

Iron Ore Pellet, A Natural and Reusable Catalyst for Synthesis of Pyrano[2,3-*d*]pyrimidine and Dihydropyrano[*c*]chromene Derivatives in Aqueous Media

Sheikhhosseini, Enayatollah*⁺

Department of Chemistry, Kerman Branch, Islamic Azad University, P.O. Box 76351-31167 Kerman, I.R. IRAN

Sattaei Mokhtari, Tayebeh

Department of Chemistry, Jiroft Branch, Islamic Azad University, P.O. Box 78617-36343 Jiroft, I.R. IRAN

Faryabi, Malihe; Rafiepour, Adeleh

Department of Chemistry, Kerman Branch, Islamic Azad University, P.O. Box 76351-31167 Kerman, I.R. IRAN

Soltaninejad, Shahla

Department of Biology, Jiroft Branch, Islamic Azad University, P.O. Box 78617-36343 Jiroft, I.R. IRAN

ABSTRACT: We wish to report a mild and efficient one-pot three component reaction of an aryl aldehyde, malononitrile and barbituric acid or 4-hydroxycoumarin for the synthesis of pyrano[2,3-*d*]pyrimidine and dihydropyrano[*c*]chromene derivatives in the presence of iron ore pellet as a natural and reusable catalyst under heterogeneous and green conditions. The present methodology offers several advantages such as excellent yields, simple procedure and work up steps, short reaction times and easy recovery of the catalyst. We have also demonstrated that the catalyst can be reused successfully after six times using the same catalyst with high yields. Use of water as the reaction medium makes the process environmentally benign.

KEY WORDS: Natural catalyst; Pyrano[2,3-*d*]pyrimidine; Dihydropyrano[*c*]chromene; Aqueous media; Heterogeneous catalyst.

INTRODUCTION

Recently, the development of environmentally benign and clean synthetic procedures has become the goal of organic synthesis. Water plays an essential role in life processes and also as a medium for organic reactions. The use of water as a reaction medium exhibits

a remarkable benefit because of its highly polarity and therefore immiscibility with the most organic compounds. Reactions in aqueous media are environmentally safe, have less carcinogenic effects with a simple work up and are especially important in industry. Thus, there is a need

* To whom correspondence should be addressed.

+ E-mail: sheikhhosseiny@gmail.com.

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for developing Multi-Component Reactions (MCR's) in water, without the use of any harmful organic solvents and catalysts [1, 2].

There is a continuous widespread interest in the synthesis of pyrano-pyrimidinones and coumarins because of the diverse biological properties associated with this system [3]. Some of these compounds show spasmolytic, diuretic, anticoagulant, antihypertensive and cardiotoxic, anti-cancer and antianaphylactic activities [4-6]. In addition, they are used as cognitive enhancers in treating neurodegenerative diseases such as Alzheimer's disease, amyotrophic lateral sclerosis, Parkinson's disease, Huntington's disease, AIDS associated dementia and Down's syndrome, schizophrenia and myoclonus [7-9].

The importance of pyrano[2,3-*d*]pyrimidine derivatives and 3,4-dihydropyrano[*c*]chromene have led many workers to synthesize them using methods including traditional thermal condition [9], electrocatalytic transformation [10], ultrasonic and microwave irradiation [11, 12]. Different catalysts such as *N*-methyl-morpholine [13], DABCO [14, 15], TEBA [16], proline and diammonium hydrogen phosphate (DAHP) [17-20], $H_{14}[NaP_3W_{30}O_{110}]$ [21], (SBA-Pr-SO₃H) [22, 23], TBAB [24], $[KAl(SO_4)_2]$ under heating [25], copper oxide nanoparticles [26], Sodium Dodecyl Sulfate (SDS) [27], Ac_2O/H_2SO_4 [28], trisodium citrate [29], selectflour [30], tetramethylguanidinium trifluoroacetate (TMGT) [31], grindstone chemistry [32], hexamethylenetetramine [33], Fe_2O_3 nanoparticles [34], silica gel [35], Ru(II) complexes [36] and DBSA [37] have been used for the synthesis of pyrano[2,3-*d*]pyrimidine and dihydropyrano[*c*] chromene derivatives.

Application of inorganic solid catalyst as an effective heterogeneous catalyst could receive considerable attention in organic synthesis owing to its unique physical and chemical properties in terms of shape, porous solids possessing acid and Lewis basic sites, selectivity and thermal stability [38, 39]. As part of our program for applying novel catalysts to multi-component reactions, herein we report an efficient one-pot three component synthesis pyrano [2, 3-*d*]pyrimidine and dihydropyrano[*c*]chromene derivatives catalyzed by iron ore pellet in aqueous media.

EXPERIMENTAL SECTION

General.

IR spectra were recorded on a Perkin-Elmer FT-IR 240-C spectrophotometer (KBr). ¹H NMR spectra

were recorded on a varian 400 MHz spectrometer. Melting points were determined using an Electrothermal 9100 and were uncorrected. The reactions were monitored by thin layer chromatography and the products were identified fully or by comparison of melting points and spectroscopic data with the previously reported ones.

General procedure for synthesis of pyrano[2,3-*d*]pyrimidine and dihydropyrano[*c*]chromens derivatives using iron ore pellet.

A mixture of malononitrile (2.2 mmol), substituted benzaldehydes (2 mmol), barbituric acid/4-hydroxycoumarin (2 mmol) and iron ore pellet (1 number) in water/ethanol or water (10 mL) was heated at reflux for 8-30 min in order to synthesize pyrano[2,3-*d*]pyrimidine and 26-40 min for dihydropyrano[*c*]chromens derivatives. Progress of the reaction was monitored by TLC. Upon completion of the reaction, the reaction mixture was allowed to cool down to room temperature. The solid was filtered off, washed with water and purified by recrystallization from ethanol. Spectral data of the selected compound is given below:

*7-Amino-2,3,4,5-tetrahydro-5-(3-nitrophenyl)-2,4-dioxo-1H-pyrano[2,3-*d*]pyrimidine-6-carbonitrile (4p)*.

M.p. = 269-270 °C. IR (KBr, cm⁻¹): 3417, 2857, 2193, 1712, 1662. ¹H NMR (400 MHz, DMSO-*d*₆) δ: 4.42 (s, 1H, CH), 7.30 (br s, 2H, NH₂), 7.01 (t, *J* = 7.6 Hz, 1H, H-Ar), 7.75 (t, *J* = 7.6 Hz, 1H, H-Ar), 8.06-8.11 (m, 2H, H-Ar), 11.10 (s, 1H, NH), 12.15 (s, 1H, NH). ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 35.4, 58.3, 88.3, 119.6, 122.8, 122.9, 130.6, 135.3, 147.2, 148.5, 150.4, 153.2, 158.9, 163.2 ppm.

*2-Amino-4,5-dihydro-4-(4-nitrophenyl)-5-oxopyrano[3,2-*c*]chromene-3-carbonitrile (6d)*

M.P. 258-260 °C. IR (KBr, cm⁻¹): 3365, 3176, 2187, 1706. ¹H NMR (400 MHz, DMSO-*d*₆) δ: 4.68 (s, 1H, CH), 7.48 (d, 1H, *J* = 8.4 Hz, H-Ar), 7.53 (d, 1H, *J* = 7.6 Hz, H-Ar), 7.58 (br s, 2H, NH₂), 7.60 (d, 2H, *J* = 8.4 Hz, H-Ar), 7.74 (td, 1H, *J* = 7.8, 1.2 Hz, H-Ar), 7.92 (dd, 1H, *J* = 8.0, 1.6 Hz, H-Ar), 8.18 (d, 1H, *J* = 8.4 Hz, H-Ar).

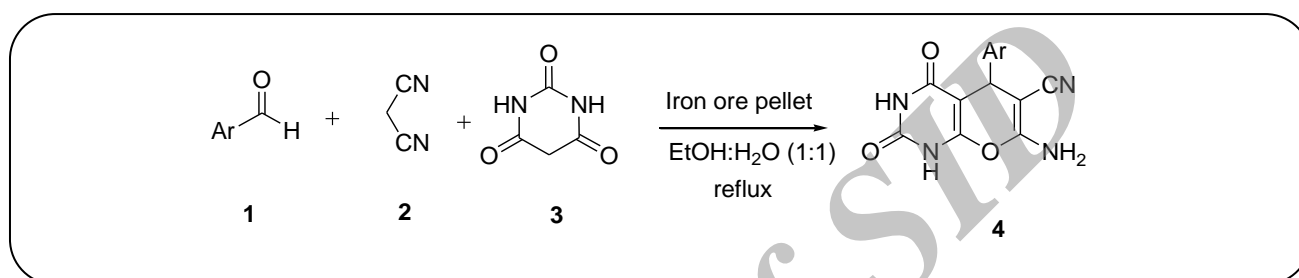
*2-Amino-4,5-dihydro -4- (3,4,5-trimethoxyphenyl)-5-oxopyrano[3,2-*c*]chromene-3-carbonitrile (6k)*

M.p. = 230-233 °C. IR (KBr, cm⁻¹): 3384, 3318, 2200, 1719. ¹H NMR (400 MHz, DMSO-*d*₆) δ: 3.64 (s, 3H, OMe),

Table 1: Reactions of 3-nitrobenzaldehyde, malonitrile and barbituric acid in the presence of iron ore pellet in different solvent

Entry	Solvent	Temperature	Time (min)	Yield(%) ^a
1	EtOH	reflux	88	21
2	MeOH	reflux	107	92
3	EtOH:H ₂ O (1:1)	reflux	8	92
4	MeOH:H ₂ O (1:1)	reflux	91	87
5	H ₂ O	r.t.	60	trace
6	H ₂ O	reflux	30	67

a) Isolated yield

**Scheme 1: Synthesis of pyrano-pyrimidinone derivatives in aqueous media.**

3.72 (s, 6H, 2OMe), 4.41 (s, 1H, CH), 6.53 (s, 2H, H-Ar), 7.38 (br s, 2H, NH₂), 7.46-7.51 (m, 2H, H-Ar), 7.72 (t, *J* = 7.6 Hz, 1H, H-Ar), 7.90 (d, *J* = 8.0 Hz, 1H, H-Ar). ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 37.2, 55.9, 57.8, 59.8, 103.8, 104.9, 113.1, 116.5, 119.2, 122.5, 124.6, 132.8, 138.6, 139.9, 152.2, 152.8, 153.5, 157.9, 159.6 ppm.

RESULTS AND DISCUSSION

The natural iron ore pellet catalyst that used in this work as it was described in reference [40] was obtained in the southern Sirjan region (Iran). To optimize the conditions, three component reaction of 3-nitrobenzaldehyde, malonitrile and barbituric acid in the presence of iron ore pellet as heterogeneous catalyst was selected as the model. It was found to be a good catalyst for preparation of pyrano-pyrimidinone derivatives (Scheme 1).

The attempts for evaluation of different solvents in preparing compound 4n in model reaction showed that carrying out the reaction in MeOH and H₂O as media had satisfactory results (Table 1, Entries 2, 6). However the best results were obtained with solvent system water/ethanol (1:1) (Table 1, Entry 3).

Afterward, a variety of aldehydes (Scheme 1) to check the viability of this protocol in obtaining a library

of pyrano-pyrimidinone derivatives were used (Table 2).

To extend scope of the iron ore pellet catalyzed multi-component reaction, 3, 4-dihydropyrano[*c*]chromene derivatives (**6a-k**) were successfully synthesized when using 4-hydroxy coumarin instead of barbituric acid in these MCRs under the optimal conditions (Scheme 2). The results are given in Table 3. The comparison of the solvent showed that water for this reaction was more suitable for dihydropyrano[*c*]chromene preparation.

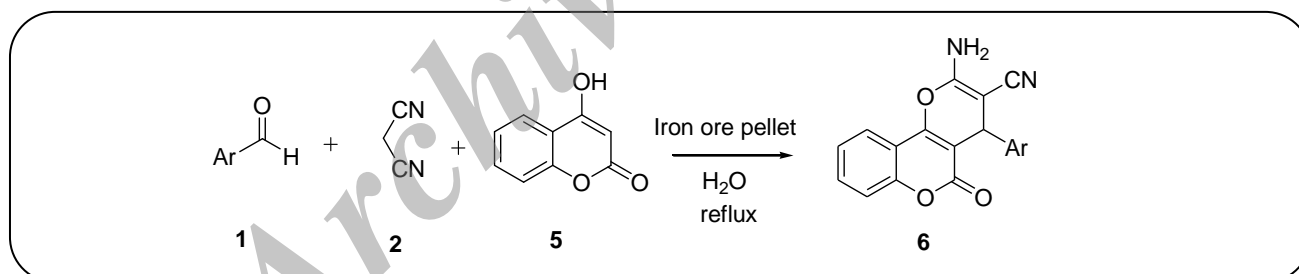
As can be seen in Tables 2 and 3, in all the cases, aromatic aldehydes substituted with either electron-donating or electron-withdrawing groups smoothly underwent the reaction and gave the products in high-excellent yields under the optimized reaction conditions. This natural solid catalyst becomes particularly interesting when it can be regenerated. In a typical experiment, after completion of the reaction, iron ore pellet was isolated by simple filtration, washed with water (10 mL) and DMSO (5 mL) three times, dried and successively used several times without the loss of activity. In fact, the reaction of benzaldehyde (Table 2, Entry 1) with malonitrile and barbituric acid has been repeated six times using the same catalyst with high yields (70-73%).

To show the efficiency of the selected method,

Table 2: Preparation of pyrano-pyrimidinone catalyzed by iore pellet at reflux in water/ethan.

Entry	Ar	Time/min	product	Yield/% ^a	M.P. (°C)	
					Found	Reported
1	C ₆ H ₅	8	4a	73	210-2012	206-209 [12]
2	2-OH-C ₆ H ₄	8	4b	91	169-170	162-163 [12]
3	4-N(Me) ₂ -C ₆ H ₄	8	4c	92	212-214	207-210 [12]
4	2-MeO-C ₆ H ₄	10	4d	93	198-201	172-175 [12]
5	4-MeO-C ₆ H ₄	10	4e	91	296-298	287-288 [13]
6	2,4-Cl-C ₆ H ₃	8	4f	91	239-240	241-242 [19]
7	3,4,5-(MeO) ₃ -C ₆ H ₂	13	4g	92	247-249	-----
8	4-NO ₂ -C ₆ H ₄	8	4h	89	230-234	239-240 [19]
9	4-Cl-C ₆ H ₄	11	4i	90	238-239	234-237 [13]
10	2,6-(Cl) ₂ -C ₆ H ₃	8	4j	85	235-241	226-227 [22]
11	3-Me-C ₆ H ₄	8	4k	89	228-229	224-225 [22]
12	2,4-(MeO) ₂ -C ₆ H ₃	8	4l	91	227-228	235-237
13	4-Br-C ₆ H ₄	30	4m	89	240-245	235-236 [22]
14	3-NO ₂ -C ₆ H ₄	8	4n	91	269-270	268-270 [19]

a) Isolated yield



Scheme 2: Synthesis of dihydropyrano[c]chromene derivatives in water.

Tables 4 and 5 compares the results obtained in the present study with some of those reported in the literature.

Although we have not yet established the mechanism of the one-pot reaction between benzaldehyde derivatives, malononitrile and barbitoric acid or 4-hydroxy coumarin in the presence of iron ore pellet, we estimate that the surface of the catalyst presents multicatalytic active sites. The basic sites polarize the C-H bond of the active methylene compound. The acidic

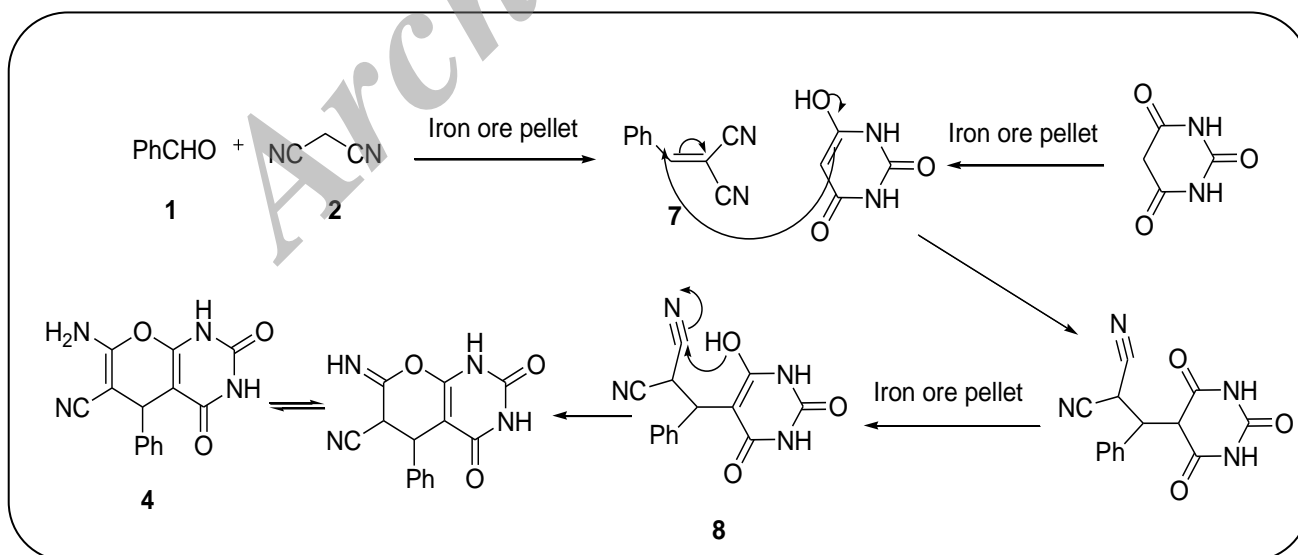
surface probably coordinates with the oxygen of the carbonyl carbon on which a partial positive charge appears. A possible explanation is presented in Scheme 2.

The higher reactivity of the iminium group is utilized to facilitate Knoevenagel condensation between aryl aldehyde 1 and malononitrile 2, which produce intermediate 7. Iron ore pellet also catalyzes the generation of a proposed enolicbarbituric acid and this intermediate adds to olefin 7 to generate 4, after proton transfer, tautomerization and hydrolysis of intermediate 8 (Scheme 3).

Table 3: Preparation of dihydropyranoc[*c*]chromene catalyzed by iore pellet at reflux in water.

Entry	Ar	Time/min	product	Yield/% ^a	M.P. (°C)	
					Found	Reported
1	C ₆ H ₅	30	6a	71	225-230	256-258 [19]
2	2-NO ₂ C ₆ H ₄	26	6b	92	255-256	258-260 [19]
3	3-NO ₂ C ₆ H ₄	29	6c	68	260-262	262-264 [19]
4	4-NO ₂ C ₆ H ₄	26	6d	91	258-260	258-260 [19]
5	4-BrC ₆ H ₅ -	31	6e	71	248-250	247-249 [31]
6	4-ClC ₆ H ₄ -	32	6f	84	245-250	263-265 [19]
7	3,4-(Me) ₂ C ₆ H ₃	28	6g	70	228-233	232-233 [33]
8	4-MeOC ₆ H ₄	35	6h	77	220-225	228-230 [36]
9	2-MeOC ₆ H ₄	33	6i	88	250-253	247-249 [33]
10	2,4-(MeO) ₂ C ₆ H ₃ -	28	6j	84	220-222	225-227 [34]
11	3,4,5-(MeO) ₃ C ₆ H ₂ -	40	6k	79	230-233	228-230 [33]

a) Isolated yield



Scheme 3: Proposed mechanism.

Table 4: Comparison of our results with some of those reported in the literature for the reaction of benzaldehyde, malononitrile and 4-hydroxycoumarin.

Entry	Reaction condition	Yield (%)	Time	Ref.
1	DAHP (10 mol%), Ethanol-Water, r.t.	85	6 h	[19]
2	S-pyroline (10 mol%), Ethanol-Water, reflux	78	3 h	[19]
3	SDS (20 mol%), water, reflux	88	2.5 h	[15]
4	RuBr ₂ (PPh ₃) ₄ , water, reflux	trace	60 min	[36]
5	RuBr ₂ (PPh ₃) ₄ , Ethanol, reflux	45	45 min	[36]
6	RuBr ₂ (PPh ₃) ₄ , Methanol, reflux	80	3 min	[36]
7	Silica gel, Ethanol, r.t.	95	4 h	[35]
8	Triethylbenzylammonium chloride, water, reflux	96	10 h	[16]
9	Iron ore pellet, Water, reflux	71	30 min	this work

Table 5: Comparison of our results with some of those reported in the literature for the reaction of aldehyde, malononitrile and barbituric acid.

Entry	Reaction condition	Yield (%)	Time	Ref.
1	TBAB, H ₂ O, reflux	80-90	25-35 min	[24]
2	DHP, EtOH, r.t.	71-81	2 h	[18]
3	US, H ₂ O	62-78	1-3h	[12]
4	L-proline, H ₂ O/EtOH, r.t.	68-86	30-90 min	[17]
5	SBA-Pr-SO ₃ H, H ₂ O/EtOH, r.t.	28	6 h	[22]
6	SBA-Pr-SO ₃ H, solvent free, 140 °C	30-90	5-45 min	[22]
7	Solvent and catalyst-free, ball milling, 96 °C	99	30-90 min	[11]
8	DABCO, H ₂ O/EtOH, r.t.	83-92	2 h	[14]
9	Iron ore pellet, H ₂ O/EtOH, reflux	73-93	8-31 min	this work

The same mechanism could be proposed for dihydropyrano[c]chromene preparation.

CONCLUSIONS

Using of iron ore pellet as natural, inexpensive, ecofriendly, non-toxic, and heterogeneous catalyst in aqueous media, short reaction time and high-excellent yield are key advantages to some reports. No harmful organic solvent is used.

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