

One-pot synthesis of dihydropyrimidones using silica-supported heteropoly acid as an efficient and reusable catalyst: Improved protocol conditions for the Biginelli reaction

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Received 30 November 2005; received in revised form 20 January 2006; accepted 23 January 2006

Available online 24 February 2006

Abstract

An efficient synthesis of 3,4-dihydropyrimidinones or thiones (DHPMs) is described, using silica-supported heteropoly acid $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ (PW/SiO₂) for the first time as the catalyst from an aldehyde, β -keto ester and urea or thiourea in acetonitrile. Compared to the classical Biginelli reaction conditions, this method consistently has the advantage of excellent yields, mild reaction conditions, ease of workup, survival of different functional groups, and short reaction times.

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Keywords: Heterogeneous catalysts; Dihydropyrimidinones or thiones (DHPMs); Supported heteropoly acid; Biginelli reaction; Multi component reactions (MCR)

1. Introduction

Heterogeneous catalysis dominates the industrial scenery mainly due to the facility of recovery and reuse of solid insoluble catalysts [1]. The comparison between heterogeneous and homogeneous catalysis has been discussed intensively [2]. Catalysis by heteropoly acids (HPAs) is a field of increasing importance [3]. HPAs have several advantages as catalysts which make them economically and environmentally attractive. They have very strong Brønsted acidity approaching the superacid region and this acid–base property can be varied over a wide range by changing the chemical composition. Solid HPAs possess a discrete ionic structure, comprising fairly mobile basic structural units-heteropoly anions and counteranions (H^+ , H_3O^+ , H_5O_2^+ , etc.)—unlike the network structure of zeolites and metal oxides, for instance. This unique structure manifests itself to have extremely high proton mobility and a ‘pseudoliquid phase’ [4], while heteropoly anions can stabilize cationic organic intermediates [3d]. In the last two decades the broad utility of HPA as acid and oxidation catalysis has been demonstrated in a wide variety of synthetically useful selec-

tive transformations of organic substrates [3–5]. Among the HPAs, Keggin family appeared rapidly as interesting candidates for strong acid-demanding reactions. Moreover, the use of supported HPAs for both increasing the active site accessibility and limiting the formation of bulky residues as much as possible has gained interest. A great variety of organic and inorganic supports, such as carbons [6], clays [7], SiO_2 [8] have already been used for supporting HPAs, but SiO_2 , which is relatively inert towards HPAs, is the one most often used [9]. Recently, the authors’ own work found silica-supported 12-tungstophosphoric acid (PW/SiO₂) to be a very efficient catalyst for Dakin–West reaction [10]. Here, another remarkable catalytic activity of PW/SiO₂ for the one-pot condensation of dicarbonyl compound (1), aldehyde (2) and urea or thiourea (3) to DHPMs (4) is reported.

DHPMs derivatives have exhibited important therapeutic and pharmacological properties as the integral backbone of several calcium channel blockers [11], antihypertensive agents [12], α_{1a} -antagonists [13], and neuropeptide Y (NPY) antagonists [14]. A broad range of biological effects including antiviral, antitumor, antibacterial and anti-inflammatory activities have been described for these compounds [15]. Additionally, their particular structure has been found in natural marine alkaloid batzalladines which are the first low molecular weight natural products reported in the literature to inhibit the binding of HIV

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gp-120 to CD4 cell, so disclosing a new path towards the development of AIDS therapy [16].

Biginelli reactions are simple one-pot, but low yielding, condensations of β -dicarbonyl compounds with aldehyde, and urea or thiourea in the presence of catalytic amount of acid to produce DHPMs [15,17]. Performing efficient chemical transformations coupling three or more components in a single operation by a catalytic process while avoiding stoichiometric toxic reagents, large amounts of solvents, and expensive purification techniques is a very important goal of the modern organic synthesis [3c]. Thus, Biginelli's reaction for the synthesis of DHPMs has received renewed interest, and several improved procedures have recently been reported [15,18–32]. However in spite of their potential utility, many of the reported one-pot protocols involve prolonged reaction times, unsatisfactory yields, cumbersome product isolation procedures, expensive reagents, stoichiometric amounts of catalysts, strongly acidic conditions, incompatibility with other functional groups and environmental pollution [24–26,33–35]. Thus in spite of a large number of methods reported for this transformation, there has been considerable interest to explore simple, milder, rapid and high-yielding protocols by employing environmentally friendly and reusable catalysts.

2. Experimental

2.1. Techniques

Surface area and porosity of HPA catalysts were measured by nitrogen physisorption on a Micromeritics ASAP 2000 instrument. Thermogravimetric analyses (TGA) were performed using Perkin-Elmer TGA 7 instrument under nitrogen flow. IR spectra were recorded with KBr pellets using a Shimadzu 470 spectrophotometer and FT-IR spectra were performed using Bomem MB 104 spectrophotometer. Tungsten content in the catalysts was measured by inductively coupled plasma (ICP atomic emission spectroscopy) on a Spectro Ciros CCd spectrometer. The products of the catalysis reaction were detected by a Bruker Avance 200 MHz NMR spectrometer.

2.2. Materials and catalysts

All chemical reagents and solvents were analytical grade and used without further purification. $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ hydrate from Aldrich, Merck and Aerosil 300 silica from Degussa were used. Silica-supported PW (PW/SiO₂) or PMo (PMo/SiO₂) catalysts were prepared by impregnating Aerosil 300 silica (S_{BET} , 300 m²/g) with an aqueous solution of PW. The mixture was stirred overnight at room temperature, followed by drying using a rotary evaporator, as described elsewhere [36]. Catalyst characterisation is given in Table 1.

2.3. Typical procedure for the synthesis of 3,4-dihydropyrimidin-2(1H)-ones and -thiones

A mixture containing an appropriate β -dicarbonyl compound (2 mmol), corresponding aldehyde (2 mmol), urea or thiourea (3 mmol) and PW/SiO₂ (9 mol%) in acetonitrile (5 mL) was

Table 1
Catalysts characterisation

Catalyst ^a	S_{BET}	Pore size	Pore volume	H ₂ O ^b (wt.%)	W ^c (wt.%)
60% PW/SiO ₂	87	145	0.34	1.8	45.6
40% PW/SiO ₂	117	227	0.67	4.8	28.9
20% PW/SiO ₂	208	145	0.75	3.5	15.4

^a Catalysts pre-treated at 150 °C/0.5 Torr for 1.5 h; PW content from preparation stoichiometry in anhydrous catalysts.

^b From TGA as a weight loss in the range of 30–300 °C.

^c W content in anhydrous catalysts from ICP. Typically, the W content from ICP was slightly lower than expected from the preparation stoichiometry.

stirred rapidly and heated at 80 °C in a preheated oil bath for an appropriate time (Table 3). After completion of the reaction as indicated by TLC, the mixture was filtered to remove the catalyst, and the filtrate was poured into crushed ice. Stirring was continued for several minutes. The solid product was filtered, washed with cold water (2 × 30 mL) and recrystallized from ethyl acetate/*n*-hexane or ethanol to afford pure product. All products were identified by comparing their spectral and physical data with those for authentic samples.

3. Results and discussion

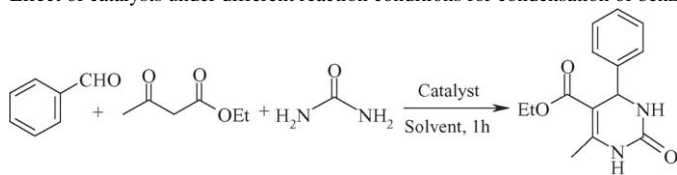
Recently, the authors found heteropoly acids, e.g. PW, PMo, and PW/SiO₂ to be very efficient catalysts for Dakin–West reaction [10,37]. These results encouraged us to explore these catalysts for the synthesis of 3,4-dihydropyrimidin-2(1H)-ones and -thiones.

Initially, the reaction of benzaldehyde, ethyl acetoacetate and urea in the presence of PW and PMo as catalysts was carried out in a one-pot condensation. Both of them showed good catalytic effects, but PW resulted a high yield for this transformation (Table 2, entries 2 and 3). However in the absence of catalyst, the reaction did not yield the desired product after 10 h (Table 2, entry 1).

Due to the increasing demand in modern organic processes for avoiding expensive purification, the use of heterogeneous catalysts presented itself as a remarkable technique toward an environmentally clean synthesis of DHPMs. This encouraged the investigation of the efficiency of PW/SiO₂ and PMo/SiO₂ as catalysts on such reactions (Table 2, entries 4 and 7). Usually, tungsten HPAs are preferred over molybdenum ones as acid catalysts because of their stronger acidity, higher thermal stability and low reducibilities [9a]. The state of HPAs on the SiO₂ surface has been reviewed [9b]. According to earlier IR and XRD studies, PW retains the Keggin structure when supported on SiO₂. PW/SiO₂ with different weight percent of PW was examined (Table 2, entries 5–7). Furthermore, the use of just 9 mol% of 40% PW/SiO₂ is sufficient to promote the reaction and no additives are required for this conversion. There are no improvements in the reaction rates and yields by increasing the amount of the catalyst from 9 to 20 mol% (Table 2, entries 7–9). It seems that acetonitrile is a much better solvent in term of yield (95%) than all other solvents tested such as ethanol, toluene, and chloroform (Table 2, entries 8 and 10–12). After a

Table 2

Effect of catalysts under different reaction conditions for condensation of benzaldehyde, ethyl acetoacetate and urea



Entry	Catalyst	Temperature (°C)	Solvent	Yield (%) ^a
1	–	80	CH ₃ CN	0 ^b
2	PW (5 mol%)	80	CH ₃ CN	92
3	PMo (5 mol%)	80	CH ₃ CN	85
4	40% PMo/SiO ₂ (5 mol% ^c)	80	CH ₃ CN	77
5	60% PW/SiO ₂ (14 mol% ^c)	80	CH ₃ CN	94
6	20% PW/SiO ₂ (9 mol% ^c)	80	CH ₃ CN	75
7	40% PW/SiO ₂ (5 mol% ^c)	80	CH ₃ CN	85
8	40% PW/SiO ₂ (9 mol% ^c)	80	CH ₃ CN	95
9	40% PW/SiO ₂ (20 mol% ^c)	80	CH ₃ CN	96
10	40% PW/SiO ₂ (9 mol% ^c)	80	C ₂ H ₅ OH	40
11	40% PW/SiO ₂ (9 mol% ^c)	80	C ₆ H ₅ CH ₃	55
12	40% PW/SiO ₂ (9 mol% ^c)	80	CHCl ₃	50
13	40% PW/SiO ₂ (9 mol% ^c)	RT	CH ₃ CN	60
14	40% PW/SiO ₂ (9 mol% ^c)	120	CH ₃ CN	83
15	40% PW/SiO ₂ (9 mol% ^c) ^d	80	CH ₃ CN	86
16	40% PW/SiO ₂ (9 mol% ^c) ^d	80	CH ₃ CN	81
17	40% PW/SiO ₂ (9 mol% ^c) ^d	80	CH ₃ CN	78

^a Isolated yield.^b After 10 h.^c Percent of PW to aldehyde.^d Catalyst reused in four successive runs; the catalyst was filtered off, washed with acetonitrile and dried at 150 °C/0.5 Torr for 1.5 h.

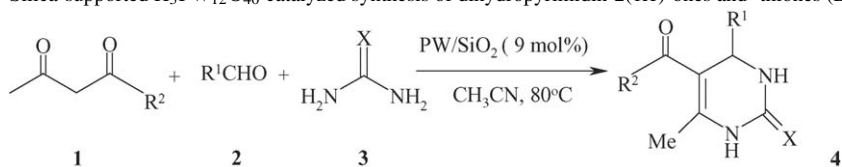
few optimization cycles, 80 °C was discovered to be a very efficient reaction temperature. Higher temperatures would lead to decreased yields because of the formation of undesired byproducts; lower reaction temperatures on the other hand required longer reaction times for complete conversion (Table 2, entries 13 and 14).



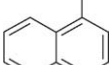

These optimum conditions were applied to a series of substituted aromatic, aliphatic and heterocyclic aldehydes. The results are shown in Table 3. Aromatic aldehydes carrying either electron-donating or electron-withdrawing substitutions in the *ortho*, *meta*, and *para* positions are reacted giving high to excellent yields (Table 3). Many of the pharmacological relevant substitution patterns on the aryl ring can thus be introduced with high efficiency [12,14]. With aliphatic aldehydes which normally show extremely poor yields in the classical Biginelli reactions, the corresponding 3,4-dihydropyrimidin-2(1H)-ones could be obtained in moderate yields and the reaction times can also be reduced from 18 h to 80 min (Table 3, entries 12–14). Acid-sensitive aldehydes such as furfural and cinnamaldehyde worked well without the formation of any side products, which are normally observed in the presence of protic acids due to their polymerization under acidic conditions (Table 3, entries 15 and 16). Apart from its simplicity, an additional important feature of the present protocol is the ability to tolerate the variation in all the three components. The results showed that besides ethyl acetoacetate, methyl acetoacetate and acetylacetone can also be used as one of the substrates (Table 3, entries 19–28). Furthermore,

thiourea has been used with similar success to provide the corresponding 3,4-dihydropyrimidin-2(1H)-thiones, which are also of much interest with regard to biological activity [15a]. For example monastrol (product of entry 31 of Table 3) is a new class of anticancer agents acting as cell division (mitosis) blockers [38]. Another important aspect of this procedure is survival of functional groups such as conjugated C=C double bond, Cl, OH, NO₂, OMe, and heterocyclic moieties under the reaction conditions. Thus, variations in all three components have been accommodated very comfortably.

After reaction, PW/SiO₂ can be filtered and treated with the reagents. This solution can be re-submitted to a new period of reaction; only a slight decrease in the yield of the DHPMs from 95 to 78% was observed after the fourth time (Table 2, entries 15–17), which is due to high porosity of the catalyst (Table 1) and deposited coke during the reaction (4–9 wt.% of carbon). In addition, when the filtered solution containing the catalyst was used after 3 months of storage, it was observed that the catalyst was quite active. Moreover FT-IR of the catalyst was checked after catalysis preparation and catalytic reaction. Characteristic peaks of Keggin type HPA were observed at about 1081, 985, 890, and 814 cm⁻¹, demonstrating that PW/SiO₂ is stable in this mild reaction conditions and does not undergo any deterioration. The authors investigated the mechanism of the Biginelli reaction in the literature [39], and proposed an *N*-acyliminium ion formed in situ by reaction of the aldehyde with urea as the key intermediate.

Table 3
Silica-supported $H_3PW_{12}O_{40}$ catalyzed synthesis of dihydropyrimidin-2(1*H*)-ones and -thiones (DHPMs)^a



Entry	R ¹	R ²	X	Time (min)	Yield ^b (%)	Reference ^c
1	C ₆ H ₅	OEt	O	60	95	[28]
2	3-NO ₂ C ₆ H ₄	OEt	O	70	94	[28]
3	4-NO ₂ C ₆ H ₄	OEt	O	65	89	[28]
4	4-CH ₃ OC ₆ H ₄	OEt	O	60	95	[28]
5	2-ClC ₆ H ₄	OEt	O	65	80	[28]
6	3-ClC ₆ H ₄	OEt	O	70	91	[28]
7	4-ClC ₆ H ₄	OEt	O	60	92	[28]
8	4-CH ₃ C ₆ H ₄	OEt	O	50	97	[28]
9	2-HOC ₆ H ₄	OEt	O	70	50	[22]
10	3-HOC ₆ H ₄	OEt	O	75	71	[28]
11	4-N(Me) ₂ -C ₆ H ₄	OEt	O	60	93	[22]
12	C-C ₆ H ₁₁	OEt	O	80	72	[23]
13	<i>n</i> -C ₃ H ₇	OEt	O	80	55	[22]
14	<i>n</i> -C ₅ H ₉	OEt	O	80	53	[23]
15	PhCH=CH	OEt	O	60	85	[28]
16		OEt	O	60	91	[28]
17		OEt	O	65	90	[28]
18		OEt	O	70	71	[22]
19	C ₆ H ₅	OMe	O	60	92	[28]
20	3-ClC ₆ H ₄	OMe	O	75	90	[20]
21	4-ClC ₆ H ₄	OMe	O	60	87	[25]
22	4-CH ₃ OC ₆ H ₄	OMe	O	60	98	[28]
23	4-NO ₂ C ₆ H ₄	OMe	O	70	75	[28]
24	4-CH ₃ C ₆ H ₄	OMe	O	60	95	[28]
25	4-N(Me) ₂ -C ₆ H ₄	OMe	O	75	91	[29]
26	C ₆ H ₅	Me	O	60	91	[24]
27	4-CH ₃ OC ₆ H ₄	Me	O	60	93	[24]
28	4-NO ₂ C ₆ H ₄	Me	O	100	84	[24]
29	C ₆ H ₅	OEt	S	60	90	[28]
30	4-CH ₃ OC ₆ H ₄	OEt	S	50	95	[28]
31	3-HOC ₆ H ₄	OEt	S	75	70	[32]
32	4-ClC ₆ H ₄	OEt	S	65	87	[28]
33	4-NO ₂ C ₆ H ₄	OEt	S	65	84	[28]
34	4-CH ₃ C ₆ H ₄	OEt	S	50	95	[28]
35		OEt	S	65	86	[28]

^a Reaction conditions: aldehyde (2 mmol), dicarbonyl compound (2 mmol), urea or thiourea (3 mmol), PW/SiO₂ (9 mol%), 80 °C.

^b Isolated yield.

^c Products were characterised by comparison of their spectroscopic data with those reported in the literature.

4. Conclusion

An efficient and important catalytic activity of PW/SiO₂ (cheap, noncorrosive, easily available, and reusable catalyst) has been studied for the synthesis of dihydropyrimidin-ones or thiones. The present procedure describes useful improvement in

the protocol condition for the Biginelli condensation. High to excellent yields, ease of workup, mild reaction conditions, short reaction times, environmentally friendly procedure, survival of different functional groups, and the ability to tolerate a variety of substituents in all three components are features of this new procedure.

Acknowledgments

The authors thank the Razi University Research Council and Kermanshah Refinery Company for support of this work.

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