m/z 378 (M^+, 1), 277 (4), 43 (100); ^{1}H NMR ($CDCl_3$) δ 1.50 (9 H, s, *t*-Bu), 2.35 (3 H, s, CH_3); ^{13}C NMR ($CDCl_3$) 21.61 (CH_3 of *t*-Bu), 27.98 (CH_3), 83.58 (C of *t*-Bu), 107.90 (C-3), 121.67, 123.95, 135.76, 138.15 (C-5,6,7,8), 158.78 (C-2), 163.19 (CO). Anal. Calcd for $C_{12}H_{12}Cl_4O_3S$: C, 38.10; H, 3.17. Found: C, 38.00; H, 2.89.

2-Methyl-3-acetyl-5,6,7,8-tetrachloro-1,4-oxathiocine (3f). Diazoacetylacetone (1.0 g, 0.008 mol) was added dropwise during 2 h to a stirred and cooled (4 °C) solution of tetrakis(acetato)-dirhodium(II) (5 mg) and 2,3,4,5-tetrachlorothiophene (8.7 g, 0.04 mol) in DCE (5 mL). After addition, the mixture was left at 10 °C for 6 days. The solvent was removed under reduced pressure, dry hexane (20 mL) was added, and the solid product was filtered off and purified by column chromatography. Elution with petroleum ether (200 mL) gave tetrachlorothiophene, and subsequent elution with chloroform (400 mL) gave the white crystalline product **3f**: 0.28 g (11%); mp 82–83 °C (microscope), 83 °C (Kofler); IR (Nujol) 1687 (C=O) cm^{-1}; MS *m/z* 235 (1), 187 (1), 149 (4), 44 (100); ^{1}H NMR ($CDCl_3$) δ 2.29 (3 H, s, CH_3), 2.52 (3 H, s, CH_3); ^{13}C NMR ($CDCl_3$) δ 21.95, 29.91 (2 CH_3), 112.38 (C-3), 121.73, 122.59, 135.58, 138.73 (C-5,6,7,8), 160.06 (C-2), 196.98 (CO). Anal. Calcd for $C_9H_6Cl_4O_2S$: C, 34.21; H, 1.91. Found: C, 34.41; H, 1.81.

2-Methyl-3-(*p*-tolylsulfonyl)-5,6,7,8-tetrachloro-1,4-oxathiocine (3g). α-Acetyl-α-(*p*-tolylsulfonyl)diazomethane (0.71 g, 0.003 mol) was dissolved in DCE (1 mL) and added slowly at room temperature to a solution of tetrakis(acetato)dirhodium(II) (5 mg) and 2,3,4,5-tetrachlorothiophene (5.33 g, 0.024 mol) in DCE (5 mL), and the mixture was stirred at room temperature for 2 weeks. After evaporation of the solvent dry hexane was added, and the solid product was purified by column chromatography. Elution with petroleum ether (200 mL) gave tetrachlorothiophene, and subsequent elution with chloroform (400 mL) gave the product **3g**: 0.33 g (26%); mp (from $CHCl_3$) 181–182 °C (microscope); IR (Nujol) 1615 cm^{-1}; MS *m/z* 432 (M^+, 6), 277 (16), 235 (34), 91 (100); ^{1}H NMR ($CDCl_3$) δ 2.35, 2.51 (6 H, 2 s, 2 CH_3), 7.27 (2 H, d, J = 9.0 Hz, 3,5-H_2), 7.85 (2 H, d, J = 9.0 Hz, 2,6-H_2); ^{13}C NMR ($CDCl_3$) δ 21.68, 21.70 (2 × CH_3), 128.40, 129.77, 139.19, 145.32 (aromatic carbons), 118.01 (C-3), 122.12, 123.48, 135.05, 136.27 (C-5,6,7,8), 161.59 (C-2). Anal. Calcd for $C_{14}H_{10}Cl_4O_3S_2$: C, 39.27; H, 2.35. Found: C, 39.42; H, 2.06.

2-Methyl-3-carbethoxy-6,7-dibromo-5,8-dichloro-1,4-oxathiocine (3h). Ethyl diazoacetoacetate (0.78 g, 0.005 mol) was added dropwise to a mixture of tetrakis(acetato)dirhodium(II) (5 mg) and 3,4-dibromo-2,5-dichlorothiophene (12.36 g, 0.04 mol) at 80 °C under nitrogen. The mixture was stirred at 75–80 °C for 15 h and cooled, and petroleum ether was added. The crude product was purified by column chromatography. Elution with petroleum ether (200 mL) gave 3,4-dibromo-2,5-dichlorothiophene, and subsequent elution with petroleum ether–ether (1:1) (400 mL) gave the product **3h**: 0.81 g (37%); oil; IR (neat) 1721 (C=O) cm^{-1}; MS *m/z* 440 (M^+, 3), 395 (7), 367 (7), 43 (100); ^{1}H NMR ($CDCl_3$) δ 1.28 (3 H, t, J = 7.5 Hz, CH_3 of Et), 2.33 (3 H, s, CH_3), 4.25 (2 H, q, J = 7.5 Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ 14.01 (CH_3 of Et), 22.03 (CH_3), 62.21 (CH_2), 106.17 (C-3), 113.98, 124.75, 131.23, 136.05 (C-5,6,7,8), 160.40 (C-2), 164.02 (CO).

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Synthesis of Quaternary Ammonium Fluoride Salts by a Solid–Liquid Halogen Exchange Process in Protic Solvents

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Both hydrophilic and lipophilic quaternary ammonium fluoride compounds are prepared by direct exchange of the corresponding halides with solid potassium fluoride containing an optimized amount of water (4.0 mol %). The procedure is most effective when methanol is applied as a solvent. A variety of quaternary ammonium fluorides were prepared in 75–97% yield.

Introduction

Quaternary ammonium fluoride salts are an important group of compounds with numerous synthetic applications, mainly as fluorinating agents and as mild bases.[1,2] Four major methods were reported in the literature for the preparation of these compounds:[3] (a) Neutralization of quaternary ammonium hydroxides with aqueous hydrogen fluoride.[4,5] (b) Reaction of silver fluoride with quaternary ammonium chlorides, bromides, or iodides.[6] (c) Anion exchange of aqueous quaternary ammonium halides with solid anion exchangers in fluoride form.[7] (d) Anion exchange between aqueous potassium fluoride (in large excess) and quaternary ammonium hydrogensulfates in organic phase.[3] These techniques suffer several limitations as follows: (a) The first three methods are limited to water-soluble starting materials and therefore cannot be applied to quaternary salts with more than 20–22 carbons. (b) The first two methods utilize relatively expensive reagents. (c) The product of method a is always contaminated with the side product bifluoride salt $R_4N{\cdot}HF_2$. (d) The last method is limited to lipophilic quaternary ammonium fluorides and requires large excess of reagent (30 equiv). Also, since the exchange is conducted in the presence of water, the ammonium fluorides are obtained as trihydrates which are rather difficult to dry.

Results and Discussion

We have examined the formation of quaternary fluorides by the direct heterogeneous liquid–liquid or solid–liquid halide exchange process (eq 1) where R is a normal alkyl

$$R_4NX + MF \rightleftharpoons R_4NF + MX \qquad (1)$$

group, X is a halide, typically bromide or chloride, and M is an alkali metal, sodium, or potassium. These anion exchange reactions are relatively fast processes, and equilibrium is usually obtained within a few minutes at room temperature in liquid–liquid systems. Longer periods of time are required for solid–liquid systems.

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In initial experiments we contacted saturated aqueous solutions of potassium fluoride with an equivalent volume of 10% (w/w) solutions of a lipophilic quaternary salt, e.g. tetrahexylammonium bromide (THAB), or aliquat 336 in toluene or *o*-dichlorobenzene at various temperatures between 25 and 85 °C for several hours. As could be expected in view of the extremely low selectivity coefficients $K^{sel}_{Cl/F}$ and $K^{sel}_{Br/F}$,[8] only minor exchange (less than 1%) took place under these conditions as was determined by conductometric titration of the organic phase by lanthanium acetate. However, upon gradual removal of water from these systems, the equilibrium 1 is increasingly shifted to the right, reaching a maximum of approximately 4.0% conversion when 0.04 mol of water was present for each mole of KF. In the absence of any solvent the conversion was higher and reached 7.0%.[9] No exchange at all was, on the other hand, observed when the potassium fluoride was carefully dried by freeze-drying.

We have previously suggested[9,10] that quaternary ammonium ion pairs can exchange anions only with hydrated or dissolved salts but are inert toward solid crystals. Therefore, when the amount of water in the system is limited, only the more hydrophilic anions are hydrated and, consequently, extracted. Upon removal of water from the mixture of reaction 1 the equilibrium is shifted to the right because the potassium chloride is dehydrated by the more hydrophilic potassium fluoride and cannot participate in the exchange process.

Interestingly, when sodium fluoride was applied instead of potassium fluoride in reaction 1, very small conversions (<1%) were detected when aqueous solutions were used. However in solid–liquid systems, with limited amount of water, no exchange was observed at all under any circumstances. We have confirmed that this is not due to a thermodynamic reason since all attempts to exchange sodium chloride with various quaternary ammonium fluorides failed as well. We therefore attribute this phenomenon to the large difference in the solubility ratio in water between KF/KCl and NaF/NaCl, which at 25 °C is 25 and 0.3, respectively. It can safely be argued that when a minor amount of water is available for hydration it is the fluoride that will remain in solution when potassium salt is used. On the other hand, when sodium fluoride is applied in reaction 1, the fluoride anion will be driven out of solution once minute amounts of sodium chloride are formed.

The maximum conversion of aliquat 336 in toluene to its fluoride form (reaction 2), applying potassium fluoride containing the optimized amount of water, was found to be 4.5% at 25 °C. This magnitude was not improved by replacing the solvent with *o*-dichlorobenzene nor by carrying out the process in the absence of any solvent or at a different temperature. A dramatic increase in the degree of exchange, up to more than 99%, was, on the other hand, observed when protic solvents, mainly alcohols, were introduced to the system.

$$(n\text{-}C_8H_{17})_3N(CH_3)Cl + KF \rightleftharpoons (n\text{-}C_8H_{17})_3N(CH_3)F + KCl \quad (2)$$

Table I. Effect of Solvent on the Conversion of Reaction between Solid Potassium Fluoride and Aliquat 336[a]

	solvent	convn, mol %
1.	50% (w) phenol in toluene	99.1
2.	methanol	96.8
3.	ethanol	89.5
4.	1-propanol	81.7
5.	1-butanol	75.5
6.	1-octanol	56.0
7.	2-propanol	30.7
8.	nitromethane	12.7
9.	chloroform	5.3
10.	acetone	4.5
11.	1,2-dichlorobenzene	4.0

[a] The experiments were conducted by contacting 1.8 M solutions of aliquat 336 with 1.25 equiv of solid potassium fluoride containing 4.0 mol % of water with effective mechanical stirring (600 rpm) at 25 °C for 3 h. Analysis by titration of both chloride and fluoride in the organic phase.

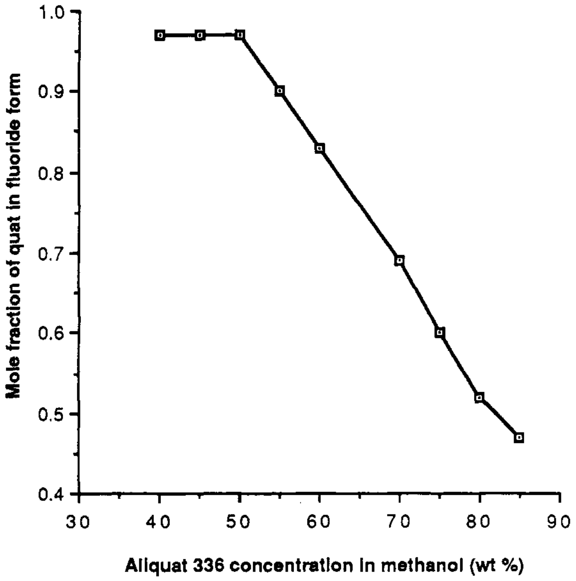

Figure 1. Effect of concentration on conversion of reaction 2.

Table I presents the degree of conversion in reaction 2 when 1.25 equiv of potassium fluoride containing 4% (w/w) water was contacted with effective mixing (600 rpm) for 3 h at 25 °C with 1.8 M solutions of aliquat 336 in various solvents. The results shown in the table clearly suggest that protic solvents with high acidity increase the conversion of reaction 1.

Though not a practical solvent, the highest conversion was measured with a 50% (w/w) of phenol in toluene. Attempts to apply solvents with even higher acidity, e.g. acetic acid, failed due to the competing formation of potassium bifluoride (eq 3). For synthetic purposes methanol is obviously the solvent of choice.

$$2KF + CH_3COOH \rightarrow KHF_2 + CH_3COOK \quad (3)$$

In another set of experiments we studied the effect of the amount of methanol on the equilibrium conversion of aliquat 336 by potassium fluoride at 25 °C. The results of these experiments are presented in Figure 1. It can be concluded that dilution of aliquat 336 by equal weight of methanol is sufficient to obtain the maximum possible conversion which is almost quantitative. In solution of 50% (w/w) there are 15 molecules of methanol for each molecule of quaternary fluoride. This figure apparently reflects the degree of solvation of the fluoride anion by methanol which is exceptionally high under these conditions due to the strong hydrogen bonding. We believe that these hydrogen bonds are the driving force for the shift of the equilibrium of reaction 1 in presence of protic solvents.

These observation are the basis of a new method for the synthesis of anhydrous quaternary ammonium fluoride

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Table II. Quaternary Ammonium Fluoride Monohydrates[a] Prepared in this Study

compound	dec,[b] °C	yield, %	Cl/F ratio[c]
$(CH_3)_4NF$[a]	180	95	3.77
$(C_2H_5)_4NF$[a]	80	83	7.21
$(n\text{-}C_3H_7)_4NF$[a]	140	86	12.40
$(n\text{-}C_4H_9)_4NF$[a]	151–3	87	15.80
$(n\text{-}C_6H_{13})_4NF$	153–5	89	24.10
$(n\text{-}C_8H_{17})_4NF$	156–8	89	30.80
$(n\text{-}C_8H_{17})_3N(CH_3)F$	168–71	93	36.20
$(n\text{-}C_{16}H_{34})N(CH_3)_3F$	246–9	93	18.40

[a] The salts were prepared as monohydrates but are relatively unstable in this form and tend to decompose unless absorb more water of hydration to form higher hydrates. [b] Measured by thermal gravimetry using a TA-3000 Mettler Thermoanalyzer. [c] Based on experimental elementary analysis.

salts. Following the exchange step, the methanol is gradually evaporated under vacuum at room temperature. The precipitation of potassium chloride formed during the evaporation is filtered and removed several times in the course of the operation. The products obtained are 95–7% pure anhydrous quaternary ammonium fluoride salt in 83–95% yield. Since these materials, particularly those with ethyl, propyl, and butyl groups, are extremely unstable, it is recommended to add several equivalents (2–4) of water at the very last step of the evaporation to yield the corresponding hydrates which are stable at room temperature. Table II presents a list of products synthesized in the course of this work with their temperature of decomposition (all the salts in the form of monohydrate). The purity of the products was verified by elementary analysis.

Experimental Section

Materials. Quaternary ammonium chlorides of bromides were purchased from Aldrich and were used without further purification.

Conductometric Assay of Fluoride Anion. The method is based on the potentiometric method reported by Linge.[11] The reagent is a mixture of 1.0 g of lanthanum acetate and 0.5 mL of glacial acetic acid dissolved in 1.0 of double-distilled water. The titration is conducted in methanol–water mixture containing 40 wt % methanol; 100-mg samples are dissolved in 30 mL of this solution and titrated by the reagent with continuous monitoring of the conductivity using El-Hamma TH-230 conductometer and electrode. The endpoint is determined graphically.

This method is applicable to both aqueous and organic samples which are soluble in the water–methanol mixture. In samples containing a nonsoluble solvent (e.g. toluene), the solvent should be evaporated prior to the test.

Chloride anion was determined by argentometric titration.

Preparation of Tricaprylmethylammonium Fluoride. A mixture of 9.15 g of aliquat 336, 40 mL of absolute methanol, and 2.2 g of potassium fluoride containing 4% by weight of water is stirred at room temperature for 15 min. The mixture is filtered, to the solution is added another fraction of 2.2 g of potassium fluoride, and the mixing is continued for an additional 15 min. After filtration 25% of the methanol is evaporated under vacuum at room temperature, the mixture is filtered again, and this procedure is repeated four times until all the methanol is removed. The oily product (8.7 g, 94% yield) was found by titration and elementary analysis to contain 96.5% tricaprylmethylammonium fluoride and 3.5% chloride.

The other quaternary fluorides were prepared in identical procedures.

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Electrochemical Synthesis of (α-Halobenzyl)silanes and Benzal Disilanes

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Electrochemical reduction of a series of substituted benzal chlorides (4) in dimethylformamide containing excess chlorotrimethylsilane affords (α-chlorobenzyl)trimethylsilanes (5) or benzal (geminal) disilanes (6), depending upon experimental conditions. Benzal bromide (13) is reduced to (α-bromobenzyl)trimethylsilane (14) cleanly and in high yield without subsequent conversion to the geminal disilane 6a, apparently because of electrode passivation by bromide ion. The reactions are conveniently carried out at constant current in an undivided cell containing a stainless steel cathode and sacrificial magnesium anode.

α-Halosilanes (1) and geminal disilanes (2) are versatile synthetic intermediates,[1] but their widespread use in organic and organosilicon chemistry has been limited by the lack of convenient methods for their preparation. For example, a recent report described an improved method of preparation of bis(trimethylsilyl)methane (3),[2] yet this method involves the use of lithium at −50 °C, conditions which would be cumbersome at best and possibly hazardous for the synthesis of large amounts of 3, and in addition, it generates 3 in only 55% yield. The conversion of benzal chloride (**4a**) to either (α-chlorobenzyl)trimethylsilane (**5a**) and benzal trimethylsilane (**6a**) is another case in point. The literature synthetic route to these substances involves reaction between **4a**, chlorotrimethylsilane, and an active metal such as magnesium in hexamethyl phosphorous triamide.[3] The reaction presumably involves formation of the Grignard reagents corresponding to **4a** and **5a**, which then react with the halosilane to form a mixture of **5a** and **6a**. It is relatively difficult in such cases to obtain good yields of the monohalide, since halides **4a** and **5a** tend to be about equally

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