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Novel acidic ionic liquids mediated zinc chloride: Highly effective catalysts for the Beckmann rearrangement

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ABSTRACT

A mild, efficient, and eco-friendly procedure for Beckmann rearrangement was catalyzed by a series of novel Brønsted acidic ionic liquids (ILs) consisiting double $-SO_3H$ cations mediated zinc chloride (ILs–$ZnCl_2$) catalytic system. High yields of amides were achieved by using 5 mol.% of ILs–$ZnCl_2$ catalysts. In addition, the catalyst system could be recycled and reused for three times.

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1. Introduction

Beckmann rearrangement, the conversion of an oxime into an amide [1], has long been an important subject for catalyst researchers. It accomplishes both the cleavage of a carbon–carbon bond and the formation of a carbon–nitrogen bond, and represents a powerful method in organic synthesis and chemical manufacturing, particularly for the preparation of ε-caprolactam from cyclohexanone oxime in industry. This reaction, however, generally requires high temperature, strong Brønsted acid and dehydrating media, which will produce large numbers of by-products and bring serious corrosion problems [2]. Great efforts have been made to overcome these problems, among which is the catalytic Beckmann rearrangement in the vapor-phase process or liquid-phase process [3–5]. But the low selectivity for ε-caprolactam and the rapid decay of the catalyst activity in the former (vapor-phase) process, and the risk of environmental problems caused by the use of organic solvents in the latter one, still both remain unsatisfactory. Therefore the matter of primary interest is accelerating reaction rates as well as improving selectivity's via more "green" or environmentally friendly chemical processes. Recently, Beckmann rearrangement in supercritical water has been reported [6–9], in which a short reaction time and excellent selectivity for ε-caprolactam was obtained and the corrosion problem was controlled to a certain extent, but very low conversion and rigorous reaction conditions make this approach utilizable only in research scope.

Ionic liquids (ILs) have attracted extensive interest as excellent alternatives to organic solvents, due to their favorable properties. Brønsted acidic ILs, which possesses the advantageous characteristics of solid acids and mineral acids, are designed to replace traditional mineral liquid acids, such as sulfuric acid and hydrochloric acid [10]. In recent years, ILs as media or catalysts in Beckmann rearrangement have been reported [11–18], affording a new approach for catalytic Beckmann rearrangement. In the search for a clean, highly efficient catalyst system for Beckmann rearrangement reaction, we synthesized a series of novel functional acidic ILs [Bis-BsImM]$[OTf]_2$ (Bs = butyl-sulfonyl, Im = imidazolium, M = methane, OTf = triflic acid) (**I**), [Bis-BsImH]$[OTf]_2$ (H = hexane) (**II**) and [Bis-BsImD]$[OTf]_2$ (D = decane) (**III**) (Scheme 1). This new type of ILs is comprised of imidazolium-based dications and triflic acid anions. Due to their unique structures, they are of quite strong acidity and very poor solubility in common organic solvents except for ethanol and methanol. Excellent yields of amides were obtained for the reaction when these novel acidic ILs were used together with $ZnCl_2$ as catalysts without producing any waste (Scheme 2). Moreover, the immiscibility of the novel acidic ILs with organic solvents makes the separation of catalysts very facile. For comparison, the performance of other acidic ILs such as [MBsIm][OTf], [HBsIm][OTf], [DBsIm][OTf], [MBsIm][CF_3COO], [MBsIm][H_2PO_4] and [MBsIm][Ts-OH] (Ts-OH = p-toluenesulfonic acid) (Fig. 1, ILs **1–6**) were also tested.

2. Experimental

2.1. General remarks

Toluene was distilled from sodium metal. Acetonitrile was distilled from calcium hydride. All other solvents and chemicals were

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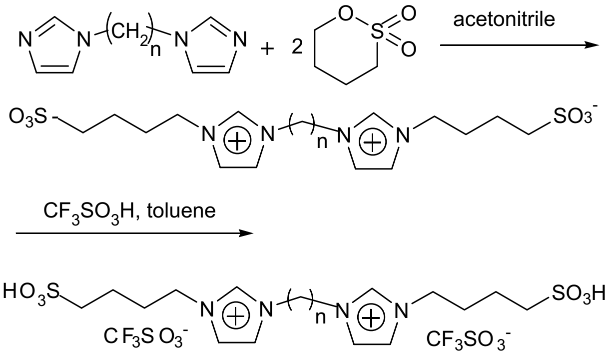
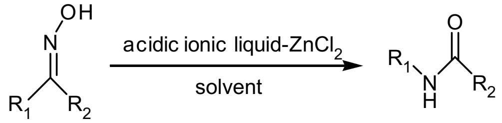
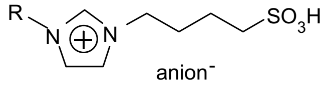


I: n= 1, [Bis-BsImM][OTf]$_2$
II: n= 6, [Bis-BsImH][OTf]$_2$
III: n= 10, [Bis-BsImD][OTf]$_2$

Scheme 1. Synthesis of the novel acidic ionic liquids.



Scheme 2. The Beckmann rearrangement of oxime catalyzed by acidic IL–$ZnCl_2$.



1 R=CH_3, anion=OTf [MBsIm][OTf]
2 R=$(CH_2)_5CH_3$, anion=OTf [HBsIm][OTf]
3 R=$(CH_2)_9CH_3$, anion=OTf [DBsIm][OTf]
4 R=CH_3, anion=CF_3COO [MBsIm][CF_3COO]
5 R=CH_3, anion=H_2PO_4[MBsIm][H_2PO_4]
6 R=CH_3, anion=Ts-OH [MBsIm][Ts-OH]

Fig. 1. The structures of [MBsIm][OTf], [HBsIm][OTf], [DBsIm][OTf], [MBsIm][CF_3COO], [MBsIm][H_2PO_4] and [MBsIm][Ts-OH].

commercially available and used without further purification. The oximes were prepared according to standard methods and their purities were established before utilization according to their melting points. The ILs **1–6** used in this study were synthesized according to previous literatures [19,20]. Their structures are shown in Fig. 1. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian INOVA 400 M spectrometer. Chemical shifts were reported in parts per million (ppm, δ).

2.2. Preparation of the novel functional acidic ionic liquids

2.2.1. [Bis-BsImM][OTf]$_2$ (I)

Preparation of bisimidazolemethane was according to literature [21], reacting one equivalent of imidazole and dichloromethane with two equivalents of potassium hydroxide in the presence of tetra-n-butylammonium bromide (TBAB, 3%). Reaction was performed at room temperature and bisimidazolemethane was isolated by extraction with ethanol followed by column chromatography. IL (**I**) was prepared according to a similar approach as reported previously [22]. According to the route in Scheme 1, bisimidazolemethane and 1,4-butane sultone were mixed in a molar ratio of 1:2 at 80 °C in anhydrous acetonitrile for 24 h. The resulting white powder was pulverized, washed with ethanol and dried in vacuo. The white powder and CF_3SO_3H were mixed in a molar ratio of 1:2 in anhydrous toluene, and heated at 80 °C for 24 h, followed by washing with acetonitrile and ether and drying in vacuo to obtain the final IL **I**. The product was a yellow viscous liquid. Yield: 91%. ^{1}H-NMR (400 MHz, D_2O): δ 9.15 (s, 2 H), 7.64 (s, 2 H), 7.62 (s, 2 H), 6.57 (s, 2 H), 4.16 (t, J = 7.2 Hz, 4 H), 2.78 (t, J = 7.2 Hz, 4 H), 1.89 (t, J = 7.6 Hz, 4 H), 1.58 (t, J = 7.2 Hz, 4 H); ^{13}C-NMR (100 MHz, D_2O): δ 136.31, 122.40, 122.29, 119.71 (q, J_{C-F} = 315.2 Hz, CF_3), 59.01, 50.03, 49.76, 27.85, 20.97.

2.2.2. [Bis-BsImH][OTf]$_2$ (II)

Bisimidazolehexane was prepared according to similar literature [23]. A mixture of 1-H-imidazole-1-propanenitrile and 1,6-dibrohxeane in ethanol was stirred at 80–90 °C for 24 h (molar ratio of 1-H-imidazole-1-propanenitrile and 1,6-dibrohxeane is 2.1:1), after the reaction was completed, the mixture was cooled, the precipitated solid was filtered and washed with cold acetone to give the imidazolium salt. The salt was then dissolved in chloroform and mixed with a 40 wt.% NaOH solution, and the mixture was stirred at room temperature for 0.5–1 h, followed by extraction with chloroform and the organic phase was washed with water for six times. The combined organic extracts were concentrated to afford yellow reddish viscous liquid and white crystal of product immediately emerged therein upon addition of a mixture of ether and water (ether /water = 2/1) in the above yellow reddish viscous liquid. The obtained white crystal was filtered, washed with ether and water and dried in vacuo to afford pure bisimidazolehexane for the preparation of IL **II**. IL **II** was prepared in an analogous procedure to the preparation of **I** described in Section 2.2.1. The product was a yellow viscous liquid. Yield: 96%. ^{1}H-NMR (400 MHz, D_2O): δ 8.64 (s, 2 H), 7.34 (s, 2 H), 7.32 (s, 2 H), 4.07 (t, J = 6.8 Hz, 4 H), 4.01 (t, J = 7.2 Hz, 4 H), 2.75 (t, J = 7.6 Hz, 4 H), 1.85 (t, J = 7.6 Hz, 4 H), 1.68 (t, J = 6.8 Hz, 4 H), 1.49(t, J = 7.6 Hz, 4 H), 1.42(t, J = 6.0 Hz, 4 H); ^{13}C-NMR (100 MHz, D_2O): δ 135.29, 122.56, 122.41, 119.71 (q, J_{C-F} = 315.2 Hz, CF_3), 50.13, 49.05, 49.54, 29.00, 28.14, 24.91, 21.01.

2.2.3. [Bis-BsImD][OTf]$_2$ (III)

The procedure was the same as described in Section 2.2.2, and a yellow viscous liquid was obtained. Yield: 97%. ^{1}H-NMR (400 MHz, D_2O) δ 8.60 (s, 2 H), 7.31(s, 2 H), 7.29 (s, 2 H), 4.04 (t, J = 6.8 Hz, 4 H), 3.98 (t, J = 6.8 Hz, 4 H), 2.72 (t, J = 7.6 Hz, 4 H), 1.81 (t, J = 7.6 Hz, 4 H), 1.64 (t, J = 6.0 Hz, 4 H), 1.53 (t, J = 7.2 Hz, 4 H), 0.95–1.06 (m, 12 H); ^{13}C-NMR (100 MHz, D_2O): δ 135.25, 122.55, 122.37, 119.71(q, J_{C-F} = 315.2 Hz, CF_3), 50.12, 49.69, 49.02, 29.14, 28.35, 28.21, 28.01, 25.32, 21.02.

2.3. General procedure for Beckmann rearrangement

The Beckmann rearrangement was processed as follows: for each reaction, the oxime 1.00 mmol, IL 0.05–0.10 mmol, $ZnCl_2$ 0.05–0.10 mmol and 5 ml solvent were charged into a 25 ml round-bottom flask equipped with a magnetic stirrer and condenser, then the reactions were allowed to proceed for 2–5 h at 80 °C. At the end of the reaction the resulting mixture was cooled and qualitative analyses were conducted with HP 6890/5793 GC–MS and quantitative analyses were conducted with Agilent 6820 GC system equipped with FID detector. GC yield was obtained from product of conversion of starting material and selectivity of amide.

3. Results and discussion

Initially, acetophenone oxime has been used as a probe molecule to investigate the feasibility of Beckmann rearrangement reac-

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