

One-pot green procedure for Biginelli reaction catalyzed by novel task-specific room-temperature ionic liquids

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Abstract

Cheap and reusable task-specific ionic liquids that bear an alkanesulfonic acid group in an acyclic trialkylammonium cation were found to be effective catalysts for synthesizing 3,4-dihydropyrimidine-2-(1*H*)-ones via the one-pot three-component Biginelli reaction. The satisfactory results were obtained with good yields, short reaction time and simplicity in the experimental procedure. The catalysts could be recycled and reused six times without noticeably decrease in the catalytic activity.

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Keywords: Biginelli reaction; Dihydropyrimidinones; Brønsted-acidic ionic liquid

1. Introduction

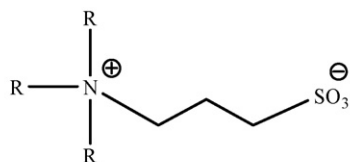
3,4-Dihydropyrimidine-2-(1*H*)-ones (DHPMs) and their derivatives are pharmacologically important compounds because of the promising biological activities, including antiviral, antibacterial, antitumor, and antihypertensive agents, α_{1a} adrenergic antagonists and neuropeptid Y (NPY) antagonists, and furthermore, these compounds have emerged as the integral backbones of several calcium channel blockers [1–6]. Some marine alkaloids containing the dihydropyrimidine core unit show interesting biological properties; batzelladine alkaloids have been found to be potent HIV gp-120-CD4 inhibitors [7–9]. The most simple and straightforward procedure, reported by Biginelli more than 100 years ago [10,11], involves the three-component acid catalyzed condensation in one-pot, but this reaction suffers from the harsh conditions, long reaction times and frequently low yields.

Recently, many synthetic methods for preparing these compounds have been developed to improve and modify this reaction by microwave [12–16] and ultrasound irradiation [17–19] and by using Lewis acids as well as Brønsted acids promoters. FeCl_3 /tetracthyl orthosilicate [20], triflates [21,22], metal bromide [23,24], polyoxometalate [25], strontium(II) nitrate [26],

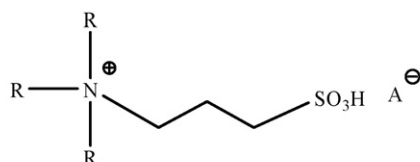
cerium(III) chloride [27], $\text{Li}(\text{OTf})$ [28], $\text{Ln}(\text{OTf})_3$ [29], heteropoly acids [30–34], ion exchange resins, polymer based solid acid [35,36], L-proline [37,38], chiral phosphoric acid [39], and TMSCl [40] were used to replace the strong protic acid used in the classic Biginelli reaction, and the search for the new readily available and green catalysts is still being actively pursued.

In recent years, task-specific room-temperature ionic liquids (TSILs) have emerged as a powerful alternative to conventional molecular organic solvents or catalysts due to their particular properties, such as undetectable vapour pressure, wide liquid range, as well as the ease of recovery and reuse [41–50]. The TSILs have also been used as catalysts for Biginelli reaction [51–55]. Peng and Deng [51,52] synthesized DHPMs in the presence of ionic liquid BMImBF_4 or BMImPF_6 , Shaabani and Rahmati [53] used room-temperature ionic liquid 1,1,3,3-tetramethylguanidinium trifluoroacetate as catalyst, Li et al. [54] reported ionic liquid (BMImSac) as catalyst, Zheng et al. [55] synthesized and used ionic liquid CMIImHSO_4 as catalyst for Biginelli reaction. However, TSILs with imidazole as the cation are relatively expensive, which hinders their industrial applications. Furthermore, typical ionic liquids consist of halogen containing anions (such as $[\text{PF}_6]^-$, $[\text{BF}_4]^-$, $[\text{CF}_3\text{SO}_3]^-$ and $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$) which in some regard limit their “greenness” [56–58]. Therefore, it is necessary to synthesize less expensive and halogen-free TSILs. Herein, we synthesized some SO_3H -functional Brønsted-acidic halogen-free TSILs that bear an alkanesulfonic acid group in an acyclic trialkylammonium

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TMAPS: R=Me; TEAPS: R=Et; TBAPS: R=n-Bu;



TSILs a: R=Me; TSILs b: R=Et; TSILs c: R=n-Bu;

A: HSO₄

Fig. 1. Structure of the TMAPS and TSILs.

cation [59] (Fig. 1), and subsequently used them as catalysts for the one-pot three-component Biginelli reaction. (Scheme 1).

2. Experimental

2.1. Materials and methods

Melting points were determined on a Perkin-Elmer differential scanning calorimeter or a Thomas Hoover apparatus and uncorrected. The IR spectra were run on a Nicolette spectrometer (KBr). ¹H NMR spectra were recorded on a Bruker DRX300 (300 MHz) spectrometer and ¹³C NMR spectra on a Bruker DRX300 (75.5 MHz) spectrometer. Elemental analyses were recorded on a Perkin-Elmer C spectrometer. Mass spectra were obtained with an automated Finnigan Trace Ultra-Trace DSQ GC/MS spectrometer. All chemicals (AR grade) were commercially available and used without further purification.

2.2. Synthesis of 3-tri-n-butylammoniopropanesulfonate (TBAPS)

Tributylamine (0.11 mol) and 1,3-propanesulfone (0.10 mol) were dissolved in 1,2-dichloroethane (20 mL) and allowed to stir under nitrogen for 24 h at 35–40 °C. A white precipitate was formed, which was filtered and washed with petroleum ether. The product was recrystallized from a mixture of chloroform, petroleum ether and acetone. White solid products were obtained in 97% yield, mp 172–173 °C.

2.3. Synthesis of 3-triethylammoniopropanesulfonate (TEAPS)

The same process as TBAPS was followed except that the reaction was carried out for 12 h at 35–40 °C. White solid products were obtained in 95% yield, mp 290–292 °C dec.

2.4. Synthesis of 3-trimethylammoniopropanesulfonate (TMAPS)

The same process as TBAPS was followed except that the reaction was carried out for 2 h at 55–60 °C. White solid products were obtained in 92% yield, mp 344–346 °C dec with darkening at 330 °C.

2.5. Synthesis of SO₃H-functional Brønsted-acidic TSILs

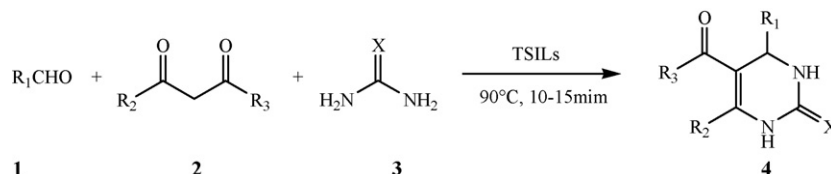
The mixture of equal molar 3-trialkylammoniopropanesulfonate (TAAPS) and acid solutions was mixed and stirred for 24 h at 40–80 °C. Then, the mixed solution was dried in a vacuum at 100 °C to remove water. The produced TSILs were washed repeatedly with diethyl ether to remove unreacted material and dried in a vacuum again.

2.5.1. TSILs a

TSILs a. IR (KBr, ν/cm^{-1}): 3523.47, 3039.71, 2953.36, 2353.79, 1477.48, 1372.97, 1234.71, 1165.38, 1052.82, 1028.36, 879.28, 846.85, 745.95, 578.71. ¹H NMR (D₂O, δ): 1.99 (m, 2H, –CH₂–), 2.73 (t, 2H, –N–CH₂–), 2.90 (s, 9H, –CH₃), 3.22 (t, $J=7.8$ Hz, 2H, –CH₂–S). ¹³C NMR (D₂O, δ): 65.00, 53.94, 47.63, 18.85. MS (m/z): 279.05 (M^+), 182.14 (100). Anal. Calcd. For C₆H₁₇NO₇S₂: C, 25.80; H, 6.13; N, 5.01; Found: C, 25.53; H, 6.14; N, 4.96. Melting points determined by DSC was –12 °C.

2.5.2. TSILs b

TSILs b. IR (KBr, ν/cm^{-1}): 3525.65, 3038.62, 2955.17, 2355.79, 1480.12, 1374.33, 1230.27, 1160.73, 1050.55, 1030.06, 877.90, 845.39, 745.25, 577.03. ¹H NMR (D₂O, δ): 1.12 (t, 9H, –CH₃), 1.97 (m, 2H, CH₂–CH₂–CH₂), 2.85 (t, 2H, –N–CH₂), 3.16 (t, 6H, –N–CH₂–), 3.22 (t, 2H, –CH₂–S). ¹³C NMR (D₂O, δ): 56.00, 52.95, 48.34, 18.93, 8.04. MS (m/z): 321.05 (M^+), 322.05, 320.15, 194.05 (100). Anal. Calcd. For C₉H₂₃NO₇S₂: C, 33.63; H, 7.21; N, 4.36; Found: C, 33.45; H, 7.24; N, 4.21. Melting points determined by DSC was –9 °C.



Scheme 1.

2.5.3. TSILs c

TSILs c. IR (KBr, ν/cm^{-1}): 3528.07, 3035.98, 2951.23, 2350.45, 1480.11, 1370.87, 1236.90, 1162.19, 1057.54, 1023.07, 871.48, 841.97, 756.76, 589.52. ^1H NMR (D_2O , δ): 0.78 (t, 9H, $-\text{CH}_3$), 1.18 (m, 6H, $-\text{CH}_2-\text{CH}_3$), 1.49 (s, 6H, $-\text{CH}_2-\text{CH}_2\text{CH}_3$), 1.96 (m, 2H, $\text{CH}_2-\text{CH}_2-\text{CH}_2$), 2.77 (t, 2H, $-\text{N}-\text{CH}_2-$), 3.06 (t, 6H, $-\text{N}-\text{CH}_2-$), 3.21 (t, 2H, $-\text{CH}_2-\text{S}$). ^{13}C NMR (D_2O , δ): 58.49, 50.66, 48.42, 23.93, 20.36, 19.16, 14.46. MS (m/z): 405.29 (M^+), 406.28, 404.28 (100). Anal. Calcd. For $\text{C}_{15}\text{H}_{35}\text{NO}_7\text{S}_2$: C, 44.42; H, 8.70; N, 3.45; Found: C, 44.27; H, 8.71; N, 3.28. Melting points determined by DSC was -7°C .

2.6. General procedure for one-pot three-component Biginelli reaction

Benzaldehyde 10 mmol, ethyl acetoacetate 10 mmol, urea 12 mmol, TSILs 0.2 mmol, and 15 mL H_2O were heated to 90°C while being stirred for 10–15 min, then cooled and left overnight. The products were filtered out, washed with ice-cold water, and then recrystallized with alcohol to afford pure 3,4-dihydropyrimidin-2-(1*H*)-ones **4**. The products were identified by IR, ^1H NMR, and physical data (mp) by comparison with those reported in the literatures.

3. Results and discussion

For the beginning of this study, the efficacy of the catalysts TSILs was tested for benzaldehyde, ethyl acetoacetate, and urea under different conditions (Table 1). It showed that no desirable product could be detected when a mixture of benzaldehyde, ethyl acetoacetate and urea (mole rate 1:1:1.2) was heated at 90°C for 10 min in the absence of TSILs (entry 1), which indicated that the catalysts should be absolutely necessary for the Biginelli reaction. Then, three-component Biginelli condensation of benzaldehyde, ethyl acetoacetate and urea in stoichiometric ratio was investigated with different amounts of TSILs (entries 2–11). It is clear that the yield was increased with the adding of TSILs and the optimal amounts of TSILs a was 0.2 mmol (entry 3), amount to 2 mol% of reactant **1**. Higher amount of the catalysts did not improve the result to a greater extent. For the

Table 1
Synthesis of DHPM under different conditions^a

Entry	Catalyst (mmol)	Isolated yield (%)
1	0	0
2	TSILs a (0.1)	86
3	TSILs a (0.2)	94
4	TSILs a (0.3)	94
5	TSILs a (0.4)	95
6	TSILs b (0.1)	76
7	TSILs b (0.2)	89
8	TSILs b (0.3)	90
9	TSILs c (0.1)	73
10	TSILs c (0.2)	82
11	TSILs c (0.3)	82
12	H_2SO_4 (0.2)	43

^a 10 mmol benzaldehyde, 10 mmol ethyl acetoacetate, 12 mmol urea, 0.2 mmol [TMPSA]HSO₄, 90°C , 10 min.

Table 2
Reusing of the ionic liquid TSILs a^a

Run	Isolated yield (%)
1	94
2	93
3	94
4	92
5	91
6	91

^a 10 mmol benzaldehyde, 10 mmol ethyl acetoacetate, 10 mmol urea, 0.2 mmol TSILs a, 90°C , 10 min. After separation of the product by filtration, the recovered solvent containing [TMPSA]HSO₄ and excess urea was reused directly.

purpose of comparison, the sulfuric acid as catalyst was tested for the Biginelli reaction under the same conditions and a yield of 43% was obtained (entry 12).

When optimizing the reaction conditions, the recycling performance of TSILs a was investigated in the reaction of benzaldehyde, ethyl acetoacetate and urea. After the separation of the products, the filtrate containing the catalyst and the excess urea was reused in the next run without further purification. A mixture of benzaldehyde, ethyl acetoacetate and urea (mole rate 1:1:1) was added to the filtrate and stirred under the same conditions. The data listed in Table 2 showed that the TSILs a could be reused six times without lowering the catalytic activity. Compared with the traditional solvents and catalysts, the easy recycling performance is an attractive property of the TSILs for the environmental protection and economic reasons.

Results on the Biginelli reaction catalyzed by TSILs a are presented in Table 3. It can easily be seen that the condensation of a series of aldehydes, 1,3-dicarbonyl compounds and urea or thiourea catalyzed by TSILs a as an environmentally

Table 3
Ionic liquid TSILs a catalyzed Biginelli reaction^a

Entry	R ₁	R ₂	R ₃	X	Time (min)	Yield ^b (%)
1	C_6H_5	Me	OEt	O	10	94
2	C_6H_5	Me	OEt	S	15	83
3	C_6H_5	Me	OMe	O	10	93
4	C_6H_5	Me	OMe	S	15	78
5	C_6H_5	Me	Me	O	10	93
6	C_6H_5	Me	Me	S	15	72
7	4- $\text{CH}_3\text{O}-\text{C}_6\text{H}_4$	Me	OEt	O	10	90
8	4- $\text{CH}_3\text{O}-\text{C}_6\text{H}_4$	Me	OMe	O	10	91
9	4- $\text{CH}_3\text{O}-\text{C}_6\text{H}_4$	Me	Me	O	10	92
10	4- $\text{NO}_2-\text{C}_6\text{H}_4$	Me	OEt	O	10	88
11	4- $\text{NO}_2-\text{C}_6\text{H}_4$	Me	OMe	O	10	88
12	4- $\text{NO}_2-\text{C}_6\text{H}_4$	Me	Me	O	10	84
13	4- $\text{Cl}-\text{C}_6\text{H}_4$	Me	OEt	O	10	92
14	4- $\text{Cl}-\text{C}_6\text{H}_4$	Me	OMe	O	10	90
15	3,4-(OMe) ₂ - C_6H_3	Me	OEt	O	10	82
16	2-OH- C_6H_4	Me	Me	O	10	87
17	2-Furyl	Me	OEt	O	10	86
18	C_6H_5	Ph	OEt	O	10	89

^a Reaction conditions: benzaldehyde 10 mmol, molar ratio of benzaldehyde, acetoacetate and urea (thiourea) was 1:1:1.2, 0.2 mmol TSILs a, 90°C . All products were characterized by IR, ^1H NMR, and their mp were in comparison with that of previous literatures.

^b Isolated yield.

benign ionic liquid at 90 °C and reaction completed within 10–15 min. Compared to the classical Biginelli method, one additional important feature of the present protocol is the ability to tolerate variation in all three components simultaneously.

Besides the β -ketoester, β -diketone (entries 5, 6, 9, 12, and 16) can also be employed without any decrease in yields. Thiourea was used as one of the substrates to provide the corresponding DHPMs in reasonable yields (entries 2, 4, and 6). Most importantly, many of the pharmacological relevant substitution patterns on the aromatic ring could be introduced without any interruption in efficiency. Aromatic aldehydes carrying either electron-donation or electron-withdrawing substituents afforded good yields of DHPMs in high purity. Another important feature of this procedure is the survival of variety of functional groups such as ethers, esters, nitro, hydroxyl, and halides under the present reaction conditions.

According to the mechanism suggested by Folkers, Johnson and Kappe, the reaction may proceed through imine formation from the aldehyde and urea, subsequent addition of the carbanion derived from 1,3-dicarbonyl compounds to the imine followed by cyclodehydration to afford DHPMs. The hydrogen ion, donated by TSILs a–c, not only helps the dehydration but also benefits the enolization of 1,3-dicarbonyl compounds to form enolate intermediate.

4. Conclusion

In summary, an efficient protocol for one-pot three-component condensation of Biginelli reaction catalyzed by ionic liquids was developed. The short reaction time, easy synthetic procedure, free of organic solvent, simple work-up in isolation of the products in good yield with high purity, and recyclability of the catalysts are features of this new procedure.

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