Journal of Molecular Catalysis A: Chemical 376 (2013) 90–97

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

A simple, eco-friendly, and recyclable bi-functional acidic ionic liquid catalysts for Beckmann rearrangement

Rajkumar Kore, Rajendra Srivastava*

Department of Chemistry, Indian Institute of Technology Ropar, Rupnagar 140001, Punjab, India

ARTICLE INFO

Article history:
Received 10 November 2012
Received in revised form 9 April 2013
Accepted 10 April 2013
Available online xxx

Keywords:
Ionic liquids
Bi-functional acid catalysts
Beckmann rearrangements
Lewis acidity
Brönsted acidity

ABSTRACT

A library of ionic liquids was prepared by varying the cations and anions. Bi-functional acidic ionic liquids were prepared by the direct combination of ionic liquids and $ZnCl_2$. Ionic liquids were investigated in the Beckmann rearrangements. A simple, eco-friendly, and recyclable bi-functional acidic ionic liquid based protocol for Beckmann rearrangement is developed, which is based on the fine tuning of the Brönsted and the Lewis acidity of ionic liquids.

1. Introduction

Beckmann rearrangement is one of the classical and most popular reactions in the organic chemistry, in which amides are formed by the acid catalyzed rearrangement of oximes [1,2]. Co-production of large amount of undesired by-product and corrosive phenomenon associated with conventional acid (H_2SO_4 and $SOCl_2$) based liquid phase protocol provided a challenging task for chemists to develop alternate methods for this reaction [3]. A variety of organic acids and inorganic solid acids based alternative routes were developed [4–12]. However, low selectivity, low reactant to catalyst ratio, corrosive and large volume of solvents, high operating temperature, and rapid catalyst deactivation are of serious concern. A green chemical method based on supercritical water was developed for Beckmann rearrangement, but low conversion and high temperature condition (646 K) provide its limited scope [13]. Rising demand of caprolactum production and environmental concern of the existed industrial process have provided ample opportunity for the researchers to find eco-friendly and economical procedure for Beckmann rearrangement.

Ionic liquid attracted significant attention to researchers due to their favorable physico-chemical properties [14–19]. Ionic liquids (ILs) have been widely investigated in the inter-disciplinary research areas [14–19]. Our research is focused on the synthesis of a library of ILs and on finding their applications in catalysis and materials synthesis [20–28]. Several ILs based catalysts have been reported for Beckman rearrangement [29–32]. However, few of them have suffered from the separation of the desired product from the reaction mixture. State of the art for the Beckmann rearrangement suggests that this reaction can be catalyzed by using Brönsted or Lewis acidic catalysts [29–33]. However, it is not precisely known whether Brönsted acid or Lewis acid or a combination of Brönsted and Lewis acid is good for this reaction. To understand this phenomenon, varieties of ILs were prepared and their performance was evaluated in the Beckmann rearrangement. In this study, a comprehensive and systematic study was made to develop a simple, economical, eco-friendly, and recyclable catalytic protocol for Beckmann rearrangement.

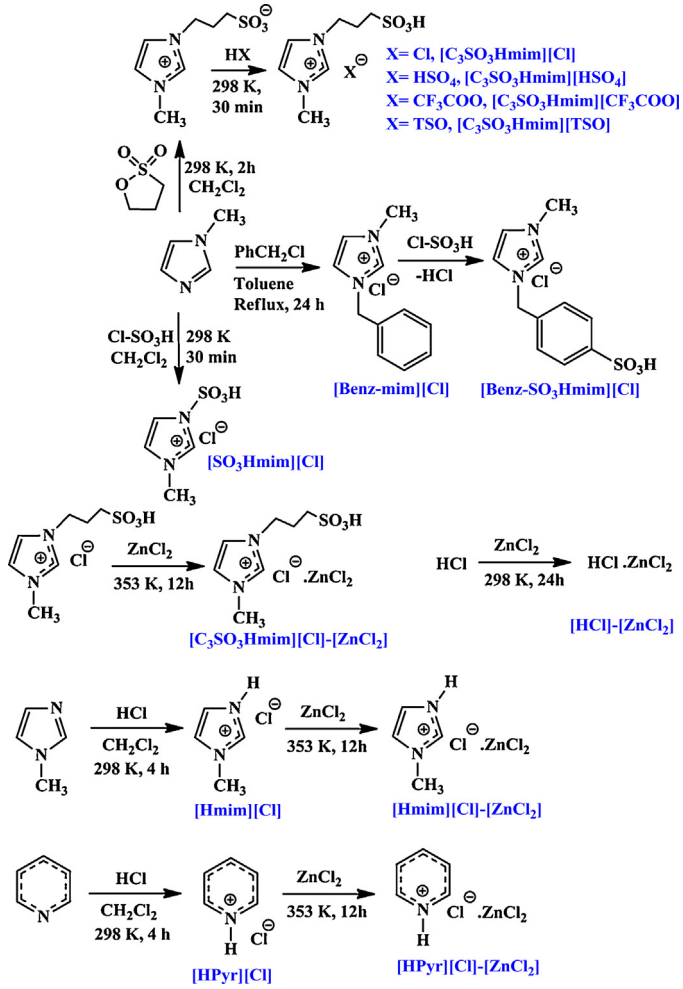
2. Experimental

2.1. Synthesis of ILs

[Bmim][Cl] is commercially available and [Hmim][Cl] was prepared by following the reported procedure (Scheme 1) [25,26]. [HPyr][Cl] was prepared by the similar procedure that was adopted for the synthesis of [Hmim][Cl]. We have already reported the synthesis of various $-SO_3H$ functionalized ILs used in this work (Scheme 1) [25,26]. However, we did not report the synthesis of metal anion (especially Zn) containing ILs, which is described as follows: In a typical synthesis, [C_3SO_3Hmim][Cl] was reacted with various amounts of $ZnCl_2$ under neat condition at 353 K for 12 h to

* Corresponding author. Tel.: +91 1881 242175; fax: +91 1881 223395.
E-mail address: rajendra@iitrpr.ac.in (R. Srivastava).

1381-1169/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molcata.2013.04.021



Scheme 1. Schematic representation for the synthesis of ILs investigated in this study.

get $[C_3SO_3Hmim][Cl]$–$[ZnCl_2]$ as a viscous liquid. With an increase of the $ZnCl_2$ mass in the reaction, the viscosity of the ionic liquid ($[C_3SO_3Hmim][Cl]$–$[ZnCl_2]$) also increased.

[Hmim][Cl]–$[ZnCl_2]$, [HPyr][Cl]–$[ZnCl_2]$, and [HCl]–$[ZnCl_2]$ were synthesized according to the similar procedure that was adopted for the synthesis of $[C_3SO_3Hmim][Cl]$–$[ZnCl_2]$. In a typical synthesis, $ZnCl_2$ was reacted with equivalent amount of ([Hmim][Cl]/[HPyr][Cl]/[HCl]) to obtain [Hmim][Cl]–$[ZnCl_2]$/[HPyr][Cl]–$[ZnCl_2]$/[HCl]$[ZnCl_2]$.

[HPyr][Cl]: IR (KBr, υ, cm^{-1}) = 615, 679, 752, 926, 1000, 1053, 1163, 1198, 1249, 1332, 1385, 1485, 1537, 1611, 1634, 2621, 2947, 3060, 3400. ^1H NMR (400 MHz, D_2O): δ (ppm) = 8.8 (d, 2H), 8.7 (t, 1H), 8.1 (t, 2H). ^{13}C NMR (400 MHz, D_2O): δ (ppm) = 145, 143, 128. Elemental analysis for C_5H_6NCl: Theoretical (%): C 51.97, H 5.23, N 12.12; Experimental (%): C 51.23, H 5.74, N 12.5.

$[C_3SO_3Hmim][Cl]$–$[ZnCl_2]$: IR (KBr, υ, cm^{-1}) = 655, 745, 1033, 1169, 1215, 1367, 1443, 1532, 1739, 2321, 2970, 3022, 3108, 3151, 3443. ^1H NMR (400 MHz, D_2O): δ (ppm) = 8.6 (s, 1H), 7.2 (s, 2H), 4.1 (t, 2H), 3.6 (s, 3H), 2.7 (t, 2H), 2.1 (m, 2H). ^{13}C NMR (400 MHz, D_2O): δ (ppm) = 134, 121, 120, 46, 44, 33, 24. MS (ESI) for $[ZnCl_3]^-$ m/z 171, $[Zn_2Cl_5]^-$ m/z 306.6, and $[Zn_3Cl_7]^-$ m/z 443.

2.2. Characterization details

Fourier transform infrared (FT-IR) spectra were recorded on Bruker Tensor-27 spectrometer in the range of 600–4000 cm^{-1} (spectral resolution = 4 cm^{-1}; number of scans = 100). UV–vis spectra were recorded on Analytikjena Specord 250 PLUS spectrophotometer. Nuclear magnetic resonance (NMR) (^1H and ^{13}C) spectra were recorded on Bruker AM, 400 MHz NMR. Electrospray ionization-mass spectrometry (ESI-MS) was performed by a Waters Q-ToF Micro equipped with ESI Source with capillary voltage of 3000 V and cone voltage 30 V. Analysis was performed in negative ion mode. Acid values of the BAILs were determined by titration with alkali solution using phenolphthalein as the indicator.

2.3. Catalytic reaction

In a typical procedure, the oxime (1.0 mmol), catalyst1 + catalyst2 (catalyst1 = ILs, 0.0–0.1 mmol); catalyst2 = metal chlorides (0.0–0.125 mmol), where metal = Al, Mn, Fe, Co, Ni, Cu, Zn, Sn, and Ce) and 4 mL acetonitrile were charged into a 25 mL round-bottom flask equipped with a magnetic stirrer and condenser. The reactions were allowed to proceed for 0.5–4 h at 298–373 K. The reaction mixture was analyzed using gas chromatography (Yonglin 6100; BP-5; 30 m × 0.25 mm × 0.25 μm). The products were identified by GC–MS (Hewlett-Packard; 30 m long, 0.25 mm i.d., with a 0.25-μm-thick capillary HP5column) and authentic samples obtained from Aldrich.

For the recovery of the ILs after the reaction, reaction mixture was evaporated. Since reactant and products are soluble in diethyl ether, therefore reaction mixture was washed 4–5 times with diethyl ether to remove the reactant and products and leaving behind the catalyst in the reaction flask. Reaction flask containing ILs were subjected to Rota-evaporation, followed by drying in vacuum to remove solvent from the ILs. Reactants were again charged into the reaction flask containing recovered ILs and reaction was performed by the above mentioned method.

2.4. Theoretical study details

The minimum-energy geometries of ILs were determined by performing DFT geometry optimizations at the B3LYP/6-31G level using the Gaussian09 program [34]. A vibrational analysis was performed to ensure the absence of negative frequencies and verify the existence of a true minimum.

3. Results and discussions

3.1. Synthesis and characterization of ILs

A library of ILs was prepared by varying the cations and anions (Scheme 1). Structure of ILs was characterized using various spectroscopic tools such as FT-IR, NMR, and Mass spectrometer. Acidity of Brönsted acidic ILs (BAILs) investigated in this study was measured using UV–visible spectrophotometer with a basic indicator by following the method reported in literature [35,36]. Acidity of BAILs was investigated in water using 4-nitroanline as indicator. With the increase of acidity of the BAILs, the absorbance of the unprotonated form of the basic indicator decreased, whereas the protonated form of the indicator could not be observed because of its small molar absorptivity and its location. Therefore, the $[I]/[IH^+]$ (I represents indicator) ratio can be determined from the differences of measured absorbance after the addition of BAILs and Hammett function, H_0, can be calculated using Eq. (1). This value can be regarded as the relative acidity of the BAILs.

$$H_0 = pK(I)_{aq} + \log\left[\frac{I}{IH^+}\right] \quad (1)$$

Under the same concentration of 4-nitroanline (3 mg/L, $pK(I)_{aq} = pK_a = 0.99$) and BAILs (50 mmol/L) in H_2O, H_0 values of all BAILs were determined. The maximal absorbance of the unprotonated form of the indicator was observed at 380 nm in water. When