388 **RESEARCH PAPER** JUNE, 388–390 JOURNAL OF CHEMICAL RESEARCH 2005

Task-specific ionic liquids as efficient, green and recyclable reagents and solvents for oxidation of olefins

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Two kinds of task-specific ionic liquids (Ils) composed of imidazolinium or pyridinium cations with a carboxy group and hydrogensulfate as counterion have been synthesised and their application in oxidation of olefins has been studied. The carbonyl compounds were obtained from the oxidation of chain olefins, and 1,2-cycloalkandiols were obtained from cycloalkenes in the novel oxidation systems which are easily manipulated. The products can be easily isolated from the reaction system and the ILs can readily be recovered and reused.

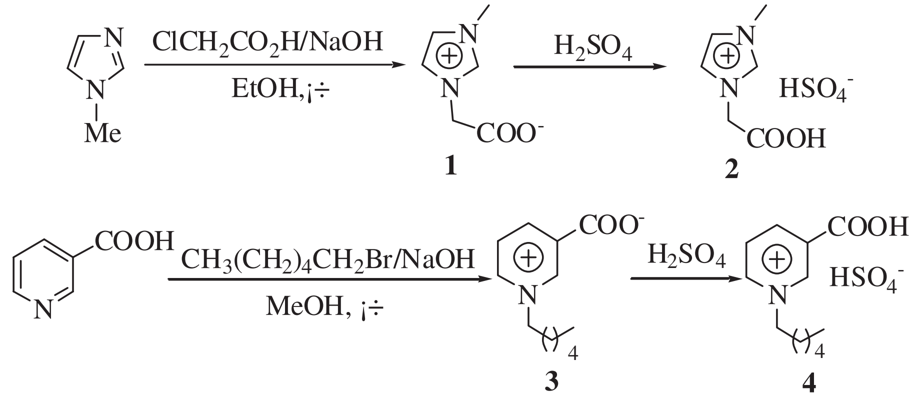
Keywords: ionic liquids, imidazolinium, pyridinium, carboxy group, olefins, oxidation

Ionic liquids (ILs) have recently gained recognition as recyclable reaction media for organic reactions, because of their properties, such as lack of significant vapour pressure, ease of reuse, absence of flammability, and tolerance for large temperature variations.[1-2] There has been also a great deal of interest in the application of the ILs as novel biphasic catalysts,[3] extraction solvents,[4] and stationary phases for chromatography.[5] Recently, task-specific ILs have shown interesting usage and developing potentialities.[6,7] Almost all the reported new task-specific ILs have been proven useful in both synthetic and separation applications.[8-20] For example, Deng *etc.* synthesised carboxyl-containing imidazolium ILs and used them to catalyse deoximation.[14b] Wasserscheid and co-workers reported Friedel–Crafts alkylation catalysed by ILs with hydrogensulfate and tetrakis(hydrogensulfato)borate anions.[20]

Organic peracids are used in large scale in organic synthesis. Reaction of carboxylic acids with H_2O_2 at low temperature in acidic conditions is one of the most important documented synthetic method for organic peracids.[21] As ILs possess the merits of easy recovery and reuse, we planned to synthesise a kind of ILs containing a carboxy group which can be used in organic synthesis after oxidising it to a peracid. In addition, we choose hydrogensulfate as the anion of Ils to meet the acidic condition, for H_2SO_4 is in general use and possesses low volatility.

Herein, we describe the synthesis of carboxy group containing ILs with hydrogensulfate as an anion and their use in oxidation of olefins. The imidazolium task-specific IL (**2**) can be prepared by alkylation of 1-methylimidazole with chloroacetic acid under basic condition followed by the addition of one equivalent 63% H_2SO_4 (80% yield, m.p. 20–21°C, Scheme 1). As the natural nicotinic acid is a biorenewable resource with a pyridine ring and carboxy group, we choose it as another starting material for the synthesis of a pyridinium ring containing, task-specific IL. The pyridinium targeted IL (**4**) was obtained by the route of Scheme 1 (86% yield m.p. 44–46°C). Both of the ILs are miscible with water, methanol, acetone, and other strong polar organic solvents and immiscible with ether, 1,1,1-trichloroethane, and other weakly polar organic solvents.

The oxidation reactions are conducted as follows. With no special precautions, **2** was mixed with 60% H_2O_2 at 0°C. After 1h, styrene was added to the mixture and the reaction was continued for 5h at 5°C. Benzyaldehyde (**6**) and styrene oxide (**7**) were obtained in 72% and 6% yield, respectively, shown in Table 1 (entry 1–2). **4** was mixed with 60% H_2O_2 at 0°C. After 1h, styrene was added to the mixture and the reaction was continued for 10h at 5°C. **6** and **7** were obtained in 70% and 5% yield, respectively, shown in Table 1 (entry 2). With this trend in hand, compound task-specific IL **2** was further used for the oxidation of several other aromatic and aliphatic olefins so as to investigate the universality of such novel oxidation system. When α-methylstyrene was used as the substrate, acetophenone was obtained in 67% (Table 1, entry 3). When 1-tetradecene was used as the substrate, tridecanal and 1,2-epoxytetradecane were obtained in 78% and 5% yield, respectively, shown in Table 1 (entry 4). When oleic acid was used as the substrate, decyl aldehyde and ω-aldehyde octanoic acid were obtained in 70% and 75% yield, respectively, shown in Table 1 (entry 5). Interestingly,



Scheme 1 Synthesis of task-specific ionic liquids.

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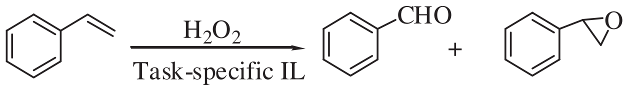
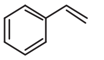
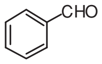
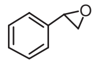
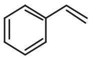
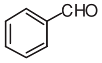
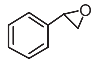
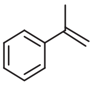
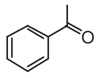
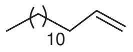
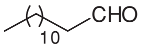
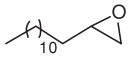
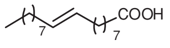
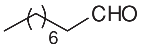
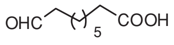
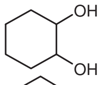
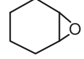
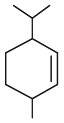
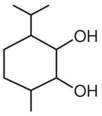
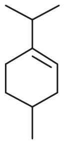
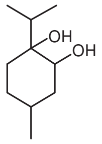


5 **6** **7**

Table 1 Oxidation of olefins in task-specific IL system

Entry	Substrate	Product	Yield[b]/%	B.p.(Lit.)/°C/mmHg
1			72	61–62/10(62/10[22])
			6	72–73/10(73–74/10[23])
2[c]			70	61–62/10(62/10[22])
			5	72–73/10(73-74/10[23])
3			67	66–67/5(67/5[22])
4			78	127–128/10(126–127/10[22])
			5	99–101/1(oil[23])
5			70	90–91/22(91–92[22])
			75	180–181/15(181–182/15[22])
6[d]			73	101–102(101–104[23])
			5	131/760(130–132/760[23])
7[d]			82	110–114/0.1(110–115/0.1[24])
8[d]			80	106–109/2(106–108/2[25])

[a]Reaction conditions: compound task-specific IL **2** (5mmol) was mixed with 60%H_2O_2 (3mmol) at 0°C. After 1h, the olefin (2mmol) was added to the mixture and the reaction was continued for 5h at 5°C. [b]Yield is based on the substrate and is determined by GC. [c]Reaction conditions: compound task-specific IL **4** (5mmol) was mixed with 60%H_2O_2 (3mmol) at 0°C. After 1h, the olefin (2mmol) was added to the mixture and the reaction was continued for 10h at 5°C. [d]*Trans*-diol was obtained.

when cyclohexene was used as the substrate, *trans*-1,2-cyclohexanediol was obtained as the main product and a small amount of cyclohexene oxide was detected (Table 1, entry 6). For the six-number-ring compounds (2-isopropyl-5-methyl-1-cyclohexene and 1-isopropyl-4-methyl-1-cyclo hexene), similar results were obtained (Table 1, entry 7–8). This shows that the chain olelfins tend to form carbonyl compounds and the cycloalkenes tend to form trans-1,2-cycloalkandiols.

To evaluate the possibility of recycling the compound task-specific ILs used for the reaction, the recovered IL (**2**) was concentrated in a vacuum (10 torr for 2h at room temperature). Then a second amount of reactants were added and the process was repeated up to 5 times. It seems that there is little decline in the rate or yield of the reaction during each cycle, shown in Table 2.

The metal-assisted oxidation by hydrogen peroxide of olefins to aldehydes or ketones and the palladium-catalysed oxidation of styrene to acetophenone in IL have been reported.[26-27] In our novel oxidation reaction system, it is probably that the epoxidation of the olefin may be the early stage of the reaction and the perhydrolysis or hydrolysis of the epoxide leads to the final product.[28] Further studies of the details of reaction mechanism are under study. In conclusion, we have designed and synthesised two kinds of new task-specific ILs by a

Table 2 Recycling of the task-specific ionic liquids **2**

Run			1	2	3	4	5
	Task-specific ILs	Products					
Yield/%[a]	**2**	**6**	72	70	73	71	70
		7	6	8	7	8	6

[a]Yield is based on the substrate and is determined by GC.

simple and straightforward procedure from cheap materials in good yields. The novel system has been successfully applied to oxidize olefins to selectively obtain aldehydes, ketones or 1,2-cycloalkandiols as the main products. The system is easily manipulated, the product can be easily isolated and the ILs can readily be recovered and reused.

Experimental

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Advance 400 spectrometer in $CDCl_3$ or DMSO with TMS as the internal standard; chemical shifts are quoted in ppm and J values are given in Hz. IR spectra were recorded on a Bruker Vector 22 spectrometer. GCMS was recorded on TRACE GC 2000/TRACE MS. Melting or boiling points are in good agreement with literature data.

A typical procedure for the oxidation of styrene in **2**: Ionic liquid **2** (5mmol) and 60% H_2O_2 (3mmol) were mixed in a 25ml flask equipped with a magnetic stir bar at 0°C. After 1h, olefin (2mmol) was added to the mixture and the reaction was continued for 5h at 5°C. Progress of the reaction was monitored by GC. The products were extracted by ether (3 × 2ml), washed with water and dried with anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the residue was chromatographed on silical gel. The formation of different products has been conformed by ^{1}H NMR and GCMS.

Synthesis of **2**: Under vigorous stirring, chloroacetic acid (9.5g) was added dropwise to a solution of 1-methylimidazole (8.2g) and NaOH (4.0g) in 200ml of methanol over 0.5h. The mixture was stirred for additional 10h under reflux and then the insoluble NaCl was removed by filtration. The residue was evaporated to dryness, extracted by CH_2Cl_2 (3 × 20ml) and then **1** was obtained, yield 11.2g, 80%. After mixing **1** with 63% H_2SO_4 (1:1 mol), the mixture was evaporated to dryness and **2**, which can be directly used in the reaction, was obtained, yield 19.0g, 100%. A little **1** was further purified by column chromatography (2:1, methanol/ethyl acetate) for characterisation. After mixing the pure **1** with 63% H_2SO_4 (1:1 mol), the mixture was evaporated to dryness and **2**, which can be directly characterised, was obtained.

Synthesis of **4**: Under vigorous stirring, 1-bromohexane (19.8g) was added dropwise to a solution of nicotinic acid (12.3g) and NaOH (4.0g) in methanol (200ml) over 0.5h. The mixture was stirred for additional 10h under reflux and then the insoluble NaCl was removed by filtration. The residue was evaporated to dryness, extracted by CH_2Cl_2 (3 × 20ml) and then **3** was obtained, yield 17.8g, 86%. After mixing **3** with 63% H_2SO_4 (1:1 mol), the mixture was evaporated to dryness and **4**, which can be directly used in the reaction, was obtained, yield 26.2g, 100%. A little **3** was further purified by column chromatography (2:1, methanol/ethyl acetate) for characterisation. After mixing the pure **3** with 63% H_2SO_4 (1:1 mol), the mixture was evaporated to dryness and **4**, which can be directly characterised, was obtained.

1: M.p. 236°C (decomposed); ^{1}H NMR (400 MHz) DMSO/$CDCl_3$(4:1)–TMS δ = 3.98 (overlap in DMSO, 3H), 5.19 (s, 2H), 7.69 (s, 1H), 7.74 (s, 1H), 9.36 (s, 1H); ^{13}C NMR (400 MHz), DMSO/$CDCl_3$(1:1)–TMS δ = 36.72, 50.50, 123.77, 124.53, 138.46, 168.50; IR 3446, 3117, 1736, 1632 cm^{-1}; Anal. Calcd. For $C_6H_8N_2O_2$: C, 51.4; H, 5.8; N, 20.0. Found: C, 51.3; H, 5.9; N, 19.9%.

2: M.p. 20–21°C, ^{1}H NMR (400 MHz) DMSO–TMS δ = 3.90 (s, 3H), 5.15 (s, 2H), 7.73 (s, 2H), 9.14 (s, 1H), 9.36 (s, br.); ^{13}C NMR (100 MHz), DMSO δ = 36.28, 50.01, 123.64, 124.14, 138.13, 168.58; IR 3157, 3115, 3092, 2899, 1736, 1580 cm^{-1}; Anal. Calcd. For $C_6H_{10}N_2O_6S$: C, 30.3; H, 4.2; N, 11.8. Found: C, 30.2; H, 4.3; N, 11.8%.

3: M.p. 193°C (decomposed); ^{1}H NMR (400 MHz) DMSO/$CDCl_3$(4:1)–TMS δ = 0.84 (t, J = 7.00 Hz, 3H), 1.26–1.34 (m, 6H), 2.00 (q, J = 6.80 Hz, 2H), 4.76 (t, J = 7.20 Hz, 2H), 7.98 (t, J = 6.60 Hz, 1H), 8.93–8.98 (m, 2H), 9.36 (s, 1H); ^{13}C NMR (100 MHz), DMSO/CDCl3(4:1)–TMS δ = 14.16, 22.26, 25.52, 30.99, 31.39, 60.94, 127.48, 140.64, 144.39, 144.85, 145.65, 185.08; IR 3416, 3057, 2957, 2930, 2859, 2199, 1643 cm^{-1}; Anal. Calcd. For $C_{12}H_{17}NO_2$: C, 69.5; H, 8.3; N, 6.8. Found: C, 69.4; H, 8.5; N, 6.7.

4: M.p. 44–46°C, ^{1}H NMR (400 MHz) DMSO–TMS δ = 0.84 (t, J = 6.75 Hz, 3H), 1.27 (m, 6H), 1.90–1.92 (m, 2H), 4.69 (t, J = 7.49 Hz 2H), 6.88 (s, br.), 8.26 (dd, J=8.06, 6.06 Hz, 1H), 8.94 (d, J = 8.06 Hz, 1H), 9.29 (d, J = 6.06 Hz, 1H), 9.57 (s, 1H); ^{13}C NMR (100 MHz), DMSO δ = 14.26, 22.27, 25.45, 31.01, 31.21, 61.53, 128.79, 131.60, 145.62, 146.43, 148.08, 163.55; IR 3431, 3083, 3058, 3010, 2920, 2855, 1716, 1635, 1592 cm^{-1}; Anal. Calcd. For $C_{12}H_{19}NO_6S$: C, 47.2; H, 6.3; N, 4.6. Found: C, 47.; H, 6.3; N, 4.6.

Received 26 November 2004; accepted 14 March 2005
Paper 04/2899

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