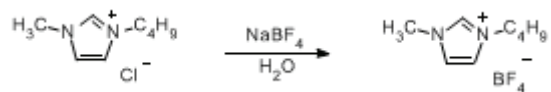


## PREPARATION OF 1-BUTYL-3-METHYLIMIDAZOLIUM TETRAFLUOROBORATE

### [1H-Imidazolium, 1-butyl-3-methyl, tetrafluoroborate (1-)]



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### 1. Procedure

1-Butyl-3-methylimidazolium chloride (30.00 g, 172 mmol) (Note 1) is placed in a 125 mL Erlenmeyer flask containing a stir bar and a thermometer. This salt is dissolved in 35 mL of distilled water and NaBF<sub>4</sub> (20.00 g, 182 mmol) (Note 2) is added in portions with stirring over 10-15 min. The NaBF<sub>4</sub> dissolves as the mixture emulsifies and cools to 14°C (Note 3). After the mixture warms back to ambient temperature, 30 mL of CH<sub>2</sub>Cl<sub>2</sub> is added and the contents are transferred to a 125 mL separatory funnel. The bottom CH<sub>2</sub>Cl<sub>2</sub> phase is separated (Note 4). The aqueous phase is extracted with an additional 20 mL of CH<sub>2</sub>Cl<sub>2</sub>. The combined CH<sub>2</sub>Cl<sub>2</sub> phases are shaken in a separatory funnel with a solution of NaBF<sub>4</sub> (10.0 g, 91 mmol) in 20 mL of water. The CH<sub>2</sub>Cl<sub>2</sub> phase is separated and dried over a mixture of 1.0 g of Na<sub>2</sub>SO<sub>4</sub> and 3.0 g of MgSO<sub>4</sub>. The mixture is filtered through a Büchner funnel and the salts are washed with an additional 15 mL of CH<sub>2</sub>Cl<sub>2</sub>. A short path distillation head is attached to the 250 mL round-bottom-flask containing the filtrate and most of the CH<sub>2</sub>Cl<sub>2</sub> is removed by distillation at 30 mm pressure. Care is taken not to heat the product above 50°C. The solvent is condensed in a receiver flask cooled in an ice-water slurry (Note 5). The last traces of CH<sub>2</sub>Cl<sub>2</sub> are removed using a rotary evaporator at 15 mm and 45 °C followed by vacuum drying at ambient temperature until the weight remains constant. The pure 1-butyl-3-methylimidazolium tetrafluoroborate (34.2–34.3 g; 89% yield) is a colorless to pale yellow, viscous liquid (Notes 6-8).

### 2. Notes

1. The submitters prepared 1-butyl-3-methylimidazolium chloride as previously described.<sup>2</sup> The checkers purchased this from Aldrich Chemical Co.
2. Sodium tetrafluoroborate (98%) was purchased from Acros Organics and used as received.
3. If the emulsion is allowed to stand for 30-60 min, then two phases results. However, there is no need to do this since addition of CH<sub>2</sub>Cl<sub>2</sub> induces rapid phase separation.
4. The product at this point is not completely chloride free. In a separate analysis by the submitters, removal of the CH<sub>2</sub>Cl<sub>2</sub> from this solution and analysis of 1.53 g of product by titration with 0.100 M AgNO<sub>3</sub> (Mohr titration; K<sub>2</sub>CrO<sub>4</sub> indicator)<sup>3</sup> required 0.6 mL of the silver nitrate solution to precipitate all of the chloride ion. This corresponds to a product containing 0.7% BMIM<sup>+</sup> Cl<sup>-</sup> and 99.3% BMIM<sup>+</sup> BF<sub>4</sub><sup>-</sup>.
5. The distilled CH<sub>2</sub>Cl<sub>2</sub> has droplets of water from the azeotrope with CH<sub>2</sub>Cl<sub>2</sub>. This distillation process helps to dry the product and allows recovery of most of the CH<sub>2</sub>Cl<sub>2</sub> used in the procedure.
6. Dissolution of 1.50 g of this liquid in 3 mL of water followed by addition of 0.100 M AgNO<sub>3</sub> gave no precipitation or cloudiness.
7. The submitters report that the water content of the product was 0.17% as determined from the <sup>1</sup>H NMR spectrum of the neat liquid by integration of the water signal at δ 2.9 and the CH<sub>2</sub> signal at δ 1.93. The product is hygroscopic and water content increases with exposure to air. The checkers could not detect water in their spectrum in CD<sub>2</sub>Cl<sub>2</sub>.
8. The product exhibits the following spectroscopic properties: IR (thin film) 3646, 3162, 3122, 2964, 2877, 1575, 1467, 1431, 1171, 1048, 850 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.66 (s, 1 H), 7.37 (s, 2 H), 4.14 (t, 2 H, *J* = 7.3 Hz), 3.89 (s, 3 H), 1.81 (quintet, 2 H, *J* = 7.4 Hz), 1.32 (sextet, 2 H, *J* = 7.3 Hz), 0.91 (t, 3 H, *J* = 7.3 Hz); <sup>13</sup>C NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 136.2, 123.8, 122.5, 49.7, 36.1, 31.9, 19.3,

13.1. Anal. Calcd for  $C_8H_{15}BF_4N_2$ : C, 42.51; H, 6.69; N, 12.37; Found: C 41.94; H, 6.85; N, 12.37; trace analysis for Cl, 636 ppm.

### Waste Disposal Information

All hazardous materials should be handled and disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

### 3. Discussion

This procedure is based on the general method recently reported in *Organic Syntheses*.<sup>2</sup> The preparation of 1-butyl-3-methylimidazolium hexafluorophosphate ( $BMIM^+ PF_6^-$ ) proceeds as described.<sup>2</sup> However, in our hands, the reported method for the preparation of 1-butyl-3-methylimidazolium tetrafluoroborate ( $BMIM^+ BF_4^-$ ; the most commonly used of the ionic liquids) was not reproducible. The product was contaminated with varying (and significant) amounts of  $BMIM^+ Cl^-$ . The use of the relatively insoluble  $KBF_4$  (0.44 g/100 mL) in the original preparation makes dissolution and subsequent reaction problematic. Thus, analysis of 0.716 g of a typical ionic liquid product produced from  $KBF_4$  by titration with 0.100 M  $AgNO_3$  required 11.1 mL of the silver nitrate solution to precipitate all of the chloride ion. This corresponds to a product containing 27%  $BMIM^+ Cl^-$  and 73%  $BMIM^+ BF_4^-$ .

The procedure described herein uses the much more soluble  $NaBF_4$  (97.3 g/100 mL). After the first cycle, the chloride content is only 0.7%, and the chloride can no longer be detected after the second cycle. In addition, the tedious process of removing water by distillation under reduced pressure is eliminated. This procedure is also useful for the preparation of the ionic liquid *n*-butyl pyridinium tetrafluoroborate, which is subject to the same chloride contamination problems when prepared from  $KBF_4$ . Finally, the amount of residual water in the product can be readily determined from the  $^1H$  NMR spectrum of the neat product.

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### References and Notes

1. Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556.
2. Dupont, J.; Consorti, C. S.; Suarez, P. A. Z.; de Sousa, R. F. *Organic Syntheses* **2002** 79, 236.
3. Christian, G. D. "Analytical Chemistry, Fifth Edition", John Wiley and Sons, Inc., New York, 1994, p. 278.
4. Contamination of  $BMIM^+ BF_4^-$  and other ionic liquids with chloride in various preparations has been noted in the literature. See Seddon, K. R.; Stark, A.; Torres, M.-J. *Pure Appl. Chem.* **2000**, 72, 2275.

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### Appendix

#### Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

1-Butyl-3-methylimidazolium chloride:  
1H-Imidazolium, 1-butyl-3-methyl-, chloride; (79917-90-1)

$NaBF_4$ : Borate(1-), tetrafluoro-, sodium; (13755-29-8)

1-Butyl-3-methylimidazolium tetrafluoroborate:  
1H-Imidazolium, 1-butyl-3-methyl-, tetrafluoroborate (1-); (174501-65-6)

