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Synthesis of 3,4-dihydropyrimidin-2(1H)-ones using Ziegler–Natta catalyst system under solvent free conditions

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Abstract

A Ziegler–Natta catalyst system ($TiCl_4$-$MgCl_2$/magnesium chloride-methanol adduct) was efficiently found to catalyze the three component Biginelli reaction of an aldehyde, β-keto ester, and urea or thiourea under solvent free conditions to afford the corresponding 3,4-dihydropyrimidin-2-(1H)-ones in excellent yields. The enhanced surface areas of $TiCl_4$-$MgCl_2$-methanol adduct plays significant role in providing an efficient synthesis of Biginelli compounds.

Keywords: Biginelli reaction; Dihydropyrimidinones; Ziegler–Natta catalyst; Solvent free; Multi-component reaction

1. Introduction

3,4-Dihydropyrimidin-2-(1H)-ones (Biginelli Products) are very important heterocyclic motif in the realm of natural and synthetic organic chemistry due to their interesting biological and pharmacological activities such as antitumour, antibacterial, antiviral and anti-inflammatory activities [1]. Recently different derivatives of 3,4-dihydropyrimidin-2-(1H)-ones have exhibited calcium channel modulators, α-1a-antagonists and neuropeptide Y (NPY) antagonist [2]. Several alkaloids have been isolated from marine sources which contain the dihydropyrimidin core unit. Most notably among these are the batzelladine alkaloids which were recently found to be potent HIV gp-120-CD4 inhibitors [3].

Today, the Biginelli reaction is considered as one of the most important multi-component reaction for generating compounds of diverse medicinal importance [4].

The most simple and straightforward procedure, reported by Biginelli in 1893, involves one pot condensation of ethylacetoacetate, benzaldehyde and urea under strongly acidic conditions. However, one serious drawback of Biginelli's reaction is the low yields obtained in the case of substituted aromatic and aliphatic aldehydes [5]. This has led to multi-step synthetic strategies that produce somewhat better yields but lack the simplicity of one pot, one step synthesis [6]. In recent years, new methods for the synthesis of 3,4-dihydropyrimidin-2-(1H)-ones have been developed by different groups. In order to improve the efficacy of the Biginelli reaction different Lewis catalyst such as $BF_3{\cdot}OEt_2$ [7], $ZrCl_4$ [8], $BiCl_3$ [9], LiBr [10], $LaCl_3{\cdot}H_2O$ [11], $Mn(OAc)_3{\cdot}2H_2O$ [12], $InCl_3$ [13], NH_4Cl [14], $Cu(OTf)_2$ [15], $In(OTf)_3$ [16], $ZnCl_2$ [17], $MgBr_2$ [18], $FeCl_3{\cdot}6H_2O$ [19], $NiCl_2{\cdot}6H_2O$ [20], VCl_3 [21], $LiClO_4$ [22], $CuCl_2$ [23], lanthanide triflate [24], $CeCl_3{\cdot}7H_2O$ [25] and $Sr(OTf)_2$ [26] have been reported. In addition, ionic liquid [27], polymer supported reagents and polymer–metal complex have been used for Biginelli reaction [28].

As increasing environmental awareness in chemical research and pharmaceutical chemistry due to their traditionally large volume of waste/product ratios is perhaps the most ripe area for greening [29]. Organic reactions under solvent free conditions have attracted considerable interest of chemist particularly from the viewpoint of green chemistry. Green chemistry approaches hold out significant potential not only for reduction of byproducts, a reduction in waste produced and lowering of energy costs, but also in development of new methodologies towards previously unobtainable materials, using existing technologies [30].

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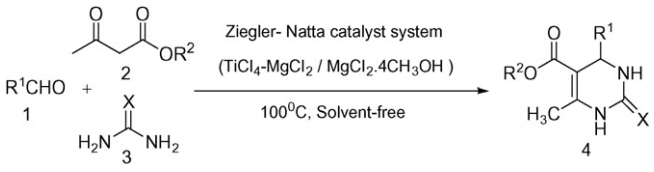
Table 1
$TiCl_4$-$MgCl_2$·$4CH_3OH$ catalyzed Biginelli condensation (4d) under different reaction conditions[a]

Catalyst	Surface area of support (m^2/g)	Catalyst (mol%)	Yield of 4d (%)[b]	Catalyst (mol%)	Yield of 4d (%)[b]
$TiCl_4$-$MgCl_2$ (anhydrous)	1.7	3	39	5	45
		10	49	20	49
$TiCl_4$-$MgCl_2$·$4CH_3OH$	16.8[c]	3	76	5	90
		10	90	20	90

[a] *Reaction conditions:* aldehyde 1 (10 mmol), β-ketoester 2 (10 mmol), urea or thiourea 3 (15 mmol) and catalyst $TiCl_4$-$MgCl_2$·$4CH_3OH$, $TiCl_4$-$MgCl_2$ 100 °C, 3 h.
[b] Surface area at 100 °C.
[c] Isolated yield.



Scheme 1.

The importance of green chemistry is most valued in medicinal chemistry.

In this communication, we wish to report the Ziegler–Natta catalyst system ($TiCl_4$-$MgCl_2$/magnesium chloride-methanol adduct) catalyzed synthesis of 3,4-dihydropyrimidin-2(1H) ones under solvent free conditions.

2. Results and discussion

The reaction of benzaldehyde, urea and ethylacetoacetate in the presence of catalytic amount of $MgCl_2$·$4CH_3OH$ impregnated $TiCl_4$ at 100 °C afforded the corresponding 3,4-dihydropyrimidin-2(1H)-ones in 90% yield (Scheme 1).

The selection of $TiCl_4$ as catalyst is done on the basis of report of Hu et al. [31], in which they found that $TiCl_4$ catalyzed Biginelli reaction is not giving good yield. In our observation, we also encountered low yield with titanium chloride as catalyst. Therefore, we thought to develop reagent by impregnation of $TiCl_4$ on inorganic supports. Inorganic supports used $MgCl_2$ and $MgCl_2$·$4CH_3OH$ adduct [32]. Selection of $MgCl_2$ as support is based on Ziegler–Natta catalyst system [33], in which $TiCl_4$ impregnated on $MgCl_2$ was used for olefin polymerization reaction very effectively. Ziegler–Natta catalyst having $MgCl_2$-supported $TiCl_4$ implies the discovery of $MgCl_2$ as co-catalyst for $TiCl_4$ and enhances the catalytic property of catalyst.

The surface area of magnesium chloride-methanol adduct is 14.1 m^2/g while that of anhydrous magnesium chloride is 1.7 m^2/g at room temperature [34]. In most of the cases, increasing the surface area of the catalyst, increases the rate of the reaction and also yield. We, therefore, prepared magnesium chloride-methanol adduct. The yield of reaction was drastically increased using $MgCl_2$·$4CH_3OH$ as co-catalyst. This is probably due to large surface area of magnesium chloride-methanol adduct (about 10 times more than anhydrous magnesium chloride) (Fig. 1).

The reaction of benzaldehyde, urea and ethylacetoacetate was selected as a model to examine the catalytic efficiency of the Ziegler–Natta catalyst system ($TiCl_4$-$MgCl_2$·$4CH_3OH$ and $TiCl_4$-$MgCl_2$ anhydrous). The reaction was carried out with different molar ratios of catalyst (3–20 mol%) and at dif-

Table 2
$TiCl_4$-$MgCl_2$·$4CH_3OH$ catalyzed synthesis of dihydropyrimidinones under solvent free condition[a]

Entry	R^1	R^2	X	Yield[b] (%)	Mp (°C)[c] (observed)	Mp (°C) (reported)
4a	1-Naphthyl	C_2H_5	O	91	256–258	–
4b	3-$CH_3OC_6H_4$	C_2H_5	O	82	205–207	207–208 [10]
4c	$C_6H_5CH{=}CH$	C_2H_5	O	84	230–232	232–235 [20]
4d	C_6H_5	C_2H_5	O	90	209–210	209–210 [10]
4e	4-ClC_6H_4	C_2H_5	O	76	215–216	216–217 [10]
4f	4-$O_2NC_6H_4$	C_2H_5	O	80	208–211	208–211 [10]
4g	4-$CH_3OC_6H_4$	C_2H_5	O	85	200–202	201–203 [12]
4h	4-$CH_3C_6H_4$	C_2H_5	O	84	205–206	169–171 [10]
4i	3-$O_2NC_6H_4$	CH_3	O	81	273–275	273–275 [10]
4j	4-$CH_3OC_6H_4$	CH_3	O	85	192–194	192–194 [12]
4k	3-$CH_3OC_6H_4$	CH_3	O	81	213–214	213–214 [10]
4l	C_6H_5	CH_3	O	90	208–210	209–212 [10]
4m	4-ClC_6H_4	CH_3	O	75	204–206	204–207 [10]
4n	4-$CH_3C_6H_4$	C_2H_5	S	70	212–214	192–194 [10]
4o	4-$(CH_3)_2NC_6H_4$	CH_3	S	70	152–153	152–155 [17]
4p	3-$CH_3OC_6H_4$	C_2H_5	S	82	150–152	150–152 [17]

[a] *Reaction conditions:* aldehyde 1 (10 mmol), β-ketoester 2 (10 mmol), urea or thiourea 3 (15 mmol), $TiCl_4$-$MgCl_2$·$4CH_3OH$ (10 mol%), 100 °C, 3 h.
[b] Isolated yield.
[c] Melting points were uncorrected.

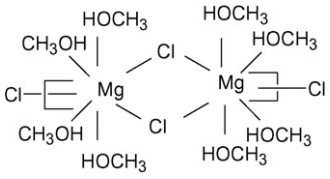


Fig. 1. Structure of $MgCl_2.4CH_3OH$ [34].

ferent temperatures (r.t., 50, 70 and 100 °C). The best results were achieved by carrying out the reaction with 0.1:1:1.5:1 mol ratios of $TiCl_4$-$MgCl_2$·$4CH_3OH$, benzaldehyde, urea and ethylacetoacetate at 100 °C for 3 h under solvent free conditions (Table 1). In order to study the generality of this procedure, a series of Biginelli compounds [35] were synthesized with similar operation. The results are listed in Table 2.

Several activated and deactivated aromatic aldehydes afforded high yields of product with high purity. Another important feature of this procedure is survival of a variety of functional groups such as ether, nitro, methoxy, halides, unsaturation, etc. under reaction conditions. Thiourea has been used with similar success to provide corresponding thioderivatives of dihydropyrimidinones, which are also of much interest with respect to their biological activities.

3. Conclusions

In conclusion, we have developed a simple and new methodology for the synthesis of 3,4-dihydropyrimidin-2-(1H)-ones by three component condensation in one pot using Ziegler–Natta catalyst system. This method offers several advantages such as inexpensive catalyst environmental friendly procedure, short reaction time, high yields simple work up procedure and easy isolation.

4. Experimental

4.1. General

4.1.1. General procedure for the preparation of $TiCl_4$-magnesium chloride-methanol adduct

$MgCl_2$ (0.10 mol) was introduced into a glass reactor equipped with a magnetic stirrer and 100 ml methanol was added. The mixture was heated to 60 °C and stirred until the $MgCl_2$ was completely dissolved. *n*-Decane (100 ml) was then added to this homogeneous solution, the mixture was stirred at 2000 rpm and heated under vacuum at 80 °C. $MgCl_2$ particles were slowly precipitated in the *n*-decane medium as the methanol evaporated. The resulting $MgCl_2$ particles were washed several times with toluene to remove residual *n*-decane and then dried under vacuum. Thus, magnesium chloride-methanol adduct [$MgCl_2$·$(CH_3OH)_n$] was obtained.

$MgCl_2$-methanol adduct (0.10 mol) was taken in 500 ml flask equipped with a water cooling reflux device and magnetic stirrer. $TiCl_4$ (0.10 mol) and toluene (200 ml) were added. The reaction mixture was stirred for 30 min in an ice bath and then refluxed for 3 h. The reaction mixture was filtered and residue was washed with toluene to give catalyst $TiCl_4$-$MgCl_2$-methanol adduct. Using the same methodology $TiCl_4$-$MgCl_2$ was prepared.

4.1.2. General procedures for preparation of 3,4-dihydropyrimidin-2-(1H)-ones using $TiCl_4$-$MgCl_2$·$4CH_3OH$ as hybrid catalyst

A mixture of aldehyde (10 mmol), β-keto ester (10 mmol) and urea or thiourea (15 mmol) and $TiCl_4$-$MgCl_2$·$4CH_3OH$ (1 mmol) was heated at 100 °C for 3 h. After cooling the reaction mixture was poured onto crushed ice and stirred for 10 min. The solid separated was filtered and was washed with cold water. It was recrystallized from hot ethanol to afford pure product. Physical data for selected compounds are given in the coming sections.

4.1.3. 5-Ethoxycarbonyl-4-(1-naphthyl)-6-methyl-3,4-dihydropyrimidin-2-(1H)-one (Entry 4a)

^{1}H NMR (200 MHz, DMSO-d_6) δ: 9.28 (s, 1H, NH), 8.31 (d, J = 7.9 Hz, 1H, ArH), 7.95 (m, 2H, ArH), 7.78 (s, 1H, NH), 7.55 (m, 4H, ArH), 6.09 (d, J = 2.7 Hz, 1H, CH), 3.82 (q, J = 7.03 Hz, 2H, OCH_2), 2.39 (s, 3H, CH_3), 0.83 (t, J = 7.03 Hz, 3H, CH_3); ^{13}C NMR (50 MHz, DMSO-d_6) δ: 165.6, 152.0, 149.0, 140.7, 133.8, 130.4, 128.8, 128.2, 126.4, 126.0, 124.6, 123.9, 99.5, 59.3, 50.1, 18.1, 14.1. IR (KBr, cm^{-1}): 3423, 3252, 2978, 1701, 1596. MS (FAB): m/z = 311 (M + H). Anal. calcd. for $C_{18}H_{18}N_2O_3$: C, 69.66; H, 5.85; N, 9.03. Found: C, 69.58; H, 5.71; N, 9.05.

4.1.4. 5-Methoxycarbonyl-4-(4-chlorophenyl)-6-methyl-3,4 dihydropyrimidin-2-(1H)-one (Entry 4e)

^{1}H NMR (200 MHz, DMSO-d_6) δ: 9.27 (s, 1H, NH), 7.78 (s, 1H, NH), 7.38 (d, J = 8.5 Hz, 2H, ArH), 7.25 (d, J = 8.5 Hz, 2H, ArH), 5.14 (d, 1H, CH), 3.53 (s, 3H, OCH_3), 2.25 (s, 3H, CH_3); ^{13}C NMR (50 MHz, DMSO-d_6) δ: 165.6, 151.9 148.9, 143.5, 131.7, 128.3, 128.0, 98.5, 53.5, 50.7, 17.7. IR (KBr, cm^{-1}): 3238, 3114, 2950, 2875, 1702, 1645. MS (FAB): m/z = 281 (M + H).

4.1.5. 5-Methoxycarbonyl-4-(4-dimethylaminophenyl)-6-methyl-3,4-dihydropyrimidin-2-(1H)-thione (Entry 4o)

^{1}H NMR (200 MHz, DMSO-d_6) δ: 9.95 (s, 1H, NH), 9.30 (s, 1H, NH), 7.16 (d, J = 9.1 Hz, 2H, ArH), 6.62 (d, J = 9.1Hz, 2H, ArH), 5.13 (s, 1H, CH), 3.60 (s, 3H, OCH_3), 2.92 (s, 6H, $N(CH_3)_2$), 2.30 (s, 3H, CH_3) ^{13}C NMR (50 MHz, DMSO-d_6) δ: 174.1, 166.2, 150.3, 144.9, 131.2, 127.4, 112.6, 101.3, 53.7, 51.3, 17.4. IR (KBr, cm^{-1}): 3280, 3185, 2928, 1710, 1651, 1613, 1583. MS (FAB): m/z = 306 (M + H). Anal. calcd. for $C_{15}H_{19}N_3O_2S$: C, 58.99; H, 6.27; N, 13.76. Found: C, 58.73; H, 6.19; N, 13.65.

4.1.6. 5-Ethoxycarbonyl-4-(3-methoxyphenyl)-6-methyl-3,4-dihydropyrimidin-2-(1H)-thione (Entry 4p)

^{1}H NMR (200 MHz, DMSO-d_6) δ: 10.37 (s, 1H, NH), 9.71 (s, 1H, NH), 7.27 (t, J = 9 Hz, 1H, ArH), 6.84 (m, 3H, ArH), 5.90 (s, 1H, CH), 4.03 (q, J = 6 Hz, 2H, OCH_2), 3.73 (s, 3H, OCH_3), 2.30 (s, 3H, CH_3), 1.12 (t, J = 6 Hz, 3H, CH_3); ^{13}C NMR (50 MHz, DMSO-d_6) δ:174.3, 165.4, 159.6, 145.3, 145.1, 130.1,

118.7, 112.8 (2), 101.1, 60.0, 55.3, 54.2, 17.5, 14.3. IR (KBr, cm^{-1}): 3157, 3122, 1710, 1651, 1596. MS (FAB); $m/z = 307$ (M + H). Anal. calcd. for $C_{15}H_{18}N_2O_3S$: C, 58.80; H, 5.92; N, 9.14. Found: C, 58.62; H, 5.81; N, 9.05.

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[35] ^{1}H NMR data of some compounds—compound 4b: ^{1}H NMR (DMSO-d_6, 200 MHz) δ: 9.21 (s, 1H), 7.53 (s, 1H), 7.23–7.31 (m, 1H), 6.82–6.86 (m, 3H), 5.14 (d, $J = 3.0$ Hz, 1H), 3.97 (q, $J = 6.9$ Hz, 2H), 3.74 (s, 3H), 2.27 (s, 3H), 1.10 (t, $J = 6.9$ Hz, 3H). Compound 4c: ^{1}H NMR (DMSO-d_6, 200 MHz) δ: 9.14 (s, 1H), 7.54 (s, 1H), 7.20–7.40 (m, 5H), 6.12–6.39 (m, 2H), 4.72 (d, $J = 3.7$ Hz, 1H), 3.99 (q, $J = 7.0$ Hz, 2H), 2.19 (s, 3H), 1.15 (t, $J = 7.0$ Hz, 3H). Compound 4d: ^{1}H NMR (DMSO-d_6, 200 MHz) δ: 8.99 (s, 1H), 7.20–7.41 (m, 6H), 5.26 (d, $J = 4.0$ Hz, 1H), 3.97 (q, $J = 7.1$ Hz, 2H), 2.31 (s, 3H), 1.12 (t, $J = 7.1$ Hz, 3H). Compound 4n: ^{1}H NMR (DMSO-d_6, 200 MHz) δ: 10.30 (s, 1H), 9.61 (s, 1H), 7.12 (d, $J = 8.0$ Hz, 2H), 6.90 (d, $J = 8.0$ Hz, 2H), 5.12 (s, 1H), 4.00 (q, $J = 6.8$ Hz, 2H), 2.72 (s, 3H), 2.29 (s, 3H), 1.11 (t, $J = 6.8$ Hz, 3H). MS (FAB): $m/z = 291$ (M + H). Anal. calcd. for $C_{15}H_{18}N_2O_2S$: C, 62.04; H, 6.25; N, 9.65. Found: C, 61.92; H, 6.18; N, 9.45.