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One-Pot Synthesis of Dihydropyrimidinones/Thiones Catalyzed by White Marble a Metamorphic Rock: an Efficient and Reusable Catalyst for the Biginelli Reaction¹

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Abstract—In this work, we report a simple, efficient and green protocol for the synthesis of dihydropyrimidinones/thiones (products of Biginelli reaction) by the use of white marble as an effective heterogeneous catalyst. Short reaction times, high product yields, simple processing procedure and reusability of the catalyst are the superior characteristics of this protocol.

Keywords: Biginelli reaction, 3,4-dihydropyrimidin-2(1H)-ones/thiones, white marble, green catalyst

INTRODUCTION

In the concept of green chemistry, which is linked to a desire of scientists to take preventive and sustainable action on the environment, research has been developed for the application of new heterogeneous natural catalysts [1, 2], in the synthesis of therapeutic chemicals or key intermediates in the manufacturing of pharmaceutical chemicals.

The dihydropyrimidinone derivatives known as “Biginelli compounds” constitute an important class of compounds exhibiting broad range of pharmacological and biological activities such as inhibitors of the calcic channels, antihypertensive agents, antioxidants, anti-tumor activity, anti-cancer and anti-inflammatory drugs [3–6]. The Biginelli reaction reported by the chemist P. Biginelli in 1893 involves the condensation of three components: a β -ketoester (ethyl acetoacetate) with an aldehyde and urea (or thiourea) under strongly acidic conditions [7]. This method of synthesis suffers however from disadvantages such as low yields in the case of certain substituted aliphatic and aromatic aldehydes with a long reaction time.

Recently, several synthetic methods for the preparation of dihydropyrimidinones to improve the efficiency of this reaction have been reported. These catalytic systems involve Mn(OAc)₃ · 2H₂O [8], trifluoroacetic acid [9], boric acid [10], CeCl₃ · 7H₂O [11], copper(II) triflate [12], LiBr [13], silica/sulfuric acid [14], zinc triflate [15], I₂ [16], bismuth triflate [17], LiClO₄ [18], NH₄Cl [19], ZrCl₄ [20], Fe(OTs)₃ · 6H₂O [21], Yb(OTf)₃ [22], benzyltriethylammonium chloride [23], AlCl₃ : ZnCl₂ (3 : 1) [24], etidronic acid [25].

However, most of these methods suffer from one disadvantage or another, such as the use of dangerous and carcinogenic solvents, high catalyst loading or not recoverable catalysts that sometimes contain toxic metals. Therefore, there is a great need for new catalytic processes which do not have these problems.

In this paper we would like to point out our work on white marble (WM) to catalyze the synthesis reaction of dihydropyrimidinones with great efficiency and excellent reusability. The catalyst can be easily recovered and still retains its catalytic activity.

We have shown that white marble could be considered as a new heterogeneous catalyst for the Biginelli reaction.

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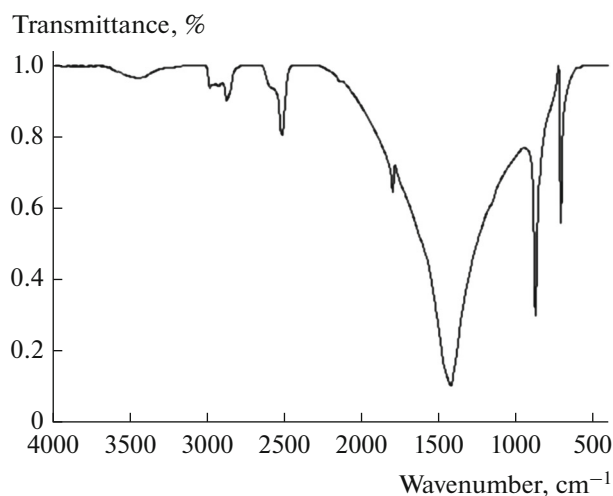


Fig. 1. FT-IR spectrum of marble powder.

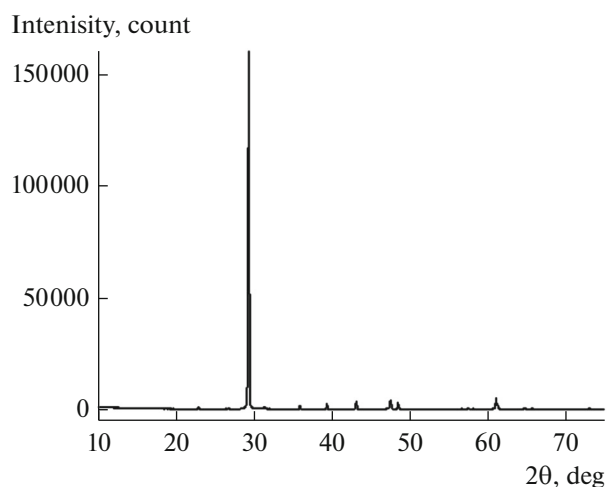


Fig. 2. XRD pattern of marble powder.

MATERIALS AND METHODS

Characterization of the Catalyst: Marble Powder

The marble powder used as a basic precursor in the preparation of catalysts is the waste from the marble works due to the cutting of white marble pieces. A sample was subjected to a treatment consisting of washing with water and ethanol followed by preliminary sieving to remove the impurities. After this operation, the grinding is carried out with sieving which makes it possible to retain the granulometry of the carbonate at a size between 63 and 125 μm . The carbonate thus obtained is dried and preserved at 100°C in the oven.

The recovered after treatment powder have been characterized by Fourier transform infrared spectroscopy (**FT-IR**), X-ray diffraction (**XRD**), the elemental analysis by energy dispersion spectroscopy (**EDS**) using a fluorescence X spectrometer and by measuring the specific surface.

FT-IR reveals several bands, in particular those attributable to carbonate ions CO_3^{2-} (Fig. 1). We have thus identified the adsorption bands characteristic of carbonates at 1480, 870 and 713 cm^{-1} . Analysis of the X-ray powder diffraction pattern (Fig. 2) showed a well-crystallized phase. The presence of calcite was confirmed by the characteristic 104 and 113 reflections at 29.41° and 39.39° (2θ) (Joint Committee on Powder Diffraction International Centre for Diffraction Data Further (JCPDS: 86-2334). Note the absence of the characteristic reflections of calcium carbonate in the different allotropes aragonite (JCPDS: 76-0606) and vaterite (JCPDS: 74-1867) [26–30].

The elemental analysis of the main constituent elements of the same samples was determined by EDS. Table 1 gives the mineralogical composition of the powder of marble used in this study. The powder of marble has an average specific surface area of 4.23 m^2/g as measured by the BET method.

Table 1. Mineralogical composition of marble powder

Compound	Concentration, %
CaO	78
P ₂ O ₅	0.156
F	3.08
SiO ₂	0.397
SO ₃	0.143
Na ₂ O	0.0874
Al ₂ O ₃	0.195
MgO	1.11
Fe ₂ O ₃	0.0723

General Procedure for the Synthesis of Dihydropyrimidinones/Thiones

In a conventional procedure, ethyl acetoacetate (1 mmol), aldehyde (1 mmol) and urea or thiourea (1.5 mmol) were mixed with WM as a catalyst (10 mol %, 0.01 g) and heated to reflux in the presence of ethanol (3 mL) as a solvent for an appropriate time. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was recovered by filtration. The filtrate was evaporated and the crude product purified by recrystallization from ethanol to give the pure product. The products were identified by comparison with melting points of the authentic compounds, and by ¹H and ¹³C NMR.

Table 2. Effect of WM mass on condensation reaction of **1a**, **2** and **3***

Entry	Catalyst, mol %	Time, min	Yield, %**
1	—	480	No reaction
2	10	45	93
3	20	45	86
4	30	45	80
5	40	45	72
6	50	45	65
7	100	45	48

* Reaction conditions: **1a** (1 mmol), **2** (1 mmol), **3** (1.5 mmol), catalyst, EtOH (3 mL), 80°C, for 45 min.

** Isolated yield.

Spectral Data of Typical Compounds

5-(Ethoxycarbonyl)-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one (4a). ¹H NMR (300 MHz, DMSO-d₆), δ, ppm: 9.17 (s, 1H, NH), 7.73 (s, 1H, NH), 7.21–7.33 (m, 5H, ArH), 5.14 (d, 1H, CH), 4.00 (q, 2H, OCH₂), 2.23 (s, 3H, CH₃), 1.09 (t, 3H, OCH₂CH₃). ¹³C NMR (300 MHz, DMSO-d₆), δ, ppm: 165.80, 152.62, 148.81, 145.33, 128.85, 127.72, 126.71, 99.74, 59.65, 54.44, 18.24, 14.53.

5-(Ethoxycarbonyl)-4-(4-chlorophenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (4b). ¹H NMR (300 MHz, DMSO-d₆), δ, ppm: 9.22 (s, 1H, NH), 7.76 (s, 1H, NH), 7.21–7.38 (m, 4H, ArH), 5.13 (d, 1H, CH), 3.99 (q, 2H, OCH₂), 2.23 (s, 3H, CH₃), 1.09 (t, 3H, OCH₂CH₃). ¹³C NMR (300 MHz, DMSO-d₆), δ, ppm: 165.67, 152.41, 149.19, 144.25, 132.25, 128.86, 128.65, 99.30, 59.72, 53.88, 18.26, 14.53.

5-(Ethoxycarbonyl)-6-methyl-4-(p-tolyl)-3,4-dihydropyrimidin-2(1H)-one (4c). ¹H NMR (300 MHz, DMSO-d₆), δ, ppm: 9.13 (s, 1H, NH), 9.12 (s, 1H, NH), 7.65–7.67 (m, 4H, ArH), 5.09 (d, 1H, CH), 3.99 (q, 2H, OCH₂), 3.31 (s, 3H, CH₃), 2.21 (s, 3H, CH₃), 1.09 (t, 3H, OCH₂CH₃). ¹³C NMR (300 MHz, DMSO-d₆), δ, ppm: 165.82, 152.63, 148.61, 142.42, 136.82, 129.35, 126.61, 99.88, 59.62, 54.09, 21.11, 18.22, 14.56.

5-(Ethoxycarbonyl)-4-(4-nitrophenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (4d). ¹H NMR (300 MHz, DMSO-d₆), δ, ppm: 9.32 (s, 1H, NH), 8.18–8.21 (d, 2H, ArH), 7.87 (s, 1H, NH), 7.47–7.50 (d, 2H, ArH), 5.26 (d, 1H, CH), 4.00 (q, 2H, OCH₂), 2.25 (s, 3H, CH₃), 1.09 (t, 3H, OCH₂CH₃). ¹³C NMR (300 MHz, DMSO-d₆), δ, ppm: 165.52, 152.46, 152.21, 149.86, 147.18, 128.12, 124.30, 98.64, 59.86, 54.15, 18.33, 14.51.

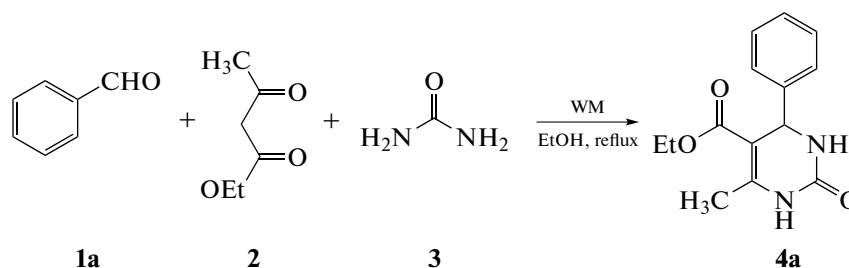
5-(Ethoxycarbonyl)-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-thione (4e). ¹H NMR (300 MHz, DMSO-d₆), δ, ppm: 10.31 (s, 1H, NH), 9.64 (s, 1H, NH), 7.19–7.35 (m, 5H, ArH), 5.17 (d, 1H, CH), 4.02 (q, 2H, OCH₂), 2.28 (s, 3H, CH₃), 1.10 (t, 3H, OCH₂CH₃). ¹³C NMR (300 MHz, DMSO-d₆), δ, ppm: 174.71, 165.59, 145.49, 143.96, 129.02, 128.14, 126.85, 101.19, 60.05, 54.51, 17.63, 14.47.

5-(Ethoxycarbonyl)-4-(4-methoxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-thione (4f). ¹H NMR (300 MHz, DMSO-d₆), δ, ppm: 10.27 (s, 1H, NH), 9.58 (s, 1H, NH), 6.86–7.43 (m, 4H, ArH), 5.10 (s, 1H, CH), 4.01 (q, 2H, OCH₂), 3.70 (s, 3H, OCH₃), 2.26 (s, 3H, CH₃), 1.11 (t, 3H, OCH₂CH₃). ¹³C NMR (300 MHz, DMSO-d₆), δ, ppm: 174.48, 165.63, 159.20, 145.21, 136.16, 128.08, 114.34, 101.42, 60.00, 55.56, 53.90, 17.60, 14.49.

RESULTS AND DISCUSSION

Evaluation of the Catalytic Activity of WM in the Synthesis of Dihydropyrimidinones

Initial studies were realized using the benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol) and urea (1.5 mmol) as the model reaction (Scheme 1). The reaction was carried out in EtOH at 80°C with a different catalyst mass. The best yield (93%) was obtained using 10 mol % of the catalyst after 45 min (Table 2). In addition, the experiment was also carried out under identical reaction conditions without the catalyst, no trace of the product was found after 480 min. It was evident that MW was the most effective catalyst among of the catalysts tested.



Scheme 1. The model reaction between benzaldehyde (**1a**), ethyl acetoacetate (**2**) and urea (**3**) in the presence of catalyst.

Effect of Solvents

The effect of various solvents (such as MeOH, EtOH, AcOEt, CH₂Cl₂, CH₃CN, THF, CHCl₃, and 1,4-dioxane) on the model reaction was studied in the presence of WM (10 mol %). The results indicate that the solvents had a significant effect on the yield of the product. The use of dioxane, AcOEt and CHCl₃ as solvent resulted in low yields (Table 3, entries 5, 7 and 10). Solvents such as H₂O, CH₃CN, tetrahydrofuran (THF) and CH₂Cl₂ gave moderate yields (Table 3, entries 4, 6, 8 and 9). The best conversion was observed when the reaction was carried out in ethanol (Table 3, entry 2). On the basis of these results, EtOH was then selected as a solvent for other investigations.

Time Effect of the Reaction

To study the effect of the reaction time (Table 4), the catalyst mass of 0.01 g (10 mol %) was chosen as the optimum mass in the presence of EtOH as solvent. The reaction mixture at 80°C for a short reaction time (45 min) gave 93% of 4a (Table 4, entry 6). However, when the reaction time was increased, the yield of the 4a started to decrease.

Study of the Reusability of the Catalyst

To accomplish this study, we examined the reuse of the catalyst. Indeed, a heterogeneous catalyst is not considered interesting in organic synthesis if it can be easily recovered and reused.

After completion of the reaction between benzaldehyde, ethyl acetoacetate and urea, the catalyst was recovered by simple filtration and then washed with water and ethanol (2 × 5 mL) to remove any trace of reagents and final products adsorbed on the catalyst, then dried in an oven at 80°C. The catalyst was reused directly in the model reaction without any additional treatments. The efficiency of the recovered catalyst was measured again by using the same reaction model. As shown in Table 5, the reaction yield reached >80% after 5 cycles. To the best of our knowledge, the reuse of this catalyst is significantly better than that for most supported catalysts reported.

Generalization

Using the optimum conditions, we have extended this study with various aldehydes, ethyl acetoacetate and urea or thiourea for the synthesis of a variety of 3,4-dihydropyrimidin-2(1H)-one derivatives/thiones (Scheme 2). The relevant data are presented in Table 6. The reactions gave the desired products with satisfactory yields (88–96%) depending on the substrate and the conditions used for the reaction (Table 6, entries 1–6).

Table 3. Effect of different solvents on the synthesis of dihydropyrimidinone (**4a**) catalyzed by WM*

Entry	Solvent	Time, min	Yield, %**
1	No solvent	60	66
2	EtOH	45	93
3	MeOH	45	81
4	H ₂ O	45	68
5	Dioxane	45	49
6	CH ₃ CN	45	64
7	AcOEt	45	52
8	THF	45	73
9	CH ₂ Cl ₂	45	69
10	CHCl ₃	45	41

* Reaction conditions: **1a** (1 mmol), **2** (1 mmol), **3** (1.5 mmol), catalyst (10 mol %), EtOH (3 mL), 80°C, for 45 min.

** Isolated yield.

Table 4. Effect of reaction time on the yield of dihydropyrimidinone (**4a**) in the presence of WM*

Entry	Time, min	Yield, %**
1	3	12
2	5	23
3	10	57
4	15	68
5	30	86
6	45	93
7	60	81
8	120	75

* Reaction conditions: **1a** (1 mmol), **2** (1 mmol), **3** (1.5 mmol), catalyst, EtOH (3 mL), 80°C, for specified time.

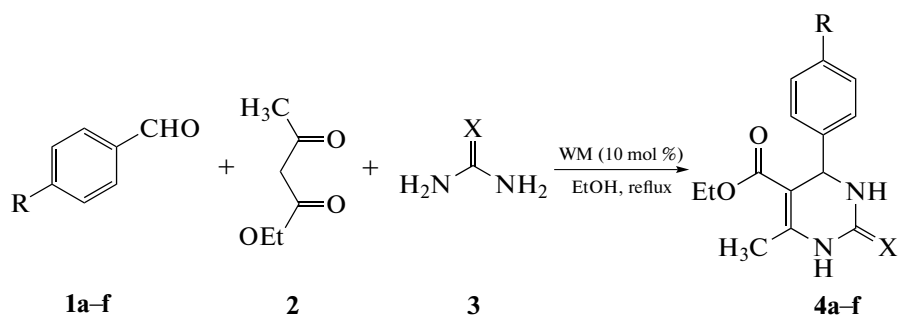
** Isolated yield.

Table 5. Reusability of WM in the synthesis of 3,4-dihydropyrimidinones*

Entry	Number of recycling runs	Time, min	Yield, %**
1	1	45	93
2	2	45	93
3	3	45	91
4	4	45	89
5	5	45	86

* Reaction conditions: **1a** (1 mmol), **2a** (1 mmol) and **3a** (1.5 mmol), catalyst (0.01 g), EtOH (3 mL), 80°C, for 45 min.

** Isolated yield.



Scheme 2. Generalization of the synthesis of dihydropyrimidinones/thiones.

Comparison of the Catalytic Activity of WM and Other Catalysts

To establish the catalytic activity of the WM, we compared the results obtained on the synthesis of 3,4-

dihydropyrimidinones with the literature data (Table 7). Based on this comparison, we see that the used catalyst (WM) presents higher yields and shorter reaction time compared to other reported systems [34–41].

Table 6. Synthesis of dihydropyrimidinones/thiones from various aromatic aldehydes with ethyl acetoacetate and urea or thiourea catalyzed by WM

Entry	Product	R	X	Time, min	Yield, %*	M.p., °C	
						found	reported
1	4a	H	O	45	93	204–206	207–208 [31]
2	4b	4-Cl	O	35	89	210–212	212–214 [32]
3	4c	4-Me	O	55	90	214–218	216–218 [32]
4	4d	4-NO ₂	O	50	96	210–214	211–212 [32]
5	4e	H	S	40	88	208–210	206–208 [31]
6	4f	4-MeO	S	25	91	150–154	153 [33]

* Isolated yield.

Table 7. Comparison of the efficiency of WM with certain catalysts reported in the literature

Entry	Catalyst	Reaction conditions	Number of recycling runs	Reaction time, h	Yield, %	Reference
1	WM (10%)	Ethanol/100°C	5 (93–86%)	0.75	93	This study
2	PS-PEG-SO ₃ H (0.3 g)	Dioxane/2-propanol/80°C	Not studied	10	80	[34]
3	Montmorillonite KSF (15%)	H ₂ O/100°C	Not studied	48	78	[35]
4	Silica-sulfuric acid (35%)	Ethanol/reflux	Not studied	6	91	[14]
5	Molybdophosphoric acid (2%)	AcOH/reflux	6 (94–85%)	4	70	[36]
6	Fe ₃ O ₄ @Silica sulfuric acid (0.05 g)	No solvent/80°C	4 (92–81%)	0.6	92	[37]
7	Triphenylphosphine (PPh ₃) (10 mol %)	No solvent/100°C	Not studied	10	70	[38]
8	Fe ₃ O ₄ @mesoporous SBA-15 (50 mg)	Ethanol/r.t.	7 (85–70%)	6	85	[39]
9	SiO ₂ -Cl (2.5 mol %)	No solvent/80°C	Not studied	3	88	[40]
10	ASA NPs (10 mol %)	No solvent/70°C	6 (94–60%)	5.3	94	[41]

CONCLUSIONS

In conclusion, we used the white marble as a new heterogeneous and effective catalyst in the reaction of Biginelli for the synthesis of 3,4-dihydropyrimidin-2-(1H)-ones and their analogues (thiones) by cyclocondensation of aldehydes, urea/thiourea and ethyl acetoacetate in ethanol. The WM showed a high reactivity with 82–96% conversion in 15–45 min at reflux for the various dihydropyrimidinone/thiones in 3 mL of ethanol. In addition, this method offers several advantages, including mild reaction conditions, low catalyst loading, short reaction times, and high yields. The catalyst can be recovered and reused up to 6 times without significant loss of activity.

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