Environmentally friendly Beckmann rearrangement of oximes catalyzed by metaboric acid in ionic liquids

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Abstract

Beckmann rearrangement of several oximes catalyzed by metaboric acid was studied in room temperature ionic liquids. Especially for conversion of cyclohexanone oxime into ε-caprolactam, excellent conversion and selectivity were obtained.
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1. Introduction

Catalytic rearrangement of oximes into the corresponding lactams has long been an important subject for catalyst researchers, particularly with respect to the commercial production of ε-caprolactam in which concentrated sulfuric acid is employed and a large amount of ammonium sulfate is produced as a by-product. Great efforts have been put into the development of the ammonium sulfate free processes. Recently, the Beckmann rearrangement in supercritical water has been reported [1–3], in which, although there were no serious corrosion problems and excellent selectivity for ε-caprolactam was obtained, very low conversion and rigorous reaction conditions make the above approach utilisable only in research. The vapor-phase rearrangement over solid acid is another alternate. Some catalysts give very high conversion and selectivity, but they suffered from the intrinsic features such as the requirement of high temperature above 250 °C and rapid deactivation of catalyst due to the coke formation [4,5].

Boric acid has low mammalian toxicity and is widely used as antiseptic in the hospital. When boric acid is heated above 100 °C, it is dehydrated and converted into metaboric acid (Scheme 1). Chandrasekhar and Gopalaiah [6] investigated solid metaboric acid catalyzed Beckmann rearrangement of ketoximes, but involved reaction conditions were rigorous (for cyclohexanone oxime instance, it requires high reaction temperatures near 140 °C and more than 40 h reaction time. Moreover, the yield is not satisfactory).

The use of room temperature ionic liquids as environmentally benign media for catalytic processes is widely recognized and accepted [7–10]. The Beckmann rearrangement was found to be efficiently progressed using ionic liquids in the presence PCl_5 or P_2O_5 as catalyst [11,12]. However, in both cases, the phosphorated compounds involved inevitably environmental problems. Hereby, more environmentally benign catalytic system should be sought (Scheme 2).
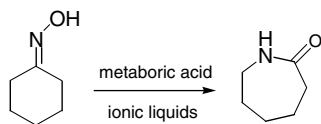
With our seeking clean, highly efficient catalyst system for Beckmann rearrangement reaction, in this paper

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$$nB(OH)_3 \ (Boric \ Acid) \xrightarrow[-n(H_2O)]{120\ °C} (HBO_2)n \ (Metaboric \ Acid: MBA)$$
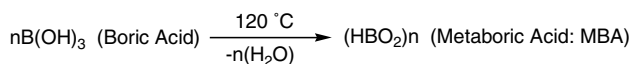
Scheme 1.

Scheme 2.

we reported that the catalytic Beckmann rearrangement of several oximes using the environmentally friendly reaction medium and acidic catalyst, i.e., RTILs and metaboric acid. Satisfactory conversion and selectivity were obtained for the transformation of cyclohexanone oxime into ε-caprolactam.

2. Experimental

The ionic liquids $BMImPF_6$ (B = butyl; M = methyl; Im = imidazolium), $BMImNO_3$, $BMImCF_3COO$ and $BPyBF_4$ (Py = pyridinium) were used in the Beckmann rearrangement reaction due to their good solubility for MBA and cyclohexanone oxime, and were synthesized according to previous papers [13–15]. $BMImTf_2N$ was used as comparison although the solubility of MBA in this ionic liquid was very poor.

Metaboric acid was converted by heating boric acid at 120 °C for 4 h, then the powdery metaboric acid was obtained by grinding with a mortar.

Several oximes, such as acetone oxime, cyclopentanone oxime, acetophenone oxime and p-nitrobenzaldehyde oxime, were employed in this work. For each reaction, oxime 2 mmol, MBA 0.5–6 mmol and 2 ml

ionic liquid were successively added into a 25 mm × 25 mm weighing bottle with cover which sealed by polytetrafluroethylene film, then the reaction was allowed to proceed on an oven at 70–90 °C. At the end of the reaction the resulting mixture was cooled and extracted with 5 ml × 2 ethyl acetate. Then qualitative analyses of the extractions were conducted on a HP 6890/5793 GC–MS with a 30 m × 0.25 mm × 0.33 μm capillary column and with chemstation containing a NIST Mass Spectral Database. Quantitative analyses were conducted on a HP 1790 GC equipped with a FID detector, 30 m × 0.25 mm × 0.33 μm capillary column. The conversion and the selectivity were calculated according to the chromatograph peak areas given by the chemstation.

3. Results and discussion

First, we used cyclohexanone oxime as probe molecular to investigate Beckmann rearrangement reaction of oxime which was catalyzed by MBA in aid of $BMImPF_6$. At reaction temperature the MBA and cyclohexanone oxime are completely soluble in $BMImPF_6$ and the final results are summarized in Table 1. It could be seen that the dosage of catalyst had greatly effect on the conversion and the selectivity of the rearrangement reaction. When molar ratio of cyclohexanone/MBA increased from 4/1 to 1/1 (Table 1, entries 1, 2), the conversion increased rapidly from 3.6% to 51.3% at 70 °C for 3 h; However, increasing molar ratio to 1/3, almost the same conversion was maintained, whereas the great increasing in the selectivity can be observed (Table 1, entry 3). The same result was represented by reaction condition at 90 °C for 3 h (Table 1, entries 4, 5, 6). It was obvious that either increasing amount of MBA or elevating the reaction

Table 1
Results of Beckmann rearrangement of cyclohexanone oxime in $BMImPF_6$

Entry	Cyclohexanone oxime/MBA (mol/mol)	T (°C)	t (h)	Con. (%)	Sel.[e] (%)
1	1:0.25	70	3	3.6	18.3
2	1:1	70	3	51.3	60.2
3	1:3	70	3	54.5	94.5
4	1:0.25	90	3	51.2	50.4
5	1:1	90	3	89.0	94.9
6	1:3	90	3	98.1	>99
7[a]	1:3	90	3	93	
8[b]	1:3	90	3	23.1	59.1
9[c]	1:3	90	3	33.7	50.4
10[d]	1:3	90	3	47.1	78.0

[a] *Isolated yield.* The resulting mixture was neutralized with ammonium hydroxide until pH = 7, then the product was purified by flash chromatograph column (silica gel).
[b] The MBA is replaced by equal molar of boric acid.
[c] The MBA is replaced by equal molar of acetic acid.
[d] The MBA is replaced by equal molar of toluene-p-sulfonic acid.
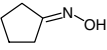[e] The byproduct is cyclohexanone.

temperature was great beneficial to the conversion of cyclohexanone oxime. From the results of Table 1, we could see that the optimum reaction condition w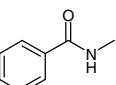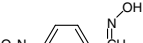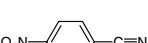as at 90 °C for 3 h and the best molar ratio of cyclohexanone oxime:MBA is 1:3 (Table 1, entries 6, 7). With this reaction condition, cyclohexanone oxime was almost completely converted into ε-caprolactam. For comparison, MBA was replaced by equal molar of boric acid at the same reaction conditions, nevertheless, only poor conversion and selectivity was obtained (Table 1, entry 8). This might be attributed to the competitive hydrolysis of oxime. As a result, the oxime was partially hydrolyzed back to cyclohexanone.

We all know that PF_6 ILs tend to hydrolyze in presence of traces of water, especially in an acid environment (in this process HF could be released). In order to investigate the action of HF formed during reaction, several other acid catalysts were further explored. When the MBA were replaced by toluene-p-sulfonic acid ($pK_a = 1.7$) and acetic acid ($pK_a = 4.74$), which have stronger acidity than the MBA has ($pK_a = 9.25$) and the hydrolysis of PF_6 ILs could be more severe under these conditions [16], no satisfactory results were observed (Table 1, entries 9, 10). So we can deduce that the MBA is the true catalyst in the rearrangement reaction.

The Beckmann rearrangement of cyclohexanone oxime in different ionic liquids was also carried out. The results were summarized in Table 2. Using hydrophilic ionic liquids, such as $BPyBF_4$, $BMImBF_4$, $BMImCF_3COO$ and $BMImNO_3$, only poor rearrangement results were obtained (Table 2, entries 1, 2, 3, 4). As a typically hydrophobic and stable enough ionic liquid, $BMImTf_2N$ was then used in the Beckmann rearrangement reaction and relatively good result was obtained. The conversion was 51.8% and the selectivity was 77.1%, respectively, although the solubility of MBA in $BMImTf_2N$ was very poor (Table 2, entries 5). In consideration of the results obtained above, it could be known that both MBA and the hydrophobic nature of ILs had a great effect on the Beckmann rear-

rangement reactions. The supposition also confirmed when the Beckmann rearrangement of cyclohexanone oxime was processed in traditional organic solvents. Using water-immiscible 1,2,3,4-tetrahydronaphthalene as reaction medium, slightly high conversion and excellent selectivity were observed (Table 2, entry 6); on the contrary, when water-miscible N,N-dimethylformamide was used in rearrangement reaction, almost the same conversion was maintained, but the selectivity decreased clearly (Table 2, entry 7). In addition, without using any solvent, the Beckmann rearrangement of cyclohexanone oxime catalyzed by solid metaboric acid had also been investigated. It was possible that the solid catalyst and the substrate could not blend well. High selectivity and low conversion were observed (Table 2, entry 8). Whereas solid metaboric acid and cyclohexanone oxime become homogenous in some ILs at the reaction temperature. It is why ILs were introduced as reaction medium for rearrangement reaction.

Table 3
Results of Beckmann rearrangement of different oximes in $BMImPF_6$

Entry[a]	Oximes	Products	By products	Con. (%)	Sel. (%)
1				98	0.5
2				48	>99
3				67	16
4			–	4.1	>99

[a] Reaction temperature 90 °C, reaction time 3h, oxime: MBA 1:3.

Table 2
Beckmann rearrangement of cyclehexanone oxime in several solvents

Entry[a]	Solvents	Con. (%)	Sel.[b] (%)
1	$BPyBF_4$	45	9.5
2	$BMImBF_4$	10.9	21
3	$BMImCF_3COO$	10.5	17
4	$BMImNO_3$	9.7	50
5	$BMImTf_2N$	51.8	77.1
6	1,2,3,4-tetrahydronaphthalene	28.7	93.2
7	N,N-dimethyllformamide	23.3	41.6
8	None	11.2	94.1

[a] Reaction temperature 90 °C, reaction time 3 h, cyclohexanone oxime:MBA 1:3.
[b] The byproduct is cyclohexanone.

The scope of the rearrangement reaction of oximes in ILs was investigated, too. Table 3 shows the results summarily. In BMImPF$_6$, the rearrangement of acetone oxime reached conversion of 98%, but only selectivity of 0.5% was obtained (Table 3, entry 1). Although, the Beckmann rearrangement of cyclopentanone oxime had excellent selectivity in the same reaction conditions, conversion of 48% had greater decrease than that of cyclohexanone oxime (Table 3, entry 2). It is possible that the ring strain provides the resistance for rearrangement [17,18]. With more steric hindrance, the rearrangement of aromatic ketoxime–acetophenone oxime had poor result (Table 3, entry 3). However, the reaction of aromatic aldoxime only gave little product of dehydration – corresponding to nitrile (Table 3, entry 4).

4. Conclusion

In conclusion, an environmentally friendly catalytic Beckmann rearrangement of typical oximes using metoboric acid as catalyst in room temperature ionic liquids was studied. Particularly with respect to cyclohexanone oxime, nearly 100% conversion and selectivity were obtained under mild reaction conditions in BMImBF$_6$. However, in other water-miscible ionic liquids the catalyst gave poor results. In comparison with previous reports in ionic liquids [11,12], this catalytic system involved is environmentally harmless; with Beckmann rearrangement of ketoximes on solid metaboric acid [6], this system is time-saving and has high catalytic activity. Further investigation is in progress.

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