Synthesis of Novel Gemini Dicationic Acidic Ionic Liquids and Their Catalytic Performances in the *Beckmann* Rearrangement

by **Xiaofei Liu**[a)][b)], **Linfei Xiao**[a)][b)], **Hugjiltu Wu**[a)][b)], **Jing Chen***[a)], and **Chungu Xia***[a)]

[a)] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R. China
(phone: +86-931-4968163; fax: +86-931-4968129; e-mail: chenj@lzb.ac.cn, cgxia@lzb.ac.cn)
[b)] Graduate University of Chinese Academy of Sciences, Beijing 100039, P. R. China

A series of novel gemini dicationic acidic ionic liquids (GDAILs), compounds **1**–**3** carrying two SO_3H groups at the cation moieties and having anions of the type $CF_3SO_3^-$, were synthesized in good yields (*Scheme 1*). Some physicochemical properties of **1**–**3** were determined; due to their unique structures, these novel GDAILs showed noticeable hydrophilic properties and strong acidities (*Table 1*). *Beckmann* rearrangements of oximes catalyzed by **1**, **2**, or **3**/zinc chloride (GDAIL/$ZnCl_2$) were investigated (*Scheme 2*); the corresponding amides were formed in up to 99% yield in the presence of 5 mol-% of GDAIL/$ZnCl_2$ catalyst under optimized conditions (*Tables 2* and *3*). The peculiar solubilities of **1**–**3** made the separation of the catalysts from the products very facile, and the catalytic system could be recycled and reused for three times.

Introduction. – Ionic liquids (ILs) have been one of the most rapidly growing areas of chemistry research in recent years. The wide range of possible cation and anion combinations allows for a large variety of tunable interactions and applications [1][2]. ILs have got broadly attention in synthesis, catalysis, separation, electrochemistry, and biochemistry [3]. Of a variety of common ILs available, most of the cations are monoquaternary species with only one quaternization center. In recent years, gemini dicationic ionic liquids (GDILs), *i.e.*, surfactant molecules possessing two hydrophobic tails on two ionic groups that are linked by a spacer, attracted increasing attention of researchers [2][4]. The GDILs usually have different chemical and physical properties from monocationic ILs such as high densities and viscosities, greater thermal stabilities, and longer liquid ranges, which make them well suited for specific applications. As recently reported, GDILs have been successfully used as electrolytes [5], as additives in chromatography [6], as agents for selectively complexing and extracting mercury(II) [7], as solvents for high-temperature organic reactions [8], and as high-temperature lubricants [9]. However, up to now, there has been no report on attempts to use a GDIL as catalyst.

We now report the synthesis of a series of novel gemini dicationic functionalized acidic ILs, *i.e.*, of 1,1′-(alkane-α,ω-diyl)bis[3-(4-sulfobutyl)-1*H*-imidazolium] trifluoro-methanesulfonates (1:2) **1**–**3**, consisting of imidazolium-based dications and triflic acid anions. Due to their unique structures, these GDAILs of a new type are strongly acidic and very poorly soluble in common organic solvents, except for EtOH and MeOH. To study the reactivity enhancement in the presence of the GDAILs **1**–**3**

during acidic catalytic reactions, we used the GDAILs together with $ZnCl_2$ as catalysts in *Beckmann* rearrangements. For comparison, the performances of other acidic ILs with only one (sulfobutyl)imidazolium unit and different tails and counterions were also tested.

Results and Discussion. – *Synthesis and Physicochemical Properties of the Gemini Dicationic Acidic Ionic Liquids* **1–3**. For the synthesis of **1–3**, 1,1′-alkanediylbis[1*H*-imidazoles] **A** were treated with butane-1,4-sultone, and then the corresponding salts **B** were reacted with triflic acid (=1,1,1-trifluoromethanesulfonic acid) (*Scheme 1*). The synthetic procedure and workup were quite simple and practical, and afforded the products **1–3** are in excellent overall yield (91–97%). The GDAILs **1–3** are viscous liquids at room temperature, being soluble in highly polar solvents such as H_2O, EtOH, and MeOH but insoluble in common organic solvents such as Et_2O, acetone, toluene, $CHCl_3$, and MeCN. These properties, together with the simple synthesis, meet the requirements for practical applications in acidic catalytic reactions.

Scheme 1. *Synthesis of the Novel Acidic Ionic Liquids* **1–3**

1 *n* = 1
2 *n* = 6
3 *n* = 10
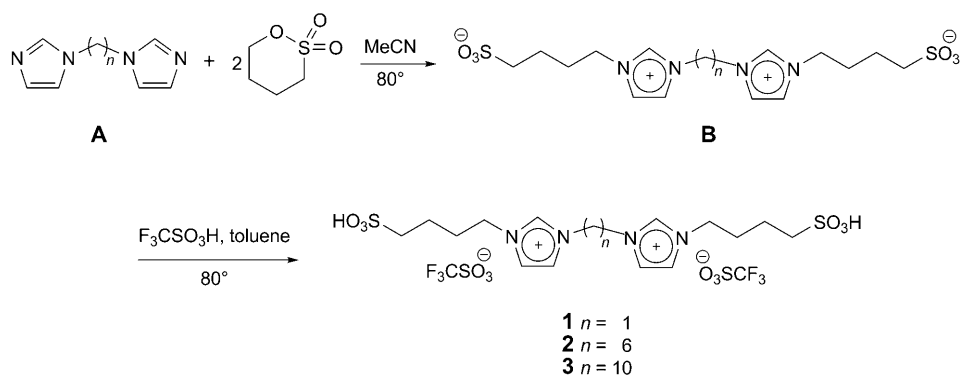
Some physicochemical properties of the novel GDAILs **1–3** and of the traditional monocationic IL **I** (see *Fig.*) are presented in *Table 1*. At room temperature (*ca.* 25°), **1–3** are liquid and have no distinct freezing points and melting points but possess lower glass-transition temperatures T_g (−30.0°, −29.2°, and −28.5°, resp.). The thermal decomposition temperatures T_d (with mass loss of 10%) of **1–3** (314°, 340°, and 343°, resp.) are lower than that of **I** (350°). This is inconsistent with general cases of common gemini dicationic ILs reported previously [2][10] which have higher thermal stabilities than monocationic ILs. The *Brønsted* acidities H_0 of ILs **1–3** and **I** were determined by the *Hammett* method as reported in [11] with UV/VIS spectroscopy. Ultimately, we obtained the acidity order of the four ILs with the following H_0 values: **3** (−0.149) < **2** (−0.115) < **1** (−0.016) < **I** (0.424), suggesting that *Brønsted* acidities of **1–3** are relatively stronger than that of the monocationic **I**. The ionic conductivities of **1–3** are smaller than that of **I** ($1.21 \cdot 10^{-1}$ Sm^{-1}) at 25°. Relatively broad electrochemical windows, 3.5–3.7 V, were observed for **1–3**, which are smaller than that of **I** (4.2 V).

Beckmann *Rearrangement Catalyzed by the IL/ZnCl₂ System. Beckmann* rearrangement, the conversion of an oxime into an amide (see *Scheme 2*), has long been an
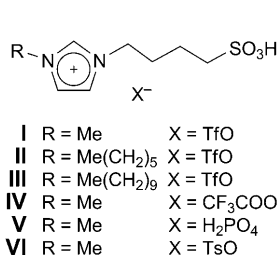
Figure. *Acidic Ils* **I–VI** *with only one (sulfobutyl)imidazolium unit and different tails and counterions, synthesized according to [12][13]* (1-methyl-3-(4-sulfobutyl)-1*H*-imidazolium 1,1,1-trifluoromethanesulfonate (1:1) (**I**), 1-hexyl-3-(4-sulfobutyl)-1*H*-imidazolium 1,1,1-trifluoromethanesulfonate (1:1) (**II**), 1-decyl-3-(4-sulfobutyl)-1*H*-imidazolium 1,1,1-trifluoromethanesulfonate (1:1) (**III**), 1-methyl-3-(4-sulfobutyl)-1*H*-imidazolium 2,2,2-trifluoroacetate (1:1) (**IV**), 1-methyl-3-(4-sulfobutyl)-1*H*-imidazolium dihydrogen phosphate (1:1) (**V**), and 1-methyl-3-(4-sulfobutyl)-1*H*-imidazolium 4-methylbenzenesulfonate (1:1) (**VI**))

	R = Me	X = TfO
I	R = Me	X = TfO
II	R = Me(CH$_2$)$_5$	X = TfO
III	R = Me(CH$_2$)$_9$	X = TfO
IV	R = Me	X = CF$_3$COO
V	R = Me	X = H$_2$PO$_4$
VI	R = Me	X = TsO

Table 1. *Some Physicochemical Properties of Gemini Dicationic Acidic Ionic Liquids*

ILs	T_g [°]	T_d [°]	H_0[a])	Ionic conductivity [S m^{-1}][b])	Electrochemical window [V][b])
1	− 30.1	313.7	− 0.016	7.23 · 10^{-2}	3.5
2	− 29.2	339.7	− 0.115	6.41 · 10^{-2}	3.4
3	− 28.5	343.1	− 0.149	4.85 · 10^{-2}	3.7
I	–	350.0	0.424	1.21 · 10^{-1}	4.2

[a]) The indicator used was 2-nitroaniline. A 0.5 mM CH$_2$Cl$_2$ solution of IL was used to determine the acidity scales because of the poor solubility of the GDAILs in CH$_2$Cl$_2$. [b]) Measured at 25°.

important subject for catalyst researchers. It accomplishes both the cleavage of a C–C bond and the formation of a C–N bond, and represents a powerful method in organic synthesis and chemical manufacturing, particularly for the industrial preparation of ε-caprolactam (= hexahydro-2*H*-azepin-2-one) from cyclohexanone oxime. This reaction, however, generally requires high temperature, strong *Brønsted* acid, and dehydrating media, which will produce a large number of by-products and bring serious corrosion problems [14]. Great efforts have been made to overcome these problems, among which is the catalytic *Beckmann* rearrangement in the vapor-phase process or liquid-phase process [15]. But the low selectivity for ε-caprolactam and the rapid decay of the catalyst activity in the vapor-phase process and the risk of environmental problems caused by the use of organic solvents in the latter liquid-phase process still remain unsatisfactory. Therefore, it is of utmost importance to accelerate reaction rates as well as to improve selectivities *via* more 'green' or environmentally friendly chemical processes. Recently, *Beckmann* rearrangement in supercritical H$_2$O has been reported [16], in which a short reaction time and excellent selectivity for ε-caprolactam was obtained, and the corrosion problem was controlled to a certain extent; but a very low conversion and rigorous reaction conditions make this approach utilizable only for research topics. In recent years, ILs as media or catalysts in *Beckmann* rearrangement have been reported [17], affording a new approach for catalytic *Beckmann* rearrangement.

Scheme 2. Beckmann *Rearrangement of Oximes to Amides Catalyzed by Acidic IL/ZnCl$_2$*
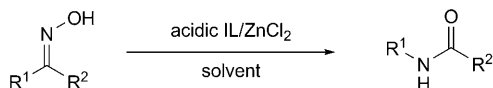
Initially, (*E*)-acetophenone oxime (= (1*E*)-1-phenylethanone oxime; R^1 = Ph, R^2 = Me) was used as a probe molecule to investigate the feasibility of the oxime *Beckmann* rearrangement to acetanilide (= *N*-phenylacetamide) in the presence of **3**/$ZnCl_2$ as catalyst (at 5 mol-%) (*Table 2*). The rearrangement failed when either **3** or $ZnCl_2$ were used as a sole catalyst (*Table 2*, *Entries 1* and *2*), while a 99% yield of acetanilide was obtained when the reaction was conducted in the presence of **3**/$ZnCl_2$ (*Table 2*, *Entry 3*). The only identified by-product was acetophenone, which was formed by deoximation of the starting (*E*)-acetophenone oxime; this implies that such a by-product can be recovered and reused, and is less detrimental to the purity of the acetanilide product.

Table 2. Beckmann *Rearrangement of (*E*)-Acetophenone Oxime Catalyzed by Acidic IL/ZnCl_2*[a])

Entry	Ionic liquid	Amount of IL [mol-%]	Reaction time [h]	Solvent	Yield[e])[f]) [%]
1[b])	**3**	5	5.0	MeCN	–
2[c])	–	0	5.0	MeCN	–
3	**3**	5	5.0	MeCN	99
4	**1**	5	5.0	MeCN	99
5	**2**	5	5.0	MeCN	99
6	**I**	10	5.0	MeCN	93
7	**II**	10	5.0	MeCN	92
8	**III**	10	5.0	MeCN	93
9	**IV**	10	5.0	MeCN	35
10	**V**	10	5.0	MeCN	5
11	**VI**	10	5.0	MeCN	47
12	**3**	2	5.0	MeCN	18
13	**3**	3	5.0	MeCN	59
14	**3**	4	5.0	MeCN	86
15	**3**	5	2.0	MeCN	25
16	**3**	5	3.0	MeCN	73
17	**3**	5	4.0	MeCN	95
18	**3**	5	5.0	EtOH	1
19	**3**	5	5.0	$MeNO_2$	10
20	**3**	5	5.0	toluene	–
21	**3**	5	5.0	solvent-free	28
22[d])	**3**	5	5.0	MeCN	94

[a]) Reaction conditions: (*E*)-acetophenone oxime (1 mmol), IL/$ZnCl_2$ 1:1 (mol ratio), solvent (5 ml), *T* 80°. [b]) $ZnCl_2$ = 0 mmol. [c]) $ZnCl_2$ = 0.05 mmol. [d]) The second cycle. [e]) GC Yield. [f]) The only by-product is acetophenone.

The effects of the various *Brønsted*-acidic ILs on the *Beckmann* rearrangement of (*E*)-acetophenone oxime were also investigated (*Table 2*). Since there were two SO_3H groups in ILs **1**, **2**, or **3** compared to one SO_3H group in the ILs **I–VI** (*Fig.*), 5 mol-% of IL/$ZnCl_2$ with respect to the oxime were used in the case of **1–3** and 10 mol-% in the case of **I–VI** to allow for the comparison of their catalytic activities. The yield of acetanilide increased slightly when the ILs with a single SO_3H group were replaced by the ILs with two SO_3H groups (see *e.g.*, *Entry 8* (93%), *vs. Entry 3* (99%)). While the differences in the alkanediyl chain length between the two imidazolium moieties did

not influence the catalytic activities (*Entries 3–5*, yields 99%), significantly different catalytic activities were observed on variation of the counterions (*Entries 6* and *9–11*). Among the ILs **I** and **IV–VI**, the highest yield of acetanilide was obtained with the **I**/ZnCl$_2$ catalyst (*Entry 6*), probably as a result of the highest *Brønsted* acidity in the case of the triflic acid anion.

To optimize the reaction conditions of the *Beckmann* rearrangement of (*E*)-acetophenone oxime (*Scheme 2*), the effect of catalyst dosage, reaction time, and solvent were also investigated (*Table 2*). The catalyst dosage had a great effect on the yield of acetanilide. When the amount of IL **3** was increased from 2 mol-% to 4 mol-% (*Entries 12* and *14*), the yield of acetanilide increased from 18% to 86% at 80°, and a further increase to 5 mol-% resulted in a 99% yield (*Entry 3*). Increasing of the reaction time had also a propitious influence on the yield of acetanilide (*Entries 15–17* and *3*), the highest yield being obtained after 5 h. Several solvents such as MeCN, MeNO$_2$, toluene, and EtOH were tested to study the solvent effect, and the reaction was also investigated under solvent-free conditions for comparison. The results show that MeCN was the most suitable solvent for this catalyst system (*Entry 3*). The yield of acetanilide was 28% under solvent-free condition (*Entry 21*), only 10% when the reaction was processed in MeNO$_2$ (*Entry 19*). When toluene or EtOH was used as solvent, no *Beckmann* rearrangement product was detected (*Entries 18* and *20*). Therefore, the solvent plays an important role in this reaction.

Then, the reusability of the **3**/ZnCl$_2$ catalyst was tested in the *Beckmann* rearrangement of (*E*)-acetophenone oxime. The two SO$_3$H groups of **1–3** cause these ILs to be more hydrophilic than the ILs **I–VI** bearing a single SO$_3$H group. The latter are soluble in some organic solvents such as MeCN, toluene, CH$_2$Cl$_2$, and alcohol to some extent, while the ILs **1–3** are hardly soluble in common organic solvents, except for MeOH and EtOH at room temperature. The immiscibility of **3** with MeCN and the good solubility of acetanilide in MeCN make the separation of the catalyst from the product quite facile, and a 94% yield of acetanilide was achieved when the catalyst was directly reused for the second time just after the organic phase was decanted and without need of supplementary ZnCl$_2$ (*Table 2*, *Entry 21*).

Finally, the generality and scope of the *Beckmann* rearrangement of various ketone oximes in the presence of **3**/ZnCl$_2$ in MeCN was investigated (*Table 3*), the by-products being only the corresponding ketones (by GC/MS). Excellent yields were obtained with aromatic ketoximes, and (*E*)-acetophenone oxime showed the best reactivity among all the oximes (*Entries 1–5*) under the given conditions. Cyclo-dodecanone oxime was also very reactive and was converted to the corresponding amide in 94% yield (*Entry 6*), this amide being useful as a staring material for the production of nylon. While cyclohexanone oxime was converted into ε-caprolactam in moderate yield (*Entry 7*), acetone oxime was extremely unreactive, and no amide was isolated (*Entry 8*).

Conclusions. – We prepared a series of novel gemini dicationic acidic ionic liquids (GDAILs) with noticeable hydrophilic properties and strong acidities and established the potential application of these GDAILs as catalysts in acidic catalytic reactions. The GDAILs-mediated ZnCl$_2$ catalyst (IL/ZnCl$_2$) demonstrated successful catalytic performances in the *Beckmann* rearrangement: satisfactory yields of amides were

Table 3. Beckmann *Rearrangement of Various Oximes Catalyzed by [3/ZnCl₂*

Entry[a])	Substrate	Product	Yield[b])[c]) [%]
1			96
2			76
3			92
4			94
5			93
6			94
7			37
8			–

[a]) Reaction conditions: oxime (1 mmol), **3** (5 mol-%), **3**/ZnCl₂ 1:1 (mol/mol), MeCN (5 ml), temperature 80°, time 5 h. [b]) Yields of isolated product. [c]) Purity of amide tested by GC; content of amide in the product > 99% (GC).

obtained in the presence of 5 mol-% of *Brønsted*-acidic ILs/ZnCl₂ as catalysts in MeCN under mild reaction conditions, especially from aromatic oximes, and the novel GDAILs could easily be separated from the products due to their immiscibility with organic solvents. Ionic liquids with triflate anions showed better catalytic activities than

acidic ILs with other anions. The performance of these novel catalyst was still excellent in a second-time reuse. Further work is in progress in our laboratories to study the mechanism of the catalytic system in the *Beckmann* rearrangement of oximes.

Experiment Part

General. Toluene was distilled over Na. MeCN was distilled over CaH_2. All other solvents and chemicals were commercially available and used without further purification. The oximes were prepared according to standard methods, and their purities were established by their melting points before utilization. The ILs **I–VI** were synthesized according to [12][13]. ^{1}H- and ^{13}C-NMR Spectra: *Varian INOVA-400-M* spectrometer; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. ESI-MS: *Waters ZQ 4000*; in *m/z* (rel. %). Elemental analyses: *Elementar Analysensysteme GmbH VarioEL*, with the software version V3.00. Ion conductivity: *Mettler FE30* digital conductivity meter at 25°. Cyclic Voltammetry: *CHI-660C* electrochemical work station; at r.t. with a glassy carbon working electrode, a Pt wire counter electrode, and a Ag/AgCl reference electrode. *Brønsted* Acidity: measurement of the H_0 values with an *Agilent 8453* UV/VIS spectrophotometer and a basic indicator. Thermal Analysis and Temp.-Dependent Phase Behavior: *Mettler-Toledo DSC822e* differential-scanning calorimeter, scan rate 10°/min, under N_2 in the circular range of −100 to 110°, with samples tightly sealed in Al pans; the glass transition temp. (T_g) and was recorded as the midpoint of the glass transition; the decomposition temp. (T_d) was recorded by thermogravimetry with 10% of mass loss by means of a *Pyris Diamond Perkin-Elmer* TG/DTA, scan rate 20°/min, under N_2, with samples tightly sealed in Al_2O_3 pans.

1,1′-Methylenebis[3-(4-sulfobutyl)-1H-imidazolium] 1,1,1-Trifluoromethanesulfonate (1:2) (**1**). As described in [18], 1,1′-methylenebis[1H-imidazol] (**A**, *n* = 1) was prepared from 1H-imidazole (1 equiv.), CH_2Cl_2, and KOH (2 equiv.) in the presence of 3% $Bu_4N \cdot Br$ soln. at r.t. Extraction with EtOH followed by column chromatography yielded **A** (*n* = 1). According to a similar approach reported previously [13], a mixture of **A** (*n* = 1; 1 equiv.) and butane-1,4-sultone (= 1,2-oxathiane 2,2-dioxide; 2 equiv.) at 80° in anh. MeCN was stirred for 24 h. The resulting white powder was pulverized, washed with EtOH, and dried *in vacuo*. The white powder and CF_3SO_3H were mixed in a molar ratio of 1:2 in anh. toluene and heated at 80° for 24 h, followed by washing with MeCN and Et_2O and drying *in vacuo*: **1** (91%). Yellow viscous liquid. ^{1}H-NMR (400 MHz, D_2O): 9.15 (*s*, 2 H); 7.64 (*s*, 2 H); 7.62 (*s*, 2 H); 6.57 (*s*, 2 H); 4.16 (*t*, *J* = 7.2, 4 H); 2.78 (*t*, *J* = 7.2, 4 H); 1.89 (*t*, *J* = 7.6, 4 H); 1.58 (*t*, *J* = 7.2, 4 H). ^{13}C-NMR (100 MHz, D_2O): 136.31; 122.40; 122.29; 119.71 (*q*, *J*(C,F) = 315.2, CF_3); 59.01; 50.03; 49.76; 27.85; 20.97. ESI-MS: 421.7. Anal. calc. for $C_{17}H_{26}F_6N_4O_{12}S_4$ (720.66): C 28.33, H 3.64, N 7.77; found: C 28.26, H 3.75, N 7.71.

1,1′-(Hexane-1,6-diyl)bis[3-(4-sulfobutyl)-1H-imidazolium] 1,1,1-Trifluoromethanesulfonate (1:2) (**2**). The starting 1,1′-(hexane-1,6-diyl)bis[1H-imidazol] (**A**, *n* = 6) was prepared according to a similar procedure [19]: A mixture of 1H-imidazole-1-propanenitrile (2.1 mol-equiv.) and 1,6-dibromohexane (1 mol-equiv.) in EtOH was stirred at 80–90° for 24 h. Then, the mixture was cooled, the precipitated solid filtered and washed with cold acetone to give the bis-imidazolium salt. The salt was then dissolved in $CHCl_3$, the soln. mixed with 40% (*w/w*) NaOH soln., and the mixture was stirred at r.t. for 0.5–1 h. Then, the mixture was extracted with $CHCl_3$, the org. phase washed with H_2O (6×), and the combined org. extract concentrated. To the obtained yellow reddish viscous liquid, Et_2O/H_2O 2:1 was added, and the immediately formed white crystals were filtered, washed with Et_2O and H_2O, and dried *in vacuo*: pure **A** (*n* = 6). As described for **1**, **A** (*n* = 6) was then transformed to **2** (96%).Yellow viscous liquid. ^{1}H-NMR (400 MHz, D_2O): 8.64 (*s*, 2 H); 7.34 (*s*, 2 H); 7.32 (*s*, 2 H); 4.07 (*t*, *J* = 6.8, 4 H); 4.01 (*t*, *J* = 7.2, 4 H); 2.75 (*t*, *J* = 7.6, 4 H); 1.85 (*t*, *J* = 7.6, 4 H); 1.68 (*t*, *J* = 6.8, 4 H); 1.49 (*t*, *J* = 7.6, 4 H); 1.42 (*t*, *J* = 6.0, 4 H). ^{13}C-NMR (100 MHz, D_2O): 135.29; 122.56; 122.41; 119.71 (*q*, *J*(C,F) = 315.2, CF_3); 50.13; 49.05; 49.54; 29.00; 28.14; 24.91; 21.01. ESI-MS: 491.8. Anal. calc. for $C_{22}H_{36}F_6N_4O_{12}S_4$ (790.80): C 33.41, H 4.59, N 7.09; found: C 33.35, H 4.67, N 7.20.

1,1′-(Decane-1,10-diyl)bis[3-(4-sulfobutyl)-1H-imidazolium] 1,1,1-Trifluoromethanesulfonate (1:2) (**3**). As described for **2**: **3** (97%). Yellow viscous liquid. ^{1}H-NMR (400 MHz, D_2O): 8.60 (*s*, 2 H); 7.31 (*s*,

2 H); 7.29 (*s*, 2 H); 4.04 (*t*, *J* = 6.8, 4 H); 3.98 (*t*, *J* = 6.8, 4 H); 2.72 (*t*, *J* = 7.6, 4 H); 1.81 (*t*, *J* = 7.6, 4 H); 1.64 (*t*, *J* = 6.0, 4 H); 1.53 (*t*, *J* = 7.2, 4 H); 0.95 – 1.06 (*m*, 12 H). ^{13}C-NMR (100 MHz, D_2O): 135.25; 122.55; 122.37; 119.71 (*q*, *J*(C,F) = 315.2, CF_3); 50.12; 49.69; 49.02; 29.14; 28.35; 28.21; 28.01; 25.32; 21.02. ESI-MS: 547.8. Anal. calc. for $C_{26}H_{44}F_6N_4O_{12}S_4$ (846.90): C 36.87, H 5.23, N 6.62; found: C 36.90, H 5.31, N 6.56.

Beckmann *Rearrangement: General Procedure.* A mixture of the oxime (1.00 mmol), IL (0.05 – 0.10 mmol), $ZnCl_2$ (0.05 – 0.10 mmol), and solvent (5 ml) was stirred for 2 – 5 h at 80°. Then, the mixture was cooled and analyzed qualitatively by GC/MS (*HP 6890/5793*) and quantitatively by GC (*Agilent-6820-GC* system, FID detector). The GC yield was obtained from the product of conversion of starting material and selectivity of amide.

REFERENCES

[1] T. Welton, *Chem. Rev.* **1999**, *99*, 2071; V. I. Pârvulescu, C. Hardacre, *Chem. Rev.* **2007**, *107*, 2615; B. Jastorff, K. Mölter, P. Behrend, U. Bottin-Weber, J. Filser, A. Heimers, B. Ondruschk, J. Ranke, M. Schaefer, H. Schröder, A. Stark, P. Stepnowski, F. Stock, R. Störmann, S. Stolte, U. Welz-Biermann, S. Ziegerta, J. Thöminga, *Green Chem.* **2005**, *7*, 362; F. van Rantwijk, R. A. Sheldon, *Chem. Rev.* **2007**, *107*, 2757; C. Cadena, J. L. Anthony, J. K. Shah, T. I. Morrow, J. F. Brennecke, E. J. Maginn, *J. Am. Chem. Soc.* **2004**, *126*, 5300; K. A. Fletcher, S. Pandey, *Langmuir* **2004**, *20*, 33; D. L. Boxall, R. A. Osteryoung, *J. Electrochem. Soc.* **2004**, *151*, E41; H. Luo, S. Dai, P. V. Bonnesen, A. C. Buchanan, J. D. Holbrey, N. J. Bridges, R. D. Rogers, *Anal. Chem.* **2004**, *76*, 3078; A. E. Visser, R. P. Swatloski, W. M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. H. Davis, R. D. Rogers, *Environ. Sci. Technol.* **2002**, *36*, 2523.
[2] J. L. Anderson, R. Ding, A. Ellern, D. W. Armstrong, *J. Am. Chem. Soc.* **2005**, *127*, 593.
[3] W. J. Swindall, *Clean Techn. Environ. Policy* **2004**, *6*, 149.
[4] R. Wang, C. M. Jin, B. Twamley, J. M Shreeve, *Inorg. Chem.* **2006**, *45*, 6396.
[5] K. Ito, N. Nishina, H. Ohno, *Electrochim. Acta* **2000**, *45*, 1295; Z. X. Zhang, L. Yang, S. C. Luo, M. Tian, K. Tachibana, K. Kamijima, *J. Power Sources* **2007**, *167*, 217.
[6] V. Pino, Q. Q. Baltazar, J. L. Anderson, *J. Chromatogr.*, *A* **2005**, *1148*, 92; J. L. Anderson, D. W. Armstrong, *Anal. Chem.* **2005**, *77*, 6453; M. Qi, D. W. Armstrong, *Anal. Bioanal. Chem.* **2007**, *388*, 889.
[7] J. D. Holbrey, A. E. Visser, S. K. Spear, W. M. Reichert, R. P. Swatloski, G. A. Broker, R. D. Rogers, *Green Chem.* **2003**, *5*, 129.
[8] X. Han, D. W. Armstrong, *Org. Lett.* **2005**, *7*, 4205.
[9] Z. Zeng, B. S. Phillips, J. C. Xiao, J. M. Shreeve, *Chem. Mater.* **2008**, *20*, 2719.
[10] Y.-S. Ding, M. Zha, J. Zhang, S.-S. Wang, *Colloids Surf.*, *A* **2007**, *298*, 201.
[11] C. Thomazeau, H. Olivier-Bourbigou, L. Magna, S. Luts, B. Gilbert, *J. Am. Chem. Soc.* **2003**, *125*, 5264.
[12] J. Z. Gui, X. H. Cong, D. Liu, X. T. Zhang, Z. D. Hu, Z. L. Sun, *Catal. Commun.* **2004**, *5*, 473.
[13] H. B. Xing, T. Wang, Z. H. Zhou, Y. Y. Dai, *Ind. Eng. Chem. Res.* **2005**, *44*, 4147.
[14] R. E. Gawly, *Org. React.* **1988**, *35*, 1.
[15] H. Ichihashi, M. Kitamura, *Catal. Today* **2002**, *73*, 23; S. Chandrasekhar, K. Gopalaiah, *Tetrahedron Lett.* **2002**, *43*, 2455; S. Chandrasekhar, K. Gopalaiah, *Tetrahedron Lett.* **2003**, *44*, 755.
[16] Y. Ikushima, K. Hatakeda, O. Sato, T. Yokoyama, M. Arai, *J. Am. Chem. Soc.* **2000**, *122*, 1908; M. Boero, T. Ikeshoji, C. C. Liew, K. Terakura, M. Parrinello, *J. Am. Chem. Soc.* **2004**, *126*, 6280; O. Sato, Y. Ikushima, T. Yokoyama, *J. Org. Chem.* **1998**, *63*, 9100; Y. Yamaguchi, N. Yasutake, M. Nagaoka, *THEOCHEM* **2003**, *639*, 137.
[17] J. J. Peng, Y. Q. Deng, *Tetrahedron Lett.* **2001**, *42*, 403; R. X. Ren, L. D. Zueva, W. Ou, *Tetrahedron Lett.* **2001**, *42*, 8441; S. Guo, Y. Q. Deng, *Catal. Commun.* **2005**, *6*, 225; J. Z. Gui, Y. Q. Deng, Z. D. Hu, Z. L. Sun, *Tetrahedron Lett.* **2004**, *45*, 2681; K. Elango, R. Srirambalaji, G. Anantharaman, *Tetrahedron Lett.* **2007**, *48*, 9059; Z. Y. Du, Z. P. Li, Y. L. Gu, J. Zhang, Y. Q. Deng, *J. Mol. Catal. A: Chem.* **2005**, *237*, 80; S. Guo, Z. Y. Du, S. G. Zhang, D. M. Li, Y. Q. Deng, *Green Chem.* **2006**, *3*, 296.
[18] E. Díez-Barra, A. de la Hoz, A. Sánchez-Migallón, J. Tejeda, *Heterocycles* **1992**, *34*, 1365.
[19] A. Horvóth, *Synthesis* **1994**, 102.