Pergamon

Tetrahedron Letters 43 (2002) 9497–9499

TETRAHEDRON
LETTERS

New dense fluoroalkyl-substituted imidazolium ionic liquids

Rajendra P. Singh, Sudha Manandhar and Jean'ne M. Shreeve*

Department of Chemistry, University of Idaho, Moscow, ID 83844-2343, USA

Received 29 October 2002; accepted 30 October 2002

Abstract—New mono and polyfluoroalkyl-substituted ionic liquids have been synthesized and characterized. The neat reaction of 1-methylimidazole (**1a**) with 1,1,1-trifluoro-3-iodopropane (**2a**) at 80°C formed the quaternary salt, 1-methyl-3-trifluoropropylimidazolium iodide (**3**), in 90% yield. Similarly, sodium imidazole (**1b**) gave good yields of the quaternary salts, 1,3-bis(trifluoropropyl)imidazolium iodide (**3b**) with an excess of **2a**, and 1,3-bis(monofluoropropyl)imidazolium bromide (**3c**) with an excess of 1-fluoro-3-bromopropane (**2b**). In water as solvent, metathesis reactions of **3** with KPF_6, $LiN(SO_2CF_3)_2$ and KSO_3CF_3, and of **3b** and **3c** with KPF_6 and $LiN(SO_2CF_3)_2$ led to **4a**–**c**, **4d**,**e**, and **4f**,**g**, respectively, in good isolated yields. Some of the di(polyfluoroalkyl)imidazolium salts are liquids with densities in excess of 1.8 g/cm^3. © 2002 Elsevier Science Ltd. All rights reserved.

Research on ambient temperature ionic liquids has been directed largely toward common salts with alkylammonium, alkylphosphonium, *N*-alkylpyridinium and *N*,*N′*-dialkylimidazolium cations and tetrachloroaluminate or frequently fluorine-containing anions. A very large fraction of the literature is devoted to 1,3-dialkylimidazolium salts.[1–4] These ionic liquids or 'designer' solvents are truly amazing in that their liquid ranges and thermal stabilities can, in some cases do, exceed a 400°C range, and, in addition, they exhibit essentially no vapor pressure. The properties of these materials are optimizable and can be tuned as need arises. Because of these unusual properties they have promise as solvents for a wide range of inorganic and organic materials and reactions, and are arguably the key to clean processes and green chemistry.[5,6] While they tend to be highly polar, their ionic species are often weakly coordinating permitting, e.g. the first biphasic oligomerization of ethene to higher α-olefins with cationic Ni complexes.[7] Other properties allow these extraordinary liquids to play roles, e.g. in high yield Stille coupling with a Pd catalyst;[8] in enhancing electrophilic nitration of aromatics giving a new life to Balz–Schiemann reactions;[9] as solvent systems for enzyme-catalyzed reactions and other biotransformations; as the electrolyte in dual intercalating molten electrolyte batteries;[6] and this is just the tip of the iceberg of things to come.

The development of ionic liquids that are air and moisture stable has markedly extended the value of these materials. However, there appear to be few examples of mono(polyfluoroalkyl)[4,10,11] (suggested as surfactants with PF_6^- as anion) and di(polyfluoroalkyl)[11] (utilized as ligands as the iodide salts in palladium complexes)-substituted imidazolium salts and, with the exception of the 1-(2,2,2-trifluoroethyl)-3-methyl derivatives,[4] their characterization has been limited.

We now report the first syntheses of the quaternary 1-methyl-3-trifluoropropyl and the 1,3-bis(polyfluoroalkyl)imidazolium iodide or bromide that were metathesized with salts containing hydrophobic anions, such as PF_6^- and $N(SO_2CF_3)_2^-$, as well as the hydrophilic anion, $CF_3SO_3^-$, to form new ionic liquids.

Initially a mixture of *N*-methyl imidazole (**1a**) with 1.2 equiv. of 2,2,2-trifluoroethyl iodide in THF was maintained at reflux for two days with no reaction of interest. The same reaction was repeated neat in a closed tube at 80°C for 24 h with the 1-methyl-3-(2,2,2-trifluoroethyl)imidazolium iodide being obtained in ~20% yield. Continuing the reaction for several days did not improve the product yield. Earlier workers had demonstrated that a trifluoroethyl group could be placed on imidazolium rings in ~20% yield and we, via a different method using trifluoroethyl iodide, observed a similar yield. We now report excellent yields when 3,3,3-trifluoropropyl iodide or 3-fluoropropyl is introduced either onto an alkyl-substituted or a polyfluoroalkyl-substituted imidazolium ring. Two moles of the fluorinated propyl iodide can be reacted with sodium imidazolate to form bis(polyfluoroalkyl)imidazolium iodide. The greater reactivity of the polyfluoropropyl group arises from an increase in S_N2 reactivity as the electron withdrawing fluorine atoms

---

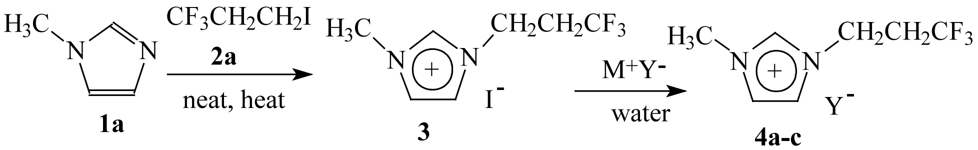
* Corresponding author.

0040-4039/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(02)02448-6

of trifluoroethyl are replaced by hydrogen allowing more successful attack by the imidazolium anion.[12] Metathesis reactions of **3** with KPF_6, KSO_3CF_3, and $LiN(SO_2CF_3)_2$ in aqueous solutions resulted in the formation of ionic liquids **4a**–**c** in good yields (Scheme 1). Products were fully characterized by spectroscopic and elemental analyses.

In order to introduce two polyfluoroalkyl substituents into the imidazole ring, sodium imidazolate (**1b**) was prepared by the reaction of NaH with imidazole in THF at 70°C for 7 h.[13,14] The reactions of 1,1,1-trifluoro-3-iodopropane (**2a**) and 1-fluoro-3-bromopropane (**2b**) with **1b** in THF even after reflux for several days (Scheme 2) were found to be sluggish at best. However, when no solvent was used, the reaction of **1b** with an excess of either **2a** or **2b** gave good yields of **3b** or **3c**. Minor amounts of polar impurities comprised of unreacted imidazole and a partially polyfluoroalkylated imidazole derivative were observed in the crude reaction mixture. When metathesis reactions of the crude mixtures of **3b**,**c** were carried out with KPF_6 and $LiN(SO_2CF_3)_2$ in aqueous solution, **4d**–**g** were precipitated in good yields with the impurities remaining in the water phase.

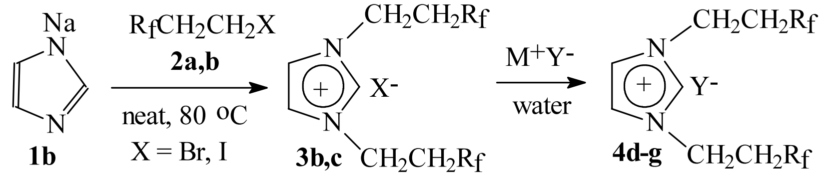
The quaternary salts and the ionic liquids are air and water stable.[15–17] Formation of the two species proceeds more smoothly with heating in the absence of solvent. The thermal stabilities of the ionic liquids having PF_6^-, $CF_3SO_3^-$ and $N(SO_2CF_3)_2^-$ anions were studied via differential scanning calorimetry and found to exceed 300°C. It is interesting to note for example that while **4a** has a melting point of 61°C, for **4d**, with the replacement of methyl by a second trifluoropropyl substituent, the melting point remains essentially constant at 69°C. However, if the anion which is hexafluorophosphate in **4a** is changed to triflate (**4c**), the melting point is 51°C and then to bis(trifluoromethanesulfonyl)amide (**4b**), the melting point is reduced to −70°C. Similarly changing the anion in **4d** (hexafluorophosphate) to bis(trifluoromethanesulfonyl)amide (**4e**), the melting temperature decreases 131°C to −62°C. This is not unique to the bis(trifluoropropyl)imidazolium case, but is also true for the bis(fluoropropyl) examples where **4f** (hexafluorophosphate) melts at 27°C, but the melting point is reduced by 107°C to −80°C for **4g** [bis(trifluoromethanesulfonyl)amide]. However, we do find that changing to anions that are less likely to hydrogen bond causes the melting point to decrease, i.e. from triflate or hexa-



M = Li, K

4a: Y = PF_6
4b: Y = $N(SO_2CF_3)_2$
4c: Y = SO_3CF_3

Scheme 1.



M = Li, K

2a: $CF_3CH_2CH_2I$
2b: $CH_2FCH_2CH_2Br$
3b: Rf = CF_3, X = I
3c: Rf = CH_2F, X = Br
4d: Rf = CF_3, Y = PF_6
4e: Rf = CF_3, Y = $N(SO_2CF_3)_2$
4f: Rf = CH_2F, Y = PF_6
4g: Rf = CH_2F, Y = $N(SO_2CF_3)_2$

Scheme 2.

fluorophosphate to bis(trifluoromethanesulfonyl)amide, often times markedly. The densities of **4e** and **4g** with two fluorine-containing substituents at 1.85 and 1.57 g/cm^3 are considerably higher than **4b** at 1.44 g/cm^3 with a single fluorinated substituent. The latter density is approximately equivalent to that of [C_3-mim]NTf_2.[14] These compounds are insoluble in water, alkanes (pentane, hexane) and diethyl ether. They are sparingly soluble in dichloromethane and chloroform, but soluble in acetone, alcohols, THF and DMF. All the final products were characterized by spectroscopic and elemental analyses.

In conclusion, new thermally stable, water-insoluble ionic liquids with alkyl/polyfluoroalkyl and, di(polyfluoroalkyl)-substituted imidazolium cations have been synthesized and characterized. Marked variations in melting points appear to be primarily a function of the anion and essentially independent of the substituents on the cation. However, the presence of fluorine markedly increases the density and may cause an increase in the melting point with constant anion in some cases. Work is being carried out to extend the understanding of the chemical and physical properties of these versatile novel compounds and to develop methodologies leading to even more dense liquids.

Acknowledgements

This work was supported by National Science Foundation (Grant No. CHE-9720365) and Petroleum Research Fund, administered by ACS. We are also grateful to Drs. G. Knerr and A. Blumenfeld for measuring MS and NMR spectra, respectively.

References

1. Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772–3789.
2. Welton, T. *Chem. Rev.* **1999**, *99*, 2071–2083.
3. Hagiwara, R.; Ito, Y. *J. Fluorine Chem.* **2000**, *105*, 221–227.
4. Bonhôte, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. *Inorg. Chem.* **1996**, *35*, 1168–1178.
5. Freemantle, M. *Chem. Eng. News* **2001**, *79*, 21–25.
6. Freemantle, M. *Chem. Eng. News* **2000**, *78*, 37–50.
7. Wasserscheid, P.; Gordon, C. M.; Hilgers, C.; Muldoon, M. J.; Dunkin, I. R. *J. Chem. Soc., Chem. Commun.* **2001**, 1186–1187.
8. Handy, S. T.; Zhang, X. *Org. Lett.* **2001**, *3*, 233–236.
9. Laali, K. K.; Gettwert, V. J. *J. Fluorine Chem.* **2001**, *107*, 31–34.
10. Merrigan, T. L.; Bates, E. D.; Dorman, S. C.; Davis, J. H., Jr. *J. Chem. Soc., Chem. Commun.* **2000**, 2051–2052.
11. Xu, L.; Chen, W.; Bickley, J. F.; Steiner, A.; Xiao, J. *J. Organomet. Chem.* **2000**, *596*, 409–416.
12. Hine, J.; Ghirardelli, R. G. *J. Org. Chem.* **1958**, *23*, 1550–1554.
13. Dyuba, S. V.; Bartsch, R. A. *J. Chem. Soc., Chem. Commun.* **2001**, 1466–1467.
14. Dyuba, S. V.; Bartsch, R. A. *Tetrahedron Lett.* **2002**, *43*, 4657–4659.
15. **1-Methyl-3-(3,3,3-trifluoropropyl)imidazolium hexafluorophosphate (4a)**: yield 95%; white solid; mp 61°C; IR (KBr film): 3180, 1579, 1403, 1344, 1255, 1147, 833, 745 cm^{-1}; ^{1}H NMR (acetone-d_6): δ 8.99 (s, 1H), 7.77 (t, 1H, J=1.7 Hz), 7.64 (t, 1H, J=1.7 Hz), 4.64 (t, 2H, J=7.0 Hz), 4.0 (s, 3H), 3.0 (q of t, 2H, J=10.4 Hz, J=7.0 Hz); ^{19}F NMR (acetone-d_6): δ −61.08 (t, 3F, J=10.4 Hz, $CH_2CH_2\underline{C}F_3$), −67.58 (d, 6F, J=708.2 Hz, PF_6); ^{31}P NMR (acetone-d_6): δ −137.86 (sept., 1P, J=708.3 Hz, PF_6); ^{13}C NMR (acetone-d_6): δ 33.66, (q, J=29.1 Hz, $CH_2\ \underline{C}H_2CF_3$), 35.99, 43.02 (q, J=3.9 Hz, $\underline{C}H_2CH_2CF_3$), 122.70, 124.27, 125.99 (q, J=276 Hz, $CH_2CH_2\underline{C}F_3$), 137.3; MS (solid probe): *m*/*z* 179 ([M^+−PF_6], 39), 164 (M^+−[PF_6−CH_3], 80), 82 (M^+−[I+$CH_2CH_2CF_3$], 69), 81 ($C_4H_5N_2^+$, 95). Anal. calcd for $C_7H_{10}F_9N_2P$: C, 25.94; H, 3.11. Found: C, 25.34, H, 3.02%.
16. **1,3-Bis(3,3,3-trifluoropropyl)imidazolium hexafluorophosphate (4d)**: yield 80%; white solid; mp 69°C; IR (KBr film): 3179, 3130, 1572, 1440, 1404, 1345, 1256, 1142, 1026, 999, 835, 742 cm^{-1}; ^{1}H NMR (acetone-d_6): δ 9.2 (s, 1H), 7.9 (d, 2H, J=1.5 Hz), 4.7 (t, 4H, J=6.4 Hz), 3.07 (q of t, 4H, J=9.4 Hz, J=6.3 Hz); ^{19}F NMR (acetone-d_6): δ −61.16 (t, 6F, J=9.03 Hz, $CH_2CH_2\underline{CF_3}$), −67.63 (d, 6F, J=707.9 Hz, PF_6^-); ^{31}P NMR (acetone-d_6): δ −137.88 (sept., 1P, J=707.8 Hz, PF_6^-); ^{13}C NMR (acetone-d_6): δ 142.9, 131.5 (q, J=271.8 Hz, $CH_2CH_2\underline{C}F_3$), 128.8 (s, 2C), 48.8 (q, J=3.7 Hz, $\underline{C}H_2CH_2CF_3$), 39.6 (q, J=29.4 Hz, $CH_2\underline{C}H_2CF_3$); MS (solid probe): *m*/*z* 261 ([M^+−PF_6], 51), 164 (M^+−[PF_6−$CH_2CH_2CF_3$], 45), 67 [PF_6−2$CH_2CH_2CF_3$], 16). Anal. calcd for $C_9H_{11}F_{12}N_2P$: C, 26.62; H, 2.73. Found: C, 26.41, H, 2.83%.
17. **1,3-Bis(3-fluoropropyl)imidazolium hexafluorophosphate (4f)**: yield 80%; viscous yellowish liquid; IR (NaCl film): 3674, 3597, 3161, 2978, 1606, 1567, 1462, 1394, 1162, 1038, 1011, 933, 831, 740 cm^{-1}; ^{1}H NMR (acetone-d_6): δ 8.89 (s, 1H), 7.67 (d, 2H, J=1.6 Hz), 4.55 (d of t, 4H, J=47.13 Hz, J=5.49 Hz), 4.43 (t, 4H, J=7.1 Hz), 2.32 (d of t of t, 4H, J=26.37 Hz, J=7.1 Hz, J=5.6 Hz); ^{19}F NMR (acetone-d_6): δ −218.27 (t of t, 2F, J=46.1 Hz, J=28.3 Hz, $CH_2CH_2CH_2\underline{F}$), −67.28 (d, 6F, J=707.9 Hz, PF_6^-); ^{13}C NMR (acetone-d_6): δ 137.0 (d, J=7.5 Hz), 123.6 (d, J=7.5 Hz), 81.6 (d, J=158.3 Hz, $CH_2CH_2\underline{C}H_2F$), 47.21 (d, J=5.27 Hz, $\underline{C}H_2CH_2CH_2F$), 31.18 (d, J=19.60 Hz, $CH_2\underline{C}H_2CH_2F$); ^{31}P NMR (acetone-$d_6$): δ −137.88 (sept., 1P, J=707.8 Hz, PF_6^-). Anal. calcd for $C_9H_{15}F_8N_2P$: C, 32.35; H, 4.52. Found: C, 32.26, H, 4.50%.