

# Perfluoroalcohols

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## Abstract

Perfluorinated primary alcohol adducts with triethylamine were prepared from lower perfluorinated acid fluorides and triethylamine monohydrofluoride. They are stable compounds and may be used as a source of R<sub>F</sub>O groups in organic syntheses.

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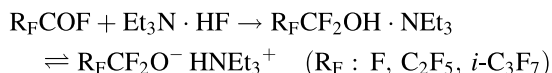
**Keywords:** Perfluoroalcohols; Triethylamine monohydrofluoride

## 1. Introduction

Perfluoroalcohols are not known as a general class of compounds [1,2]. The CF<sub>2</sub>OH and CFOH groups are unstable and decompose into hydrogen fluoride and perfluorinated carbonyl compounds. This is especially true for primary perfluoroalcohols, although secondary perfluorocyclobutanol with a fluorine atom directly attached to the carbon that also carries the hydroxyl, has been isolated [3].

## 2. Results and discussion

We have found that perfluoroalcohols give adducts with triethylamine that are stable and have good solubility in organic solvents. We prepared primary fluoroalcohols by triethylammonium fluoride addition to fluorinated acid fluorides and observed the formation of stable perfluoroalcohol adducts with the amine. No adduct formation was observed for nonfluorinated acid fluorides PhCOF and CH<sub>3</sub>COF.



The adducts were characterized by NMR spectra, which show broad unresolved absorptions of the CF<sub>2</sub>O group, and also an acidic OH/NH adsorption. The hydrogen atom may be bound to an oxygen atom from the acid fluoride or we may have the triethylammonium salt of perfluorinated alkoxides.

The alkoxides are a well documented species in fluorine chemistry [2,4,5]. They are usually made by reaction of fluorinated acid fluorides with fluoride ion. The source of fluoride ion is generally alkali metal fluorides of cesium and potassium. Potassium perfluoroalkoxides are widely used in industry for the preparation of polyfluoroethers (stable fluids) or trifluorovinyl ethers (monomers) from HFPO [6].

The formation of perfluoroalkoxides is an equilibrium reaction and an unfavorable equilibrium position could presumably be shifted to the right by increasing the fluoride ion concentration.



This is the main obstacle for the metal fluorides. The more active cesium fluoride is almost insoluble in polar nonhydroxylic organic solvents. The lack of a suitable solvent system for the reagents is the main experimental difficulty in fluoride ion reactions. One way of circumventing the solubility difficulty would be to use more soluble fluoride such as tetraethylammonium fluoride and this compound has been used with some success [7,8]. It is a rather active catalyst, soluble in organic solvents but it is very hygroscopic, difficult to prepare in a pure state and thermally unstable. In general, it is not a viable alternative to the alkali metal fluorides. So, there is still a great need for a readily available system that is very soluble in organic solvents, especially if derived simply from hydrogen fluoride.

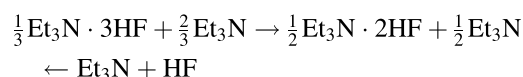
Fluoroalcohol–triethylamine adducts are completely soluble in polar solvents like diglyme, acetonitrile, THF, dioxane, acetone, methylenechloride and the like and in this respect they have an advantage over alkali metal fluoroalkoxides. The adducts are as soluble as tetraethylammonium fluoroalkoxides but do not require tetratethylammonium

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fluoride synthesis—an extra step in the tetraethylammonium alkoxide preparation. Also there is no problem concerning triethylammonium fluoride instability and storage. This raises the question: why has triethylammonium fluoride not been previously used in place of tetraethylammonium fluoride in popular syntheses with perfluoroalkoxide anions? The answer is: because triethylammonium fluoride is unknown as an individual and pure compound. And also we have found that triethylammonium bifluoride or triethylamine trihydrogenfluoride do not react with perfluorinated acid fluorides.

Tertiary amines and hydrogen fluoride form a series of associated species with the general formula  $R_3N \cdot nHF$  ( $n = 1, 2, 3$ , etc.). Solid triethylammonium bifluoride [9] and liquid triethylamine trihydrofluoride (available from Aldrich) are well known. The NMR spectra of trialkylamine-hydrogen fluoride salts,  $R_3N \cdot nHF$ , in methylene chloride solution showed separate signals attributable to the monofluorides of triethylamine and tributylamine [10], but these monofluorides could not be isolated as pure individual compounds [11]. They only appear to exist as equilibrium mixtures with the polyhydrogen fluorides and free trialkylamine. Surprisingly, many authors do not distinguish between tertiary amine mono- and poly-hydrogen fluorides. For instance, in the Fieser Monograph Series “Reagent for Organic Synthesis” triethylamine polyhydrogen fluoride was named as “triethylamine hydrofluoride” [12].

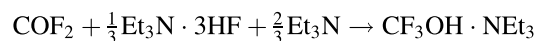
We tried to prepare triethylammonium monofluoride by two methods, by addition of the needed quantity of free triethylamine to the triethylamine trihydrofluoride and by addition of hydrogen fluoride to an excess of the amine. In both cases, solid triethylammonium bifluoride was the main or the only reaction product and the excess of triethylamine was not consumed even with heating.



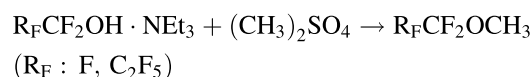
For the synthesis of perfluoroalcohol–triethylamine adducts, we used a 1:1 molar mixture of triethylammonium bifluoride with free triethylamine prepared from triethylamine trihydrofluoride and triethylamine (later in this text, we use the name “triethylammonium fluoride” for this mixture). To this suspension cooled to  $-70^\circ C$ , a low  $M_w$  perfluorinated acid fluoride may be added as a liquid. Only a slight exotherm was observed when the mixture was left to warm to room temperature with gradual dissolving of the acid fluoride and triethylammonium bifluoride. To accomplish the adduct formation, the mixture was usually heated at  $35$ – $40^\circ C$  for 10 min to yield a clear, slightly colored, liquid product. There is no pressure remaining in the reactor at the end of the reaction and it may be opened to add a second reactant or solvent or to take a sample for NMR studies. The reaction equation is as follows:



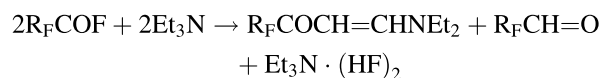
This technique is not the best method when the acid fluoride is added to triethylammonium fluoride in a solvent because a huge exotherm will occur. It is better to bubble the acid fluoride into the solution and that was the only method we used for carbonyldifluoride, which is noncondensed at  $-78^\circ C$ . But even  $COF_2$  is exothermically and quickly consumed while bubbling. The initial suspension of solid triethylammonium bifluoride (which may be partly insoluble when a relatively small amount of solvent is used) is gradually and completely dissolved because of the trifluoromethanol complex formation.



Perfluoroalcohol–triethylamine adducts may be easily alkylated by dimethylsulfate (DMS) to give hydrofluoroethers and there is no need to use any solvent in this reaction.



The best yield of heptafluoropropylmethyl ether was 70% and approximately 28% of perfluoropropionyl fluoride was returned as ethylpentafluoropropionate after treatment by ethanol of the low boiling material distilled out of the reaction mixture. This is the result of partial decomposition of heptafluoropropanol–triethylamine adduct back to acid fluoride and triethylammonium fluoride. Methylbromide reacts with perfluoropropanol–triethylamine adduct to give a low yield (9%) of heptafluoropropylmethyl ether  $C_3F_7OCH_3$ . More active benzylbromide reacts with heptafluoropropanol–triethylamine adduct at room temperature to give a reasonable yield (43%) of heptafluoropropylbenzyl ether ( $C_3F_7OCH_2Ph$ ). Alkylhalides like  $CH_3Br$  require higher temperature for alkylation and in this case, reversible formation of initial perfluoroacid fluoride and its known [13] reduction by triethylamine became the main side reaction.



There are probably some other tertiary amines, that may be better in these reactions, but we did not research this possibility.

### 3. Experimental details

Analytical data was provided by Specialty Materials Manufacturing Division analytical group at 3M. The  $^1H$  and  $^{19}F$  NMR spectra were acquired using a Varian UNITY plus 400 FT NMR spectrometer and include 400 MHz  $^1H$  and 376 MHz  $^{19}F$  spectra. Use of  $p$ -HFX as the cross-integration standard [14] facilitates the cross-correlation of various fluorine and proton signals intensities for

quantitative purposes. GC/MS analysis was performed using an HP 5890 Series 2 gas chromatograph with a 105 m  $\times$  0.32 mm Rtx-5 capillary column to introduce the sample to a Finnigan SSQ-700 mass spectrometer. The samples were ionized using chemical ionization with methane as the reagent gas. A gas chromatograph HP 5890 Series 2 with J&W Scientific fused silica capillary column DB 210 (30 m  $\times$  0.325 mm) with FID detector was used for GC analysis.

### 3.1. Reaction of triethylamine with hydrogen fluoride

An excess of triethylamine (4.347 g, 43.0 mmol) was added to liquid HF (0.664 g, 33.2 mmol) at  $-78^\circ\text{C}$ . The resulting solid and liquid mixture was melted and unreacted triethylamine was separated after cooling as an upper liquid layer to give 2.519 g of white solid mixture of  $\text{Et}_3\text{NH}^+\text{HF}_2^-$ .  $^{19}\text{F}$  NMR ( $\text{CD}_3\text{CN}$ ):  $-152.70$  ( $\text{F}_2^-$ , s, b),  $^1\text{H}$  NMR: 11.09 ( $\text{NH}^+$ ) and  $\text{Et}_3\text{NH}^+\text{F}^-$   $^{19}\text{F}$  NMR:  $-126.12$  ( $\text{F}^-$ , s, b). Cross-correlation of fluorine and proton signal intensities gives: HF as  $\text{H}_2\text{F}_2$  41.41% (F NMR),  $\text{Et}_3\text{N}$  45.62% (H NMR) and HF as HF 12.97% (F NMR), which corresponds 77 mol% triethylammonium bifluoride and 23 mol% triethylammonium monofluoride mixture.

### 3.2. Reaction of triethylamine with triethylamine trihydrogenfluoride

To 0.963 g (5.98 mmol) of triethylamine trihydrogenfluoride was added 1.207 g (11.9 mmol) triethylamine. Immediately a white crystalline solid formation was observed. The mixture was heated until all solid was melted to give the layered liquid material, which after cooling and separation gave 1.266 g (8.97 mmol) of solid triethylammonium bifluoride (100% yield) and 0.878 g (8.69 mmol) of unreacted triethylamine.

### 3.3. Reaction of triethylammonium fluoride with perfluorinated acid fluorides (typical experiment)

To a suspension of triethylamine trihydrogenfluoride (0.33 mol) and triethylamine (0.67 mol) perfluoroacyl fluoride (1 mol) was added while cooling. The addition without solvent may be accomplished simply by pouring liquid acyl fluoride into the amines mixture at a temperature lower than its boiling point. Usually gaseous acyl fluoride was condensed in a trap and poured at  $-70^\circ\text{C}$  into a mixture of triethylamine and its trihydrogenfluoride in an ACE GLASS Inc. heavy-wall glass pressure tube with Ace-Thred PTFE cap, FETFE “O-ring” and magnetic bar stirrer. After leaving the tube reactor to warm to room temperature, the acyl fluoride gradually reacts with the amines mixture to give a clear and slightly colored solution. To accomplish the adduct formation the reaction mixture may be heated at  $40^\circ\text{C}$  for 10–15 min. The products are crystalline solid at approximately  $0^\circ\text{C}$  and liquid at room temperature. They

are stable and do not lose gaseous acyl fluoride at atmospheric pressure and may be stored in a polyethylene bottle for many days.

The reaction of perfluorinated acyl fluoride with the mixture of triethylamine trihydrogenfluoride and triethylamine in solvents (diglyme, acetonitrile, THF, dichloromethane, etc.) is an exothermic process and needs cooling. The perfluoroalcohol–triethylamine adduct may be prepared without solvent, which may be added to the adduct if necessary. The following adducts were prepared:

- $\text{CF}_3\text{OH}\cdot\text{NEt}_3$ ,  $^{19}\text{F}$  NMR ( $\text{CD}_3\text{CN}$ ):  $-33.18$  ( $\text{CF}_3$ , vb),  $^1\text{H}$  NMR: 11.37 (H, b), 3.00 ( $\text{CH}_2$ , q), 1.22 ( $\text{CH}_3$ , t).
- $\text{CF}_3\text{CF}_2\text{CF}_2\text{OH}\cdot\text{NEt}_3$ ,  $^{19}\text{F}$  NMR (diglyme):  $-81.16$  ( $\text{CF}_3$ , s),  $-126.44$  ( $\text{CF}_2$ , s),  $-45.8$  ( $\text{OCF}_2$ , vb);  $^1\text{H}$  NMR: 11.8 (H, b), 2.80 ( $\text{CH}_2$ , q), 1.05 ( $\text{CH}_3$ , t).
- $(\text{CF}_3)_2\text{CFCF}_2\text{OH}\cdot\text{NEt}_3$ ,  $^{19}\text{F}$  NMR ( $\text{CD}_3\text{CN}$ ):  $-72.79$  ( $\text{CF}_3$ , d),  $-180.72$  (CF, h),  $-51$  ( $\text{CF}_2$ , vb);  $^1\text{H}$  NMR: 12.46 (H, b), 2.87 ( $\text{CH}_2$ , q), 1.17 ( $\text{CH}_3$ , t).

The NMR spectrum of  $\text{C}_3\text{F}_7\text{OH}\cdot\text{NEt}_3$  was originally run in a Teflon NMR tube at  $22^\circ\text{C}$  and then run at  $-45$ ,  $-20$ ,  $50$ ,  $75$  and  $100^\circ\text{C}$  with no resolution of the broad  $\text{OCF}_2$  signal. The combined proton and fluorine NMR spectral data showed no acid fluoride at any temperature. The sample contains a minor amount of perfluoropropionic acid at the 5 mol% level and several very minor impurities, which increase to about 5 mol% at  $75$  and  $100^\circ\text{C}$ . One of these increasing impurities appears to be the aminoketone  $\text{C}_2\text{F}_5\text{COCH}=\text{CHN}(\text{C}_2\text{H}_5)_2$ .

### 3.4. Heptafluoropropylmethyl ether (3M HFE 301)

A mixture of pentafluoropropionyl fluoride (7.25 g, 44 mmol), Aldrich triethylamine trihydrogenfluoride (2.41 g, 15 mmol) and triethylamine (3.0 g, 30 mmol) was heated at  $35$ – $40^\circ\text{C}$  for 30 min in ACE GLASS Inc. pressure tube until homogenization was completed. To the clear liquid at  $0^\circ\text{C}$  was added dimethylsulfate (5.81 g, 46 mmol) and 0.19 g Adogen and the whole mixture agitated at  $45$ – $47^\circ\text{C}$  for 5.5 h. In vacuum (25 Torr) from the reactor distilled out low boiling material in cold trap ( $-78^\circ\text{C}$ ) containing 1.1 g of ethanol. The trap content washed  $\text{H}_2\text{O}$  and dried  $\text{MgSO}_4$  to give 8.33 g a mixture of (GC (%)): 68%  $\text{C}_3\text{F}_7\text{OCH}_3$  MS (CI): 201 [50 ( $\text{M}+1$ ) $^+$ ], 181 [100 ( $\text{M}-\text{F}$ ) $^+$ ], (calculated yield 6.15 g, 70%); 2.5%  $\text{C}_2\text{F}_5\text{COOCH}_3$ , (calculated yield 0.2 g, 2.6%) and 28%  $\text{C}_2\text{F}_5\text{COOC}_2\text{H}_5$  (calculated yield 2.36 g, 28%).

### 3.5. Methyltrifluoromethyl ether (HFE 134a)

Carbonyldifluoride from a steel cylinder was bubbled through the agitated mixture of triethylamine trihydrogenfluoride (1.67 g, 10 mmol) and triethylamine (2.10 g, 21 mmol) in 2.71 g diglyme in a two-neck flask with a condenser at  $0^\circ\text{C}$  and end bubbler. The exothermic reaction was ended when an excess of the carbonyl fluoride began to

escape through the end bubbler. There was consumed 2.11 g (32 mmol) of  $\text{COF}_2$ . The reaction mixture was transferred to a stainless steel tube pressure reactor, 4.14 g (33 mmol) of dimethylsulfate was added, and the mixture was heated at 70 °C for 17 h. In trap (−78 °C) vented out 1.80 g  $\text{CH}_3\text{OCF}_3$  with purity (by GC) 84% (yield 49%), MS (CI): 101 [92 ( $\text{M} + 1$ )<sup>+</sup>], 81 [100 ( $\text{M} - 1$ )<sup>+</sup>];  $^1\text{H}$  and  $^{19}\text{F}$  NMR ( $\text{CH}_3\text{CN}$ ): −61.91 ( $\text{CF}_3$ , s), 3.75 ( $\text{CH}_3$ , s).

### 3.6. Benzylheptafluoropropyl ether

The mixture of pentafluoropropionyl fluoride (3.1 g, 19 mmol), triethylamine trihydrogenfluoride (1.03 g, 6 mmol), triethylamine (1.3 g, 13 mmol), benzylbromide (3.37 g, 20 mmol) and 0.1 g Adogen were heated in the ACE GLASS Inc. pressure tube at 40–45 °C for 22 h. Methanol (1.5 g) was added at 0 °C and the reaction mixture washed  $\text{H}_2\text{O}$  and dried to give 4.3 g of the product consisting of (GC (%)): 52%  $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_2\text{Ph}$   $^1\text{H}$  &  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ): −81.88 ( $\text{CF}_3$ , t), −129.77 ( $\text{CF}_2$ , t), −86.44 ( $\text{OCF}_2$ , m), 4.99 ( $\text{CH}_2$ , s), 7.2–7.4 ( $\text{C}_6\text{H}_5$ ); MS (CI): 276 [100 ( $\text{M}$ )<sup>+</sup>], 91 [100 ( $\text{M} - \text{C}_3\text{F}_7\text{O}$ )<sup>+</sup>], calculated yield 43%; 28%  $\text{PhCH}_2\text{Br}$ ; 4%  $\text{PhCH}_2\text{F}$ ; 11%  $\text{C}_2\text{F}_5\text{COOCH}_3$ ; 4%  $\text{C}_2\text{F}_5\text{COOCH}_2\text{Ph}$ ; 0.8%  $\text{C}_2\text{F}_5\text{CONEt}_2$  and 0.2%  $\text{C}_2\text{F}_5\text{COCH}=\text{CHNEt}_2$  MS (CI): 246 [100 ( $\text{M} + 1$ )<sup>+</sup>], 226 [60 ( $\text{M} - \text{F}$ )<sup>+</sup>], 198 [50 ( $\text{M} - \text{COF}$ )<sup>+</sup>], 126 [56 ( $\text{M} - \text{C}_2\text{F}_5$ )<sup>+</sup>].

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