Preparation of ε-Caprolactam via Beckmann Rearrangement of Cyclohexanone Oxime: A Mild and Recyclable Process

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(Received July 13, 2004; CL-040826)

A recyclable liquid phase process for preparation of ε-caprolactam via the Beckmann rearrangement of cyclohexanone oxime is developed by utilizing Lewis acidic ionic liquid as catalyst and a mixture of supercritical CO_2 and chloroform as extractant.

Room temperature ionic liquids (RTILs) have recently received recognition as green and promising solvents for synthetic chemistry.[1] One of the most interesting developments in this field is the combination of ionic liquids with super critical CO_2 ($scCO_2$), another commonly used green solvent with good extraction ability, by which it provides an attractive route to solve the difficulties faced by traditional homogenous reaction system, such as the product separation and catalyst recycle. A few examples of the applications of ionic liquids + $scCO_2$ in products separation and organic compounds extraction are reported up to now.[2]

The rearrangement of a ketoxime to corresponding amide, known as the Beckmann rearrangement, is an important reaction both in organic synthesis and chemical manufacturing, particularly for preparation of ε-caprolactam from cyclohexanone oxime in industry. Traditionally, this reaction is carried out in a non-catalytic liquid phase process in the presence of excess sulfuric acid. To overcome the well-known disadvantages caused by the utilization of sulfuric acid in industry, a host of catalytic Beckmann rearrangement systems, proceeded in either vapor phase or liquid phase process, are developed.[3]

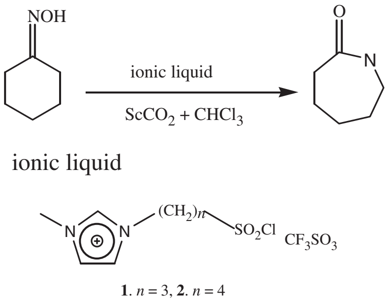

Figure 1. Beckmann rearrangement of cyclohexanone oxime.

Recently, much attention is paid to liquid phase catalytic Beckmann rearrangement that involved employing ionic liquids as reaction medium or catalyst. Deng et al. had first reported an approach for liquid phase catalytic Beckmann rearrangement by utilization of ionic liquids as reaction medium in the presence of PCl_5.[4] A following work by Ren et al. showed that P_2O_5 is also a suitable catalyst for this reaction in ionic liquid.[5] Although in those two cases, satisfactory conversion and selectivity of oximes could be achieved, products separation is still a serious problem and there is not yet a suitable way to make a recycling of ionic liquid and catalyst, especially for the catalysts, which are sensitive to water and prone of hydrolysis to produce acidic waste.

Gui et al. have demonstrated recently that a kind of sulfonyl chloride modified ionic liquids, with $PF_6{}^-$ as anion to provide water immisciblity, could act as suitable catalysts for the Beckmann rearrangement.[6] Although product could be separated by water extraction, there still failed in the issue of recycling ionic liquids, which were found to be remarkably deactivated after water extraction.

In this paper, we present what we believe to be the first example of a recyclable ionic liquid system for preparation of ε-caprolactam via the Beckmann rearrangement of cyclohexanone oxime, which involved the utilization of our previous reported Lewis acidic ionic liquid[7] as catalysts and a mixture of supercritical CO_2 and chloroform as extractant (Figure 1). We think this system might provide an attractive alternative to solve the difficulties so for suffered by ionic liquid system for the Beckmann rearrangement.

Results of the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam in the presence of a Lewis acidic ionic liquid, which is used in either a stoichiometric or a catalytic amount. are summarized in Table 1.[8] As can be seen from the table, Lewis acidic ionic liquids have shown high activity for the Beckmann reaction. When they are used in a stoichiometric amount, the reaction could be finished in 15 min with nearly 100% conversion and selectivity (Entries 1 and 2). In the cases of catalytic amount, their performance is strongly associated with mole ratio of oxime/ionic liquids and reaction temperature. When the reaction is carried out with a mole ratio of oxime/ionic liquid as 2, for example, the reaction could be completely finished within 1 h at room temperature, while keep the color of reaction system unchanged (Entry 3). Nevertheless, further increasing the ratio to 5 will lead to a violent reaction that would finish instantaneously at temperature above 50 °C. Although GC analysis demonstrated in this case both the conversion and selectivity could still keep near 100%, it is unfortunately observed that the reaction system turned to a black and viscous mixture after reaction (Entry 4), which believed to be caused by the strong heat produced from the exothermic reaction of Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam. In comparison with other catalyst systems that reported so far for liquid phase Beckmann rearrangement, these Lewis acidic ionic liquids display a relative higher activity, which, therefore, makes it possible to carry out the Beckmann rearrangement under very mild condition.

Table 1. Beckmann rearrangement of cyclohexanone oxime[a]

Entry	IL	IL /Oxime	Temp. /°C	Con. /%	Sel. /%
1	**1**	1:1	r.t.	99.4	>99
2	**2**	1:1	r.t.	99.6	>99
3	**1**	1:2	r.t.	99.3	>99
4	**1**	1:5	50	100	100

[a]Ionic liquid: 1 mmol.

Table 2. Recycle of ionic liquid **1** after extraction[a]

Run	Time /min.	Temp. /°C	Con. /%	Sel. /%	Yield /%
1	15	r.t.	99.4	>99	>95
2	60	40	71.3	95.6	>95
3	60	40	69.7	94.8	>95
4	60	40	70.1	95.1	>95

[a]Ionic liquid **1**: 4 mmol, Ionic liquid **1**/Oxime: 1:1.

Once the reaction is over, more attention is paid to the product separation and ionic liquid recycling for Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam. As mentioned above, one of the major difficulties concerning the liquid phase Beckmann rearrangement process is the existence of interaction between acidic catalyst and basic amide product. According to our preliminary experiments, we believe that this kind of interaction also exists between the Lewis acidic ionic liquid and ε-caprolactam, because a common liquid–liquid extraction, for instance, using benzene or cyclohexane as extractant, can not offer an effective extraction of product from the after-reaction viscous mixture. Then we turn to employ $scCO_2$ as extractant and the apparatus involved is illustrated in Figure 2. Though pure $scCO_2$ extraction also provides no positive result, it is found that when a co-solvent, such as water, ethanol, ethyl ether, or chloroform, is used simultaneously during the $scCO_2$ extraction, ε-caprolactam could be completely extracted from the ionic liquid. Among all the co-solvents that have been examined, chloroform has been demonstrated to possess the least negative effect on the maintenance of activity and recycling of the ionic liquid. Results of recycling the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam in the presence of Lewis acidic ionic liquid **1** via a $scCO_2$ + chloroform extraction are listed in Table 2. As can be seen, there is a decrease of the conversion of cyclohexanone oxime after first recycle, which we think probably caused by the degradation of a certain amount of ionic liquid during the process that breaking the interaction between ionic liquid and ε-caprolactam. It is interesting, however, to observe that, with the recycling goes on, the conversion of cyclohexanone oxime can keep at about 70% by slightly increasing the reaction temperature and prolonging the reaction time.

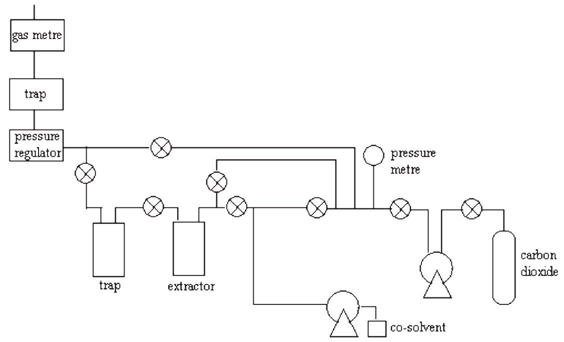

Figure 2. Apparatus for extraction with $scCO_2$ + chloroform.

Although the details of reaction mechanism and deactivation of ionic liquid are not very clear at this stage, it is demonstrated herein the feasibility of combination of ionic liquid and $scCO_2$ as an alternative route for exploring novel and recyclable liquid phase process for the Beckmann rearrangement. Owing to the designable properties of ionic liquids, we think the above system could be further optimized and efforts on designing a suitable batch reactor and increasing the recycling efficiency are under conducting now.

In conclusion, ionic liquids and $scCO_2$ + chloroform are respectively applied as catalysts and extractant for the Beckmann rearrangement. To our knowledge, this is the first example of a recyclable ionic liquid process for preparation of ε-caprolactam via Beckmann rearrangement of cyclohexanone oxime.

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8 In a typical experiment the oxime and ionic liquid were charged into a 10-mL glass test tube with the mole ratio of ionic liquid/oxime ranged from 0.2 to 1. After mixing the ionic liquid and oxime with a spoon for 3 min, put the test tube in an oil bath at the desired temperature. The whole reaction was monitored by a gas chromatograph equipped with a FID detector (Shimadzu GC-14A, ULBON HR-52 capillary column 25 m × 0.32 mm).

Published on the web (Advance View) September 18, 2004; DOI 10.1246/cl.2004.1350