A Novel and Eco-friendly Method for the Preparation of Ionic Liquids

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Abstract: A novel and eco-friendly method is described for the direct preparation of a series of ionic liquids containing alkylimidazolium-based cations and hexafluorophosphate-based (or tetrafluoroborate-based) anions in a one-pot procedure by using ionic liquids themselves as solvents.

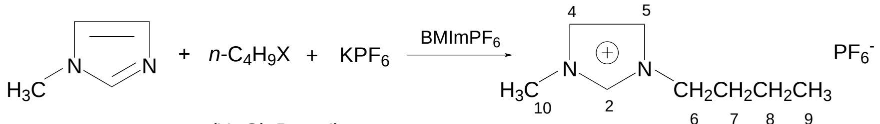
Key words: ionic liquid, alkylimidazolium, hexafluorophosphate, tetrafluoroborate

As the use of conventional volatile solvents required in various organic synthetic processes is of ecological concern, the room temperature ionic liquids (RTILs), also referred to as designer solvents, have drawn powerful attention due to their unique chemical characters.[1,2] Such characters as negligible vapor pressure, thermal stability, favorable solubility of many and various chemicals, high recovery and recycling potential, have made RTILs emerge as a new green alternative to volatile organic solvents in the applications of organic synthesis, catalysis, biocatalysis, polymerization, and so on.[3–6] As more and more synthesis can be proceeded in these novel solvent systems with good yield and high selectivity, RTILs have shown great promise in commercial applications.[7]

However, despite their successful applications as reaction medium in synthetic processes, a practical method for the preparation of RTILs, especially in large-scale production, is still not available. The conventional procedures for their preparation usually include two steps: with alkylimidazolium hexafluorophosphate based RTILs as example, firstly, alkylimidazolium halides are prepared; secondly, the obtained halides react with hexafluorophosphoric acid or its corresponding salts.[8] A large excess of alkyl halides/volatile organic solvents, such as acetone, toluene and CH_3CN, is always used as the reaction medium in the two steps, and in some cases expensive silver salts are required, all of them remain much to be improved. Quite recently, Varma and Namboodiri disclosed an improved preparation of RTILs by using microwaves.[9,10] Although the microwave-assisted method avoided using organic solvents as the reaction medium, the procedure was still difficult to achieve on large-scale preparation.

Accordingly, we have recently been interested in the development of not only environmentally benign but also facile approaches to the preparation of RTILs and disclose herein our study results of a method using RTILs themselves as reaction medium, which can be carried out directly and effectively from three components of *N*-methylimidazole (MIm) [or 1,2-dimethylimidazole (DMIm)], alkyl halide, and hexafluorophosphate (or tetrafluoroborate) salt in a one-pot procedure to prepare alkylimidazolium hexafluorophosphate and alkylimidazolium tetrafluoroborate based RTILs. The method is in accordance with the principles of green chemistry in three aspects: 1) usage of an environmental benign solvent and inexpensive materials, 2) elimination of an additional process required in the two-step procedure to separate and purify the formed intermediate of quaternary alkylimidazolium halide (QImX), since QImX reacted with hexafluorophosphate (or tetrafluoroborate) salt directly in situ to generate the desired ionic liquid and 3) avoiding the tedious process for the desired product isolation from solvent, since two of them were the same materials.

Initially the method was evaluated to the preparation of $BMImPF_6$ (Scheme 1) and the results are presented in Table 1. As can be seen, the reactivity of halides is in the order of *n*-butyl iodide > *n*-butyl bromide > *n*-butyl chloride (entries 1, 5 and 7); *n*-butyl chloride was relatively less reactive and required longer reaction time, while the higher reactivity of *n*-butyl bromide and *n*-butyl iodide provided good yields with shorter reaction time. Hence, *n*-



Scheme 1

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Table 1 Direct Preparation of $BMImPF_6$

Entry	n-C_4H_9X	mol	MIm (mol)	KPF_6 (mol)	$BMImPF_6$ (g)[a]	Temp (°C)	Time (h)	Isolated Yield (%)
1	n-C_4H_9Cl	0.08	0.05	0.05	10.0	80	25	74
2		0.08	0.05	0.05	10.0	80	35	83
3		3.2	2.0	2.0	400.0	80	35	86
4	n-C_4H_9Br	0.05	0.05	0.05	10.0	60	15	75
5		0.05	0.05	0.05	10.0	80	15	85
6		2.0	2.0	2.0	400.0	80	15	87
7	n-C_4H_9I	0.05	0.06	0.05	10.0	80	10	85

[a] Used as solvent.

butyl bromide may be the favorable choice, since it has higher reactivity than *n*-butyl chloride and is more stable in air and less expensive than *n*-butyl iodide. The increase of temperature/time gave the corresponding increase in yields (entries 1,2, 4 and 5), which reflected that the reaction process was also sensitive to the reaction temperature and time. Anyway, the established reaction procedure was conducted successfully and the higher yields were achieved under the conditions investigated, compared with the literatures,[11,12] in a two-step procedure, 64% yield of 1-*n*-butyl-3-methylimidazolium chloride (BMImC) was obtained from *N*-methylimidazole and *n*-butyl chloride in refluxing toluene under N_2 for 24 hour, and 91% yield of $BMImPF_6$ was achieved from BMImC and sodium hexafluorophosphate after stirring for 24 hours at room temperature in acetone.

Then, the method was extended to the preparation of alkylimidazolium hexafluorophosphates and alkylimidazolium tetrafluoroborates based RTILs and the results are summarized in Table 2. All the products listed in Table 2 were characterized by IR and ^{1}H NMR spectroscopy; the spectroscopic data were identical with those of the authentic sample or in the literature.[8,12] As can be seen, the method was found to be general and applicable to the RTILs bearing alkyl chains of varying lengths (R′) or different alkylimidazoles (R). It did not matter what kind of hexafluorophosphate salt or tetrafluoroborate salt was employed (entries 1, 3 and 10–12). Yields of up to 87% were obtained under mild conditions.

We believe that the method developed is a promising green route for the facile and direct preparation of the most extensively used RTILs of alkylimidazolium hexafluorophosphates and alkylimidazolium tetrafluoroborates. There are many major advantages such as eco-friendliness, simple procedure, and high yield achieved in mild conditions. The present method is suitable for applications both in laboratory preparation and in large-scale manufacture. The extension of this method for other RTILs is still under way in our laboratory.

All starting materials were commercially available and were used without further purification. IR spectra were recorded on a Bruker Equinox 55 spectrometer. ^{1}H NMR spectra were obtained on a Bruker Avance 500 (TMS as internal standard).

1-*n*-Butyl-3-methylimidazolium Hexafluorophosphate; General Procedure

In a 50 mL round-bottomed flask, fitted with a reflux condenser and a mechanical stirrer, were placed KPF_6 (9.2 g, 0.05 mol), *N*-methylimidazole (4.1 g, 0.05 mol), *n*-butyl chloride (7.4 g, 0.08 mol) and $BMImPF_6$ (10.0 g); the stirrer was started and the mixture was heated up to 80 °C. After 35 h of stirring, the mixture was treated with water (15 mL) to dissolve the formed KCl and then the aq phase was removed, the left $BMImPF_6$ phase was washed with water (15 mL × 3), followed by drying on a Rotavapor under vacuum, to give $BMImPF_6$ (21.8 g), which contained 11.8 g of freshly formed $BMImPF_6$ (83.1% yield).

IR (film): 3170 [γ(CH), aromatic], 2966 and 2878 [γ(CH), aliphatic], 1573 and 1467 [γ(C=C)], 842 [γ(PF)] cm^{-1}.

^{1}H NMR (DMSO): δ = 9.09 (s, 1 H, H_2), 7.75 and 7.69 (2 s, 2 H, H_4, H_5), 4.16 (t, 2 H, *J* = 7.16 Hz, H_6), 3.84 (s, 3 H, H_{10}), 1.76 (m, 2 H, H_7), 1.26 (m, 2 H, H_8), 0.90 (t, 3 H, *J* = 7.38 Hz, H_9).

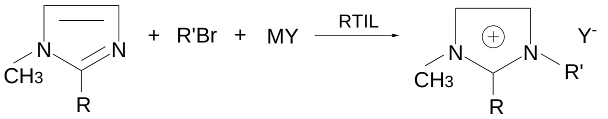
1-*n*-Butyl-3-methylimidazolium Tetrafluoroborate; General Procedure

$NaBF_4$ (220.0 g, 2 mol), *N*-methylimidazole (164.0 g, 2 mol), *n*-butyl bromide (274.0 g, 2 mol) and $BMImBF_4$ (400.0 g) were charged successively into a 1 L round-bottomed flask fitted with a reflux condenser and a mechanical stirrer. The reaction proceeded at 80 °C for 15 h. After the completion of the reaction, the mixture was transferred to a 2 L round-bottomed flask, treated with water (500 mL) and extracted with CH_2Cl_2 (300 mL × 3). Then the combined extracts were evaporated to remove the solvent, and gave $BMImBF_4$ (800.5 g), which contained 400.5 g of freshly formed $BMImBF_4$ (88.6% yield).

IR (film): 3162 [γ(CH) aromatic], 2965 and 2877 [γ(CH) aliphatic], 1574 and 1467 [γ(C=C)], 1060 [γ(BF)] cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 8.83 (s, 1 H, H_2), 7.33 and 7.29 (2 s, 2 H, H_4, H_5), 4.19 (t, 2 H, *J* = 7.45 Hz, H_6), 3.96 (s, 3 H, H_{10}), 1.85 (m, 2 H, H_7), 1.37 (m, 2 H, H_8), 0.96 (t, 3 H, *J* = 7.38 Hz, H_9).

Table 2 Direct Preparation of RTILs[a]



Entry	R	R′	MY	RTIL[b]	Product	Isolated Yield (%)
1	H	$CH_2(CH_2)_2CH_3$	KPF_6	$BMImPF_6$	$BMImPF_6$	87
2	H	$CH_2(CH_2)_2CH_3$	NH_4PF_6	$BMImPF_6$	$BMImPF_6$	89
3	H	$CH_2(CH_2)_2CH_3$	$NaPF_6$	$BMImPF_6$	$BMImPF_6$	88
4	H	$CH_2(CH_2)_3CH_3$	KPF_6	$PeMImPF_6$	$PeMImPF_6$	93
5	H	$CH_2(CH_2)_4CH_3$	KPF_6	$HMImPF_6$	$HMImPF_6$	92
6	H	$CH_2(CH_2)_5CH_3$	KPF_6	$HeMImPF_6$	$HeMImPF_6$	93
7	H	$CH_2(CH_2)_6CH_3$	KPF_6	$OMImPF_6$	$OMImPF_6$	93
8	H	$CH(CH_3)CH_2CH_3$	KPF_6	$MPMImPF_6$	$MPMImPF_6$	89
9	H	$CH(CH_3)(CH_2)_2CH_3$	KPF_6	$MBMImPF_6$	$MBMImPF_6$	92
10	H	$CH_2(CH_2)_2CH_3$	KBF_4	$BMImBF_4$	$BMImBF_4$	90
11	H	$CH_2(CH_2)_2CH_3$	NH_4BF_4	$BMImBF_4$	$BMImBF_4$	88
12	H	$CH_2(CH_2)_2CH_3$	$NaBF_4$	$BMImBF_4$	$BMImBF_4$	89
13	H	$CH_2(CH_2)_4CH_3$	$NaBF_4$	$HMImBF_4$	$HMImBF_4$	94
14	H	$CH_2(CH_2)_6CH_3$	$NaBF_4$	$OMImBF_4$	$OMImBF_4$	92
15	H	$CH(CH_3)CH_2CH_3$	$NaBF_4$	$MPMImBF_4$	$MPMImBF_4$	88
16	H	$CH(CH_3)(CH_2)_2CH_3$	$NaBF_4$	$MBMImBF_4$	$MBMImBF_4$	91
17	CH_3	$CH_2(CH_2)_2CH_3$	KPF_6	$BDMImPF_6$	$BDMImPF_6$	93
18	CH_3	$CH_2(CH_2)_4CH_3$	KPF_6	$HDMImPF_6$	$HDMImPF_6$	95
19	CH_3	$CH_2(CH_2)_2CH_3$	$NaBF_4$	$BDMImBF_4$	$BDMImBF_4$	94
20	CH_3	$CH_2(CH_2)_4CH_3$	$NaBF_4$	$HDMImBF_4$	$HDMImBF_4$	93

[a] All the preparations were run with MIm (or DMIm) (2 mol), R′Br (2 mol) and MY (2 mol) in 400 g RTIL at 80 °C for 15 h.
[b] Used as solvent.

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