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12-Molybdophosphoric acid: A recyclable catalyst for the synthesis of Biginelli-type 3,4-dihydropyrimidine-2(1H)-ones

Majid M. Heravi [a,*], Khadijeh Bakhtiari [a], Fatemeh F. Bamoharram [b]

[a] *Department of Chemistry, School of Sciences, Azzahra University, Vanak, Tehran 1234, Iran*
[b] *Department of Chemistry, Azad University of Mashad, Khorasn Branch, Mashad, Iran*

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Abstract

A simple and one-pot method for the synthesis of dihydropyrimidones is reported. 12-molybdophosphoric acid in refluxing acetic acid catalyzes this three-component condensation reaction to afford the corresponding pyrimidinones in good yields.

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Keywords: Biginelli reaction; Dihydropyrimidinones; Keggin-type heteropolyacid; HPA; 12-Molybdophosphoric acid

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1. Introduction

The Biginelli's reaction consists in the condensation of an aldehyde, a β-ketoester and urea in the presence of an acid catalyst [1]. However, this reaction suffers from the harsh conditions, long reaction times and frequently low yields.

3,4-Dihydropyrimidin-2(1H)-ones are interesting compounds and play an important role in synthetic, therapeutic and bioorganic chemistry [2].

In recent years, new methods for preparation of dihydropyrimidinones have been the subject of research for organic chemists. Consequently, the development of newer Lewis acid catalysts for this purpose has continued with the availability of a wide range of such reagents namely, $BF_3 \cdot OEt_2/CuCl$ [3], lanthanide triflate [4], indium trichloride [5], vanadium (III) chloride [6], cupric chloride [7], LiBr [8], zirconium (IV) chloride [9], lithium perchlorate [10], and polymer-supported ytterbium (II) reagent [11] as well as Bronsted acids, such as *p*-toluene sulfonic acid [12], silica sulfuric acid [13] and KHSO4 [14]. Also, montmorilonite KSF [15], natural HEU-type zeolite [16] and HY-zeolite [17] have been employed as heterogeneous catalyst for the synthesis of dihydropyrimidinones.

Due to the importance of Biginelli reaction products, the discovery and introduction of better and milder conditions using new catalysts has been under attention. Along this line, using heteropoly acids (HPAs), which are low in toxicity, highly stable towards humidity, recyclable and air stable have found more attention. In this paper, we describe an one-pot method for the Biginelli reaction using 12-molybdophosphoric acid, $H_3PMo_{12}O_{40}$, a recyclable catalyst from the Keggin-type heteropolyacids (Scheme 1).

2. Experimental

All products are known compounds, which were satisfactory characterized by physical and spectra data [3,4,9,12,27–33].

2.1. Preparation of dihydropyrimidinones

2.1.1. General procedure

A solution of aldehyde (10 mmol), β-ketoester (15 mmol) and urea or thiourea (15 mmol) in acetic acid (5 mL) was treated with $H_3PMo_{12}O_{40}$ (2 mol%, 0.03 g). The mixture was heated at reflux temperature and the progress of the reaction was monitored by TLC using

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[*] Corresponding author. Tel.: +98 2188041344; fax: +98 2188047861.
E-mail address: mmh1331@yahoo.com (M.M. Heravi).

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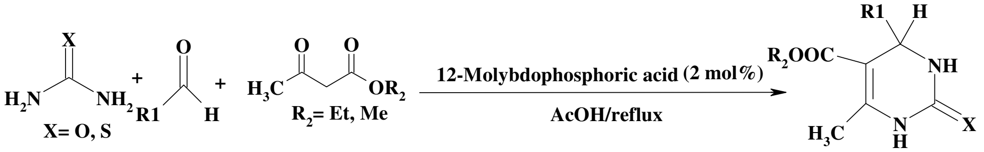

Scheme 1.

petroleum ether: ethylacetate as eluent. Upon completion of the reaction, the mixture was cooled to room temperature. Heteropolyacid then filtered off and the solution poured into ice-water (30 mL). The resulting solid product was then removed by filtration and recrystallized from absolute ethanol to give pure product.

3. Results and discussion

Due to the ever-mounting environmental concern in the field of chemistry, it is advisable to use easily recovered and recycled catalysts, especially expensive or toxic metallic ones for the next use [34]. In this respect, only few of the aforementioned catalysts meet this criterion of green chemistry. For example, the recovery of ytterbium triflate from water seems cumbersome since water must be removed through heating and then drying under vacuum at 100°C for 2 h [4]. In the case of polymer-supported Yb (III) resin, the activity of recycled resin is much lower than that of the original one thus limiting the recyclability [11]. Therefore, there is still room for further search for recyclable catalysts to be used in the Biginelli-type that can convert a variety of aldehydes to pyrimidinones in high yields under mild reaction conditions.

In the past two decades, the broad utility of HPAs as acid and oxidation catalysts in solution as well as in the solid state for various industrial processes has been demonstrated for a wide variety of synthetically transformation of organic substrates [18,24].

Heteropolyacids are more reactive catalysts than conventional inorganic and organic acids for reactions in solution [19]. Heteropolyacids have been used as catalyst for many of organic transformations, such as synthesis of acylals [20], tetrahydropyranilation of phenols [21], thioacetalization and transacetalization reactions [22]. They are also used as industrial catalysts for several Liquid-phase reactions [23], including alcohol dehydration [24], alkylation [25] and esterification [26].

Heteropolyacids (HPAs) as catalyst for fine organic synthetic processes have been developed for industrial related to fine chemicals, such as the flavors, pharmaceuticals and food industries [35].

In the present communication, Urea, ethylaceto acetate, and aldehydes were converted to the corresponding pyrimidinones in a three-component one-pot Biginelli-type reaction in the presence of a catalytic amount of 12-molybdophosphoric acid, $H_3PMo_{12}O_{40}$. The best condition to prepare the dihydropyrimidinones were achieved when 2 mol% of HPA, 1.5 equivalent of both urea (or thiourea) and ethylaceto acetate and 1 equivalent of aldehyde were heated under reflux for 4–7 h, affording the desired product in good yields (Table 1). We found that this method is effective with a variety of substituted aromatic aldehydes independently of the nature of the substituents in the aromatic ring, representing an improvement to the classical Biginelli's methodologies.

Recently, Kappe proposed that the first step of the Biginelli reaction, the acid catalyzed formation of acylimine

Table 1
Biginelli reaction using $H_3PMo_{12}O_{40}$

Entry	R_1	R_2	X	Time (h)	Yield (%)[a]	M.p. (°C)	
						Found	Reported[lit]
1	Ph-	Et	O	5	80	204	205–206[3]
2	4-Me-Ph	Et	O	4	75	214	214–215[3]
3	4-MeO-Ph	Et	O	4	70	203	201–203[3]
4	4-Cl-Ph	Et	O	6	80	216	214–215[3]
5	4-Br-Ph	Et	O	6	65	215	213–215[28]
6	2-NO_2-Ph	Et	O	4.5	67	221	218–220[29]
7	3-NO_2-Ph	Et	O	6	72	230	227–229[12]
8	4-NO_2-Ph	Et	O	7	70	211	209–211[3]
9	2-furyl-	Et	O	5	60	205–206	203–205[9]
10	Ph-	Et	S	4	57	204–205	205–206[4]
11	4-MeO-Ph	Et	S	4	50	152–154	152–153[27]
12	Ph-	Me	O	5	65	208–211	207–210[3]
13	4-Cl-Ph	Me	O	5.5	70	205–208	204–207[31]
14	3-NO_2-Ph	Me	O	5	60	279–280	278–279[32]

[a] Yields refer to the isolated pure products.

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