J. Iran. Chem. Soc., Vol. 7, No. 3, September 2010, pp. 646-651.

JOURNAL OF THE
Iranian
Chemical Society

3-Methyl-1-Sulfonic Acid Imidazolium Chloride as a New, Efficient and Recyclable Catalyst and Solvent for the Preparation of *N*-Sulfonyl Imines at Room Temperature

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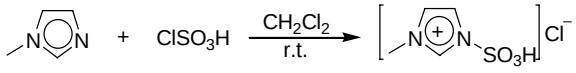
(Received 9 August 2009, Accepted 11 September 2009)

New Brønsted acidic ionic liquid, 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl} was used as an efficient, green and reusable catalyst and solvent for the synthesis of *N*-sulfonyl imines *via* the condensation of sulfonamides with aldehydes as well as isatin. The reactions proceeded at room temperature and the title compounds were obtained in high to excellent yields and in relatively short reaction times.

Keywords: Brønsted acidic ionic liquid, 3-Methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl}, *N*-Sulfonyl imine, Sulfonamide, Aldehyde

INTRODUCTION

Ionic liquids are the subject of considerable current interest as benign reaction media in organic synthesis because of their unique properties such as non-volatility, non-flammability, safety, recyclability and ability to dissolve a wide range of materials [1]. During the past decade, a variety of ionic liquids have been demonstrated as efficient and practical alternatives to organic solvents for many important organic transformations [1]. These green solvents have also been used as catalysts in various organic reactions [2]. As part of our ongoing research to extend the application of acidic catalysts and reagents in organic synthesis [3], we have synthesized 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl}as a new Brønsted acidic ionic liquid, from the reaction of 1-methylimidazole with chlorosulfonic acid at room temperature (Scheme 1). We believe that this novel ionic liquid can be applied as a catalyst as well as solvent for different organic transformations. We found out that the synthesis of *N*-sulfonyl imines from sulfonamides and carbonyl compounds can be efficiently achieved in [Msim]Cl. This is the first report of the application of this novel ionic liquid in organic synthesis.



Scheme 1

Imines bearing electron-withdrawing *N*-substituents are useful intermediates in organic synthesis [4]. Among them, *N*-sulfonyl imines are the center of attention for organic chemists because the sulfonyl moiety has proven to be a powerful activating group of the C=N bond in these compounds. As a consequence, *N*-sulfonyl imines have been widely used in organic synthesis [5]. Furthermore, they are excellent substrates in nucleophilic additions [6], reductions [7], aza Diels-Alder reactions [8], aziridine [9] and oxaziridine

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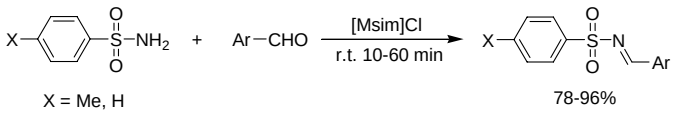
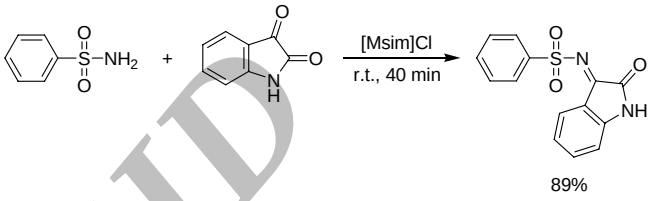
synthesis [10], as well as ene reactions [11]. Several routes toward the synthesis of *N*-sulfonyl imines have been developed *via* Lewis and Brønsted acid catalyzed reactions of sulfonamides with aldehyde precursors [12], rearrangement of oxime *o*-sulfinates [13], tellurium mediated reaction of aldehydes with chloramines T by utilization of the *in situ* generated *N*,*N'*-ditosyltellurodiimide [14], application of *N*-sulfinyl sulfonamides instead of sulfonamides to generate sulfonyl imine *in situ via* a [2+2] cycloaddition and extrusion of sulfur dioxide [15], generation of sulfonamidosulfones and basic elimination [16], and catalyzed isomerization or rearrangement of *N*-sulfonyl aziridines [17]. However, most of the reported methods suffer from drawbacks like long reaction times, unsatisfactory yields, harsh conditions, the use of expensive reagents, the use of multi-steps and cumbersome procedures, and no agreement with the green chemistry protocols. Moreover, it is worth noting that the preparation of *N*-sulfonyl imines under mild reaction conditions has been scarcely reported in the literature [12f,i]. Therefore, development of an efficient, one-step, mild and environmentally friendly procedure for the synthesis of *N*-sulfonyl imines is in order.

Considering the above mentioned routs for the synthesis in question, herein we report a new procedure in which an imidazolium salt as an ionic liquid has been used as a recyclable catalyst and media for the preparation of *N*-sulfonyl imines at room temperature (Schemes 2 and 3).



Scheme 2



Scheme 3

EXPERIMENTAL

Chemical and Apparatus

All chemicals were purchased from Merck or Fluka Chemical Companies. All compounds were identified by comparison of their melting points and/or NMR data with those reported for the authentic samples. The ^{1}H NMR (250 MHz) and ^{13}C NMR (62.9 MHz) were run on a Bruker Avance DPX-250, FT-NMR spectrometer (δ in ppm). Microanalyses were performed on a Perkin-Elmer 240-B microanalyzer. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

Preparation of Ionic Liquid [Msim]Cl

A round-bottomed flask (100 ml) was charged with 1-methylimidazole (0.410 g, 5 mmol) in dry CH_2Cl_2 (50 ml), and then chlorosulfonic acid (0.605 g, 5.2 mmol) was added dropwise over a period of 5 min at room temperature. After the addition was completed, the reaction mixture was stirred for 20 min, halted for 5 min, and the CH_2Cl_2 was decanted. The residue was washed with dry CH_2Cl_2 (3 × 50 ml) and dried under vacuum to give [Msim]Cl as a viscous colorless oil in 92% yield, 0.912 g.

General Procedure for the Preparation of *N*-Sulfonyl Imines and Recycling of [Msim]Cl

To a mixture of compounds consisting of sulfonamide (2 mmol) and carbonyl compound (2 mmol) in a round-bottomed flask (10 ml) was added [Msim]Cl (0.792 g, 4 mmol). The resulting mixture was stirred at room temperature for the appropriate time (Table 2). Afterward, the reaction mixture was extracted with dry ethyl acetate (2 × 20 ml) and the organic extracts were combined. The mixture was concentrated to 4 ml, and *n*-hexane (12 ml) was added to the mixture and was allowed to stand at room temperature for 5-6 h. The target molecules were collected by filtration, washed with *n*-hexane and dried. The remaining ionic liquid was dried and used for the next run under identical reaction conditions.

Spectral Data of [Msim]Cl

Viscous colorless oil; ^{1}H NMR (DMSO-d_6): δ (ppm) 3.77 (s, 3H, CH_3), 7.46 (s, 1H), 7.51 (s, 1H), 8.84 (s, 1H), 13.96 (s, 1H); ^{13}C NMR (DMSO-d_6): δ 36.5, 120.6, 124.2, 138.6; Anal. Calcd. for $C_4H_7ClN_2O_3S$: C, 24.19; H, 3.55; N, 14.10. Found:

C, 24.41; H, 3.69; N, 13.92.

Selected Physical and Spectral Data of the Products

(E)-*N*-Benzylidenebenzenesulfonamide (Table 2, entry 2). White solid; m.p.: 76-78 °C (Lit. [12j] m.p.: 76-78 °C); ^{1}H NMR ($CDCl_3$): δ 7.61 (m, 6H), 8.02 (m, 4H), 9.05 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 127.1, 128.3, 129.5, 130.3, 131.7, 132.8, 134.0, 136.1.0, 171.2.

(E)-*N*-(2-Oxoindolin-3-ylidene)benzenesulfonamide (Table 2, entry 15). Orange solid; m.p.: 144-145 °C (Lit. [12j] m.p.: 143-144 °C); ^{1}H NMR (DMSO-d_6): δ 6.89 (m, 1H), 7.05 (m, 1H), 7.34 (m, 2H), 7.48 (m, 1H), 7.56 (m, 2H), 7.84 (m, 2H), 11.00 (s, 1H); ^{13}C NMR (DMSO-d_6): δ 112.2, 117.8, 122.7, 124.6, 125.5, 128.8, 131.7, 138.3, 144.1, 150.7, 159.3, 184.3.

RESULTS AND DISCUSSION

In order to optimize the reaction conditions, the condensation of 4-methylbenzenesulfonamide (2 mmol) with benzaldehyde (2 mmol) was selected as a model reaction in the presence of [Msim]Cl (4 mmol) as the catalyst and solvent at room temperature (Scheme 1). Interestingly, the catalytic activity of the ionic liquid was excellent and the product was produced in 92% yield after 30 min. To evaluate the efficiency and the capacity of [Msim]Cl in comparison with the reported Brønsted acidic ionic liquids, the model reaction was tested in some of these ionic liquids, including [Hmim]HSO_4, [Hmim]Tfa, [Hmim]OTs, [Hmim]BF_4 and [Bmim]HSO_4. The results are summarized in Table 1. As can be seen from Table 1, [Msim]Cl afforded the product in higher yield and shorter reaction time.

Afterward, 4-methylbenzenesulfonamide and benzenesulfonamide were condensed with various aldehydes as well as with isatin in order to assess the applicability and scope of the catalyst; the respective results are displayed in Table 2. As Table 2 indicates, all reactions proceeded efficiently in the presence of [Msim]Cl at room temperature and the *N*-sulfonyl imines were produced in high to excellent yields in relatively short reaction times. In this study, the influence of electron-withdrawing substituents, electron-releasing substituents and halogens on the aromatic ring of aldehydes upon results of the reaction was investigated. The results showed that electron-withdrawing substituents and halogens increased the reaction yields (Table 2, entries 3 and 4 as well as 8-11); however, electron-releasing substituents slightly decreased the yields (Table 2, entries 5, 6 and 7). Moreover, the condensation of sulfonamides with dicarbonyl compounds as well as isatin can be powerfully carried out using [Msim]Cl as the catalyst and solvent (Scheme 2 and Table 2, entries 12 and 15).

Table 1. The Condensation of 4-Methylbenzenesulfonamide with Benzaldehyde in Different Brønsted Acidic Ionic Liquids at Room Temperature

Entry	Ionic liquid	Time (min)	Yield (%)[a]
1[b]	[Msim]Cl	30	92
2	[Hmim]HSO_4	70	68
3[c]	[Hmim]Tfa	90	56
4	[Hmim]OTS	90	61
5	[Hmim]BF_4	90	49
6	[Bmim]HSO_4	90	57

[a]Isolated pure product.

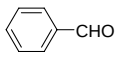
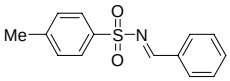
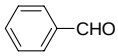
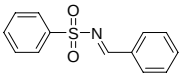
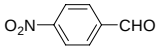
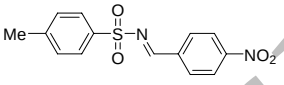
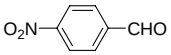
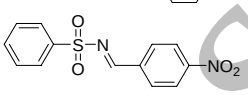
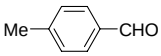
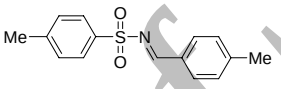
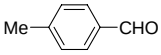
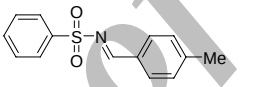
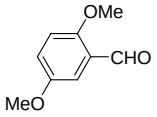
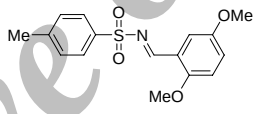
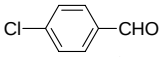
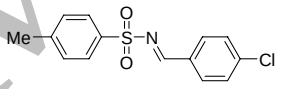
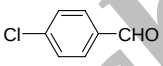
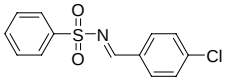
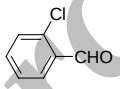
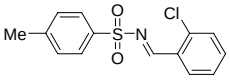
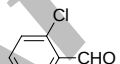
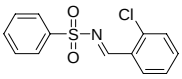
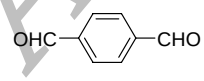
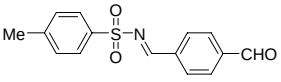
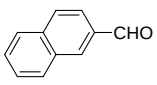
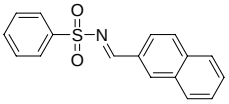
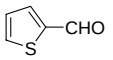
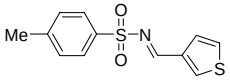
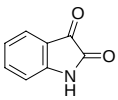
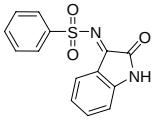
In another study, the efficiency and applicability of this new catalyst was compared with some reported catalysts for the preparation of *N*-sulfonyl imines (Table 3). As is shown in Table 3, [Msim]Cl afforded the products in higher yields and in extremely milder reaction conditions.

Ease of recycling is a desirable feature of ionic liquids. It must be mentioned that [Msim]Cl was partially hydrolyzed during the reaction without loss of its reusability. For the reaction 4-methylbenzenesulfonamide with benzaldehyde (model reaction), no significant loss of the product yield was observed when the ionic liquid was used after three times recycling (see Table 4).

CONCLUSIONS

In summary, we have introduced ionic liquid, 3-methyl-1-sulfonic acid imidazolium chloride, as a novel, efficient and reusable catalyst and solvent in organic synthesis. In this work, this acidic ionic liquid has been used successfully as the

Table 2. Preparation of *N*-Sulfonyl Imines from Sulfonamides and Aldehydes as well as Isatin in [Msim]Cl at Room Temperature

Entry	Carbonyl compound	Product	Time (min)	Yield (%)[a]
1			30	92
2			30	90
3			10	96
4			10	95
5			30	89
6			30	87
7			50	86
8			20	95
9			20	92
10			20	94
11			25	95
12[b]			60	78
13			30	91
14			15	93
15			40	89

[a]Isolated pure product. [b]In this reaction, bis-*N*-sulfonyl imine was obtained in very low yield.

Table 3. The Comparative Condensation of 4-Methylbenzenesulfonamide with Benzaldehyde Using the Reported Catalysts *vs*. [Msim]Cl

Entry	Reagent and conditions	Time (min)	Yield (%)	Ref.
1	[Msim]Cl , r.t.	30	92	-
2	$CaCO_3$, K10 Clay, $CH(OMe)_3$, Microwave	6	69	[5a]
3	Silica chloride, solvent-free, 120 °C	180	75	[12a]
4	$Si(OEt)_4$, 160 °C	360	68	[12b]
5	$TiCl_4$, NEt_3, 0 °C, CH_2Cl_2	25	58	[12c]
6	Silphox (1 g), 110 °C	180	85	[12g]
7	P_2O_5/SiO_2, solvent-free, 110 °C	120	91	[12h]
8	$Ph(p\text{-}MeOC_6H_4)_2Cl$, MeCN, 40 °C	45	85	[12i]
9	MgO, Microwave, 110 °C	12	80	[12k]

Table 4. The Reaction of 4-Methylbenzenesulfonamide with Benzaldehyde in the Presence of Recycled [Msim]Cl at Room Temperature

Entry	Cycle	Time (min)	Yield (%)
1	1st run	30	92
2	2nd run	30	91
3	3rd run	33	90
4	4th run	37	88

[a]Isolated pure product.

catalyst and solvent for the efficient synthesis of *N*-sulfonyl imines *via* the condensation of sulfonamides with aldehydes as well as isatin at room temperature.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the partial support of this work by the Research Affairs Office of Bu-Ali Sina University (Grant number 32-1716 entitled development of chemical methods, reagent and molecules.), and Center of Excellence in Development of Chemical Methods (CEDCM), Hamedan, I.R. Iran.

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