



Catalytic Beckmann rearrangement of ketoximes in ionic liquids

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Abstract—Under mild conditions and without any additional organic solvents, Beckmann rearrangements of several ketoximes were performed in the catalytic media consisting of room temperature ionic liquid based on 1,3-dialkylimidazolium or alkylpyridinium salts and phosphorated compounds. Excellent conversion and selectivity was achieved for cyclohexanone oxime as the substrate, while Beckmann fragmentation of cyclopentanone oxime was observed. © 2001 Elsevier Science Ltd. All rights reserved.

It is well known that the most common media for the Beckmann rearrangement to manufacture ϵ -caprolactam in chemical industry are excess or stoichiometric amounts of those strong Brønsted acids or Lewis acids, i.e. concentrated sulfuric acid, phosphorous pentachloride in ether, hydrogen chloride in a mixture of acetic acid and acetic anhydride, causing large amounts of by-products and serious corrosion problems.¹ Although a great number of the vapor-phase Beckmann rearrangement processes have been reported, low selectivity for ϵ -caprolactam and rapid decay of activity generally resulted partially because of high reaction temperatures.^{1–4} Liquid-phase catalytic rearrangement under milder conditions, on the contrary, can afford high selectivity, in which solvent plays an important role.⁵ A relatively large amount of organic solvent such as *N,N*-dimethylformamide (DMF),^{6,7} however, was generally needed, which would cause environmental problems due to the volatility and toxicity. Nevertheless, relatively few liquid-phase catalytic methods have been developed.

The use of room temperature ionic liquids as environmentally benign media for catalytic processes or chemical extractions is becoming widely recognized and accepted.^{8,9} Our new approach reported herein involved the use of room temperature ionic liquids based on 1,3-dialkylimidazolium or alkylpyridinium salts and an acidic phosphorated compound as catalytic media for

the catalytic Beckmann rearrangement of several oximes. Satisfactory conversion and selectivity were obtained for the transformation of cyclohexanone oxime into ϵ -caprolactam.

1-*n*-Butyl-3-methylimidazolium trifluoroacetate (BMIm-TFA), tetrafluoroborate (BMImBF₄) and *n*-butylpyridinium tetrafluoroborate (BPyBF₄) were, respectively, synthesized according to the procedures reported in the previous literatures.^{10,11}

For each Beckmann rearrangement reaction, cyclohexanone, acetone or cyclopentanone oxime (10 mmol) and ionic liquid (5–10 mmol, about 1–2 ml) were charged into a 50 ml round-bottomed flask equipped with a magnetic stirrer and thermometer. Then the powder of a phosphorous compound (1–2 mmol) was added with vigorous stirring at room temperature, there was no requirement for any other additional solvent. The reaction was allowed to proceed for 2 hours at desired temperatures. At the end of the reaction the resulting mixture was cooled, mixed with 5 ml of water, extracted twice with dichloromethane (5 ml $\times$ 2), and then dried with anhydrous sodium sulfate.

The resulting products were analyzed on a Hewlett–Packard 6890/5793 GC-MS equipped with a HP 5MS column (30 m long, 0.25 mm i.d., film thickness of 0.25 μ m). The concentration of reactant and product was directly given by the system of GC-MS chemstation according to the area of each chromatograph peak.

The experimental results are summarized in Tables 1 and 2. Firstly, the Beckmann rearrangement of cyclo-

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Table 1. Beckmann rearrangement of cyclohexanone oxime in the combined catalytic media of ionic liquids and phosphorated compounds

Entry	Ionic liquid	(mmol)	Phosphorated compounds	(mmol)	<i>T</i> (°)	Conv. (%)	Selectivity (%)			Catalyst turnover ^b
							ϵ -Caprolactam	Cyclohexanone	Others ^a	
1	BMImTFA	5	PCl ₅	2	80	96.6	95.2	3.9	0.9	4.83
2	BPyBF ₄	5	PCl ₅	2	80	~100	~99.0	Trace	Trace	5.0
3	BMImBF ₄	5	PCl ₅	2	80	97.8	89.9	9.0	1.1	4.89
4	BMImBF ₄	10	PCl ₅	2	80	83.6	80.0	18.6	1.4	4.18
5	BMImBF ₄	15	PCl ₅	2	80	42.2	24.1	74.1	1.8	2.1
6	BMImTFA	5	PCl ₅	1	70	30.1	50.1	48.3	1.6	3.01
7	BMImTFA	5	PCl ₅	1	80	53.8	81.1	17.8	1.1	5.38
8	BMImTFA	5	PCl ₅	1	90	70.8	75.4	22.4	2.2	7.08
9	BMImBF ₄	5	POCl ₃	2	80	60.3	94.8	4.1	1.1	3.02
10	BMImBF ₄	5	P ₂ O ₅	2	80	29.4	32.7	66.0	1.3	1.47
11	BPyBF ₄	5	PCl ₅	1	80	66.0	95.0	3.8	1.2	6.6
12	BPyBF ₄	5	PCl ₅	1.5	80	97.2	96.1	2.9	1.0	6.48

^a Including: α -chlorocyclohexanone, cyclohexane, 2-cyclohexen-1-one oxime and 2-cyclohexylidenecyclohexanone.^b Catalyst turnover: mol oxime/mol phosphorated compound.**Table 2.** Beckmann rearrangement of acetone and cyclopentanone oximes in BMImBF₄/PCl₅ catalytic media

Entry	Substrate	Ionic liquid	(mmol)	Phosphorated compounds	(mmol)	Oxime conv. (%)	Product distribution (%)		Catalyst turnover (r)
13	Acetone oxime	BMImBF ₄	5	PCl ₅	2	89.1	<i>N</i> -Ethyl acetamide	(66.8)	4.46
14	Cyclopentanone oxime	BMImBF ₄	5	PCl ₅	2	23.5	acetone	(33.2)	1.18
							Cyclopentanone	(54.9)	
							5-chlorovaleronitrile	(40.4)	
							pentanenitrile	(4.7)	

Reaction conditions: 80°C, 2 h.

hexanone oxime in different ionic liquids was carried out (entries 1, 2 and 3). If only pure ionic liquid was used as catalytic medium there was no detectable transformation. The transformation could, however, proceed effectively when both ionic liquid and acidic phosphorated compound, e.g. phosphorous pentachloride were used. Only a small amount of ionic liquid, i.e. 5 mmol (ca. 1 ml) was used and effective enough in comparison with the related previous work,⁶ in which the ratio of substrate(mmol)/solvent(ml) was 70.7 mmol/45 ml, which is much smaller than that of 10 mmol/1 ml used in this work. Although there was no great difference in conversion between entries 1–3, the experimental results indicated that almost 100% of conversion and 99% of selectivity for ϵ -caprolactam could be achieved with BPyBF₄ ionic liquid (entry 2), indicating that both the cation and anion of the ionic liquid were playing a role in the reaction. The main side reaction was deoximation, and therefore cyclohexanone was formed. Some other by-products (ca. 1% in concentration), including α -chlorocyclohexanone (excluding entry 10) and cyclohexane were also detected. The amounts of the ionic liquid added had strong impact on the catalytic performance. It is interesting to note that both the conversion and selectivity were obviously reduced when the amount of ionic liquid added was increased from 5 to 15 mmol (entries 3, 4 and 5). Slightly lower conversion and selectivity would be obtained if the ionic liquid was mixed together with acidic phosphorated compound before the reactant substrate was added, and the details about such a phenomenon are not clear at this stage. There existed a suitable reaction temperature, i.e. ca. 80°C for achieving a maximum selectivity for ϵ -caprolactam (entry 7), although the conversion of cyclohexanone oxime and the corresponding number of the catalyst turnover would greatly increase with increasing temperature (entries 6, 7 and 8). The performance of different phosphorated compounds on the Beckmann rearrangement of cyclohexanone oxime were also investigated (entries 3, 9 and 10). Phosphorous pentachloride showed the highest catalytic activity and selectivity for ϵ -caprolactam, while phosphorous pentoxide showed a very low activity and selectivity, though it was reported that phosphorous pentoxide exhibited excellent activity and selectivity in P₂O₅–DMF system for the liquid-phase Beckmann rearrangement.⁶ Finally, the experimental results indicated that increasing the amounts of phosphorous pentachloride favored both the conversion and the selectivity (entries 2, 11 and 12), although the catalyst turnover number was decreased with the increase of the amounts of phosphorous pentachloride.

In order to investigate the scope and limitation of such catalytic media consisting of ionic liquid and phosphorated compound as one of the promising catalysts for the Beckmann rearrangement, other ketoximes, i.e. acetone and cyclopentanone oximes as the substrates were also tested in the BImBF₄/PCl₅ catalytic medium (Table 2). Acetone oxime, entry 13, has been isomerized

to the corresponding *N*-methylacetamide with 89.1% conversion and 66.8% selectivity, and the by-product was acetone. As for cyclopentanone oxime, entry 14, the conversion was low in comparison with the cyclohexanone or acetone oximes and corresponding lactam was not observed. But it is worth noting that Beckmann fragmentation of cyclopentanone oxime was observed unexpectedly, and cyclopentanone 54.9%, 5-chlorovaleronitrile 40.4% and pentanenitrile 4.7% were obtained as the products. It is possible that the ring strain provides the driving force for fragmentation.^{12,13}

The experimental results showed that the Beckmann rearrangements of cyclohexanone and acetone oximes in the catalytic media consisting of room temperature ionic liquid based on 1,3-dialkylimidazolium or alkylpyridinium salts and phosphorous pentachloride could proceed with high conversion and selectivity, while Beckmann fragmentation of cyclopentanone oxime was observed in the same catalyst system. At this stage, the catalyst turnovers are still not high enough, but such catalyst systems and reaction conditions used in this work have not been optimized yet. It is possible that the ionic liquid could be recyclable since it can easily be separated from the water containing used phosphorated compound with a suitable organic solvent after the products were extracted as mentioned above. To our knowledge, it is the first time that Beckmann rearrangement of ketoximes was performed in the catalytic media consisting of room temperature ionic liquid and phosphorated compounds under mild conditions and without any additional organic solvents.

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