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Review

Synthesis, characterization and catalytic application of novel ionic liquids based on thiazolium cation

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ABSTRACT

A new series of thiazolium based ionic liquids were designed and synthesized. Their typical physical properties were also studied. The introduction of hydroxyl, vinyl, sulfonic, carboxylic and methoxycarbonyl groups promoted the remarkable change on the general properties of these ionic liquids. The synthesized products were characterized by ^{1}H NMR, FT-IR, TG, mass spectra and elemental analysis. The catalytic activity of these functionalized ionic liquids was investigated in the preparation of benzimidazole derivatives, N-substituted pyrroles and 4-Hydroxy-6-methyl-[(1-phenylimino) ethyl)]-2H-pyran-2-one derivatives. This procedure gave the desired products in short reaction time with high to excellent yields.

Contents

1. Introduction

Ionic liquids (ILs) have been attracting considerable attention in recent time due to their unique physico-chemical properties [1]. Initially, ionic liquids were usually used as alternative reaction solvents, but today they have been employed as catalysts for different reactions [2,3]. Great efforts have been made to promote the development of "task-specific" ILs that have functional groups tethered to their cations or anions [4]. The most common ionic liquids in use are those with alkylammonium, alkylphosphonium, N-alkylpyridinium and 1, 3-dialkylimidazolium cations [5]. These still play a major role, but the attention is slowly shifting towards new structural types. Thiazoles are structurally similar to imidazoles, with a sulfur atom replacing imidazole nitrogen. Because of the nucleophilic nitrogen atom in thiazole ring, alkylation with haloalkane at nitrogen forms a quaternary ammonium salt. Up to now, thiazolium salts have been successfully used as catalysts in various reactions, such as a benzoin condensation reaction [6], the Stetter reaction [7], Sila–Stetter reaction [8] and the synthesis of α-amidoketones [9]. Despite their importance from a

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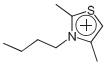
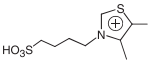
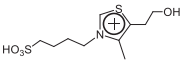
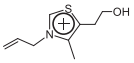
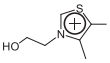
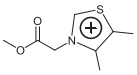
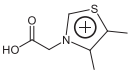
Table 1
Structure of room temperature ionic liquids in this study.

Entry	Cations	Anions	Mp/°C	Yield/%[a]
1		Br^-	160–162 °C	29.5
2		Br^-	154–156 °C	25.8
3		Br^-	126–128 °C	75.9
4		Br^-	136–137 °C	54.5
5		HSO_4^-	Liquid	66.5
6		HSO_4^-	Liquid	98.6
7		Br^-	Liquid	86.5
8		Br^-	100–102 °C	87.9
9		Cl^-	120–122 °C	46.5
10		Cl^-	149–151 °C	59.5
11		Br^-	166–168 °C	64.5

[a] Isolated yield.

catalytic and synthetic point of view, relatively few methods for their preparation have been reported.

In recent years, the benzimidazoles have been attracting considerable attention because of their applications as antiparasitic, antimicrobial, antitumor and antihistaminic agents [10–12]. A number of methods are available for the construction of benzimidazole derivatives, and two protocols are generally used. In these procedures, phenylenediamines and carboxylic acids or their derivatives are usually condensed under harsh dehydrating conditions [13,14]. Another alternative approach is the condensation of phenylenediamines and aldehydes in the presence of a wide spectrum of oxidative reagents. Unfortunately, many of these processes suffer limitations, such as drastic reaction conditions [15–18], toxic solvents [19,20], low isolation yields [21–23], co-occurrence of several side reactions [24,25], prolonged reaction time [26] and use of metals and non-recyclable catalysts [27–30]. Later on, Saha et al. reported that a high yield of benzimidazoles could be achieved by a treatment of o-phenylenediamine with many aryl aldehydes in ionic liquid [pmim]BF_4 without any other solvent or catalyst [31]. However, this method is not very satisfactory due to drawbacks such as considerable amounts of ionic liquid and a long reaction time. Therefore, the discovery of mild and practical routes for synthesis of 2-substituted benzimidazoles continues to attract the attention of researchers.

To the best of our knowledge, very little effort has been made to prepare and utilize ionic liquids incorporating the thiazolium moiety. Herein, we first report the preparation of various thiazolium-based ionic liquids containing additional functional groups in the alkyl side chain. Their melting point, thermal stability, conductivity and solubility properties in common solvents were investigated. As part of a program directed at the utilization of functionalized ionic liquids in homogeneous catalysis [32,33], we apply the new synthesized compounds as efficient catalysts for a facile synthesis of benzimidazole derivatives. In this manner, their catalytic performance in the aforesaid cyclo-

Table 2
Solubility of new ionic liquids in some common solvents.

ILs	EtOH	DMF	DMSO	CH_3CN	$CHCl_3$	Et_2O	H_2O	EtOAc	$(CH_3)_2CO$[a]
1	misc	misc	misc	misc	pm	imisc	misc	imisc	imisc
2	misc	misc	misc	misc	misc	imisc	misc	imisc	imisc
3	misc	misc	misc	misc	misc	pm	misc	imisc	imisc
4	misc	misc	misc	misc	imisc	imisc	misc	imisc	imisc
5	pm	pm	pm	imisc	imisc	imisc	misc	imisc	imisc
6	pm	pm	pm	imisc	imisc	imisc	misc	imisc	imisc
7	misc	misc	misc	misc	imisc	imisc	misc	imisc	imisc
8	misc	misc	misc	misc	misc	pm	misc	imisc	imisc
9	misc	misc	misc	misc	misc	pm	misc	imisc	imisc
10	misc	misc	misc	pm	misc	pm	misc	imisc	imisc
11	misc	misc	misc	pm	pm	imisc	misc	imisc	imisc

[a] misc: miscible; imisc: immiscible; and pm: partially miscible.

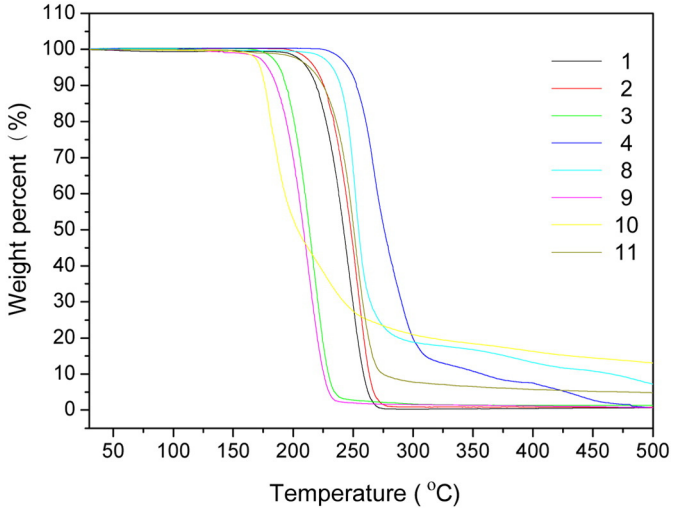


Fig. 1. TGA curves of ionic liquids 1–4 and 8–11.