Available online at www.sciencedirect.com
ScienceDirect
Journal of Fluorine Chemistry 127 (2006) 1261–1264
www.elsevier.com/locate/fluor

Short communication

A novel method for preparation of imidazolium tetrafluoroborate ionic liquids

Minato Egashira *, Yuji Yamamoto, Tsubasa Fukutake, Nobuko Yoshimoto, Masayuki Morita

Faculty of Engineering, Yamaguchi University, Tokiwadai 2-16-1, Ube, Yamaguchi 755-8611, Japan

Received 8 May 2006; received in revised form 11 July 2006; accepted 14 July 2006
Available online 21 July 2006

Abstract

A new method for the preparation of substituted imidazolium tetrafluoroborate salt, some of which are known as versatile room temperature ionic liquids, is proposed. The new method based on *N*-methylation of imidazole provided tetrafluoroborate derivatives containing no counterions, with shorter time and lower cost than conventional ion-exchange method.

Keywords: Ionic liquid; Syntheses; *N*-Methylation

1. Introduction

Room temperature ionic liquids have been attracted from many research fields due to their unique properties such as high conductivity and non-volatility. Tetrafluoroborates with substituted imidazolium cations are known as versatile ionic liquids as well as some kinds of sulfoneimide salts. In particular, many electrochemical researches have concerned with 1-ethyl-3-methyl imidazolium tetrafluoroborate ($EMIBF_4$) as the first-proposed stable ionic liquid system, exhibiting low viscosity and conductivity as high as 10^{-2} S cm^{-1} [1,2]. However, for the practical use in electrochemical devices, the purity and production cost of such ionic liquids should be paid attention.

Apart from hydrophobic ionic liquids such as sulfoneimide salts, tetrafluoroborate ionic liquids are difficult to be supplied with sufficient purity and cost for electrochemical usage. Ionic liquids are frequently prepared with so-called ‘‘ion-exchange’’ method [1–4]. An example for ‘‘ion-exchange’’ preparation of $EMIBF_4$ is as shown in Scheme 1.

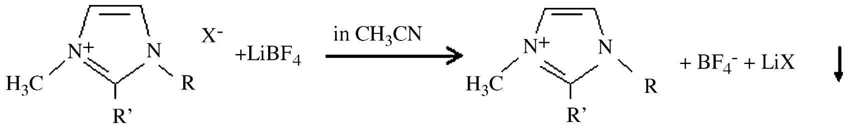
In case of the preparation of hydrophobic ionic liquids, ionic liquid phase is spontaneously isolated from solution phase of counter ions in sources by using water as solvent for ionic sources. In addition, the isolation process of ionic liquid phase from aqueous solution is generally as fast as 20 h. In contrast, when a hydrophilic ionic liquid such as $EMIBF_4$ is prepared, ionic liquid phase would not be isolated spontaneously and thus other process to isolate counter ions is necessary. In many cases, counter ions are to be deposited by using non-aqueous solvent, or using $AgBF_4$ and halides as sources. However, the deposition of counter ion salts is generally as slow as 3–4 days. In addition, the contamination of counter ions is inevitable in this process because counter ions also have significant solubility in solvent. Therefore, it is difficult to obtain a large quantity of hydrophilic ionic liquid with a sufficient purity. A syntheses route using a neutralization of corresponding acid and base is possible to provide a metal-free ionic liquid product [5], while the strong acid such as HBF_4 is in general difficult to handle.

Recently some synthetic methods have been proposed for the preparation of hydrophilic ionic liquids [6–8]. Ignat’ev and Welz-Biermann introduced a new method to prepare imidazolium triflate ionic liquids based on the *N*-alkylation of alkylimidazole with alkyltriflate [7]. Ohno introduced some preparation routes of ionic liquids via the quarterization of tertiary amine [8]. The concept of *N*-alkylation of alkylimidazole appears to be useful for the preparation of hydrophilic ionic liquids without contamination of counter ions. In the present study, the authors have proposed a novel preparation route of alkylimidazolium tetrafluoroborate salt based on *N*-alkylation. As long as the authors’ knowledge, this has been the first trial to prepare one of the most versatile ionic liquid, $EMIBF_4$, via *N*-alkylation.

---

* Corresponding author. Tel.: +81 836 85 9212; fax: +81 836 85 9201.
E-mail address: minato@yamaguchi-u.ac.jp (M. Egashira).

0022-1139/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2006.07.010



Scheme 1. An example for conventional "ion-exchange" process for the preparation of substituted imidazolium tetrafluoroborate.

2. Results and discussion

Trimethyloxonium tetrafluoroborate (Me_3OBF_4), called Meerwein reagent, is known as a methylation reagent [9]. When this reagent is reacted with *N*-alkylimidazole, the reaction illustrated in Scheme 2 is expected. The yields of the crude products when the Scheme 2 reaction is assumed are summarized in Table 1. According to Scheme 2, when *N*-ethylimidazole, *N*-methylimidazole or 1,2-dimethylimidazole is the reactant, the expected product is $EMIBF_4$, 1,3-dimethylimidazolium tetrafluoroborate ($DMIBF_4$) and 1,2,3-trimethylimidazolium tetrafluoroborate ($TMIBF_4$), respectively. The CHN gravimetric ratios of these crude products by elemental analyses were also included, compared with calculated values. On the syntheses of $EMIBF_4$, the yield is rather reasonable value and obtained CHN ratios corresponded to expected ones. In contrast, when the expected product was $DMIBF_4$ or $TMIBF_4$, the CHN ratios were far from expected ones. On the syntheses of $DMIBF_4$, the yield also exceeded to 100%. Such deviation observed for the syntheses of $DMIBF_4$ is possibly due to the contamination of a significant amount of water. If the $DMIBF_4$:H_2O ratio is assumed to be 1:1, the CHN ratio is calculated to be C, H, N = 29.7%, 4.9%, 15.2%, respectively. These values are very close to the obtained ones for the reaction with *N*-methylimidazole. By accepting the assumption of water association, the rigorous yield of $DMIBF_4$ is calculated to be a reasonable value as ca. 97%. The expected water source is atmospheric moisture because the reaction was carried out under an ambient atmosphere. On the other hand, for the reaction with 1,2-dimethylimidazole such an assumption of association with water provides no reasonable CHN ratios compared with obtained ones. Even the product from *N*-ethylimidazole has several percent of deviation in CHN ratio compared with calculated ones for $EMIBF_4$. Such deviation indicates that the existence of some organic impurities, possibly by-products, unreacted materials, or impurities form reagents.

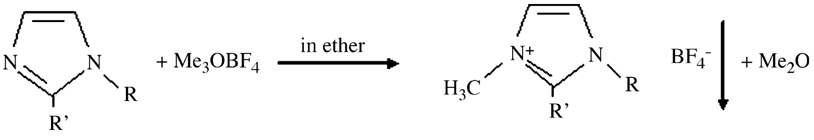
The ^{1}H NMR spectra (obtained by JNM-400, JEOL Co.) of the products from *N*-methyl and *N*-ethylimidazole dissolved in d^6-dimethylsulfoxide (DMSO) are shown in Fig. 1. On both spectra only the peaks attributed to DMI^+ or EMI^+, and impurity in solvent (proton-substituted DMSO) are observable and other indication is very small. The position (as indicated in Fig. 1) and the relative intensity of each peaks corresponded to the expected values for $DMIBF_4$ and $EMIBF_4$. These spectra confirm that the expected reaction quantitatively progressed to provide $DMIBF_4$ and $EMIBF_4$ without significant side reaction. These results clearly indicates that the deviation of the CHN values of the product from *N*-ethylimidazole compared with the ones for $EMIBF_4$ is due to the existence of small amount of unreacted *N*-ethylimidazole.

When 1,2-dimethylimidazole was reacted, the crude product appeared to contain a large amount of by-product. By washing with acetone, white powder was obtained. After vacuum drying, the gravimetric yield of washed product was 88% from crude one. CHN analyses and ^{1}H NMR measurements were carried out. The gravimetric CHN ratio of washed product was C:H:N = 35.8%, 5.5%, 14.2%, respectively. The ^{1}H NMR spectra for the washed product is shown in Fig. 2. The spectrum feature, both peak position and intensity, of washed product corresponded to those for $TMIBF_4$. These results indicate that $TMIBF_4$ was possible to be purified by washing the crude product of the reaction in Scheme 2 using 1,2-dimethylimidazole. The molar yield of purified $TMIBF_4$ from the reactant was 56%. The re-calculated yields of each tetrafluoroborate salts are also summarized in Table 1.

$EMIBF_4$ prepared in the present study showed ca. 14 mS cm^{-1} of conductivity at 25 °C. This conductivity value is similar to that reported recently for carefully purified $EMIBF_4$ [10]. The conductivity result indicated that the product here corresponds to a target tetrafluoroborate salt in view of electrochemical property.

The differential scanning calorimetery (DSC) profile of the product by *N*-ethylimidazole upon heating at the temperature range from -100 to 50 °C was shown in Fig. 3. The DSC profile shows a couple of exothermic and endothermic peak around -20 and 0 °C. An exothermic peak around -20 °C is attributed to the glass transition process and an endothermic peak around 0 °C is attributed to the melting point of $EMIBF_4$. The latter peak appears to be in a different position from 15 °C, a frequently reported value. However, the similar profile to Fig. 3 was proposed by Choudhury et al. for $EMIBF_4$ after applied zone melting process [11]. Such DSC profile as Fig. 3 may be a characteristic for $EMIBF_4$ with high purity, or the polymorphism of $EMIBF_4$ may provide such a difference.

These results have assured the reaction in Scheme 2 as a novel preparation method of imidazolium tetrafluoroborate



Scheme 2. Expected *N*-alkylation process for the preparation of substituted imidazolium tetrafluoroborate.

Table 1
Details of reactions described in Scheme 2

Reactant/material	Elemental analyses (wt.%)			Yield for crude product (wt.%)	Yield (wt.%)
	C	H	N		
N-Ethylimidazole	35.1	5.4	14.3	98	94
N-Methylimidazole	29.5	5.5	14.2	106	97
1,2-Dimethylimidazole					
Before purified	31.4	4.3	15.2	64	
After purified	35.8	5.5	14.2		56
EMIBF$_4$ (calculated)	36.4	5.6	14.2	–	–
DMIBF$_4$ (calculated)	32.6	4.9	15.2	–	–
TMIBF$_4$ (calculated)	36.4	5.6	14.2	–	–

ionic liquids with facility and high yield over 90%. Furthermore, the expected cost for the production of EMIBF$_4$ with this method is lower than that with conventional ion-exchange methods due to the lower cost of sources and the facility of removal process of ionic impurities as well as shorter reaction time. In the present study there are some evidences that a small amount, in some cases a significant amount, of water is contaminated in the products. The origin of the contaminated water is considered to be a reaction atmosphere. For further improvement of purity and water level for imidazolium tetrafluoroborate salt, the refinement of reaction condition, in particular reaction atmosphere, and the purity level of reagent, is necessary. Nevertheless, the present report exhibits the potential of this new preparation method of the versatile ionic liquids without containing metal species in the product.

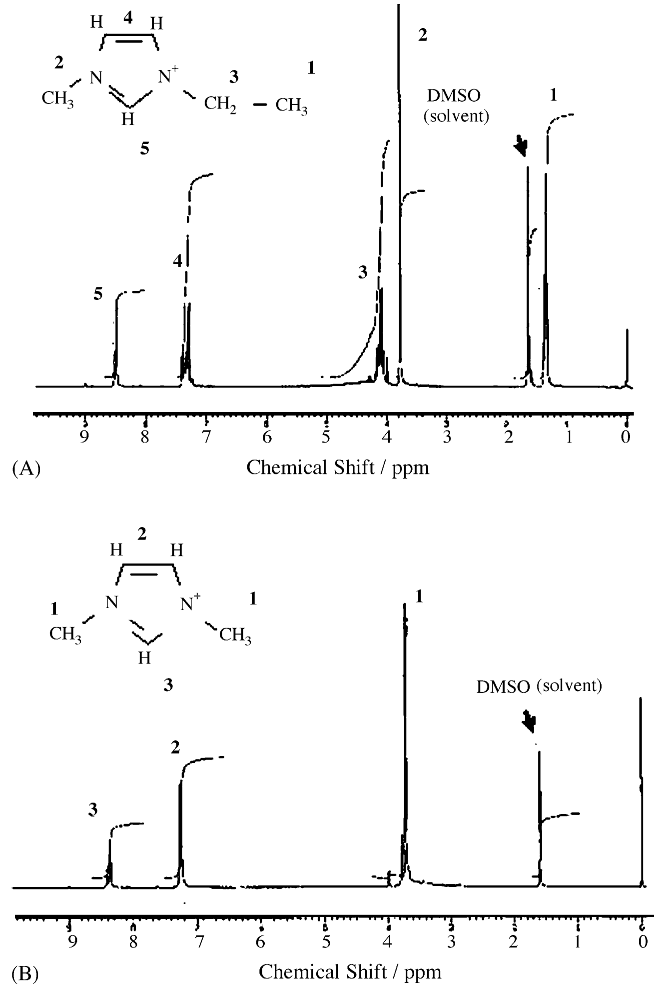


Fig. 1. ^{1}H NMR spectra for products of reaction described in Scheme 2. (A) Reactant *N*-ethylimidazole and (B) reactant *N*-methylimidazole.

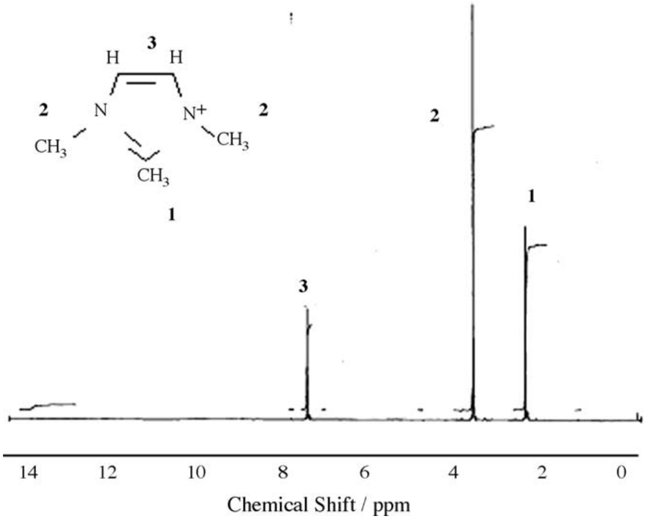


Fig. 2. ^{1}H NMR spectra for washed products of reaction described in Scheme 2 with 1,2-dimethylimidazole.

3. Experimental

The typical preparation procedure of EMIBF$_4$ was as follows: *N*-ethylimidazole (6.51 g; Tokyo Kasei Co.) was dissolved in ca. 40 ml of diethyl ether (Wako Pure Chemical Co.), and then 10 g of Me$_3$OBF$_4$ (Wako Pure Chemical Co.) was gradually added into the ether solution under magnetic stirring. A significant amount of transparent liquid precipitate was immediately observed. After 20 h of stirring, ether was decanted off from the two-phase liquid product. The lower phase liquid was washed by diethyl ether followed by decantation several times. The lower liquid was then dried into vacuum at 100 °C during 10 h. On the preparation of

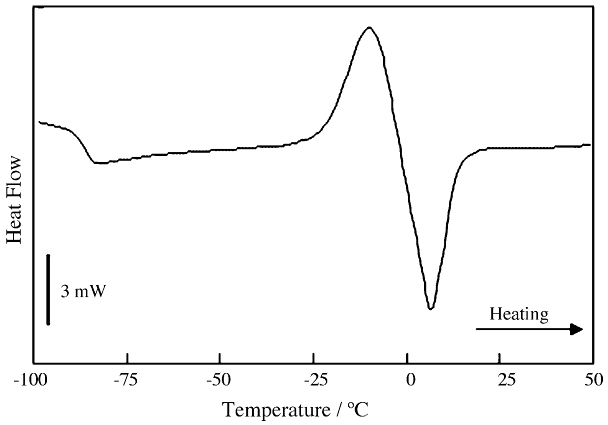


Fig. 3. DSC profile of the product from *N*-ethylimidazole.

$DMIBF_4$ or $TMIBF_4$, *N*-methylimidazole (5.62 g; Tokyo Kasei Co.) or 1,2-dimethylimidazole (6.51 g; Tokyo Kasei Co.) was dissolved into diethyl ether instead of *N*-ethylimidazole. When 1,2-dimethylimidazole was used as reactant, the obtained precipitate was slightly colored slurry. All the procedures except for vacuum drying were carried out under ambient atmosphere.

The slurry from the reaction with 1,2-dimethylimidazole was collected in an alternative bottle, and then ca. 10 ml of acetone (Wako Pure Chemical Co.) was added. Immediately after the addition of acetone, white precipitate was observed in the acetone solution. The precipitate was collected by filtration.

DSC measurement was carried out using a sealed Al pan prepared in a glove bag with Ar flow. Al_2O_3 was used as reference. The pans for sample and reference were set in the apparatus (DSC-50, Shimazu Co., Japan), kept at 100 °C at 5 min, cooled to -100 °C at the rate of 10 $^\circ C\,min^{-1}$, and then heated to 50 °C at the rate of 5 $^\circ C\,min^{-1}$. Ar gas was flown during measurement.

Acknowledgements

The authors thank Dr. Takaaki Sonoda in Institute for Materials Chemistry and Engineering, Kyushu University, and Dr. Yasuhiro Umebayashi in Graduate School of Science, Kyushu University, for their assistance on the measurement of elemental analyses and fruitful discussion.

References

[1] J.S. Wilkes, M.J. Zaworotko, J. Chem. Soc., Chem. Commun. (1992) 965–968.
[2] J. Fuller, R.T. Carlin, R.A. Osteryoung, J. Electrochem. Soc. 144 (1997) 3881–3886.
[3] V.R. Koch, L.A. Dominey, C. Nanjundiah, M.J. Onderechen, J. Electrochem. Soc. 143 (1996) 798–803.
[4] P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasunderam, M. Grätzel, Inorg. Chem. 35 (1996) 1168.
[5] K. Matsumoto, R. Hagiwara, R. Yoshida, Y. Ito, Z. Mazej, P. Benkic, B. Zemva, O. Tamada, H. Yoshino, S. Matsubara, Dalton Trans. (2004) 144.
[6] K.R. Seddon, A.J. Carmichael, M.J. Earle, PCT Int. Appl., WO, 2001040146, 2003.
[7] N.V. Ignat'ev, U. Welz-Biermann, in: Proceedings of the First International Congress on Ionic Liquids, Salzburg, Austria, (2005), p. 57.
[8] H. Ohno, Ionsei-Ekitai (Ionic Liquids), CMC Publishing Co., 2003.
[9] H. Boehme, M. Daehne, W. Lehners, E. Ritter, Justus Liebigs Ann. Chem. 723 (1969) 34.
[10] T. Nishida, Y. Tashiro, M. Yamamoto, J. Fluorine Chem. 120 (2003) 135.
[11] A.R. Choudhury, N. Winterton, A. Steiner, A.I. Cooper, K.A. Johnson, J. Am. Chem. Soc. 127 (2005) 16792.