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of Reliable Methods
for the Preparation
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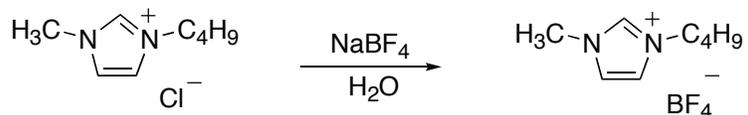
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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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**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 NaBF₄ (20.00 g, 182 mmol) (Note 2) is added in portions with stirring over 10-15 min. The NaBF₄ dissolves as the mixture emulsifies and cools to 14 °C (Note 3). After the mixture warms back to ambient temperature, 30 mL of CH₂Cl₂ is added and the contents are transferred to a 125 mL separatory funnel. The bottom CH₂Cl₂ phase is separated (Note 4). The aqueous phase is extracted with an additional 20 mL of CH₂Cl₂. The combined CH₂Cl₂ phases are shaken in a separatory funnel with a solution of NaBF₄ (10.0 g, 91 mmol) in 20 mL of water. The CH₂Cl₂ phase is separated and dried over a mixture of 1.0 g of Na₂SO₄ and 3.0 g of MgSO₄. The mixture is filtered through a Büchner funnel and the salts are washed with an additional 15 mL of CH₂Cl₂. A short path distillation head is attached to the 250 mL round-bottom-flask containing the filtrate and most of the CH₂Cl₂ 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 CH₂Cl₂ 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.² 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_2Cl_2 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_2Cl_2 from this solution and analysis of 1.53 g of product by titration with 0.100 M AgNO_3 (Mohr titration; K_2CrO_4 indicator)³ required 0.6 mL of the silver nitrate solution to precipitate all of the chloride ion. This corresponds to a product containing 0.7% $\text{BMIM}^+ \text{Cl}^-$ and 99.3% $\text{BMIM}^+ \text{BF}_4^-$.

5. The distilled CH_2Cl_2 has droplets of water from the azeotrope with CH_2Cl_2 . This distillation process helps to dry the product and allows recovery of most of the CH_2Cl_2 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_3 gave no precipitation or cloudiness.

7. The submitters report that the water content of the product was 0.17% as determined from the ^1H NMR spectrum of the neat liquid by integration of the water signal at δ 2.9 and the CH_2 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_2Cl_2 .

8. The product exhibits the following spectroscopic properties: IR (thin film) 3646, 3162, 3122, 2964, 2877, 1575, 1467, 1431, 1171, 1048, 850 cm^{-1} ; ^1H NMR (500 MHz, CD_2Cl_2) 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); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 136.2, 123.8, 122.5, 49.7, 36.1, 31.9, 19.3, 13.1. Anal. Calcd for $\text{C}_8\text{H}_{15}\text{BF}_4\text{N}_2$: 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.

Safety and 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*.² The preparation of 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM⁺ PF₆⁻) proceeds as described.² However, in our hands, the reported method for the preparation of 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM⁺ BF₄⁻; 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 KBF₄ (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 KBF₄ by titration with 0.100 M AgNO₃ 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⁺ BF₄⁻.

The procedure described herein uses the much more soluble NaBF₄ (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 KBF₄. Finally, the amount of residual water in the product can be readily determined from the ¹H NMR spectrum of the neat product.

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. *Org. Synth.* **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⁺ BF₄⁻ 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.

Appendix
Chemical Abstracts Nomenclature; (Registry Number)

- 1-Butyl-3-methylimidazolium chloride: 1H-Imidazolium, 1-butyl-3-methyl-, chloride; (79917-90-1)
- NaBF₄: Borate(1-), tetrafluoro-, sodium; (13755-29-8)
- 1-Butyl-3-methylimidazolium tetrafluoroborate: 1H-Imidazolium, 1-butyl-3-methyl, tetrafluoroborate (1-); (174501-65-6)

