Clean Beckmann rearrangement of cyclohexanone oxime in caprolactam-based Brønsted acidic ionic liquids†‡

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The Beckmann rearrangement of cyclohexanone oxime to afford caprolactam in a novel caprolactam-based Brønsted acidic ionic liquid as catalyst and reaction medium proceeded with high conversion and selectivity at 100 °C. The occurrence of the Beckmann rearrangement of cyclohexanone oxime in such a Brønsted acidic IL was also confirmed with *in situ* FT-Raman observation. The key point is that the caprolactam product was one component of the ionic liquid, and a dynamic exchange between the resulting caprolactam product and the caprolactam from the ionic liquid is expected. Therefore, the strong chemical combination between the caprolactam product and the acidic ionic liquid was greatly decreased and the desired product in the solid was recovered through extraction with organic solvent after the reaction.

Introduction

Caprolactam has been an important intermediate for the production of nylon synthetic fibers and resins. The commercial production of ε-caprolactam has been realized through the rearrangement of cyclohexanone oxime known as the Beckmann rearrangement, in which a large amount of oleum was employed as catalyst and reaction medium and a large amount of ammonium sulfate as by-product was produced because ammonium hydroxide was used to neutralize the sulfuric acid to release the desired product. As particular attention has been paid to the environmental impact of chemical industry processes, a clean Beckmann rearrangement process has long been expected, and great efforts have been put into the development of ammonium sulfate free processes.[1] For example, vapor-phase Beckmann rearrangements catalyzed by solid acid such as modified molecular sieves were reported.[2] A higher reaction temperature (*ca.* 300 °C) was necessary for such processes and rapid deactivation of catalyst was unavoidable due to coke formation.[3] Recently, it was reported that the Beckmann rearrangement has also been carried out in supercritical water with a short reaction time and excellent selectivity.[4] However, it is too rigorous to be used in an industrial application. More recently, Al-containing MCM-41 materials were reported to be more effective catalysts for both liquid and vapour-phase Beckmann rearrangement of cyclohexanone oxime in comparison to zeolites and other mesoporous catalysts.[5] However, the conversions and selectivities could not simultaneously reach more than 80% and some ring-opening byproducts and tars were also formed. Very recently, a one-step catalytic Beckmann rearrangement from cyclohexanone to caprolactam using an AlPO catalyst doped with manganese and magnesium with 68% of conversion and 78% of selectivity was reported[6] and reviewed.[7] The reaction conditions were very mild (80 °C), but the conversion and selectivity need to be further improved before practical application. Therefore, to develop a liquid-phase catalytic Beckmann rearrangement without formation of ammonium sulfate as by-product is highly desirable.

Room temperature ionic liquids (RTILs) as new reaction media and catalysts have been widely recognized and accepted.[8] Previously reported work[9] suggested that, for a Beckmann rearrangement catalyzed with a strong Brønsted acid, the first step was protonization of ketoxime to form a positively charged intermediate. A strong electrostatic field possessed with RTILs may stabilize such a charged intermediate, thus making RTILs a favorable reaction media for Beckmann rearrangement. Efforts to use RTILs as reaction media for Beckmann rearrangement of cyclohexanone oxime have been made in our group and by other colleagues.[10] Although good results have been obtained, phosphorous compounds like P_2O_5 and PCl_5 catalysts are environmentally unfriendly and are difficult to reuse. Brønsted acidic RTILs consisting of sulfonyl chloride as reaction media and catalysts were also tested for Beckmann rearrangement of cyclohexanone oxime without any additional co-catalyst and solvent,[11] but the synthetic procedure for such RTILs was so complicated that they would be too expensive to be used for Beckmann rearrangement in practice. Another problem was that the resulting caprolactam would chemically combine with the RTILs due to the basicity of caprolactam and the acidity of the RTILs, which made it almost impossible to separate the desired product from the RTILs after reaction. Therefore, the key for designing RTIL as catalyst and reaction medium for liquid-phase Beckmann rearrangement is that the desired ε-caprolactam product could be easily separated from the reaction system.

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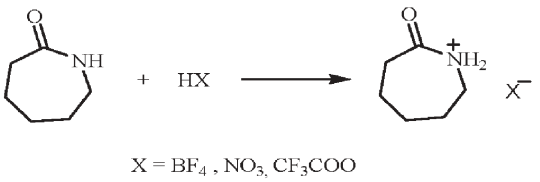
‡ Electronic supplementary information (ESI) available: Differential scanning calorimetry (DSC) (Fig. S1); thermogravimetric (TG) (Fig. S2); cyclic voltammograms (Fig. S3); NMR spectral data (Fig. S4–S7); ESI-MS (Fig. S8). See DOI: 10.1039/b513139a



Scheme 1 Preparation of caprolactam cation-based ILs.

Recently, we had successfully developed a new family of lactam cation-based Brønsted acidic ILs through a simple and atom-economic neutralization between lactam, such as caprolactam and butyrolactam, and a Brønsted acid and their physicochemical properties were preliminarily characterized and investigated (Scheme 1).[12]

In this work, we wish to report our new finding that the above-mentioned caprolactam cation (abbreviated as [NHC])-based Brønsted acidic ILs could be effective catalysts and reaction media for Beckmann rearrangement of cyclohexanone oxime to caprolactam. In comparison with dialkyl imidazolium, caprolactam is cheaper, more environmentally benign, and available on an industrial scale, which would be attractive in industry if incorporated into RTILs as catalyst and medium for Beckmann rearrangement. From another aspect, the separation of the desired product from acidic ionic liquids as catalyst and reaction medium is a great challenge in the Beckmann rearrangement reaction of cyclohexanone oxime to caprolactam. Because the rearrangement reaction product is one component of ILs used in this work, it can be conjectured that there would be a dynamic exchange between caprolactam ILs and the produced caprolactam during the rearrangement reaction (Scheme 2), and the strong chemical combination between caprolactam and acidic catalyst would be largely avoided. That is to say that the product separation from the acidic ILs system through organic solvent extraction and the recycling of ILs would be easily facilitated.

Experimental

Measurement and analysis

The ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AMX FT 400 MHz NMR spectrometer. Chemical shifts were reported in parts per million (ppm, δ). Electrospray ionization mass spectra were recorded on a Bruker Daltonics APEX II 47e FTMS. The Hammett Brønsted acid scales (H_0) of ILs were determined by using Agilent 8453 UV-vis spectrophotometer with a modified method.[12,13] The thermal properties were examined by DSC-Q100 (TA Instruments Inc.) differential scanning calorimeter and Pyrid Diamond TG thermo gravimetric analyzer (Perkin Elmer Co.) with a scan rate of 20 °C min^{-1}. Electrochemical stability was analyzed by cyclic voltammetry using a CHI660A Instruments Electrochemical Work Station at room temperature. The ionic conductivity was determined with a conductivity meter (DDS-11A) produced by Shanghai YULONG Scientific Instrument Co. Ltd. *In situ* FT-Raman studies were conducted during the Beckmann rearrangement with a Thermo Nicolet 5700 FT-Raman spectrometer with AsGaIn detector and Nd:YAG laser (1064 nm). The IL and cyclohexanone oxime with a 1 : 1 molar ratio was charged into a transparent glass capillary tube specified for FT-Raman measurement and sealed. The tube containing the reaction mixture was then fixed into the sample chamber and was heated to 100 °C with a self-made electric heating device, and in the meantime, the spectra were continuously recorded during the reaction.

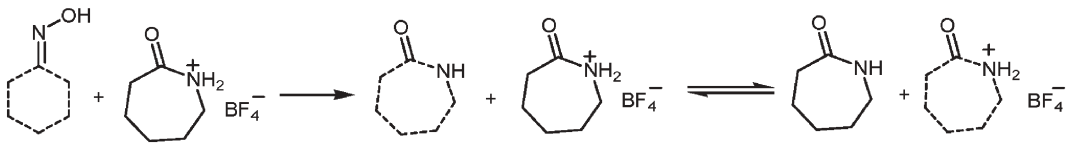
Preparation of ILs

[NHC][BF_4] was prepared as follows: 11.3 g (0.1 mol) caprolactam was dissolved in 22 g (0.1 mol) 40% fluoroboric acid water solution, and was stirred for 30 min at room temperature, and then water was evaporated with a spin-evaporator. The residual trace water was removed under vacuum (5–10 mmHg) for 4 h at 90 °C and a light yellow clear liquid was obtained with a yield of 20.0 g (99%). ^{1}H-NMR (400 MHz, d_6-DMSO): δ 1.45–1.66 (m, 6H), 2.38 (t, 2H), 3.10 (t, 2H), 8.26 (s, 1H), 11.98 (s, 1H). ^{13}C-NMR (100 MHz, d_6-DMSO): δ 22.86, 29.15, 30.08, 35.42, 42.18, 179.25. ESI-MS for cation: *m/z* 114.0912 *versus* calculated 114.0913.

[NHC][NO_3] and [NHC][CF_3COO] were also prepared with the same procedure as for [NHC][BF_4]. For the purpose of comparison, methylimidazolium tetrafluoroborate, [HMIm][BF_4], was prepared according to the previously reported literature.[14] Their spectra data are listed here. [NHC][NO_3]: mp 45 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) 1.65–1.82 (m, 6H), 2.57 (t, 2H), 3.35 (d, 2H), 8.38(s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) 22.61, 29.04, 30.16, 35.69, 42.91, 179.27; ESI-MS for cation: *m/z* 114.0912 *versus* calculated 114.0913. [NHC][CF_3COO]: ^{1}H-NMR (400 MHz, $CDCl_3$): 1.65–1.82 (m, 6H), 2.51 (q, 2H), 3.27 (q, 2H), 8.06(s, 1H), 15.89 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) 22.74, 28.86, 30.25, 35.76, 42.83, 115.23 (q, CF_3), 160.99, 181.02; ESI-MS for cation: *m/z* 114.0910 *versus* calculated 114.0913. [HMIm][BF_4]: mp 49 °C. ^{1}H-NMR (400 MHz, d_6-DMSO) 4.07 (s, 3H), 7.65 (t, 1H), 7.66 (t, 1H), 8.84 (s, 1H), 12.65 (s, 1H).

General procedure for the Beckmann rearrangement reaction

The Beckmann rearrangement of cyclohexanone oxime was processed as follows: 0.565 g (5 mmol) cyclohexanone oxime and the corresponding amount of ionic liquid (molar ratio of IL/substrate = 2/1–4/1) were charged into a 10 ml round-bottomed flask equipped with a magnetic stirrer. Then the



Scheme 2 Possible dynamic exchange between caprolactam and [NHC][BF_4].

Table 1 Some physicochemical properties of caprolactam-based ILs

ILs	T_g/°C	T_d/°C	H_0	Conductivity/S cm^{-1}	Viscosity/cP	E/V
[NHC][BF_4]	−74.0	239	−0.22	7.31×10^{-4}	503	2.0
[NHC][CF_3COO]	−73.0	135	3.35	3.83×10^{-4}	28	2.1
[NHC][NO_3]	—[a]	188	2.08	8.40×10^{-4}	—[b]	2.2

[a] No glass temperature was observed. [b] It is solid at 25 °C.

reaction was continued for 3–5 h at the desired temperature (80–100 °C). After the reaction the resulting mixture was dissolved with 5 ml acetone for GC-MS and GC analyses. Qualitative analyses were conducted with a HP 6890/5973 GC-MS with chemstation containing a NIST Mass Spectral Database. Quantitative analyses were conducted with an Agilent 6820 GC equipped with a FID using an external standard method.

After the reaction, the product separation was conducted as follows: the resulting liquid mixture was extracted with organic solvents such as ether or CCl_4 three times, the organic phase containing desired product was evaporated at an elevated temperature to remove organic solvent, and solid caprolactam was obtained.

Since the rearrangement reaction product is one component of ILs, a parallel experiment for recovery of the carprolactam was also conducted so as to obtain a precise yield resulting from the rearrangement of cyclohexanone oxime, *i.e.* the resulting liquid mixture after reaction was neutralized with 30% ammonium hydroxide solution until pH = 7.0, then separated by a silica gel column chromatograph with 1 : 1 CH_2Cl_2/hexane as eluents to obtain total and pure caprolactam which resulted from the rearrangement of cyclohexanone oxime and from the caprolactam-based IL. The isolated and real yield was obtained according to the following calculation: yield% = [isolated caprolactam by column chromatograph − caprolactam released from [NHC][BF_4]]/cyclohexanone oxime added.

Results and discussion

Physicochemical properties of caprolactam cation-based ILs

Some physicochemical properties of caprolactam cation-based ILs used in this work are summarized in Table 1. At room temperature (*ca.* 20 °C), [NHC][BF_4] and [NHC][CF_3COO] are liquid and have no distinct freezing points and melting points but possess lower glass transition temperatures (−74 °C and −73 °C, respectively). The thermal decomposition temperatures (T_d, with mass loss of 10%) of [NHC][BF_4], [NHC][CF_3COO] and [NHC][NO]$_3$ ILs are 239, 135 and 188 °C, respectively, suggesting that the thermal stability of caprolactam-based ILs are not higher in comparison with that of [BMIm][BF_4] but high enough for a general chemical process (at or below 100 °C). The resulting Hammett Brønsted acid scales (H_0) using UV-vis spectroscopy were −0.22, 3.35, and 2.08 for [NHC][BF_4], [NHC][CF_3COO], and [NHC][NO_3], respectively, suggesting that Brønsted acidity of [NHC][BF_4] was relatively strong. The ionic conductivities of caprolactam-based ILs are slightly smaller than that of [BMIm][PF_6] (1.4×10^{-3} S cm^{-1} [15]). Relatively narrow electrochemical windows, *i.e. ca.* 2.0–2.2 V were observed due to the presence of active H in these ILs.

Beckmann rearrangement of cyclohexanone oxime over caprolactam-based ILs

The results of Beckmann rearrangement of cyclohexanone oxime to caprolactam over caprolactam-based ILs and [HMIM][BF_4] (just for the purpose of comparison) as catalyst and reaction medium are summarized in Table 2. Firstly, the effect of molar ratio of [NHC][BF_4]/oxime on rearrangement reaction was examined at 80 °C. The conversion and the selectivity increased greatly with the increase of molar ratio of [NHC][BF_4]/oxime from 2/1 to 4/1 (entries 1–3). Since higher viscosity of reaction mixture resulted if the oxime was added into [NHC][BF_4] with a higher molar ratio, which may prevent the reaction proceeding to a certain extent, additional reactions under different agitation rates were further conducted. The conversion, however, only increased *ca.* 1% when the agitation rate was changed from 200 rpm to 1000 rpm (entries 4 and 5). This indicated that the agitation rate, or expressed more precisely, the viscosity of the reaction mixture, has little effect on the conversion of the BR reaction, and the amount of the IL used as reaction medium and catalyst has a strong impact on the conversion. Another important point derivated from the above experiment is that the Beckmann rearrangement of cyclohexanone oxime does occur in such a Brønsted acidic IL as catalyst and reaction medium although its Brønsted acidity is much lower than that of oleum, in other words, it may not be necessary to use a strong Brønsted acid as catalyst and reaction medium for a Beckmann rearrangement.

Table 2 Results of Beckmann rearrangement of cyclohexanone oxime to caprolactam

Entry	ILs	ILs/oxime	T/°C	t/h	Conv. (%)	Sel. (%)
1	[NHC][BF_4]	2 : 1	80	3	12.3	64.5
2	[NHC][BF_4]	3 : 1	80	3	47.8	90.1
3	[NHC][BF_4]	4 : 1	80	3	61.8	91.2
4[a]	[NHC][BF_4]	3 : 1	80	3	47.5	90.3
5[a]	[NHC][BF_4]	3 : 1	80	3	48.4	89.7
6	[NHC][BF_4]	3 : 1	100	3	77.5	90.2
7	[NHC][BF_4]	3 : 1	100	4	93.4	87.2
8	[NHC][BF_4]	3 : 1	100	5	95.1	85.1
9	[NHC][BF_4]	4 : 1	100	4	92.6	88.9
10	[NHC][CF_3COO]	3 : 1	100	4	92.3	52.1
11	[NHC][NO_3]	3 : 1	100	4	71.4	58.3
12	[HMIm][BF_4]	3 : 1	100	4	43.8	33.1
13	[NHC][BF_4]	3 : 1	100	4	Isolated yield = 79.6%[b]	
14	[NHC][BF_4]	3 : 1	100	4	Isolated yield = 42%[c]	

[a] The agitation rates for entries 4 and 5 were 200 rpm and 1000 rpm, respectively. [b] The yield by column chromatography after neutralization with ammonium hydroxide. [c] The yield by ether extraction of the resulting mixture.

In order to confirm the occurrence of a Beckmann rearrangement of cyclohexanone oxime in such a Brønsted acidic IL, *in situ* FT-Raman was conducted (Fig. 1). For the pure cyclohexanone oxime (a), there is a strong peak at 1660 cm^{-1} (ν(C=N)), which is assigned to the characteristic band of cyclohexanone oxime. For the pure [NHC][BF_4] (b), there is a peak at 1690 cm^{-1} (ν(C=O)), which was shifted from the original 1636 cm^{-1} (ν(C=O)) which is assigned to the characteristic band of pure caprolactam (g).[16] Such a shift from 1636 to 1690 cm^{-1} may be attributed to the protonation of N after combination between caprolactam and HBF_4, which could be assigned to the characteristic band of caprolactam in [NHC][BF_4]. As for the mixture of cyclohexanone oxime and [NHC][BF_4] before reaction (c), a new peak at 1673 cm^{-1} appeared, which is assigned to ν(C=N) in cyclohexanone oxime in which N was protonized due to the presence of [NHC][BF_4]. At 100 °C and as the reaction proceeded, the peak strength at 1673 cm^{-1} was gradually reduced, indicating that cyclohexanone oxime was transformed. At the same time, the peak strength at 1636 cm^{-1}, which could be assigned to the characteristic band of caprolactam, became stronger. This means that the Beckmann rearrangement of cyclohexanone oxime to caprolactam did occur.

Based on the experimental results obtained, the Beckmann rearrangement of cyclohexanone oxime in different Brønsted acidic ILs and for different reaction time at constant temperature (100 °C) was further tested. With a 3/1 [NHC][BF_4]/oxime molar ratio, the conversion increased to 77.5% and further reached 95.1% when the reaction time was increased from 3 to 5 h although the corresponding selectivity for the desired product decreased slightly (entries 6–8). At this temperature, the conversion and selectivity approached a constant even if the [NHC][BF_4]/oxime molar ratio increased to 4/1 (entry 9). It is worth noting that, although the selectivity for the desired product was not very high, the byproduct was only cyclohexanone, implying that such a byproduct could be recovered, reused and was less detrimental to the purity of the caprolactam product. When [NHC][BF_4] was replaced by [NHC][CF_3COO] and [NHC][NO_3], poor conversions and selectivities were obtained (entries 10 and 11). For the purpose of comparison, [HMIm][BF_4], (H_0 = 1.605) as catalyst and reaction medium under the above-mentioned optimum conditions was also tested (entry 12). Lower conversions and selectivities were also obtained. These experimental results suggested that the acidity of ILs was important but not the unique factor for the rearrangement reaction, and both cation and anion RTIL have a strong impact on the rearrangement reaction although a detailed reaction mechanism is still not clear at this stage. In order to precisely determine the amount of caprolactam transformed from cyclohexanone oxime during the rearrangement reaction, the resulting liquid mixture of entry 5 was also neutralized with 30% ammonium hydroxide until pH = 7.0 to dissociate all the caprolactam molecule, including those from [NHC][BF_4]. Then the resulting solution was separated by a silica gel column using 1 : 1 CH_2Cl_2/hexane as eluent. After evaporation of the eluent, total caprolactam (2.14 g) was obtained as a light yellow solid. When subtracting caprolactam from the IL (1.69 g), 0.45 g caprolactam product which was derived from rearrangement of the cyclohexanone oxime, could be obtained, corresponding to 79.6% of isolated yield (containing *ca.* 2% of cyclohexanone oxime) (entry 13). This result is just slightly lower than the GC yield of entry 5 (81.4%).

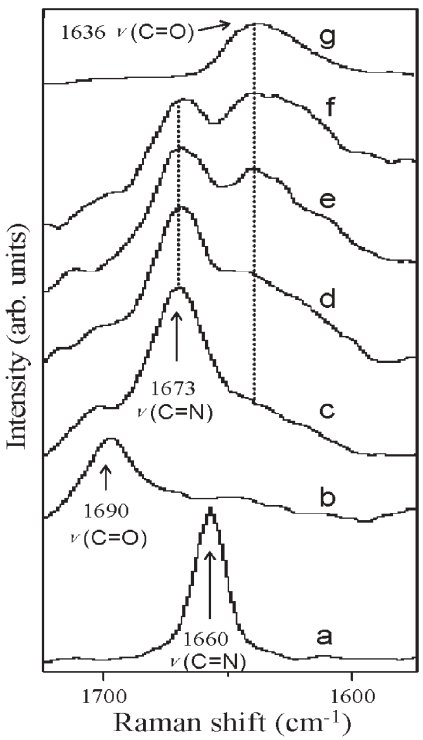


Fig. 1 *In situ* Raman spectra of Beckmann rearrangement of cyclohexanone oxime in [NHC][BF_4] with a molar ratio of 1 : 1 at 100 °C. (a) Pure cyclohexanone oxime; (b) pure [NHC][BF_4]; (c) 0 min (reaction mixture); (d) 20 min; (e) 60 min; (f) 100 min; (g) pure caprolactam.

The product separation from the reaction system is a key step for a clean Beckmann rearrangement. The extraction with organic solvents was preliminarily adopted in this work, and ether as extracting solvent to recover the caprolactam from the resulting liquid mixture after reaction was employed due to its immiscibility with the IL and good solubility for caprolactam. When the resulting liquid mixture after reaction of entry 7 was extracted with ether three times (15 ml × 3) and then the upper ether phase containing caprolactam was evaporated at 40 °C to remove ether, a white solid (containing *ca.* 2% of cyclohexanone) could be recovered in *ca.* 42% of isolated yield (entry 14). This means that, on the one hand, a dynamic exchange between the caprolactam IL and the produced caprolactam does exist, and a strong chemical combination between caprolactam and acidic catalyst would be greatly avoided in the reaction system used in this work. On the other hand, there is still some chemical interaction between caprolactam product and acidic IL since not all caprolactam product could be recovered through the extraction. It can be conjectured that such an interaction may be derived from the hydrogen bond between caprolactam and acidic IL, and such an interaction could be further reduced through adjusting the extraction conditions.

Conclusions

In conclusion, the Beckmann rearrangement of cyclohexanone oxime to afford caprolactam over a novel caprolactam tetrafluoroborate Brønsted acidic IL as catalyst and reaction medium was successfully followed with high conversion and selectivity under mild reaction conditions. The strong chemical combination between caprolactam product and acidic [NHC][BF_4] was largely avoided. Preliminary results of direct product extraction using ether from the IL system suggested that product recovery without neutralization is possible. The catalyst system, reaction conditions and separation method could be further optimized. A possible reaction mechanism and separation mechanism using *in situ* FT-IR and FT-Raman is now underway.

Acknowledgements

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