Boron trioxide–alumina as a heterogeneous catalyst in a facile solvent free one-pot synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones

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B_2O_3/Al_2O_3 has been found to be a new and highly efficient heterogeneous catalyst for the one-pot synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones by the Biginelli reaction under solvent-free conditions. 3,4-Dihydropyrimidin-2(1*H*)-ones have important pharmacological and biological activities.

Keywords: B_2O_3/Al_2O_3, 3,4-dihydropyrimidin-2(1*H*)-ones, Biginelli reaction, solvent-free synthesis

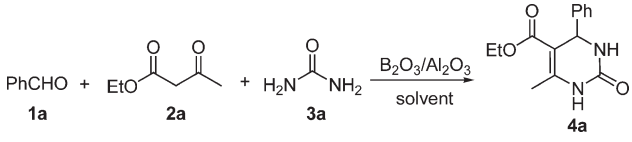
3,4-Dihydropyrimidin-2(1*H*)-ones[1] have recently attracted interest because of their wide range of pharmacological and biological activities.[2–5] In 1893, Biginelli was the first to synthesise 3,4-dihydropyrimidin-2(1*H*)-ones by the one-pot three-component condensation reaction of an aromatic aldehyde, urea, and ethyl acetoacetate.[6] However, the original reactions often afforded poor to moderate yields and were conducted under strongly acidic conditions.[7] These might limit the scope of the reaction. Consequently, many improved methods have been reported for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones in the presence of various catalysts.[8–22] Although the reported methodologies are suitable for certain syntheses, some of these procedures suffer from disadvantages, such as a long reaction time, low yield, the use of volatile organic solvents, requirement of excess reagents or costly catalysts and harsh reaction conditions. Owing to the importance of 3,4-dihydropyrimidin-2(1*H*)-ones from the pharmaceutical, industrial and synthetic points of view, introduction of an efficient method for the preparation of these compounds is still in demand.

In recent years, heterogeneous organic reactions have been recently performed with immobilised reagents on solid supports.[23] These procedures offer several intrinsic advantages such as clean reactions, easy separation of the products, the recovery and reuse of catalyst, and the minimisation of waste production. To the best of our knowledge, only two examples have been described in which B_2O_3/Al_2O_3 as a heterogeneous catalyst has been used for the synthesis of β-amino alcohols[24] and β-enamino ketones/esters[25] in the field of organic synthesis.

As part of our continuing interest in the development of new synthetic methodologies,[26,27] we report that B_2O_3/Al_2O_3 is an efficient heterogeneous catalyst for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones by the Biginelli reaction under solvent-free conditions.

Initially, the one-pot, three-component reaction of benzaldehyde, ethyl acetoacetate and urea was chosen as a model reaction to identify the optimal reaction conditions. The results are listed in Table 1. First, the effect of solvents was tested. Among the solvents screened (*e.g.* CH_3CH_2OH, CH_3CN, CH_2Cl_2, and THF), ethanol is a better solvent than other solvents tested (Table 1, entries 1–4). We were pleased to discover that the reaction occurred efficiently to afford the corresponding 3,4-dihydropyrimidin-2(1*H*)-one **4a** in 88% yield when 0.03 g B_2O_3/Al_2O_3 and 1–1.15 mmol substrates were used under solvent-free conditions (Table 1, entry 6). Moreover, we observed that the yields were affected by the amount of B_2O_3/Al_2O_3 that was used and by the reaction temperature. Decreasing the amount of the catalyst or the reaction temperature led to lower yields (Table 1, entries 6–10) of the product. On the other hand, **4a** was obtained in 38% yield when only Al_2O_3 was used as a catalyst (Table 1, entry 11). In contrast, only a trace amount of the product was obtained in the absence of B_2O_3/Al_2O_3 (Table 1, entry 12), which provided further proof that B_2O_3/Al_2O_3 plays an important role in this transformation.

Table 1 Optimisation of the reaction conditions[a]



Entry	Solvent	Temp./°C	Time/h	Yields/%
1	CH_3CH_2OH	75	4	58
2	CH_3CN	75	4	50
3	CH_2Cl_2	40	4	43
4	THF	60	4	32
5	none	75	4	86
6	none	75	6	88
7	none	50	6	71
8	none	90	3	85
9	none	75	4	73[b]
10	none	75	4	87[c]
11	none	75	4	38[d]
12	none	75	6	Trace[e]

[a] All reactions were run with **1a** (1.0 mmol), **2a** (1.5 mmol), **3a** (1.0 mmol) and B_2O_3/Al_2O_3 (0.03 g, 15% w/w) in 3 mL of solvent at 75 °C. Isolated yield.
[b] B_2O_3/Al_2O_3 (0.01 g, 15% w/w) was used as a catalyst.
[c] B_2O_3/Al_2O_3 (0.04 g, 15% w/w) was used as a catalyst.
[d] Al_2O_3 (0.02 g) was used as a catalyst.
[e] Without catalyst.

Having the optimal conditions in hand, the substrate scope of the Biginelli reaction was investigated, and several structurally diverse 3,4-dihydropyrimidin-2(1*H*)-ones **4** were prepared (Table 2).

As shown in Table 2, we investigated the influence of the electronic features of the aromatic aldehydes on the reaction. It was observed that the substituent group on the phenyl ring had no obvious effects on the yield of the Biginelli reaction (Table 2, entries 1–4). For example, *p*-fluorobenzaldehyde and *p*-methoxybenzaldehyde afforded the corresponding products **4b** and **4c** in 90% and 85% yields, respectively. Moreover, we also examined the one-pot, three-component reaction of aldehydes, dicarbonyl compounds and thiourea (Table 2, entries 5–9). The corresponding 3,4-dihydropyrimidin-2(1*H*)-thiones **4e–i** were also obtained in high yields. Aacetylacetone was also a good partner for the Biginelli reaction and the corresponding products **4j–l** were isolated in 91%, 89%, 87% yields,

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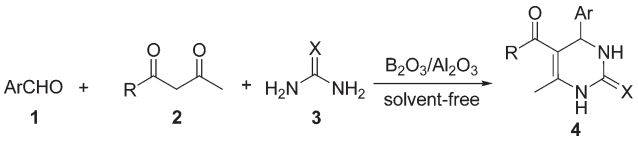
Table 2 Scope for synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones[a]



Entry	Ar	R	X	Products	Yield/%
1	C_6H_5	OEt	O	**4a**	88
2	*p*-(F)C_6H_4	OEt	O	**4b**	90
3	*p*-(OMe)C_6H_4	OEt	O	**4c**	85
4	*p*-(Me)C_6H_4	OEt	O	**4d**	89
5	*p*-(OMe)C_6H_4	OEt	S	**4e**	84
6	*p*-(Me)C_6H_4	OEt	S	**4f**	86
7	*p*-(F)C_6H_4	OEt	S	**4g**	91
8	*p*-(OMe)C_6H_4	CH_3	S	**4h**	89
9	*p*-(F)C_6H_4	CH_3	S	**4i**	93
10	*p*-(OMe)C_6H_4	CH_3	O	**4j**	91
11	*p*-(F)C_6H_4	CH_3	O	**4k**	89
12	C_6H_5	CH_3	O	**4l**	87

[a]All reactions were run with **1** (1.0 mmol), **2** (1.5 mmol), **3** (1.0 mmol) and B_2O_3/Al_2O_3 (0.03 g, 15% w/w) at 75 °C for 6 h under solvent-free conditions. Isolated yield.

respectively (Table 2, entries 10–12). In general, B_2O_3/Al_2O_3-catalysed reactions proceeded smoothly and gave the corresponding products in good to excellent yields.

Conclusion

In summary, B_2O_3/Al_2O_3 is a highly efficient heterogeneous catalyst for the Biginelli reaction under solvent-free conditions, affording the corresponding 3,4-dihydropyrimidin-2(1*H*)-ones in good yields. The present protocol involves a simple work-up, is environmentally benign, and affords high yields using of the catalytic amounts of the cheap heterogeneous catalyst as well as solvent-free conditions. Investigations on further application of the protocol are currently underway in our laboratory.

Experimental

Chemicals and apparatus

Unless otherwise noted, the reagents were purchased and used without further purification. NMR spectroscopy was performed on a Bruker-300 spectrometer using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts are given in δ relative to TMS, the coupling constants *J* are given in Hz. Column chromatography was performed using EM Silica gel 60 (300–400 mesh). All known compounds afforded analytical data identical to those reported literature previously.

Typical procedure for the preparation of B_2O_3/Al_2O_3[28]

85 g of γ-Al_2O_3 (JRC-ALO-7: 180 m^2 g^{-1}) was first impregnated with an aqueous solution of H_3BO_3 (26.64g of boric acid and 50 ml of water), followed by calcination at 773 K for 5 h. The B_2O_3 contents were 15 wt%. The white mixture (B_2O_3/Al_2O_3) of 100 g was obtained.

Synthesis of 3,4-dihydropyrimidin-2(1H)-ones; general procedure

B_2O_3/Al_2O_3 (0.03 g, 15% w/w) was added to a magnetically stirred mixture of aldehyde (1 mmol), dicarbonyl compound (1.5 mmol), and urea or thiourea (1 mmol), and the reaction mixture was stirred at 75 °C for 6 h under solvent-free conditions. After the completion of the reaction, as monitored by TLC and GC-MS analysis, the reaction mixture was cooled to room temperature and diluted with ethyl acetate. The catalyst was separated by filtration, then the solution was washed with ethyl acetate and dried over anhydrous sodium sulfate, filtered and the solvent was evaporated under vacuum. The residue was purified by silica gel chromatography using ethyl acetate-hexane as an eluent to afford the pure product of **4**. The physical and spectral data of compounds **4a–l** are as follows.

Ethyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4a**): Solid, m.p. 203–204 °C, (lit.[14] 202–203 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 8.12 (br s, 1H, NH), 7.25–7.32 (m, 5H), 5.76 (br s, 1H, NH), 5.40 (d, *J* = 2.74 Hz, 1H), 4.03 (q, *J* = 7.12 Hz, 2H), 2.34 (s, 3H), 1.59 (t, *J* = 7.12 Hz, 3H). ^{13}C MNR (75 MHz, $CDCl_3$): δ ppm 128.7, 127.9, 126.6, 101.3, 60.0, 55.7, 18.6, 14.1.

Ethyl 4-(4-fluorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4b**): Solid, m.p. 175–176 °C, (lit.[14] 171–173 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 8.64 (br s, 1H, NH), 7.25–7.30 (m, 2H), 6.95–7.00 (m, 2H), 6.29 (br s, 1H, NH), 5.37 (d, *J* = 2.22 Hz, 1H), 4.07 (q, *J* = 7.04 Hz, 2H), 2.32 (s, 3H), 1.04 (t, *J* = 7.04 Hz, 3H). ^{13}C MNR (75 MHz, $CDCl_3$): δ ppm 165.5, 162.2 ($^1J_{CF}$ = 244.86 Hz), 153.7, 146.4, 139.6 ($^4J_{CF}$ = 3.08 Hz), 128.2 ($^3J_{CF}$ = 8.18 Hz), 115.4 ($^2J_{CF}$ = 21.38 Hz), 101.2, 60.0, 54.9, 18.5, 14.1.

Ethyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4c**): Solid, m.p. 192–193 °C, (lit.[14] 190–192 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 8.24 (br s, 1H, NH), 7.23–7.28 (m, 2H), 6.83–6.86 (m, 2H), 5.80 (br s, 1H, NH), 5.38 (d, *J* = 2.54 Hz, 1H), 4.09 (q, *J* = 7.11 Hz, 2H), 3.80 (s, 3H), 2.34 (s, 3H), 1.18 (t, *J* = 7.11 Hz, 3H). ^{13}C MNR (75 MHz, $CDCl_3$): δ ppm 165.7, 159.3, 153.5, 145.9, 136.1, 127.8, 114.0, 101.6, 59.9, 55.2, 18.6, 14.1.

Ethyl 6-methyl-2-oxo-4-p-tolyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4d**): Solid, m.p. 207–208 °C, (lit.[19] 209–212 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 8.42 (br s, 1H, NH), 7.20–7.23 (m, 2H), 7.10–7.13 (m, 2H), 5.96 (br s, 1H, NH), 5.37 (d, *J* = 2.74 Hz, 1H), 4.08 (q, *J* = 7.10 Hz, 2H), 2.33 (s, 3H), 2.31 (s, 3H), 1.18 (t, *J* = 7.10 Hz, 3H). ^{13}C MNR (75 MHz, $CDCl_3$): δ ppm 165.7, 153.6, 146.2, 140.9, 137.5, 129.3, 126.4, 101.4, 59.9, 55.3, 21.0, 18.5, 14.1.

Ethyl 4-(4-methoxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4e**): Solid, m.p. 125–126 °C, (lit.[14] 123–125 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 8.46 (br s, 1H, NH), 7.84 (br s, 1H, NH), 7.18–7.22 (m, 2H), 6.81–6.84 (m, 2H), 5.33 (d, *J* = 2.90 Hz, 1H), 4.08 (q, *J* = 7.11 Hz, 2H), 3.77 (s, 3H), 2.35 (s, 3H), 1.17 (t, *J* = 7.11 Hz, 3H). ^{13}C MNR (75 MHz, $CDCl_3$): δ ppm 174.0, 165.3, 159.4, 142.6, 134.7, 128.0, 114.0, 103.0, 60.3, 55.4, 55.2, 18.0, 14.0.

Ethyl 6-methyl-2-thioxo-4-p-tolyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4f**): Solid, m.p. 192–194 °C, (lit.[14] 190–193 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 8.18 (br s, 1H, NH), 7.68 (br s, 1H, NH), 7.10–7.20 (m, 4H), 5.35 (d, *J* = 2.91 Hz, 1H), 4.09 (q, *J* = 7.11 Hz, 2H), 2.35 (s, 3H), 2.32 (s, 3H), 1.17 (t, *J* = 7.11 Hz, 3H). ^{13}C MNR (75 MHz, $CDCl_3$): δ ppm 179.1, 170.0, 147.3, 144.2, 142.8, 134.2, 131.4, 107.7, 65.1, 60.6, 25.8, 22.9, 18.8.

Ethyl 4-(4-fluorophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**4g**): Solid, m.p. 194–195 °C, (lit.[29] 191–192 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 8.30 (br s, 1H, NH), 7.79 (br s, 1H, NH), 7.23–7.28 (m, 2H), 6.97–7.04 (m, 2H), 5.38 (d, J = 2.52 Hz, 1H), 4.05–4.15 (m, 2H), 2.36 (s, 3H), 1.15–1.26 (m, 3H). ^{13}C MNR (75 MHz, $CDCl_3$): δ ppm 174.3, 165.1, 162.5 ($^1J_{CF}$ = 245.78 Hz), 142.8, 138.3 ($^4J_{CF}$ = 3.15 Hz), 128.5 ($^3J_{CF}$ = 8.33 Hz), 115.8 ($^2J_{CF}$ = 21.68 Hz), 102.9, 60.5, 55.4, 18.2, 14.1.

1-(4-(4-Methoxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidin-5-yl)ethanone (**4h**): Solid, m.p. 194–195 °C, (lit.[20] 191–192 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 7.87 (br s, 1H, NH), 7.39 (br s, 1H, NH), 7.15–7.26 (m, 4H), 5.40 (d, J = 2.37 Hz, 1H), 2.35 (s, 3H), 2.32 (s, 3H), 2.12 (s, 3H). ^{13}C MNR (75 MHz, $CDCl_3$): δ ppm 195.3, 174.2, 141.5, 138.6, 138.5, 129.8, 126.7, 111.5, 56.3, 30.2, 21.1, 19.3.

1-(4-(4-Fluorophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidin-5-yl)ethanone (**4i**): Solid, m.p. 208–209 °C, (lit.[21] 209–211 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 7.58 (br s, 1H, NH), 7.24–7.29 (m, 2H), 7.06 (br s, 1H, NH), 7.00–7.06 (m, 2H), 5.47 (d, J = 2.85 Hz, 1H), 2.36 (s, 3H), 2.18 (s, 3H). ^{13}C MNR (75 MHz, $CDCl_3$): δ ppm 195.1, 174.5, 162.4 ($^1J_{CF}$ = 242.55 Hz), 145.2, 129.6, 128.0 ($^3J_{CF}$ = 8.78 Hz), 115.8 ($^2J_{CF}$ = 21.30 Hz), 110.9, 53.4, 30.9, 18.7.

5-Acetyl-4-(4-methoxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (**4j**): Solid, m.p. 178–179 °C, (lit.[21] 177–179 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 8.53 (br s, 1H, NH), 7.18–7.26 (m, 2H), 6.82–6.86 (m, 2H), 6.12 (br s, 1H, NH), 5.37 (d, J = 2.94 Hz, 1H), 3.77 (s, 3H), 2.31 (s, 3H), 2.09 (s, 3H). ^{13}C MNR (75 MHz, $CDCl_3$): δ ppm 195.3, 159.4, 153.3, 145.7, 135.1, 127.8, 114.3, 110.6, 55.4, 55.2, 30.2, 19.5.

5-Acetyl-4-(4-fluorophenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (**4k**): Solid, m.p. 257–259 °C, (lit.[22] 260–261 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 8.44 (br s, 1H, NH), 7.24–7.29 (m, 2H), 6.97–7.03 (m, 2H), 6.08 (br s, 1H, NH), 5.44 (d, J = 2.94 Hz, 1H), 2.33 (s, 3H), 2.14 (s, 3H). ^{13}C MNR (75 MHz, $CDCl_3$): δ ppm 194.9, 162.4 ($^1J_{CF}$ = 245.78 Hz), 153.0, 145.7, 128.3 ($^3J_{CF}$ = 8.25 Hz), 115.9 ($^2J_{CF}$ = 21.68 Hz), 110.9, 55.1, 30.5, 19.7.

5-Acetyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one (**4l**): Solid, m.p. 233–235 °C, (lit.[21] 234–235 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 9.17 (br s, 1H, NH), 7.81 (br s, 1H, NH) 7.22–7.33 (m, 5H), 5.23 (d, J = 3.16 Hz, 1H), 2.27 (s, 3H), 2.08 (s, 3H). ^{13}C MNR (75 MHz, $CDCl_3$): δ ppm 194.6, 152.5, 148.5, 144.6, 128.9, 127.7, 126.8, 109.9, 54.2, 30.7, 19.3.

We are grateful for financial support from the Science and Technology Department of Zhejiang Province (No. 2010C33061), the Opening Foundation of Zhejing Provincial Top Key Discipline (No. 100061200129), and the Wenzhou Science & Technology Bureau Program (No. S20100004).

Received 22 December 2011; accepted 18 February 2012
Paper 1101056 doi: 10.3184/174751912X13318334808777
Published online: 17 April 2012

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