Research Article

1-Methyl-3-(2-(sulfooxy)ethyl)-1H-imidazol-3-ium Chloride as a New and Green Ionic Liquid Catalyst for One-Pot Synthesis of Dihydropyrimidinones under Solvent-Free Condition

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Received 8 June 2012; Revised 11 September 2012; Accepted 15 September 2012

Academic Editor: Francisco José Hernández Fernández

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An efficient and simple method for the preparation of 1-methyl-3-(2-(sulfooxy)ethyl)-1H-imidazol-3-ium chloride {(MSEI)Cl} as an acidic ionic liquid is described. One-pot multicomponent condensation of 1,3-dicarbonyl compounds, urea/thiourea and aldehydes at 80°C affords the corresponding compounds in high yields and in short reaction times by using (MSEI)Cl.

1. Introduction

First reported for multicomponent reaction involves a three-component, one-pot condensation of an aldehyde, α,β -ketoester, and urea under strongly acidic conditions discovered by Biginelli in 1893 [10]. In the past few decades, interest in this reaction has increased dramatically since dihydropyrimidinones have a wide range of biological activities, acting as calcium channel antagonists, anti-hypertensive, anti-bacterial and anti-inflammatory agents, while also possessing cytotoxic activity [11–17]. In order to improve the efficiency of Biginelli reaction, a variety of catalysts have been reported which of them $H_4PMo_{11}VO_{40}$, [18], Dowex-50W [19], $H_3PW_{12}O_{40}/SiO_2$ [20], $MgBr_2$ [21], polymer-supported 4-aminofomoyldiphenylammonium triflate [22], $NaHSO_4/SiO_2$ [23], $FeCl_3$ [24], $ZrCl_4$ [25], $Cu(OTf)_2$ [26], $Bi(OTf)_3$ [27], ytterbium triflate [28], NH_2SO_3H [29], 12-Molybdophosphoric acid [30], natural HEU type zeolite [31], $Sr(OTf)_2$ [32], covalently anchored sulfonic acid onto silica [33], $ZrOCl_2 \cdot 8H_2O$ [34], silica triflate [35], $Fe(HSO_4)_3$ [36], TCICA [37], PPh_3 [38], CaF_2 [39], [bmim] BF_4 -immobilized Cu(II) acetylacetonate [40], [bmim] $[FeCl_4]$ [7], ionic liquid-sunder ultrasound irradiation [41], and melamine trisulfonic acid [42] are examples. Ionic liquids (ILs), which have been widely promoted as green solvents, are attracting much attention for applications in many fields of chemistry and industry due to their chemical and thermal stability, low

vapor pressure, and high-ionic-conductivity properties. Over the last few years, ILs have been popularly used as solvents for organic synthesis, catalysis, and also been used as media for extraction processes [43, 44]. But some of the mentioned methods encounter drawbacks such as the requiring expensive reagents, long reaction times, low yields of the products and tedious workup. The advantages of the present procedure are simplicity of operation, short reaction times, inexpensive reagents, green condition, and the high yields of products.

We synthesized the bronsted acidic ionic liquid 1-methyl-3-(2-(sulfooxy)ethyl)-1H-imidazol-3-ium chloride [45] as an efficient and reusable catalyst for the synthesis of DHPMs derivatives.

2. Experimental

IR spectra of the compounds were obtained on a PerkinElmer spectrometer version 10.03.06 using a KBr disk. The 1H nuclear magnetic resonance (1H NMR) spectra were recorded on a Bruker AQS 400 Avance instrument at 400 MHz in dimethyl sulfoxide ($DMSO-d_6$) using tetramethylsilane as an internal standard. The progress of reaction was followed with thin-layer chromatography (TLC) using silica gel SILG/UV 254 and 365 plates. All the products are known compounds and were characterized by comparing the IR, 1H NMR, and ^{13}C NMR spectroscopic data and their melting points with the literature values.

FIGURE 1

FIGURE 2: Comparison IR spectrum of ionic liquid 3, bronsted acidic ionic liquid 4.

SCHEME 2: Synthesis of 3,4-dihydropyrimidin-2(1H)-ones and -thiones.

TABLE 1: Temperature and time effect on dihydropyrimidinones synthesis.

$\text{PhCHO} + \text{H}_2\text{N}-\overset{\text{O}}{\parallel}\text{C}-\text{NH}_2 + \text{Me}-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{Me} \xrightarrow{\text{BAIL}} \text{Me}-\overset{\text{O}}{\parallel}\text{C}-\text{C}(\text{Ph})=\text{C}(\text{Me})-\text{NH}-\overset{\text{O}}{\parallel}\text{C}-\text{NH}$			
Entry	Temperature (°C)	Time (min)	Yield (%)
1	r.t.	90	36
2	50	90	45
3	80	30	93
4	100	30	91
5	120	30	90

TABLE 2: Dihydropyrimidinones synthesis catalyzed by Brønsted acidic ionic liquid (BAIL).

Entry	R ₁	R ₂	X	Time (min)	Yield (%)	M.p. (°C)	
						Found	Reported
1	Ph	Me	O	30	93	231–233	235–236 [1]
2	4-OH-C ₆ H ₄	Me	O	30	95	254–256	256–258 [2]
3	4-Me-C ₆ H ₄	Me	O	30	92	231–232	228–229 [1]
4	4-MeO-C ₆ H ₄	Me	O	30	90	175–177	177–179 [2]
5	4-Cl-C ₆ H ₄	Me	O	30	92	223–224	224–226 [3]
6	4-NO ₂ -C ₆ H ₄	Me	O	45	85	227 (dec)	229 (dec) [2]
7	3-NO ₂ -C ₆ H ₄	Me	O	45	82	246–248	248–250 [1]
8	Ph	OEt	O	45	88	203–205	201–202 [1]
9	2-OH-C ₆ H ₄	OEt	O	45	92	200–202	201–203 [3]
10	4-Me-C ₆ H ₄	OEt	O	45	90	170–172	170–171 [1]
11	4-MeO-C ₆ H ₄	OEt	O	45	87	198–200	199–201 [4]
12	4-Cl-C ₆ H ₄	OEt	O	45	86	211–213	209–210 [1]
13	3-NO ₂ -C ₆ H ₄	OEt	O	60	78	225–227	226–227 [4]
14	Ph	Me	S	75	81	230–231	232–233 [5]
15	2-OH-C ₆ H ₄	Me	S	75	83	239–241	242–243 [3]
16	4-Me-C ₆ H ₄	Me	S	75	80	221–223	222–224 [5]
17	4-NO ₂ -C ₆ H ₄	Me	S	90	73	106–107	108–110 [6]
18	Ph	OEt	S	105	75	206–208	208–209 [5]
19	4-Me-C ₆ H ₄	OEt	S	105	72	193–194	193–194 [1]
20	4-NO ₂ -C ₆ H ₄	OEt	S	120	70	214–216	209–212 [3]

TABLE 3: Comparison of catalytic ability of catalysts.

Entry	Catalyst	Time (min) condition	Yield (%) (reference)
1	[BMIM]FeCl ₄	120	90
		90°C, s.f. ^a	[7]
2	[HMIM]Tfa	45	90
		50°C, s.f.	[4]
3	[BMIM]BF ₄	30	99
		100°C, s.f.	[8]
4	[HMIM]HSO ₄	90	96
		80°C, s.f.	[9]
5	[MSEI]Cl	30	93
		80°C, s.f.	—

^as.f.: solvent free condition.

SCHEME 3: Mechanism of synthesis of 3,4-dihydropyrimidin-2(1H)-ones and -thiones.

TABLE 4: Formation of DHMP in different solvents and comparison with solvent-free condition.

$\text{PhCHO} + \text{H}_2\text{N}-\text{C}(=\text{O})-\text{NH}_2 + \text{Me}-\text{C}(=\text{O})-\text{CH}_2-\text{C}(=\text{O})-\text{Me} \xrightarrow{\text{BAIL}} \text{Product}$				
Entry	Solvent	Time (h)	Temperature (°C)	Yield (%)
1	Ethanol	4	Refluxing	81
2	H ₂ O	4	Refluxing	<20
3	MeCN	4	Refluxing	70
4	CH ₂ Cl ₂	8	Refluxing	38
5	Solvent-free	0.5	80	93

TABLE 5: Recovery of catalyst.

Number	Reaction	Yield (%)
1	First	91
2	Second	91
3	Third	90
4	Forth	88

2.1. Preparation of Bronsted Acidic Ionic Liquid. 1-Methylimidazole **1** (4.1 g, 50 mmol) and 2-chloroethanol **2** (4.02 g, 50 mmol) were added in a flask containing 10 mL of CHCl₃, and the mixture was refluxed for 8 h and removed CHCl₃ under vacuum. Unreacted 1-methylimidazole or 2-chloroethanol was extracted with ether (3 × 10 mL) to give 1-methyl-3-(2-hydroxyethyl) imidazolium chloride (yield 95%). IR spectrum of compound **3**: OH (3200–3600 cm⁻¹), C=C (1450, 1575 cm⁻¹), and C=N (1643 cm⁻¹) (Figure 2).

A stoichiometric amount of 97% chlorosulfonic acid (3.4 mL, 50 mmol) in CCl₄ (10 mL) was added dropwise to

compound **3** over a period of 45–60 min at 0°C, and HCl gas was evolved in an alkali trap immediately (Scheme 1). The mixture was washed with CCl₄ (3 × 10 mL) to remove the unreacted chlorosulfonic acid (yield 92%). IR spectrum of compound **4**: OH (3200–3600 cm⁻¹), C=C (1440, 1579 cm⁻¹), C=N (1648 cm⁻¹), S=O (1019 cm⁻¹), and S–O (623 cm⁻¹) (Figures 1 and 2) [44].

2.2. General Procedure for the Preparation of DHPMs. A mixture of an aromatic aldehyde (1 mmol), β-dicarbonyl (1 mmol), urea/thiourea (1.5 mmol), and catalyst (50 mg) was finely mixed together in a test tube at 80°C for the times reported in (Table 2). During the reaction process, a solid product spontaneously formed. The completion of the reaction was monitored by TLC. The reaction mixture was cooled to room temperature and then cold water (20 mL) was added to the reaction mixture and stirred for 10–15 min. During this time, crystals of the product formed which were collected by filtration and dried and then recrystallized

from ethanol to afford the pure product. The results are summarized in Table 2. The aqueous layer (including BAIL) was separated, and its solvent was evaporated to obtain pure BAIL. The recycled catalyst was used for the next run under identical reaction conditions.

3. Results and Discussion

The one-pot synthesis of 3,4-dihydropyrimidin-2(1H)-ones and -thiones was achieved by the three-component condensation of aldehydes, dicarbonyl, and urea or thiourea in presence of bronsted acidic ionic liquid is conducted at 80°C, and the results are summarized in Table 1. The procedure gives products in good yields, short reaction times and avoids the use of organic solvents (handling, cost, safety, pollution) (Table 4). Environmental friendly ionic liquid afforded a valuable alternative to promote a numerous efficient catalytic systems that have already been proposed for the achievement of DHPMs. As long as, the reaction rate and the yields are depending on electron donating/withdrawing effect of the groups on the benzene ring in benzaldehydes. Aryl aldehydes containing electron-donating substituent gave excellent yields of the products in a shorter reaction time. The mechanism of the Biginelli reaction established by Kappe [6] proposed that the key step in this cyclocondensation process should involve the formation of N-acyliminium ion intermediate (Scheme 3).

According at Table 2 the using of thiourea and ethylacetoacetate increased reaction time, and also the using of thiourea reduces the efficiency of Biginelli reaction. Thiourea stability of negatively charged than urea and low nucleophiles property of thiourea than urea at intermediate State. The catalyst is reusable and can be applied several times without any decrease in the yield of the reaction. As it can be seen from Table 3, (MSEI)Cl as a catalyst afforded the good results with respect to the another ionic liquid catalysts.

4. Conclusions

In summary, we have developed the use of bronsted acidic ionic liquid 1-methyl-3-(2-(sulfooxy)ethyl)-1H-imidazol-3-ium chloride as an inexpensive, easy to handle, noncorrosive and environmentally benign catalyst for the Biginelli reaction from an aldehyde, a β -dicarbonyl, and urea or thiourea. The advantages of the present procedure are simplicity of operation, very short reaction times compared with other procedures for the preparation of dihydropyrimidinones derivatives, and the high yields of products. In this reaction the catalyst can be were easily recyclable after removing starting materials and water (Table 5).

Acknowledgments

The authors gratefully acknowledge partial support of this work by Payame Noor University (PNU) of Ilam.

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