NEW TRISUBSTITUTED IMIDAZOLIUM-BASED ROOM TEMPERATURE IONIC LIQUIDS+

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Received March 17, 2006
Accepted June 29, 2006

Reaction of 1-decyl-2-methylimidazole (**1**) with linear bromoalkanes **2a**, **2b** in refluxing acetonitrile leads to the formation of quaternary bromide salts **3a**, **3b** in excellent isolated yields. Quaternary salts **3a**, **3b** were metathesized with KPF_6 (**4a**), $LiNTf_2$ (**4b**), $LiBF_4$ (**4c**), or KOTf (**4d**) in water to form the ionic liquids **5a**–**5h** in very good yields. These new ionic liquids are liquid at ambient temperature, immiscible with water, miscible with acetone and chloroform and thermally stable up to 350 °C.

Keywords: Ionic liquids; Imidazolium quaternary salts; Imidazoles; Alkylation; Green solvents; Quaternization; Thermal stability.

Synthesis, properties and applications of ionic liquids have been the focal points of vigorous research activities, as evidenced by the appearance of large numbers of publications[1–6]. Much research has been done and various kinds of ionic liquids have been developed but today, the research on ionic liquids is still at the peak due to their great applications in various fields of science[7–9]. In general, ionic liquids are made up of positively and negatively charged ions creating salts whose melting points are less than 100 °C. They are thermally stable and have wide liquid ranges which allow reactions at low and high temperatures. Generally, ionic liquids are non-volatile, non-flammable, and have almost no vapor pressure. Very common applications of ionic liquids include: solvents for various organic and inorganic reactions[7,8], catalysts[9], and battery electrolytes[10–12]. We have studied this chemistry to see the effect of longer alkyl group and higher number of substitution (on the imidazolium cation) on the nature of the ionic liquids at room temperature and their thermal stability.

+ Presented at 17th Winter Fluorine Conference, ACS Division of Fluorine Chemistry, St. Pete Beach, Florida, January 9–14, 2005.

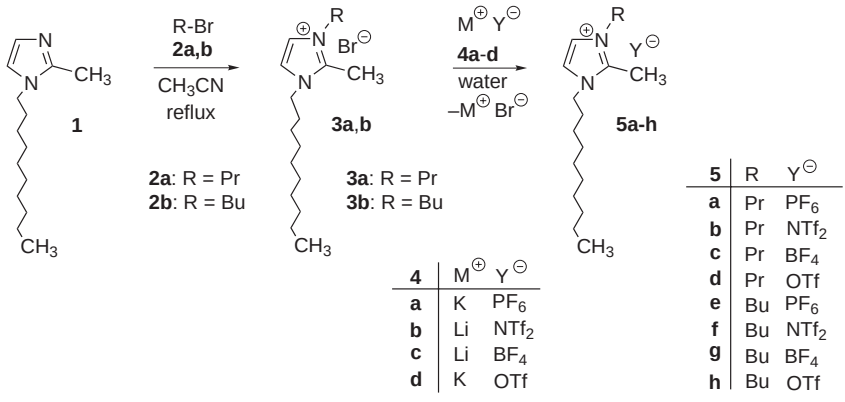
Collect. Czech. Chem. Commun. 2006, Vol. 71, No. 9, pp. 1265–1269

doi:10.1135/cccc20061265

RESULTS AND DISCUSSION

Based on literature, imidazolium-based ionic liquids are mentioned most frequently[13,14]. There are mainly three kinds of imidazolium-substituted cations in ionic liquids: monosubstituted, disubstituted, and trisubstituted. The chemistry of mono- and disubstituted imidazolium ions is well explored. Some studies on trisubstituted imidazolium ions have been also made but shorter alkyl chains have been used and the synthesized ionic liquids are solid at room temperature[15]. Here, we report the reactions of 1-decyl-2-methylimidazole **1** with linear bromoalkanes **2a**, **2b** followed by metathesis reactions of quaternary salts **3a**, **3b** with KPF_6, $LiNTf_2$, $LiBF_4$, or KOTf, which led to the formation of room temperature ionic liquids **5a**–**5h** in good yields.

In a general procedure, 1-decyl-2-methylimidazole (**1**) and linear bromoalkanes **2a**, **2b** were refluxed overnight in acetonitrile. Removal of the solvent at reduced pressure led to the isolation of liquid salts **3a**, **3b** in nearly quantitative yields (Scheme 1). The metathesis reaction of **3a**, **3b** with KPF_6 (**4a**), $LiNTf_2$ (**4b**), $LiBF_4$ (**4c**), or KOTf (**4d**), using water as a solvent, resulted in ionic liquids **5a**–**5h** in >88% isolated yields (Scheme 1).



SCHEME 1

When freshly synthesized, quaternary salts **3a**, **3b** are liquid at room temperature, however, **3b** slowly solidifies upon storage at room temperature for one week. These salts are soluble in water, acetone, and chloroform and insoluble in pentane and hexane. All the ionic liquids **5a**–**5h** are liquid at room temperature and stable in air. They are insoluble in water, pentane, and hexane, but soluble in acetone and chloroform. They are thermally

stable up to 350 °C as determined by TGA. Densities of these compounds range from 1.0 to 1.5 g/cm^3.

In conclusion, we report the synthesis of new trisubstituted imidazolium-based ionic liquids which are liquid at room temperature and thermally more stable in comparison to some known di- and trisubstituted imidazolium based ionic liquids. Due to these properties they might be useful as substitutes for organic solvents which are used in high temperature reactions.

EXPERIMENTAL

Stringent precautions were taken to exclude moisture during the synthesis of quaternary salts. All the reagents used were analytical grade. 1-Decyl-2-methyl-imidazole, 1-bromopropane, 1-bromobutane, acetonitrile, KPF_6, $LiNTf_2$, $LiBF_4$, and KOTf were obtained from commercial suppliers. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Brucker spectrometer operating at 300, 282, and 75 MHz, respectively. Chemical shifts are reported in ppm (δ-scale) relative to the appropriate standard, $CFCl_3$ for ^{19}F, and TMS for ^{1}H and ^{13}C NMR. Coupling constants (*J*) are given in Hz. The IR spectra (ν in cm^{-1}) were recorded using the neat sample on a Thermo Nicolet (Model No. Nexus 40 IR) spectrometer and mass spectra were recorded as solid probe using HP 5890/5970 Gas Chromatograph/Mass Spectrometer. Densities were measured at 25 °C using pycnometer. Elemental analyses were performed by Desert Analytics, Tucson.

General Procedure for 1-Decyl-2-methyl-3-propylimidazolium Bromide (**3a**) and 3-Butyl-1-decyl-2-methylimidazolium Bromide (**3b**)

1-Decyl-2-methylimidazole (**1**; 225 mmol) was dissolved in acetonitrile (200 ml) and 1-bromopropane (**2a**) or 1-bromobutane (**2b**; 230 mmol) was added portionwise at room temperature. The reaction mixture was refluxed for 24 h. Volatile materials were removed in vacuo and trapped at –196 °C. The obtained liquid product was dissolved in acetone (100 ml) and mixed with hexane (350 ml). The immiscible bottom layer was separated and evacuated for 3 h to yield **3a** or **3b**.

1-Decyl-2-methyl-3-propylimidazolium bromide (**3a**). Yield 92%; light yellow viscous liquid. IR (KBr film): 2928, 1568, 1465, 1262, 844, 748. ^{1}H NMR ($CDCl_3$): 7.26 (d, 1 H, *J* = 5.5); 7.28 (d, 1 H, *J* = 5.5); 3.95–4.07 (overlapped triplet, 4 H, *J* = 7.5); 2.56 (s, 3 H); 1.6–1.8 (m, 6 H); 1.1–1.4 (m, 12 H); 0.86 (t, 3 H, *J* = 7.5); 0.79 (t, 3 H, *J* = 7.5).

3-Butyl-1-decyl-2-methylimidazolium bromide (**3b**). Yield 90%; light yellow viscous liquid. IR (KBr film): 2930, 1575, 1468, 1260, 840, 752. ^{1}H NMR ($CDCl_3$): 7.28 (d, 1 H, 5.5); 7.29 (d, 1 H, *J* = 5.5); 3.96–4.08 (overlapped triplet, 4 H, *J* = 7.5); 2.52 (s, 3 H); 1.6–1.8 (m, 6 H); 1.1–1.4 (m, 14 H); 0.85 (t, 3 H, *J* = 7.5); 0.78 (t, 3 H, *J* = 7.5).

General Metathesis Reaction of 1-Decyl-2-methyl-3-propylimidazolium Bromide (**3a**) and 3-Butyl-1-decyl-2-methylimidazolium Bromide (**3b**) with M^+Y^- (**4a**–**4d**)

Quaternary salt **3a** or **3b** (90 mmol) was dissolved in water (100 ml) and metal salt **4a**–**4d** (91 mmol) solution in water (150 ml) was added with vigorous stirring at room temperature.

The products **5a**–**5d** formed as insoluble liquids. The mixture was stirred for 1 h and insoluble liquid was separated by decantation. It was washed with water (2 × 40 ml) and dried in vacuo for 5 h.

1-Decyl-2-methyl-3-propylimidazolium hexafluorophosphate (**5a**). Yield 90%; light yellow liquid. IR (KBr film): 2924, 1579, 1466, 1258, 842, 751. ^{1}H NMR ($CDCl_3$): 7.25 (d, 1 H, *J* = 5.5); 7.24 (d, 1 H, *J* = 5.5); 3.96–4.08 (overlapped triplet, 4 H, *J* = 7.5); 2.54 (s, 3 H); 1.6–1.8 (m, 6 H); 1.1–1.4 (m, 12 H); 0.85 (t, 3 H, *J* = 7.5); 0.78 (t, 3 H, *J* = 7.5). ^{13}C NMR ($CDCl_3$): 9.2, 10.6, 14.1, 22.7, 23.0, 26.3, 29.0, 29.3, 29.4, 29.5, 29.6, 31.9, 48.6, 49.9, 121.1, 121.3, 143.2. ^{19}F NMR ($CDCl_3$): –73.0 (d, 6 F, *J* = 706). MS (EI), *m/z* (%): 266 {[(M + H) – PF_6], 55}, 265 [(M – PF_6), 38], 250 {[M – (PF_6 + CH_3)], 30}, 236 {[M – (PF_6 + C_2H_5)], 20}, 222 {[M – (PF_6 + C_3H_7)], 24}. Density 1.2 g/cm^3. For $C_{17}H_{33}F_6N_2P$ (410.4) calculated: 49.75% C, 8.04% H, 6.82% N; found: 49.79% C, 7.80% H, 6.61% N.

1-Decyl-2-methyl-3-propylimidazolium ditriflimide (**5b**). Yield 90%; light yellow liquid. IR (KBr film): 2924, 1574, 1462, 1349, 1176, 1059, 733. ^{1}H NMR ($CDCl_3$): 7.20 (d, 1 H, 5.6); 7.19 (d, 1 H, *J* = 5.6); 3.96–4.08 (overlapped triplet, 4 H, *J* = 7.6); 2.55 (s, 3 H); 1.62–1.85 (m, 6 H); 1.11–1.41 (m, 12 H); 0.90 (t, 3 H, *J* = 7.3); 0.82 (t, 3 H, *J* = 6.7). ^{19}F NMR ($CDCl_3$): –79.2 (s, 6 F). Density 1.4 g/cm^3. For $C_{19}H_{33}F_6N_3O_4S_2$ (545.6) calculated: 41.83% C, 6.05% H, 7.64% N; found: 41.53% C, 5.82% H, 7.61% N.

1-Decyl-2-methyl-3-propylimidazolium tetrafluoroborate (**5c**). Yield 89%; light yellow liquid. IR (KBr film): 2922, 1580, 1460, 1346, 1282, 1050, 752. ^{1}H NMR ($CDCl_3$): 7.20 (d, 1 H, *J* = 5.6); 7.21 (d, 1 H, *J* = 5.6); 3.95–4.05 (overlapped triplet, 4 H, *J* = 7.6); 2.55 (s, 3 H); 1.60–1.85 (m, 6 H); 1.11–1.40 (m, 12 H); 0.90 (t, 3 H, *J* = 7.3); 0.80 (t, 3 H, *J* = 6.7). ^{19}F NMR ($CDCl_3$): –152.2 (s, 4 F). Density 1.3 g/cm^3. For $C_{17}H_{33}BF_4N_2$ (352.3) calculated: 57.97% C, 9.37% H, 7.95% N; found: 57.68% C, 9.04% H, 7.71% N.

1-Decyl-2-methyl-3-propylimidazolium triflate (**5d**). Yield 88%; light yellow liquid. IR (KBr film): 2928, 1550, 1445, 1340, 735. ^{1}H NMR ($CDCl_3$): 7.24 (d, 1 H, 5.5); 7.26 (d, 1 H, *J* = 5.5); 3.95–4.05 (overlapped triplet, 4 H, *J* = 7.7); 2.53 (s, 3 H); 1.4–1.6 (m, 6 H); 1.1–1.5 (m, 12 H); 0.84 (t, 3 H, *J* = 7.5); 0.77 (t, 3 H, *J* = 7.5). ^{19}F NMR ($CDCl_3$): –78.9 (s, 3 F). Density 1.3 g/cm^3. For $C_{18}H_{33}F_3N_2O_3S$ (414.5) calculated: 52.17% C, 7.97% H, 6.76% N; found: 52.36% C, 8.00% H, 6.41% N.

3-Butyl-1-decyl-2-methylimidazolium hexafluorophosphate (**5e**). Yield 92%; light yellow liquid. IR (KBr film): 2915, 1575, 1471, 1250, 833, 742. ^{1}H NMR ($CDCl_3$): 7.22 (d, 1 H, 5.5); 7.24 (d, 1 H, *J* = 5.5); 3.95–4.05 (overlapped triplet, 4 H, *J* = 7.5); 2.55 (s, 3 H); 1.4–1.6 (m, 6 H); 1.1–1.5 (m, 14 H); 0.85 (t, 3 H, *J* = 7.5); 0.78 (t, 3 H, *J* = 7.5). ^{13}C NMR ($CDCl_3$): 9.5, 11.0, 14.1, 23.0, 22.8, 23.2, 26.7, 29.0, 29.2, 29.5, 29.6, 29.8, 32.0, 48.3, 50.1, 121.1, 121.2, 143.1. ^{19}F NMR ($CDCl_3$): –74.0 (d, 6 F, *J* = 705). MS (solid probe), *m/z* (%): 280 {[(M + H) – PF_6], 36}, 279 [(M – PF_6), 15], 264 {[M – (PF_6 + CH_3)], 10}, 250 {[M – (PF_6 + C_2H_5)], 12}, 236 {[M – (PF_6 + C_3H_7)], 15}, 222 {[M – (PF_6 + C_4H_9)], 16}. Density 1.3 g/cm^3. For $C_{18}H_{35}F_6N_2P$ (424.5) calculated: 50.90% C, 8.24% H, 6.54% N; found: 50.88% C, 7.79% H, 6.64% N.

3-Butyl-1-decyl-2-methylimidazolium ditriflimide (**5f**). Yield 92%; light yellow liquid. IR (KBr film): 2924, 1566, 1462, 1354, 1198, 1050. ^{1}H NMR ($CDCl_3$): 7.20 (d, 1 H, 5.5); 7.22 (d, 1 H, *J* = 5.5); 3.95–4.05 (overlapped triplet, 4 H, *J* = 7.5); 2.52 (s, 3 H); 1.4–1.6 (m, 6 H); 1.1–1.5 (m, 14 H); 0.84 (t, 3 H, *J* = 7.5); 0.77 (t, 3 H, *J* = 7.5). ^{19}F NMR ($CDCl_3$): –78.5 (s, 6 F). Density 1.4 g/cm^3. For $C_{20}H_{35}F_6N_3O_4S_2$ (559.6) calculated: 42.94% C, 6.25% H, 7.50% N; found: 42.63% C, 5.97% H, 7.55% N.

3-Butyl-1-decyl-2-methylimidazolium tetrafluoroborate (**5g**). Yield 88%; light yellow liquid. IR (KBr film): 2920, 1584, 1462, 1289, 1046, 755. ^{1}H NMR ($CDCl_3$): 7.27 (d, 1 H, 14); 7.26

(d, 1 H, *J* = 14); 3.96–4.08 (overlapped triplet, 4 H, *J* = 8); 2.55 (s, 3 H); 1.6–1.8 (m, 6 H); 1.1–1.4 (m, 14 H); 0.87 (t, 3 H, *J* = 7.5); 0.78 (t, 3 H, *J* = 7.5). ^{19}F NMR ($CDCl_3$): –153.4 (s, 4 F). Density 1.4 g/cm^3. For $C_{18}H_{35}BF_4N_2$ (366.3) calculated: 58.96% C, 9.55% H, 7.64% N; found: 58.56% C, 9.24% H, 7.55% N.

3-Butyl-1-decyl-2-methylimidazolium triflate (**5h**). Yield 88%; light yellow liquid. IR (KBr film): 2924, 1560, 1466, 1271, 1154, 1033, 833, 745. ^{1}H NMR ($CDCl_3$): 7.25 (d, 1 H, 5.5); 7.27 (d, 1 H, *J* = 5.5); 3.95–4.05 (overlapped triplet, 4 H, *J* = 7.7); 2.55 (s, 3 H); 1.4–1.6 (m, 6 H); 1.1–1.5 (m, 14 H); 0.84 (t, 3 H, *J* = 7.5); 0.78 (t, 3 H, *J* = 7.5). ^{19}F NMR ($CDCl_3$): –78.2 (s, 3 F). Density 1.3 g/cm^3. For $C_{19}H_{35}F_3N_2O_3S$ (428.6) calculated: 53.23% C, 8.17% H, 6.53% N; found: 53.36% C, 8.12% H, 6.49% N.

We are thankful to the management team of ARC for their kind support.

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