



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at [http://www.nap.edu/catalog.php?record\\_id=12654](http://www.nap.edu/catalog.php?record_id=12654)). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

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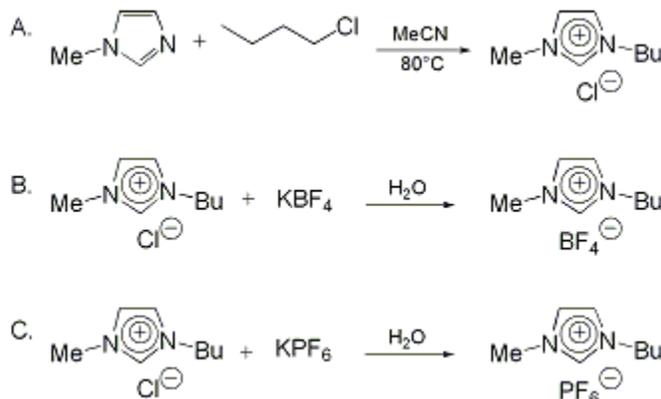
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*September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions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

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## PREPARATION OF 1-BUTYL-3-METHYL IMIDAZOLIUM-BASED ROOM TEMPERATURE IONIC LIQUIDS

[ 1H-Imidazolium, 1-butyl-3-methyl-, chloride (1<sup>-</sup>); 1H-Imidazolium, 1-butyl-3-methyl-, tetrafluoroborate (1<sup>-</sup>); 1H-Imidazolium, 1-butyl-3-methyl-, hexafluorophosphate (1<sup>-</sup>) ]



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### 1. Procedure

*Caution! 1-Chlorobutane is an irritant and a possible carcinogen.*

*A. 1-Butyl-3-methylimidazolium chloride*. A 2-L, three-necked, round-bottomed flask is equipped with a heating oil bath, a nitrogen inlet adapter, an internal thermometer adapter, an overhead mechanical stirrer, and a reflux condenser. The flask is flushed with nitrogen and charged with 151.5 g (1.85 mol, 1 equiv) of freshly distilled N-methylimidazole (Note 1), 100 mL of acetonitrile (CH<sub>3</sub>CN, Note 2) and 220 g (2.4 mol, 1.3 equiv) of 1-chlorobutane (Note 3), and brought to a gentle reflux (75–80°C internal temperature). The solution is heated under reflux for 48 hr (Note 4) and then cooled to room temperature (Note 5). The volatile material is removed from the resulting yellow solution under reduced pressure (Note 6). The remaining light-yellow oil is re-dissolved in dry acetonitrile (250 mL) and added dropwise via cannula to a well-stirred solution of 1000 mL of dry ethyl acetate (Note 7) and one seed crystal of 1-butyl-3-methylimidazolium chloride (Note 8) placed in a 2-L, three-necked, round-bottomed flask, equipped with a nitrogen inlet adapter and an overhead mechanical stirrer (Note 9). The imidazolium salt begins to crystallize exothermically almost immediately, and after the addition of the acetonitrile solution is completed, the flask is cooled at –30°C for 2 hr. The supernatant solution is removed via filtration through a filter cannula and the resulting white solid (Note 10) is dried under reduced pressure (0.1 mbar, 0.001 mm) at 30°C for 6 hr to afford 1-butyl-3-methylimidazolium chloride 289.5 g (89%), mp 66–67°C (Notes 11 and 12).

*B. 1-Butyl-3-methylimidazolium tetrafluoroborate, (BMI · BF<sub>4</sub>)*. A 1-L, one-necked, round-bottomed flask (Note 13) is charged with 91.6 g (0.52 mol, 1 equiv) of finely powdered 1-butyl-3-methylimidazolium chloride, 66.1 g (0.52 mol, 1 equiv) of potassium tetrafluoroborate (Note 14) in 200 mL of distilled water. The reaction mixture is stirred at room temperature for 2 hr affording a heterogeneous mixture (Note 15). The water is removed under reduced pressure (0.1 bar, 0.1 mm) at 80°C until constant weight. To the remaining suspension are added 100 mL of dichloromethane (Note 16) and 35 g of anhydrous magnesium sulfate. After 1 hr of standing the suspension is filtered and the

volatile material is removed under reduced pressure (0.1 bar, 0.1 mm) at 30°C for 2 hr to afford 107.5 g (0.48 mol, 91%) of **1-butyl-3-methylimidazolium tetrafluoroborate** as a light yellow, viscous liquid, mp -74°C (Notes 17 and 18).

*C. 1-Butyl-3-methylimidazolium hexafluorophosphate*. A 1-L, one-necked, round-bottomed flask (Note 13) is charged with 65.6 g (0.37 mol, 1 equiv) of **1-butyl-3-methylimidazolium chloride**, and 69.3 g (0.37 mol, 1 equiv) of **potassium hexafluorophosphate** (Note 19) in 70 mL of distilled water. The reaction mixture is stirred at room temperature for 2 hr affording a two-phase system. The organic phase is washed with 3 × 50 mL of water and dried under reduced pressure (0.1 mbar, 0.001 mm). Then 100 mL of **dichloromethane** and 35 g of anhydrous **magnesium sulfate** are added. After 1 hr, the suspension is filtered and the volatile material is removed under reduced pressure (0.1 bar, 0.1 mm) at 30°C for 2 hr to afford 86.4 g (0.29 mol, 81%) of **1-butyl-3-methylimidazolium hexafluorophosphate** as a light yellow viscous liquid, mp 10°C (Notes 20 and 21).

## 2. Notes

1. **N-Methylimidazole** is commercially available. The submitters used a product from Aldrich Chemical Company, Inc. (99%) dried over **potassium hydroxide** (KOH) pellets and distilled (210-212°C).
2. **Acetonitrile** (Merck) is distilled over **phosphorus pentoxide** (P<sub>2</sub>O<sub>5</sub>).
3. **1-Chlorobutane** (Merck) is used as received.
4. The external temperature should not exceed 85°C.
5. The consumption of **N-methylimidazole** (R<sub>f</sub> = 0.4) can be followed by TLC using Merck Silica gel 60 and **ethyl acetate** as eluent (developed using I<sub>2</sub>).
6. The volatile material (**acetonitrile** and the excess of **1-chlorobutane**) is captured in a liquid nitrogen trap. This solution (35 wt% in **1-chlorobutane**, determined by GC) can be stored in a dark flask and used for further synthesis.
7. **Ethyl acetate** (Merck) is distilled over P<sub>2</sub>O<sub>5</sub>.
8. The seed crystal is obtained by dissolving a sample (≈1 g) of the crude imidazolium salt in a minimum amount of **acetonitrile** (3 mL); this solution is allowed to stand at -30°C overnight. The checkers observed spontaneous crystallization upon removal of volatile materials.
9. A 150-rpm agitation speed is used and the rate of the addition will determine the morphology of the imidazolium salt (from finely divided powder to solid blocks that are difficult to powder).
10. If solid blocks are obtained they should be ground before drying.
11. Differential scanning calorimetry is performed at a heating rate of 2°C/min from 20°C to 100°C. The checkers used a conventional melting point apparatus.
12. The product has the following spectral properties: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 0.80 (t, 3 H, <sup>3</sup>J<sub>HH</sub> = 7.3), 1.23 (m, 2 H), 1.75 (m, 2 H), 3.98 (s, 3 H), 4.19 (t, 2 H, <sup>3</sup>J<sub>HH</sub> = 7.4), 7.46 (s, 1 H), 7.63 (s, 1 H), 9.55 (s, 1 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 13.6, 19.6, 32.3, 36.6, 49.8, 122.3, 124.0, 137.8; IR (neat film/NaCl plate) cm<sup>-1</sup>: 3137, 3046, 2959, 2935, 2873, 1571, 1465, 1382, 1336, 1172.
13. The reaction is performed in air without any special precaution.
14. **Potassium tetrafluoroborate** (Strem Chemicals Inc.) was used as received. **Sodium tetrafluoroborate** can be also used although it is much more expensive.
15. Although BMI · BF<sub>4</sub> is soluble in water at room temperature, the presence of **potassium chloride** (KCl) gives a salting-out effect, affording two phases. By adding more water a homogeneous colorless solution can be obtained.
16. **Dichloromethane** (Merck and Co., Inc.) was used as received.
17. A glass transition (-74°C) is obtained by differential scanning calorimetry performed at the cooling rate of 10°C/min from 20°C to -150°C followed by an isothermal at this temperature for 10 min and then heated to 30°C, at the same heating rate. When the cooling rate was decreased to 2 or 1°C/min, the crystallization transition at -73°C was barely observable.
18. The product has the following spectral properties: <sup>1</sup>H NMR (300 MHz, acetone-d<sub>6</sub>) δ: 0.95 (t, 3 H, <sup>3</sup>J<sub>HH</sub> = 7.3), 1.37 (m, 2 H), 1.93 (m, 2 H), 4.07 (s, 3 H), 4.40 (t, 2 H, <sup>3</sup>J<sub>HH</sub> = 7.1), 7.79 (s, 1 H), 7.85 (s, 1 H), 9.55 (s, 1 H); <sup>13</sup>C NMR (75 MHz, acetone-d<sub>6</sub>) δ: 13.1, 19.3, 32.2, 35.9, 49.4, 122.7, 124.0, 138.9; IR (neat film/NaCl plate) cm<sup>-1</sup>: 3160, 3119, 2963, 2938, 2876, 1573, 1171, 1059. For comparison with the literature data see Ref. 2.
19. **Potassium hexafluorophosphate** (Strem Chemicals Inc.) is used as received. **Sodium hexafluorophosphate** can be also used although it is much more expensive.

20. A glass transition ( $-75^{\circ}\text{C}$ ) and two broad bands close to  $0^{\circ}\text{C}$  are obtained by differential scanning calorimetry performed at the cooling rate of  $10^{\circ}\text{C}/\text{min}$  from  $20^{\circ}\text{C}$  to  $-150^{\circ}\text{C}$  followed by an isothermal at this temperature for 10 min and then heated to  $30^{\circ}\text{C}$  at the same rate. If the heating rate is lowered to 2 or  $1^{\circ}\text{C}/\text{min}$ , a crystallization peak is obtained at  $10^{\circ}\text{C}$ .

21. The product has the following spectral properties:  $^1\text{H}$  NMR (300 MHz, acetone- $d_6$ )  $\delta$ : 0.96 (t, 3 H,  $^3J_{\text{HH}} = 7.3$ ), 1.37 (m, 2 H), 1.93 (m, 2 H), 4.05 (s, 3 H), 4.36 (t, 2 H,  $^3J_{\text{HH}} = 7.3$ ), 7.68 (s, 1 H), 7.74 (s, 1 H), 8.95 (s, 1 H);  $^{13}\text{C}$  NMR (75 MHz, acetone- $d_6$ )  $\delta$ : 13.0, 19.3, 32.1, 36.0, 49.6, 122.7, 124.1, 137.0; IR (neat film/NaCl plate)  $\text{cm}^{-1}$ : 3171, 3125, 2965, 2939, 2878, 1571, 1167, 836. For comparison with the literature data see Ref. 2.

### Waste Disposal Information

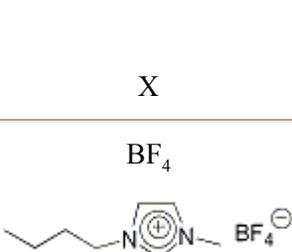
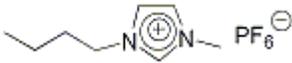
All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

### 3. Discussion

The primary advantage in the first step of the method described here (using 1-chlorobutane diluted in MeCN) is that it eliminates long reaction periods<sup>3</sup> and allows the use of secondary alkyl halides without competitive elimination reactions. For example, the reaction of sec-butyl bromide with N-methylimidazole using the classical method (in neat alkyl halide) produces, along with the desired product, 20-30% of butenes and 1-methylimidazole hydrobromide. In the second step, the use of water as solvent allows the anion metathesis reaction to be quantitative in a very short time and allows the easy purification of the ionic liquids. Moreover, employing the potassium salt avoids the use of corrosive and difficult to handle hexafluorophosphoric acid<sup>3</sup> and the expensive silver tetrafluoroborate.<sup>4</sup>

The ionic liquids 1-butyl-3-methylimidazolium tetrafluoroborate ( $\text{BMI}\cdot\text{BF}_4$ ) and 1-butyl-3-methylimidazolium hexafluorophosphate ( $\text{BMI}\cdot\text{PF}_6$ ) have a broad application as "green" solvents for organic synthesis,<sup>5</sup> extraction technologies,<sup>6</sup> electrochemistry,<sup>7</sup> biphasic organometallic catalysis<sup>8</sup> and as stationary phases for GC.<sup>9</sup> In particular these room temperature ionic liquids are highly thermal- and electrochemically stable, they possess negligible vapor pressure, have relatively low viscosity and high density (see Table).<sup>10</sup> The most important advantage of the use of these ionic liquids as solvents, in particular for biphasic organometallics, is that it allows the facile separation of the products from the reaction (in most of the cases by simple decanting) and the recovered ionic catalyst solution can be reused. Moreover, ionic liquids can improve or promote reactions that occur with difficulty or do not occur at all in classical organic solvents.

TABLE<sup>10</sup>  
PHYSICAL CHEMICAL PROPERTIES FOR 1-BUTYL-3-METHYLIMIDAZOLIUM BASED IONIC LIQUIDS

| X  | mp ( $^{\circ}\text{C}$ ) | $\eta_{30}$ (P) | $\rho_{30}$ (g mL $^{-1}$ ) | $K_{60}$ (S cm $^{-1}$ ) $10^{-2}$ | EW (V) |
|--|---------------------------|-----------------|-----------------------------|------------------------------------|--------|
| <br>$\text{BF}_4$ | -74                       | 2.33            | 1.15                        | 0.864                              | 6.1    |
| <br>$\text{PF}_6$ | 10                        | 3.12            | 1.37                        | 0.656                              | 7.0    |

$\eta_{30}$  = viscosity at 30°C;  $\rho_{30}$  = density at 30°C;  $K_{60}$  = electrical conductivity at 60°C;  
EW = electrochemical window.

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## References and Notes

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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 (10); (79917-90-1)

1-Butyl-3-methylimidazolium tetrafluoroborate:  
1H-Imidazolium, 1-butyl-3-methyl-, tetrafluoroborate(1-) (13); (174501-65-6)

1-Butyl-3-methylimidazolium hexafluorophosphate:  
1H-Imidazolium, 1-butyl-3-methyl-, hexafluorophosphate(1-) (13); (174501-64-5)

N-Methylimidazole:  
Imidazole, 1-methyl- (8);  
1H-Imidazole, 1-methyl (9); (616-47-7)

1-Chlorobutane:  
Butane, 1-chloro- (8,9); (109-69-3)

Potassium tetrafluoroborate:  
Borate(1-), tetrafluoro-, potassium (8,9); (14075-53-7)

Potassium hexafluorophosphate:  
Phosphate(1-), hexafluoro-, potassium (8,9); (17084-13-8)

