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Barium (II) chloride: An efficient catalyst for the multicomponent synthesis of 3,4-dihydropyrimidin-2-(1*H*)-ones under solvent free conditions

Nepram Sushuma Devi*, O.Mukherjee Singh, M.Dhaneshwar Singh

Department of Chemistry, Manipur University, Canchipur - 795 003, Manipur, (INDIA)

E-mail: nsushuma@gmail.com

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ABSTRACT

An efficient multicomponent synthesis of 3,4-Dihydropyrimidin-2-(1*H*) ones catalysed by $BaCl_2$ under solvent free condition is described herein. The mild reaction conditions, high yields and shorter reaction period illustrate the good synthetic utility of this method.

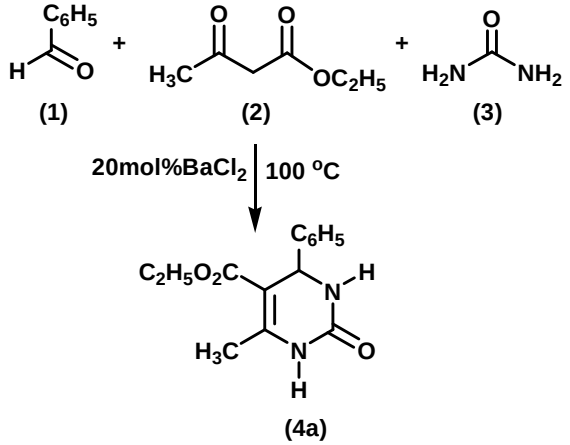
KEYWORDS

Barium(II) chloride;
Biginelli reaction;
Dihydropyrimidine;
High yield;
Solvent free.

INTRODUCTION

The multicomponent reactions (MCRs) are one of the most important protocols in organic synthesis and medicinal chemistry. In 1893 Pietro Biginelli first reported the Bronsted acid or Lewis acid catalysed synthesis of 3,4-dihydropyrimidin-2(*1H*)-ones by a simple one pot condensation reaction of an aromatic aldehyde, urea and ethylacetoacetate[1]. In recent years, dihydropyrimidinones (DHPMs) and their derivatives occupied an important place in medicinal and synthetic organic chemistry, because of their pharmaceutical and therapeutic properties such as antibacterial, antifungal, antiviral, antitumor and anti-inflammatory actions[2-6]. Several marine natural products containing the dihydropyrimidine-5-carboxylate core were found to be potent HIVgp-120-CD4 inhibitors[7]. Therefore, the synthesis of this heterocyclic nucleus has gained great importance in organic synthesis.

The multicomponent synthesis of dihydropyrimidinones, first reported by Biginelli in 1893, suffer from low yields (20–50%) of products in the cases of substituted aromatic and aliphatic aldehydes. In order to improve the efficiency of the Biginelli reaction, different Lewis acid catalysts such as $ZrCl_4$[8], $BiCl_3$[9], LiBr[10], $Mn(OAC)_3.2H_2O$[11], $InCl_3$[12], $Cu(OTf)_3$[13], $Zn(OTf)_2$[14], $FeCl_3.6H_2O$[15], $LiClO_4$[16] and



Scheme 1 : Condensation of benzaldehyde (1), ethylacetoacetate (2) and urea (3) catalyzed by $BaCl_2$ under solvent free conditions

chloroacetic acid[17] have been reported to be effective for this one-pot reaction. Recently, there has been reports on the Bronsted base-catalyzed synthesis of dihydropyrimidines by one-pot three-component Biginelli-type reaction[18]. Biginelli compounds 3,4-dihydropyrimidine-2-(1*H*)-ones are also synthesized in high yields using lactic acid organocatalyst[19]. However, $BaCl_2$ has not been reported as an efficient catalyst in Biginelli cyclocondensation reaction. Our new approach reported herein involves the use of barium chloride as catalyst for the Biginelli condensation reaction under solvent-free conditions.

EXPERIMENTAL

Materials and methods

Reagents were commercially purchased from Aldrich and used without further purification. Commercial solvents were used after distillation. Melting points were determined on a 'Veego MP-I' capillary melting point apparatus and are uncorrected. The IR spectra were recorded on a Perkin Elmer 983 and Shimadzu IR-408 spectrometers. Infrared spectra were recorded as thin films on KBr plates with *v* max in cm^{-1}. ^1H NMR spectra were taken in commercial DMSO-d_6 on a multinuclear spectrometer with all chemical shifts being reported in parts per million δ relative to internal tetramethylsilane (TMS, δ 0.0). Data are reported as follows: chemical shift (multiplicity [singlet (s), doublet (d), triplet (t), quartet (q), broad (brs), and multiplet (m)], coupling constants [Hz], and integration). ^{13}C NMR spectra were taken on a multinuclear spectrometer (200 MHz), using diluted solutions of each compound in DMSO-d_6 as the solvent, and the chemical shifts are reported in ppm (δ unit) downfield from tetramethylsilane as the internal standard. Mass measurements were carried out with Jeol JMSD-300 spectrometer. Masses (MS) are reported in unit of mass over charge (m/z), the molecular or base peaks and relative intensities are indicated by (M) and (%) respectively. Elemental analyses were performed on a Heracus CHN-O-Rapid Analyzer. Column chromatography was performed on Merck Silica Gel 60 (230-400 mesh) using analytical reagent grade hexane and ethyl acetate as eluents.

TABLE 1 : Effect of amount of catalyst on the yield of the dihydropyrimidine (4a)

Entry	$BaCl_2$ (mol%)	yield(%)[a]
1	5	65
2	10	79
3	20	96
4	25	96

[a]Isolated yield

General procedure for the preparation of dihydropyrimidine (4a-m)

To a mixture of aldehyde 1 (10 mmol), β-dicarbonyl compound 2 (10 mmol) and urea or thiourea 3 (12 mmol), $BaCl_2.2H_2O$ (20 mol %) was added at room temperature. After it was stirred for 5 min, the resulting mixture was heated at 100°C in a preheated oil bath for 20-30 min (monitored by TLC). The reaction mixture was brought to room temperature, crushed ice and 100 mL of cold water was added and stirred for 5-10 min. The solid was filtered under suction (water aspirator), washed with ice-cold water (100 mL), and then recrystallized from hot ethanol to afford pure product. The structures were fully established from spectral and analytical data which are given below.

5-ethoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1*H*)-one (4a)

m.p. 208-209°C (209-210°C); IR (KBr): 3228, 3105, 1709, 1605, 1240 cm^{-1}; ^1H NMR: δ 9.21 (s, 1H, NH), 7.76 (s, 1H, NH), 7.23-7.34 (m, 5H, C_6H_5), 5.15 (s, 1H, CH), 3.97 (q, J = 7.1 Hz, 2H, OCH_2CH_3), 2.25 (s, 3H, CH_3), 1.09 (t, J = 7.1 Hz, 3H, OCH_2CH_3); ^{13}C NMR: δ 165.2; 152.1, 148.3, 144.7, 128.3, 127.2, 126.1, 99.2, 59.1, 53.8, 17.7, 14.0; EIMS: m/z: 260 (M^+), 232, 184, 156, 138, 43; Anal. Calcd. for $C_{14}H_{16}N_2O_3$: C, 64.60; H, 6.20; N, 10.76. Found: C, 64.64; H, 6.25; N, 10.92.

5-ethoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1*H*)-thione (4b)

m.p. 190-192°C (191-193°C); IR (KBr): 3259, 3195, 3100, 1710, 1690 cm^{-1}; ^1H NMR: δ 10.37 (s, 1H, NH); 9.68 (s, 1H, NH), 7.19-7.35 (m, 5H), 5.17 (s, 1H), 4.07 (q, J = 7.1 Hz, 2H), 2.28 (s, 3H), 1.10 (t, J = 7.1 Hz, 3H), Anal. Calcd. for $C_{14}H_{16}N_2O_2S$: C, 60.85, H, 5.84, N, 10.14; Found: C, 60.83, H, 5.82, 10.13.

5-ethoxycarbonyl-4-(2-hydroxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1*H*)-one (4c)

m.p. 199-200°C (200-202°C); IR (KBr): 3317, 3090, 1380, 1280, 1114 cm^{-1}; ^1H NMR: δ 9.36 (s, 1H, OH), 9.12 (s, 1H, NH), 7.65 (s, 1H, NH), 7.02-6.62 (m, 4H, C_6H_4), 5.05 (s, 1H, CH), 3.99 (q, J = 7.1 Hz, 2H, OCH_2CH_3), 2.28 (s, 3H, CH_3), 1.11 (t, J = 7.0 Hz, 3H, OCH_2CH_3).

5-ethoxycarbonyl-4-(2-hydroxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1*H*)-thione (4d)

m.p. 181-182°C (183-185C); IR (KBr): 3060, 2959, 1741, 1361, 1246 cm^{-1}; ^1H NMR: δ 9.40 (s, 1H, OH), 9.14 (s, 1H, NH), 7.68 (s, 1H, NH), 7.03-6.66 (m, 4H, C_6H_4), 5.07 (s, 1H, CH), 3.43 (q, J = 7.2 Hz, 2H, OCH_2CH_3), 2.30 (s, 3H, CH_3), 1.15 (t, J = 7.1 Hz, 3H, OCH_2CH_3).

5-ethoxycarbonyl-4-(4-dimethylaminophenyl)-6-methyl-3,4-dihydropyrimidin-2(1*H*)-one (4e)

m.p. 253-254°C (256-258°C) ; IR (KBr): 3200, 3100, 1700, 1685 cm^{-1}; ^1H NMR: δ 8.90 (s, 1H, NH), 8.95 (s, 1H, NH), 7.19 (d, J = 9.1 Hz, 2H, Ar), 6.62 (d, J = 9 .1 Hz, 2H, Ar), 5.18 (s, 1H, CH), 4.0 (q, J = 7.6 Hz, 2H, -OCH_2), 2.87 (s, 6H, $N(CH_3)_2$), 2.25 (s, 3H, CH_3), 1.20 (t, J = 7.6 Hz, 3H, CH_3),; EIMS: m/z (%): 303 (75), 274 (100), 257 (15), 230 (78), 155 (20).

5-ethoxycarbonyl-4-(4-dimethylaminophenyl)-6-methyl-3,4-dihydropyrimidin-2(1*H*)-thione (4f)

m.p. 209-210°C (209-210°C); IR (KBr): 3327, 3169, 2986, 1671, 1650, 1616, 1580, 1524, 1466, 1364, 1322, 1188, 1099 cm^{-1}; ^1H NMR: δ 10.23 (s, 1H, NH), 9.54 (s, 1H, NH), 7.01 (d, 2H, J = 8.4 Hz, ArH), 6.66 (d, 2H, J = 8.4 Hz, ArH), 5.05 (s, 1H, CH), 3.99 (q, 2H, J = 6.8 Hz, OCH_2CH_3), 2.86 (s, 6H, $N(CH_3)_2$), 2.27 (s, 3H, CH_3), 1.12 (t, 3H, J = 6.8 Hz, OCH_2CH_3); ^{13}C NMR: δ 173.8, 165.3, 149.9, 144.3, 131.2, 127.1, 112.2, 101.2, 59.5, 53.5, 40.1, 17.1, 14.1; EIMS: m/z: 320.1; Anal. Calcd. for $C_{16}H_{21}N_3O_2S$: C, 60.21; H, 6.63; N; 13.16. Found: C, 60.28; H, 6.60; N; 13.18.

5-ethoxycarbonyl-6-methyl-4-(4-methylphenyl)-3,4-dihydropyrimidin-2(1*H*)-one (4g)

m.p. 204-206°C (205-206°C); IR (KBr): 3165, 1688, 1633 cm^{-1}; ^1H NMR: δ 9.15 (s, 1H, NH), 7.80 (s, 1H, NH), 7.10 (s, 4H, C_6H_4), 5.09 (s, 1H, CH), 3.96 (q, J = 7.1 Hz, 2H, OCH_2CH_3), 2.23 (s, 3H, C_6H_5-CH_3), 1.08 (t, J = 7.1 Hz, 3H, OCH_2CH_3); ^{13}C NMR: δ 165.3, 152.2, 148.1, 141.9,136.3, 128.8, 126.1, 99.5, 59.1, 53.7, 20.6, 17.7, 14.1; EIMS: m/z (%): 274 (M^+, 28), 183 (100); Anal. Calcd. for $C_{15}H_{18}O_3N_2$: C, 6 5.66; H, 6.62; N; 10.22. Found: C, 65.39; H, 6.69; N; 10.13.

5-ethoxycarbonyl-4-(4-methoxyphenyl)-6-methyl-3,4-dihydropyrimidin2(1*H*)-one (4h)

m.p. 200-202°C (199-201°C); IR (KBr): 3241,1700, 1637 cm^{-1}; ^1H NMR: δ 9.17 (s, 1H, NH), 7.68 (s, 1H, NH), 7.15 (d, J = 8.6 Hz, 2H; arom CH), 6.88 (d, J = 8.5 Hz, 2H; arom CH), 5.09 (s,1H, CH), 3.98 (q, J = 7.0 Hz, 2H, OCH2), 3.71 (s, 3H, OCH_3), 2.24 (s, 3H, CH_3), 1.10 (t, J = 7.0 Hz, 3H, CH_3); Anal. Calcd. for $C_{15}H_{18}N_2O_4$: C, 62.07; H, 6.20; N, 9.66. Found: C, 61.65; H, 6.21; N 9.58.

5-ethoxycarbonyl-4-(4-hydroxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1*H*)-one (4i)

m.p. 237-238°C (236-238°C); ^1H NMR: δ 9.34 (s, 1H, OH), 9.10 (s, 1H, NH), 7.64 (s, 1H, NH), 7.03-6.65 (m, 4H, C_6H_4), 5.02 (s, 1H, CH), 3.96 (q, J = 7.0 Hz, 2H, OCH_2CH_3), 2.21 (s, 3H, CH_3), 1.08 (t, J = 7.0 Hz, 3H, OCH_2CH_3).

4-(4-chlorophenyl)-5-(ethoxycarbonyl)-6-methyl-3,4-dihydropyrimidin-2(1*H*)-one (4j)

m.p. 215-216°C (216-217C); IR (KBr): 3241, 1700, 1645 cm^{-1}; ^1H NMR: δ 9.26 (s, 1H, NH), 7.79 (d, J = 3.1 Hz, 1H, NH), 7.40 (d, J = 0.5 Hz, 2H arom CH), 7.25 (d, J = 8.5 Hz, 2H; arom CH), 5.14 (s, 1H, CH), 3.99 (q, J = 7.0 Hz, 2H, OCH_2), 2.25 (s, 3H, CH_3), 1.09 (t, J = 7.0 Hz, 3H, CH_3); Anal. Calcd. for $C_{14}H_{15}N_2O_3Cl$: C, 57.14; H, 5.10; N 9.52. Found: C, 56.99; H, 5.09; N, 9.60.

5-ethoxycarbonyl-4-(3,4-dimethoxyphenyl)-6-ethyl-3,4-dihydropyrimidin-2(1*H*)-one (4k)

m.p. 173-175°C (174-175°C); IR (KBr): 3253, 1721, 1687 cm^{-1}; ^1H NMR: δ 8.90 (s, 1H, NH), 7.25 (s, 1H, NH), 6.80-6.85 (m, 3H), 5.25 (s, 1H), 4.05 (q, J = 7.1 Hz, 2H), 3.85 (s, 6H), 2.30 (s, 3H), 1.15 (t, J = 7.1 Hz, 3H); ^{13}C NMR: δ 165.7, 157.1, 147.9, 145.8,

139.6, 135.8, 120.6, 114.8, 113.9, 106.7, 59.7, 56.5, 49.6, 17.4, 13.5; EIMS: m/z (%): 320 (M^+), 292, 273, 247, 138, 97. Anal. Calcd. for $C_{16}H_{20}N_2O_5$: C, 59.99; H, 6.90; N, 8.74. Found: C, 59.84; H, 6.25; N, 8.92.

5-ethoxycarbonyl-6-methyl-4-(3,4-dioxymethylenephenyl)-3,4dihydropyrimidin-2(1*H*)-one (4l)

m.p. 189-190°C (188-190°C); IR (KBr): 3353, 1701, 1647 cm^{-1}; ^1H NMR: δ 1.15 (t, J = 7.1 Hz, 3H), 2.35 (s, 3H), 4.10 (q, J = 7.1 Hz, 2H), 5.95 (s, 2H), 6.75-6.85 (m, 3H), 8.25 (s, 1H, NH), 8.90 (s, 1H, NH); ^{13}C NMR : δ 13.7, 17.9, 49.8, 59.7, 91.5, 106.7, 113.9, 114.9, 120.4, 135.8, 145.8, 147.9, 156.6, 165.9; EIMS: m/z: 304 (M^+), 275, 258, 231, 183, 69. Anal. Calcd. for $C_{15}H_{16}N_2O_5$: C, 59.21; H, 5.30; N, 9.21. Found: C, 59.24; H, 5.23; N, 9.32.

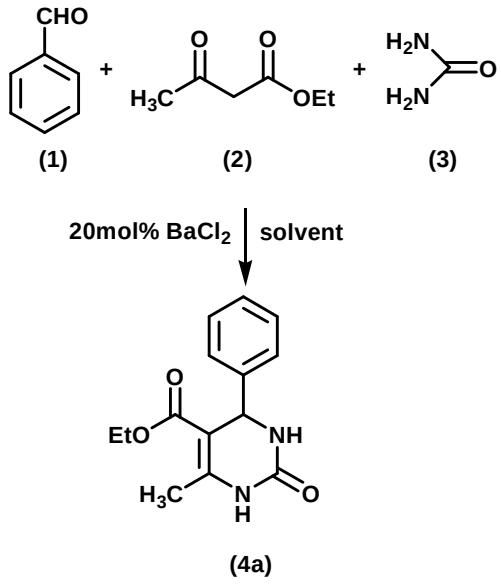
5-ethoxycarbonyl-6-methyl-4-naphthyl-3,4-dihydropyrimidin-2(1*H*)-one(4m)

m.p. 246-247°C (247-248°C); IR (KBr): 3253, 1699, 1647, 1435 cm^{-1}; ^1H NMR: δ 0.95 (t, J = 7.1 Hz, 3H), 2.45 (s, 3H), 3.95 (q, J = 7.1 Hz, 2H), 6.91 (s, 2H), 7.45-7.60 (m, 5H), 7.85 (t, J = 8.2 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 8.35 (d, J = 8.2 Hz, 1H), 9.15 (s, 1H, NH); ^{13}C NMR: δ 13.0, 17.1, 46.6, 59.5, 106.7, 123.9, 124.8, 125.6, 126.0, 126.4, 126.9, 128.9, 132.8, 133.6, 134.1, 139.7, 156.8, 165.7; EIMS: m/z: 310 (M^+), 217, 176, 231, 133, 69. Anal. Calcd. for $C_{18}H_{18}N_2O_3$: C, 69.66; H, 5.85; N, 9.03. Found: C, 69.60; H, 5.23; N, 9.03. Found: C, 69.60; H, 5.23; N, 9.22.

RESULTS AND DISCUSSION

Barium Chloride is an inexpensive and commercially available compound that can be used in practice without any special precautions. Previously, the reaction of benzaldehyde **(1)** (1.06g, 10 mmol), ethylacetoacetate **(2)** (1.30g, 10 mmol) and urea **(3)** (0.72g, 12 mmol) was investigated using 20 mol% $BaCl_2$ at 100°C under solvent free conditions (Scheme 1). The solid mass was heated under the same temperature for 30min (monitored by TLC). The resulting solid was crushed, washed with cold water (200 mL) and filtered under suction (water aspirator). The solid mass was dried and recrystallized from hot ethanol to afford the analytically pure product **(4a)** with 96% yield (TABLE 1). The

TABLE 2 : Biginelli reaction of benzaldehyde (1), ethylacetoacetate (2) and urea (3) catalyzed by $BaCl_2$ under different solvent conditions



(4a)

Entry	Solvent	time	Yield(%)[b]
1	Water	5h	50
2	Acetonitrile	3h	91
3	Benzene	6h	73
4	Tetrahydrofuran	4h	81
5	Ethanol	3h	83
6	No solvent	30 min	96

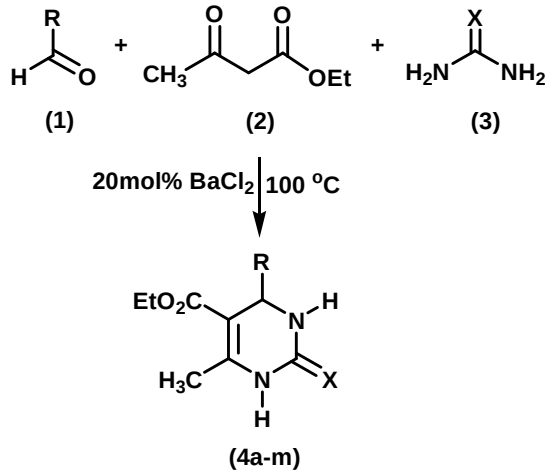
[b]**Isolated yield**

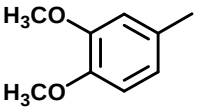
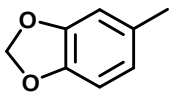
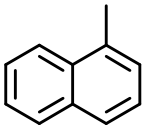
reaction proceeds very smoothly in a shorter time period. The structure of 5-ethoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1*H*)-one **(4a)** was confirmed with the help of analytical and spectroscopic data.

Further we investigated the effect of the amount of catalyst on the yield of the reaction (TABLE 1). Increase of $BaCl_2$ from 5% to 20% increases the yield of the reaction 65% to 96%. Further increase of catalyst has no effect on the yield of the reaction. Thus the reaction is optimized to 20 mol% $BaCl_2$.

As an extensive investigation, we have elaborated the $BaCl_2$ catalyzed one-pot Biginelli reaction under different solvents by taking the mixture of benzaldehyde **(1)**, ethylacetoacetate **(2)** and urea **(3)** as a representative example. The corresponding dihydropyrimidinone **(4a)** was obtained in moderate to good yield. The aqueous condition requires refluxing with longer time **(5h)** of reaction which ended finally with 50% overall yield. Refluxing the same reaction mixture under acetonitrile af-

TABLE 3 : Biginelli reaction of aldehyde (1), ethylacetoacetate (2) and urea or thiourea (3) catalyzed by $BaCl_2$ under solvent free conditions



Entry	R	X	[c]yield(%)	m.p.(°C) found	m.p.(°C) reported
4a	C_6H_5	O	96	208-209	209-210[22]
4b	C_6H_5	S	90	190-192	191-193[21]
4c	2-OHC_6H_4	O	95	199-200	200-202[15]
4d	2-OHC_6H_4	S	86	181-182	183-185[20]
4e	4-$Me_2NC_6H_4$	O	85	253-254	256-258[23]
4f	4-$Me_2NC_6H_4$	S	85	209-210	209-210[21]
4g	4-$CH_3C_6H_4$	O	90	204-206	205-206[21]
4h	4-$CH_3O\ C_6H_4$	O	96	200-202	199-201[24]
4i	4-HOC_6H_4	O	90	237-238	236-238[22]
4j	4-ClC_6H_4	O	92	215-216	216-217[22]
4k		O	90	173-175	174-175[3]
4i		O	92	189-191	188-190[3]
4m		O	89	246-247	247-248[3]

[c]Isolated yield

fords good yield of **(4a)** (91%). However, this condition also requires longer heating **(3-4h)** and the yield of dihydropyrimidine **(4a)** in both the conditions are found still lesser than the solvent free condition which needs only 30 minutes heating at 100°C with an excellent yield of 96%. The same reaction was also carried out in tetrahydrofuran, benzene, ethanol etc. The yield of the solvent-free condition was compared with different solvent conditions (TABLE 2). The products obtained under solvent-free conditions are of high purity and do not require any chromatographic separation. The solvent-free conditions are much better in terms of yield and shorter reaction times. In addition, the reactions are very clean, and no side product was obtained in any run. The same process was successfully extended to a wide range of structurally varied aldehydes, urea or thiourea, and β-ketoesters to afford the corresponding dihydropyrimidinones **(4a-m)** in good to excellent yields (TABLE 3). All the known compounds were checked further by comparison with the m.p. of the literature reports.

CONCLUSION

In conclusion, we have successfully described the synthesis of dihydropyrimidines by a three component condensation in one pot using catalytic amount of barium chloride under solvent free condition. The present procedure has many obvious advantages including simplicity of the methodology, ease of product isolation (only simple filtration), good yields and shorter reaction period.

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