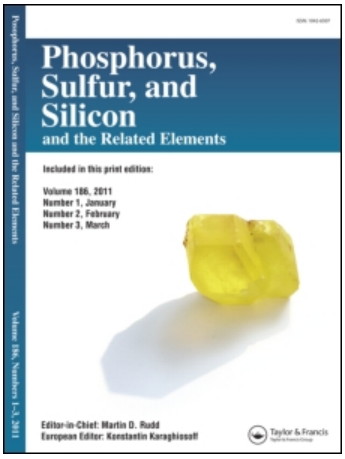

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Environmentally Friendly Preparation of 3,4-Dihydropyrimidin-2(1H)-thiones Catalyzed by $Al(H_2PO_4)_3$

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An efficient, facile, simple, and green synthetic protocol for the Biginelli reaction has been developed for the preparation of 3,4-dihydropyrimidin-2(1H)-thione derivatives under thermal and microwave irradiation, solvent-free conditions, in the presence of aluminum hydrogen phosphate, $Al(H_2PO_4)_3$, as an environmentally friendly heterogeneous recyclable catalyst, in high to excellent yields and short reaction time. In addition, the catalyst could be easily recovered from the reaction mixture by simple filtration and reused several times without any loss of activity.

Keywords $Al(H_2PO_4)_3$; Biginelli reaction; 3,4-dihydropyrimidin-2(1H)-thione; heterogeneous catalyst; multicomponent reaction

INTRODUCTION

Dihydropyrimidinones (DHPMs) and their derivatives have attracted interest in medicinal chemistry, because they exhibit a wide range of biological, pharmacological and therapeutic properties.[1] The dihydropyrimidinones (DHPMs) can serve as the integral backbones of several calcium channel blockers.[2] They are also reported to have antibacterial, antiviral, antitumor, antiinflammatory, α-1a-antagonist, and neuropeptide Y (NPY) antagonist activities.[3] Recently, structurally simple DHPM derivatives have emerged as a mitotic kinesin Eg5 motor protein inhibitor for the development of anticancer drugs.[4] Furthermore, the dihydropyrimidinone moiety in batzelladine alkaloids A and B inhibit the binding of HIV envelope protein gp-120 to human CD4 cells,

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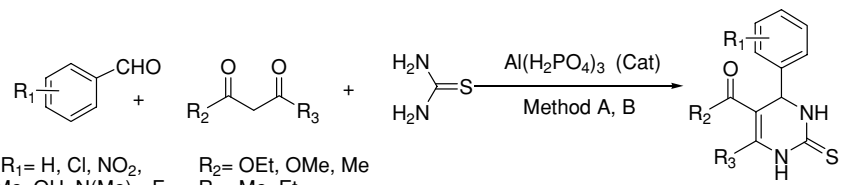
so that they are potential compounds in AIDS therapy.[5] In addition, the antioxidant activity of this ring system has been reported for retarding a variety of human diseases, including diabetes and various neurodegenerative diseases.[6]

The classical Biginelli reaction of an aldehyde, 1,3-dicarbonyl, and urea or thiourea requires strongly acidic conditions with relatively low yields, high reaction times, and harsh conditions.[7] In order to improve the efficiency of the Biginelli reaction, several Lewis and Brønsted catalysts, such as chlorotrimethylsilane,[8] ferric chloride/tetraethyl orthosilicate,[9] ruthenium(III) chloride,[10] N-bromosuccinimide,[11] ferric and nickel chloride hexahydrates,[12] ammonium chloride,[13] polystyrenesulfonic acid (PSSA),[14] Yb(III)-resin and polymer-supported scavengers,[15] $ZrCl_4$ or $ZrOCl_2$,[16] vanadium(III) chloride,[17] sulfonic acid functionalized silica,[18] ion exchange resins,[19] Ziegler–Natta,[20] PW, PMo, SiW,[21] chloroacetic acid,[22] ferric chloride and boric acid,[23] iron(III) trifluoroacetate and trifluoromethanesulfonate,[24] sulphamic acid,[25] alkylammonium and alkylimidazolium perhaloborates, phosphates, aluminates,[26] 1,1,3,3-tetrametylguanidinium trifluoroacetate,[27] and $ZnBr_2$ using α-(benzotriazolyl)alkyl urea derivatives[28] have been developed. However, many of these methods are not environmentally sound in that they are toxic chemicals, have low yields and very long reaction times, and use heavy metallic salts that pollute the environment. Hence, there is a clear need for a simple and practical methodology for the synthesis of this useful class of molecules on a large scale. Therefore, introducing clean processes and utilizing ecofriendly and green catalysts that can be simply recycled at the end of reactions have been under constant attention. The demand for an environmentally benign procedure with heterogeneous and reusable catalyst, prompted us to develop a safe alternate method for the synthesis of 3,4-dihydropyrimidin-2(1H)-thione derivatives in the presence of $Al(H_2PO_4)_3$ as a solid acid catalyst (Scheme 1).



SCHEME 1

This catalyst is safe, easy to handle, environmentally benign, presents fewer disposal problems, and is stable in reaction media. $Al(H_2PO_4)_3$ has been used as catalyst for nitration of organic compounds with nitric acid.[29]

RESULTS AND DISCUSSION

In order to carry out the Biginelli condensation in a more efficient way that minimizes the time, temperature, and amount of catalyst, the reaction of benzaldehyde, ethyl acetoacetate, and thiourea was selected as model to investigate the effects of the catalyst at different reaction temperatures (70, 100, and 120°C) and tdiffering amounts of catalyst (8, 16, 31, and 39 mol%) for method A and the different power of microwave irradiation (180 and 300 W) and the different amount of catalyst (16 and 31 mol%) for method B. The best result was obtained by carrying out the reaction with 1:1.2:1.5 molar ratios of aldehyde, 1,3-dicarbonyl compound, thiourea, and 16 mol% of $Al(H_2PO_4)_3$ at 120°C (Method A) or 31 mol% of $Al(H_2PO_4)_3$ at 180 W microwave power (Method B) in solvent-free conditions (Table I).

Using these optimized reaction conditions, the scope and efficiency of these procedures were explored for the synthesis of a wide variety

TABLE I Synthesis of Ethyl 1,2,3,4-Tetrahydro-6-methyl-4-phenyl-2-thioxopyrimidine-5-carboxylate from the Reaction of Benzaldehyde, Ethylacetoacetate, and Thiourea Using Different Quantities of $Al(H_2PO_4)_3$ as Catalyst

Entry	Catalyst (Mol %)	T (°C)	MW Power (W)	Method A[a] Time (min)/ Yield(%)[b]	Method B[a] Time (min)/ Yield (%)[b]
1	39	120	–	19/95	–
2	31	120	–	22/90	–
3	16	120	–	25/92	–
4	8	120	–	38/78	–
5	16	100	–	60/85	–
6	16	70	–	95/50	–
7	16	–	300	–	20/76
8	31	–	300	–	10/75
9	31	–	180	–	20/82

[a]Molar ratio: benzaldehyde (1 mmol), ethylacetoacetate (1.2 mmol), and thiourea (1.5 mmol).

[b]Yields refer to the isolated pure product.

TABLE II $Al(H_2PO_4)_3$ Catalyzed Synthesis of 3,4-Dihydropyrimidin-2(1H)-thiones Under Solvent-Free Thermal and Microwave Irradiation Conditions

				Method A	Method B	
Entry	R_1	R_2	R_3	Time (min)/ Yield (%)[a] [lit. Yield (%)][ref]	Time (min)/ Yield (%)[a]	m.p.°C (lit m.p)[ref]
1	H	C_2H_5O	CH_3	25/(88–92)[b] [56][16]	20/(78–82)[b]	206–207(206–207)[16]
2	3-Cl	C_2H_5O	CH_3	40/85 [60.1][16]	20/80	196–198(192–196)[16]
3	4-NO_2	C_2H_5O	CH_3	60/75 [91][27]	20/65	108–110(107–108)[27]
4	3-MeO	C_2H_5O	CH_3	50/84 [82][20]	20/83	150–152(150–152)[20]
5	4-HO	C_2H_5O	CH_3	45/65 [79][22]	20/68	194–196(193–195)[22]
6	H	CH_3O	CH_3	50/90 [83][22]	20/91	221–223(221–222)[22]
7	3-NO_2	CH_3O	CH_3	45/78 [90][25]	20/72	237–239(237)[25]
8	4-HO	CH_3O	CH_3	40/70 [88][25]	20/63	226–228(227)[25]
9	4-$(Me)_2N$	CH_3O	CH_3	30/92 [70][20]	20/83	152–154(152–153)[20]
10	H	CH_3	CH_3	20/95 [83][16]	15/90	216–217(214–215)[16]
11	2-Cl	CH_3	CH_3	50/86 [90.1][16]	15/89	173–174 (173–174)[16]
12	3-Cl	CH_3	CH_3	30/89 [89][16]	15/84	244–246(243–245)[16]
13	4-F	CH_3	CH_3	25/90 [89][26]	15/86	209–211(209–212)[26]
14	4-NO_2	CH_3	CH_3	45/81 [74][26]	15/74	207–209 (207–209)[26]
15	H	CH_3O	C_2H_5	45/80 [30.4][23]	20/81	166–168 (168–169)[23]
16	4-Cl	CH_3O	C_2H_5	40/75 [25.87][23]	20/72	161–162 (161–163)[23]
17	3-NO_2	CH_3O	C_2H_5	60/60 [16.06][23]	20/56	200–202 (201–203)[23]

[a]Yields refer to the pure isolated products. All known products have been reported previously in the literature and were characterized by comparison of melting points, and IR and NMR spectra with authentic samples.[14–27]

[b]Yield after the fifth recovery of the catalyst.

of substituted 3,4-dihydropyrimidin-2(1H)-thiones, and the results are summarized in Table II.

As shown in Table II, aromatic aldehydes with both electron-withdrawing and electron-donating substituents reacted efficiently with thiourea and methyl/ethyl acetoacetate, acetylacetone, or methyl propionylacetate afforded to the corresponding 3,4-dihydropyrimidin-2(1H)-thiones without the formation of any side products, in high to excellent yields (Table II, Entries 1–17). This protocol significantly improves the yields of Biginelli products, and the reaction was carried out under solvent-free conditions without using any toxic solvents.

In a typical experiment, after a period of time that the reaction was completed, the mixture was diluted with ethyl acetate and the heterogeneous catalyst was recovered. In every experiment, the entirety of the catalyst was easily recovered from the reaction mixture. The reusability

TABLE III Comparison Results of $Al(H_2PO_4)_3$ with Other Catalysts Reported in the Literature

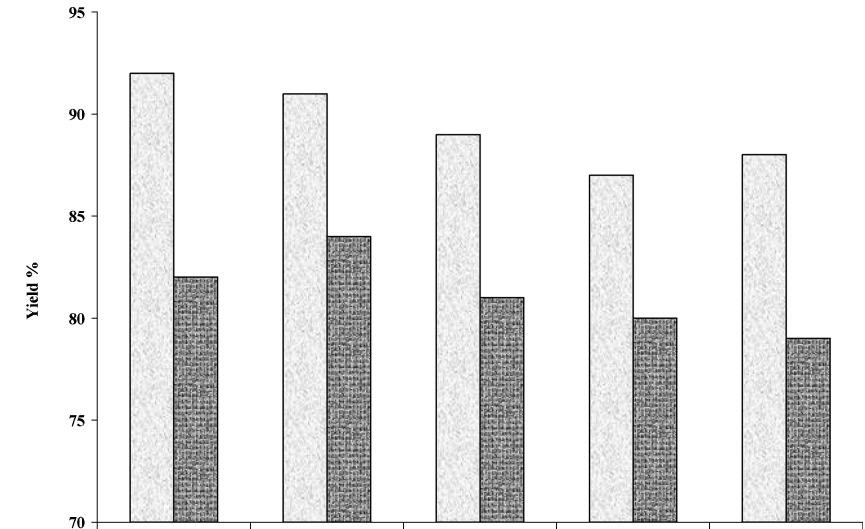
Entry	Catalyst[Ref]	Conditions Method A (Catalyst)	Time/Yield (%)	Conditions Method B (Catalyst)	Time/Yield (%)
1	$Al(H_2PO_4)_3$	Solvent-free/ 120°C (16 mol%)	20–60 min/ 60–95	Solvent-free/ 180 W (31 mol %)	15–20 min/56–91
2	NH_4Cl[13]	Solvent-free/100°C	3 h/78–88 (40 mol%)	–	–
3	PSSA[14]	–	–	Solvent-free/ 100 W (20 mol%)	20 min/86–88
4	Chloroacetic acid[22]	Solvent-free/90°C (10 mol%)	3 h/79–87	–	–

of the catalysts is one of the most important benefits that makes them useful for commercial applications. Thus the recovery and reusability of aluminum hydrogen phosphate, $Al(H_2PO_4)_3$, was investigated. The separated catalyst can be reused after washing with ethyl acetate and drying at 100°C. The reusability of the catalyst was checked by using the reaction of benzaldehyde, ethyl acetoacetate, and thiourea in the presence of $Al(H_2PO_4)_3$ under thermal and microwave conditions. The results indicate that the catalyst can be used five times without any loss of activity (Table II, Entry 1).

To show the merit of the present work in comparison with reported results in the literature, we compared results of $Al(H_2PO_4)_3$ with ammonium chloride,[13] polystyrenesulfonic acid (PSSA),[14] and chloroacetic acid[22] in the synthesis of 3,4-dihydropyrimidin-2(1H)-thione compounds. As shown in Table III, $Al(H_2PO_4)_3$ can act as effective catalyst with respect to reaction times, yields, and the obtained products.

CONCLUSION

In conclusion, we have developed a simple, cost-effective, and green procedure for the synthesis of 3,4-dihydropyrimidin-2(1H)-thione derivatives using recyclable $Al(H_2PO_4)_3$ catalyst under heterogeneous catalysis conditions. Furthermore, the solvent-free microwave irradiation and thermal conditions, high yield of products, short reaction time, ease of work-up, compatibility with various functional groups, and the ecologically clean procedure will make the present method a useful



	1	2	3	4	5
Method A	92	91	89	87	88
Method B	82	84	81	80	79

FIGURE 1 The reusability of $Al(H_2PO_4)_3$ in the reaction of benzaldehyde, ethyl acetoacetate, and thiourea under thermal (Method A) and microwave (Method B) conditions.

and important addition to the present methodologies for the Biginelli synthesis.

EXPERIMENTAL

All reagents were purchased from Merck and Aldrich and used without further purification. All yields refer to isolated products after purification. Products were characterized by comparison with authentic samples and by spectroscopy data (IR, ^{1}H NMR). The NMR spectra were recorded on a Bruker Avance DEX 300 MHz instrument. The spectra were measured in DMSO-d_6 relative to TMS (0.00 ppm). IR spectra were recorded on a JASCO FT-IR 460plus spectrophotometer. Melting points were determined in open capillaries with a BUCHI 510. TLC was performed on silica-gel PolyGram SIL G/UV 254 plates.

Preparation of $Al(H_2PO_4)_3$

The catalyst was prepared by taking a mixture of alumina (neutral) and concentrated phosphoric acid (88%) in a silica boat maintaining the

molar ratio of alumina: H_3PO_4 as 1:3 and heating at 200–220°C on a hot sand bath. The mixture was stirred at the stipulated temperature until the swampy mass solidified and then the temperature was reduced to around 100°C. The whole was then placed in a vacuum desiccator and cooled to ambient temperature. The catalyst thus prepared was finally transferred and stored in an airtight sample vial. The catalyst has been reported previously in the literature, and was characterized by comparison of IR spectroscopy and the powder XRD with known samples.[29] The IR spectrum and powder XRD pattern matched well with the literature.

Typical Experimental Procedure for the One-Pot Preparation of 5-(Ethoxycarbonyl)-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-thione

A mixture of benzaldehyde (1 mmol), ethyl acetoacetate (1.2 mmol), thiourea (1.5 mmol), and $Al(H_2PO_4)_3$ (16 mol % for method A or 31 mol% for method B) was stirred at 120°C (Method A) or the mixture was inserted in a microwave oven (Samsung, model KE300R) and heated at 180 W (Method B) for the appropriate time (Table II). After completion of the reaction as indicated by TLC, the resulting solidified mixture was diluted with ethyl acetate (5 mL) and the catalyst was separated by simple filtration and washed by ethyl acetate (2 × 5 mL). The filtrate obtained was washed with water (2 × 10 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvent under reduced pressure yielded crude product, which was purified by recrytallization with ethanol to afford pure product in 92% and 82% yields for methods A and B, respectively.

5-(Ethoxycarbonyl)-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-thione (Table II, Entry 1)

^{1}H NMR: $\delta = 9.19$ (s, 1H), 7.73 (s, 1H), 7.22 (m, 5H), 5.14 (d, $J = 3.6$ Hz, 1H), 3.40 (q, $J = 6.9$ Hz, 2H), 2.24 (s, 3H), 1.09 (t, $J = 6.9$ Hz, 3H) ppm; IR (KBr, cm^{-1}): 2940, 1980, 1940, 1810, 1650, 1240, 1050, 790.

The spectral data of some representative products are given below:

5-(Methoxycarbonyl)-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-thione (Table II, Entry 6)

^{1}H NMR: $\delta = 10.37$ (s, 1H), 9.68 (s, 1H), 7.21–7.37 (m, 4H), 5.18 (s, 1H), 3.55 (s, 3H), 2.30 (s, 3H) ppm; IR (KBr, cm^{-1}): 3340, 1662, 1600, 1566.

5-(Methoxycarbonyl)-6-methyl-4-(4-(dimethylamino)phenyl)-3,4-dihydropyrimidin-2(1H)-thione (Table II, Entry 9)

^{1}H NMR: $\delta = 9.95$ (s, 1H), 9.30 (s, 1H), 7.16 (d, $J = 9.1$ Hz, 2H), 6.62 (d, $J = 9.1$ Hz, 2H), 5.13 (s, 1H), 3.60 (s, 3H), 2.92 (s, 6H), 2.30 (s, 3H) ppm; IR (KBr, cm^{-1}): 3280, 3185, 2928, 1710, 1651.

5-Acetyl-6-methyl-4(2-chlorophenyl)-3,4-dihydropyrimidin-2(1H)-thione (Table II, Entry 11)

^{1}H NMR: $\delta = 10.36$ (s, 1H), 9.65 (d, $J = 2.5$ Hz, 1H), 7.48– 7.44 (m, 1H), 7.35–7.31 (m, 2H), 7.27–7.26 (m, 1H), 5.70 (d, $J = 5$ Hz, 1H), 2.38 (s, 3H), 2.12 (s, 3H) ppm; IR (KBr, cm^{-1}): 3252, 1710, 1659, 855.

5-Acetyl-6-methyl-4(4-fluorophenyl)-3,4-dihydropyrimidin-2(1H)-thione (Table II, Entry 13)

^{1}H NMR: $\delta = 10.35$ (s, 1H), 9.75 (s, 1H), 8.20 (d, $J = 7.5$ Hz, 2H), 7.55 (d, $J = 7.5$ Hz, 2H), 5.40 (d, $J = 7.4$ Hz, 1H), 2.35 (s, 3H), 2.25 (s, 3H) ppm; IR (KBr, cm^{-1}): 3288, 3144, 2896, 2765, 1697, 1637.

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