J. Org. Chem. **1993**, *58*, 7294–7295

N,N,N-Trimethyl-1-adamantylammonium Fluoride, a Completely Anhydrous Quaternary Ammonium Fluoride Salt[1]

Kenneth M. Harmon,* Barbara A. Southworth,
Karen E. Wilson, and Patricia K. Keefer

*Department of Chemistry, Oakland University,
Rochester, Michigan 48309*

Received August 2, 1993

There has been considerable interest in the use of quaternary ammonium fluorides as an organic solvent soluble source of fluoride ion in anhydrous conditions.[2] However, simple tetra-*n*-alkylammonium fluorides cannot be prepared in anhydrous condition due to Hofmann-type elimination to alkene, trialkylamine, and tetraalkylammonium hydrogen difluoride.[2–4] Tetramethylammonium fluoride can be prepared in anhydrous form[5,6] but it is not particularly soluble in common organic solvents.

Recently, and quite inadvertently, we prepared anhydrous *N,N,N*-trimethyl-1-adamantylammonium fluoride (TMAAF) during a study of the hydrates of this salt.[7] Since mention of this fact appeared ancillary to an infrared study of molecular structure, it is likely that it will not come to the attention of chemists that would be interested in this compound from a synthetic viewpoint. Also, the reported preparation would be quite expensive on a large scale, and we have developed a simpler route. For these reasons it seems useful to make a brief report in this journal.

The original route involved treatment of aqueous TMAABr with Ag_2O, neutralization of the resulting TMAAOH solution with hydrofluoric acid, dehydration *in vacuo* to $TMAAF\cdot 3H_2O$, dissolution in D_2O, and again drying *in vacuo*. Deuteration is necessary; TMAAF forms a hemihydrate, $TMAAF\cdot 0.5H_2O$, which contains an $F{-}H{-}O{-}H{-}F^{2-}$ molecular ion bound by covalent three-center bonds. Water cannot be removed from this species by drying *in vacuo*, azeotropic distillation under benzene, dissolution in 2-propanol and treatment with molecular sieve, or extended storage over P_2O_5. However, $TMAAF\cdot 0.5D_2O$ may be dried *in vacuo* to yield anhydrous material. The difference in the behavior of $TMAAF\cdot 0.5H_2O$ and $TMAAF\cdot 0.5D_2O$ on attempted dehydration presumably results from different hydrogen bond types in the two hydrates. Examples are known where the nature of proton potential well is significantly altered on deuteration,[8,9] and infrared spectra suggest this may be the case with $TMAAF\cdot 0.5H_2O$ and $TMAAF\cdot 0.5D_2O$.[7]

This preparation has two major problems. The use of Ag_2O would be expensive on a large scale, and on occasion samples are contaminated with residual Ag metal from photoreduction of colloidal AgBr (see Experimental Section). Also, the need to prepare $TMAAF\cdot 0.5D_2O$ is time consuming (deuteration must be repeated three times for complete replacement) and again expensive on a large scale.

We have previously prepared anhydrous tetramethylammonium fluoride[6] by the method of Tunder and Siegel,[5] which involves metathesis of tetramethylammonium chloride and potassium fluoride in alcohol solvent. We find that this method can be used to prepare anhydrous TMAAF (IR Figure 1D).

All operations must be conducted with completely dry reagents in a highly efficient glove box. TMAAF is extraordinarily hygroscopic. Although material prepared by metathesis was completely anhydrous, as shown by the IR spectrum, and was carefully packaged for shipment, the analysis received was for the hemihydrate.

Figure 1 also illustrates spectra that might be of use to persons preparing TMAAF; these include $TMAAF\cdot 3H_2O$ and $TMAAF\cdot 0.5H_2O$ (unwanted but not unlikely) and the 1:2 adduct of TMAAF and 2-propanol (an intermediate compound).

The stability of the $TMAA^+$ cation results from the presence of methyl groups which are compatible with the extremely basic anhydrous fluoride ion,[5,6] and the bridgehead position of the $(CH_3)_3N^+$ group which, following Bredt's rule, resists elimination. We have investigated fluoride hydrates of several other quaternary ammonium ions which form stable fluoride ion monohydrates and, for structural reasons, may well resist elimination and yield anhydrous fluorides by the metathesis method. These include the *N*-methylquinuclidinium,[10] *N,N'*-dimethyltriethylenediammonium,[11] and hexamethonium[12] ions.

Experimental Section

Aldrich anhydrous methanol, 2-propanol, and potassium fluoride were used as supplied. TMAACl was prepared as previously reported[13,14] by reaction of methyl chloride with *N,N*-dimethyl-1-adamantamine in ether solvent. (This reaction is quite slow and gives incomplete conversion; however, TMAABr or TMAAI, which form in high yield, cannot be used as KBr and KI are too soluble in alcohol solvent.) Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer as Nujol mulls on CsI plates. Analyses were by Galbraith Laboratories Inc., Knoxville, TN. All operations were carried out in an efficient dry box.

Metahasis Method. A solution of TMAACl (1.23 g, 5.35 mmol) in methanol (15 mL) was added to a solution of KF (0.32 g, 5.35 mmol) in methanol (6 mL) and the resulting mixture allowed to stand 1 h. Precipitated KCl was removed on a glass frit (dry N_2 push) and the methanol solution evaporated *in vacuo* at 25 °C to a white powder. This powder was then treated with 2-propanol (25 mL) and again filtered on the same glass frit to remove residual KCl . Total recovery of KCl was 0.40 g, 5.36 mmol). The 2-propanol solution was dried *in vacuo* for 12 h at 25 °C to yield a soft, white powder. NMR analysis[13] showed this material to contain 2.1 mol of 2-propanol per mol of TMAAF. This adduct was heated *in vacuo* at 45 °C for 12 h to yield anhydrous TMAAF. An IR spectrum (Figure 1D) showed no trace of water or alcohol.

Although the sample was anhydrous by IR (contrast Figure 1D with the spectrum of the hemihydrate, Figure 1B), the sample

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[1] Acknowledgement is gratefully made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this work.

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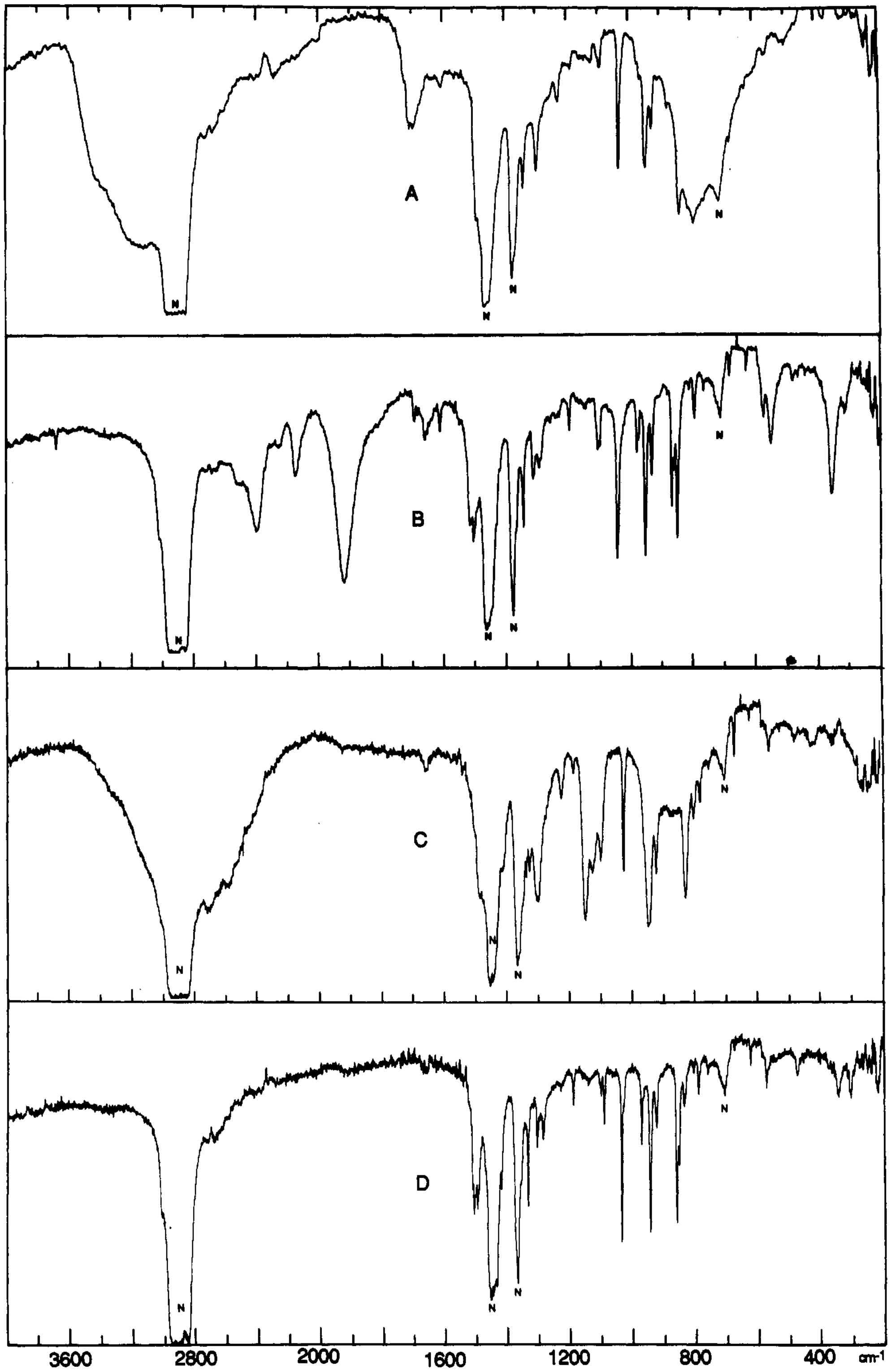

Figure 1. Infrared spectra (Nujol mulls on CsI plates) of *N,N,N*-trimethyl-1-adamantylammonium fluoride compounds: A, trihydrate; B, hemihydrate; C, adduct with 2 mol of 2-propanol; D, anhydrous fluoride. Units are cm^{-1} (wavenumbers); % *T*. Peaks marked N are from Nujol.

gained water on shipment and was analyzed for the hemihydrate. Anal. Calcd for $C_{13}H_{24}NF{\cdot}0.5H_2O$: C, 69.99; H, 10.98; N, 6.52; F, 8.32. Found: C, 69.78; H, 11.06; N, 6.18; F, 8.46.

Ag_2O/D_2O Method. The general method for preparation of fluorides[11] and the specific preparation of TMAAF[7] have been described previously in detail. As the method has drawbacks (see above) it will not be described further. The sample submitted for analysis was contaminated by metallic Ag. A solution in water gave no precipitate with NaCl solution; a solution in nitric acid gave AgCl precipitate with NaCl solution. Calcd for $C_{13}H_{24}NF$: ratios C/H, 6.45; C/N, 11.14; C/F, 8.08. Found: ratios C/H, 6.45; C/N, 11.13; C/F, 8.20. Calcd %: C, 73.19; H, 11.34, N, 6.57; F, 9.06. Found %: C, 70.36; H, 10.91; N, 6.32; F, 8.58; corrected for Ag content: C, 73.17; H, 11.35; N, 6.57; F; 8.92.