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Low melting and slightly viscous ionic liquids via protonation of trialkylamines by perfluoroalkyl β-diketones ☆

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Abstract—New trialkylammonium perfluoroalkyl β-diketonate salts are obtained in one-step reactions by taking advantage of proton transfer from perfluoroalkyl β-diketones to tertiary amines. The charge associated with the β-diketonate anion is considerably delocalized, which may play a role in giving rise to low melting and thermally stable salts with low viscosities and densities.

While there are a large number of quaternary tetraalkyl ammonium salts,[1–3] few quaternary trialkyl ammonium (R_3NH^+) compounds have been reported. Some of the former claim to have real world applications, such as glutardialdehyde bisulfite trialkylamine salts that are bactericides for use against sulfate-reducing bacteria especially in the petroleum industry.[4] Similar applications have been suggested for monoquaternized diamines some of which are trialkylammonium,[5] and longer chain trialkyl ammonium derivatives of higher fatty acid–sulfuric acid anhydrides.[6] Simple trialkyl salts, such as $R_3NH^+NCS^-$ (R = methyl, ethyl, *n*-propyl, *n*-butyl) and $R_3NH^+TsO^-$ (R = methyl, ethyl) are relatively low melting and have been utilized as a new class of polar stationary phases for gas chromatography.[7,8]

Wasserscheid et al.[9] reported a straightforward one-pot, two-step synthesis of new functionalized ionic liquids from Michael-type reactions by first protonating a tertiary amine, such as *N*-methylimidazole, with a strong acid to form an ammonium salt. The latter was then reacted with an α,β-unsaturated compound at 70 °C for 16 h to form a viscous room temperature ionic liquid. In contrast, the analogous pyridinium salts tended to have low viscosities, for example, pyridinium methoxyethyl sulfate at 154 mPa s.

It has been shown with several diketones, for example, acetylacetone and trifluoromethyl acetylacetone that in the presence of CHF_2Cl and triethylamine, the amine increases the percentage of the enol by ~8% over pure acetylacetone arising either from proton transfer to the amine to give Et_3NH^+ (hydrogen bonded to the enolate anion) or involving a bifurcated hydrogen bond instead of proton transfer. However, although studies such as these were carried out in various solvent systems, products formed between the diketone and the amine have rarely been reported.[10]

We now describe an interesting new family of trialkylammonium perfluoroalkyl β-diketonates obtained from reactions between perfluoroalkyl β-diketones and tertiary amines in one-step, room temperature syntheses.

In our continuing interest[11–15] in the development of low melting compounds, particularly those that are fluorine containing, a new series of stable room temperature liquid quaternary trialkylammonium perfluoroalkyl β-diketonates are produced via a single reaction step. β-Diketones are readily available, widely used reagents, but until now advantage has not been taken of reactions of these compounds as proton transfer reagents to form quaternary salts with trialkylamines (Scheme 1, Table 1). An attractive feature of the perfluoroalkyl β-diketonate anion, just as with the bis(trifluoromethanesulfonyl) amide anion, is the considerable delocalization of the electron cloud over the molecular backbone,

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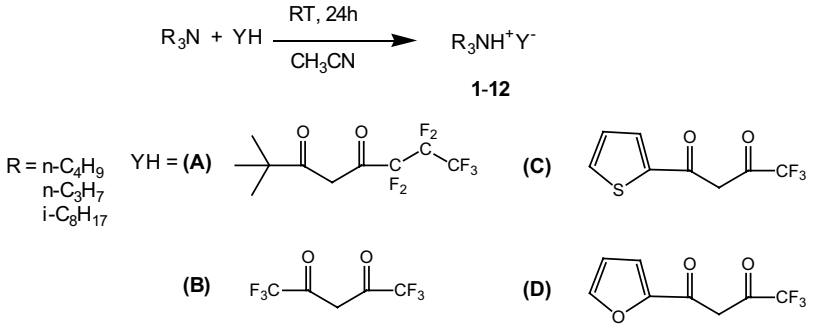

Scheme 1.

Table 1. Synthesis and properties of trialkylammonium perfluoroalkyl β-diketonate liquid salts

$R_3NH^+Y^-$	R	YH	Yield (%)	MP (°C)	Viscosity/cP		d (g/cm^3)
					25 °C	40 °C	25 °C
H_2O					0.89	0.66	0.997
1	n-C_4H_9	**A**	95	−65	9.50	2.50	0.86
2	n-C_4H_9	**B**	90	−93[a]	16.80	6.80	0.68
3	n-C_4H_9	**C**	90	52	—	—	—
4	n-C_4H_9	**D**	95	−65	317.40	3.60	1.02
5	n-C_3H_7	**A**	90	−83	16.00	6.00	0.96
6	n-C_3H_7	**B**	90	−10	—	—	0.73
7	n-C_3H_7	**C**	95	−65	—	—	1.27
8	n-C_3H_7	**D**	90	−82	10.87	3.87	1.25
9	i-C_8H_{17}	**A**	90	−96[a]	8.34	2.86	0.82
10	i-C_8H_{17}	**B**	95	−11	3.44	1.60	0.80
11	i-C_8H_{17}	**C**	90	−86[a]	172.22	44.11	0.94
12	i-C_8H_{17}	**D**	90	−92[a]	140.20	39.58	1.14

[a] Melting point determined by direct measurement. All others obtained via DSC.

which may tend to reduce hydrogen bonding in these liquid systems. By using β-diketones as proton transfer reagents, a large range of quaternary trialkylamino salts were synthesized. These compounds are thermally stable to >300 °C and unexpectedly have sub-ambient melting points and viscosities as low as 3.44 cP.

Each of the reactions proceeds readily to give the diketonate in high yield at room temperature. For example, compound **2** was obtained when a solution of 2 mmol (0.27 gm) of tri(n-butyl)amine in 10 mL of anhydrous acetonitrile, and 2.0 mmol of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (**B**) in 5 mL of acetonitrile were stirred in a 50 mL round-bottomed flask at 25 °C. The solvent was removed under vacuum to give the crude compound. It was purified by column chromatography using a silica gel column (70–230 mesh), and eluted with an acetonitrile–ethyl acetate (70/30) mixture to give **2** in 90% yield as a low melting liquid (−93 °C). Compounds **1**, **3**–**12** were obtained in a similar manner in high yields.

The solid compound (**3**) was purified by recrystallization from ethyl acetate–hexane, (75/25). Its single crystal X-ray structure was determined and is given in Figure 1.[16] The hydrogen of the tributylammonium cation [(n-Bu)$_3$NH$^+$] is located almost in the center of the beta-dicarbonyl grouping. There is a bifurcated hydrogen bond to both oxygen atoms (N...O 2.749, 2.796 Å). The

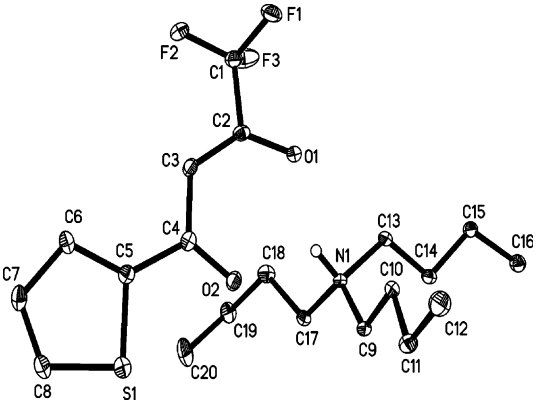

Figure 1. An ORTEP drawing of **3**. Thermal ellipsoids are shown at 30% probability. All hydrogen atoms except for H1 have been omitted for clarity.

charge appears to be delocalized over the OC–CH–CO fragment (O1–C2, 1.256(2); C2–C3, 1.378(3); C3–C4 1.423(3); C4–O2, 1.245(2) Å).[17]

The thermal properties of **1**–**12** were investigated by differential scanning calorimetry. Remarkably all of the diketonate-amine adducts, except **3**, formed by the interaction of tributylamine and thenoyl diketone (**C**), are liquids at room temperature with well defined melting points below 0 °C (Table 1) and with surprising

thermal stabilities to ~300 °C giving rise to long liquid ranges. The thermal stabilities of these adducts seem to be essentially independent of the tertiary amine employed. Although there are some differences in the melting points, there does not appear to be a systematic correlation between anion or cation and the melting point.

As shown in Table 1, the viscosities of these compounds at 25 and 40 °C are, in some cases, remarkably low. In fact, these are the least viscous of any reported ionic salts. Also, there is a very appreciable decrease observed in the viscosity of these materials at 40 °C. Again there seems to be little correlation between the compositions of these adducts and the viscosities observed. These liquids fulfil exactly the criteria of a Newtonian model (viscosity dependent on temperature alone) and therefore are Newtonian ionic liquids. Most of these adducts can be stirred and poured readily at room temperature, while others tend to be more lethargic.

Reduced reaction rates and competitive unimolecular side reactions occur in highly viscous liquids in addition to concomitant handling difficulties, for example, dissolution, decantation, and filtration. Although, in general, the viscosities of nonhaloaluminate alkylimidazolium-based liquids are higher than the analogous haloaluminate salts, one of the least viscous, inert families of low melting salts is that based on the bis(trifluoromethanesulfonyl) amide, $N(Tf)_2^-$ ion,[1,18,19] for example, 1-ethyl-3-5-methylimidazolium bis(trifluoromethanesulfonyl)amide ($\eta = 34$ cP, 20 °C). Introducing the dicyanamide anion gives a viscosity of 21 cP at 25 °C.[20] In the latter study, several new quaternary ammonium, pyrrolidinium, and imidazolium dicyanamide salts showed different solubility profiles from the analogous bis(trifluoromethanesulfonyl) amides and have potential donor characteristics as the anion is a powerful ligand. The densities of these stable β-diketonates, as determined with a pycnometer, lie in the range 0.68–1.27 g/cm^3 at 25 °C. Salts of the diketones **A** and **B** are less dense in comparison with diketones **C** and **D**, which are comprised of a bulky thenoyl or furyl group, respectively. Also, not unexpectedly, the liquids formed from the more highly fluorinated diketone **A** tend to be denser than those obtained with **B**.

These adducts are appreciably soluble in water and aliphatic hydrocarbons, and they are miscible in all proportions with many organic solvents ranging in polarity from toluene to methanol. This new synthesis provides the opportunity for the production of inexpensive, useful ionic liquids. Of particular interest are the exceptionally long liquid range, the nonviscous nature, and the rather high thermal stability (to ~300 °C). While we have reported only compounds formed from fluorine-containing diketones, the solvent characteristics can be modified with change in the composition of the latter compounds.

In summary, we have found a one-step route to low melting ionic liquids with a heretofore unexplored anion type. This has led to a large variety of stable liquids of low density and having unexpectedly low viscosities. This may provide a break through in solvent systems for replacing organic solvents in synthetic chemistry.

Supporting information available. Experimental procedures for **1**–**12**, and characterization data for compounds **3**, **4**, **8**–**12**. CCDC 223840 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; deposit@ccdc.cam.ac.uk).

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17. X-ray data for **3**. Empirical formula: $C_{20}H_{32}F_3NO_2S$. Formula weight: 407.53. Crystal color, habit: yellow block. Crystal dimensions: $0.35\times0.15\times0.08\,mm^3$. Crystal system: triclinic. Lattice parameters: $a = 9.7272(19)$ Å, $b = 9.863(2)$ Å, $c = 12.483(3)$ Å, $\alpha = 88.11(3)°$, $\beta = 83.93(3)°$, $\gamma = 65.26(3)°$, $V = 1081.5(4)$ Å^3. Space group: P-1. Z value = 2. $D_{calcd} = 1.251\,mg/m^3$ F_{000} 436. Diffractometer: Bruker/Siemens SMART APEX. Residuals: $R = 0.0536$, $R_w = 0.1216$.
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