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FTIR study on deactivation of sulfonyl chloride functionalized ionic materials as dual catalysts and media for Beckmann rearrangement of cyclohexanone oxime

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Abstract

Several novel sulfonyl chloride functionalized ionic materials were used as media and catalysts for Beckmann rearrangement of cyclohexanone oxime and satisfactory results were achieved under mild conditions. The effects of all parameters were discussed. Moreover, the deactivation of ionic liquid catalytic system during the recycle was investigated by using FTIR spectroscopy and mass balance calculation. The trapping of acidic ionic material with basic product is proved to be mainly responsible for the difficulties encountered in the reuse of this type of material. A possible mechanism was conjectured.

Keywords: Beckmann rearrangement; Cyclohexanone oxime; Caprolactam; Sulfonyl chloride functionalized ionic materials; IR investigation

1. Introduction

The rearrangement of a ketoxime to the corresponding amide is a powerful method in organic synthesis and is known as the Beckmann rearrangement [1]. This reaction, however, generally requires a large amount of a strong Brønsted acid such as sulfuric acid and forms ammonium sulfate as a byproduct [2]. So more and more attentions have been paid to improve this important process for a long time. In the vapor-phase process, a few examples of the Beckmann rearrangement catalyzed by solid acid such as modified molecular sieves were reported and good results were achieved [3–5]. The vapor-phase reaction, however, suffers from its intrinsic features such as the requirement of high temperature and rapid deactivation of catalyst due to the coke formation [6,7]. Without using other media and catalysts, Beckmann rearrangement were carried out in supercritical water with fast reaction time and excellent selectivity [8–10]. But it is too rigorous to fulfill in industrial application. Liquid-phase catalytic rearrangement in organic solvents, on the contrary, can partially overcome the above-mentioned problems, in which solvent plays an important role [11]. A relatively large amount of organic solvent, however, was generally needed [12–14], which would also cause environmental problems because of the volatility and toxicity. Some of them involved the use of noble metal compound and/or organic strong acid as catalysts [15,16].

Recently, ionic liquids have gained recognition as environmentally benign alternatives to more volatile organic solvents and functional materials in many fields because of their interesting properties such as wide liquid range, negligible vapor pressure, high thermal stability and good solvating ability for a wide range of substrates and catalysts [17–22]. Beckmann rearrangement was also found to be efficiently progressed with satisfactory conversions and selectivities using ionic liquids as reaction media in the presence of phosphorus compounds [23,24], but they produced irritant gas of HCl and needed longer reaction time. Subsequently Sun et al. [25] and Yokoyama et al. [26] reported that functionalized ionic

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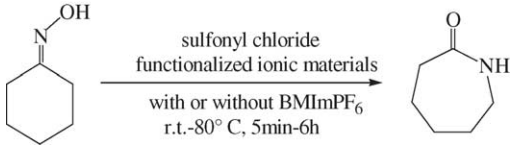


Scheme 1. Beckmann rearrangement of cyclohexanone oxime over SCFIMs.

liquid containing chlorosulfonyl group could promote this reaction. However, the efficiency of these catalytic systems is still far from satisfactory, particularly for the reuse of ionic liquids. Additionally the reason of deactivation and the reaction mechanism have not yet been discussed in detail.

As an extension of our recent investigation on the clean Beckmann rearrangement of cyclohexanone oxime (CHO) in room temperature ionic liquids, we report herein the catalytic Beckmann rearrangement of CHO over sulfonyl chloride functionalized ionic materials (SCFIMs) under mild conditions and satisfactory conversions and excellent selectivities were obtained. (Scheme 1). Mass balance calculation and IR spectroscopy were then used to investigate the cause of deactivation of SCFIMs during the process. Furthermore, a possible mechanism of Beckmann rearrangement of CHO over SCFIMs was also conjectured.

2. Experimental

All solvents and chemicals used were commercially available and used without further purification unless otherwise stated. Cyclohexanone oxime, trifluoromethanesulfonic acid (99% of purity with water content <0.1%), 1,4-butane sultone (99% of purity) were purchased from Fluka chemical corporation; benzene was dried for 3 days over 5 Å molecular sieve prior to use; others were all purchased from Beijing Chemical Reagent Corporation Ltd.

2.1. Instrumental analysis and measurements

The C and H elemental analysis were performed on a Yanaco CHN FOER MT-3 element analyzer. IR spectra were recorded on a Nicolet NEXUS 670 FTIR spectrometer using liquid film or KBr tablet. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were obtained as solutions in deuterium-substituted reagent. Chemical shifts were reported in parts per million (ppm, δ).

2.2. Synthesis and characterization of SCFIMs

The SCFIMs were prepared by three-step reactions through 1-methylimidazole, pyridine and triphenylphosphine quaternized first with 1,4-butane sultone to form zwitterions, as described in previous literatures [27,28], which then reacted with an acid to yield acidic ionic compounds. The resulting products readily underwent reaction with thionyl chloride to form the target ionic materials (Scheme 2). Here we take the synthesis of 1-(4-chlorosulfonylbutyl)-3-methylimidazolium trifluoromethanesulfonate (**1a**) as an example and describe as follows.

1-(Butyl-4-sulfonate)-3-methylimidazolium zwitterion and 1-(4-sulfonyl butyl)-3- methylimidazolium trifluoromethanesulfonate were prepared according to the procedures we have described formerly [29,30]. Then thionyl chloride was added with an excess of 5 mol times and refluxed for 24 h. The unreacted thionyl chloride was removed by evaporation. The brown viscous liquid was formed with yield of 97% and in high purity. ^{1}H NMR (400 MHz, d_6-DMSO):δ9.21 (s, 1H), 7.79 (t, J = 2.0, 1H), 7.73 (t, J = 1.8, 1H), 4.21 (t, J = 6.8, 2H), 3.88 (t, J = 7.0, 3H), 2.68 (t, J = 7.6, 2H), 1.91 (quint, J = 8.0, 2H), 1.59 (q, J = 7.6, 2H). ^{13}C NMR (100 MHz, d_6-DMSO):δ136.81, 123.78, 122.47, 121.08 (q, $J_{C–F}$ = 320.0, CF_3), 50.59, 48.63, 35.92, 28.61, 21.53. IR (cm^{-1}): 3156, 3116, 1369, 1165, 593. $C_9H_{14}F_3O_5N_2S_2Cl$ (386.58): calcd: C 27.96, H 3.62. Found: C 27.81, H 3.72.

The spectral data of other SCFIMs are listed herein.

2.2.1. 1-(4-Chlorosulfonylbutyl)-3-methylimidazolium trifluoroacetate (*1b*)

An orange liquid with yield of 95%. ^{1}H NMR (400 MHz, d_6-DMSO): δ9.43(s, 1H), 7.88(t, J = 2.0, 1H), 7.81(t, J = 1.8, 1H), 4.30(t, J = 7.2, 2H), 3.93(s, 3H), 3.69(t, J = 6.4, 2H), 1.97(quint, J = 7.2, 2H), 1.72(q, J = 6.4, 2H). ^{13}C NMR (100 MHz, d_6-DMSO): δ137.04, 123.98, 122.62, 50.79, 48.82, 36.19, 28.86, 27.37, 21.71.

2.2.2. 1-(4-Chlorosulfonylbutyl)-3-methylimidazolium p-toluenesulfonate (*1c*)

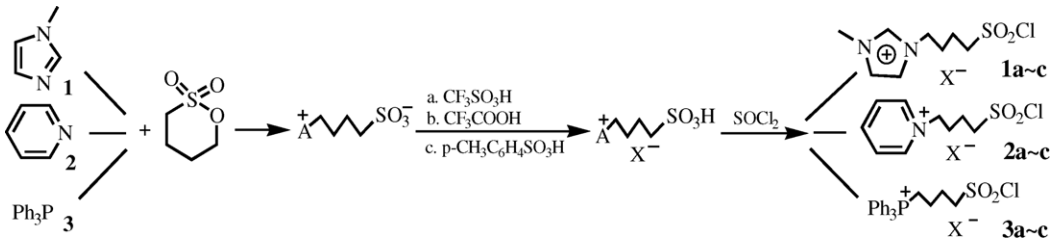
A dark brown viscous liquid with yield of 92%. ^{1}H NMR (400 MHz, d_6-DMSO): δ9.51(s, 1H), 7.89(t, J = 1.6, 1H), 7.79(t, J = 1.6, 1H), 4.24(t, J = 6.8, 2H), 3.84(s, 3H), 3.64(t, J = 6.8, 2H), 1.87(quint, J = 7.2, 2H), 1.65(q, J = 6.8, 2H). ^{13}C NMR(100 MHz, d_6-DMSO): δ136.86, 128.35, 123.68, 122.28, 47.92, 44.71, 35.80, 28.63, 27.02.

2.2.3. 1-(4-Chlorosulfonylbutyl)pyridinium trifluoromethanesulfonate (*2a*)

A dark brown semisolid with yield of 96%. ^{1}H NMR (400 MHz, d_6-DMSO): δ9.07(s, 2H), 8.53(s, 1H), 8.09(s, 2H), 4.60(s, 2H), 2.65(s, 2H), 1.97(s, 2H), 1.56(s, 2H). ^{13}C NMR(100 MHz, d_6-DMSO): δ146.10, 145.31, 128.68, 125.64(q, $J_{C–F}$ = 320.0, CF_3), 60.89, 50.86, 30.26, 21.74.

2.2.4. 1-(4-Chlorosulfonylbutyl)pyridinium trifluoroacetate (*2b*)

A brown semi-solid with yield of 95%. ^{1}H NMR (400 MHz, d_6-DMSO): δ9.32(d, J = 3.6, 2H), 8.62(t, J = 7.6, 1H), 8.18(t, J = 6.8, 2H), 4.76(t, J = 7.2, 2H), 3.65(t, J = 6.8, 2H), 2.01(quint, J = 7.2, 2H), 1.69(quint, J = 6.8, 2H). ^{13}C-NMR(100 MHz, d_6-DMSO): δ145.64, 144.97, 128.18, 59.64, 44.67, 28.46.



A= 1, 2, 3; X=CF_3SO_3(a), CF_3COO(b), p-$CH_3C_6H_4SO_3$(c)

Scheme 2. Synthesis of sulfonyl chloride functionalized ionic materials.

*2.2.5. 1-(4-Chlorosulfonylbutyl)pyridinium p-toluenesulfonate (**2c**)*

A dark brown slurry with yield of 93%. ^{1}H NMR (400 MHz, D_2O): δ7.21(d, J = 2.8, 2H), 6.89(t, J = 7.6, 1H), 6.42(d, J = 3.2, 2H), 3.00(t, J = 8.0, 2H), 1.98(q, J = 5.6, 2H), 0.52(quint, J = 6.4, 2H), 0.18(quint, J = 6.0, 2H). ^{13}C NMR(100 MHz, D_2O): δ148.23, 146.77, 130.88, 63.68, 46.94, 30.85, 30.63.

*2.2.6. Triphenyl(4-chlorosulfonylbutyl)phosphonium trifluoromethanesulfonate (**3a**)*

A pale brown solid with yield of 94%. Melting point: 90–92 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.84(s, 3H), 7.72(m, J = 3.2, 12H), 3.88(t, J = 6.4, 2H), 3.41(q, J = 7.2, 2H), 2.34(t, J = 6.8, 2H), 1.93(d, J = 3.6, 2H). ^{13}C NMR(100 MHz, $CDCl_3$): δ135.37, 133.45, 130.62, 117.63 (q, $J_{C–F}$ = 320.0, CF_3), 64.17, 24.80, 21.65, 20.30.

*2.2.7. Triphenyl(4-chlorosulfonylbutyl)phosphonium trifluoroacetate (**3b**)*

A yellow powder with yield of 92%. Melting point: 222–225 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.83(m, J = 7.6, 15H), 4.02(s, 2H), 3.73(s, 2H), 2.25(s, 2H), 1.84(s, 2H). ^{13}C NMR (100 MHz,$CDCl_3$): δ134.90, 133.77, 130.42, 118.46, 44.69, 37.87, 31.82, 21.73, 19.67.

*2.2.8. Triphenyl(4-chlorosulfonylbutyl)phosphonium p-toluenesulfonate (**3c**)*

A yellow solid with yield of 90%. Melting point: 221–223 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.88(q, J = 7.6, 6H), 7.79(q, J = 6.4, 3H), 7.71(m, J = 3.6, 6H), 4.01(q, J = 8.0, 2H), 3.73(t, J = 6.0, 2H), 2.24(t, J = 6.4, 2H), 1.83(q, J = 7.2, 2H). ^{13}C NMR (100 MHz,$CDCl_3$): δ134.91, 133.71, 130.42, 118.46, 44.61, 31.88, 21.42, 19.62.

2.3. General procedure of Beckmann rearrangement of CHO

In a typical experiment, CHO (3 mmol) and SCFIM (3 mmol) were charged into a 25 ml round-bottomed flask equipped with a magnetic stirrer at room temperature (ca. 25 °C) to 80 °C for 5 min to 6 h. At the end of the reaction, the mixture was extracted with benzene (6 ml × 3), and the combined benzene phase was analyzed by GC/MS. Then benzene was removed under reduced pressure and the crude product was obtained. The residual of the extraction was treated at 100 °C for 30 min with ca. 1–5 mm Hg vacuum to remove volatile compounds for another run.

2.4. Qualitative and quantitative analysis

The qualitative analysis of liquid reaction mixture was carried out on a Hewlett-Packard 6890/5973 GC/MS equipped with a HP 5MS column (30 m) with helium as carrier gas. The column temperature was raised from 80 to 260 °C at a heating rate of 10 °C/min. The quantitative analysis of the extract solution was carried out on a temperature-programmed Agilent 6820 GC equipped with a FID detector. The concentration of reactant and product was directly given by the system of GC chemstation according to the area of each chromatograph peak.

3. Results and discussion

Owing to the presence of SO_2Cl group in the frameworks, the ionic liquids allowed us to explore the Beckmann rearrangement of CHO. During the process, the major product of the reaction was ε-caprolactam. Two byproducts were detected respectively at different temperature conditions. When the reaction was carried out at <80 °C, the parent ketone, cyclohexanone, was formed as the only byproduct. However, at 80 °C or higher, a trace amount (<0.5%) of dehydrated dimer of caprolactam, hexahydro-1-(3,4,5,6-tetrahydro-2H-azepin-7-yl)-2H-azepin-2-one (CAS: 22993-71-1), was detected by GC/MS.

3.1. Effects of different ionic materials

Several SO_2Cl-functionalized ionic materials with varying anions and cations were examined in the Beckmann rearrangement of CHO, and the results are summarized in Table 1. Because ionic materials **1a**–**1c** are liquid with low viscosity at room temperature, Beckmann rearrangement reaction can be performed in neat SCFIMs. In the case of **2a**–**c** and **3a**–**c**, which are slurry, semisolid or powder, a common ionic liquid, e.g., $BMImPF_6$, must be utilized as medium to facilitate the contact between substrate and catalyst. On screening, ionic

Table 1
Catalytic Beckmann rearrangement of CHO over SCFIMs[a]

Entry	SCFIL	Reaction medium	*t* (h)	Conc. (%)	Sel. (%)
1	**1a**	–	1	100	97.2
2	**1b**	–	1	100	90.4
3	**1c**	–	1	61.0	14.3 (85.7)[b]
4	**2a**	$BMImPF_6$	1	63.6	92.5
5	**2b**	$BMImPF_6$	1	48.6	74.7
6	**2c**	$BMImPF_6$	1	93.3	3.0 (97.0)[b]
7	**3a**	$BMImPF_6$	5	97.5	94.6
8	**3b**	$BMImPF_6$	5	15.3	39.9
9	**3c**	$BMImPF_6$	5	68.8	22.3 (77.7)[b]

[a] Reaction conditions: SCFIL 3 mmol, CHO 3 mmol, $BMImPF_6$ 5 ml, 80 °C.
[b] The main product is reversed to cyclohexanone with selectivities in brackets.

liquid **1a** is found to be the best catalyst for the Beckmann rearrangement of CHO (entry 1). SCFIM **1b** and **3a** are also capable of catalyzing this reaction, however the efficiency is slightly inferior as compared with that of **1a** (entries 1, 2 and 7). It is interesting to note that CHO is effectively consumed in three SO_2Cl-functionalized *p*-toluenesulfonate ionic materials, however, major selectivity in favor of cyclohexanone were obtained (entries 3, 6 and 9). This observation implies that the SO_2Cl-functionalized toluenesulfonate ionic materials, especially the pyridinium-based ionic material **2c**, should be the potential catalysts for the deoximation of CHO.

3.2. Optimization of reaction conditions

Having established that the best catalyst was **1a**, we studied the effects of reaction parameters, including reaction time, temperature and the dosage of **1a**, on the Beckmann rearrangement of CHO. The results in Table 2 showed that 80 °C is the best choice for the reaction temperature, while 50 °C is sufficient to achieve a high activity of ionic material **1a** for the rearrangement. The reaction time can be greatly reduced by increasing the temperature, which is shown in entries 3 and 6. Further inspection reveals that the amount of SCFIM also affects the reaction apparently. Optimal activity is achieved in the presence of 1.0 equivalents of **1a** in the reaction mixture (entries 3–5). Ultimately, an ultrafast Beckmann rearrangement of CHO is obtained over SCFIM **1a** at 80 °C for 5 min, which shows 100% of conversion of CHO and 98.0% of selectivity to ε-caprolactam (entry 6). Unfortunately, it is an obvious exothermic process evidenced by the appreciable increase of the system temperature. Therefore, we introduced the Beckmann rearrangement to ionic liquid $BMImPF_6$ as well as to benzene to compare the efficiency of SCFIM. The results show that after 30 min reaction in $BMImPF_6$, CHO could react completely with only a slight loss of selectivity (entry 7). As expected, intense exotherm observed in neat **1a** is alleviated by the use of $BMImPF_6$ as medium. However, when benzene was employed as solvent instead of $BMImPF_6$, an obvious decrease in the selectivity to ε-caprolactam is observed (entry 8).

Table 2
Optimization of reaction conditions over SCFIM **1a**[a]

Entry	Medium	**1a**/CHO (mol)	*T* (°C)	*t* (h)	Conc. (%)	Sel. (%)
1	–	1/1	RT	2	49.6	100.0
2	–	1/1	RT	6	68.3	99.5
3	–	1/1	50	6	92.2	99.0
4	–	1/2	50	6	81.2	98.6
5	–	3/1	50	6	96.7	97.9
6[b]	–	1/1	80	5 min	100.0	98.0
7	$BMImPF_6$	1/1	80	30 min	100.0	95.3
8	Benzene	1/1	80	30 min	100.0	88.5
9[c]	–	1/1	80	5 min	73.3	40.9

[a] Reaction conditions: **1a** 3 mmol, $BMImPF_6$ (or benzene) 5 ml.
[b] The crude product was obtained with yield of 64% and purity of 97%.
[c] The reuse of catalytic system in the second run.

3.3. Yield and purity analysis of crude product

When the reaction (Table 2, entry 6) was completed, the crude product was obtained with yield of 64% by extraction with benzene and then removing benzene under reduced pressure. The purity of crude product was analyzed by using GC outside standard method and showed 97%. The main impurities include 1.5% of cyclohexanone and 0.4% dehydrated dimer of caprolactam. The rest 1% of impurity might be SCFIM **1a** solved in benzene and other unidentified compounds.

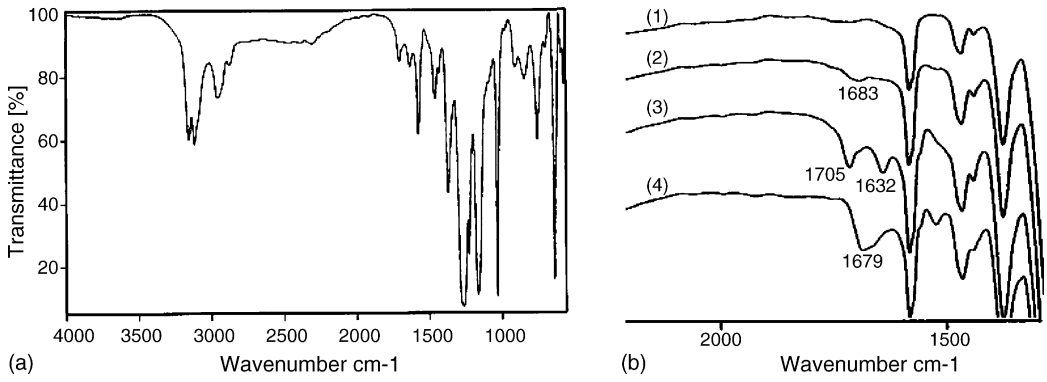
3.4. Reuse of SCFIM *1a*

Once the reaction was completed, the product was extracted with benzene; the residual was treated at 100 °C for 30 min under vacuum of ca. 1–5 mmHg to remove volatile compounds for recycling. The reuse of **1a** reveals that only 73.3% of conversion of CHO and 40.9% of selectivity to caprolactam are obtained (entry 9). This implies that the SCFIM **1a** is partially deactivated to the species of which is advantageous for the formation of cyclohexanone.

3.5. FTIR spectra investigation

Sun et al. [25] ascribed the deactivation to the conversion of SO_2Cl into SO_3H, which is considered to be active for the deoximation of CHO. In order to examine whether some of **1a** have been transformed into corresponding sulfonic acid after reaction, we first determined the pH values of neat **1a** and the resultant mixture in Table 2, entry 6. The value of 3.9 and 4.0 respectively shows that there was no significant change in acidic scale between the two samples. The FTIR spectrum of the resultant mixture in Table 2, entry 6 was also recorded and no characteristic peak of acidic hydroxyl group is observed (Scheme 3a). Obviously the deactivation cannot be attributed to the partial conversion of **1a** into corresponding $–SO_3H$ compound.

We further examined the rearrangement using FTIR spectra. Four samples of neat **1a** (1), the mixture of **1a** and CHO (to coat film in IR test conveniently, 5 mmol **1a** and 1 mmol CHO



Scheme 3. IR spectra of rearrangement samples.

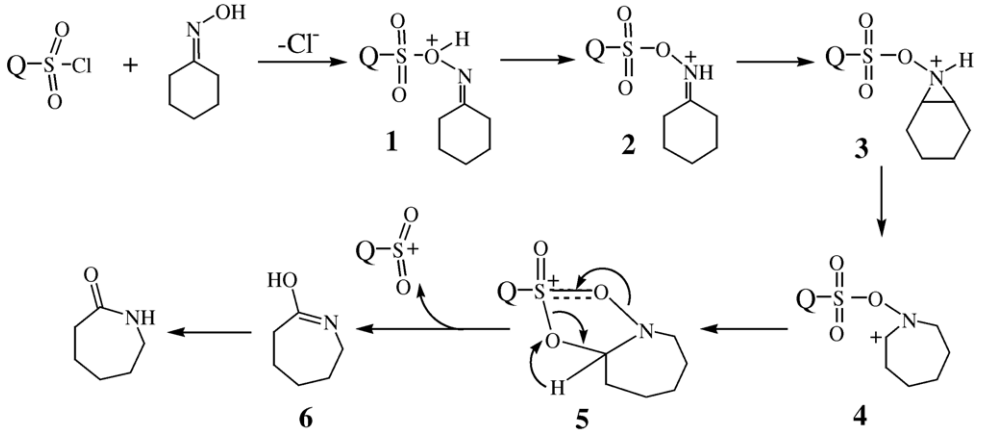
were mixtured) before reaction (2), the mixture after reaction (3), and the mixture of **1a** and caprolactam (5 mmol **1a** and 1 mmol caprolactam) (4) were recorded and their spectra are illustrated in Scheme 3b. Compared these spectra with each other, we found that the absorbance peak of caprolactam in the resultant mixture shifted to low wavenumber from 1679 to 1632 cm^{-1}, which implies that the product could interact with acidic ionic material after the reaction. Obviously it is the main reason of which the ionic catalytic system could not be reused. However, a moderate activity was obtained in the second run, indicating that this interaction is not extensive and only part of caprolactam can readily combine with the ionic material. Moreover, the composition of caprolactam and acidic ionic material could be capable of promoting the deoximation of CHO, as a result cyclohexanone was formed in a selectivity of ca. 59.1% in the second run. Further investigation is in progress.

3.6. Mass balance calculation

With these results in hand, we next explored the extent of this interaction. How much did caprolactam form composition and how much did it exist freely? We examined the rearrangement of 1 mmol CHO (0.113 g) over 5 mmol **1a** under 80 °C for 30 min and 99.2% of CHO conversion and 97.4% of selectivity to caprolactam were achieved. A benzene solution containing 0.113 g of caprolactam was concocted and used as external standard. GC analysis revealed that the actual yield of caprolactam was 0.0722 g, just 66.1% of calculated GC yield (0.113 g × 0.992 g × 0.974 g). That was to say, only 66.1% of product existed freely and about 33% of product could be trapped by the acidic ionic compound. This result is approximately close to the isolated yield obtained by benzene extraction.

3.7. Possible mechanism of Beckmann rearrangement over SCFIMs

Scheme 4 shows the possible mechanism of Beckmann rearrangement over SCFIMs. At first the electrophilic attack of the $–SO_2Cl$ group to oxygen atom of oxime is encountered, which leads to elimination of chloride ion to form oxygenium salt of species **1**, then a three-member-ring nitrogenium cation and five-member-ring sulfonium salt might be formed, and finally $Q\text{-}SO_2^+$ is released and the product is yielded. Species **3** and **5** should be the key intermediates during the rearrangement. The detail is now undergoing.



Scheme 4. Possible mechanism of Beckmann rearrangement over SCFIMs, (Q represents the remaining group of SCFIMs).

4. Conclusions

In conclusion, nine novel SCFIMs were screened as catalysts and media for Beckmann rearrangement of cyclohexanone oxime and satisfactory results were achieved. 1-(4-chlorosulfonylbutyl)-3-methylimidazolium trifluoromethanesulfonate is shown to be a highly efficient dual medium-catalyst for this reaction. But the reuse of this SCFIM is not satisfactory. The FTIR investigations reveal that this fact cannot be ascribed to the transformation of the $–SO_2Cl$ group into the corresponding $–SO_3H$. GC quantitative analysis and mass balance calculation demonstrate that the basic product can be partially trapped by acidic ionic material, which may be the main reason for the deactivation of SCFIMs. A possible mechanism is conjected and the details are in progress.

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References

[1] R.E. Gawly, Org. React. 35 (1988) 1, and references therein.
[2] Y. Izumi, S. Sato, K. Urabe, Chem. Lett. (1983) 1649.
[3] P. Albers, K. Seibold, T. Haas, G. Prescher, W.F. Hölderich, J. Catal. 176 (1998) 561.
[4] G.P. Heitmann, G. Dahlhoff, W.F. Hölderich, J. Catal. 186 (1999) 12.
[5] G.P. Heitmann, G. Dahlhoff, J.P.M. Niederer, W.F. Hölderich, J. Catal. 194 (2000) 122.
[6] R. Maheswari, K. Shanthi, T. Sivakumar, S. Narayanan, Appl. Catal. A: Gen. 248 (2003) 291.
[7] M. Ishida, T. Suzuki, H. Ichihashi, A. Shig, Catal. Today 87 (2003) 187, and references therein.
[8] Y. Ikushima, K. Hatakeda, O. Sato, T. Yokoyama, M. Arai, Angew. Chem. Int. Ed. 38 (1999) 2910.
[9] Y. Ikushima, O. Sato, M. Sato, K. Hatakeda, M. Arai, Chem. Eng. Sci. 58 (2003) 935.
[10] Y. Ikushima, K. Hatakeda, O. Sato, T. Yokoyama, M. Arai, J. Am. Chem. Soc. 122 (1908).
[11] M.T. Nguyen, G. Raspoet, L.G. Vanquickenborne, J. Am. Chem. Soc. 119 (1997) 2552.
[12] H. Sato, H. Yoshioka, Y. Izumi, J. Mol. Catal. A: Chem. 149 (1999) 25.
[13] Y. Izumi, Chem. Lett. (1999) 2171.
[14] L. Luca, G. Giacomelli, A. Porcheddu, J. Org. Chem. 67 (2002) 6272.
[15] M. Arisawa, M. Yamaguchi, Org. Lett. 3 (2001) 311.
[16] J. Ollivier, US 6252065B1, 2001.
[17] T. Welton, Chem. Rev. 99 (1999) 2071.
[18] J. Dupont, R.F. de Souza, P.A.Z. Suarez, Chem. Rev. 102 (2002) 3667.
[19] P. Wasserscheild, W. Keim, Angew. Chem. Int. Ed. 39 (2000) 3772.
[20] H. Olivier-Bourbigou, L. Magna, J. Mol. Catal. A: Chem. 182–183 (2002) 419.
[21] C. Baudequin, J. Baudoux, J. Levillain, D. Cahard, A.-C. Gaumont, J.-C. Plaqueventa, Tetrahedron: Asym. 14 (2003) 3081.
[22] R. Sheldon, Chem. Commun. (2001) 2399.
[23] J. Peng, Y. Deng, Tetrahedron Lett. 42 (2001) 403.
[24] R. Ren, L. Zueva, W. Qu, Tetrahedron Lett. 42 (2001) 8441.
[25] J. Gui, Y. Deng, Z. Hu, Z. Sun, Tetrahedron Lett. 45 (2004) 2681.
[26] K. Qiao, C. Yokoyama, Chemistry Lett. (2004) 472.
[27] Z. Fei, D. Zhao, T.J. Geldbach, R. Scopelliti, P.J. Dyson, Chem. Eur. J. 10 (2004) 4886.
[28] H. Ohno, M. Yoshizawa, W. Ogihara, Electrochim. Acta 48 (2003) 2079.
[29] Y. Gu, F. Shi, Y. Deng, J. Mol. Catal. A: Chem. 212 (2004) 71.
[30] Zhengyin Du, Zuopeng Li, Youquan Deng. Synth. Commun. 10 (2005).