in all the ^{1}H-NMR spectra. The sum of the calculated protons in the figure is equal to that in the formula. Data of ^{1}H-NMR spectra are confirmed by IR spectra i.e. the peaks at 3428, 3285, and 1613 are related to the OH, NH and carbonyl group. The NO$_2$ group's peak appeared in 1585 and 1516.

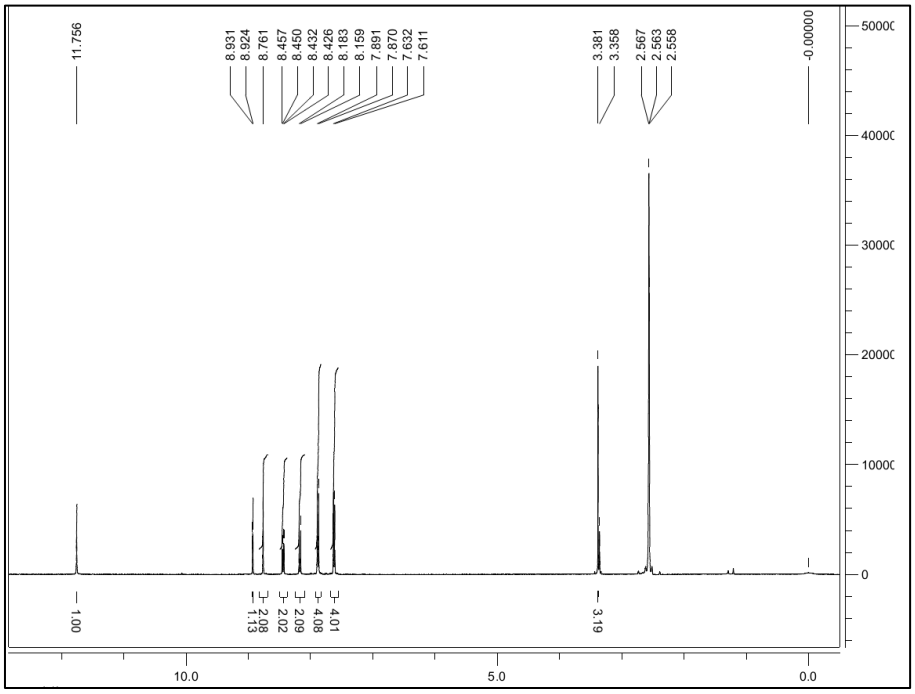
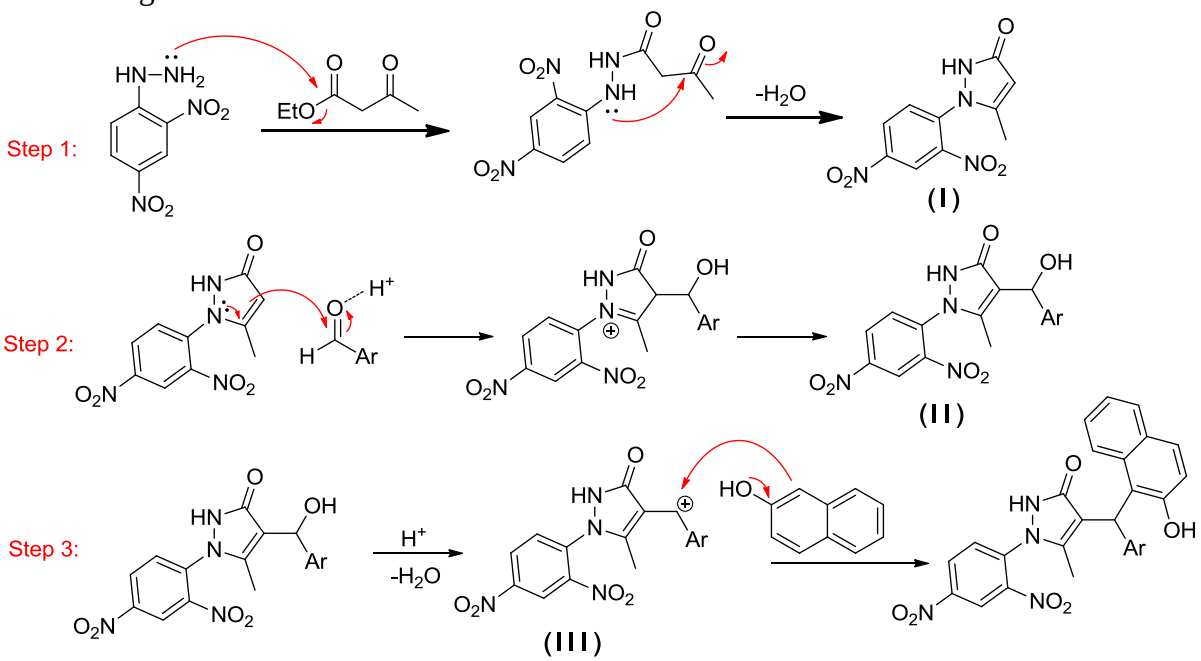


Figure 1. ^{1}H-NMR spectrum of *4-((4-chlorophenyl)(2-hydroxynaphthalen-1-yl)methyl)-1-(2,4-dinitrophenyl)-5-methyl-1H-pyrazol-3(2H)-one* (**4A**) as a model compound

Proposed mechanism

In a plausible mechanism, which is shown in Scheme 3, we suggest the pyrazolone (**I**) ring forms through the reaction of 2,4-dinitrophenylhydrazine and ethyl acetoacetate. Then, the pyrazolone ring attacks the activated aromatic aldehyde (aromatic aldehyde activates by the Brønsted acid catalyst) to form (**II**). In the presence of H^{+}, (**II**) converts to (**III**) by losing a molecule of H_2O. Finally, *β*-naphthol attacks (**III**) to form the target molecule.



Scheme 3. The proposed mechanism for the synthesis of the pyrazolone derivatives

Conclusion

In this work, we report the synthesis of the new pyrazolone derivatives *via* the one-pot condensation reaction of ethyl acetoacetate, aromatic aldehydes, 2,4-dinitrophenylhydrazine, and *β*-naphthol; in the presence of three Brønsted acid catalysts i.e. silica sulfuric acid (SSA), tetra-*n*-butyl ammonium hydrogen sulfate ($TBAHSO_4$) and [2,2′-Bipyridine]-1,1′-diium tricyanomethanide {[2,2′-BPyH][$C(CN)_3]_2$}. Products were obtained in reasonably good yields. They were characterized by ^{1}H-NMR, ^{13}C-NMR and IR studies. We compared the obtained results of these catalysts. In most cases, the results were comparable. But, sometimes$TBAHSO_4$ and {[2,2′-BPyH][$C(CN)_3]_2$} give the better results to the SSA in terms of the reaction time and yields. Even though, isolation of SSA from products was easier than the separation of two other catalysts.

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