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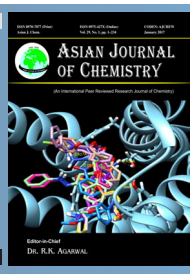

Microwave Promoted $Y(NO_3)_3 \cdot 6H_2O$ Catalyzed Biginelli Synthesis of Dihydropyrimidin-2-ones

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Biginelli synthesis of 3,4-dihydropyrimidinones from aldehydes, β-keto ester and urea using yttrium nitrate hexahydrate, as an efficient catalyst are demonstrated under microwave condition. This method offers significant advantages, such as high yields, short reaction times, easy isolation and mild reaction conditions. We have also investigated mechanism of $Y(NO_3)_3$ catalyzed 3,4-dihydropyrimidinones synthesis and identified the key intermediate benzal-bisurea by LC-MS.

Keywords: Biginelli reaction, Yttrium nitrate, Dihydropyrimidinones, Multicomponent reaction, Mechanistic study.

INTRODUCTION

Dihydropyrimidinones have attracted considerable attention in the last few decades as they show a broad spectrum of biological activity such as calcium channel blockers (nifedipine) [1], anti-hypertensive, α_{1a} adrenoceptor-selective antagonists [2], antibacterial [3], antitumor and anti-inflammatory agents [4,5]. Moreover, many natural products of biological interest contain dihydropyrimidinones moiety. Therefore, the synthesis of these heterocyclic compounds has gained considerable attention [6-9]. Synthesis of dihydropyrimidinones consists of three-component condensation reaction of aldehydes, β-keto esters and urea in acidic solution of EtOH as described by the pioneer work of Biginelli [10]. The method is simple but suffers from many disadvantages such as often quite low yield of the desired dihydropyrimidinones, various side reactions. Therefore, considerable attention has been paid to develop convenient and efficient method for synthesis of dihydropyrimidinones. After development of the three component protocol by Biginelli [10], a number of improved methods have been appeared by using Lewis acid catalyst *e.g.*, $BF_3 \cdot OEt$ [11], $InBr_3$ [12], $NiCl_2 \cdot 6H_2O$ [13], $CoCl_2 \cdot 6H_2O$ or $LaCl_3 \cdot 7H_2O$ [14], $Bi(OTf)_3$ [15], $FeCl_3$ [16], TMS-Cl [17], copper(II) trifluoroacetate [18], $RuCl_3$ [19], $Ca(NO_3)_2 \cdot 4H_2O$ [20], Fe-Al/clay [21], ionic liquids [22-24], $B(C_6F_5)_3$ [25]. However, such processes require very long reaction time and in many cases require special attention for dealing with moisture sensitive Lewis acid. In continuation of our present interest for water soluble, air stable Lewis acid, we found yttrium nitrate hexa-hydrate [26] as an efficient catalyst for promoting Biginelli reaction under microwave heating condition in ethanol at 70 °C. Bhanage *et al.* [27] for the first time observed $[Y(NO_3)_3 \cdot 6H_2O]$ as an efficient catalyst for synthesis of dihydropyrimidinones under solvent free condition at 70 °C and also demonstrated the possibility of catalyst recyclability. They proposed similar mechanism as proposed by Kappe [1]. However, while synthesizing dihydropyrimidinones, we found that the recycled catalyst from the filtrate of the water-diluted reaction mixture always contaminated with the product and starting materials and use of recycled catalyst give contaminated products. Moreover, mechanism of Beginelli synthesis of dihydropyrimidinones has been studied by many workers and found to be catalyst (Lewis acid) dependent. Herein, we wish to explore of the use of $[Y(NO_3)_3 \cdot 6H_2O]$ as a catalyst for Biginelli synthesis of dihydropyrimidinones under microwave condition and mechanistic details.

EXPERIMENTAL

Reactions were carried out under microwave irradiation (500 watt) condition at 70 °C.

General procedure under microwave: A mixture of ethyl acetoacetate (1.54 mmol), aromatic or aliphatic aldehyde (1.54 mmol), urea (1.84 mmol) and $Y(NO_3)_3 \cdot 6H_2O$ (30.7 μmol) in 10 mL Ethanol in a 100 mL round bottom flask fitted condenser was subjected to microwave heating at 70 °C for appropriate time as mentioned in the Table-1. Then the reaction mixture was allowed to cool at room temperature and H_2O (20 mL) was added. The precipitate appeared was collected by filtration and washed with water. The solid obtained was further washed with *n*-Hexane to remove excess aldehyde to get analytically pure product.

NMR spectra were recorded in Bruker 400 MHz NMR spectrometer in DMSO solvent. The data so obtained were found to be in good agreement with that reported in literature.

Ethyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (1): White solid, m.p.: 202-203 °C; LCMS: Calculated MS 260.12 for $C_{14}H_{16}N_2O_3$ [M], Found *m/z* = 261.0 $[MH]^+$; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.17 (s, 1H), 7.72 (s, 1H), 7.21-7.32 (m, 5H), 5.14 (s, 1H), 3.98 (q, *J* = 7.2 Hz, 2H), 2.24 (s, 3H), 1.08 (t, *J* = 7.2, 3H).

5-Acetyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1*H*)-one (2): White solid, m.p.: 202-203 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.17 (s, 1H), 7.81 (s, 1H), 7.34-7.32 (m, 2H), 7.25 (m, 3H), 5.2 (d, *J* = 3 Hz, 1H), 2.2 (s, 3H), 2.1 (s, 3H).

Ethyl 4-(4-hydroxy-3-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (3): Light yellow solid, m.p.: 232-233 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.11 (s, 1H), 8.89 (s, 1H), 7.6 (s, 1H), 6.80 (s, 1H), 6.7 (d, *J* = 8.4 Hz, 1H), 6.6 (d, *J* = 8.4 Hz, 1H), 5.05 (s, 1H), 3.96-4.01 (q, *J* = 7.2 Hz, 2H), 3.72 (s, 3H), 2.22 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 3H).

Ethyl 4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4): White solid, m.p.: 214-216 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.23 (s, 1H), 7.75 (s, 1H), 7.38 (d, *J* = 8.8 Hz, 2 H), 7.24 (d, *J* = 8.8 Hz, 2H), 5.14 (d, *J* = 2.8 Hz, 1H), 3.97 (q, *J* = 7.2 Hz, 2 H), 2.24 (s, 3 H), 1.09 (t, *J* = 7.2 Hz, 3H).

Ethyl 4-(2-hydroxy-3-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5): Light yellow; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.07 (s, 1H), 8.71 (s, 1H), 7.08 (s, 1H), 6.83-6.84 (m, 1H), 6.69 (t, *J* = 8 Hz, 1H), 6.57 (d, *J* = 8 Hz, 1H), 5.52 (s, 1H), 3.98 (q, *J* = 7.2 Hz, 2H), 3.77 (s, 3H), 2.26 (s, 3H), 1.03 (t, *J* = 7.2 Hz, 3H).

Ethyl 4-(4-bromophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (6): White solid, m.p.: 185-186 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.23 (s, 1H), 7.76 (s, 1H), 7.52 (d, 2 H), 7.17-7.19 (d, 2H), 5.14 (d, *J* = 3.2 Hz, 1H), 3.95-4.00 (q, *J* = 7.2 Hz, 2H), 2.24 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H).

Ethyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (7): White solid, m.p.: 201-202 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.14 (s, 1H), 7.66 (s, 1H), 7.14 (d, *J* = 8.4 Hz, 2 H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.08 (d, *J* = 2.8 Hz, 1H), 3.97 (q, *J* = 7.2 Hz, 2H), 3.71 (s, 3H), 2.23 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H).

Ethyl (E)-6-methyl-2-oxo-4-styryl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (8): Off white solid, m.p.: 157-159 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.14 (s, 1H), 7.59 (s, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.31 (t, *J* = 8.4 Hz, 2H), 7.21 (t, *J* = 2.8 Hz, 1H), 6.33 (d, *J* = 15 Hz, 1H), 6.18 (dd, *J* = 15, 6 Hz, 1H), 4.72 (s, 1H), 4.07 (q, *J* = 7.2 Hz, 2H), 2.23 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H).

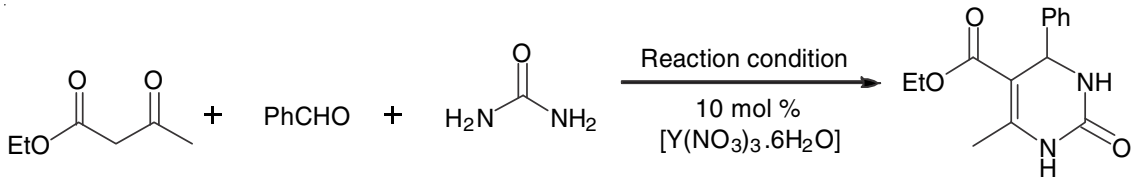
Ethyl (E)-6-methyl-2-oxo-4-(prop-1-en-1-yl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (9): Off white solid, m.p.: 163 °C; LCMS: Calculated MS 224.12 for $C_{11}H_{16}N_2O_3$ [M], Found *m/z* = 225.5 (MH^+); ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.01 (s, 1H), 7.35 (s, 1H), 5.4 (s, 2H), 4.47 (s, 1H), 4.05 (q, *J* = 7.2 Hz, 2H), 2.15 (s, 3H), 1.61(s, 3 H), 1.18 (t, *J* = 7.2 Hz, 3H).

Ethyl 4-(2-bromophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (10): White solid, m.p.: 196 °C; LCMS: Calculated MS 338.03 for $C_{14}H_{15}BrN_2O_3$ [M], Found *m/z* = 339.1 $[MH]^+$ and 341.1 $[MH+1]^+$ with intensity ratio ~1:1; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.26 (s, 1H), 7.68 (s, 1H), 7.57 (d, *J* = 8 Hz, 1H), 7.38 (t, *J* = 8 Hz, 1H), 7.30 (dd, *J* = 8, 3 Hz, 1H), 7.19 (t, *J* = 8 Hz, 1H), 5.59 (s, 1H), 3.90 (q, *J* = 7 Hz, 2H), 2.30 (s, 3H), 0.99 (t, *J* = 7 Hz, 3H).

RESULTS AND DISCUSSION

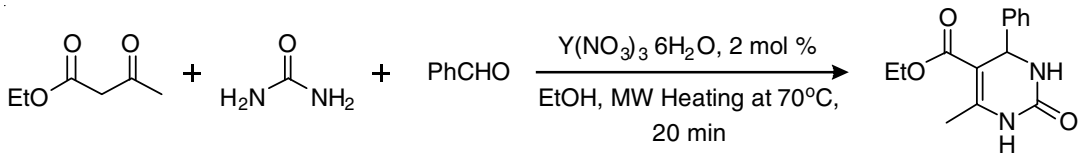
Initially, we have carried out the reaction under refluxing condition in ethanol, as described by Bhanage and co-workers [27] and found that a mixture of benzaldehyde, ethyl acetoacetate (EAA) and urea with 10 mol % $Y(NO_3)_3{\cdot}6H_2O$ gave 87 % isolated yield after 3 h (**Scheme-I**). Same reaction mixture, also subjected to microwave heating at 70 °C for 10 min resulted in 92 % isolated yield. The desired product in both the conditions can be isolated in a very simple way. Addition of water gave solid precipitate which can be isolated by filtration.

After observing the catalytic effect of yttrium nitrate in the Biginelli reaction under microwave condition, we have searched suitable solvent system for microwave condition. Here we have used ethyl acetoacetate, benzaldehyde and urea for optimization of reaction condition as shown in the (**Scheme-II**). Water as solvent fails to produce desired products under refluxing condition. Neat reaction condition, as yttrium nitrate is immiscible, is not a suitable reaction condition for microwave heating. The best result can be obtained in ethanol as reacting medium. The method requires an equimolecular mixture of ethyl acetoacetate, urea and benzaldehyde. Same reaction also carried out with different amount of catalyst loading in ethanol under microwave condition and found that only 2 mol % catalyst is sufficient for catalyzing the reaction to get 95 % isolated yield within 20 min. Whereas, under



Reaction condition	Time	Yield (%)
Refluxing in EtOH	3 h	87
MW Heating at 70°C in EtOH	10 min	92

Scheme-I: $Y(NO_3)_3$ catalyzed Biginelli reaction



Scheme-II: Optimization of reaction condition

similar reaction condition without catalyst the starting materials were remained unaltered.

In order to find out applicability to other substrates, various aldehydes and 1,3-diketo compounds were selected as shown in the Table-1. We have synthesized all the compounds (**1-10**) mentioned in the Table-1 under microwave heating condition in ethanol. Products **1-8** were identified by the comparison of observed melting point with the literature [13] and ^{1}H NMR in DMSO. The method is also applicable for aliphatic aldehyde (entry 8, 9). *o*-Vanillin also gives desired product and requires further purification. Formation of the compound **9** and **10** is confirmed by ^{1}H NMR and LCMS. Compound **9** shows a molecular ion peak at *m/z* 225.5 corresponds to the protonated molecular ion peak $[MH]^+$ of compound **9**. The presence of $[MH]^+$ and $[MH+2]^+$ in almost equal intensity in the mass spectrum of compound **10** certainly indicates the presence of one bromine atom in the product structure. The structure of **10** was further confirmed by ^{1}H NMR in DMSO.

Mechanistic study: Flokers and Jhonson [28] suggested mechanism of acid catalyzed formation of **1** from urea, benzaldehyde and ethyl acetoacetate. They suggested the possibility of involvement of the intermediate **11b**, **12** and less likely **13** by studying rate of formation of dihydropyrimidone **1** from this presynthesized intermediates (**Scheme-II**). They also pointed out the intermediate **13** is less favourable in the presence of high concentration acid catalyst.

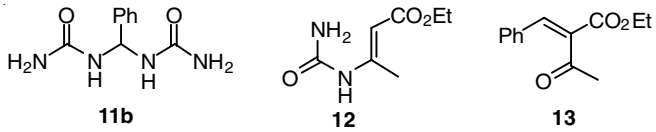
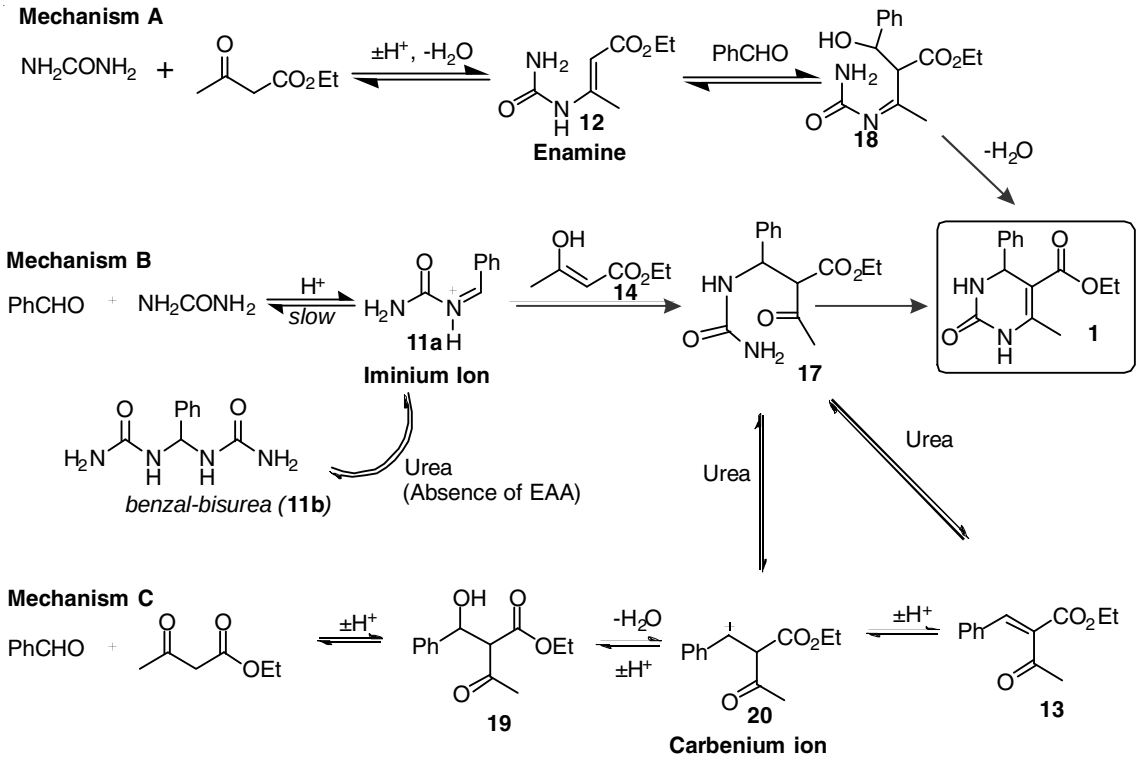


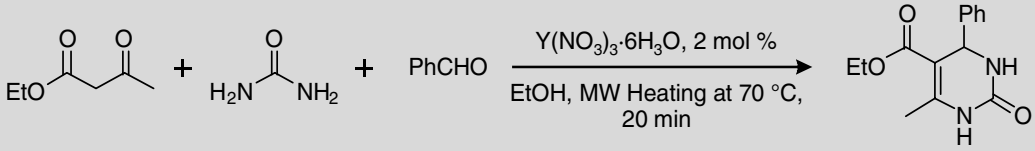
Fig. 1. Intermediate proposed by Folkers and Johnsons [28]

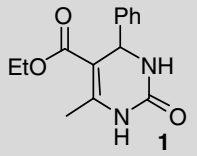
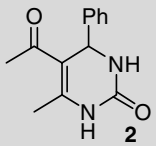
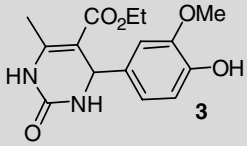
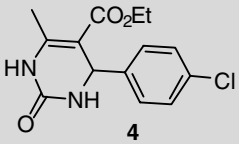
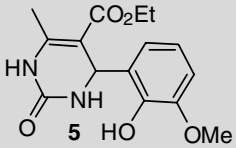
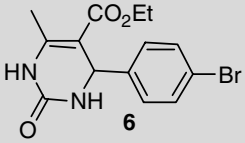
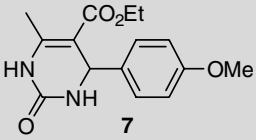
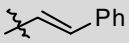
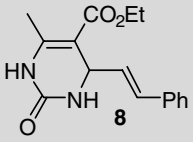
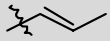
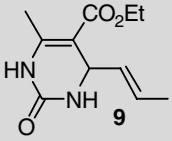
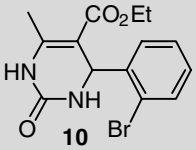
Mechanistic investigation was further detailed by Sweet and Fissekis [29]. Their proposed mechanism is based on the slow formation of carbenium ion **20** which leads to the Knoevenagel condensation product **13**. Product **1** formed after combing urea either with **20** or **13** giving **17** followed by dehydration (Mechanism C, **Scheme-III**). Furthermore reexamination of the mechanism of the Biginelli dihydropyrimidine synthesis carried out by Kappe [28]. They observed that there is no evidence of formation of aldol product **19** or **13** from the mixture ethyl acetoacetate and benzaldehyde in CD_3OH/HCl by ^{1}H NMR and ^{13}C NMR spectroscopy. Furthermore they detected benzal-bisurea (as originally proposed by Folkers and Johnson) from the mixture of benzaldehyde and urea (Mechanism B, **Scheme-III**) but not any intermediate **11a** or its hydrated form. According to Kappe, proposed mechanism for dihydropyridone formation involved slow formation of iminium ion **11a** which then rapidly combine with enol of ethyl acetoacetate (**14**). In absence of ethyl acetoacetate, **11a** rapidly attached with another molecule of urea forming benzal-bisurea **11b** and proved that the mechanistic proposal put forward by Folkers and Johnson in 1933 was correct [28].



Scheme-III: Acid catalyzed Beginelli reaction mechanism

TABLE-1
$Y(NO_3)_3 \cdot 6.H_2O$ CATALYZED 3,4-DIHYDROPYRIMIDINONES SYNTHESIS



Entry	R	Ar	Product	Time (min)	Yield (%)
1	OEt	Ph	 **1**	20	95
2	Me	Ph	 **2**	5	92
3	OEt	4-HO-3-MeOC_6H_3	 **3**	20	88
4	OEt	4-Cl-C_6H_4-	 **4**	20	97
5	OEt	2-HO-3-MeOC_6H_3-	 **5**	25	75
6	OEt	4-Br-C_6H_4-	 **6**	25	90
7	OEt	4-MeOC_6H_4-	 **7**	20	86
8	OEt		 **8**	20	65
9	OEt		 **9**	15	75
10	OEt	2-BrC_6H_4-	 **10**	20	67

All the reactions are carried out in 1.54 mmol scale, under microwave heating condition at 70 °C. Yield mentioned here are isolated yield.

In the present study, for mechanistic investigation we have carried out two separate experiments as mentioned in the Figs. 2 and 3. Liquid chromatography (Fig. 1a) of the reaction mixture containing benzaldehyde, urea and $Y(NO_3)·6H_2O$ comprised mainly benzal-biurea and its complex with Y(III) ion. The fraction eluted at 1.28 min (Fig. 2a) is assigned to the urea benzal-bisurea $PhCH(NHCONH_2)_2$ (**11b**) as detected in the mass spectrum (Fig. 2b) of the fraction. Fig. 2c shows the mass spectrum of the fraction eluted at 2.07 min, which is mainly comprised peaks of yttrium metal-containing ions. Formation of **11b** in the similar condition reveals that in the mechanism expected by Bhanage *et al.* [27] is essentially correct.

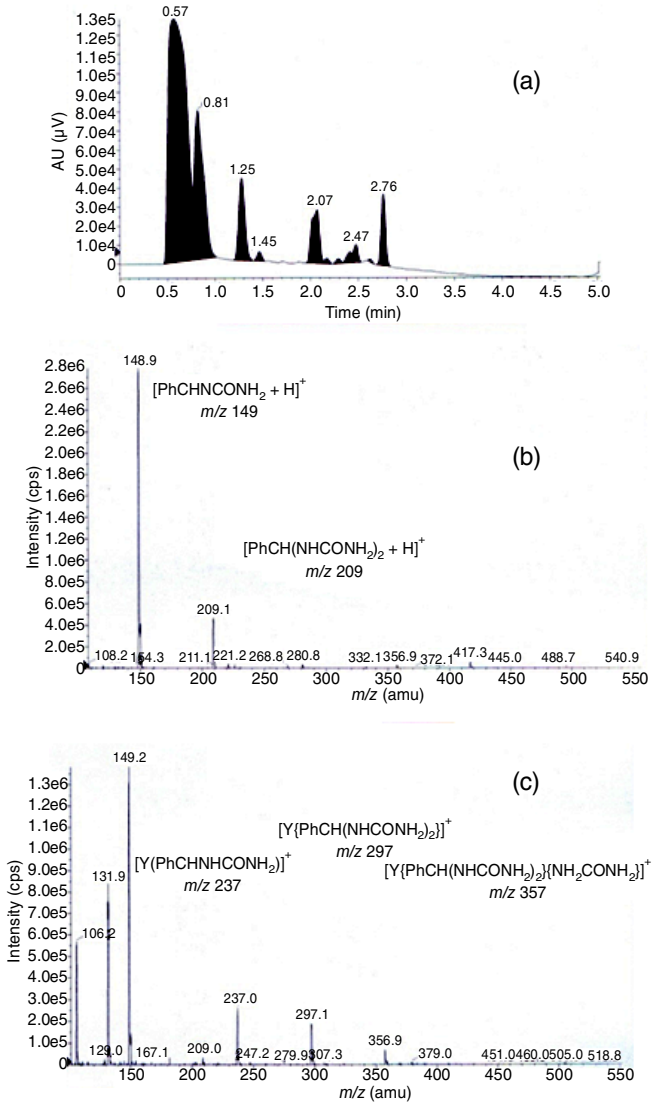


Fig. 2. LC-MS of the reaction mixture containing benzaldehyde and urea (equimolar) and 10 mol % yttrium nitrate in ethanol, heated at 70 °C under microwave for 20 min (a) Liqid chromatogram using column-ZORBAX EXT (4.6 × 50 mm, 5 m), NH_4OAc (10 mM):ACN::90:10. (b) Mass spectra of the fraction eluted at 1.28 min (c) Mass spectra of the fraction eluted at 2.07 min

In order to consider the carbenium ion **20** (**Scheme-II**) intermediate proposed by Sweet and Fissekis [29], another experiment was carried out by mixing equimolar ratio of ethyl acetoacetate and PhCHO in presence of 10 mol % $Y(NO_3)_3·6H_2O$ in ethanol and heated at 70 °C under microwave for 20 min and LC-MS was performed. The fraction eluted at 3.12 and 3.27 min (Fig. 2a) assigned to the complex of Y(III) ion with EAA [30]. *m/z* 366 is the $[M+1]^+$ ion of the complex $[Y(EAA-H)_2(H_2O)]^+$. Mass at *m/z* 131 is the protonated ethyl acetoacetate. Other fragmented ions are assigned as mentioned in the Table-2. As LC-MS do not support the formation of either of the intermediate **13**, **19** and **20** the mechanism suggested by Sweet and Fissekis [29] has excluded from the possibilities, at least for this $Y(NO_3)_3$ mediated Beginelli reaction. The fraction eluted at 2.8 min (Fig. 3b) is the hydrated complex of yttrium metal with the benzoic acid $[Y(H_2O)_6(PhCOO)_2]$ (calculated mass for $C_{14}H_{22}O_{10}Y$ +1 = 440.03, observed *m/z* = 440.3).

TABLE-2
MASS ANALYSIS OF THE FRACTION ELUTED AT 3.12 min

S. No.	Ion[a]	Calculated[b]	Observed *m/z*
1	$[Y(EAA-H)_2(H_2O)] + 1$	365 + 1 = 366	366.1
2	[Y(EAA-H)(EAA)] + 1	348 + 1 = 349	348.8
3	$\{[Y(EAA-H)_2]-OH\}$	330 + 1 = 331	331.1
4	{[Y(EAA-H)2]-EtO} + 1	302 + 1 = 303	303.0
5	$[Y(EAA-H)_2]$-EtO-OH	285	284.8
6	[Y(EAA-H) + 1	218 + 1 = 219	218.8
7	[Y(EAA-H)-EtO	173	172.8
8	$[Y(EAA-H)-EtO-H_2O$	155	155.2

[a]Y = Yttrium, EAA = Ethyl acetoacetate, EAA-H = Enolate of EAA.
[b]Calculated mass are monoisotopic mass.

Finally, the enamine mechanism (**Scheme-II**, Mechanism C) is not favourable as the equilibrium position for enamine (**12**) formation do not favour under the experimental condition. Formation of benzal-bisurea as major product in the mixture of PhCHO, urea and yttrium nitrate clearly suggest that the mechanism suggested by Bhanage *et al.* [27] is essentially correct.

Conclusion

In summary, we have investigated $Y(NO_3)_3·6H_2O$ as an efficient catalyst for the synthesis of dihydropyrimidinones from β-ketoester (or 1,3-diketo compounds), urea and aldehydes in ethanol under microwave heating. The method is very simple and efficient from the experimental point of view. We have also observed experimental evidence in favour of the mechanism proposed by Bhanage *et al.* [27].

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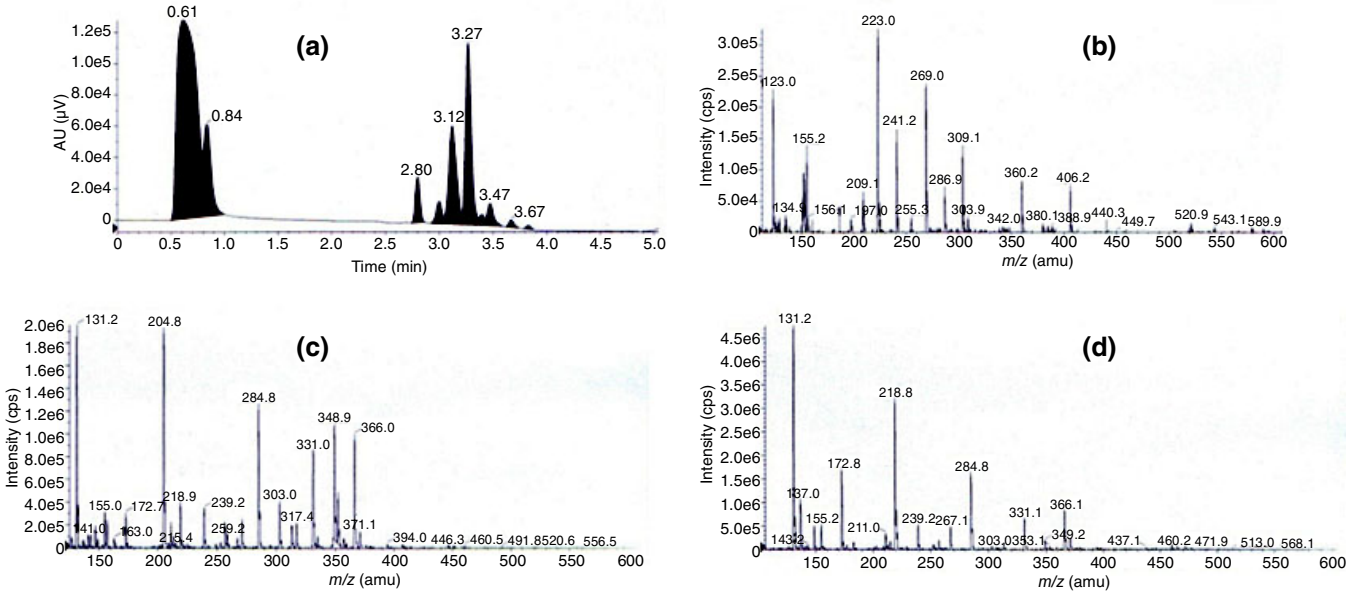

Fig. 3. LC-MS of the reaction mixture containing equimolar mixture ethyl acetoacetate and benzaldehyde in presence of 10 mol % yttrium nitrate, heated at 70 °C under microwave for 20 min in ethanol. (a) Liquid chromatogram using ZORBAX EXT (4.6 × 50 mm, 5 m) column, NH_4OAc (10 mM):ACN::90:10. (b) Mass spectra of the fraction eluted at 2.80 min. (c) Mass spectra of the fraction eluted at 3.12 min. (c) Mass spectra of the fraction eluted at 3.27 min

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