Available online at www.sciencedirect.com
ScienceDirect
Journal of Fluorine Chemistry 129 (2008) 108–111
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/fluor

A green and novel procedure for the preparation of ionic liquid

Dong Fang [a,b], Jian Cheng [a], Kai Gong [a], Qun-Rong Shi [a], Xin-Li Zhou [a], Zu-Liang Liu [a,*]

[a] School of Chemical Engineering, Nanjing University of Science & Technology, Nanjing 210094, Jiangsu, PR China
[b] Jiangsu Provincial Key Laboratory of Coastal Wetland Bioresources & Environmental Protection, Yancheng 224002, Jiangsu, PR China

Received 13 July 2007; received in revised form 8 September 2007; accepted 10 September 2007
Available online 14 September 2007

Abstract

A green and novel procedure is described for the preparation of a series of ionic liquid containing alkylimidazolium-based or *N*-alkylpyridinium-based cations and hexafluorophosphate-based or tetrafluoroborate-based anions in one-pot solvent-free conditions to give excellent yields with shortened time.

Keywords: Green procedure; Ionic liquids; Preparation

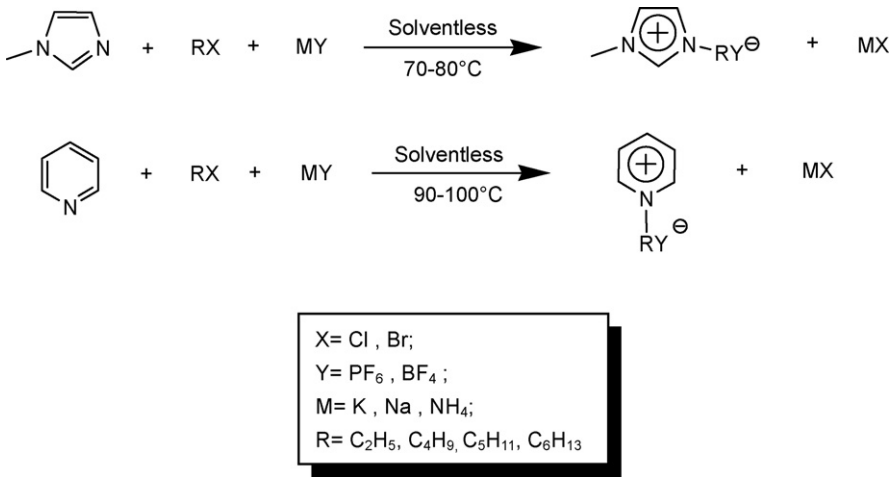
1. Introduction

Since the beginning of the Green Chemistry movement 10 years ago, the need for alternative solvents for reactions has been one of the major issues we have faced. In recent years, air- and water-stable ionic liquids (ILs) have emerged as a powerful alternative to conventional molecular organic solvents due to their particular properties, such as undetectable vapor pressure, wide liquid range, as well as ease of recovery and reuse, and making ILs a greener alternative to volatile organic solvents [1–3].

The vast majority of ionic liquid chemistry based on nitrogen-containing heterocycles focuses on the use of 1-alkyl-3-methylimidazolium and *N*-alkylpyridinium cations. 1-Alkyl-3-methylimidazolium hexafluorophosphate ($AMImPF_6$), 1-alkyl-3-methylimidazolium tetrafluoroborate ($AMImBF_4$), *N*-alkylpyridinium tetrafluoroborate ($APyBF_4$) and *N*-alkylpyridinium hexafluorophosphate ($APyPF_6$) are typically ionic liquids used as solvent or catalysts to extraction [4,5], polyborane reactions [6], hydroxylation of alkyl halides with water [7], syntheses of tribenzohexadehydro[12]annulene [8], fluorodediazoniation [9], regioselective nitration of aromatic compounds [10], oxidation [11], etc. There are two basic methods for the preparation of these ionic liquids: metathesis of a halide salt (Finkelstein step) with, for instance, a silver, group 1 metal or ammonium salt of the desired anion and acid–base neutralization reactions, but either way need the preparation of the imidazolium or pyridinium halides via alkylation (Menschutkin step) using a large molar excess of haloalkane (10–400%) for as long as 72 h at refluxing condition, and then RTILs was prepared with variable yields and much longer reaction time. Currently, the disadvantage of ionic liquids outweigh their excellent solvent properties and designer solvent features, which will always constrain their applicability [12]. Kralisch also suggested spicing up the ionic liquid research efficient for energetic, environmental and economic balances [13]. There are some non-conventional synthetic methods using microwave (MW) or ultrasonic irradiation (US) to improve access to these RTILs. Seddon and Deetlefts published a MW-assisted, solvent-free preparation of ionic liquids leading to reasonable good yields [14]. Namboodiri and Varma [14–17] synthesized imidazolium halides, and then RTILs under US or MW solventless, respectively in an open test tube. Khadilkar and Rebeiro [18] synthesized imidazolium and pyridinium halides under MW solventless in a closed vessel. Leveque et al. reported an improved preparation of ionic liquids by US [19,20]. Xu et al. prepared the ionic liquids with target ionic liquids as solvents, but the method for ionic liquids used as solvents was not indicated [21]. Each line of work has achieved great improvements in yield and reaction time; however, the search for the new readily available and green scale-up procedure is still being actively pursued [22]. We found that $BMImPF_6$, $BMImBF_4$, $APyBF_4$ and $APyPF_6$ can be prepared with stoichiometric amounts of 1-methylimidazole or pyridine,

* Corresponding author. Tel.: +86 25 84318865; fax: +86 25 84318865.
E-mail address: liuzuliang302@163.com (Z.-L. Liu).

0022-1139/$ – see front matter
doi:10.1016/j.jfluchem.2007.09.004



Scheme 1. Novel procedure for RTILs.

alkylhalides and potassium, sodium or ammonium salt of hexafluorophosphate or tetrafluoroborate in one-pot under solvent-free condition (Scheme 1).

2. Experimental

Melting points were determined on a Thomas Hoover apparatus and are reported uncorrected. The IR spectra were run on a Nicolete spectrometer and expressed in cm^{-1} (KBr). ^1H NMR spectra were recorded on Bruker DRX300 (300 MHz) and ^{13}C NMR spectra on Bruker DRX300 (75.5 MHz) spectrometer. All chemicals (AR grade) were commercially available and used without any further purification.

2.1. The general procedure for the synthesis of ionic liquids

2.1.1. The synthesis of 1-butyl-3-methylimidazolium hexafluorophosphate ($BMImPF_6$)

1-Methylimidazol 0.05 mol, 1-bromobutane 0.05 mol and potassium salt of hexafluorophosphate 0.05 mol were stirred in a three-necked flask with a reflux condenser at 80 °C for 3.5 h. Then, 10 mL water was added and bi-phase of water/ionic liquids formed, the immiscible ionic liquids $BMImPF_6$ layer was separated from the water phase, washed with quantitative fresh deionized water until the water phase will not react with $AgNO_3$ aq. and then with diethyl ether (3× 15 mL). The ionic liquids were dried in vacuum at 120 °C for 2 h, yielded 93% of colorless to pale yellow liquids product. The compound was analyzed by ^1H NMR, ^{13}C NMR, and FT-IR spectroscopy, and the spectral data tally with the structure.

^1H NMR (300 MHz, acetone-d_6): δ 8.95 (s, 1H, CH), 7.75 (s, 1H, CH), 7.65 (s, 1H, CH), 4.32 (t, 2H, CH_2), 4.02 (s, 3H, CH_3), 1.90 (m, 2H, CH_2), 1.40 (m, 2H, CH_2), 0.94 (t, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.02, 124.38, 123.00, 49.84, 36.20, 32.31, 19.58, 13.29. IR (cm^{-1}): 3171.46, 3124.90, 2965.68, 2938.72, 2877.92, 1575.14, 1467.21, 1386.54, 1339.39, 1169.63, 844.79, 751.95.

The TGA analyses show that $BMImPF_6$ is thermally stable up to 360 °C.

2.1.2. The synthesis of 1-butyl-3-methylimidazolium tetrafluoroborate ($BMImBF_4$)

1-Methylimidazol 0.05 mol, 1-bromobutane 0.05 mol and sodium salt of tetrafluoroborate 0.05 mol were stirred in a three-necked flask with a reflux condenser at 80 °C for 3.5 h. Upon completion of the reaction, the mixture was diluted with 50 mL of acetonitrile, after elimination of the precipitated salt (KBr or NaBr), the filtrate was then filtered through a pad of celite to remove the residual halide salt and finally concentrated by rotary evaporation to afford a colorless to pale yellow liquid with a yield of 98%, without reaction with $AgNO_3$ aq. The BMImBF4 was then further dried under high vacuum at 80 °C for 6 h. The compound was analyzed by ^1H NMR, ^{13}C NMR, and FT-IR spectroscopy, and the spectral data tally with the structure.

^1H NMR (300 MHz, acetone-d_6): δ 9.51 (s, 1H, CH), 7.89 (s, 1H, CH), 7.83 (s, 1H, CH), 4.42 (t, 2H, CH_2), 4.09(s, 3H, CH_3), 1.92 (m, 2H, CH_2), 1.38 (m, 2H, CH_2), 0.93 (t, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.44, 124.34, 122.98, 49.72, 36.53, 32.48, 19.62, 13.37. IR (cm^{-1}): 3144.76, 3071.25, 2960.55, 2935.58, 2873.65, 1571.90, 1465.51, 1382.92, 1337.38, 1170.21, 1062.29, 754.75.

The TGA analyses show that $BMImBF_4$ is thermally stable up to 340 °C.

2.1.3. The synthesis of N-butylpyridinium tetrafluoroborate ($BPyBF_4$)

The same procedure was used as for $BMImBF_4$ except that ammonium or sodium salt of tetrafluoroborate was used and the reaction was carried out at 100 °C for 4 h and colorless liquid was obtained with a yield of 92%.

2.1.4. The synthesis of N-alkylpyridinium hexafluorophosphate ($APyPF_6$)

The same procedure was used as for $BMImPF_6$ except that the reaction was carried out at 100 °C for 4 h, recrystallized with 95% ethanol and white crystal product was obtained with a yield of 93%, mp 64–64.5 °C.

Table 1
The preparing of room-temperature ionic liquid in one-pot solvent-free conditions

Entry	RTILs	R	X	Y	M	Time (h)	T (°C)	Yield[a] (%)
1	$EMImPF_6$	C_2H_5	Br	PF_6	K	4.0	70	91
2	$BMImPF_6$	C_4H_9	Br	PF_6	K	3.5	80	93
3	$PMImPF_6$	C_5H_{11}	Br	PF_6	K	3.5	80	90
4	$HMImPF_6$	C_6H_{13}	Br	PF_6	K	3.5	80	86
5	$EMImBF_4$	C_2H_5	Br	BF_4	K	4.0	70	94
6	$BMImBF_4$	C_4H_9	Cl	BF_4	K	3.5	80	98
7	$PMImBF_4$	C_5H_{11}	Br	BF_4	K	3.5	80	94
8	$HMImBF_4$	C_6H_{13}	Br	BF_4	K	3.5	80	91
9	$EPyPF_6$	C_2H_5	Br	PF_6	Na	4.0	70	90
10	$BPyPF_6$	C_4H_9	Cl	PF_6	Na	3.0	100	93
11	$PPyPF_6$	C_5H_{11}	Br	PF_6	Na	3.5	100	90
12	$HPyPF_6$	C_6H_{13}	Br	PF_6	Na	3.5	100	89
13	$EPyBF_4$	C_2H_5	Br	BF_4	NH_4	4.0	70	90
14	$BPyBF_4$	C_4H_9	Cl	BF_4	Na	3.0	100	92
15	$PPyBF_4$	C_5H_{11}	Br	BF_4	Na	3.5	100	91
16	$HPyBF_4$	C_6H_{13}	Br	BF_4	Na	3.5	100	88

[a] Isolated yield.

3. Results and discussion

The other ionic liquids could be prepared by the same procedure using C_2H_5Br, C_3H_7Br, $C_5H_{11}Br$, $C_6H_{13}Br$, etc. as alkylation's reagents. Various RTILs were investigated and the results were listed in Table 1.

Using conventional heating methods, the first step in ionic liquid synthesis is time-consuming; the second step is also a long-time procedure. From Table 1, it can be seen that this method needs 3.0–4.0 h totally, in contrast to the several-day time needed using conventional methods; the reaction time could be strongly decreased.

It is important to note that all of the halides used in this study were efficiently converted to the corresponding ionic liquids. The alkyl chlorides were relatively not less reactive and provided excellent yields under the same reaction conditions as the alkyl bromides (entries 6, 10, 14). In contrast to the reported rate at which the quaternisation of 1-methylimidazole or pyridine proceeds follows the conventional order: R–I > R–Br > R–Cl. The ethyl bromide required relatively longer reaction time; the reaction temperature was relatively lower for its lower bp (entries 1, 5, 9, 13), however, the yield was not decreased.

Due to evaporative loss, the Menschutkin step usually requires a large molar excess of the haloalkane to obtain good yields. For example, a 100% molar excess of 1-chlorobutane or 2-bromobutane has previously been used to prepare [C_4mim]Cl (76% yield) and [C_4mim]Br (61% yield), respectively. In contrast, all the preparations in the current study required no excess of the appropriate haloalkane to obtain 86–98% yields.

In our experiment, we found that both KPF_6 and $NaPF_6$ could be used for preparing imidazolium hexafluorophosphate ($BMImPF_6$), KBF_4 and $NaBF_4$ for imidazolium tetrafluoroborate ($BMImBF_4$). In our paper, we used KPF_6 for $BMImPF_6$ and KBF_4 for $BMImBF_4$. It is important that, the most difficulty in solvent-free conditions is the sufficient mix of the reactant, especially when the reactant could not form uniform phase. Hence, the KPF_6 used in our work was powder instead of crystal to facilitate the mix under vigorous stirring. However, for crystal reactant, the reaction time should be prolonged (more than 4 h) and the reaction temperature should be heightened (110–120 °C) to carry out the reaction completely. In case of pyridinium hexafluorophosphate ($APyPF_6$), same reactant could be used as for $BMImPF_6$. But for pyridinium tetrafluoroborate, only NH_4BF_4 and $NaBF_4$ could be employed, and no desired products could be obtained with KBF_4, the reason is still being investigated.

4. Conclusion

We have developed a very efficient, quick, and practical method for the preparation of ionic liquids, in contrast to the several-day time needed using conventional methods that require a large excess of alkylhalides/organic solvent as reaction media or concentrated acid. The synthesis can be performed on flexible reaction scales compared to non-conventional methods under microwave or ultrasonic irradiation. It should greatly contribute to the realization of the environmental benign process.

Acknowledgements

This work was financially supported by the Educational Committee of Jiangsu Province (07KJD530238), Jiangsu Provincial Key Laboratory of Coastal wetland Bioresources & Environmental Protection, (JLCBE07020) Nanjing University of Science & Technology (no. 2006001).

References

[1] M.J. Earle, K.R. Seddon, Pure Appl. Chem. 72 (2000) 1391–1398.
[2] R. Sheldon, Chem. Commun. 8 (2001) 2399–2407.
[3] J.S. Wilkes, J. Mol. Catal. A: Chem. 214 (2004) 11–17.
[4] J. Liu, G. Jiang, Y. Chi, Y. Cai, Q. Zhou, J. Hu, Anal. Chem. 21 (2003) 5870–5876.
[5] J.H. Wang, D.H. Cheng, X.Y. Chen, Z. Du, Z.L. Fang, Anal. Chem. 79 (2007) 620–625.
[6] U. Kusari, Y.Q. Li, M.G. Bradley, L.G. Sneddon, J. Am. Chem. Soc. 126 (2004) 8662–8663.
[7] D.W. Kim, D.J. Hong, J.W. Seo, H.S. Kim, H.K. Kim, C.E. Song, D.Y. Chi, J. Org. Chem. 69 (2004) 3186–3189.
[8] Y. Li, J.Y. Zhang, W. Wang, Q. Miao, X. She, X. Pan, J. Org. Chem. 70 (2005) 3285–3287.
[9] J. Heredia-Moya, K.L. Kirk, J. Fluorine Chem. 128 (2007) 674–678.
[10] K. Smith, S.F. Liu, G.A. EI-Hiti, Ind. Eng. Chem. Res. 44 (2005) 8611–8615.
[11] R.Y. Tang, P. Zhong, Q.L. Lin, J. Fluorine Chem. 128 (2007) 636–640.
[12] J.H. Clark, S.J. Tavener, Org. Process Res. Dev. 11 (2007) 149–155.
[13] D. Kralisch, A. Stark, S. Korsten, G. Kreisel, Green Chem. 7 (2005) 301–309.
[14] M. Deetlefs, K.R. Seddon, Green Chem. 5 (2003) 181–186.
[15] V.V. Namboodiri, R.S. Varma, Org. Lett. 4 (2002) 3161–3163.
[16] V.V. Namboodiri, R.S. Varma, Tetrahedron Lett. 43 (2002) 5381–5383.
[17] R.S. Varma, V.V. Namboodiri, J. Chem. Soc. Chem. Commun. 7 (2001) 643–644.
[18] B.M. Khadilkar, G.L. Rebeiro, Org. Process Res. Dev. 6 (2002) 826–828.

[19] J.M. Leveque, J.L. Luche, C. Petrier, R. Roux, W. Bonrath, Green Chem. 4 (2002) 357–360.
[20] J.M. Leveque, S. Desset, J. Suptil, C. Fachinger, Draye, W. Bonrath, G. Cravotto, Ultra Sonochem. 13 (2006) 189–193.
[21] D.Q. Xu, B.Y. Liu, S.P. Luo, Z.Y. Xu, Y.C. Shen, Synthesis 17 (2003) 2626–2628.
[22] A.K. Burrell, R.E. Del Sesto, S.N. Baker, T.M. McCleskey, G.A. Baker, Green Chem. 9 (2007) 449–454.