POLYFLUOROALKYL DERIVATIVES OF METALLOIDS AND NONMETALS

R. E. Banks and R. N. Haszeldine

Department of Chemistry, Faculty of Technology, University of Manchester, England

I. Introduction

Fluorine was isolated by Moissan in 1886, but for many years investigation of its chemistry was restricted by the difficulties encountered in its preparation and use. During the 1930's, however, several important discoveries were made which changed the whole outlook, and gave an impetus to fluorine chemistry which has remained to the present day.

The first stimulus came in 1930 when Midgley introduced dichlorodifluoromethane as an inert, nontoxic refrigerant which had such outstanding advantages over other types of refrigerants that it rapidly became a major industrial chemical. A number of simple chlorofluoro-methanes and -ethanes are now manufactured and, in addition to their original use as refrigerants, they find wide application as aerosol propellants. Certain of these chlorofluoro-methanes and -ethanes can be converted into fluoroolefins, and in the late 1930's it was disclosed that chlorotrifluoroethylene and tetrafluoroethylene can be polymerized to give materials of remarkable chemical and thermal stability. At about the same time it was found that the direct action of fluorine on carbon in the presence of a mercury catalyst gives rise to a series of stable fluorocarbons, both acyclic (C_nF_{2n+n}) and cyclic (C_nF_{2n}); these are analogous to the familiar homologous series of hydrocarbons. The marked chemical and thermal stability of these fluorocarbons is related to the high carbon-fluorine bond dissociation energy, and to the steric shielding effect and high electronegativity of the fluorine atoms.

The Second World War brought with it a great demand for materials suitable for use as sealants, coolants, lubricants, and buffer gases in chemical plants manipulating such highly corrosive substances as uranium hexafluoride. This led to the commercial development of fluorocarbons, polytetrafluoroethylene, and polychlorotrifluoroethylene, and the production of elementary fluorine on an industrial scale. When the restrictions on these wartime developments were lifted, it was clear that fluorine chemistry was firmly established as a new branch of chemical science.

Commercial interest in fluorocarbons and their derivatives is still based upon their chemical and thermal stability, but during the last decade much academic work has centered around the investigation of fluorocarbons and fluorohydrocarbons containing the familiar functional groups of organic chemistry. The availability of these compounds, and especially the perfluoroalkyl iodides, e.g., CF_3I, has enabled polyfluoroalkyl* derivatives of many elements other than carbon to be synthesized. Study of such compounds has shown that their properties and reactions are often markedly different from those of their hydrocarbon analogs; new types of chemical reactions emerge and many strange structures and valence states become stabilized when fluorine, the most electronegative of the elements, is present.

This chapter deals with the chemistry and properties of the known polyfluoroalkyl derivatives of mercury, boron, silicon, nitrogen, phosphorus, arsenic, antimony, oxygen, sulfur, and selenium (*1*). The accent has been mainly on the preparative side so far, but it is clear that a great deal of interesting physical and physical-inorganic chemistry awaits development; such development is badly needed to provide a better understanding of the phenomena observed.

II. Mercury

The perfluoroalkyl mercurials, the first compounds to be prepared containing a polyfluoroalkyl group attached to a metalloid or metal atom, show properties, e.g., hydrolytic instability, typical of many other organometalloidal fluorine compounds. Their physical properties are listed in Table I.

A. Preparation

1. Perfluoroalkylmercuric Iodides

Trifluoroiodomethane, pentafluoroiodoethane, and heptafluoroiodopropane react readily with mercury under the influence of heat and/or ultraviolet light to yield stable, crystalline mercurials of the type $R_F \cdot HgI$, where R_F = perfluoroalkyl (e.g., CF_3, C_2F_5, C_3F_7) (*6*, *9*, *59*, *67*):

$$CF_3I + Hg \xrightarrow{\text{ultraviolet light, } 150^\circ} CF_3 \cdot HgI, \quad (80\%) \qquad (1)$$

$$C_2F_5I + Hg \xrightarrow{\text{ultraviolet light, } 120^\circ} C_2F_5 \cdot HgI, \quad (60\%) \qquad (2)$$

$$C_2F_5I + Hg \xrightarrow{240^\circ} C_2F_5 \cdot HgI, \quad (88\%) \qquad (3)$$

$$C_3F_7I + Hg \xrightarrow{220^\circ} C_3F_7 \cdot HgI \qquad (4)$$

* The term *polyfluoroalkyl* will be used to denote any alkyl group containing a high proportion of fluorine (e.g., CHF_2; $CF_3 \cdot CHF \cdot CF_2$; $CF_3 \cdot CFCl$). The term *perfluoroalkyl* refers specifically to a completely fluorinated alkyl group (e.g., CF_3, C_2F_5, C_3F_7).

TABLE I

PHYSICAL PROPERTIES OF POLYFLUOROALKYL DERIVATIVES OF MERCURY

Compound	m.p. (°C, sealed tube)	Compound	m.p. (°C, sealed tube)
$(CF_3)_2Hg$	163	$C_2F_5 \cdot HgI$	98[a]
$CF_3 \cdot HgCl$	76	$C_2F_5 \cdot HgOH$	220–225
$CF_3 \cdot HgBr$	83		
$CF_3 \cdot HgI$	112.5[a]	$(CF_3 \cdot CH_2)_2Hg$	40
$CF_3 \cdot HgOH$	130/10^{-5} mm[c]	$(CF_3 \cdot CHF)_2Hg$	78–79
$CF_3 \cdot HgNO_3$	100/10^{-5} mm[c]		
$(C_2F_5)_2Hg$	106–107	$(CF_3 \cdot CFCl)_2Hg$[b]	93–95
$C_2F_5 \cdot HgF$	99–100	$CF_3 \cdot CFCl \cdot HgF$	118
$C_2F_5 \cdot HgCl$	103–104		
$C_2F_5 \cdot HgBr$	78–79	$C_3F_7 \cdot HgI$	77.0–77.5[a]

[a] These melting points are affected appreciably, while remaining sharp, by traces of mercury iodides formed during purification or on storage. This renders the values quoted somewhat uncertain.

[b] Not pure.

[c] Sublimation temperature.

The reactions may be carried out in sealed Pyrex or silica tubes, and the crude materials, isolated by ether extraction, are purified by vacuum sublimation. Light of wavelength ~2200Å decomposes the mercurials, and when silica reaction vessels are used the lower ends should be shielded to prevent irradiation of the product collecting there.

2. *Bis(polyfluoroalkyl) Mercurials*

The standard method for the direct conversion of alkyl iodides into dimercurials by reaction with sodium amalgam leads to complete decomposition when applied to trifluoroiodomethane. Application of other standard methods to trifluoromethylmercuric iodide, e.g., reaction with alkaline sodium stannite, alkaline ferrous hydroxide, or sodium, also fails to yield the dimercurial $Hg(CF_3)_2$, and in the first two cases fluoroform is liberated. Reaction of trifluoromethylmercuric iodide with aqueous potassium iodide or with potassium cyanide—reagents often used to remove the elements of mercuric iodide from an alkyl mercuric iodide—also fails to yield the dimercurial; fluoroform is the only product.

The use of amalgams of silver, copper, or cadmium was ultimately developed for the synthesis of bis(perfluoroalkyl) mercurials from the per-

fluoroalkyl mercuric iodide, or directly from the parent perfluoroalkyl iodide (*60*). Satisfactory yields are obtained:

$$CF_3 \cdot HgI \xrightarrow{Cd/Hg,\ 120\text{-}130^\circ} Hg(CF_3)_2 \quad (80\text{-}90\%) \qquad (5)$$

$$CF_3I \xrightarrow{Cd/Hg,\ 25^\circ} Hg(CF_3)_2 \quad (40\%) \qquad (6)$$

$$C_2F_5I \xrightarrow{Cd/Hg,\ 30^\circ} Hg(C_2F_5)_2 \quad (60\%) \qquad (7)$$

A recent method for preparing polyfluoroalkyl mercurials consists of heating anhydrous mercuric fluoride with a fluoroolefin at 50–150° in a steel autoclave (*79b, 140, 141*):

$$HgF_2 + CF_2{:}CF_2 \longrightarrow Hg(CF_2 \cdot CF_3)_2 \quad (56\%) \qquad (8)$$

$$HgF_2 + CF_2{:}CHF \longrightarrow Hg(CHF \cdot CF_3)_2 \quad (66\%) \qquad (9)$$

$$HgF_2 + CF_2{:}CH_2 \longrightarrow Hg(CH_2 \cdot CF_3)_2 \quad (66\%) \qquad (10)$$

$$HgF_2 + CF_2{:}CFCl \begin{cases} \xrightarrow{AsF_3\ \text{solvent}} Hg(CFCl \cdot CF_3)_2 \quad (31\%) \\ \xrightarrow{\text{no solvent}} CF_3 \cdot CFCl \cdot HgF \quad (24\%) \end{cases} \qquad (11)$$

This method offers much promise, since fluoroolefins are relatively easy to prepare, and some are of commercial importance. Proof of the direction of addition to an unsymmetrical olefin, implied by the formulas above, rests on nuclear magnetic resonance spectra for H^1 and F^{19}; the direction is consistent with addition involving ionic intermediates, and chemical proof of structure has been obtained for the compound $CF_3 \cdot CFCl \cdot HgF$ (*79b*). The reaction of mercuric fluoride with tetrafluoroethylene in the absence of a solvent (AsF_3) can become explosive.

Bistrifluoromethylmercury can also be prepared (84% yield) by heating tristrifluoromethylphosphine [$(CF_3)_3P$; VI,A] with mercuric oxide (*84b*).

B. Properties and Reactions

1. Perfluoroalkylmercuric Iodides

Perfluoroalkylmercuric iodides are white crystalline solids which are soluble in common organic solvents such as ether, acetone, alcohol, and cyclohexane, and show a general resemblance to their hydrocarbon analogs. Trifluoromethyl- and pentafluoroethyl-mercuric iodide are soluble in water, and may be recrystallized from this solvent. Aqueous solutions decompose with deposition of mercurous and mercuric iodide; the gas evolved from aqueous trifluoromethylmercuric iodide is probably mainly fluoroform. Trifluoromethylmercuric hydroxide is not formed and the reaction is not, therefore, a simple hydrolysis. The specific conductiv-

ity of an 0.125 M solution of the mercurial in water at 25° is 5.5×10^{-5} ohm^{-1} cm^{-1}, and this value increases as the decomposition proceeds. When treated with a solution of potassium iodide, an aqueous solution of the mercurial turns yellow and becomes alkaline, and fluoroform is evolved; the complex K_2HgI_4 is formed:

$$CF_3 \cdot HgI + 3I^- + H_2O \rightarrow CHF_3 + OH^- + HgI_4^= \quad (12)$$

Heptafluoropropylmercuric iodide is substantially insoluble in water.

Trifluoromethylmercuric iodide is converted into the free base, trifluoromethylmercuric hydroxide, by the action of moist silver oxide. Aqueous solutions of the hydroxide are alkaline to phenolphthalein and react with acids to form salts. Trifluoromethylmercuric chloride, bromide, fluoride, and nitrate may thus be prepared in high yield (*59*):

$$CF_3 \cdot HgI \xrightarrow{\text{"AgOH"}} CF_3 \cdot HgOH \begin{cases} \xrightarrow{HCl\ aq.} CF_3 \cdot HgCl \\ \xrightarrow{HBr\ aq.} CF_3 \cdot HgBr \\ \xrightarrow{HF\ aq.} CF_3 \cdot HgF \\ \xrightarrow{HNO_3\ aq.} CF_3 \cdot HgNO_3 \end{cases} \quad (13)$$

Trifluoromethylmercuric nitrate can also be prepared by the action of silver nitrate on an aqueous solution of the iodide:

$$CF_3 \cdot HgI + AgNO_3 \rightarrow CF_3 \cdot HgNO_3 + AgI \quad (14)$$

Similar conversions have been carried out starting from pentafluoroethylmercuric iodide (*9*).

Trifluoromethylmercuric hydroxide is a weaker electrolyte than methylmercuric hydroxide (Table II), but a stronger electrolyte than phenyl-

TABLE II
CONDUCTIVITY DATA

Compound	Concentration	Specific conductivity (ohm^{-1} cm^{-1} $\times 10^5$)
$CF_3 \cdot HgOH$	$M/16$	1.1
$CH_3 \cdot HgOH$	$M/16$	13.4
$CF_3 \cdot HgNO_3$	$M/16$	900
$CH_3 \cdot HgNO_3$	$M/16$	660
$CF_3 \cdot HgNO_3$	$M/1024$	30
$C_6H_5 \cdot HgNO_3$	$M/1024$	10
KCl	$M/100$	140

mercuric hydroxide. The conductivity of trifluoromethylmercuric nitrate, on the other hand, approaches that of a neutral strong electrolyte, and is

greater than that of either methyl- or phenyl-mercuric nitrate, since hydrolysis of the trifluoromethylmercuric nitrate occurs yielding a strongly acid aqueous solution.

Trifluoromethyl- and pentafluoroethyl-mercuric iodide react almost quantitatively with iodine at 120° to give the corresponding perfluoroalkyl iodide and mercuric iodide, e.g.,

$$CF_3{\cdot}HgI + \text{excess } I_2 \xrightarrow{120^\circ} CF_3I(92\%) + HgI_2 \qquad (15)$$

2. Bis(polyfluoroalkyl) Mercurials

Bistrifluoromethylmercury (*60*) is a white crystalline solid, density 4.22, with a characteristic pungent smell. It can be purified by extraction with organic solvents, followed by sublimation at atmospheric pressure. A preliminary crystallographic investigation (*60*) indicates that the unit cell is cubic [a = 8.11 Å; 4 molecules $Hg(CF_3)_2$ per unit cell] with mercury atoms located in the 000, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, and $0\frac{1}{2}\frac{1}{2}$ positions. The molecule is linear. Bistrifluoromethylmercury decomposes slowly above 160°, and is thus less stable than dimethylmercury, which is only slightly decomposed at 300°. The photochemical and pyrolytic decomposition affords trifluoromethyl radicals which will initiate the polymerization of olefins such as ethylene, tetrafluoroethylene, and other unsaturated compounds. Bispentafluoroethylmercury is also decomposed by heat and light of wavelength <2500 Å. Thus, irradiation of the dimercurial in silica apparatus yields mercury and perfluoro-*n*-butane (*9*):

$$Hg(C_2F_5)_2 \xrightarrow{\text{ultraviolet light}} Hg(92\%) + 2C_2F_5\cdot \rightarrow C_4F_{10}\ (80\%) \qquad (16)$$

A 40% yield of perfluorobutane is obtained by a purely thermal reaction at 250°.

Halogens react with bistrifluoromethyl- and bispentafluoroethylmercury, either thermally or photochemically, converting them into mercuric halide and the corresponding fluoroalkyl halide:

$$Hg(CF_3)_2 \begin{cases} \xrightarrow{\text{excess } Cl_2,\ 100\text{-}150^\circ} 2CF_3Cl\ (95\%) + HgCl_2 \\ \xrightarrow{\text{excess } Br_2,\ 100\text{-}150^\circ} 2CF_3Br\ (92\%) + HgBr_2 \\ \xrightarrow{\text{excess } I_2,\ 100\text{-}150^\circ} 2CF_3I\ (97\%) + HgI_2 \end{cases} \qquad (17)$$

$$Hg(C_2F_5)_2 \xrightarrow{\text{excess } Cl_2,\ \text{ultraviolet light}} 2C_2F_5Cl\ (33\%) + HgCl_2 \qquad (18)$$

Bistrifluoromethylmercury can be converted into trifluoromethylmercuric iodide or trifluoromethylmercuric chloride by reaction with mercuric iodide or chloride at 170°:

$$Hg(CF_3)_2 + HgI_2 \rightarrow 2CF_3{\cdot}HgI\ (75\%) \quad (19)$$

$$Hg(CF_3)_2 + HgCl_2 \rightarrow 2CF_3{\cdot}HgCl\ (62\%) \quad (20)$$

The reaction with mercuric iodide requires more vigorous conditions than with normal aliphatic and aromatic dimercurials. Use of acetone as a solvent enables lower reaction temperatures (140°) to be employed, but yields are lower (~50%), and fluoroform becomes a product.

The perfluoroalkyl group R_F is readily cleaved from the mercurial in aqueous media, to give the fluorohydrocarbon R_FH. Thus, fluoroform is evolved after treatment of bistrifluoromethylmercury with zinc or magnesium amalgam, or with magnesium metal and magnesium iodide, followed by addition of water. Aqueous sodium stannite solution reduces bis(perfluoroalkyl) mercurials at room temperature, e.g.,

$$Hg(CF_2{\cdot}CF_3)_2 \rightarrow Hg + 2CF_3{\cdot}CHF_2 \quad (21)$$

The perfluoroalkyl group shows pseudohalogen character in such hydrolyses in alkaline solution:

$$Hg(CF_3)_2 + 2H_2O \xrightarrow{OH^-} 2CHF_3 + Hg(OH)_2 \quad (22)$$

although the perfluoroalkyl zinc or magnesium compounds may well be intermediates in the reactions involving zinc or magnesium amalgams:

$$Hg(CF_3)_2 \xrightarrow{Mg/Hg} Mg(CF_3)_2 \xrightarrow{2H_2O} 2CHF_3 + Mg(OH)_2 \quad (23)$$

Alkyl mercurials are quite stable hydrolytically under similar conditions.

Attempts to replace the mercury in bistrifluoromethylmercury by direct reaction with metals such as zinc and magnesium did not lead to the isolation of zinc or magnesium fluoroalkyls as such (*60*). Krespan (*140*), however, claims that bis(polyfluoroalkyl) mercurials of the type $Hg(CXY{\cdot}CF_3)_2$, where X or Y is halogen or hydrogen, but only one of X or Y is fluorine, react with magnesium amalgam to yield compounds $Mg(CXY{\cdot}CF_3)_2$. The same author also reports the reaction of bispentafluoroethylmercury with sulfur to yield bispentafluoroethyl disulfide:

$$Hg(CF_2{\cdot}CF_3)_2 + 3S \xrightarrow{250^\circ} CF_3{\cdot}CF_2{\cdot}S_2{\cdot}CF_2{\cdot}CF_3 + HgS \quad (24)$$

C. Perfluoroalkylhalogenomercurates

Bistrifluoromethylmercury is moderately soluble in water [437 g/liter (*144*)], in sharp contrast to dimethylmercury, a covalent liquid, b.p. 96°, and insoluble in water. Aqueous solutions of bistrifluoromethylmercury have a small, though definite, conductivity [$\kappa = 12 \times 10^{-6}$ ohm^{-1} cm^{-1} ($M/4$ solution)], which is of the same order of magnitude as that of mercuric cyanide. Hydrolysis of the mercurial does not occur, since fluoroform

is not evolved, and complex ion formation of the type $Hg^{++}[Hg(CF_3)_4]^=$ was tentatively suggested (*60*). More recent work (*67*) has shown that the addition of halide ion increases the conductivity of the aqueous mercurial, though by an amount less than would arise from the halide alone. Perfluoroalkylhalogenomercurate (II) anions of the type $[HgR_FX_3]^=$ and $[Hg(R_F)_2X_2]^=$ are thus indicated, and this possibility is supported by the fact that heptafluoro-*n*-propylmercuric iodide, which is only slightly soluble in water, dissolves readily in the presence of halide ion.

When an aqueous solution of bistrifluoromethylmercury is titrated with a potassium halide solution, and the conductivity measured as a function of the ratio $KX:Hg(CF_3)_2$, a change of slope is observed in the conductivity curve at values for this ratio of 1 and 2, thus revealing the existence of complexes $KHg(CF_3)_2X$ and $K_2Hg(CF_3)_2X_2$. Similar results are obtained for the conductometric titrations of trifluoromethylmercuric iodide and heptafluoro-*n*-propylmercuric iodide with potassium halide in aqueous, or aqueous methanolic solutions, with breaks in the curves occurring at halide:mercurial ratios of 1:1 and 2:1. This indicates the formation in aqueous solution of the ionic species $[Hg(CF_3)IX]^-$, $[Hg(CF_3)IX_2]^=$, $[Hg(C_3F_7)IX]^-$, and $[Hg(C_3F_7)IX_2]^=$.

In the titration of trifluoromethylmercuric bromide with potassium halides there are similar breaks at ratios of 1:1 and 2:1 for potassium iodide, and 2:1 for potassium bromide, but none with potassium chloride. The formation of $[Hg(CF_3)BrI]^-$, $[Hg(CF_3)BrI_2]^=$, and $[Hg(CF_3)Br_3]^=$ is deduced; it is probable that $[Hg(CF_3)Br_2]^-$, $[Hg(CF_3)BrCl]^-$, and $[Hg(CF_3)BrCl_2]^=$ are unstable.

The perfluoroalkylhalogenomercurate (II) anions are related to the tetrahalogenomercurate (II) ions, for which the order of stability is iodo > bromo > chloro; the ion $(HgF_4)^=$ is known, but is hydrolyzed in aqueous solution. Further evidence for the existence of the above anions is provided by a study of the X-ray diffraction patterns of the residue obtained by evaporation of an aqueous solution containing potassium halide and bistrifluoromethylmercury (or potassium halide and heptafluoro-*n*-propylmercuric iodide) in a 1:1 or 2:1 molar ratio. Lines characteristic of the reactants are absent. However, with a halide:mercurial ratio of 3:1, lines are observed which are characteristic of the halide, but not of the mercurial.

The interpretation of the results of the conductometric titrations and X-ray analyses is supported by the preparation and analysis of insoluble compounds containing the perfluoroalkylhalogenomercurate ions $[Hg(CF_3)I_3]^=$, $[Hg(C_3F_7)I_3]^=$, and $[Hg(CF_3)_2I_2]^=$ by reaction of aqueous solutions containing these ions with salts of ethylenediamine–transition metal complexes. These compounds are shown in Table III. All the com-

pounds in Table III resemble the corresponding compounds containing the $HgX_4^=$ anion.

TABLE III

SALTS OF PERFLUOROALKYLHALOGENOMERCURATES

Compound[a]	Color	Compound	Color
$Cu(en)_2HgCF_3I_3$	dark purple	$Ni(en)_3Hg(CF_3)_2I_2$	violet
$Cd(en)_2HgCF_3I_3$	white	$Zn(en)_3Hg(CF_3)_2I_2$	white
$Ni(en)_3HgCF_3I_3$	violet	$Zn(en)_3HgC_3F_7I_3$	white

[a] en = ethylenediamine.

The appearance of a white precipitate, which gave fluoroform on hydrolysis with aqueous alkali, when triphenylarsonium chloride is added to an aqueous solution of bistrifluoromethylmercury, suggests that other salts could be isolated by suitable choice of cation.

The Hg—C_3F_7 bond is hydrolyzed less readily than the Hg—CF_3 bond. Thus, whereas compounds containing the trifluoromethyl group are hydrolyzed by hot water to give fluoroform quantitatively, compounds containing the heptafluoro-*n*-propyl group require hot ethanolic potassium hydroxide for complete liberation of heptafluoropropane.

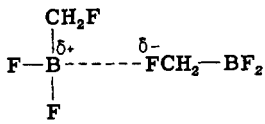
The above anionic complexes of mercury containing organic radicals in the anion were the first to be reported (Section VIII,A,*2*,*b*), although compounds of the type $LiMPh_3$ had been characterized for the other elements of Group IIB (*202*). Their relative stabilities are in the order $LiZnPh_3 > LiCdPh_3 > LiHgPh_3$ (not formed). This order of stability is the reverse of that of the tetrahalogenometallate ions. Only zinc alkyls react with alkyls of the alkali or the alkaline-earth metals to form compounds containing tetraalkylmetallate ions (*78*, *79a*, *124*) and, although perfluoroalkyl derivatives of zinc and cadmium have been described (*97*, *160*), no derived complexes, other than solvates of the zinc compounds, are known. The existence of compounds such as $K_2[Hg(CF_3)_2I_2]$ is consistent with the formation of complex ions containing mercury(II) and halide or pseudohalide ions, and again exemplifies the pseudohalogen character of the trifluoromethyl group in certain of its reactions.

III. Boron

The literature contains no reference to the successful preparation in the free state of a perfluoroalkyl derivative of boron of the type $(R_F)_3B$, since compounds containing the R_FB group readily lose boron trifluoride (*22*, *144*, *145*).

Claims have been made concerning the formation of R_F—B bonds (R_F = CF_3, C_3F_7) in reactions between bis(perfluoroalkyl) mercurials and

boron halides or alkylboron halides, and between heptafluoro-*n*-propyllithium and tri-*B*-chloro-tri-*N*-phenylborazole, but these are based only on indirect evidence. For example, aqueous alkaline hydrolysis of a solid residue obtained in the last reaction yielded heptafluoro-*n*-propane, C_3F_7H (*145*). The experiments with the *B*-halogenoborazole were carried out to test the hypothesis that the decomposition of a perfluoroalkyl boron compound to boron trifluoride or its derivatives could be substantially reduced by eliminating or weakening the acceptor properties of the boron atom. This follows from observations on the physical and chemical properties of fluoromethylboron difluoride, $CH_2F{\cdot}BF_2$, which is prepared in almost quantitative yield by the reaction of diazomethane with boron trifluoride in the gas phase at −40° (*80*). This fluoroalkylboron compound, m.p. −47°, b.p. (extrapolated) 7°, has a value of 30.5 for Trouton's constant and an observed molecular weight 3.4% higher than that calculated for the monomer. It has been suggested that association occurs in both the vapor and liquid phases, and that spectral data indicate association through the fluorine atom of the alkyl group (*80*):



This suggestion is supported by the lack of association in methylboron difluoride and trimethylboron. Fluoromethylboron difluoride readily loses boron trifluoride.

Stable compounds containing the trifluoromethylfluoroborate anion, $[CF_3{\cdot}BF_3]^-$, in which the acceptor properties of the boron atom are fully satisfied, have been briefly described recently. They were prepared as follows (*38*):

$$(CH_3)_3Sn{\cdot}Sn(CH_3)_3 + CF_3I \xrightarrow[\text{ultraviolet light}]{\text{heat or}} CF_3{\cdot}Sn(CH_3)_3 + (CH_3)_3SnI \quad (25)$$

$$CF_3{\cdot}Sn(CH_3)_3 + BF_3 \xrightarrow{CCl_4\ \text{soln.}} (CH_3)_3Sn^+[CF_3{\cdot}BF_3]^- \quad (26)$$

$$(CH_3)_3Sn^+[CF_3{\cdot}BF_3]^- + KF \xrightarrow{\text{aq. soln.}} K^+[CF_3{\cdot}BF_3]^- + (CH_3)_3SnF \quad (27)$$

The perfluorovinylboron compounds $CF_2{:}CF{\cdot}BF_2$ (b.p. −14°), $CF_2{:}CF{\cdot}BCl_2$ (b.p. 48°), $(CF_2{:}CF)_2BCl$ (b.p. 100.5°), and $(CF_2{:}CF)_3B$ (b.p. 104.9°) have been prepared as follows (*133a,b*):

$$2CF_2{:}CF{\cdot}MgBr + (CH_3)_2SnCl_2 \longrightarrow (CF_2{:}CF)_2Sn(CH_3)_2 + 2MgBrCl \quad (28)$$

$$\begin{array}{l} (CF_2{:}CF)_2Sn(CH_3)_2 \xrightarrow{BCl_3} (CF_2{:}CF)_2BCl \quad + \quad CF_2{:}CF{\cdot}BCl_2 \\ \qquad\qquad\qquad\qquad \downarrow (CF_2{:}CF)_2Sn(CH_3)_2 \qquad \downarrow SbF_3 \\ \qquad\qquad\qquad\qquad (CF_2{:}CF)_3B \qquad\qquad CF_2{:}CF{\cdot}BF_2 \end{array} \quad (29)$$

All these compounds are unstable over extended periods of time, even when kept at −78°, and decompose to give boron trifluoride. They are readily hydrolyzed to the olefin $CF_2{:}CHF$ when heated with water.

IV. Silicon

Interest in polyfluoroalkylsilicon chemistry has been stimulated by the need for polymeric materials suitable for use at the extremes of temperature associated with high-speed aircraft. The conventional dimethyl silicone rubbers may be used at temperatures up to 260°, but they are swollen or dissolved by many hydrocarbon fuels and lubricants. In order to overcome this difficulty, and also in an effort to obtain materials with enhanced thermal stability, researches were initiated to develop silicones containing pendant polyfluoroalkyl groups. These have already met with some success, and a methyl-3,3,3-trifluoropropyl silicone rubber

$$[(CF_3{\cdot}CH_2{\cdot}CH_2)(CH_3)Si{\cdot}O{\cdot}]_n$$

known as Silastic LS-53 has been developed on a commercial scale by the Dow Corning Corporation.

A. Preparation

Polyfluoroalkyl silicon compounds can be prepared by four general methods.

(*a*) Reaction of a silicon halide with a lithium polyfluoroalkyl or with a polyfluoroalkyl Grignard reagent (*98, 150, 151, 158, 170, 171*), e.g.,

$$n\text{-}C_3F_7Li + (C_2H_5)_2SiCl_2 \longrightarrow \begin{matrix} n\text{-}C_3F_7{\cdot}Si(C_2H_5)_2Cl \\ + \\ (n\text{-}C_3F_7)_2Si(C_2H_5)_2 \end{matrix} \quad (30)$$

$$CF_3{\cdot}MgI + SiCl_4 \longrightarrow CF_3{\cdot}SiCl_3 + (CF_3)_2SiCl_2 \quad (31)$$

$$CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}MgCl + Si(OCH_3)_4 \longrightarrow CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}Si(OCH_3)_3 \quad (32)$$

(*b*) Reaction of a polyfluoroalkyl chloride, bromide, or iodide with elemental silicon in the presence of a catalyst, usually copper (*166, 185*), e.g.,

$$CF_3Br + Si/Cu \xrightarrow{400°} CF_3{\cdot}SiF_3 \quad (33)$$

$$C_2F_5Cl + Si/Cu \xrightarrow{400\text{-}500°} (C_2F_5)_2SiCl_2 \quad (34)$$

(*c*) Reaction of a compound containing an Si—H bond with an unsaturated fluoro compound in the presence of ultraviolet light, a peroxide, or a noble-metal catalyst (*75, 76, 77, 104, 109, 111, 115, 152, 169, 172, 191, 199*), e.g.,

$$CF_2{:}CF_2 + SiHCl_3 \xrightarrow{\text{ultraviolet light}} CHF_2{\cdot}CF_2{\cdot}SiCl_3 \quad (35)$$

$$CF_2{:}CFCl + SiHCl_3 \xrightarrow{\text{ultraviolet light}} CHFCl{\cdot}CF_2{\cdot}SiCl_3 \quad (36)$$

$$CF_2{:}CFCl + SiHCl_3 \xrightarrow{Pt/C,\ 160^\circ} CHF_2{\cdot}CFCl{\cdot}SiCl_3 \quad (37)$$

$$CF_2{:}CF_2 + CH_3{\cdot}SiHCl_2 \xrightarrow{\text{ultraviolet light}} CHF_2{\cdot}CF_2{\cdot}Si(CH_3)Cl_2 \quad (38)$$

$$CF_3{\cdot}CH{:}CH_2 + SiH_4 \xrightarrow{\text{ultraviolet light}} CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}SiH_3 + (CF_3{\cdot}CH_2{\cdot}CH_2)_2SiH_2 + (CF_3{\cdot}CH_2{\cdot}CH_2)_3SiH \quad (39)$$

It should be noted that the reaction of the compound $SiHCl_3$ with chlorotrifluoroethylene in the presence of a noble metal gives the compound $CHF_2{\cdot}CFCl{\cdot}SiCl_3$, i.e., the direction of addition of the chlorosilane to the double bond of the olefin is the reverse of that found when the reaction is catalyzed by ultraviolet light. This suggests that when a noble metal is present the reaction probably involves the following ionic intermediates:

$$\overset{\delta+}{CF_2}{:}\overset{\delta-}{CFCl} \qquad \overset{\delta-}{H}\overset{\delta+}{SiCl_3}$$

(*d*) Free-radical reaction of a polyfluoroalkyl bromide or iodide with an alkenyl silicon compound (*77*, *190*), e.g.,

$$CF_3I + CH_2{:}CH{\cdot}Si(CH_3)_3 \xrightarrow{\text{ultraviolet light}} CF_3{\cdot}CH_2{\cdot}CHI{\cdot}Si(CH_3)_3 \quad (40)$$

Neither method (a) nor (b) is a satisfactory route to perfluoroalkyl derivatives of silicon. The formation and manipulation of lithium perfluoroalkyls and perfluoroalkyl Grignard reagents is not easy, and can be accompanied by numerous by-products (*93*, *96*, *144*), so that these reagents have not been widely used for the formation of R_F—Si bonds. The usefulness of the Rochow "direct synthesis" (*178*) in the fluorocarbon field [method (b)] is very doubtful, and there is conflicting evidence in the literature. The first reported attempt (*127*) to prepare a perfluoroalkyl silicon compound by the interaction of a perfluoroalkyl halide (in this case CF_3Cl, C_2F_5Cl, and cyclo-C_4F_7Cl) and a silicon-copper alloy at 500–1000° resulted in the formation of only silicon tetrahalides and organic breakdown products; but claims have subsequently appeared in the patent literature (*166*, *185*) that such preparations have been successful. It is said, for example, that the reaction of bromotrifluoromethane with a silicon-copper alloy at 400° can be made to yield $CF_3{\cdot}SiF_3$ and $CF_3{\cdot}SiBrF_2$.

From the known properties of polyfluoroalkyl silicon compounds it seems very unlikely that compounds such as $(C_2F_5)_2SiCl_2$ and $CF_3{\cdot}SiBrF_2$ could be prepared in this way. The compound $CF_3{\cdot}SiF_3$ can probably

TABLE IV

PHYSICAL PROPERTIES OF POLYFLUOROALKYL DERIVATIVES OF SILICON

Compound	m.p. (°C)	b.p. (°C/mm Hg)	n_D^t (t °C)	d_4^t (t °C)
$CF_3{\cdot}SiF_3$	—	−42	—	—
$CF_3{\cdot}SiCl_3$	—	35[a]	—	—
$(CF_3)_2SiCl_2$	—	25[a]	—	—
$CHF_2{\cdot}CH_2{\cdot}SiCl_3$	—	104–105.5	1.4050 (20)	1.43 (25)
$CH_2F{\cdot}CF_2{\cdot}SiCl_3$	—	96.4–96.8	—	—
$CHF_2{\cdot}CF_2{\cdot}SiCl_3$	—	84.5–85	1.367 (18)	—
$CF_2Cl{\cdot}CF_2{\cdot}SiCl_3$	—	102	—	—
$CFCl_2{\cdot}CF_2{\cdot}SiCl_3$	—	138	—	—
$CHFCl{\cdot}CF_2{\cdot}SiCl_3$	—	120–121	—	—
$CHF_2{\cdot}CH_2{\cdot}Si(CH_3)Cl_2$	—	113–113.2/743.5	1.3991 (20)	1.2790 (20)
$CHF_2{\cdot}CF_2{\cdot}Si(CH_3)Cl_2$	—	95.2/753	1.3689 (20)	1.3879 (20)
$CHFCl{\cdot}CF_2{\cdot}Si(CH_3)Cl_2$	—	124.5/734	1.4000 (20)	1.4211 (20)
$CHF_2{\cdot}CF_2{\cdot}Si(C_2H_5)Cl_2$	—	119.7/748	1.3819 (20)	1.3527 (20)
$CHF_2{\cdot}CFCl{\cdot}Si(C_2H_5)Cl_2$	—	154/754	1.4120 (20)	1.4170 (20)
$CHF_2{\cdot}CF_2{\cdot}Si(CH_3)_2H$	—	62.3	—	—
$CHF_2{\cdot}CF_2{\cdot}Si(OCH_3)_3$	—	98/190	—	—
$H{\cdot}[CF_2{\cdot}CF_2]_2{\cdot}SiCl_3$	—	90/195	—	—
$H{\cdot}[CF_2{\cdot}CF_2]_2{\cdot}Si(CH_3)Cl_2$	—	140–144	—	—
$(CHF_2{\cdot}CF_2)_2Si(CH_3)_2$	—	120	—	—
$H{\cdot}[CF_2{\cdot}CF_2]_3SiCl_3$	—	128/205	—	—
$C_3F_7{\cdot}Si(C_2H_5)Cl_2$	—	83.5/92	1.3871 (20)	1.6577
$C_3F_7{\cdot}Si(C_2H_5)_2Cl$	—	119/743	1.3538 (20)	—
$C_3F_7{\cdot}Si(CH_3)(OC_2H_5)Cl$	—	49–54/18	1.3329 (20)	—
$C_3F_7{\cdot}Si(CH_3)_2$	—	88	1.3222 (20)	—
$C_3F_7{\cdot}Si(CH_3)(C_2H_5)(CH{:}CH_2)$	—	82–83/2	1.3568 (20)	1.27 (20)
$(C_3F_7)_2Si(CH_3)Cl$	—	64.5–65/158	1.3168 (20)	—
$(C_3F_7)_2Si(OC_2H_5)Cl$	—	49–54/18	1.3329 (20)	—

$(C_3F_7)_2Si(CH_3)_2$	—	133.5	1.3110 (20)	1.57 (20)
$(C_3F_7)_2Si(CH_3)(C_2H_5)$	—	61/4	1.3344 (20)	1.55 (20)
$(C_3F_7)_2Si(C_2H_5)_2$	—	148	—	—
$(C_3F_7)_3Si{\cdot}CH_3$	—	130–3	1.3078 (20)	1.65 (20)
$CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}SiHCl_2$	—	90–91	—	—
$CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}SiCl_3$	—	113	—	—
$CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}Si(CH_3)Cl_2$	—	125	—	—
$CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}Si(CH_3)_3$	—	94.3–95.1/750	1.3576 (20)	0.896 (20)
$CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}Si(C_2H_5)_3$	—	166.1–167.8/753	1.3962 (20)	0.961 (20)
$CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}Si(CH_3)(OCH_3)_2$	—	96.5–96.8/251	1.3576 (20)	1.0954 (20)
$CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}Si(OCH_3)_3$	—	144/760	1.3547 (20)	1.137 (20)
$(CF_3{\cdot}CH_2{\cdot}CH_2)_2SiCl_2$	—	162–163	—	—
$(CF_3{\cdot}CH_2{\cdot}CH_2)_2Si(OCH_3)_2$	—	100.5/57	1.3531 (20)	1.256 (20)
$CF_3{\cdot}CH_2{\cdot}CHI{\cdot}SiCl_3$	—	79/25	—	—
$CF_3{\cdot}CH_2{\cdot}CHI{\cdot}Si(CH_3)_3$	—	72/20	—	—
$CF_3{\cdot}CH(CH_3){\cdot}CH_2{\cdot}Si(CH_3)Cl_2$	—	139	—	—
$CF_2Br{\cdot}CH_2{\cdot}CHBr{\cdot}Si(CH_3)_3$	—	95/25	—	—
$CF_2Br{\cdot}CH{:}CH{\cdot}Si(CH_3)_3$	—	66–68/52	—	—
$CF_3{\cdot}C(:CCl_2){\cdot}Si(CH_3)_3$	—	157/756	1.4322 (20)	1.243 (20)
$CF_3{\cdot}C(:CCl_2){\cdot}Si(C_2H_5)_3$	—	119/28	1.4532 (22)	1.193 (20)
$CF_3{\cdot}C(:CCl_2){\cdot}SiCl_3$	—	77.5–78.5/35	—	—
$CF_3{\cdot}C(:CCl_2){\cdot}Si(CH_3)Cl_2$	—	76–76.5/32	—	—
$CF_3{\cdot}CCl(CHCl_2){\cdot}SiCl_3$	—	78–78.5/3.8	—	—
$CF_3{\cdot}CF_2{\cdot}CHF{\cdot}CH_2{\cdot}SiCl_3$	—	127–128.8/758	—	—
$CF_3{\cdot}CF_2{\cdot}CHF{\cdot}CH_2{\cdot}Si(CH_3)Cl_2$	—	128–129.1/746	—	—
$CF_3{\cdot}CF_2{\cdot}CHF{\cdot}CH_2{\cdot}Si(CH_3)_3$	—	109.8–111.5/747	1.3441 (20)	1.133 (20)
$CF_3{\cdot}CF_2{\cdot}CHF{\cdot}CH_2{\cdot}Si(CH_3)(C_2H_5)_2$	—	154–155/747	1.3687 (20)	1.115 (20)
$CF_3{\cdot}CF_2{\cdot}CHF{\cdot}CH_2{\cdot}Si(C_2H_5)_3$	—	173.1/753	1.3800 (20)	1.110 (20)
$CF_2Cl{\cdot}CFCl{\cdot}CH_2{\cdot}CHI{\cdot}SiCl_3$	—	124/~1	—	—
$CF_2Cl{\cdot}CFCl{\cdot}CH{:}CH{\cdot}SiCl_3$	—	79[a]	—	—
$CF_2Cl{\cdot}CFCl{\cdot}CH_2{\cdot}CHI{\cdot}Si(CH_3)Cl_2$	—	108/25	—	—

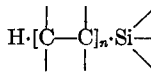
TABLE IV (*Continued*)

Compound	m.p. (°C)	b.p. (°C/mm Hg)	n_D^t (t °C)	d_4^t (t °C)
$CF_2Cl{\cdot}CFCl{\cdot}CH_2{\cdot}CHI{\cdot}Si(CH_3)_3$	—	99–100/9	—	—
$CF_2Cl{\cdot}CFCl{\cdot}CH{:}CH{\cdot}Si(CH_3)_3$	—	57–59/15	—	—
$CF_2{:}CF{\cdot}CH{:}CH{\cdot}Si(CH_3)_3$	—	25/25	—	—
$[CF_2Cl{\cdot}CFCl{\cdot}CH_2{\cdot}CHI{\cdot}SiO_{1.5}]_n$	48	—	—	—
$C_3F_7{\cdot}CH_2{\cdot}CH_2{\cdot}Si(CH_3)Cl_2$	—	147/760	—	—
$C_3F_7{\cdot}CH_2{\cdot}CH_2{\cdot}Si(CH_3)(OC_2H_5)_2$	—	92/42	1.3502 (20)	—
$C_3F_7{\cdot}CH_2{\cdot}CH_2{\cdot}Si(OC_2H_5)_3$	—	92.5–93/25	1.211 (20)	—
$(C_3F_7{\cdot}CH_2{\cdot}CH_2)_2Si(OH)_2$	64.5–65	—	—	—
$(C_3F_7{\cdot}CH_2{\cdot}CH_2)_2Si(OC_2H_5)_2$	—	117.5–118/25	—	—
$(C_3F_7{\cdot}CH_2{\cdot}CH_2)_3SiOH$	—	151–153	1.3378 (20)	—
$(C_3F_7{\cdot}CH_2{\cdot}CH_2)_3SiCl$	34–35	133–134/15	—	—
$(C_3F_7{\cdot}CH_2{\cdot}CH_2)_4Si$	—	71–72/25	—	—
$[(C_3F_7{\cdot}CH_2{\cdot}CH_2)_3Si]_2O$	66.5–67.0	—	—	—

[a] Calculated from vapor pressure measurements.

be obtained in low yield by this general route, since trifluoroiodomethane reacts with a silicon-copper alloy at 450–500° with short contact time to give, after rapid quenching, a low yield (5–8%) of trifluoromethylsilicon trifluoride (*92*, *112*). The carbon-iodine bond in trifluoroiodomethane breaks homolytically far more readily than the carbon-bromine bond in bromotrifluoromethane, but it should be noted that even under the much milder reaction conditions thus possible, compounds containing Si—I groups are not formed, and the trend is toward the formation of silicon tetrafluoride (the main product) and its trifluoromethyl derivatives. Compounds such as $CF_3{\cdot}SiF_3$ decompose rapidly at the temperatures needed for their formation by this route.

Method (*c*) is the best method for the preparation of partially fluorinated alkylsilanes, and is an extension of a reaction widely used for the preparation of alkylsilicon compounds. The reaction of a silane containing one Si—H group with a fluoroolefin under the influence of ultraviolet light, or in the presence of organic peroxides, yields products of the type



where the value of n depends on the conditions of the reaction, the ratio silane:fluoroolefin, and the olefin used. The value of n can be controlled particularly easily in the reaction of $SiHCl_3$ with C_2F_4; thus a trichlorosilane:olefin ratio of 4:1 gives the compound $H{\cdot}[CF_2{\cdot}CF_2]{\cdot}SiCl_3$ (i.e., $n = 1$) in ~60% yield, whereas with a ratio of 1.2:1 the yield of compound with $n = 1$ falls to ~35% with a ~65% yield of products where $n > 1$. When the silane contains two hydrogen atoms (e.g., R_2SiH_2), the products of the reaction with tetrafluoroethylene, for example, contain substances having the general formula $H{\cdot}[CF_2{\cdot}CF_2]_x{\cdot}SiR_2{\cdot}[CF_2{\cdot}CF_2]_y{\cdot}H$ (*75*):

$$R_2SiH_2 + x\,CF_2{:}CF_2 \xrightarrow{\text{ultraviolet light}} R_2SiH{\cdot}[CF_2{\cdot}CF_2]_x{\cdot}H \qquad (41)$$

$$R_2SiH{\cdot}[CF_2{\cdot}CF_2]_x{\cdot}H + y\,CF_2{\cdot}CF_2 \xrightarrow{\text{ultraviolet light}} R_2Si\begin{matrix}[CF_2{\cdot}CF_2]_x{\cdot}H \\ [CF_2{\cdot}CF_2]_y{\cdot}H\end{matrix} \qquad (42)$$

B. Properties and Reactions

The physical properties of polyfluoroalkylsilicon compounds are listed in Table IV.

The Si—H bond in a polyfluoroalkylsilane is not attacked by water, but dilute aqueous alkali readily cleaves it, with the formation of hydrogen. If the polyfluoroalkyl group contains fluorine on a carbon atom close to

silicon, the polyfluoroalkyl group is liberated quantitatively as the fluorohydrocarbon or as the olefin, e.g.,

$$CHF_2 \cdot CF_2 \cdot SiCl_3 \xrightarrow{NaOH\ aq.} CHF_2 \cdot CHF_2 \quad (43)$$

$$CHF_2 \cdot CH_2 \cdot SiCl_3 \xrightarrow{NaOH\ aq.} CHF{:}CH_2 \quad (44)$$

The pseudohalogen character of a polyfluoroalkyl group is again apparent.

Aqueous hydrolysis of a polyfluoroalkylsilicon di- or tri-halide yields the polyfluoroalkyl-silicone or -polysiloxane, e.g.,

$$(CHF_2 \cdot CF_2)_2SiCl_2 \xrightarrow{H_2O} [(CHF_2 \cdot CF_2)_2Si \cdot O]_n \quad (45)$$

$$CHF_2 \cdot CF_2 \cdot SiCl_3 \xrightarrow{H_2O} [CHF_2 \cdot CF_2 \cdot Si \cdot O_{1.5}]_n \quad (46)$$

A whole range of such polymers in which the fluorine is situated α, β, or γ to silicon in the $\overset{\gamma}{C}—\overset{\beta}{C}—\overset{\alpha}{C}—Si$ system has been prepared in this way.

The thermal and hydrolytic stabilities of polyfluoroalkyl-silicones and -polysiloxanes depend very markedly on the position of the fluorine relative to the silicon, as illustrated in Table V for polysiloxanes (*110*).

TABLE V

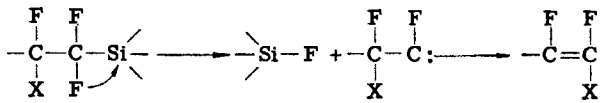
THE THERMAL AND HYDROLYTIC STABILITIES OF POLYFLUOROALKYL POLYSILOXANES

Polysiloxane	Thermal stability[a]	Hydrolytic stability[b]
$[CHF_2 \cdot CF_2 \cdot Si \cdot O_{1.5}]_n$	8% decomp. at 172° 67% decomp. at 240°	Si—C fission
$[CHF_2 \cdot CH_2 \cdot Si \cdot O_{1.5}]_n$	14% decomp. at 170° 75% decomp. at 220°	Si—C fission
$[CF_3 \cdot CH_2 \cdot CH_2 \cdot Si \cdot O_{1.5}]_n$	4% decomp. at 450° 80% decomp. at 500°	Inert

[a] Sample heated in a sealed, evacuated, silica tube for 6 hr.

[b] Sample shaken with 10% aqueous sodium hydroxide at 20°.

The breakdown products which arise from the pyrolysis of polyfluoroalkylpolysiloxanes also depend on the position of the fluorine relative to silicon. When fluorine is in the α-position, thermal breakdown appears to occur by α-elimination of fluorine initiated by an internal nucleophilic attack on silicon by the α-fluorine, and followed by rearrangement of the carbene thus formed:

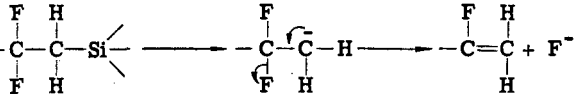


(47)

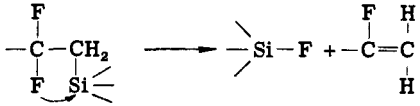
When fluorine is present in only the β-position, decomposition involves quantitative olefin formation by β-elimination, e.g.,

$$[CHF_2 \cdot CH_2 \cdot Si \cdot O_{1.5}]_n \longrightarrow n\,CHF:CH_2 + \frac{n}{4}\,SiF_4 + \frac{3n}{4}\,SiO_2 \qquad (48)$$

This reaction is possibly initiated by heterolytic fission of the C—Si bond or internal nucleophilic attack from the β-position:



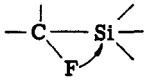
(49)



(50)

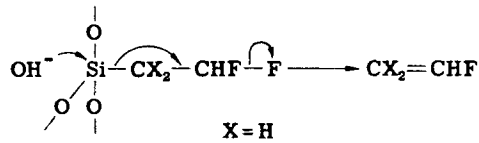
When fluorine is in both α and β positions, thermal breakdown occurs by both α- and β-elimination processes, and is accompanied by carbonization.

Evidence for the carbene-type mechanism has been obtained in separate experiments using the compounds $CHFCl \cdot CF_2 \cdot SiCl_3$ and $CFCl_2 \cdot CF_2 \cdot SiCl_3$ (*109*). For example, the pyrolysis of the first of these compounds yields the olefin CHF:CFCl as the major organic product together with small amounts of CF_2:CHCl. The primary step in this pyrolysis is considered to be an internal nucleophilic attack on silicon by a fluorine in the α-position

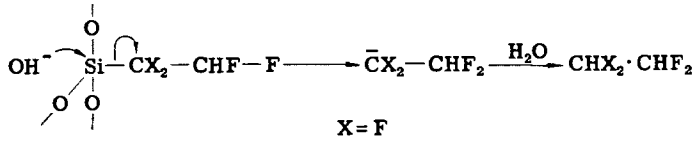


followed, or possibly accompanied, by migration of a chlorine atom from the β-carbon atom, thus giving rise to the olefin CHF:CFCl. The other olefin, CF_2:CHCl, results from β-elimination of fluorine following simple C—Si fission, or from internal nucleophilic attack of a fluorine in the β-position, or from a combination of both.

Silicones and polysiloxanes containing fluorine in the α- or β-position relative to silicon are readily hydrolyzed by aqueous base yielding fluorohydrocarbons or olefins, and this is clearly to be attributed to the increased sensitivity of the silicon atom to nucleophilic attack when attached to an electron-attracting polyfluoroalkyl group, e.g.,



X = H (51)



X = F (52)

There is a marked change when fluorine is in the γ-position with respect to the silicon atom. Thermal stability is then excellent, and even strong aqueous base fails to cleave the Si—C bond. For example, the polysiloxane $[CF_3 \cdot CH_2 \cdot CH_2 \cdot Si \cdot O_{1.5}]_n$ dissolves in boiling 40% NaOH, but is reformed when the solution is diluted and acidified. The marked thermal and chemical stability of the γ,γ,γ-trifluoropropyl-silicone and -polysiloxane, combined with a distinct resistance to swelling or disintegration by hydrocarbon liquids, will probably be utilized in commercial silicones for use under special conditions.

V. Nitrogen

Aliphatic amines are best regarded as derivatives of ammonia, formed by stepwise replacement of hydrogen by alkyl groups. One class of polyfluoroalkyl derivative of nitrogen, the polyfluoroalkylamines [e.g., $CF_3 \cdot CH_2 \cdot NH_2$, $(CF_3)_2NH$, $(CH_3)_2(CF_3 \cdot CH_2)N$], can be considered as fluoro derivatives of alkylamines, but the second class, the perfluoroamines [e.g., $C_2F_5 \cdot NF_2$, $(CF_3)_2NF$, $(CF_3)_2(C_2F_5)N$], should be thought of as derived from nitrogen trifluoride and as such have no counterpart in hydrocarbon chemistry. The perfluoroamines are strikingly different from both the polyfluoroalkylamines and the alkylamines, and it is with the known members of this group and a few closely related compounds that the following discussion is mainly concerned.

A. Perfluoroamines

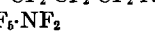
1. Preparation

In contrast to the indirect methods used to prepare perfluoroalkyl derivatives of phosphorus, arsenic, and antimony (see Section VI,A,*1*; B,*1*; C,*1*), many perfluoroalkyl nitrogen compounds can be made by direct or indirect fluorination of the corresponding amines, of amine derivatives, or of cyanides.

Moissan was the first investigator to treat a cyanide with fluorine, but

TABLE VI

FLUORINATION OF ORGANIC COMPOUNDS CONTAINING NITROGEN*

Starting Material	Fluorinating agent (diluent/temp °C)	Perfluoroalkyl nitrogen compound obtained	Reference
HCN	$CoF_3(N_2/200–250)$	$CF_3·NF_2$[a]	*40*
		$C_2N_2F_6$	
ClCN	AgF_2(—/80–100)	$CF_3·N:N·CF_3$	*42, 71, 73*
	NaF(—/235)	$CF_3·N:N·CF_3$	*197*
BrCN	AgF_2(—/100)	$CF_3·N:N·CF_3$	*42*
ICN	IF_5(—/80–140)	$CF_3·N:N·CF_3$	*48*,[b] *116*,[c] *175*
	AgF_2(—/100)	$CF_3·N:N·CF_3$	*42*
	HgF_2(—/160)	$(FCN)_3$	*123*
$K_3Fe(CN)_6$	$F_2(N_2)$	$CF_3·NF_2$	*40*
	NaF(—/235)	$CF_3·N:N·CF_3$	*197*
$K_4Fe(CN)_6$	$F_2(N_2)$	$CF_3·NF_2$	*40*
$CH_3·CN$	$F_2(N_2/85–275)$	$CF_3·CF_2·NF_2$	*43, 91*
		$CF_2:NF$	
	HgF_2(—/150–180)	$CH_3·CF_2·NF_2$	*123, 163*
		$CH_3·CF:NF$	
		$CH_2:CF·NF_2$	
		$CH_2:C:NF$	
$CH_2(CN)_2$	$F_2(N_2/250)$	$CF_3·NF_2$[a]	*4*
		$C_2F_5·NF_2$	
		$C_3F_7·NF_2$[d]	
		$F_2N·(CF_2)_3·NF_2$[d]	
			
$CF_3·CN$	$F_2(N_2/220)$	$C_2F_5·NF_2$	*91*
		$CF_2:NF$[a]	
	$CoF_3(N_2/200–250)$	$C_2F_5·NF_2$	*40*
	F_2(He/30–47)	$C_2F_5·N:N·C_2F_5$	*3*
	F_2(He/275)	$C_2F_5·NF_2$	*3*
		$CF_2:NF$[a]	
$C_2F_5·CN$	F_2(He/54–65)	$C_3F_7·N:N·C_3F_7$	*3*
	F_2(He/275)	$C_3F_7·NF_2$	*3*
$CH_3·SCN$	$F_2(N_2/95)$	$CF_2:NF$[a]	*3*
		$SF_5·CN$	
		$SF_5·CF_2·NF_2$	
$CH_3·NH_2$	$CoF_3(N_2/190)$	$CF_3·NF_2$	*88*
	$F_2(N_2/100)$	$CF_3·NF_2$[a]	*74*
		$C_2F_5·NF_2$[a]	
		$(CF_3)_2NF$[a]	
$(CH_3)_2NH$	$F_2(N_2/275)$	$CF_3·NF_2$[a]	*74*
		$C_2F_5·NF_2$[a]	
		$(CF_3)_2NF$[a]	
		$(CF_3)_3N$	
		$(CF_3)_2N·N(CF_3)_2$	

* Some of the products listed in this table are best prepared by electrochemical fluorination (see p. 361).

TABLE VI (*Continued*)

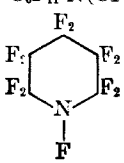
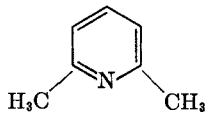
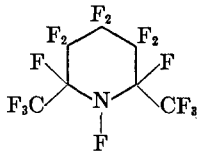
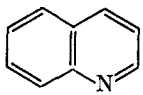
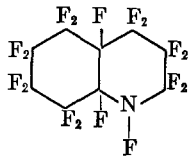
Starting material	Fluorinating agent (diluent/temp °C)	Perfluoroalkyl nitrogen compound obtained	Reference
	$F_2(N_2/120)$	$CF_3{\cdot}NF_2$[a] $(CF_3)_2NF$ $CF_3{\cdot}N{:}N{\cdot}CF_3$[a] $(CF_3)_2N{\cdot}N(CF_3)_2$	*74*
$H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$	$F_2(N_2/250)$	$CF_3{\cdot}NF_2$ $C_2F_5{\cdot}NF_2$ $CF_3{\cdot}N{:}N{\cdot}CF_3$	*74*
$(CH_3)_3N$	$CoF_3(N_2/130–220)$	$(CF_3)_2NF$	*193*
	$CoF_3(N_2/250)$	$CF_3{\cdot}NF_2$ $(CF_3)_2NF$ $(CF_3)_3N$ $(CF_3)_2N{\cdot}N(CF_3)_2$	*89*
	$F_2(N_2/275)$	$CF_3{\cdot}NF_2$[a] $CF_3{\cdot}CF_2{\cdot}NF_2$[a] $(CF_3)_2NF$[a] $(CF_3)_3N$ $CF_3{\cdot}NF{\cdot}NF{\cdot}CF_3$[e] $(CF_3)_2N{\cdot}NF{\cdot}CF_3$[e] $(CF_3)_2N{\cdot}N(CF_3)_2$[e]	*74*
$(CH_3)_2(C_2H_5)N$	$CoF_3(N_2/250)$	$(CF_3)_2(C_2F_5)N$	*89*
$(CH_3)(C_2H_5)_2N$	$CoF_3(N_2/260)$	$(CF_3)(C_2F_5)_2N$	*89*
$(C_2H_5)_3N$	$CoF_3(N_2/270)$	$(C_2F_5)_3N$	*89*
$(C_3H_7)_3N$	$CoF_3(N_2/300)$	$(C_3F_7)_3N$	*89*
$(C_3H_7)_2(\text{iso-}C_4H_9)N$	$CoF_3(N_2/320)$	$(C_3F_7)_2(\text{iso-}C_4F_9)N$	*89*
$(C_4H_9)_3N$	$CoF_3(N_2/350)$	$(C_4F_9)_3N$	*89*
$CO(NH_2)_2$	$F_2(—/0)$	HNF_2	*146*
$HCONHCH_3$	$F_2(He/275)$	$CF_3{\cdot}NF_2$ $CF_2{:}NF$[a] $(CF_3)_2NF$	*3*
$HCON(CH_3)_2$	$F_2(N_2/115)$	$(CF_3)_2NF$ $CHF_2{\cdot}NF{\cdot}NF{\cdot}CF_3$[g]	*4*
	$F_2(He/275)$	$(CF_3)_2NF$[f] $(CF_3)_3N$ $(CF_3)_2N{\cdot}N(CF_3)_2$	*3*
$C_6H_5{\cdot}NH_2$	$F_2(N_2/290)$	$C_6F_{11}{\cdot}NF_2$	*88*
	$CoF_3(N_2/300)$	$C_6F_{11}{\cdot}NF_2$	
$C_6H_5{\cdot}NHCH_3$	$CoF_3(N_2/300)$	$CF_3{\cdot}NF_2$	*88*
$C_6H_5{\cdot}N(CH_3)_2$	$CoF_3(N_2/300)$	$(CF_3)_2NF$ $C_6F_{11}{\cdot}N(CF_3)_2$[e]	*88*
	$F_2(N_2/280)$ $CoF_3(N_2/350)$		*88* *88*

TABLE VI (*Continued*)

Starting material	Fluorinating agent (diluent/temp °C)	Perfluoroalkyl nitrogen compound obtained	Reference
	$F_2(N_2/300)$ $CoF_3(N_2/350)$		*87* *87*
	$CoF_3(N_2/400)$		*105*

[a] Not isolated in the pure state.
[b] These authors quote a 35% yield of $CF_3{\cdot}N{:}N{\cdot}CF_3$.
[c] These authors quote a 60% yield of $CF_3{\cdot}N{:}N{\cdot}CF_3$.
[d] Probably isomeric mixtures.
[e] Probably formed.
[f] 38% yield.
[g] This structure is only tentative.

he did not characterize the products (*161*). Some forty years later, Ruff and Giese (*179*) demonstrated the formation of perfluoromethylamine, $CF_3{\cdot}NF_2$, from the reaction between fluorine and silver cyanide at 0°. A material of molecular formula $C_2N_2F_6$, probably $CF_3{\cdot}N{:}N{\cdot}CF_3$, and trifluoronitrosomethane, $CF_3{\cdot}NO$, which probably derived its oxygen from traces of silver nitrate present in the silver cyanide, were also isolated.* This work was followed by the discovery that hexafluoroazomethane, $CF_3{\cdot}N{:}N{\cdot}CF_3$ can be obtained from the fluorination of cyanogen iodide with iodine pentafluoride (*180*), a reaction which is still recognized as the standard method of preparation for this compound. More recent work on the fluorination of organic nitrogen compounds and cyanides with elemental fluorine or metallic fluorides is summarized in Table VI.

Apart from the few exceptions noted, no real estimate of the yields of the products listed in Table VI can be made, but in general they are poor (1–15%). Poor yields result from the highly energetic reactions used, and from the difficulties which are encountered in the separation of the desired products from complex mixtures, which often contain fluorocarbons. The fluorination of some nitrogen compounds leads also to the formation of

* These early studies have been reviewed in some detail by Bigelow (*20*). See also the comments of one of the authors on the isomerization of $CF_3{\cdot}NO$ (*129*).

TABLE VII

PREPARATION OF $(CF_3)_2N{\cdot}COF$ AND $(CF_3)_2N{\cdot}CF_2{\cdot}COF$ BY ELECTROCHEMICAL FLUORINATION

Starting material (g)	Products (g)	Starting material (g)	Products (g)
$HCON(CH_3)_2$ (1139)	$(CF_3)_2N{\cdot}COF$ (170)	$(CH_3)_2N{\cdot}CON(CH_3)_2$ (196)	$(CF_3)_2N{\cdot}COF$ (46)
$(CH_3)_2N{\cdot}COCl$ (256)	$(CF_3)_2N{\cdot}COF$ (174)[a]		$(CF_3)_2N{\cdot}CON(CF_3)_2$[b] (10)
$(C_2H_5)_2N{\cdot}COCl$ (595)	$(CF_3)_2N{\cdot}COF$ (40)	$(CH_3)_2N{\cdot}CH_2{\cdot}CON(CH_3)_2$	$(CF_3)_3N$
	$CF_2{\cdot}O{\cdot}CF_2{\cdot}CF_2{\cdot}N{\cdot}C_2F_5$[b] (241)		$(CF_3)_2N{\cdot}COF$
$(C_4H_9)_2N{\cdot}COCl$ (1176)	$(CF_3)_2N{\cdot}COF$ (not recorded)		$(CF_3)_2N{\cdot}CF_2{\cdot}COF$[d]
	$CF_2{\cdot}O{\cdot}CF(C_2F_5){\cdot}CF_2{\cdot}N{\cdot}C_4F_9$[b] (211)		$(CF_3)_2N{\cdot}CF{\cdot}O{\cdot}CF_2{\cdot}N(CF_3){\cdot}CF_2$[b]
$O(CH_2{\cdot}CH_2)_2N{\cdot}COCl$ (604)	$(CF_3)_2N{\cdot}COF$ (34)		
	$O(CF_2{\cdot}CF_2)_2N{\cdot}COF$[c] (30)		$CF_3{\cdot}N{\cdot}CF_2{\cdot}O{\cdot}CF_2{\cdot}CF_2$[b]
$CF_3{\cdot}CON(CH_3)_2$ (569)	$CF_3{\cdot}COF$ (65)	$(CH_3)_2N{\cdot}CH_2{\cdot}CO_2CH_3$	$(CF_3)_2N{\cdot}CF_2{\cdot}COF$[d]
	$(CF_3)_2N{\cdot}COF$ (137)		
	$CF_3{\cdot}CON(CF_3)_2$[b] (48)		

[a] This represents a 37% yield. Under certain conditions it is possible to obtain some $(CF_3)_2N{\cdot}COCl$ from this fluorination.

[b] This structure is proposed on the basis of IR, NMR, and elemental analyses.

[c] Assumed structure.

[d] 6% yield.

extremely reactive substances (of which $CF_2{:}NF$ is a known example) which attack hydrocarbon greases and mercury. This causes extra difficulties, and such compounds have often been destroyed to facilitate purification of more stable products, so that a complete picture of the reaction products is not obtained.

The electrochemical method of fluorination has been applied to the preparation of perfluoroalkyl nitrogen compounds by Simons, who discovered this important fluorination technique (*184*). He claims the preparation of a large number of simple [e.g., $(C_2F_5)_3N$] and mixed [e.g., $(C_2F_5)(C_3F_7)_2N$] perfluoro tertiary amines by this method, but quotes a yield only in the case of perfluorotriethylamine (27%) (*134*).* More recently the electrochemical method has been used (*204*, *205*, *207*) to prepare *N*,*N*-bistrifluoromethylcarbamyl fluoride, $(CF_3)_2N{\cdot}COF$, and bistrifluoromethylaminodifluoroacetyl fluoride $(CF_3)_2N{\cdot}CF_2{\cdot}COF$ (Table VII).

2. Properties and Reactions

The perfluoroamines are colorless, odorless, nonbasic, water-insoluble compounds which resemble fluorocarbons in many respects. They are dense, highly volatile, have low refractive indices and surface tensions, and resist chemical attack. To date, the perfluoro tertiary amines have received the most attention while the perfluoro primary and secondary amines, which are not so readily available, remain relatively unexplored. There are indications, however, that some interesting chemistry would arise from a study of the reactions of the N—F bonds in these latter compounds. Nitrogen trifluoride, for example, normally a very stable compound, can be made to react with perfluoro compounds containing C—C and C—N multiple bonds (*53a,b*):

$$NF_3 + CF_3{\cdot}CF{:}CF_2 \xrightarrow{NaF,\ 520°} CF_3{\cdot}CF{:}N{\cdot}CF_3 + \text{fluorocarbons} \qquad (53)$$

$$NF_3 + CF_3{\cdot}CF{:}CF_2 \xrightarrow{CsF,\ 320°} \begin{array}{l} CF_2{:}CF{\cdot}CF(CF_3){\cdot}NF_2 \\ + \\ (CF_3)_2CF{\cdot}NF_2 \\ + \\ (CF_3)_2C{:}NF \\ + \\ \text{fluorocarbons} \end{array} \qquad (54)$$

$$NF_3 + CF_3{\cdot}C{:}N \xrightarrow{CsF,\ 520°} \begin{array}{l} CF_3{\cdot}NF_2 + (CF_3)_2NF \\ + \\ CF_3{\cdot}N{:}CF_2 \\ + \\ (CNF)_3 \end{array} \qquad (55)$$

* Perfluoropiperidine, $C_5F_{10}NF$, is best prepared by the electrochemical fluorination of pyridine (*122*, *184*).

$$NF_3 + CF_3\cdot N{:}CF_2 \xrightarrow{CsF,\ 200^\circ} (CF_3)_2N\cdot CF{:}N\cdot CF_3$$
$$\xrightarrow[CsF,\ 500^\circ]{NF_3} (CF_3)_2N\cdot CF_2\cdot NF\cdot CF_3 \qquad (56)$$

The reported physical constants of the perfluoroamines and related compounds are listed in Table VIII. Note that replacement of a >CF— group in a fluorocarbon by a nitrogen atom scarcely affects the boiling

TABLE VIII
PHYSICAL PROPERTIES OF PERFLUOROAMINES

Compound[c]	m.p. (°C)	b.p. (°C/mm Hg)	n_D^t (t°C)	d_4^t (t°C)
NF_3	−208.5	−129	—	—
$CF_3\cdot NF_2$	−122.1	−75	—	—
$C_2F_5\cdot NF_2$	−183	−38	—	—
$C_3F_7\cdot NF_2$	−168	0	—	—
$(CF_3)_2NF$	−171	−37	—	—
$(CF_3)_3N$	−114	−10.9[a]	—	—
$(C_2F_5)_3N$	—	70.3[a]	1.262 (25)	1.736 (25)
$(C_3F_7)_3N$	—	129.5–130.5	1.279 (25)	1.822 (25)
$(CF_3)_2(C_2F_5)N$	—	20.5	—	—
$(CF_3)(C_2F_5)_2N$	—	45.5–46.5	1.253 (25)	—
$(C_4F_9)_3N$	—	179.1–179.5	1.291 (25)	1.873 (25)
$(C_5F_{11})_3N$[b]	—	215–216.5	1.301 (26)	1.923 (25)
$(C_6F_{13})_3N$	—	258	1.305 (20)	1.922 (27)
$(C_2F_5)_2(C_3F_7)N$	—	93	1.270 (25)	1.764 (27)
$(C_3F_7)_2(C_2F_5)N$	—	111/732	1.273 (24)	1.794 (24)
$(iso\text{-}C_3F_7)_2(C_2F_5)N$	—	108/736	1.279 (28)	—
$(C_2F_5)_2(C_4F_9)N$	—	113/743	1.275 (26)	1.792 (27)
$(C_3F_7)_2(iso\text{-}C_4F_9)N$	—	146–148	1.283 (25)	1.841 (25)

[a] Calculated from vapor pressure measurements.

[b] Isomeric mixture.

[c] Unless stated, all perfluoroalkyl groups containing more than two carbon atoms are assumed to be unbranched.

point, density, or refractive index [e.g., cf. CF_4, b.p. −128° and NF_3, b.p. −129°; C_2F_6, b.p. −79° and $CF_3\cdot NF_2$, b.p. −75°; C_3F_8, b.p. −39° and $(CF_3)_2NF$, b.p. −37°; C_7F_{16}, b.p. 82°, $[n]_D^{25}$ 1.267, $[d]_4^{25}$ 1.741 and $(C_2F_5)_3N$, b.p. 70.3°, $[n]_D^{25}$ 1.262, $[d]_4^{25}$ 1.736].

The perfluoro tertiary amines are unaffected by treatment with hot concentrated acids, alkalis, or oxidizing agents, but are decomposed by fusion with alkali metals. This reaction is used to determine their fluorine and nitrogen content. The failure of the perfluoroamines to react with acids demonstrates the nonbasic character of the nitrogen atom, which can be associated with the inductive effect of the highly electronegative fluorine and/or perfluoroalkyl substituents. The resistance of the perfluoroamines to attack by aqueous alkalis contrasts sharply with the hydrolytic insta-

bility of perfluoroalkyl derivatives of the other Group VB elements (see Section VI,A,*5*; B,*4*; C,*2*).

Controlled pyrolysis of perfluoro tertiary amines, preferably in the presence of metal fluoride catalysts, gives rise to perfluoroazomethines, i.e., perfluoro(alkylenealkylamines), with concurrent formation of fluorocarbons such as CF_4, C_2F_4, C_2F_6, C_3F_6, C_3F_8, C_4F_8, and C_4F_{10} (*168*). Thus, perfluoro(tri-*n*-propylamine), initially reported to be converted into perfluoro(methylene-*n*-propylamine):

$$(C_3F_7)_3N \xrightarrow{660\text{–}665^\circ,\ AlF_3} C_3F_7{\cdot}N{:}CF_2 + \text{fluorocarbons} \qquad (57)$$

is now known to give the isomeric compound $C_2F_5{\cdot}CF{:}N{\cdot}CF_3$ (*13*).

Recent reports show that pyrolytic defluorination of perfluoroethylamine, -propylamine, and -dimethylamine can be achieved by use of prefluorinated copper shot (*3*):

$$CF_3{\cdot}CF_2{\cdot}NF_2 \xrightarrow{\Delta} CF_3{\cdot}C{:}N \qquad (58)$$

$$CF_3{\cdot}CF_2{\cdot}CF_2{\cdot}NF_2 \xrightarrow{\Delta} C_2F_5{\cdot}C{:}N \qquad (59)$$

$$(CF_3)_2NF \xrightarrow{515^\circ} CF_3{\cdot}N{:}CF_2 \qquad (60)$$

No experimental details are given for the first two defluorination reactions; defluorination of the secondary amine $(CF_3)_2NF$ is accompanied by formation of carbon dioxide and carbonyl fluoride, presumably through admission of air during the pyrolysis.

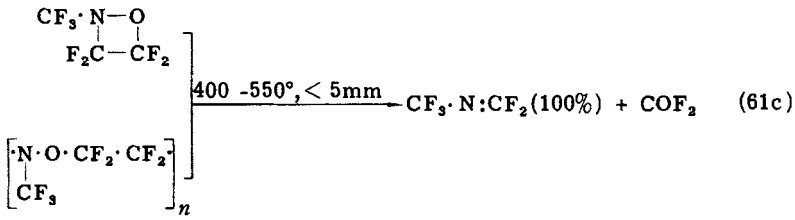
B. Perfluoro(methylenemethylamine), $CF_3{\cdot}N{:}CF_2$

Two convenient methods have been developed for the preparation of perfluoro(methylenemethylamine) in quantity. The first involves the pyrolysis of perfluoro(2-methyl-1,2-oxazetidine), or a related copolymer of trifluoronitrosomethane and tetrafluoroethylene, as shown below (% yields in parentheses) (*8*, *10*, *11*):

$$CF_3{\cdot}CO_2H \xrightarrow{Ag_2CO_3} CF_3{\cdot}CO_2Ag\ (100\%) \xrightarrow{I_2} CF_3I \quad (96\%) \qquad (61a)$$

$$CF_3I \xrightarrow[\text{ultraviolet light}]{NO,} CF_3{\cdot}NO\ (85\%) \begin{cases} \xrightarrow{C_2F_4,\ 150^\circ} CF_3{\cdot}N(O){-}CF_2{-}CF_2{-}O \quad (97\%) \\ \xrightarrow{C_2F_4,\ 20^\circ} CF_3{\cdot}N(O){-}CF_2{-}CF_2{-}O \quad (28\%) \end{cases} \qquad (61b)$$

$$\left[\cdot N(CF_3){\cdot}O{\cdot}CF_2{\cdot}CF_2{\cdot}\right]_n^{+} \quad (64\%)$$



The second method involves the pyrolysis of *N,N*-bistrifluoromethylcarbamyl fluoride (*120, 204*):

$$(CF_3)_2N\cdot COF \xrightarrow{575^\circ,\ Ni} CF_3\cdot N:CF_2\ (96\%) + COF_2 \qquad (62)$$

The starting material in this case is prepared in 37% yield by the electrochemical fluorination of *N,N*-dimethylcarbamyl chloride (see Table VII).

Perfluoro(methylenemethylamine) is a colorless gas whose boiling point

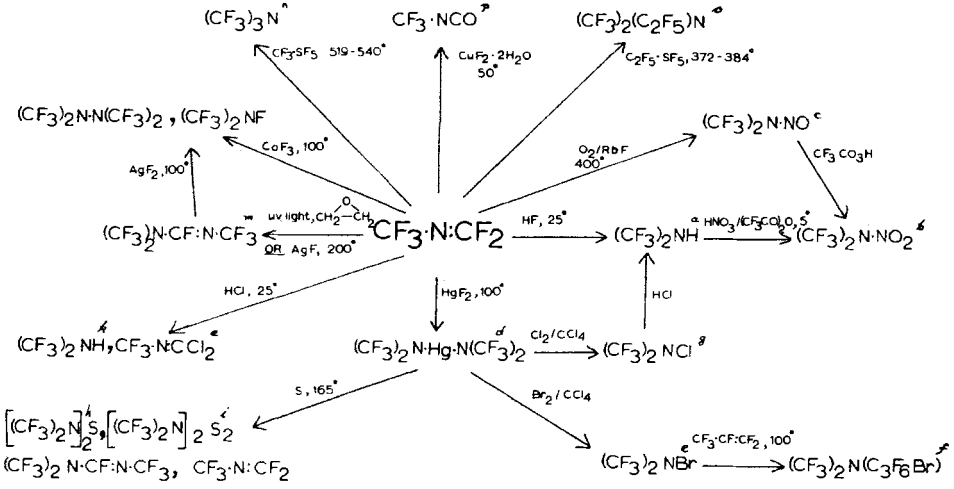


FIG. 1. The reactions of perfluoro(methylenemethylamine).

[a] Yield: 95–100% by reaction with HF.

[b] Yield: 43% by nitration of $(CF_3)_2NH$; low yield of impure material obtained from the oxidation of $(CF_3)_2N\cdot NO$.

[c] Yield: 30%.

[d] Yield: 79%.

[e] Yield: 90%.

[f] Yield: 76%. Probably a mixture of $(CF_3)_2N\cdot CF_2\cdot CFBr\cdot CF_3$(I) and $(CF_3)_2N\cdot CF(CF_3)\cdot CF_2Br$(II), with (I) predominating.

[g] Quoted as "not in good yield."

[h] Yield: 25%.

[i] Yield: 21%.

[k] Yield: 54%.

[l] Yield: 26%.

[m] Yield: 78% by irradiation method; 95% by reaction with AgF.

[n] Yield: 60%.

[o] Yield: 46%.

[p] Yield: 83%.

(−33.7°) is close to that of hexafluoropropylene (−29°). It is rapidly and quantitatively hydrolyzed, via trifluoromethyl isocyanate, $CF_3 \cdot NCO$, to carbon dioxide, ammonium fluoride, and hydrogen fluoride when treated with an excess of water. Hydrolysis with a limited amount of water (*14*), or with cupric fluoride dihydrate (*209*), allows the isocyanate to be isolated in 50–83% yield. Methanolysis is likewise rapid and the products are dimethyl ether, dimethyl carbonate, and ammonium fluoride. Aqueous alkali degrades perfluoro(methylenemethylamine) at room temperature to fluoride, carbonate, and cyanate ions.

The chemistry of perfluoro(methylenemethylamine) has been investigated mainly with a view to making a comparison with hexafluoropropylene, in particular, and perfluoroolefins in general. The reactions discovered to date are shown in Fig. 1 (*11, 12, 14, 15, 52, 56, 120, 206, 209, 210*).

For comparison, the lower members of the aliphatic alkylenealkylamines (azomethines) are believed to be cyclic trimers from molecular weight and vapor-density determinations; they are hydrolyzed to the parent amine and the aldehyde by dilute acids or aqueous bases, and when treated with ethanolic sodium hydroxide yield both the parent amine and, by reduction, the secondary amine, e.g.,

$$C_4H_9 \cdot N{:}CH_2 \rightarrow C_4H_9 \cdot NH_2 + C_4H_9 \cdot NHCH_3$$

They are said to combine readily with bromine or iodine to give solids believed to be dihalides:

$$RCH{:}NR' \xrightarrow{X_2} RCHX \cdot NXR'$$

(X = Br or I; R = alkyl; R′ = alkyl or H), but no proof of structure is available. Perfluoro(methylenemethylamine) fails to react with chlorine at room temperature, and is recovered unchanged when heated with iodine. This sharp contrast with unsubstituted alkylenealkylamines is not unexpected in view of the marked differences between addition reactions of olefins and the corresponding perfluoroolefins (e.g., $CH_3 \cdot CH{:}CH_2$ and $CF_3 \cdot CF{:}CF_2$).

C. Polyfluoroalkylamines

Primary and secondary polyfluoroalkylamines $R_F \cdot NH_2$ and $(R_F)_2NH$ (R_F = perfluoroalkyl) are unknown, with the exception of bistrifluoromethylamine, $(CF_3)_2NH$. This can be obtained in almost quantitative yield by the addition of anhydrous hydrogen fluoride to the double bond in perfluoro(methylenemethylamine) (*12, 206*). It was first obtained by Ruff and Willenberg (*180*) as an impurity in the hexafluoroazomethane prepared by the reaction of cyanogen iodide with iodine pentafluoride. The hydrogen was presumably supplied as hydrogen fluoride by moisture enter-

ing the reaction mixture and combining with the iodine pentafluoride. Evidence so far obtained indicates that primary perfluoroalkylamines, e.g., $CF_3 \cdot NH_2$, are unstable; facile loss of HF occurs in solvents of high dielectric constant (cf. the unknown alcohols $R_F \cdot CF_2 \cdot OH$), and all attempts to effect their preparation have failed.

Bistrifluoromethylamine is a colorless gas which boils at $-6°$, 13° lower than dimethylamine. This difference is probably due in part to the decreased basicity of nitrogen when a perfluoroalkyl group is attached. There is no reaction between bistrifluoromethylamine and hydrogen chloride, boron trifluoride, trifluoroacetyl chloride, or trifluoroacetic anhydride (*206*). The amine is rapidly converted by water into carbon dioxide and fluoride and ammonium ions; this is essentially hydrolysis under acid conditions. Decomposition in alkaline solution causes complete breakdown to fluoride, carbonate, and cyanate ions, and it is thus probable that the initial reaction is loss of hydrogen fluoride to give perfluoro(methylenemethylamine):

$$(CF_3)_2NH \xrightarrow{-HF} CF_3 \cdot N{:}CF_2 \xrightarrow{H_2O} CF_2 \cdot NCO \xrightarrow{OH^-} F^-, CO_2, NH_4^+ \qquad (63)$$

Loss of hydrogen fluoride is also the first step in the reaction of bistrifluoromethylamine with the trichloride of phosphorus or boron at elevated temperatures (100–140°)(206):

$$(CF_3)_2NH \longrightarrow CF_3 \cdot N{:}CF_2 + HF \qquad (64a)$$

$$3HF + MCl_3 \longrightarrow MF_3 + 3HCl \quad (M = P, B) \qquad (64b)$$

$$\begin{aligned} CF_3 \cdot N{:}CF_2 &\xrightarrow{+HCl} CF_3 \cdot NH \cdot CF_2Cl \\ &\xrightarrow{-HF} CF_3 \cdot N{:}CClF \\ &\xrightarrow{+HCl} CF_3 \cdot NH \cdot CCl_2F \\ &\xrightarrow{-HF} CF_3 \cdot N{:}CCl_2 \end{aligned} \qquad (64c)$$

Nitration of bistrifluoromethylamine with a mixture of concentrated nitric acid and trifluoroacetic anhydride gives a 43% yield of the nitramine $(CF_3)_2N \cdot NO_2$, b.p. 17° [cf. $(CH_3)_2N \cdot NO_2$, b.p. 187°].

Many partially fluorinated amines such as $CF_3 \cdot CH_2 \cdot NH_2$ and $(CF_3 \cdot CH_2)_2NH$ have been prepared by the application of standard reactions to fluoroorganic starting materials. Although the polyfluoroalkyl group has distinct influence on the nitrogen atom (e.g., cf. $CF_3 \cdot CH_2 \cdot NH_2$, $pK_b = 5.7$; $CH_3 \cdot CH_2 \cdot NH_2$, $pK_b = 3.25$), the compounds resemble the alkylamines in many respects and, as such, are of interest to the organic chemist.

VI. Phosphorus, Arsenic, and Antimony

A. Phosphorus

1. Preparation of Polyfluoroalkyl Phosphorus Compounds

Perfluoroalkyl derivatives of phosphorus are prepared by heating phosphorus with a perfluoroalkyl iodide in a sealed Pyrex glass tube or a stainless steel autoclave. So far, only the trifluoromethyl and heptafluoro-*n*-propyl compounds have been reported (*17*, *32*, *65*).

Trifluoroiodomethane reacts with either red or white phosphorus at 195–230° to yield a mixture of tristrifluoromethylphosphine, $(CF_3)_3P$, iodobistrifluoromethylphosphine, $(CF_3)_2PI$, diiodotrifluoromethylphosphine, $CF_3 \cdot PI_2$, and phosphorus iodides. Using white phosphorus at 230° the above derivatives are formed in the ratio 7:2:1, and increasing temperature favors the formation of the tris compound. Increased yields of the iodo-compounds, which, because of the reactivity of the iodine atoms, are of greater chemical interest, may be achieved by using red phosphorus at a lower temperature. Thus, the reaction of red phosphorus with trifluoroiodomethane at 200° yields the phosphines in the ratio 3:5:1.6, with 96% utilization of the trifluoroiodomethane. The introduction of phosphorus triiodide into the reaction mixture also increases the proportion of iodobistrifluoromethylphosphine in the complex equilibria:

$$(CF_3)_3P \rightleftharpoons (CF_3)_2PI \rightleftharpoons CF_3 \cdot PI_2 \rightleftharpoons CF_3I + P \qquad (65)$$

Reaction of an excess of phosphorus with trifluoroiodomethane at temperatures above 250° gives phosphorus tri- and penta-fluoride and hexafluoroethane as major products. It has been found possible to obtain a mixture of the trifluoromethyl phosphines by heating a mixture of phosphorus, iodine, and silver trifluoroacetate, so that the trifluoroiodomethane is produced *in situ* (*32*). Using this technique, however, the yield of material containing P—CF_3 bonds is reduced.

The reaction between phosphorus and heptafluoro-1-iodopropane begins at 200° and is conveniently carried out at 220–230° (*65*). Surprisingly, no trisheptafluoro-*n*-propylphosphine, $(C_3F_7)_3P$, is formed, but only a 7:3 mixture of bisheptafluoro-*n*-propyliodophosphine, $(C_3F_7)_2PI$, and diiodoheptafluoro-*n*-propylphosphine, $C_3F_7 \cdot PI_2$, with 60% utilization of the heptafluoroiodopropane. This result is obtained even when conditions should, by analogy with the behavior of trifluoroiodomethane, favor the production of the tris compound.

Fluoroalkylphosphines can be obtained in good yield by the light- or heat-catalyzed reaction of phosphine with fluoroolefins (*29*, *70*, *165*), for example:

$$PH_3 + CF_2{:}CF_2 \rightarrow CHF_2{\cdot}CF_2{\cdot}PH_2 + (CHF_2{\cdot}CF_2)_2PH + H_2P{\cdot}CF_2{\cdot}CF_2{\cdot}PH_2 \quad (66)$$

$$PH_3 + CF_2{:}CH_2 \rightarrow CHF_2{\cdot}CH_2{\cdot}PH_2 \quad (67)$$

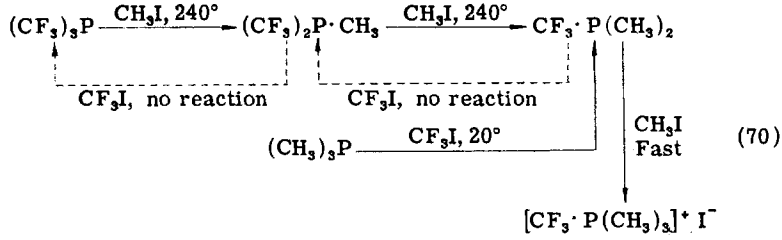
Short-chain, peroxide-initiated polymerization of tetrafluoroethylene in the presence of a dialkyl phosphite yields polyfluoroalkyl phosphonic esters:

$$HP(O)(OR)_2 + nCF_2{:}CF_2 \rightarrow H{\cdot}[CF_2{\cdot}CF_2]_n{\cdot}P(O)(OR)_2 \quad (68)$$

and the compounds where $R = CH_3$, C_2H_5, etc., and $n = 1$, 2, and 3 have been isolated (*24*). The di-ethyl, -isopropyl, and -*n*-butyl esters of difluoromethylphosphonic acid have been prepared (*187*) by the interaction of chlorodifluoromethane and the appropriate sodium dialkylphosphite in an inert solvent (benzene):

$$CHF_2Cl + Na^+[PO(OR)_2]^- \rightarrow CHF_2{\cdot}P(O)(OR)_2 + NaCl \quad (69)$$

A convenient route to the mixed methyl-trifluoromethyl compounds $(CF_3)_nM(CH_3)_{3-n}$ (M = P, As) lies in the exchange reaction between the compounds $(CF_3)_3M$ and methyl iodide at elevated temperatures (*107*, *108*). The reaction scheme for the phosphorus compounds is:



(70)

In contrast to this, dimethyltrifluoromethylarsine yields methylbistrifluoromethylarsine when heated with trifluoroiodomethane (see Section VI,B,*1*).

2. Properties and Reactions of Trifluoromethyl Phosphorus Compounds

a. Tristrifluoromethylphosphine. Tristrifluoromethylphosphine is a water-stable, colorless liquid which boils (17°) some 20° below its methyl analog, and is spontaneously inflammable in air. Compounds comparable in molecular weight to tristrifluoromethylphosphine are triphenylphosphine, b.p. >360°, and tributylphosphine, b.p. 150°/5 mm. The influence of the strongly electronegative trifluoromethyl groups is to be seen in the absence of compound formation between tristrifluoromethylphosphine and sulfur, carbon disulfide, silver iodide, mercuric iodide, boron trifluoride, or platinous chloride (*16*, *17*). The trifluoromethyl group acts like a pseudohalogen in this respect (cf. phosphorus trichloride, which reacts with sulfur

only at 140°, and does not form a carbon disulfide addition compound; and phosphorus trifluoride, which fails to react with sulfur even at 440°).

Nickel carbonyl and an excess of tristrifluoromethylphosphine will react at room temperature to form a mixture of $(CF_3)_3P{\cdot}Ni(CO)_3$ and $[(CF_3)_3P]_2Ni(CO)_2$; formation of the disubstituted compound is favored at higher temperatures (*34*, *64*). These substitution compounds are colorless liquids which decompose rapidly at temperatures above 70° or when exposed to bright sunlight. The bonding in these compounds involves the donation of electrons by the nickel to the empty *d* orbitals of the phosphorus atom, as with corresponding complexes involving phosphorus trichloride and related compounds (*126*, *201*). Attempts to prepare tetrakis(tristrifluoromethylphosphine)nickel, $[(CF_3)_3P]_4Ni$, by the reaction of tristrifluoromethylphosphine with tetrakis(trichlorophosphine)nickel at temperatures up to 60° have so far failed.

Chlorine reacts vigorously with trialkylphosphines to give a mixture of chloroalkylphosphines, but tristrifluoromethylphosphine reacts smoothly with chlorine at −40° to produce tristrifluoromethylphosphorus dichloride, $(CF_3)_3PCl_2$, quantitatively (*17*). The methyl analog of this pentavalent phosphorus compound has not been reported, although the phenyl analog can be prepared at −80° (*132*). Tristrifluoromethylphosphorus dichloride is a white solid, which distils without decomposition at 71°/370 mm, but decomposes vigorously near the normal boiling point (107°). Iodine reacts quantitatively with tristrifluoromethylphosphine at temperatures above 100° to give the iodotrifluoromethylphosphines, trifluoroiodomethane, and phosphorus triiodide; the compound $(CF_3)_3PI_2$ is not formed.

Tristrifluoromethylphosphine reacts rapidly with oxygen to give breakdown products, and not the oxide $(CF_3)_3PO$; by contrast, trimethylphosphine is easily converted to its oxide on exposure to the air. Tristrifluoromethylphosphine oxide is formed in 70% yield, however, when tristrifluoromethylphosphorus dichloride is treated with anhydrous oxalic acid (*167*):

$$(CF_3)_3PCl_2 + H_2C_2O_4 \rightarrow (CF_3)_3PO + CO + CO_2 + 2HCl \qquad (71)$$

The oxide is a liquid, b.p. 23.5°, which reacts with water to yield bistrifluoromethylphosphinic acid:

$$(CF_3)_3PO + H_2O \rightarrow (CF_3)_2PO(OH) + CHF_3 \qquad (72)$$

Alkyl and aryl tertiary phosphine oxides form stable hydrates.

b. Bistrifluoromethyl- and trifluoromethyl-phosphine. Bistrifluoromethylphosphine and trifluoromethylphosphine are obtained by the reduction of the corresponding iodotrifluoromethylphosphines. Bistrifluoromethylphosphine, b.p. 1°, is prepared in 65% yield by the reduction of iodobistrifluoro-

methylphosphine with hydrogen at 100° in the presence of a Raney nickel catalyst (*19*), or in 35% yield by the action of an excess of an acid (hydrogen chloride, phosphoric acid, trifluoroacetic acid) in the presence of mercury (*33*):

$$(CF_3)_2PI \begin{cases} \xrightarrow{H_2/Ni} (CF_3)_2PH + CHF_3 + HF + PH_3 \\ \xrightarrow[HCl,\,Hg]{} (CF_3)_2PH + (CF_3)_2PCl + (CF_3)_4P_2 \end{cases} \quad (73)$$

The reaction of tetrakistrifluoromethyldiphosphine, $(CF_3)_2P{\cdot}P(CF_3)_2$, (see Section VI,A,*2*,*c*) with hydrogen in the presence of Raney nickel also gives bistrifluoromethylphosphine in low yield (28%). Unsuccessful attempts have been made to prepare the phosphine by the lithium aluminum hydride reduction of iodobistrifluoromethylphosphine (cf. the successful preparation of bis- and mono-trifluoromethylarsine, Section VI,B,*2*,*b*), and by a photochemical reaction between the iodo compound and hydrogen:

$$(CF_3)_2PI \xrightarrow{\text{Ultraviolet light}} (CF_3)_2P\cdot \xrightarrow{H_2} (CF_3)_2PH$$

Trifluoromethylphosphine, b.p. −25.5° is prepared in very low yield (6%) by the lithium aluminum hydride reduction of diiodotrifluoromethylphosphine, but the use of hydrogen and Raney nickel fails. This may be because trifluoromethylphosphine forms a complex with nickel, since there is evidence that bistrifluoromethylphosphine forms a complex with Raney nickel from which it is released only after heating at low pressure. Diiodotrifluoromethylphosphine is not reduced by anhydrous hydrazine, or by zinc and hydrochloric acid (cf. the preparation of trifluoromethylarsine, Section VI,B,*2*,*b*), but trifluoromethylphosphine is formed in 24% yield when the iodo compound is hydrolyzed in highly concentrated aqueous solution followed by freeze-drying of the resulting solution of trifluoromethylphosphonous acid:

$$CF_3{\cdot}PI_2 \xrightarrow{H_2O} CF_3{\cdot}P(OH)_2 \rightarrow CF_3{\cdot}PH_2 \quad (74)$$

Trifluoromethylphosphine has also been prepared in low yield (13%) by heating phosphine with trifluoroiodomethane at 240° (*107*).

Bistrifluoromethylphosphine and trifluoromethylphosphine are spontaneously inflammable in air. Unlike dimethylphosphine, bistrifluoromethylphosphine does not form addition compounds with methyl iodide, carbon disulfide, silver iodide, or chloroplatinic acid. When heated with an excess of dry iodine at 280°, it is decomposed with the production of an

approximately equimolar mixture of fluoroform and trifluoroiodomethane (*19*):

$$(CF_3)_2PH \xrightarrow{\text{excess } I_2,\ 280^\circ} CHF_3 + CF_3I \tag{75}$$

c. Perfluoroalkyl Compounds Containing P—P *Bonds:*

(i) *Tetrakistrifluoromethyldiphosphine.* Iodobistrifluoromethylphosphine reacts almost quantitatively with mercury at room temperature to give tetrakistrifluoromethyldiphosphine, a stable, colorless, liquid (*17*):

$$2(CF_3)_2PI + Hg \rightarrow (CF_3)_2P{\cdot}P(CF_3)_2 + HgI_2 \tag{76}$$

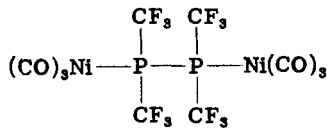
Iodobistrifluoromethylarsine reacts similarly with mercury (see Section VI,B,*2*,*c*), but whereas cacodyl, the methyl analog of the arsenic compound, is well known, the preparation of the methyl derivative of diphosphine has only recently been accomplished. The linking of two phosphorus atoms by the reaction described above is novel in phosphorus chemistry, and few compounds containing the P—P bond are known. An insight into the possible course of the reaction is given through the conversion of iodobistrifluoromethylphosphine into bistrifluoromethylphosphine by treatment with an acid in the presence of mercury (*33*). When the compound $(CF_3)_2PI$ is treated with mercury, and the volatile compound $(CF_3)_4P_2$ removed (95% yield), treatment of the nonvolatile residue with dry hydrogen chloride yields an amount of $(CF_3)_2PH$ which accounts for the missing 5% of $CF_3{\cdot}P$ groups. From this it would appear that a phosphorus-mercury bond is first established, possibly as $(CF_3)_2P{\cdot}Hg_2I$ (*33*) which is converted into either $(CF_3)_2PH$ by the action of the acid, or into $(CF_3)_4P_2$ by the action of unchanged $(CF_3)_2PI$. If this thesis is valid, a variety of new materials containing the $(CF_3)_2P$ group might be made by shaking $(CF_3)_2PI$ with mercury in the presence of halides of polyvalent metals or nonmetals.

The reaction of tetrakistrifluoromethyldiphosphine with trifluoroiodomethane gives a mixture of $(CF_3)_3P$ and $(CF_3)_2PI$; a similar, but slower, reaction occurs with methyl iodide (*45*):

$$(CF_3)_2P{\cdot}P(CF_3)_2 + CF_3I \xrightarrow{70^\circ} (CF_3)_3P + (CF_3)_2PI \tag{77}$$

$$(CF_3)_2P{\cdot}P(CF_3)_2 + CH_3I \xrightarrow{150^\circ} (CF_3)_2P{\cdot}CH_3 + (CF_3)_2PI \tag{78}$$

Tetrakistrifluoromethyldiphosphine reacts with nickel carbonyl at room temperature to yield the compound



with displacement of carbon monoxide (*34*). This coordination compound is a slightly volatile, red-black solid. It is stable at 100°, is insoluble in water, but dissolves in cyclohexane, benzene, ether, carbon tetrachloride, or methyl alcohol to give permanganate-colored solutions. Oxygen discharges the color of these solutions and causes a green powder to be precipitated.

(ii) *1,2-Bistrifluoromethyldiphosphine and 1,2,3-tristrifluoromethyltriphosphine.* 1,2-Bistrifluoromethyldiphosphine, $(CF_3{\cdot}PH)_2$, and 1,2,3-tristrifluoromethyltriphosphine, $H_2(CF_3{\cdot}P)_3$, have received brief attention (*154*). They are prepared by the aqueous hydrolysis of tetrakistrifluoromethylcyclotetraphosphine and pentakistrifluoromethylcyclopentaphosphine (these cyclophosphines are described below):

$$(CF_3{\cdot}P)_4 \xrightarrow{H_2O,\ 140°} (CF_3{\cdot}PH)_2,\ CF_3{\cdot}PH_2,\ HPO(OH)_2,\ CHF_3 \qquad (79)$$

$$(CF_3{\cdot}P)_5 \xrightarrow{H_2O/(CH_3{\cdot}O{\cdot}CH_2{\cdot}CH_2)_2O,\ 50°} H_2(CF_3{\cdot}P)_3,\ (CF_3{\cdot}PH)_2,\ CF_3{\cdot}PH_2 \qquad (80)$$

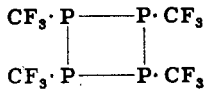
The diphosphine is stable at temperatures up to 250°, above which it decomposes, the main reaction being

$$(CF_3{\cdot}PH)_2 \rightarrow CF_3{\cdot}PH_2 + (CF_3{\cdot}P)_4 \qquad (81)$$

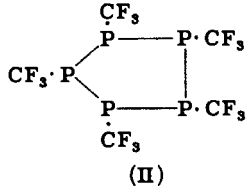
1,2,3-Tristrifluoromethyltriphosphine decomposes on an active nickel surface at 25° to give a mixture of $CF_3{\cdot}PH_2$, $(CF_3{\cdot}P)_4$, and $(CF_3{\cdot}P)_5$.

(iii) *Trifluoromethylcyclopolyphosphines.* The room-temperature reaction of diiodotrifluoromethylphosphine with mercury leads quantitatively to the production of two new compounds containing the P—P bond—tetrakistrifluoromethylcyclotetraphosphine (I), and pentakistrifluoromethylcyclopentaphosphine (II) (*153*, *154*):

$$CF_3{\cdot}PI_2 \xrightarrow{Hg} (CF_3{\cdot}P)_4\ (60\%) + (CF_3{\cdot}P)_5\ (40\%) \qquad (82)$$



(I)



(II)

Higher cyclic polymers $(CF_3{\cdot}P)_x$ are formed, together with useful yields of the tetramer and pentamer, when tetrakistrifluoromethyldiphosphine or bistrifluoromethylphosphine is heated to 350°:

$$(CF_3)_2P\cdot P(CF_3)_2 \xrightarrow{350°} (CF_3\cdot P)_4 + (CF_3\cdot P)_5 + (CF_3\cdot P)_x \quad (83)$$

$$(CF_3)_3PH \xrightarrow{350°} (CF_3\cdot P)_4 + (CF_3\cdot P)_5 + (CF_3\cdot P)_x + CHF_3 \quad (84)$$

Both the tetramer and pentamer are unstable at this temperature and so must be removed from the reaction zone as soon as they are formed. No open-chain polyphosphines are formed in these reactions.

Tetrakistrifluoromethylcyclotetraphosphine (the tetramer) is a colorless solid which melts to a colorless liquid. It crystallizes in a variety of forms, and though it is not obviously soluble in water at room temperature, it is soluble in benzene, acetone, carbon tetrachloride, hexane, ether, acetic acid, trifluoroacetic acid, and the fluorocarbon ether $C_8F_{16}O$. It dissolves in methyl alcohol with decomposition, and reacts vigorously with liquid ammonia. The tetramer is stable up to 280° *in vacuo* in a sealed glass tube, but at 314° it is completely decomposed to tristrifluoromethylphosphine and a small nonvolatile residue containing phosphorus. It is spontaneously inflammable in air, being oxidized to carbonyl fluoride, phosphoryl fluoride, and a heterogeneous phosphorus-containing solid. Controlled oxidation in the fluoroether $C_8F_{16}O$ at temperatures of 0–22° leads to the formation of a mixture of polymeric anhydrides, $(CF_3\cdot PO_2)_x$, which reacts vigorously with water, in a manner reminiscent of phosphoric anhydride, to yield trifluoromethylphosphonic acid, $CF_3\cdot PO(OH)_2$, and intermediate polyphosphonic acids such as trifluoromethyldiphosphonic acid, $[CF_3\cdot PO(OH)]_2O$.

When the tetramer is treated with an excess of iodine at room temperature or 110°, it is converted quantitatively into diiodotrifluoromethylphosphine, and with an excess of chlorine at sub-zero temperatures trifluoromethylphosphorus tetrachloride, $CF_3\cdot PCl_4$, is produced. This last compound is converted into dichlorotrifluoromethylphosphine when shaken with mercury at room temperature:

$$(CF_3\cdot P)_4 \xrightarrow{\text{Excess } Cl_2} 4CF_3\cdot PCl_4 \xrightarrow{\text{Excess Hg}} 4CF_3\cdot PCl_2 \quad (85)$$

These reactions, which are quantitative, are in accord with the cyclic structure allotted to the tetramer. No reaction is observed between the tetramer and (*a*) hydrogen chloride or boron trifluoride at temperatures below 300°, (*b*) hydrogen chloride in benzene solution, (*c*) diborane at temperatures in the range 25–70°, or (*d*) concentrated sulfuric acid at 100°. The tetramer is somewhat soluble in the last reagent and may be recrystallized unchanged from the solutions formed. When the tetramer is treated with nickel carbonyl at 0° in toluene solution, a vigorous displacement of carbon monoxide occurs, and an oily mixture with average composition $[Ni_{1.77}(CO)_{4.45}(CF_3\cdot P)_4]_x$ can be isolated (*34*).

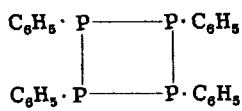
Pentakistrifluoromethylcyclopentaphosphine (the pentamer), a liquid,

is insoluble in water but miscible with organic solvents. It is less stable thermally than the tetramer, into which it is converted at 255° (56% yield):

$$(CF_3{\cdot}P)_5 \xrightarrow{255^\circ} (CF_3{\cdot}P)_4 + (CF_3)_3P + (CF_3)_4P_2 + P_4 \qquad (86)$$

It reacts quantitatively with iodine and chlorine to yield diiodobistrifluoromethylphosphine and trifluoromethylphosphorus tetrachloride respectively, which proves that its structure is of the same type as the tetramer. The polymeric material $(CF_3{\cdot}P)_x$ from the pyrolysis of tetrakistrifluoromethylphosphine or bistrifluoromethylphosphine also reacts with chlorine in a similar fashion. The reaction of chlorine with any of the $CF_3{\cdot}P$ polymers is vigorous and must be controlled by cooling, otherwise phosphorus pentachloride and chlorotrifluoromethane are produced in preference to trifluoromethylphosphorus tetrachloride.

The stability of the above phosphorus ring compounds may be due to supplementation of the P—P σ-bonding by π-bonds involving interaction of the lone pairs on the phosphorus atoms with neighboring phosphorus 3*d*-orbitals (*153*). Some support for this view is given by a study of the ultraviolet absorption spectra of the tetramer and pentamer. A trimer is not to be expected because of bond strain, and a dimer would require 3*p*–3*p* π-bonding, which is not favored. A hexamer should be capable of existence and may well be present in the polymeric material $(CF_3{\cdot}P)_x$ described above. It is interesting to note that the compound originally called "phosphobenzol" and written as $C_6H_5{\cdot}P{:}P{\cdot}C_6H_5$ (*139*) is now considered to be tetraphenylcyclotetraphosphine (III) (*142*):



(III)

This compound is prepared in 87% yield by the addition of dichlorophenylphosphine to an ethereal solution of phenylphosphine. It is oxidized by fuming nitric acid to benzenephosphonic acid, and chlorine and bromine convert it quantitatively into dichloro- and dibromo-phenylphosphine, respectively.

d. Tetrakistrifluoromethyldiphosphoxane. A stable diphosphoxane $(CF_3)_2P{\cdot}O{\cdot}P(CF_3)_2$, is obtained in 79% yield when iodobistrifluoromethylphosphine is treated with fresh silver carbonate at room temperature (*84a*):

$$2(CF_3)_2PI + Ag_2CO_3 \rightarrow (CF_3)_2P{\cdot}O{\cdot}P(CF_3)_2 + CO_2 + 2AgI \qquad (87)$$

This diphosphoxane is stable at 150° in a sealed glass tube, but decomposes when heated for several days at 250° to give $(CF_3)_3P$, $(CF_3)_2PF$, PF_3, and carbon monoxide. It is inert to Lewis acids such as boron trifluoride, but with trimethylamine forms a 1:1 complex which has a dissociation pressure of 0.04 mm at −78° and is completely dissociated at −20°. Reaction with hydrogen chloride at 100° converts the diphosphoxane to the phosphinous acid $(CF_3)_2P{\cdot}OH$ in 92% yield (*84a*):

$$(CF_3)_2P{\cdot}O{\cdot}P(CF_3)_2 + HCl \xrightarrow{100°} (CF_3)_2P{\cdot}OH + (CF_3)_2PCl \qquad (88)$$

The acidity of $(CF_3)_2P{\cdot}OH$ is demonstrated by the formation of the stable, nonvolatile, salt $[(CH_3)_3NH]^+[(CF_3)_2P{\cdot}O]^-$ from which 81% of the original phosphinous acid can be liberated by treatment with hydrogen chloride.

e. Halogenotrifluoromethylphosphines. Iodobistrifluoromethyl- and diiodotrifluoromethyl-phosphine are oily liquids (colorless and yellow, respectively) which fume in air, readily attack mercury at room temperature (see Section VI,A,*2*,*c*), and liberate iodine on exposure to light. Neither has a hydrocarbon analog. The monoiodo compound is spontaneously inflammable in an excess of air. Both compounds disproportionate when heated, the following equilibria being set up (*17*):

$$2(CF_3)_2PI \rightleftharpoons (CF_3)_3P + CF_3{\cdot}PI_2 \qquad (89a)$$

$$2CF_3{\cdot}PI_2 \rightleftharpoons (CF_3)_2PI + PI_3 \qquad (89b)$$

$$(CF_3)_3P + I_2 \rightleftharpoons (CF_3)_2PI + CF_3I \qquad (89c)$$

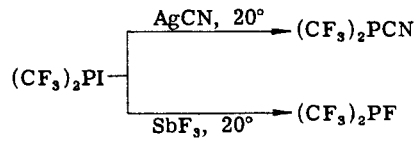
Thus, when iodobistrifluoromethylphosphine is heated in a sealed tube for 48 hours at 205°, it is converted into a mixture of the compounds $(CF_3)_3P$, $CF_3{\cdot}PI_2$, CF_3I, PI_3, C_2F_6, and unchanged $(CF_3)_2PI$ (47%). Diiodotrifluoromethylphosphine after 48 hours at 240° yields a mixture of the compounds $(CF_3)_3P$, $(CF_3)_2PI$, CF_3I, PI_3, and unchanged $CF_3{\cdot}PI_2$ (13%).

It has already been noted that the iodophosphines are reactive. When they are treated with silver halides almost quantitative yields of the corresponding halogen compounds are formed (*17*), e.g.,

$$(CF_3)_2PI \xrightarrow{AgCl,\ 20°} (CF_3)_2PCl \qquad (90)$$

$$CF_3{\cdot}PI_2 \xrightarrow{AgCl,\ 20\text{-}100°} CF_3{\cdot}PCl_2 \qquad (91)$$

The monoiodo compound is readily converted into cyanobistrifluoromethylphosphine and fluorobistrifluoromethylphosphine (*17*, *35*):



(92)

Cyanobistrifluoromethylphosphine is a colorless, spontaneously inflammable liquid.

Iodobistrifluoromethylphosphine reacts with phosphine in the gas phase at 20° and ~300 mm to give phosphonium iodide, phosphorus iodide and bistrifluoromethylphosphine (*86*).

Chlorobistrifluoromethylphosphine is a spontaneously inflammable liquid which does not attack mercury. It combines with chlorine at low temperatures to form bistrifluoromethylphosphorus trichloride, a colorless liquid which fumes in air and has an odor like that of phosphorus pentachloride. Bistrifluoromethylphosphinic azide, $(CF_3)_2PN_3$, is obtained in ~70% yield when $(CF_3)_2PCl$ is treated with lithium azide at 0°C (*192*). This phosphinic azide can undergo explosive decomposition even at −196°, but controlled decomposition has been achieved at 50–60°/37 mm to yield a polymeric bistrifluoromethylphosphonitrile:

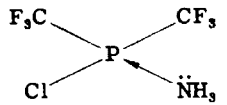
$$n(CF_3)_2PN_3 \xrightarrow{\Delta} [(CF_3)_2P{\cdot}N]_n + nN_2. \tag{93}$$

The phosphonitrile liberates fluoroform when treated with aqueous base.

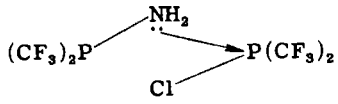
f. Aminobistrifluoromethylphosphine. Chlorobistrifluoromethylphosphine reacts readily with ammonia, methylamine, dimethylamine, and aniline to give good yields of the aminophosphines $(CF_3)_2P{\cdot}NH_2$, $(CF_3)_2P{\cdot}NHCH_3$, $(CF_3)_2P{\cdot}N(CH_3)_2$, and $(CF_3)_2P{\cdot}NHC_6H_5$ (*86*). These amino compounds are colorless liquids which are readily oxidized in air. They are stable in sealed Pyrex tubes at 0°, and do not react with mercury. It is not possible to obtain the compound $(CF_3)_2P{\cdot}NH{\cdot}P(CF_3)_2$ by increasing the ratio $(CF_3)_2PCl:NH_3$ in a vapor-phase reaction. This has been explained by assuming that in the reaction

$$(CF_3)_2PCl + 2NH_3 \rightarrow (CF_3)_2P{\cdot}NH_2 + NH_4Cl \tag{94}$$

an intermediate complex A is formed which later loses hydrogen chloride to give the amino compound. The strong inductive effect of the trifluoromethyl groups in this last compound then prevents the formation of a complex of the type B and hence no further reaction occurs (*86*).



(A)



(B)

However, it is not necessary to postulate the formation of a complex of type A, but merely to assume that the reaction proceeds by a normal S_N2-type displacement at the phosphorus. On this basis, further reaction of $(CF_3)_2P{\cdot}NH_2$ with more chlorophosphine is inhibited because the amino compound will show only weak nucleophilic character due to the decreased basicity of the nitrogen.

An alternative but less satisfactory method for the preparation of aminobistrifluoromethylphosphine involves the slow ammonolysis of tristrifluoromethylphosphine at $-70°$ (*86*):

$$(CF_3)_3P + NH_3 \rightarrow (CF_3)_2P{\cdot}NH_2 + CHF_3 \qquad (95)$$

Aminobistrifluoromethylphosphine is not obtained when iodobistrifluoromethylphosphine and sodamide are allowed to interact, and this contrasts with the behavior of the phosphorus halides, which react readily with sodamide. The reaction of ammonia with alkylhalogenophosphines has not been reported, and compounds of the type $R_2P{\cdot}NH_2$ have not been described.

Aminobistrifluoromethylphosphine (b.p. 67°) is considerably less volatile than tristrifluoromethylphosphine (b.p. 16°) or chlorobistrifluoromethylphosphine (b.p. 21°), and this, coupled with the high value of Trouton's constant (25.2), may imply that association is present in the liquid phase due to the presence of hydrogen bonds (—F · · · · H—N<). The amino compound is unaffected by the action of heat *in vacuo* up to 250°, above which it decomposes with the formation of fluoroform, phosphorus fluorides, nitrogen, and hydrogen cyanide. The hydrolysis of aminobistrifluoromethylphosphine is discussed later (Section VI,A,*5*,*a*). Hydrogen chloride reacts vigorously with the compound at $-64°$ to yield chlorobistrifluoromethylphosphine:

$$(CF_3)_2P{\cdot}NH_2 + 2HCl \rightarrow (CF_3)_2PCl + NH_4Cl \qquad (96)$$

Chlorine attacks the P—N bond of the aminophosphine to yield a mixture of $(CF_3)_2PCl_3$, CF_3Cl, ammonium chloride, and unchanged $(CF_3)_2P{\cdot}NH_2$. It might be considered that the hydrogen atoms in $(CF_3)_2P{\cdot}NH_2$ should be acidic [compare the behavior of sulfamide, which forms a silver salt, $(AgNH)_2SO_2$]. However, salts $(CF_3)_2P{\cdot}NHM$ (M = Na, Ag) have not been found, and the only evidence for the acidic nature of the hydrogens is that solutions of the amino compound in pyridine are better electrolytes than the pure solvent ($\kappa_{solv.} = 1.07 \times 10^{-6}$ ohm^{-1} cm^{-1}; $\kappa_{soln.} = 5.6 \times 10^{-6}$ ohm^{-1} cm^{-1}, $\lambda_m = 0.03$ ohm^{-1} cm^2 mole^{-1}). This may possibly be attributed to the existence in solution of $[(CF_3)_2P{\cdot}NH]^-$ $[C_5H_5NH]^+$ ion pairs (*86*). In the same connection, dimethylaminobistrifluoromethylphosphine does not form a quaternary salt with methyl iodide, which again indicates the absence of basic character for the nitrogen.

Chlorobistrifluoromethylphosphine and hydrogen sulfide do not react together at 20° (vapor phase) or at 76° (liquid phase) (*86*).

3. Heptafluoro-n-propyl Phosphorus Compounds

The halogenoheptafluoropropylphosphines (*65*) have received far less attention than the trifluoromethyl compounds. Iodobisheptafluoro-*n*-propylphosphine and heptafluoro-*n*-propyldiiodophosphine are yellow liquids which disproportionate and decompose when heated at 220° in sealed tubes, but without yielding trisheptafluoro-*n*-propylphosphine [cf. $(CF_3)_2PI$, $CF_3 \cdot PI_2$, Section VI,A,*2*,*e*].

$$(C_3F_7)_2PI \xrightarrow{220°/48\ hr} (C_3F_7)_2PI(75\%), C_3F_7 \cdot PI_2(2\%), C_3F_7I(16\%), PI_3 \quad (97)$$

$$C_3F_7 \cdot PI_2 \xrightarrow{220°/48\ hr} C_3F_7 \cdot PI_2(18\%), (C_3F_7)_2PI(36\%), C_3F_7I(16\%), PI_3 \quad (98)$$

Silver chloride converts the iodo compounds quantitatively into the corresponding chloro compounds, $(C_3F_7)_2PCl$ and $C_3F_7 \cdot PCl_2$. These disproportionate less readily than their iodo precursors. The monochloro derivative adds chlorine at low temperatures to form bisheptafluoro-*n*-propylphosphorus trichloride, $(C_3F_7)_2PCl_3$, which decomposes at 125° to a mixture of chlorobisheptafluoro-*n*-propylphosphine and 1-chloroheptafluoropropane. The compound $(C_3F_7)_2PCl$ also reacts with ammonia to give aminobisheptafluoro-*n*-propylphosphine, and with ethyl alcohol to give ethylbisheptafluoro-*n*-propylphosphinite:

$$(C_3F_7)_2PCl + 2NH_3 \rightarrow (C_3F_7)_2P \cdot NH_2 + NH_4Cl \quad (99)$$

$$(C_3F_7)_2PCl + C_2H_5OH \rightarrow (C_3F_7)_2P \cdot OC_2H_5 + HCl \quad (100)$$

The reaction of mercury with bisheptafluoro-*n*-propyliodophosphine yields a colorless liquid which, by analogy with the corresponding reaction with iodobistrifluoromethylphosphine, should be tetrakisheptafluoro-*n*-propyldiphosphine.

The main difference between the heptafluoro-*n*-propyl- and trifluoromethyl-phosphines, apart from volatility, lies in the slower hydrolysis of the former (see Section VI,A,*5*,*a*; *5*,*b*).

4. Electrolytic Conductance of Solutions of Halogenotrifluoromethylphosphines (66)

Many derivatives of phosphine readily add a halogen molecule to produce, formally at least, a compound in which a phosphorus(V) atom is covalently bound to five univalent atoms or groups:

$$PX_3 + Y_2 \rightarrow PX_3Y_2 \quad (101)$$

When these atoms or groups are electron-attracting, the pentavalent phosphorus compound may, under certain conditions, exhibit ionic properties. A simple example of this dual behavior is afforded by phosphorus pentachloride, which exists as trigonal bipyramidal molecules in the vapor phase and as ions PCl_4^+ PCl_6^- in the solid state; these ions are also present in solutions of phosphorus pentachloride in solvents of high dielectric constant. When X is an electronegative organic group (e.g., phenoxy), the adduct may also dissociate ionically. Thus, the following equilibria occur in acetonitrile:

$$2(C_6H_5\cdot O)_3P + 2Br_2 \rightleftharpoons 2(C_6H_5\cdot O)_3PBr_2 \rightleftharpoons [(C_6H_5\cdot O)_3PBr]^+ + [(C_6H_5\cdot O)_3PBr_3]^- \quad (102)$$

This knowledge has prompted an investigation aimed at determining whether the pseudohalogen character of the trifluoromethyl group will enable halogenotrifluoromethylphosphines to follow the general pattern outlined above for P(V) halides and related compounds. Tristrifluoromethylphosphorus dichloride, $(CF_3)_3PCl_2$ was found to be a conductor and bistrifluoromethylphosphorus trichloride, $(CF_3)_2PCl_3$, a nonconductor in acetonitrile, a solvent which has been widely used as an ionizing medium for nonmetallic halides and polyhalides. By analogy, the following ionization is suggested:

$$2(CF_3)_3PCl_2 \rightleftharpoons [(CF_3)_3PCl]^+ + [(CF_3)_3PCl_3]^- \quad (103)$$

Attempts to prepare tristrifluoromethylphosphorus dibromide, $(CF_3)_3PBr_2$, failed, but conductometric titration evidence suggested that an ionic compound having this formula does exist in acetonitrile solutions.

A reason for the difference in behavior of the two chlorotrifluoromethylphosphoranes has been advanced on the basis of a study of the C—F stretching region in their infrared spectra. Bistrifluoromethylphosphorus trichloride appears to have a symmetrical bipyramidal structure in which the apices are occupied by trifluoromethyl groups, and it has been postulated that a phosphorus pentahalide ionizes in a suitable medium via heterolytic fission of an apical bond. This, together with the fact that the CF_3^- ion has not been observed in any system to date is suggested as an explanation of the nonionic behavior of bistrifluoromethylphosphorus trichloride. The infrared spectrum of the dichloro analog does not lead to the assignment of a definite structure to the compound. It seems probable that this compound exists in a mixture of configurations, at least one of which contains an apical phosphorus-chlorine bond which is the site of ionization.

5. The Hydrolysis of Perfluoroalkyl Derivatives of Phosphorus

a. Trifluoromethyl Compounds. The compounds $(CF_3)_3P$, $(CF_3)_2PX$, $CF_3\cdot PX_2$ (X = F, Cl, Br, I, or CN) are hydrolyzed to fluoroform rapidly and quantitatively at room temperature (*17, 18, 19*):

$$(CF_3)_3P \xrightarrow{NaOH\ aq.} 3CHF_3 \quad (104)$$

$$(CF_3)_2PX \xrightarrow{NaOH\ aq.} 2CHF_3 \quad (105)$$

$$CF_3 \cdot PX_2 \xrightarrow{NaOH\ aq.} CHF_3 \quad (106)$$

This reaction, which has been of great analytical value because fluoroform is a gas, b.p. −84°, and so can be easily estimated, has no counterpart among the alkyl phosphorus compounds. In sharp contrast, hydrolysis of tetrakistrifluoromethyldiphosphine yields only three moles of fluoroform, and one trifluoromethyl group is broken down to fluoride, carbonate, and a trifluoromethyl phosphorus acid:

$$(CF_3)_2P \cdot P(CF_3)_2 \xrightarrow{NaOH\ aq.} 3CHF_3,\ F^-,\ CO_3^=,\ CF_3 \cdot P\ acid \quad (107)$$

The destruction of a fluorocarbon group under such mild conditions is rare in fluorine chemistry, and the reaction has been investigated in some detail (*19*). It is now clear that the hydrolysis of tetrakistrifluoromethyldiphosphine involves the initial fission of the P—P bond:

$$(CF_3)_2P \cdot P(CF_3)_2 \xrightarrow{NaOH\ aq.} (CF_3)_2PH + (CF_3)_2P \cdot OH \quad (108)$$

The acid $(CF_3)_2P \cdot OH$ is the intermediate formed when iodobistrifluoromethylphosphine is hydrolyzed by base, and is thus known to liberate two moles of fluoroform:

$$(CF_3)_2PI \xrightarrow{NaOH\ aq.} (CF_3)_2P \cdot OH \xrightarrow{NaOH\ aq.} 2CHF_3 \quad (109)$$

It follows that bistrifluoromethylphosphine should decompose in basic solution to give one trifluoromethyl group as fluoroform and one trifluoromethyl group as a trifluoromethyl phosphorus acid and fluoride and carbonate. This has been confirmed experimentally (*19*), and there is no doubt as to the course of the hydrolysis of tetrakistrifluoromethyldiphosphine.

Support for this scheme is given by the reaction of the tetrakis compound with water or dilute acid at 100°. Half of the fluorine appears as fluoroform, and both trifluoromethylphosphine and bistrifluoromethylphosphine are produced. Fluoroform arises by decomposition of bistrifluoromethylphosphinous acid to give trifluoromethylphosphonous acid, and the subsequent decomposition of the latter at 100°:

$$\begin{array}{ccccc} (CF_3)_2P \cdot P(CF_3)_2 & \xrightarrow{H_2O} & (CF_3)_2PH & + & (CF_3)_2POH \\ & & \downarrow H_2O,\ 100° & & \downarrow H_2O,\ 100° \\ & & CF_3 \cdot PH_2 + F^- + CO_3^= & & CHF_3 + CF_3 \cdot PHO(OH) \\ & & & & \downarrow H_2O,\ 100° \\ & & & & CHF_3 \end{array} \quad (110)$$

The only partial decomposition of bistrifluoromethylphosphine, to give trifluoromethylphosphine (1 mole), fluoride and carbon dioxide, but no fluoroform, accounts for the liberation of 3 moles of fluoroform when tetrakistrifluoromethyldiphosphine is treated with aqueous alkali, and of only 2 moles when heated with water.

The aminotrifluoromethylphosphines are unstable to hydrolytic agents, which bring about rupture of the P—N bond as well as one or both of the P—C bonds (*86*). Aminobistrifluoromethylphosphine is hydrolyzed by water and dilute acid at 20° with liberation of one mole of fluoroform:

$$(CF_3)_2P{\cdot}NH_2 + 2H_2O \rightarrow CF_3{\cdot}PHO(ONH_4) + CHF_3 \quad (111)$$

$$(CF_3)_2P{\cdot}NH_2 + HCl + 2H_2O \rightarrow CF_3{\cdot}PHO(OH) + NH_4Cl + CHF_3 \quad (112)$$

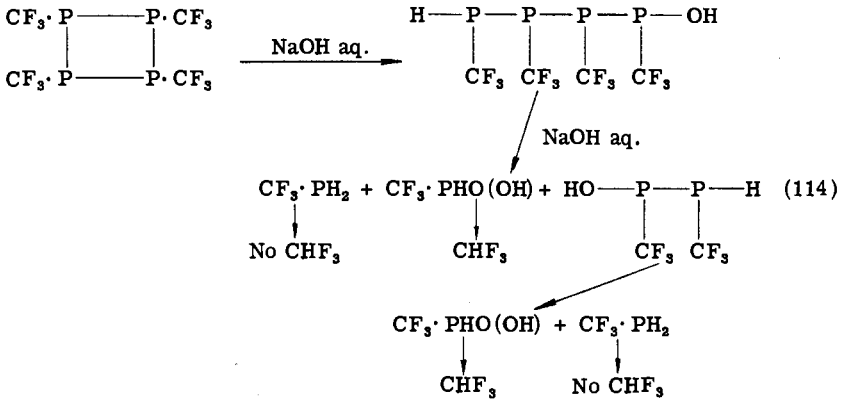
Alkaline hydrolysis at 20° removes two trifluoromethyl groups quantitatively as fluoroform:

$$(CF_3)_2P{\cdot}NH_2 + 2NaOH + H_2O \rightarrow Na_2HPO_3 + NH_3 + 2CHF_3 \quad (113)$$

The aminophosphines $(CF_3)_2P{\cdot}NHMe$, $(CF_3)_2P{\cdot}NMe_2$, and $(CF_3)_2P{\cdot}NHPh$ undergo similar alkaline hydrolysis at 80–100°, but only in the case of the last compound is aqueous hydrolysis at 20° quantitative.

The compounds $(CF_3)_3P{\cdot}Ni(CO)_3$ and $[(CF_3)_3P]_2Ni(CO)_2$ are readily hydrolyzed by an excess of aqueous alkali at 100°, all the fluorine appearing as fluoroform (*64*).

Tetrakistrifluoromethylcyclotetraphosphine is hydrolyzed by aqueous alkali at room temperature with the liberation of 2 moles of fluoroform (*154*). This result is expected if the $CF_3{\cdot}P$ units are equally and quantitatively converted into trifluoromethylphosphine and trifluoromethylphosphonous acid; the first of these yields no fluoroform, while the second produces 1 mole of fluoroform (see above):



(114)

The pentamer is hydrolyzed by aqueous alkali with liberation of 2.5 of its trifluoromethyl groups as fluoroform by a similar process (*154*). The

aqueous hydrolyses of the tetramer and pentamer have already been noted (Section VI,A,*2*,*c*).

b. Heptafluoro-n-propyl compounds. Heptafluoro-*n*-propylphosphines are more resistant to hydrolysis than the trifluoromethylphosphines, but the broad picture is very similar (*65*). Again, hydrolysis plays a major role in the analysis of these compounds, aided by the volatility of heptafluoropropane (b.p. $-18°$).

c. Mixed methyl-trifluoromethyl compounds. Investigation of the aqueous alkaline hydrolysis of the compounds $(CH_3)_3M$, $CF_3{\cdot}M(CH_3)_2$, $(CF_3)_2M{\cdot}CH_3$, and $(CF_3)_3M$ (M = P, As, or Sb) (*107*, *108*) shows that: (*a*) the trimethyl compounds are stable under the conditions used; (*b*) all the trifluoromethyl compounds yield fluoroform quantitatively with 15–20% aqueous sodium hydroxide at 20°; (*c*) for a given M the rate of hydrolysis increases markedly with the number of trifluoromethyl groups attached to M; (*d*) for a given number of trifluoromethyl groups in the compound the rate of hydrolysis increases in the order P < As < Sb. For compounds of the type $CF_3{\cdot}M(CH_3)_2$, the difference in the rates of hydrolysis of the arsenic and antimony compounds is much greater than the difference between the phosphorus and arsenic compounds.

The hydrolysis results are consistent with initial nucleophilic attack by hydroxide ion on the central atom; increase in the number of trifluoromethyl groups attached to M and/or increase in the electropositive character of M facilitate hydrolysis. Conversely, basicity is reduced. Thus trimethylphosphine gives a stable silver iodide complex, dimethyltrifluoromethylphosphine gives a readily dissociated complex, and methylbistrifluoromethylphosphine and tristrifluoromethylphosphine are virtually nonbasic in this sense (*107*). Neither tristrifluoromethylphosphine nor methylbistrifluoromethylphosphine form stable complexes with boron trifluoride, and the former phosphine does not coordinate with platinous chloride. In contrast, the compounds $(CH_3)_3P,BF_3$; $(CF_3)(CH_3)_2P,BF_3$; $[(CH_3)_3P]_2PtCl_2$; $[(CF_3)(CH_3)_2P]_2PtCl_2$; and $[(CF_3)_2(CH_3)P]_2PtCl_2$ have been isolated and characterized (*16*). Basicity decreases in the order P > As > Sb as shown by the ease of formation of quaternary compounds with methyl iodide at room temperature [e.g., $CF_3{\cdot}P(CH_3)_2$ reacts much faster than $CF_3{\cdot}As(CH_3)_2$], by the formation of compounds with carbon disulfide, and by complex-formation with silver iodide [e.g., $CF_3{\cdot}P(CH_3)_2$ gives a silver iodide complex; $CF_3{\cdot}As(CH_3)_2$ does not]. Trifluoromethyl derivatives of arsenic and antimony are very weak bases.

6. Perfluoroalkyl Phosphorus Acids

a. Trifluoromethyl compounds (*18*, *19*, *63*). Trifluoromethylphosphonous acid, $CF_3{\cdot}P(OH)_2$, is produced when the iodo compounds are treated with water:

$$CF_3{\cdot}PI_2 \xrightarrow{H_2O} CF_3{\cdot}P(OH)_2 \quad (115)$$

$$(CF_3)_2PI \xrightarrow{H_2O} (CF_3)_2P{\cdot}OH \xrightarrow{H_2O} CF_3{\cdot}P(OH)_2 + CHF_3 \quad (116)$$

The phosphonous acid has not been isolated in the pure state, since it disproportionates when it is heated in concentrated aqueous solution:

$$3CF_3{\cdot}P(OH)_2 \rightarrow CF_3{\cdot}PH_2 + 2CF_3{\cdot}PO(OH)_2 \quad (117)$$

Trifluoromethylphosphonous acid co-distils with water at low pressure, is monobasic, and yields fluoroform when its dilute aqueous solutions are heated or treated with an excess of alkali. The acid is, in fact, $CF_3{\cdot}PHO(OH)$, and as expected has reducing properties, although it is weaker in this respect than phosphorous or methylphosphonous acids. Infrared spectroscopic examination of its monosodium salt, which can be isolated as a stable solid, shows that the structure of this salt is $CF_3{\cdot}PH(:O)(ONa)$ rather than $CF_3{\cdot}P(OH)(ONa)$.

Oxidation of solutions of trifluoromethylphosphonous acid with hydrogen peroxide yields the white, crystalline trifluoromethylphosphonic acid, $CF_3{\cdot}PO(OH)_2$. This acid is dibasic, and is one of the strongest acids of phosphorus known (see Table IX).

TABLE IX
pK VALUES FOR SOME ACIDS OF PHOSPHORUS

Compound	pK_1	pK_2
Pyrophosphoric acid, $H_4P_2O_7$	0.85	1.96
Trifluoromethylphosphonic acid, $CF_3{\cdot}PO(OH)_2$	1.16	3.93
Phosphorous acid, H_3PO_3	1.80	6.15
Methyl dihydrogen phosphate, $CH_3O{\cdot}PO(OH)_2$	1.54	6.31
Ethyl dihydrogen phosphate, $C_2H_5O{\cdot}PO(OH)_2$	1.60	6.62
Trichloromethylphosphonic acid, $CCl_3{\cdot}PO(OH)_2$	1.63	4.81
Phosphoric acid, H_3PO_4	1.97	6.82
Phenylphosphonic acid, $C_6H_5{\cdot}PO(OH)_2$	2.2	—
Methylphosphonic acid, $CH_3{\cdot}PO(OH)_2$	2.48	7.34
Ethylphosphonic acid, $C_2H_5{\cdot}PO(OH)_2$	2.45	7.85

Bistrifluoromethylphosphinous acid, $(CF_3)_2P{\cdot}OH$, is unstable in aqueous solution and decomposes immediately to give $CF_3{\cdot}P(OH)_2$ and fluoroform.

Bistrifluoromethylphosphinic acid, $(CF_3)_2PO(OH)$, is a stable liquid and is readily prepared by the sequences:

$$(CF_3)_2PI \xrightarrow{AgCl} (CF_3)_2PCl \xrightarrow{Cl_2} (CF_3)_2PCl_3 \xrightarrow{H_2O} (CF_3)_2PO(OH) \quad (118)$$

or

$$(CF_3)_3P \xrightarrow{Cl_2} (CF_3)_3PCl_2 \xrightarrow{H_2O} [(CF_3)_3P(OH)_2] \rightarrow (CF_3)_2PO(OH) + CHF_3 \quad (119)$$

This monobasic acid is the strongest of the known acids of phosphorus and is in marked contrast to its methyl analog, as shown in Table X. Bistri-

TABLE X

$CF_3 \cdot P(OH)_2$	$K = 9.8 \times 10^{-2}$	$CH_3 \cdot PHO(OH)$	—
$CF_3 \cdot PO(OH)_2$	$K_1 = 6.8 \times 10^{-2}$	$CH_3 \cdot PO(OH)_2$	$K_1 = 4.2 \times 10^{-3}$
	$K_2 = 1.2 \times 10^{-4}$		$K_2 = 1.8 \times 10^{-8}$
$(CF_3)_2PO(OH)$	$K = >10^{-1}$	$(CH_3)_2PO(OH)$	$K = 8.3 \times 10^{-4}$
cf. H_3PO_4	$K_1 = 7.5 \times 10^{-3}$,	$K_2 = 6.2 \times 10^{-8}$,	$K_3 = 4.8 \times 10^{-13}$
H_3PO_3	$K_1 = 1.6 \times 10^{-2}$,	$K_2 = 7 \times 10^{-7}$	

fluoromethylphosphinic acid liberates only 1 mole of fluoroform when treated with an excess of aqueous base, since the alkali-stable trifluoromethylphosphonic acid is thereby produced:

$$(CF_3)_2PO(ONa) \xrightarrow{\text{NaOH aq.}} CF_3 \cdot PO(ONa)_2 + CHF_3 \qquad (120)$$

Since $CF_3 \cdot PO(OH)_2$ and $(CF_3)_2PO(OH)$ are highly ionized in aqueous solution, their strengths cannot easily be compared with those of other acids. The conductivities of a whole series of acids in anhydrous acetic acid have been measured in order to make such comparisons possible. The weaker acids are incompletely ionized in acetic acid as solvent, and this reveals the spread in acid strength. The results are expressed graphically in Fig. 2, and the order of acid strengths is

$$HClO_4 > (CF_3)_2PO(OH) > H_2SO_4 > CF_3 \cdot PO(OH)_2, HCl$$

Bistrifluoromethylphosphinic acid is thus one of the strongest acids known.

It must not be assumed from a consideration of the facile loss of fluoroform from certain of the derivatives of phosphorus mentioned above [$(CF_3)_3P$; $(CF_3)_2PX$ (X = I, CN, or Cl); $CF_3 \cdot PX_2$ (X = I or Cl); $CF_3 \cdot P(OH)_2$; $(CF_3)_2P \cdot OH$; $(CF_3)_2PO(OH)$] that the C—Z bond in a compound CF_3—Z is always susceptible to hydrolytic attack. On the contrary, the CF_3—Z bond is usually very resistant to hydrolytic attack, as exemplified by the compounds CF_3I, $CF_3 \cdot CO_2H$, $(CF_3)_3N$, $CF_3 \cdot SF_5$, $CF_3 \cdot [CF_2]_n \cdot CF_3$, and $(CF_3)_2S$. Trifluoromethylphosphonic acid is at present the only trifluoromethyl derivative of phosphorus known to have a marked resistance to hydrolysis. Decomposition of the CF_3 group to fluoride and carbonate is unusual in fluorine chemistry, but is found with $CF_3 \cdot OF$, $(CF_3)_2NH$, $(CF_3)_2O_2$, and $CF_3 \cdot SH$, as well as with $(CF_3)_2PH$, as noted above.

b. Heptafluoro-n-propyl Compounds (65). Heptafluoro-*n*-propylphosphonous acid, $C_3F_7 \cdot PHO(OH)$, is conveniently prepared by the action of

water on dichloroheptafluoro-*n*-propylphosphine. It is a strong monobasic acid which can be oxidized by aqueous hydrogen peroxide to heptafluoro-*n*-propylphosphonic acid, isolated as a dihydrate $C_3F_7{\cdot}PO(OH)_2{,}2H_2O$.

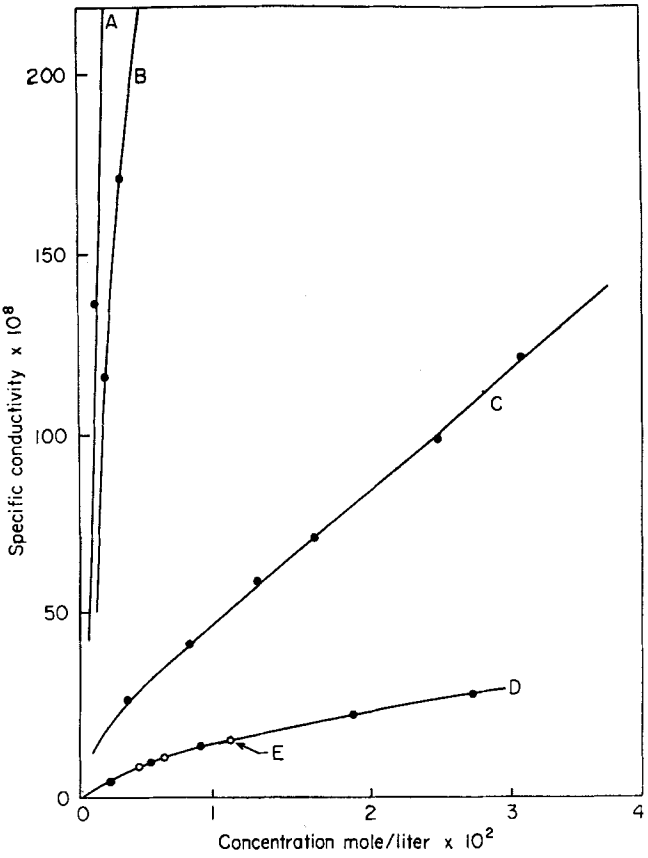


FIG. 2. Conductivities in acetic acid. (*A*) $HClO_4$; (*B*) $(CF_3)_2PO(OH)$; (*C*) H_2SO_4; (*D*) $CF_3{\cdot}PO(OH)_2$; (*E*) HCl.

Heptafluoro-*n*-propylphosphonic acid is a strong acid ($pK_1 = 0.9$, $pK_2 = 3.96$), and is stable to aqueous alkaline hydrolysis at 125°. Bisheptafluoro-*n*-propylphosphinic acid is prepared from bisheptafluoro-*n*-propylphosphorus trichloride by addition of the stoichiometric amount of water:

$$(C_3F_7)_2PCl_3 \rightarrow (C_3F_7)_2PO(OH) \qquad (121)$$

It is a white deliquescent solid which sublimes without decomposition at 66–68° *in vacuo* and is a strong monobasic acid.

7. Trifluoromethylphosphinoborines

The high chemical and thermal stability of the cyclic dimethylphosphinoborine trimer $[(CH_3)_2P{\cdot}BH_2]_3$ led to the suggestion that in this compound the P—B dative σ-bond is supplemented by weak multiple π-bonding in which the B—H bonding electrons enter the phosphorus *d*-levels (*31*). If this is the case, then this supplementary bonding will increase in importance if the methyl groups attached to the phosphorus atom are replaced by more electronegative groups. At the same time, however, the P—B bond will be weakened through decrease in donor properties of the phosphorus atom. The net result when the methyl groups are replaced by trifluoromethyl groups is a weakening of the ring structure, but the moderate stability of $[(CF_3)_2P{\cdot}BH_2]_3$ does show that nonclassical bonds are of great importance in determining stability.

The air-stable, solid trimer $[(CF_3)_2P{\cdot}BH_2]_3$ is prepared by the reaction of diborane with either fluorobistrifluoromethylphosphine or bistrifluoromethylphosphine (*35*). The reaction with bistrifluoromethylphosphine, which can be catalyzed by dimethyl ether, also yields traces of a tetramer $[(CF_3)_2P{\cdot}BH_2]_4$:

$$(CF_3)_2PH + B_2H_6 \xrightarrow{22°,\ CH_3{\cdot}O{\cdot}CH_3} [(CF_3)_2P{\cdot}BH_2]_3,\ [(CF_3)_2P{\cdot}BH_2]_4,\ (CF_3)_2P{\cdot}CH_3,\ B(OCH_3)_3,\ CH_4,\ H_2 \quad (122)$$

The trimer is stable at 155° *in vacuo*, but decomposes at 200° with the formation of boron trifluoride, fluoroform, and a brown solid of unknown structure. It is attacked very slowly by hydrogen chloride at 150°, but is decomposed quantitatively by methanolic hydrogen chloride at 85°:

$$[(CF_3)_2P{\cdot}BH_2]_3 \xrightarrow{HCl/CH_3OH,\ 85°} (CF_3)_2PH,\ B(OCH_3)_3,\ CH_3Cl,\ H_2 \quad (123)$$

Aqueous sodium hydroxide decomposes the trimer at room temperature and fluoroform is liberated. The tetramer (m.p. 116°) is decomposed by methanolic hydrogen chloride at 93°.

By comparison, the solid trimer $[(CH_3)_2P \cdot BH_2]_3$, is stable to moist air, water, or concentrated sodium hydroxide at 100°, and hydrochloric acid at 240°, but is decomposed by hydrogen chloride or hydrochloric acid at 300° (*31*):

$$[(CH_3)_2P{\cdot}BH_2]_3 \xrightarrow{HCl\ aq.,\ 300°} (CH_3)_2PO(OH),\ B(OH)_3,\ H_2 \quad (124)$$

This trimer begins to decompose at 400°, and is destroyed at 510° with the production of elementary phosphorus and methyl boranes.

The physical properties of the polyfluoroalkyl derivatives of phosphorus are listed in Table XI (pages 388–389).

B. Arsenic

Only the trifluoromethyl derivatives of arsenic have been studied in any detail; their reactions parallel those of the phosphorus analogs, with some differences which can be related to the relative positions of arsenic and phosphorus in the Periodic Table. Again, as in the case of phosphorus, the perfluoroalkyl iodides have played the major role in the preparation of these compounds, but there is evidence that fluoroolefins may prove to be important in this respect.

1. Preparation of Polyfluoroalkyl Arsenic Compounds

The normal methods used for the preparation of organoarsenic compounds from alkyl iodides (e.g., by reaction with sodium arsenide) are, in general, not applicable to the polyfluoroalkyl compounds. However, finely powdered arsenic reacts with trifluoroiodomethane at 220–240° in a stainless steel autoclave or glass Carius tube to yield tristrifluoromethylarsine, $(CF_3)_3As$, iodobistrifluoromethylarsine, $(CF_3)_2AsI$, and diiodotrifluoromethylarsine, $CF_3{\cdot}AsI_2$ in the ratio 6:2:1 by weight (*27*, *61*, *200*). There is evidence that the following equilibria are set up in this reaction:

$$2(CF_3)_2AsI \rightleftharpoons (CF_3)_3As + CF_3{\cdot}AsI_2 \quad (125a)$$

$$2CF_3{\cdot}AsI_2 \rightleftharpoons (CF_3)_2AsI + AsI_3 \quad (125b)$$

$$(CF_3)_3As + AsI_3 \rightleftharpoons (CF_3)_2AsI + CF_3{\cdot}AsI_2 + CF_3I + As \quad (125c)$$

At equilibrium, under optimum conditions, the yields of the iodotrifluoromethylarsines are low, but may be increased by using a mixture of arsenic and arsenic triiodide. Arsenic reacts in a similar manner with pentafluoroiodoethane (*5*); at 230° trispentafluoroethylarsine, $(C_2F_5)_3As$, and iodobispentafluoroethylarsine, $(C_2F_5)_2AsI$, are formed. Preliminary experiments (*65*) on the reaction between arsenic and heptafluoroiodopropane at 200–220° have been carried out, but attempts to isolate heptafluoropropyl derivatives of arsenic from the products failed because of the presence of large amounts of fluorocarbons formed in side reactions.

Mixed methyltrifluoromethylarsines $[(CF_3)_nAs(CH_3)_{3-n}]$ can be prepared by: (i) Grignard reactions using methylmagnesium iodide and the iodotrifluoromethylarsines (*61*, *100*); (ii) radical-exchange reactions between tristrifluoromethylarsine and methyl iodide or between trimethylarsine and trifluoroiodomethane (*107*, *108*); and (iii) the coupling of iododimethylarsine or diiodomethylarsine with trifluoroiodomethane in the presence of mercury (*45*).

$$CF_3{\cdot}AsI_2 \xrightarrow{CH_3{\cdot}MgI} CF_3{\cdot}As(CH_3)_2 + (CF_3)(CH_3)AsI \quad (126)$$

$$(CF_3)_2AsI \xrightarrow{CH_3{\cdot}MgI} (CF_3)_2As{\cdot}CH_3 \quad (127)$$

TABLE XI

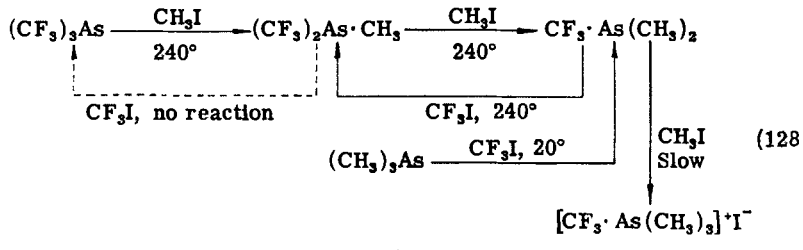
PHYSICAL PROPERTIES OF POLYFLUOROALKYL DERIVATIVES OF PHOSPHORUS

Compound	m.p. (°C)	b.p. (°C/mm Hg)	n_D^t (t °C)	d_4^t (t °C)
$CF_3 \cdot P(CH_3)_2$	—	46.8[a]	—	—
$CF_3 \cdot PH_2$	—	−26.5[a]	—	—
$CF_3 \cdot PCl_2$	—	37	—	—
$CF_3 \cdot PI_2$	—	69/29	1.630 (20)	—
$CF_3 \cdot PCl_4$	−52.5 to −52	104[a]	—	—
$(CF_3)_2P \cdot CH_3$	−104.9 to −104.6	35.2[a]	—	—
$(CF_3)_2PH$	−137.4 to −137	1[a]	—	—
$(CF_3)_2POH$	−21.3 to −21.1	61.4[a]	—	—
$(CF_3)_2P \cdot OC_2H_5$	—	74 ± 1[a]	—	—
$(CF_3)_2PF$	−149.9 to −149.6	−11.85[a]	—	—
$(CF_3)_2PCl$	—	21	—	—
$(CF_3)_2PI$	—	72–73	1.403 (15)	—
$(CF_3)_2PCN$	—	48	1.3248 (20)	—
$(CF_3)_2PO(OH)$	—	137–138/238	—	—
$(CF_3)_2P \cdot NH_2$	−87.6	67.1[a]	—	—
$(CF_3)_2P \cdot NHCH_3$	−46.5	73.2[a]	—	—
$(CF_3)_2P \cdot N(CH_3)_2$	−81.5	83.2[a]	—	—
$(CF_3)_2P \cdot NHC_6H_5$	1.7	182.1[a]	—	—
$(CF_3)_2PN_3$	—	57 mm at 0°[b]	—	—
$(CF_3)_2PCl_3$	−26 to −25	82/355	—	—
$(CF_3)_3P$	—	17.3[a]	—	—
$(CF_3)_3PO$	—	23.6[a]	—	—
$(CF_3)_3PCl_2$	24.0–25.5	107[a]	—	—
$CF_3 \cdot PH \cdot PH \cdot CF_3$	—	69.5[a]	—	—
$(CF_3)_2P \cdot P(CF_3)_2$	—	83–84	—	—
$(CF_3)_2P \cdot O \cdot P(CF_3)_2$	−53.1 to −52.6	78.3[a]	—	—
$(CF_3 \cdot P)_4$	66.3–66.4	145[a]	—	1.54 (66.4)

$(CF_3 \cdot P)_5$	−33	190[a]	—	1.60 (25)
$[(CF_3)_2PN]_n$	90–94	—	—	—
$(CF_3)_3P \cdot Ni(CO)_3$	−71.5 to −70.5	107.5 ± 1[a]	—	—
$[(CF_3)_2P \cdot Ni(CO)_3]_2$	105	0.5 mm at 20°[b]	—	—
$[(CF_3)_3P]_2Ni(CO)_2$	−31.5 to −30	<1 mm at 20°[b]	—	—
$[(CF_3)_2P \cdot BH_2]_3$	30.3–30.4	176.6[a]	—	—
$CHF_2 \cdot PO(OC_2H_5)_2$	—	85.6–86.5/12	—	1.1934 (20)
$CHF_2 \cdot PO(OC_3H_7)_2$	—	89–90/12	1.3870 (20)	1.1153 (20)
$CHF_2 \cdot PO(OC_4H_9)_2$	—	124–125/12	1.4084 (20)	1.0913 (20)
$CHF_2 \cdot CH_2 \cdot PH_2$	—	52–53/758	—	—
$CHF_2 \cdot CF_2 \cdot PH_2$	—	20.7[a]	—	—
$CHFCl \cdot CF_2 \cdot PH_2$	—	67	—	—
$CHCl_2 \cdot CF_2 \cdot PH_2$	—	109.5–110.5	—	—
$(CHF_2 \cdot CF_2)_2PH$	—	91–92	—	—
$(CHFCl \cdot CF_2)_2PH$	—	138–142	—	—
$(CHCl_2 \cdot CF_2)_2PH$	—	180–184	—	—
$H_2P \cdot CF_2 \cdot CF_2 \cdot PH_2$	—	69–72	—	—
$H_2P \cdot CFCl \cdot CF_2 \cdot PH_2$	—	107–109	—	—
$H_2P \cdot CCl_2 \cdot CF_2 \cdot PH_2$	—	ca. 140	—	—
$C_3F_7 \cdot PCl_2$	−90	86.4 ± 1[a]	—	—
$C_3F_7 \cdot PI_2$	−18	190 ± 2[a]	—	—
$(C_3F_7)_2P \cdot OC_2H_5$	−47	140–141[a]	—	—
$(C_3F_7)_2P \cdot NH_2$	−23	143 ± 1[a]	—	—
$(C_3F_7)_2PCl$	−75	118–119[a]	—	—
$(C_3F_7)_2PI$	−108	135[a]	—	—
$(C_3F_7)_2PCl_3$	—	184 ± 2[a]	—	—
$C_3F_6H \cdot PH_2$	—	45–48	—	—
$(CH_3)_2CH \cdot CF_2 \cdot PH_2$	—	75–77	—	—

[a] Calculated from vapor pressure measurements.

[b] Vapor pressure.



(128)

$$CH_3 \cdot AsI_2 + 2Hg + 2CF_3I \xrightarrow{20^\circ} (CF_3)_2As \cdot CH_3 + 2HgI_2 \quad (129)$$

$$(CH_3)_2AsI + Hg + CF_3I \xrightarrow{20^\circ} CF_3 \cdot As(CH_3)_2 + HgI_2 \quad (130)$$

Dimethyltrifluoromethylarsine can also be prepared by the thermal decomposition of dimethyltrifluoroacetoxyarsine, which is prepared from chlorodimethylarsine and silver trifluoroacetate (*47*), and by the interaction of tetramethyldiarsine with trifluoroiodomethane at room temperature (*45*):

$$(CH_3)_2AsCl + CF_3 \cdot CO_2Ag \xrightarrow{60^\circ} CF_3 \cdot CO_2As(CH_3)_2 + AgCl \quad (131a)$$

$$CF_3 \cdot CO_2As(CH_3)_2 \xrightarrow{205^\circ} CF_3 \cdot As(CH_3)_2 + CO_2 \quad (131b)$$

$$(CH_3)_2As \cdot As(CH_3)_2 + CF_3I \xrightarrow{20^\circ} CF_3 \cdot As(CH_3)_2 + (CH_3)_2AsI \quad (132)$$

Reactions of type (iii) above have also been used to prepare heptafluoropropyldimethylarsine (*45*), methylphenyltrifluoromethylarsine, phenylbistrifluoromethylarsine, and diphenyltrifluoromethylarsine (*46*):

$$(CH_3)_2AsI + C_3F_7I \xrightarrow{Hg,\ 20^\circ} C_3F_7 \cdot As(CH_3)_2 \quad (133)$$

$$C_6H_5 \cdot AsI_2 + 2CF_3I \xrightarrow{Hg,\ 20^\circ} (CF_3)_2As \cdot C_6H_5 \quad (134)$$

$$(C_6H_5)_2AsI + CF_3I \xrightarrow{Hg,\ 20^\circ} CF_3 \cdot As(C_6H_5)_2 \quad (135)$$

There is no reaction between tristrifluoromethylarsine and iodobenzene at 240°, and the reaction of trifluoroiodomethane with triphenylarsine at 210° gives a mixture of products which includes fluoroform, benzotrifluoride, benzene, and arsenic triiodide, but no phenyltrifluoromethylarsines (*46*).

Dichloropentafluoroethylarsine has been obtained by the reaction of tetrafluoroethylene with arsenic trichloride in the presence of catalytic amounts of aluminium trichloride (*28*):

$$3CF_2{:}CF_2 + 2AsCl_3 \xrightarrow{AlCl_3,\ 70\text{–}100^\circ} 2CF_3 \cdot CF_2 \cdot AsCl_2 + CF_2{:}CCl_2 \quad (136)$$

The formation of dichloropentafluoroethylarsine (45–50% yield based on C_2F_4) instead of the expected tetrafluoro-β-chloroethyldichloroarsine,

$CF_2Cl{\cdot}CF_2{\cdot}AsCl_2$, [cf. $CH_2{:}CH_2 + AsCl_3 \xrightarrow{AlCl_3} CH_2Cl{\cdot}CH_2{\cdot}AsCl_2$] is explained by the ability of aluminium trichloride to replace fluorine by chlorine in fluorocarbons (*94*, *164*), and the following reaction scheme has been put forward (*28*):

$$CF_2{:}CF_2 + AlCl_3 \rightarrow CF_2{:}CCl_2 + AlF_2Cl \quad (137a)$$

$$CF_2{:}CF_2 + AlF_2Cl + AsCl_3 \rightarrow CF_3{\cdot}CF_2{\cdot}AsCl_2 + AlFCl_2 \quad (137b)$$

$$CF_2{:}CF_2 + 2AlFCl_2 \rightarrow CF_2{:}CCl_2 + 2AlF_2Cl \quad (137c)$$

Apparently, 1,1-dichlorodifluoroethylene does not react with arsenic trichloride under these conditions because the only arsenical produced is dichloropentafluoroethylarsine. Presumably, in step (137b) the compound $CF_2Cl{\cdot}CF_2{\cdot}AsCl_2$ is first produced, then fluorinated by the aluminum chlorodifluoride to yield the pentafluoroethyl derivative. It would be expected, however, that the chlorine atoms attached to the arsenic would be far more likely to undergo halogen-exchange reactions (see Section VI,B,*2*,*c*), and so the above mechanism seems to be inadequate.

2. Properties and Reactions of Polyfluoroalkyl Arsenic Compounds

The physical properties of polyfluoroalkyl arsenic compounds are listed in Table XII.

a. Tristrifluoromethylarsine. Tristrifluoromethylarsine is a colorless, pungent-smelling liquid, b.p. 33.3° [cf. $As(CH_3)_3$, b.p. 49°]. It is soluble in ether but not in water, and is unaffected by 3*N* hydrochloric acid. It does not ignite in air, and shows no tendency toward compound formation with sulfur, carbon disulfide, mercuric chloride, trifluoroiodomethane, or methyl iodide, although it partakes in radical-exchange reactions with the last compound. Methylbistrifluoromethyl- and dimethyltrifluoromethyl-arsine do not form complexes with silver iodide [cf. $CF_3{\cdot}P(CH_3)_2$], but dimethyltrifluoromethylarsine forms a quaternary salt with methyl iodide indicating that the donor properties of the arsenic lone-pair electrons are not completely lost by the introduction of a trifluoromethyl group.

The pyrolysis of tristrifluoromethylarsine at 350–410° in platinum and silica vessels has been studied in detail (*5*). The major volatile product is hexafluoroethane, and this is compatible with the primary fission of the carbon-arsenic bond to give rise to a trifluoromethyl radical which can then dimerize or abstract a similar radical from another arsine molecule:

$$(CF_3)_3As \rightarrow CF_3\cdot + \cdot As(CF_3)_2 \quad (138a)$$

$$CF_3\cdot + CF_3\cdot \rightarrow C_2F_6 \quad (138b)$$

$$CF_3\cdot + (CF_3)_3As \rightarrow C_2F_6 + \cdot As(CF_3)_2 \quad (138c)$$

The reaction is homogeneous, of the first order, and has an activation energy of 57.4 kcal/mole. The activation energy for the homogeneous, first-order

decomposition of trimethylarsine at 400–460° is 54.6 kcal/mole, and if this energy is identified with the dissociation energy of the carbon-arsenic bond it is clear that the replacement of hydrogen by fluorine causes little change

TABLE XII

PHYSICAL PROPERTIES OF POLYFLUOROALKYL DERIVATIVES OF ARSENIC

Compound	m.p. (°C)	b.p. (°C/mm Hg)	n_D^t (t, °C)	d_4^t (t, °C)
$CF_3 \cdot AsH_2$	—	−12.5/753	—	—
$CF_3 \cdot AsCl_2$	—	71	1.431 (20)	—
$CF_3 \cdot AsBr_2$	—	118/745	1.528 (20)	—
$CF_3 \cdot AsI_2$	—	100/48	1.688 (20)	—
$CF_3 \cdot As(CH_3)_2$	—	58.0[a]	—	—
$CF_3 \cdot As(CH_3)(C_6H_5)$	—	186	—	—
$CF_3 \cdot As(C_6H_5)_2$	—	86–88/10^{-3}	—	—
$CF_3 \cdot As(C_6H_5)_2Br_2$	110[c]	—	—	—
$(CF_3)_2AsH$	—	19[a]	—	—
$(CF_3)_2AsF$	—	25	—	—
$(CF_3)_2AsCl$	—	46	1.351 (19)	—
$(CF_3)_2AsBr$	—	59.5/745	1.398 (20)	—
$(CF_3)_2AsI$	—	92	1.425 (25)	—
$(CF_3)_2As \cdot CN$	—	89.5	1.359 (20)	—
$(CF_3)_2As \cdot SCN$	—	117	1.445 (20)	—
$(CF_3)_2As \cdot CH_3$	—	52	—	—
$(CF_3)_2As \cdot C_6H_5$	—	160	—	—
$(CF_3)_2AsCl_3$	—	93–95/722	1.423 (20)	—
$(CF_3)_2AsO_2H$	150[b]/10^{-3}	—	—	—
$(CF_3)_3As$	—	33.3[a]	—	—
$(CF_3)_3AsF_2$	—	57–58	—	—
$(CF_3)_3AsCl_2$	—	98.5	1.386 (19)	—
$(CF_3)_2As \cdot As(CF_3)_2$	—	106–107	1.372 (19)	—
$(CF_3)_2As \cdot O \cdot As(CF_3)_2$	—	95–97[c]	1.3554 (20)	—
$C_2F_5 \cdot AsH_2$	—	26–27	1.331 (20)	—
$C_2F_5 \cdot AsF_2$	—	47–48	1.3472 (20)	2.0754 (20)
$C_2F_5 \cdot AsCl_2$	—	86–87	1.4063 (20)	1.9221 (20)
$(C_2F_5)_2AsI$	—	120	—	—
$(C_2F_5)_3As$	—	96.3	—	—
$C_3F_7 \cdot As(CH_3)_2$	—	93	—	—

[a] Calculated from vapor pressure measurements.

[b] Sublimes with decomposition.

[c] With decomposition.

in the bond dissociation energy. The thermal decomposition of trispentafluoroethylarsine is fundamentally similar to that of the trifluoromethyl compound; at 280° in silica the activation energy for the first-order, homogeneous reaction is 48.0 kcal/mole, and the products are arsenic and a mixture of saturated fluorocarbons in which decafluoro-*n*-butane predominates:

$$(C_2F_5)_3As \xrightarrow{280°} \tfrac{3}{2}C_4F_{10} + As \quad (139)$$

Tristrifluoromethylarsine is decomposed by ultraviolet light to arsenic and hexafluoroethane.

Tristrifluoromethylarsine reacts with nitric oxide or nitrosyl chloride to give very low yields (2–4%) of trifluoronitrosomethane (*128*):

$$(CF_3)_3As + 3NOCl \xrightarrow{100°} 3CF_3 \cdot NO + AsCl_3 \quad (140)$$

$$(CF_3)_3As + 3NO \xrightarrow{\text{ultraviolet light}} 3CF_3 \cdot NO + As \quad (141)$$

b. Bistrifluoromethylarsine and Trifluoromethylarsine. Attempts to prepare trifluoromethylarsine, $CF_3 \cdot AsH_2$, and bistrifluoromethylarsine, $(CF_3)_2AsH$, by the direct action of hydrogen on the compound $(CF_3)_2As$ failed, as did indirect attempts using lithium aluminium hydride (*61*). The thermal reaction of hydrogen with tristrifluoromethylarsine at 220–240° gave fluoroform, and arsenic was deposited as a mirror; this result is to be expected from a consideration of the thermal stabilities of the three arsines. Photochemically-initiated hydrogenation gave similar breakdown products. Iodobistrifluoromethyl- and diiodotrifluoromethyl-arsine can be converted into bistrifluoromethylarsine and trifluoromethylarsine respectively by reduction with lithium aluminium hydride or, in higher yield, by a zinc-copper couple and hydrochloric acid (*61*):

$$(CF_3)_2AsI \xrightarrow{Zn/Cu,\ HCl} (CF_3)_2AsH(43\%) + (CF_3)_2As \cdot As(CF_3)_2(37\%) \quad (142)$$

$$CF_3 \cdot AsI_2 \xrightarrow{Zn/Cu,\ HCl} CF_3 \cdot AsH_2(98\%) \quad (143)$$

Pentafluoroethylarsine has been obtained from the dichloride (*28*):

$$C_2F_5 \cdot AsCl_2 \xrightarrow{Zn,\ HCl\ aq.} C_2F_5 \cdot AsH_2 \quad (144)$$

Bistrifluoromethylarsine decomposes thermally at 220–240° according to the equation:

$$3(CF_3)_2AsH \rightarrow (CF_3)_3As + 2As + 3CHF_3 \quad (145)$$

Trifluoromethylarsine is stable at temperatures up to 220°, but at 330° it decomposes to arsenic, fluoroform, and hydrogen.

c. Halogenoperfluoroalkylarsines. Iodobistrifluoromethyl- and diiodotrifluoromethyl-arsine are yellow oils, which are not inflammable in air, and which are insoluble in, and stable to, water at room temperature. They have been used to synthesize the compounds $CF_3 \cdot AsCl_2$, $(CF_3)_2As \cdot O \cdot As(CF_3)_2$, and $(CF_3)_2AsX$ (X = F, Cl, CN, SCN, OCN) in high yield by reaction with the appropriate silver or mercury salts (*61*, *200*). Iodobistrifluoromethylarsine is converted by reaction with mercury at room tem-

perature into tetrakistrifluoromethyldiarsine, a water-stable liquid, b.p. 106–107° [cf. $(CH_3)_2As{\cdot}As(CH_3)_2$, b.p. ~170°]:

$$2(CF_3)_2AsI + Hg \rightarrow (CF_3)_2As{\cdot}As(CF_3)_2 + HgI_2 \qquad (146)$$

Fission of the As—As bond in tetrakistrifluoromethyldiarsine can be accomplished by heating the latter with trifluoroiodomethane or, less readily, with methyl iodide (*45*):

$$(CF_3)_2As{\cdot}As(CF_3)_2 \xrightarrow[CF_3I,\ 75°]{} (CF_3)_3As + (CF_3)_2AsI \qquad (147)$$
$$(CF_3)_2As{\cdot}As(CF_3)_2 \xrightarrow[CH_3I,\ 105°]{} (CF_3)_2As{\cdot}CH_3 + (CF_3)_2AsI$$

Carbon-arsenic bond fission occurs when liquid tristrifluoromethylarsine is allowed to react at low temperatures with fluorine diluted with nitrogen, and arsenic trifluoride and carbon tetrafluoride are the only products. Fluorination with cobalt trifluoride at 100° gives the same products, together with small amounts of fluorobistrifluoromethylarsine and difluorotrifluoromethylarsine (*61*). Tristrifluoromethylarsine difluoride, $(CF_3)_3AsF_2$, has been prepared by the interaction of silver fluoride and tristrifluoromethylarsenic dichloride at room temperature. Difluoropentafluoroethylarsine, $C_2F_5{\cdot}AsF_2$, has been prepared by a halogen exchange reaction between dichloropentafluoroethylarsine and ammonium fluoride (*28*).

Chlorine reacts readily with tristrifluoromethylarsine, and by suitable adjustment of the reaction conditions the compounds $(CF_3)_2AsCl$, $CF_3{\cdot}AsCl_2$, $(CF_3)_3AsCl_2$, or $(CF_3)_2AsCl_3$ can be obtained (*61*):

$$\begin{array}{ccc} & & (CF_3)_2AsCl + CF_3{\cdot}AsCl_2 + CF_3Cl \\ & & \uparrow \text{20°, 1.5 hr (vapor phase)} \\ CF_3Cl + (CF_3)_2AsCl_3 & \xleftarrow[\text{(liquid phase)}]{\text{20°, 1 month}} & (CF_3)_3As + Cl_2 \\ & \swarrow \text{20°, 84 hr (liquid phase)} \quad \searrow \text{125°, 24 hr} & \\ & (CF_3)_3AsCl_2 + CF_3Cl \qquad CF_3Cl + AsCl_3 & \end{array} \qquad (148)$$

Tristrifluoromethylarsenic dichloride, b.p. 98.5°, can be distilled without decomposition, but on prolonged heating at 125° it decomposes into the compounds $(CF_3)_3As$, $(CF_3)_2AsCl$, $CF_3{\cdot}AsCl_2$, CF_3Cl, and $AsCl_3$. It reacts with mercury at room temperature, and is converted into tristrifluoromethylarsine.

No evidence has been obtained for the formation of a pentavalent arsenic compound, $(CF_3)_3AsBr_2$, from bromine and tristrifluoromethylarsine; at $-5°$ arsenic tribromide is deposited and bromotrifluoromethane, bromobistrifluoromethylarsine, and dibromotrifluoromethylarsine are formed. Likewise, neither methylphenyltrifluoromethylarsine nor phenylbistrifluoromethylarsine yield stable pentavalent dibromides when treated with bromine in carbon tetrachloride solution at 20°. Under these last conditions, however, diphenyltrifluoromethylarsine yields diphenyltrifluoromethylarsenic dibromide, a colorless, hygroscopic solid which decomposes at 120° in a sealed tube to give bromotrifluoromethane and bromodiphenylarsine (*46*).

Appreciable reaction occurs between iodine and tristrifluoromethylarsine only at temperatures above 100°; iodobistrifluoromethylarsine, diiodotrifluoromethylarsine, trifluoroiodomethane, and arsenic triiodide are the products, and hence a useful route is provided to these reactive iodoarsines.

3. Ammonolysis and Aminolysis of Trifluoromethylarsenic Compounds (44)

Chlorobistrifluoromethylarsine reacts with primary and secondary amines in the gas phase to give aminoarsines in good yield:

$$(CF_3)_2AsCl + 2HNRR' \rightarrow (CF_3)_2As{\cdot}NRR' + RR'NH, HCl \qquad (149)$$

The methylamino-, ethylamino-, and dimethylamino-compounds have been made, and their properties and reactions are similar to those reported for the analogous phosphorus compounds. Evidence has been sought—but with negative results—to demonstrate the acidity of the hydrogen atom in compounds of the type $(CF_3)_2As{\cdot}NHR$.

Chlorobistrifluoromethylarsine reacts with liquid ammonia at low temperatures to yield $[(CF_3)_2As]_2NH$, and the same compound is formed, together with aminobistrifluoromethylarsine, $(CF_3)_2As{\cdot}NH_2$, by a gas-phase reaction at room temperature. With an excess of liquid ammonia at 20° both chlorobistrifluoromethyl- and dichlorotrifluoromethyl-arsine are almost completely converted into fluoroform. These reactions indicate a major difference between the alkyl and trifluoromethyl arsenicals; chlorodimethylarsine and ammonia react together in the liquid phase at $-46°$ to yield unidentified solid products, while dichloromethylarsine and dichlorophenylarsine both form solids of the type $(RAs{:}NH)_x$, where R = CH_3 or C_6H_5 (*125*).

No reaction occurs between ammonia and tristrifluoromethylarsine in the gas phase, but with liquid ammonia at 20°, solvolysis is almost complete with liberation of fluoroform. If the reaction is carried out at $-64°$, or with an excess of the arsine, aminobistrifluoromethylarsine and

$[(CF_3)_2As]_2NH$ can be isolated. Tetrakistrifluoromethyldiarsine is converted almost quantitatively into fluoroform when it is treated with liquid ammonia.

4. The Hydrolysis of Trifluoromethyl Derivatives of Arsenic

All trifluoromethyl derivatives of arsenic yield fluoroform, or a mixture of fluoroform and fluoride ion, on alkaline hydrolysis; cyanobistrifluoromethylarsine and dimethylaminobistrifluoromethylarsine are exceptional because they are hydrolyzed by water alone with the liberation of fluoroform (*44*, *61*). Investigation of the aqueous alkaline hydrolysis of tristrifluoromethylarsine and the mixed methyltrifluoromethyl-, methylphenyl trifluoromethyl-, and phenyltrifluoromethyl-arsines has shown that the rate increases as the number of trifluoromethyl groups increases and that alkyltrifluoromethylarsines are more easily hydrolyzed than aryltrifluoromethylarsines (*46*, *108*). Tetrakistrifluoromethyldiarsine yields 83% of the fluorine as fluoroform and 17% as fluoride ion when it is treated with aqueous base. This can be explained as follows [cf. $(CF_3)_2P{\cdot}P(CF_3)_2$, Section VI,A,*5*,*a*]:

$$\begin{array}{l} (CF_3)_2As{\cdot}As(CF_3)_2 \xrightarrow{H_2O} (CF_3)_2As{\cdot}OH + (CF_3)_2AsH \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow OH^- \qquad\qquad \downarrow OH^- \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad 2CHF_3 \qquad CHF_3, F^-, CO_3^= \end{array} \qquad (150)$$

In a separate experiment, the hydrolysis of bistrifluoromethylarsine was shown to give fluoroform (66%) and fluoride ion (34%) as expected from the above reaction scheme.

5. Trifluoromethyl Arsenic Acids

Attempts to prepare the arsenic acids $CF_3{\cdot}As(OH)_2$ and $(CF_3)_2As{\cdot}OH$ by hydrolysis of the corresponding iodo-compounds failed, since the iodo-compounds are stable to water (cf. their phosphorus analogs, Section VI,A,*6*,*a*), and react with aqueous base by loss of fluoroform. Reaction of the iodo compounds with aqueous hydrogen peroxide, however, yields bistrifluoromethylarsinic acid, $(CF_3)_2AsO(OH)$, and trifluoromethylarsonic acid, $CF_3{\cdot}AsO(OH)_2$ (*62*). Dichloropentafluoroethylarsine is similarly oxidized by aqueous hydrogen peroxide to the arsonic acid, reduction of which can be effected by sulfur dioxide in 50% hydrochloric acid (*28*):

$$C_2F_5{\cdot}AsCl_2 \underset{SO_2/HCl\ aq.}{\overset{H_2O_2\ aq.\ ;\ 0^\circ}{\rightleftharpoons}} C_2F_5{\cdot}AsO(OH)_2 \qquad (151)$$

Bistrifluoromethylarsinic acid behaves as a dibasic acid in aqueous solution; two points of inflection occur in the titration curve corresponding

to $(CF_3)_2As(OH)_2{\cdot}ONa$ and $(CF_3)_2As(OH)(ONa)_2$. The acid decomposes rapidly in solutions of pH >7 with the liberation of fluoroform.

Trifluoromethylarsonic acid is a stable white solid which resembles arsenic acid in that it undergoes progressive dehydration *in vacuo*, forming first a pyro-acid and then an anhydride:

$$CF_3{\cdot}AsO(OH)_2 \xrightarrow{35°/10^{-2}mm} CF_3{\cdot}As(O)(OH){\cdot}O{\cdot}As(O)(OH){\cdot}CF_3 \xrightarrow{73°/10^{-2}mm} CF_3{\cdot}AsO_2 \qquad (152)$$

The trifluoromethylarsenic acids are considerably stronger than their methyl analogues, as shown by the data in Table XIII, and are thus highly

TABLE XIII

DISSOCIATION CONSTANTS

$CF_3{\cdot}AsO(OH)_2$	$K_1 = 7.5 \times 10^{-2}$	$CH_3{\cdot}AsO(OH)_2$	$K_1 = 2.5 \times 10^{-4}$
	$K_2 = 3 \times 10^{-6}$		$K_2 = 5.7 \times 10^{-9}$
$(CF_3)_2AsO(OH)$	$K = 3.8 \times 10^{-2}$	$(CH_3)_2AsO(OH)$	$K_a = 7.5 \times 10^{-7}$
			$K_b = 5.6 \times 10^{-13}$

(cf. H_3AsO_4, $K_1 = 5 \times 10^{-3}$, $K_2 = 8.3 \times 10^{-8}$, $K_3 = 6 \times 10^{-10}$)

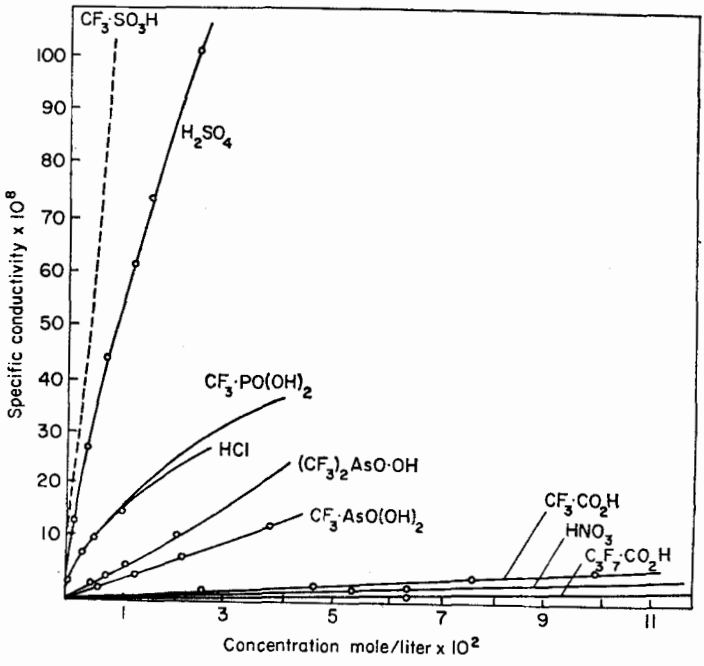


FIG. 3. Conductivities in acetic acid.

ionized in aqueous solution. Conductivity measurements in anhydrous acetic acid have been carried out to enable comparisons of acid strengths to be made. The results are shown in Fig. 3, and it will be seen that certain acids which are strong in aqueous solution are weak in acetic acid (HNO_3, $CF_3{\cdot}CO_2H$, $C_3F_7{\cdot}CO_2H$). Attachment of a perfluoroalkyl group to an atom other than carbon (e.g., P, As) thus produces a stronger acid and effectively utilizes the electron-attracting power of a perfluoroalkyl group. The arsenic acids are about as strong as hydrogen chloride, but appreciably weaker than their phosphorus analogues. The order of acid strengths is thus:

$$HClO_4 > (CF_3)_2PO(OH) > HBr > H_2SO_4 > CF_3{\cdot}PO(OH)_2,$$
$$HCl > (CF_3)_2AsO(OH) > CF_3{\cdot}CO_2H, HNO_3, C_3F_7{\cdot}CO_2H$$

If the values of equivalent conductivities at a particular concentration are taken as a qualitative measure of the extent of ionization (it being assumed

TABLE XIV

$HClO_4$	360	$CF_3{\cdot}PO(OH)_2$	9	$CF_3{\cdot}CO_2H$	1
$(CF_3)_2PO(OH)$	250	HCl	9	HNO_3	1
HBr	180	$(CF_3)_2AsO(OH)$	3.5	$C_3F_7{\cdot}CO_2H$	1
H_2SO_4	32	$CF_3{\cdot}AsO(OH)_2$	2.5		

that the anionic conductivities are approximately equal), the relative strengths of the acids, with $CF_3{\cdot}CO_2H$, HNO_3, and $C_3F_7{\cdot}CO_2H$ being taken as unity, are shown in Table XIV.

C. Antimony

The polyfluoroalkyl derivatives of antimony have received less attention than those of nitrogen, phosphorus, or arsenic. Only the trifluoromethyl derivatives have been prepared, the route employed being the direct reaction of trifluoroiodomethane with the element. Trifluoromethyl derivatives of trivalent antimony boil 30–50° higher than the corresponding arsines, and 50–60° higher than the corresponding phosphines.

1. Preparation of Trifluoromethyl Antimony Compounds

The trifluoromethyl derivatives of antimony are prepared from trifluoroiodomethane with distinctly greater difficulty than are the corresponding phosphorus or arsenic compounds, since they are less stable thermally. Under optimum conditions (165–175° at pressures >50 atm), the main product (90%) from the reaction of finely divided antimony with trifluoroiodomethane is tristrifluoromethylstibine, $(CF_3)_3Sb$, together with small amounts of iodobistrifluoromethylstibine, $(CF_3)_2SbI$, and diiodotrifluoromethylstibine, $CF_3{\cdot}SbI_2$ (*50*). The proportions of the iodo-compounds

can be increased by use of a mixture of antimony and antimony triiodide, and this suggests that a series of equilibria of the type described previously (Sections VI,A,*1*; VI,B,*1*) is involved. Fluorocarbons are produced when the reaction temperature is allowed to rise above 175°, probably by conversion of tristrifluoromethylstibine into tetrafluoroethylene, followed by polymerization initiated by trifluoromethyl radicals arising from homolytic fission of the CF_3—Sb bond (*5*, *50*) in accord with the scheme:

$$(CF_3)_3Sb \rightarrow (CF_3)_2Sb\cdot + CF_3\cdot \qquad (153a)$$

$$(CF_3)_3Sb \rightarrow CF_3{\cdot}SbF_2 + C_2F_4 \xrightarrow{CF_3\cdot} CF_3{\cdot}[CF_2{\cdot}CF_2]_n{\cdot}CF_3 \qquad (153b)$$

Carbon tetrafluoride is another product—arising by the action of antimony fluorides on trifluoroiodomethane.

Dimethyltrifluoromethylstibine can be prepared by the reaction of trimethylstibine with trifluoroiodomethane at room temperature (*107*):

$$2(CH_3)_3Sb + CF_3I \rightarrow CF_3{\cdot}Sb(CH_3)_2 + [(CH_3)_4Sb]^+I^- \qquad (154)$$

2. Properties and Reactions of Trifluoromethyl Antimony Compounds

The physical properties of trifluoromethyl antimony compounds are listed in Table XV.

TABLE XV

PHYSICAL PROPERTIES OF TRIFLUOROMETHYL DERIVATIVES OF ANTIMONY

Compound	m.p. (°C)	b.p. (°C/mm Hg)
$CF_3{\cdot}Sb(CH_3)_2$	—	85.8[a]
$CF_3{\cdot}SbBr_2$	—	34/2.5
$CF_3{\cdot}SbI_2$[b]	4–8	>200[c]
$(CF_3)_2SbCl$	—	~88[c]
$(CF_3)_2SbBr$	—	113
$(CF_3)_2SbI$	−42	16/8
$(CF_3)_2SbCl_3$	27	13/5[d]
$(CF_3)_3Sb$	−58	71.7[a]
$(CF_3)_3Sb,C_5H_5N$	39	~127[a]
$(CF_3)_3SbCl_2$	−34	101[a]
$(CF_3)_3SbCl_2$, H_2O	51	—
$(CF_3)_3SbBr_2$	−16	—
$(CF_3)_2Sb{\cdot}Sb(CF_3)_2$	—	34/14.1

[a] Calculated from vapor pressure measurements.

[b] Not pure.

[c] With disproportionation.

[d] Vapour pressure of the solid.

Tristrifluoromethylstibine is a mobile, colorless liquid, b.p. 71.7° [cf. $(CH_3)_3Sb$, b.p. 80°], which is readily oxidized by air with the formation of carbonyl fluoride and carbon dioxide. It is stable to water at 100° and to

concentrated hydrochloric acid at 20°, but is completely destroyed by concentrated hydrochloric acid at 100°, with almost quantitative conversion of the trifluoromethyl groups into fluoroform. Aqueous alkaline hydrolysis to fluoroform is rapid and quantitative at room temperature, as it is with almost all other trifluoromethyl derivatives of arsenic and antimony. Tristrifluoromethylstibine does not react with aluminium chloride, mercuric chloride, sulfur, or palladous chloride, and the antimony is thus not a donor atom, as it is in trimethylstibine. On the other hand it functions clearly as an acceptor in the reaction of tristrifluoromethylstibine with pyridine, when a 1:1 compound, $(CF_3)_3Sb,C_5H_5N$, is formed. Vapor pressure studies on this complex suggest that it dissociates in the vapor phase, as often found with weak complexes. Antimony trichloride also shows acceptor properties and yields complexes with ammonia, quinoline, dimethyl sulfide, and other organic donors.

The reactions of tristrifluoromethylstibine with halogens, by oxidation of the antimony to the pentavalent state and/or replacement of trifluoromethyl by halogen, resemble those of tristrifluoromethyl-phosphine or -arsine. Exothermic reaction with chlorine at $-40°$ to $-50°$ gives tristrifluoromethylantimony dichloride, $(CF_3)_3SbCl_2$, a labile liquid which decomposes at room temperature with liberation of chlorotrifluoromethane, in direct contrast to trimethylantimony dichloride, which is a white solid stable up to 150°. Tristrifluoromethylantimony dichloride forms 1:1 complexes with water and pyridine, which again illustrates the pseudohalogen character of the trifluoromethyl group—antimony pentachloride is known to form many stable 1:1 complexes, including those with water, ether, and pyridine.

The reaction of bromine with tristrifluoromethylstibine at $-30°$ yields tristrifluoromethylantimony dibromide, which decomposes when kept at room temperature:

$$(CF_3)_3SbBr_2 \rightarrow (CF_3)_2SbBr + CF_3Br \qquad (155)$$

The existence of this dibromide is interesting because antimony pentabromide is unknown. Bromination of tristrifluoromethylstibine at 20° yields a mixture of bromobistrifluoromethylstibine, dibromotrifluoromethylstibine, and bromotrifluoromethane. The first compound disproportionates slowly when kept at room temperature:

$$2(CF_3)_2SbBr \rightleftharpoons (CF_3)_3Sb + CF_3{\cdot}SbBr_2 \qquad (156a)$$

$$2CF_3{\cdot}SbBr_2 \rightleftharpoons (CF_3)_2SbBr + SbBr_3 \qquad (156b)$$

Iodine does not react with tristrifluoromethylstibine at low temperatures, but at 20° cleavage occurs with the formation of iodobistrifluoromethylstibine and trifluoroiodomethane. Further reaction of the iodobis-

trifluoromethylstibine with iodine at room temperature gives diiodotrifluoromethylstibine:

$$(CF_3)_3Sb \xrightarrow{I_2} (CF_3)_2SbI \xrightarrow{I_2} CF_3{\cdot}SbI_2\ (+\ SbI_3 + CF_3I) \qquad (157)$$

[cf. $(CF_3)_3P$ and $(CF_3)_3As$ which react with iodine only at 180° and 100° respectively]. Iodobistrifluoromethylstibine disproportionates on exposure to heat or light to give products analogous to those from the bromocompound.

The iodine atom in iodobistrifluoromethylstibine is reactive, as in the corresponding phosphorus or arsenic compound, but disproportionation often occurs faster than a simple replacement reaction. Reaction with silver chloride gives chlorobistrifluoromethylstibine, a compound that disproportionates readily to tristrifluoromethylstibine and antimony trichloride. Mercury or, better, zinc reacts with iodobistrifluoromethylstibine to give tetrakistrifluoromethyldistibine, which is a pale yellow liquid. This distibine, in contrast to the analogous phosphorus and arsenic compounds (Section VI,A,*5,a*; B,*4*), liberates almost the whole of its fluorine as fluoroform on treatment with aqueous alkali, and only 1–2% as fluoride. Chlorine cleaves the Sb—Sb bond at −78° to form the trichloride $(CF_3)_2SbCl_3$; and bromine or iodine, at room temperature and 90° respectively, decompose the distibine quantitatively with the production of the appropriate halotrifluoromethane and antimony trihalide.

Tristrifluoromethylstibine is decomposed quantitatively by liquid ammonia at room temperature to give fluoroform and antimony nitride (*44*), and almost quantitatively by dimethylamine at 20° to give fluoroform. The rate of ammonolysis of the compounds $(CF_3)_3M$ (M = P, As, Sb) appears to increase in the order P < As < Sb, and this is the order also found for alkaline hydrolysis (see Section VI,A,*5,c*).

3. Tristrifluoromethylantimonic Acid and Its Derivatives (162)

Tristrifluoromethylantimony dichloride reacts with controlled amounts of water to give mono- and di-hydrates. The dihydrate undergoes reversible hydrolysis in aqueous solution, according to the equation

$$(CF_3)_3SbCl_2,\ 2H_2O + 4H_2O \rightleftharpoons 3H_3O^+ + 2Cl^- + [(CF_3)_3Sb(OH)_3]^- \qquad (158)$$

and if the solution is treated with silver oxide and the resulting solution of the silver salt decomposed with hydrochloric acid, a solution of tristrifluoromethylantimonic acid is obtained.

Tristrifluoromethylantimonic acid is unique among the antimonic acids, since it is a strong acid ($pK = 1.85$), and stable in aqueous solution. Its solutions do not give precipitates when treated with solutions containing metal ions (e.g., Na^+, Ag^+, Mg^{2+}, Al^{3+}, Th^{4+}), but a benzene complex

$Ag(CF_3)_3Sb(OH)_3,C_6H_6$ has been prepared from a solution of silver tristrifluoromethylantimonate. Similar complexes are known with silver perchlorate, silver trifluoroacetate, and silver trifluoromethanesulfonate, but with few other silver salts. Pyridinium tristrifluoromethylantimonate $[C_5H_5NH]^+[(CF_3)_3Sb(OH)_3]^-$ can be prepared by treating an aqueous solution of silver tristrifluoromethylantimonate with pyridinium chloride, followed by removal of the silver chloride by filtration, and freeze-drying of the clear solution thus obtained. This pyridinium salt reacts with the acids HX to form salts of the type $[C_5H_5NH]^+[(CF_3)_3SbX_3]^-$ where X = halogen. The tristrifluoromethylantimonate ion is fairly stable in alkaline solution at room temperature, but at 70° concentrated aqueous alkali brings about hydrolysis as follows:

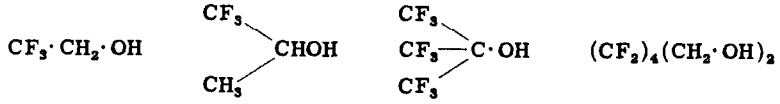
$$[(CF_3)_3Sb(OH)_3]^- + 3H_2O \rightarrow 3CHF_3 + [Sb(OH)_6]^- \qquad (159)$$

The resistance of tristrifluoromethylantimonic acid to hydrolysis is greater than that of the trifluoromethyl oxyacids of arsenic and of bistrifluoromethylphosphinic acid, although not as great as that of trifluoromethylphosphonic acid.

VII. Oxygen

A. Hydroxy Compounds

Polyfluoroalkyl hydroxy compounds, i.e., fluoroalcohols, merit only brief attention here. Fluorine in the α-position of the alkyl group relative to the hydroxyl group is unstable, and attempts to prepare and isolate hydroxy compounds of the type $R_F \cdot CF_2 \cdot OH$ or $(R_F)_2CF \cdot OH$ (where R_F = polyfluoroalkyl) have failed. However, primary, secondary, and tertiary alcohols, and glycols, such as (I), (II), (III), and (IV) below, are quite stable and are prepared by methods familiar in hydrocarbon chemistry, e.g., by the reduction of fluorinated acids and their derivatives, and by use of Grignard reagents.



(I) (II) (III) (IV)

Fluorine-containing alcohols are acidic because of the inductive effect of the fluorine; this effect reaches a maximum in the tertiary perfluoroalkyl compounds (e.g., III) which have ionization constants approaching that of phenol (1×10^{-10}). The reactions associated with hydrocarbon alcohols are modified by the presence of fluorine in the molecule; for example, tri-

fluoroethanol is much less reactive as an alcohol, and does not react with phosphorus pentabromide to give 1,1,1-trifluorobromoethane, nor is it readily converted into the ether $(CF_3 \cdot CH_2)_2O$ by conventional methods.

The literature concerning fluoroalcohols has been reviewed recently (*149*).

B. Trifluoromethyl Hypofluorite

1. Preparation

Methanol, carbonyl fluoride, or carbon monoxide each react with an excess of fluorine (diluted with nitrogen) at 170° in the presence of a silver difluoride catalyst to give good yields (50–70%) of a stable, gaseous compound $CF_3 \cdot OF$, which has been named trifluoromethyl hypofluorite by its discoverers (*135*). Carbonyl fluoride is an intermediate in the preparation of trifluoromethyl hypofluorite from both methanol and carbon monoxide, and it appears that the reaction of fluorine with carbonyl fluoride involves addition to the carbonyl double bond. Attention has been drawn to the analogy between this reaction and the saturation of a carbonyl group with hydrogen in hydrocarbon chemistry, and to the fact that further examples of such fluorine addition might be found (*147*). However, higher homologues of trifluoromethyl hypofluorite could not be obtained by reaction of fluorine with perfluoracyl fluorides; such reactions lead only to the formation of trifluoromethyl hypofluorite (*49*).

It has been reported that trifluoromethyl hypofluorite can be prepared in good yield by the direct fluorination of carbon dioxide (*49*), and also that it occurs in the products of the fluorination of oxygen-containing organic compounds (*36*), e.g., ethyl alcohol, acetic acid, acetone, ethylene glycol, and cyclohexanone.

The most simple laboratory method for preparing trifluoromethyl hypofluorite in high yield is to pass a mixture of fluorine and carbon monoxide in the volume ratio of somewhat more than 2:1 through copper tubing heated to 400° with a residence time of ~1 minute (*37*).

The formation of trifluoromethyl hypofluorite from fluorine and carbonyl fluoride is reversible at temperatures above 275°. The equilibrium

$$CF_3 \cdot OF \rightleftharpoons COF_2 + F_2 \qquad (160)$$

has been studied in a nickel apparatus over the temperature range 367–467°, to give the molar heat of formation of trifluoromethyl hypofluorite from the gaseous elements at 25° as 481.4 kcal exothermic (*174*). Using this value, the O—F bond in $CF_3 \cdot OF$ is calculated to have a strength of 47 kcal per mole, which compares well with the value of 45 kcal derived for the same bond in oxygen difluoride.

2. Properties and Reactions

Pure trifluoromethyl hypofluorite is a colorless gas with an odor reminiscent of fluorine or oxygen difluoride. It boils at −95°, and can be stored under pressure in steel cylinders which have been pretreated with fluorine; it has been cooled to −215° without solidification. Pyrex glass is unaffected by trifluoromethyl hypofluorite at moderate temperatures, but hydrocarbon greases (slowly) and mercury (rapidly) are attacked at room temperature. If, however, chlorofluorocarbon lubricants (Kel-F greases) are used and the mercury in manometers is protected by a film of Kel-F oil, the compound can be handled satisfactorily in a conventional glass vacuum apparatus. The infrared and Raman spectra of trifluoromethyl hypofluorite have been analyzed (*143*).

Some chemical reactions of trifluoromethyl hypofluorite have been investigated (*2, 135, 173, 174*), but much work remains to be done. Lithium, mercury, nickel, sulfur, or hydrogen react to give fluorides and carbonyl fluoride (*173*):

$$CF_3\cdot OF \begin{cases} \xrightarrow{Li,\ 25^\circ} LiF + COF_2 \\ \xrightarrow{Hg,\ 25^\circ} Hg_2F_2 + COF_2 \\ \xrightarrow{S,\ 25^\circ} SF_4 + COF_2 \\ \xrightarrow{H_2,\ 25^\circ} 2HF + COF_2 \\ \xrightarrow{Ni,\ >\ 477^\circ} NiF_2 + COF_2 \end{cases} \qquad (161)$$

Lithium carbonate and sodium chloride undergo anion-displacement reactions, e.g.,

$$CF_3\cdot OF + 2Li_2CO_3 \rightarrow 3CO_2 + 4LiF + \tfrac{1}{2}O_2 \qquad (162)$$

Trifluoromethyl hypofluorite combines with carbonyl fluoride at elevated temperatures to yield bistrifluoromethyl peroxide (*174*):

$$CF_3\cdot OF + COF_2 \xrightarrow{250\text{–}300^\circ} CF_3\cdot O\cdot O\cdot CF_3 \qquad (163)$$

This compound is the major product (60% yield) when a mixture of fluorine and carbon monoxide in the volume ratio 3:2 is passed over silver difluoride at 180° with a contact time of 90 minutes. Bistrifluoromethyl peroxide is a stable, colorless gas (b.p. −37°), which liberates iodine quantitatively from aqueous iodide solutions in the presence of ultraviolet light:

$$CF_3\cdot O\cdot O\cdot CF_3 + 3I^- + 2H_2O \rightarrow I_3^- + 2CO_2 + 4HF + 2F^- \qquad (164)$$

This reaction was discovered by Swarts (*188*) who prepared the peroxide in low yield by electrolyzing aqueous solutions containing trifluoroacetate ion.

Trifluoromethyl hypofluorite combines with sulfur trioxide at 245–260° to give low yields of trifluoromethylperoxyfluorosulfonate, $CF_3{\cdot}O{\cdot}O{\cdot}SO_2F$, a colorless liquid which melts at −117° and boils at 12.9°. Sulfur dioxide and trifluoromethyl hypofluorite react at 175–180° to yield a complex mixture of products from which compounds have been isolated (*37*) corresponding to the formulas $CF_3{\cdot}O{\cdot}SO_2F$, $CF_3{\cdot}O{\cdot}SO_2{\cdot}O{\cdot}CF_3$, $CF_3{\cdot}O{\cdot}SO_2{\cdot}O{\cdot}SO_2F$, and $CF_3{\cdot}O{\cdot}SO_2{\cdot}O{\cdot}SO_2{\cdot}O{\cdot}CF_3$.

In accord with a high energy of activation, trifluoromethyl hypofluorite can safely be mixed with methane, chloroform, or carbon tetrachloride, and the mixture exploded by a spark (*2*). The reactions which occur are:

$$CH_4 + CF_3{\cdot}OF \xrightarrow{\text{spark}} C,CO,HF \tag{165}$$

$$CHCl_3 + CF_3{\cdot}OF \xrightarrow{\text{spark}} CF_4,CF_3Cl,CF_2Cl_2,CFCl_3,CO,HF \tag{166}$$

$$CCl_4 + CF_3{\cdot}OF \xrightarrow{\text{spark}} CF_4,CF_3Cl,CF_2Cl_2,CFCl_3,CO \tag{167}$$

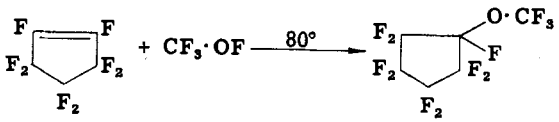
When sparked alone trifluoromethyl hypofluorite decomposes into fluorine and carbonyl fluoride. The reaction with methane follows a different, controlled course under the influence of ultraviolet light:

$$CH_4 + CF_3{\cdot}OF \xrightarrow[\text{(in glass)}]{\text{ultraviolet light}} CH_3F,CH_2F_2,CHF_3,CF_4,CO_2,SiF_4 \tag{168}$$

Ethylene reacts explosively with trifluoromethyl hypofluorite at room temperature, but quantitative addition of the elements of $CF_3{\cdot}OF$ to the olefinic double bond occurs when the reactants, diluted with nitrogen, are mixed slowly while being irradiated with ultraviolet light:

$$CH_2{:}CH_2 + CF_3{\cdot}OF \xrightarrow{\text{ultraviolet light}} CF_3{\cdot}O{\cdot}CH_2{\cdot}CH_2F \tag{169}$$

This observation reveals a novel route to trifluoromethyl ethers, but apart from the above example this reaction has only been applied with definite success to the preparation of perfluoro(methylcyclopentyl) ether from perfluorocyclopentene (*173*):



(170)

Rather surprisingly, tetrafluoroethylene and trifluoromethyl hypofluorite react explosively below room temperature (*173*):

$$C_2F_4 + CF_3{\cdot}OF \rightarrow 2CF_4 + CO \tag{171}$$

When this reaction is controlled by allowing the gaseous reactants (with or without diluent nitrogen) to diffuse slowly together at room temperature,

a white wax reminiscent of polytetrafluoroethylene is formed. This product does not appear to have been investigated in any detail.

The oxidizing power of trifluoromethyl hypofluorite is illustrated by its ability to liberate chlorine, bromine, and iodine from aqueous solutions of their salts, and oxygen from aqueous alkali (*135*). Two wet methods of analysis are based on these reactions. The first involves the reaction:

$$CF_3{\cdot}OF + 3I^- + H_2O \rightarrow 2F^- + 2HF + CO_2 + I_3^- \qquad (172)$$

and subsequent titration of iodine with standard thiosulfate solution. In the second, trifluoromethyl hypofluorite is treated with *N* sodium hydroxide solution, and the fluoride ion formed is precipitated and weighed as lead chlorofluoride:

$$CF_3{\cdot}OF + 6OH^- \rightarrow CO_3^{=} + 4F^- + \tfrac{1}{2}O_2 + 3H_2O \qquad (173)$$

Measurement of the volume of oxygen liberated when the gas reacts with moist pellets of potassium hydroxide also provides a means of analysis. The reaction of trifluoromethyl hypofluorite with water at room temperature is very slow, and use is made of this to free freshly prepared material from carbonyl fluoride.

C. Polyfluoroalkyl Ethers

Perfluoroalkyl ethers, e.g., $(CF_3)_2O$, can be prepared by vapor-phase fluorination of hydrocarbon ethers or, more conveniently, by electrochemical fluorination of a solution of an ether in anhydrous hydrogen fluoride. The boiling point of a perfluoroalkyl ether $R_F{\cdot}O{\cdot}R'_F$ is close to that of the fluorocarbon $R_F{\cdot}R'_F$ (Table XVI) and, like the fluorocarbons, per-

TABLE XVI
The Boiling Points of Fluorocarbons $R_F{\cdot}R'_F$ and Perfluoroethers $R_F{\cdot}O{\cdot}R'_F$

Fluorocarbon ($R_F{\cdot}R'_F$)		b.p. (°C)	Perfluoroether ($R_F{\cdot}O{\cdot}R'_F$)	b.p. (°C)
$CF_3{\cdot}CF_3$	(C_2F_6)	−79	$CF_3{\cdot}O{\cdot}CF_3$	−61
$CF_3{\cdot}C_2F_5$	(C_3F_8)	−38	$CF_3{\cdot}O{\cdot}C_2F_5$	−29
$C_2F_5{\cdot}C_2F_5$	(C_4F_{10})	−2	$C_2F_5{\cdot}O{\cdot}C_2F_5$	0
$C_2F_5{\cdot}C_3F_7$	(C_5F_{12})	29.5	$C_2F_5{\cdot}O{\cdot}C_3F_7$	28
$C_3F_7{\cdot}C_3F_7$	(C_6F_{14})	57	$C_3F_7{\cdot}O{\cdot}C_3F_7$	54

fluoroalkyl ethers are characterized by chemical inertness and thermal stability. They are not cleaved by hydrogen iodide, do not form stable addition compounds with boron trifluoride, and in fact show few properties normally associated with ethers. Cleavage does occur when they are heated

with aluminium trichloride, and this reaction provides a means for structure determination (194), e.g.,

$$(n\text{-}C_6F_{13})_2O \xrightarrow{AlCl_3,\ 230^\circ} n\text{-}C_5F_{11}\cdot COCl + n\text{-}C_5F_{11}\cdot CCl_3 \qquad (174)$$

Cyclic perfluoroethers may also be cleaved using this procedure to give ω,ω,ω-trichloroperfluoroacyl chlorides, e.g.,

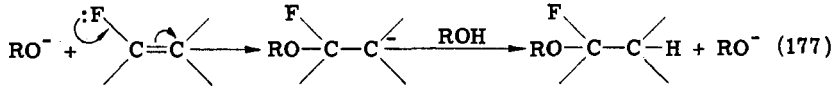
$$\overbrace{CF_2\cdot(CF_2)_3\cdot O} \xrightarrow{AlCl_3,\ 170^\circ} CCl_3\cdot[CF_2]_2\cdot COCl \qquad (175)$$

Perfluoroethyl ether shows a pyrolytic stability comparable with most fluorocarbons. When its vapor is passed slowly over a bed of sodium fluoride pellets contained in a nickel tube heated to 800°, carbonyl fluoride and low-molecular weight fluorocarbons are obtained (*55*):

$$C_2F_5\cdot O\cdot C_2F_5 \xrightarrow{NaF,\ 800^\circ} C,\ COF_2,\ C_2F_6,\ C_3F_6,\ C_3F_8,\ i\text{-}C_4F_8 \qquad (176)$$

Even at this temperature only 68% of the ether is converted.

Mixed alkyl-polyfluoroalkyl ethers, e.g., $CHF_2\cdot CF_2\cdot O\cdot CH_3$, have received considerable attention because of their reactivity (compared with the perfluoroethers), and the relative ease with which they can be prepared from readily available fluorine compounds (*149, 189*). The main method of synthesis of these ethers involves the base-catalyzed reaction of hydrocarbon alcohols with fluoroolefins, a reaction first announced in 1946 (*85*). The alkoxide ion always adds to the carbon atom of the olefin which is substituted by the greater number of fluorine atoms, and the following mechanism has been advanced (*159*):



(177)

Ethers with polyfluorinated groups on both sides of the oxygen atom can be synthesized in fair yield from sodium 1,1-di-H-perfluoroalkoxides and halogenofluoroalkanes (Williamson-type reaction), e.g. (*121*):

$$CF_3\cdot CH_2\cdot ONa + CF_2Cl\cdot CH_3 \rightarrow CF_3\cdot CH_2\cdot O\cdot CF_2\cdot CH_3 + NaCl \qquad (178)$$

It has already been noted that the oxygen atom in perfluoroethers has little or no basic character, an effect due to the strongly electron-withdrawing character of perfluoroalkyl groups. Solubility in concentrated acids and the formation of complexes with Lewis acids is suppressed by fluorine substitution on one side of the ether function, and completely prevented by substitution on both sides. A CF_2 group in the α-position is quite sensitive to hydrolysis unless protected by a CHF_2 or a $R_F\cdot CHF$ group in the β-position.

VIII. Sulfur and Selenium

A. Sulfur

The ability of fluorine, with its high electronegativity and small atomic radius, to stabilize unusual chemical structures, and the ability of sulfur to exhibit several valence states enables many compounds containing sulfur and fluorine to exist. Of these the polyfluoroalkyl sulfur compounds have proved to be of particular interest, and a fair amount of activity has centered on their preparation and investigation during the last decade. It is convenient to divide these compounds into three main groups: (a) derivatives of sulfur hexa- and tetra-fluoride e.g., $CF_3{\cdot}SF_5$, $CF_2(SF_3)_2$; (b) derivatives containing bivalent sulfur, e.g., $CF_3{\cdot}S{\cdot}S{\cdot}CF_3$; and (c) the perfluoroalkane sulfonic acids, e.g., $CF_3{\cdot}SO_3H$.

1. Derivatives of Sulfur Hexa- and Tetra-fluoride

a. Preparation. The first known member of this group, trifluoromethylsulfur pentafluoride, was prepared in low yield (10–20%) by the reaction of methanethiol with cobalt trifluoride, or with elementary fluorine in the presence of a silver difluoride catalyst (*182*). A better yield (40%) is obtained by passage of carbon disulfide over cobalt trifluoride:

$$CS_2 \xrightarrow{CoF_3,\ 200\text{–}250^\circ} CF_3{\cdot}SF_5 + CF_4 + SF_6 \qquad (179)$$

The direct fluorination of carbon disulfide produces a more complex mixture of products (*198*):

$$CS_2 \xrightarrow{F_2/N_2,\ 48^\circ} CF_3{\cdot}SF_5,\ CF_3{\cdot}SF_3,\ SF_5{\cdot}CF_2{\cdot}SF_5,\ SF_3{\cdot}CF_2{\cdot}SF_5,\ CSF_2,\ CF_4,\ SF_6,\ SF_4,\ S_2F_{10} \qquad (180)$$

The compound of molecular formula $CSHF_7$ also obtained as a product of the direct fluorination of methanethiol reacts spontaneously with 6*N* sodium hydroxide solution with quantitative conversion of its fluorine to fluoride; its precise structure remains unknown.

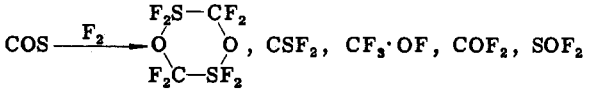
Other reported direct fluorinations of sulfur-containing organic compounds concern methyl thiocyanate (*3*) and carbonyl sulfide (*21*). The direct fluorination of methyl thiocyanate apparently provides the only known route to the potentially important compound pentafluorosulfur nitrile, $SF_5{\cdot}CN$:

$$CH_3{\cdot}SCN \begin{cases} \xrightarrow{(I)} SF_5{\cdot}CN,\ CF_4 \\ \xrightarrow{(II)} CF_3{\cdot}SF_5, SF_5{\cdot}CN,\ SF_5{\cdot}CF_2{\cdot}NF_2,\ CF_2{:}NF,\ CF_4,\ SF_6,\ S_2F_{10} \end{cases} \qquad (181)$$

(I): reaction temperature 90°; molar ratio $F_2 : CH_3{\cdot}SCN : N_2$, 4 : 1 : 100;

(II): reaction temperature 95°; molar ratio $F_2 : CH_3{\cdot}SCN : N_2$, 6 : 1 : 90.

The direct fluorination of carbonyl sulfide yields a fraction which has been tentatively identified as the perfluorinated dimer of the starting material:



$$COS \xrightarrow{F_2} \begin{matrix} F_2S{-}CF_2 \\ O \quad\quad O \\ F_2C{-}SF_2 \end{matrix}, \; CSF_2, \; CF_3{\cdot}OF, \; COF_2, \; SOF_2 \qquad (182)$$

Fluorination of carbonyl sulfide with cobalt trifluoride (*183*) at about 200° led only to the formation of carbonyl fluoride and sulfur hexafluoride.

The electrochemical method of fluorination (*184*) has been widely applied to sulfur-containing organic compounds. This method yields compounds with sulfur in its highest valence state, namely, hexavalent, sometimes with smaller amounts of compounds containing tetravalent sulfur. Thus, the electrochemical fluorination of dimethyl sulfide yields trifluoromethylsulfur pentafluoride and bistrifluoromethylsulfur tetrafluoride (*39*):

$$CH_3{\cdot}S{\cdot}CH_3 \xrightarrow[\text{fluorination}]{\text{electrochemical}} CF_3{\cdot}SF_5 + (CF_3)_2SF_4 \qquad (183)$$

The compound $CF_3{\cdot}SF_5$ is formed by fission of one of the carbon-sulfur bonds accompanied by complete fluorination; this reaction predominates so that the compound $(CF_3)_2SF_4$ is obtained in only low yield. Trifluoromethylsulfur pentafluoride is also formed by the electrochemical fluorination of carbon disulfide (*39*, *183*), but in addition small yields of the compounds $CF_2(SF_5)_2$ and $CF_2(SF_3)_2$ are isolated (*39*):

$$CS_2 \rightarrow CF_3{\cdot}SF_5 + CF_2(SF_5)_2 + CF_2(SF_3)_2 \qquad (184)$$

Table XVII lists the sulfur-containing organic compounds which have been fluorinated electrochemically and the products obtained, together with an indication of the yields. It should be emphasized that separation of pure compounds from the often complex reaction mixtures is usually difficult.

b. Properties and reactions. The compounds containing sulfur in its highest valence state show the marked chemical and thermal stability expected for derivatives of sulfur hexafluoride; the derivatives of sulfur tetrafluoride show the expected instability. Trifluoromethylsulfur pentafluoride can be recovered unchanged after 60 hours at 100° in 20% aqueous or alcoholic potassium hydroxide (*39*); it is superior to sulfur hexafluoride as a gaseous electrical insulator at low pressures, but is decomposed by an electric spark to a mixture of carbon tetrafluoride and sulfur tetrafluoride (*148*).

Thermal decomposition of perfluoroalkyl derivatives of sulfur hexafluoride (*52*, *54*, *56*, *58*, *157*) occurs according to the general equations:

$$R_F{\cdot}SF_5 \xrightarrow{\Delta} R_FF + R_F{\cdot}R_F + SF_4 \qquad (185)$$

TABLE XVII

DERIVATIVES OF SULFUR HEXA- AND TETRA-FLUORIDE PREPARED BY ELECTROCHEMICAL FLUORINATION

Starting compound (g)	Product (g)	Reference
CS_2 (55)	$CF_3{\cdot}SF_5$ (>90% yield) $CF_2(SF_5)_2$[a] (0.5% yield) $CF_2(SF_3)_2$[a] (0.5% yield)	*39*
$(CH_3)_2S$ (16.9)	$CF_3{\cdot}SF_5$ (30.5) $(CF_3)_2SF_4$ (3.5)	*39*
$(CH_2{\cdot}S)_2$ (282)	$CF_3{\cdot}SF_5$ (149) $CH_3{\cdot}SF_5$[b] $CH_3{\cdot}SF_4{\cdot}CH_2F$[b]	*57*
$(CH_2{\cdot}S)_3$ (470)	CS_2 (25) $CF_3{\cdot}SF_5$ (90) $CF_2(SF_5)_2$[b] (55) $(CF_2{\cdot}SF_4)_2$[b] $CF_3{\cdot}SF_4{\cdot}CF_2{\cdot}SF_5$[b]	*57*
$(C_2H_5)_2S$ (198)	$C_2F_5{\cdot}SF_5$[b] (46) $(C_2F_5)_2SF_4$[b] (1.25)	*122*
$(n\text{-}C_3H_7)_2S$ (826)	$C_3F_7{\cdot}SF_5$[b] (375) $(C_3F_7)_2SF_4$[b] (389)	*122*
$(n\text{-}C_4H_9)_2S$ (1746)	$C_4F_9{\cdot}SF_5$[b] } (724) $CF_2{\cdot}(CF_2)_3{\cdot}SF_4$[b] } $(C_4F_9)_2SF_4$[b] (659)	*122*
$(n\text{-}C_4H_9S)_2$ (1964)	$C_4F_9{\cdot}SF_5$[b] } (833) $CF_2{\cdot}(CF_2)_3{\cdot}SF_4$[b] } $(C_4F_9)_2SF_4$[b] (180)	*122*
$CH_3{\cdot}S{\cdot}(CH_2)_2{\cdot}S{\cdot}CH_3$ (370)	$CF_3{\cdot}SF_5$ (170) $C_2F_5{\cdot}SF_4{\cdot}CF_3$[b] (90) $(C_2F_5)_2SF_4$[b] (28) $(C_2F_4{\cdot}SF_4)_2$[a] (6) $CF_3{\cdot}SF_4{\cdot}(CF_2)_2{\cdot}SF_5$[a] (19)	*57*
$S(CH_2{\cdot}CH_2{\cdot}SH)_2$ (26)	$C_2F_5{\cdot}SF_5$ (17)	*113*
$HS{\cdot}CH_2{\cdot}CO_2H$ (500)	$CF_3{\cdot}SF_5$ (35) $SF_5{\cdot}CF_2{\cdot}COF$ (20) $SF_5{\cdot}CF_2{\cdot}CO_2H$ (30)	*106*
$CH_3{\cdot}S{\cdot}CH_2{\cdot}COCl$ (615)	$CF_3{\cdot}SF_5$ (60) $(CF_3)_2SF_4$ (63) $C_2F_5{\cdot}SF_4{\cdot}CF_3$[b] (24) $CF_3{\cdot}SF_4{\cdot}CF_2{\cdot}COF$[b] (32) $(CF_3{\cdot}SF_4)_2$[b] (10)	*208*
$[(C_2H_5)_2N{\cdot}CH_2{\cdot}CH_2{\cdot}S]_2$ (62)	$(C_2F_5)_2N{\cdot}CF_2{\cdot}CF_2{\cdot}SF_5$[a] (30)	*122*
$(CH_3)_2SO_2$ (25)	$(CF_3)_2SO_2$ (2.3)	*114*
$(n\text{-}C_4H_9)_2SO$ (81)	$C_4F_9{\cdot}SF_5$ (3) $(C_4F_9)_2SF_4$[b] (4)	*122*
$C_8H_{17}{\cdot}SH$ (90)	$C_8F_{17}{\cdot}SF_5$ (48)	*114*

TABLE XVII (*Continued*)

Starting compound (g)	Product (g)	Reference
$\lceil CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2\rceil$ (100)	$C_4F_9{\cdot}SF_5$ $(C_2F_5)_2SF_4$[b] $C_3F_7{\cdot}SF_4{\cdot}CF_3$[b] (60) $\lceil CF_2{\cdot}(CF_2)_3{\cdot}SF_4\rceil$[b]	*122*
$\lceil CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}S\rceil$ (650)	$C_2F_5{\cdot}O{\cdot}C_2F_5$ (164) $C_2F_5{\cdot}SF_5$ (67) $C_2F_5{\cdot}O{\cdot}(CF_2)_2{\cdot}SF_5$[a] (95) $\lceil CF_2{\cdot}CF_2{\cdot}O{\cdot}CF_2{\cdot}CF_2{\cdot}SF_4\rceil$ (400)	*57*

[a] Structure assigned only on the basis of elemental analysis.

[b] Structure assigned on the basis of NMR and elemental analysis, and, in some cases, IR analysis.

$$(R_F)_2SF_4 \xrightarrow{\Delta} R_F{\cdot}R_F + SF_4 \quad (R_F = CF_3, C_2F_5, \text{or } C_4F_9) \tag{186}$$

Trifluoromethylsulfur pentafluoride and pentafluoroethylsulfur pentafluoride are decomposed quantitatively when heated in closed vessels to 423° and 380°, respectively; temperatures in the region of 500° are required when the decompositions are carried out in flow systems:

$$CF_3{\cdot}SF_5 \xrightarrow{\Delta} CF_4 + C_2F_6 + SF_4 \tag{187}$$

$$C_2F_5{\cdot}SF_5 \xrightarrow{\Delta} C_2F_6 + C_4F_{10} + SF_4 \tag{188}$$

The decomposition products accord with a free radical mechanism, e.g.,

$$CF_3{\cdot}SF_5 \rightarrow CF_3{\cdot} + F{\cdot} + SF_4 \tag{189a}$$

$$2CF_3{\cdot} \rightarrow C_2F_6 \tag{189b}$$

$$CF_3{\cdot} + F{\cdot} \rightarrow CF_4 \tag{189c}$$

and this is supported by the production of the bromo compound C_4F_9Br when the compound $(C_4F_9)_2SF_4$ is pyrolyzed at 550° in the presence of bromine (*181*):

$$(C_4F_9)_2SF_4 + Br_2 \xrightarrow{550°} 2C_4F_9Br + SF_4 \tag{190}$$

Phosphonitrilic fluorides are formed during the reaction between trifluoromethylsulfur pentafluoride and phosphorus nitride at 710° (*157*):

$$CF_3{\cdot}SF_5 + P_3N_5 \xrightarrow{710°} C_2F_6, SF_4, PF_3, (PNF_2)_3, (PNF_2)_4 \tag{191}$$

The products obtained when the trifluoromethylsulfur compounds are co-pyrolyzed in continuous-flow experiments with hexafluoropropylene and perfluoro(methylenemethylamine) would also suggest radical intermediates:

$$CF_3{\cdot}SF_5 + CF_3{\cdot}CF{:}CF_2 \xrightarrow{425\text{–}518^\circ} SF_4 + C_1\text{—}C_7 \text{ fluorocarbons} \quad (192)$$

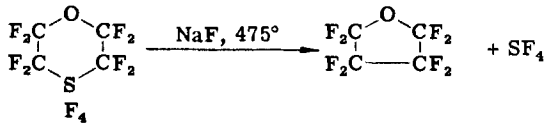
$$(CF_3)_2SF_4 + CF_3{\cdot}CF{:}CF_2 \xrightarrow{518^\circ} SF_4 + C_5F_{12} \text{ (mixed isomers)} \quad (193)$$

$$CF_3{\cdot}SF_5 + CF_3{\cdot}N{:}CF_2 \xrightarrow{NaF,\ 519^\circ} (CF_3)_3N + SF_4 \quad (194)$$

Pentafluoroethylsulfur pentafluoride reacts with perfluoro(methylenemethylamine) at 384° in a stainless steel autoclave to yield the tertiary amine perfluoro(dimethylethylamine):

$$C_2F_5{\cdot}SF_5 + CF_3{\cdot}N{:}CF_2 \rightarrow C_2F_5{\cdot}N(CF_3)_2 \quad (195)$$

An interesting pyrolysis, and one which again demonstrates the thermal stability of perfluoroethers, is that of perfluorothioxane tetrafluoride (*56*):



(196)

Electrochemical fluorination provides a potential route to perfluoroalkyl derivatives of sulfur hexafluoride containing in the molecule a conventional reactive group of organic chemistry, e.g., —CO_2H, —C⋮N, —SO_3H, which would make synthesis possible. So far, however, only compounds containing the carboxyl group have been prepared, and these in low yield (see Table XVII). Thus, electrochemical fluorination of thioglycolic acid yields α,α-difluoro-α-(trifluorothio)acetic acid, $SF_3{\cdot}CF_2{\cdot}CO_2H$, and α,α-difluoro-α-(pentafluorothio)acetic acid, $SF_5{\cdot}CF_2{\cdot}CO_2H$ (*106*). The silver salts of these acids decarboxylate when treated with chlorine at −23° [cf. silver salts of polyfluoroalkane carboxylic acids (*90*, *95*)]:

$$SF_5{\cdot}CF_2{\cdot}CO_2Ag \xrightarrow{Cl_2} [SF_5{\cdot}CF_2{\cdot}CO_2Cl] \rightarrow SF_5{\cdot}CF_2Cl + CO_2 \quad (197)$$

Silver α,α-difluoro-α-(trifluorothio)acetate reacts immediately with chlorine, but by complete breakdown to carbon dioxide, carbonyl fluoride, and thionyl fluoride and, by attack on the reaction vessel, silicon tetrafluoride. Chlorodifluoromethylsulfur pentafluoride is a colorless gas, b.p. 16.5°, which is stable to dilute aqueous alkali.

The physical properties of perfluoroalkyl derivatives of sulfur hexa- and tetra-fluoride are listed in Table XVIII.

TABLE XVIII

THE PHYSICAL PROPERTIES OF DERIVATIVES OF SULFUR HEXA- AND TETRA-FLUORIDE

Compound	m.p. (°C)	b.p. (°C/mm Hg)	n_D^t (t, °C)	d_4^t (t, °C)
$CF_3 \cdot SF_5$	—	−20[a]	—	—
$C_2F_5 \cdot SF_5$	—	13.5	—	—
$C_3F_7 \cdot SF_5$	—	42	1.2594 (25)	1.801 (25)[b]
$C_4F_9 \cdot SF_5$	—	70.5	1.2701 (15)	1.839 (25)[b]
$C_8F_{17} \cdot SF_5$	—	156–157	—	—
$(CF_3)_2 \cdot SF_4$	—	20.5	—	—
$(C_2F_5)_2 \cdot SF_4$	—	70	1.2754 (25)	1.836 (25)[b]
$(C_3F_7)_2 \cdot SF_4$	—	116	1.2856 (25)	1.865 (25)[b]
$(C_4F_9)_2SF_4$	—	154	1.2943 (25)	1.903 (25)[b]
$CF_3 \cdot SF_3$	−110	−7	—	—
$CF_2(SF_5)_2$	—	59.6	1.2884 (25)	2.041 (25)
$CF_2(SF_3)_2$	—	35	—	—
$[(CF_2)_2SF_4]_2$	76	82/61	—	—
$(CF_2 \cdot SF_4)_3$	—	144.5	1.3258 (25)	2.162 (25)
$CF_2Cl \cdot SF_5$	—	16.5	—	—
$SF_5 \cdot CF_2 \cdot COF$	—	21.5–22.5	—	—
$SF_3 \cdot CF_2 \cdot CO_2H$	—	132.5	—	—
$SF_3 \cdot CF_2 \cdot SF_5$	−51	26	—	—
$SF_5 \cdot CF_2 \cdot NF_2$	−153	9.5	—	—
$CF_3 \cdot SF_4 \cdot CF_2 \cdot COOCH_3$	—	123	1.3259 (30)	—
$CF_3 \cdot SF_4 \cdot CF_2 \cdot CF_3$	—	47.1	—	—
$CF_3 \cdot SF_4 \cdot (CF_2)_2 \cdot SF_5$	—	112–112.5	1.3041 (25)	2.002 (25)
$\ulcorner CF_2 \cdot CF_2 \cdot O \cdot CF_2 \cdot CF_2 \cdot SF_4$	17.1	80.3	1.3041 (25)	1.9031 (25)
$CF_3 \cdot SF_4 \cdot CF_2 \cdot SF_5$	—	87.8–88.1	1.3010 (25)	—
$C_2F_5 \cdot O \cdot (CF_2)_2 \cdot SF_5$	—	65	1.2598 (25)	1.772 (25)
$(C_2F_5)_2N \cdot CF_2 \cdot CF_2 \cdot SF_5$	—	124	1.2921 (25)	1.86 (25)[b]
$(CF_3)_2SO_2$	—	15.6[a]	—	—

[a] Calculated from vapor pressure measurements.

[b] d_{25}.

2. *Derivatives Containing Bivalent Sulfur*

a. Preparation of Polyfluoroalkyl Sulfides. The trifluoromethyl derivatives of bivalent sulfur have received the most attention, and their chemistry is well developed. Knowledge of the other polyfluoroalkyl compounds is limited.

Trifluoromethyl sulfides can be prepared in several ways. The direct action of sulfur on trifluoroiodomethane in a stainless steel autoclave at 310° yields a mixture consisting mainly of the disulfide (*25, 26, 99*):

$$CF_3I + S \xrightarrow{310°} CF_3 \cdot S_2 \cdot CF_3(75\%) + CF_3 \cdot S_3 \cdot CF_3(12\%) + CF_3 \cdot S_4 \cdot CF_3(1\%) \qquad (198)$$

A more convenient synthesis involves a reaction which at first sight seems strange (*99*):

$$CS_2 + IF_5 \xrightarrow{195^\circ} CF_3{\cdot}S_2{\cdot}CF_3(76\%) + CF_3{\cdot}S_3{\cdot}CF_3(7\%), \qquad (199)$$

but which probably involves the following steps:

$$CS_2 \xrightarrow{I_2} CI_3{\cdot}SI \qquad (\text{cf. } CS_2 \xrightarrow{Cl_2} CCl_3{\cdot}SCl) \qquad (199a)$$

$$CI_3{\cdot}SI \xrightarrow{IF_5} CF_3{\cdot}SI \qquad (\text{cf. } CI_4 \xrightarrow{IF_5} CF_3I) \qquad (199b)$$

$$2CF_3{\cdot}SI \longrightarrow 2CF_3{\cdot}S{\cdot} \longrightarrow CF_3{\cdot}S{\cdot}S{\cdot}CF_3 \qquad (199c)$$

The fluorination of carbon disulfide with mercuric fluoride at temperatures above 300° also yields bistrifluoromethyl disulfide together with smaller amounts of the monosulfide (*156*).

A very simple method for preparing bistrifluoromethyl disulfide and trifluoromethanesulfenyl chloride from relatively inexpensive and readily available reactants has recently formed the basis of a patent claim (*196*). This method consists of heating an alkali metal fluoride with thiocarbonyl chloride or trichloromethanesulfenyl chloride, preferably in the presence of an organic solvent of high dielectric constant such as acetonitrile or cyclic tetramethylene sulfone:

$$CSCl_2 + NaF \xrightarrow{245^\circ} CF_3{\cdot}S_2{\cdot}CF_3 + CS_2 \qquad (200)$$

$$CCl_3{\cdot}SCl + NaF \xrightarrow{209\text{–}247^\circ} CF_3{\cdot}SCl + CF_3{\cdot}S_2{\cdot}CF_3 \ (+ \text{traces of } CF_2Cl{\cdot}SCl,\ CF_3{\cdot}S_3{\cdot}CF_3,\ CF_3{\cdot}S_4{\cdot}CF_3) \qquad (201)$$

The reaction of sulfur with iodo compounds has been extended as follows (*72*, *103*, *117*, *118*, *138*):

$$C_3F_7I + S \xrightarrow{250^\circ} (C_3F_7)_2S_n \qquad (n = 1\text{–}3) \qquad (202)$$

$$C_4F_9{\cdot}CFI{\cdot}CF_3 + S \xrightarrow{172\text{–}176^\circ} [C_4F_9{\cdot}CF(CF_3)]_2S_n \qquad (n = 2\text{–}5) \qquad (203)$$

$$CF_2Cl{\cdot}CFClI + S \xrightarrow{187^\circ} (CF_2Cl{\cdot}CFCl)_2S_n \qquad (n = 2\text{–}5) \qquad (204)$$

$$CHF_2{\cdot}(CF_2)_5{\cdot}CH_2I + S \xrightarrow{250\text{–}270^\circ} [CHF_2{\cdot}(CF_2)_5{\cdot}CH_2]_2S_n \qquad (n = 1 \text{ and } 2) \qquad (205)$$

The thermal or light-initiated reaction of black mercuric sulfide with iodoperfluoroalkanes also gives rise to perfluoroalkyl sulfides (*119*).

Chlorofluoroalkyl sulfides have been prepared by the addition-reaction of sulfur mono- or di-chloride with the fluoroolefins tetrafluoroethylene, chlorotrifluoroethylene, and 1,1-difluoroethylene (*7*, *136*, *137*, *176*), and also by the replacement of chlorine by fluorine in chloromethyl sulfides (*23*, *195*), e.g.,

$$CF_2{:}CF_2 + S_2Cl_2 \xrightarrow{100\text{–}120^\circ} CF_2Cl{\cdot}CF_2{\cdot}SCl + (CF_2Cl{\cdot}CF_2)_2S_n \quad (n = 1\text{–}3) \tag{206}$$

$$CCl_3{\cdot}S{\cdot}CH_2Cl \xrightarrow{SbF_3,\ SbCl_5;\ 80^\circ} CF_3{\cdot}S{\cdot}CH_2Cl + CF_2Cl{\cdot}S{\cdot}CH_2Cl \tag{207}$$

The asymmetrical sulfide $CF_3{\cdot}S{\cdot}CH_3$ can be prepared by the application of the above chlorine-exchange reaction to α,α,α-trichlorodimethyl sulfide (*195*); difluoromethyl methyl sulfide, $CHF_2{\cdot}S{\cdot}CH_3$, is obtained by the reaction of chlorodifluoromethane with sodium methylmercaptide (*186*). Many other asymmetrical fluorine-containing sulfides have been prepared by the base-catalyzed addition of thiols to fluoroolefins, (*177*) e.g.,

$$RSH + CF_2{:}CFCl \rightarrow RS{\cdot}CF_2{\cdot}CHFCl \quad (R = \text{alkyl}) \tag{208}$$

b. The Properties and Reactions of Polyfluoroalkyl Sulfides and Their Derivatives. Bistrifluoromethyl disulfide is a liquid, b.p. 34.6°; electron diffraction and infrared spectroscopic measurements (*99*) show that the molecule contains an unbranched sulfur chain. This is also true for the trisulfide $CF_3{\cdot}S_3{\cdot}CF_3$, and further evidence for this is derived from the synthesis of the trisulfide from trifluoromethanesulfenyl chloride and hydrogen sulfide (see below). The monosulfide, $CF_3{\cdot}S{\cdot}CF_3$, is readily prepared by the photolysis of the disulfide:

$$CF_3{\cdot}S_2{\cdot}CF_3 \xrightarrow{\text{ultraviolet light}} CF_3{\cdot}S{\cdot}CF_3 + S \tag{209}$$

Irradiation of the trisulfide likewise yields the monosulfide (*99*):

$$CF_3{\cdot}S_3{\cdot}CF_3 \xrightarrow{\text{ultraviolet light}} CF_3{\cdot}S{\cdot}CF_3 + CF_3{\cdot}S_2{\cdot}CF_3 \xrightarrow{\text{ultraviolet light}} CF_3{\cdot}S{\cdot}CF_3 + S \tag{210}$$

Bistrifluoromethyl sulfide is stable to heat and to attack by strong acid or strong alkali. In sharp contrast, the disulfide is decomposed rapidly and quantitatively at room temperature by dilute aqueous alkali to give fluoride, carbonate, and sulfide, but no fluoroform. This complete destruction of two trifluoromethyl groups under such mild conditions proceeds as follows:

$$\begin{array}{l} CF_3{\cdot}S_2{\cdot}CF_3 \xrightarrow{H_2O} CF_3{\cdot}SH + CF_3{\cdot}S{\cdot}OH \\ \qquad\qquad\qquad\quad \downarrow \bar{O}H \qquad\qquad \downarrow \bar{O}H \\ \qquad\qquad\qquad\quad F^-, S^=, CO_3^= \quad F^-, S^=, CO_3^= \end{array} \tag{211}$$

i.e., an initial hydrolytic fission of the S—S link is followed by breakdown of the thiol and the sulfenic acid.

(i) *Trifluoromethanethiol.* Trifluoromethanethiol can be synthesized from bistrifluoromethyl disulfide as follows (*99*):

$$CF_3{\cdot}S_2{\cdot}CF_3 + Hg \xrightarrow{\text{ultraviolet light}} (CF_3{\cdot}S)_2Hg \quad (212a)$$

$$(CF_3{\cdot}S)_2Hg + 2HCl \longrightarrow 2CF_3{\cdot}SH + HgCl_2 \quad (212b)$$

It was the first compound known with a perfluoroalkyl group linked to an electronegative atom which also carries a hydrogen atom. Although stable in a vacuum apparatus, it is decomposed quantitatively and rapidly by aqueous base to give fluoride, sulfide, and carbonate. In ionizing solvents, or in the presence of an acceptor for hydrogen fluoride, decomposition of trifluoromethanethiol occurs as follows (*103*):

$$CF_3{\cdot}SH \rightarrow CSF_2 + HF \quad (213)$$

and the thiocarbonyl fluoride formed often undergoes further reactions. Aqueous hydrolysis of trifluoromethanethiol proceeds slowly to yield carbonyl sulfide as the end product:

$$CF_3{\cdot}SH \xrightarrow{H_2O} HF + CSF_2 \xrightarrow{H_2O} COS + 2HF \quad (214)$$

Anhydrous ammonia reacts with trifluoromethanethiol to yield, as major products, trifluoromethyl fluorodithioformate, a yellow liquid, and bistrifluoromethyl trithiocarbonate, a red liquid (*103*):

$$CF_3{\cdot}SH \xrightarrow{NH_3} CSF_2 + (HF) \quad (215a)$$

$$CF_3{\cdot}SH + CSF_2 \xrightarrow{NH_3} CF_3{\cdot}S{\cdot}CSF + (HF) \quad (215b)$$

$$CF_3{\cdot}S{\cdot}CSF + CF_3{\cdot}SH \xrightarrow{NH_3} (CF_3{\cdot}S)_2CS + (HF) \quad (215c)$$

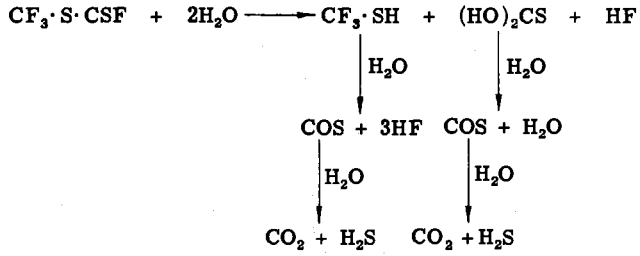
Ammonia is clearly essential to the last two reactions by acting as an acceptor for hydrogen fluoride, since trifluoromethanethiol fails to yield bistrifluoromethyl trithiocarbonate when heated with thiocarbonyl chloride, or when treated with trifluoromethyl fluorodithioformate alone or in sulfur dioxide solution. Anhydrous sodium or potassium fluoride can also be used as acceptors for hydrogen fluoride in the above reaction scheme (*155*). The trithiocarbonate has also been synthesized by the following routes (*103*):

$$2(CF_3{\cdot}S)_2Hg + CSCl_2 \xrightarrow{50^\circ} (CF_3{\cdot}S)_2CS + 2CF_3{\cdot}S{\cdot}HgCl \quad (216)$$

$$(CF_3{\cdot}S)_2Hg + CF_3{\cdot}S{\cdot}CSF \xrightarrow{70^\circ} (CF_3{\cdot}S)_2CS + CF_3{\cdot}S{\cdot}HgF \quad (217)$$

These provide proof of structure and establish the relationship between the fluorodithioformate and the trithiocarbonate. Photochemical reaction of the fluorodithioformate with chlorine yields chlorotrifluoromethane, thus showing the presence of a CF_3 group, and the formation of a small amount of trifluoromethanethiol by reaction with water indicates a $CF_3{\cdot}S$ group.

Hydrolysis is slow at room temperature but rapid and complete at 75°. The aqueous solution then contains most of the fluorine as fluoride ion and 13% of the sulfur as sulfide ion. Carbonyl sulfide, carbon dioxide, and a small amount of trifluoromethanethiol are volatile products:



(218)

Bistrifluoromethyl trithiocarbonate similarly yields carbonyl sulfide when treated with water.

Photochemical decomposition of trifluoromethanethiol (*99*) yields hydrogen, sulfur, fluoroform, bistrifluoromethyl disulfide, and bistrifluoromethyl sulfide by a series of reactions involving $CF_3{\cdot}S$ and CF_3 radicals.

(ii) *Trifluoromethanesulfenyl chloride.* Bistrifluoromethyl disulfide fails to react with iodine at temperatures up to 290°, and this resistance of the F_3C—S bonds to fission, with concomittant production of trifluoroiodomethane, may be compared with the ready conversion of the trifluoromethyl derivatives of arsenic and phosphorus into the iodo compound at moderate temperatures (see Section VI,A,*2*,*a*; B,*2*,*c*). In Pyrex apparatus, chlorine reacts with bistrifluoromethyl disulfide in the presence of ultraviolet light to yield trifluoromethanesulfenyl chloride; the same product is obtained when chlorine reacts with bis(trifluoromethylthio)mercury at low temperatures (*99*):

$$CF_3{\cdot}S_2{\cdot}CF_3 \xrightarrow{Cl_2,\ \text{ultraviolet light}} 2CF_3{\cdot}SCl \tag{219}$$

$$(CF_3{\cdot}S)_2Hg \xrightarrow{Cl_2,\ -22^\circ} CF_3{\cdot}SCl,\ CF_3{\cdot}S_2{\cdot}CF_3,\ CF_3{\cdot}S{\cdot}HgCl \tag{220}$$

Trifluoromethanesulfenyl chloride is a golden yellow liquid, b.p. −0.7°, which undergoes the characteristic reactions of an acid chloride and thus resembles the alkyl and aryl sulfenyl chlorides. It readily combines with mercury or with compounds which contain the S—H bond (*68*, *99*):

$$2CF_3{\cdot}SCl + Hg \rightarrow CF_3{\cdot}S_2{\cdot}CF_3 + HgCl_2 \tag{221}$$

$$CF_3{\cdot}SCl + CF_3{\cdot}SH \rightarrow CF_3{\cdot}S_2{\cdot}CF_3 + HCl \tag{222}$$

$$2CF_3{\cdot}SCl + H_2S \rightarrow CF_3{\cdot}S_3{\cdot}CF_3 + 2HCl \tag{223}$$

$$CF_3{\cdot}SCl + C_2H_5{\cdot}SH \rightarrow CF_3{\cdot}S_2{\cdot}C_2H_5 + HCl \tag{224}$$

These reactions suggest that the di- and tri-sulfides contain unbranched sulfur chains.

Trifluoromethanesulfenyl chloride reacts with ammonia at $-45°$ to give an almost quantitative yield of trifluoromethanesulfenamide, $CF_3{\cdot}S{\cdot}NH_2$. At room temperature, and using a higher proportion of the sulfenyl chloride, the product is trifluoromethanesulfenimide, $(CF_3{\cdot}S)_2NH$; apparently, no $(CF_3{\cdot}S)_3N$ is formed (*68*). Methylamine, dimethylamine, and aniline behave similarly, and form $CF_3{\cdot}NHCH_3$, $CF_3{\cdot}S{\cdot}N(CH_3)_2$, and $CF_3{\cdot}S{\cdot}NHC_6H_5$. Phosphine reacts with trifluoromethanesulfenyl chloride to yield bis- and tris-(trifluoromethylthio)phosphine, $(CF_3{\cdot}S)_2PH$ and $(CF_3{\cdot}S)_3P$ (*68*). No comparable reaction has been reported between phosphine and alkyl or aryl sulfenyl halides, although similar products might be expected. Preliminary experiments on the reaction of sulfur dichloride with phosphine show that hydrogen chloride is eliminated and a viscous oil is formed which appears to be $Cl{\cdot}S{\cdot}PH_2$. Trifluoromethanesulfenyl chloride is reduced by arsine to trifluoromethanethiol (*68*).

Hydrolysis of trifluoromethanesulfenyl chloride by water yields trifluoromethanesulfenic acid, $CF_3{\cdot}S{\cdot}OH$, which has not been isolated, since it disproportionates to give the thiol and trifluoromethanesulfinic acid (*102*):

$$2CF_3{\cdot}S{\cdot}OH \rightarrow CF_3{\cdot}SH + CF_3{\cdot}SO_2H \qquad (225)$$

The sulfinic acid is stable in aqueous solution and can be isolated as its sodium salt, a monohydrate. It is conveniently prepared by the reaction of trifluoromethanesulfonyl chloride with zinc dust and water in the absence of air (*102*):

$$CF_3{\cdot}SCl + 2Cl_2 + 2H_2O \longrightarrow CF_3{\cdot}SO_2Cl + 4HCl \qquad (226a)$$

$$CF_3{\cdot}SO_2Cl \xrightarrow{Zn/H_2O} CF_3{\cdot}SO_2H \qquad (226b)$$

Trifluoromethanesulfinic acid liberates fluoroform on treatment with aqueous base, and is readily oxidized to trifluoromethanesulfonic acid.

(iii) *Bis(trifluoromethylthio)mercury.* Bis(trifluoromethylthio)mercury is important in its own right, besides being an intermediate in the conversion of bistrifluoromethyl disulfide to trifluoromethanethiol and trifluoromethanesulfenyl chloride. The yield of mercurial from the reaction of mercury with the disulfide is very high (90%) (*99*), but a simple and more direct synthesis is to be found in the reaction of mercuric fluoride with carbon disulfide at 250° (*156*):

$$3HgF_2 + 2CS_2 \xrightarrow{250°} (CF_3{\cdot}S)_2Hg + 2HgS \qquad (227)$$

The average yields of mercurial are 72% and 48% for static and flow experiments, respectively. At higher temperatures (>300°) bistrifluoromethyl disulfide is the major product from this reaction.

Bis(trifluoromethylthio)mercury is a white crystalline solid, m.p. 39–40°, which sublimes readily at atmospheric pressure and is soluble in water and a wide variety of organic solvents. These properties may be

compared with those of bis(methylthio)mercury which has a high melting point (175°), and is insoluble in water and most organic solvents. Serious skin burns result from contact with bis(trifluoromethylthio)mercury, and tests on rats have shown that when taken orally it causes severe damage to the stomach and kidneys, followed by death. Fortunately, the sweet and penetrating odor of the mercurial is easily recognized. Heat is evolved when the mercurial is dissolved in organic solvents with donor properties, and the complexes formed can be isolated in several cases, e.g., $(CF_3{\cdot}S)_2Hg,2P(C_6H_5)_3$ and $(CF_3{\cdot}S)_2Hg,HC(:S){\cdot}N(CH_3)_2$ (*156*). The relative stabilizing power of the ligands appears to be $PR_3 > NR_3 > SR_2 > OR_2$ (R = alkyl or aryl), i.e., completely analogous to that found in mercuric halide complexes. A conductometric study of the reaction between bis(trifluoromethylthio)mercury and tetramethylammonium or potassium iodide in acetone solution has shown that the complex anion $[Hg(S{\cdot}CF_3)_2I]^-$ can exist under conditions where hydrolysis is excluded (*130, 131*).

Lead and thallium react with bis(trifluoromethylthio)mercury at moderate temperatures to yield the corresponding metal fluoride, and colored mixtures containing bistrifluoromethyl trithiocarbonate. Finely divided copper reacts exothermically with the mercurial at 80–100°; further heating at 150°, followed by extraction of the solid product with ether, enables a pale green compound ($CF_3{\cdot}S{\cdot}Cu$) to be isolated, although it is difficult to free from ether. The white silver salt of trifluoromethanethiol, $CF_3{\cdot}S{\cdot}Ag$, can be prepared by mixing the mercurial with aqueous silver nitrate (*156*). The trichlorides of phosphorus and arsenic react with bis(trifluoromethylthio)mercury at room temperature to form compounds of the type $RMCl_2$, R_2MCl, and R_3M, where R = $CF_3{\cdot}S$, M = P or As (*69*). Mercuric chloride reacts readily with bis(trifluoromethylthio)mercury in ethereal solution, and converts it to trifluoromethylthiomercuric chloride, $CF_3{\cdot}S{\cdot}HgCl$ (*69*). This last compound was first prepared from the mercurial as follows:

$$(CF_3{\cdot}S)_2Hg + CF_3{\cdot}SCl \rightarrow CF_3{\cdot}S{\cdot}HgCl + CF_3{\cdot}S_2{\cdot}CF_3 \qquad (228)$$

The compounds $CF_3{\cdot}S{\cdot}HgNO_3$ and $CF_3{\cdot}S{\cdot}HgOCOCH_3$ can be obtained by the action of an aqueous solution of the appropriate silver salt on $CF_3{\cdot}S{\cdot}HgCl$. Mercuric bromide does not react with bis(trifluoromethylthio)mercury under the conditions used with mercuric chloride, but trifluoromethanesulfenyl bromide is formed in a reaction with bromine:

$$(CF_3{\cdot}S)_2Hg \xrightarrow{Br_2,\ 20°} CF_3{\cdot}SBr + CF_3{\cdot}S_2{\cdot}CF_3 + HgBr_2 \qquad (229)$$

Bistrifluoromethyl disulfide is the only product formed when bis(trifluoromethylthio)mercury is treated with iodine in carbon tetrachloride solution. Attempts to prepare the nitroso compound $CF_3{\cdot}S{\cdot}NO$ by reaction with nitrosyl chloride at low temperatures failed (*69*):

$$(CF_3\cdot S)_2Hg \xrightarrow{NOCl} CF_3\cdot S_2\cdot CF_3 + CF_3\cdot SCl + NO + HgCl_2 \qquad (230)$$

Organic compounds containing reactive chlorine undergo simple metathetical reactions with bis(trifluoromethylthio)mercury (*156*), e.g.,

$$(CF_3\cdot S)_2Hg \begin{cases} \xrightarrow{tert\text{-}C_4H_9Cl} tert\text{-}C_4H_9\cdot S\cdot CF_3 \\ \xrightarrow{CH_2:CH\cdot CH_2Cl} CH_2{:}CH\cdot CH_2\cdot S\cdot CF_3 \\ \xrightarrow{CH_3\cdot COCl} CH_3\cdot CO\cdot S\cdot CF_3 \\ \xrightarrow{CCl_3\cdot SCl} CCl_3\cdot S_2\cdot CF_3 \end{cases} \qquad (231)$$

(iv) *Other fluoroalkyl sulfides.* Little detailed chemistry has been carried out with the other known fluoroalkyl sulfides. Heptafluoro-*n*-propanethiol can be prepared by a method analogous to that used for trifluoromethanethiol (*103*):

$$C_3F_7I \xrightarrow{S} C_3F_7\cdot S_2\cdot C_3F_7 \xrightarrow{Hg,\ ultraviolet\ light} (C_3F_7\cdot S)_2Hg \xrightarrow{HCl} C_3F_7\cdot SH \qquad (232)$$

The over-all yield from the disulfide is low because the preparation and isolation of the mercurial is troublesome.

Aqueous alkaline hydrolysis of the compound $C_3F_7\cdot SH$ is more complicated than expected, since by analogy with the hydrolysis of the compound $CF_3\cdot SH$, formation of pentafluoropropionic acid with liberation of two atoms of fluorine as fluoride and one atom of sulfur as sulfide per molecule of thiol would be anticipated:

$$C_3F_7\cdot SH \xrightarrow{OH^-} C_2F_5\cdot CO_2H,\ 2F^-,\ S^= \qquad (233)$$

In fact three atom-equivalents of fluoride are formed at temperatures ranging from 20–140°, but the nature of the organic end product has not been determined. The liberation of an extra fluorine as fluoride is not, however, due to the formation of tetrafluoroethylene from sodium pentafluoropropionate ($CF_3\cdot CF_2\cdot CO_2Na \rightarrow C_2F_4 + CO_2 + NaF$), since no volatile products are detected.

The alkaline hydrolysis of bis(heptafluoro-*n*-propyl) disulfide at room temperature proceeds according to the scheme:

$$\begin{array}{l} C_3F_7\cdot S\cdot S\cdot C_3F_7 \xrightarrow{OH^-} C_3F_7\cdot SH + C_3F_7\cdot S\cdot OH \\ \qquad\qquad\qquad\qquad\quad \downarrow OH^- \qquad\qquad \downarrow OH^- \\ \qquad\qquad\qquad\qquad\quad 3F^-,\ S^= \qquad \tfrac{1}{2}C_3F_7\cdot SH + \tfrac{1}{2}C_3F_7\cdot SO_2H \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow OH^- \qquad\qquad \downarrow OH^- \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad 1\tfrac{1}{2}F^-,\ \tfrac{1}{2}S^= \qquad No\ F^- \end{array} \qquad (234)$$

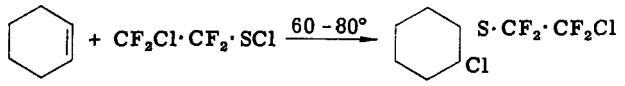
Heptafluoro-*n*-propanesulfenyl chloride can be prepared by photochemical chlorination of the disulfide. When it is heated with silver fluoride at 125–160° some halogen exchange occurs with the formation of what is thought to be heptafluoro-*n*-propanesulfenyl fluoride, but the main product is the parent disulfide (*138*).

Bis(2-chloro-1,1,2,2-tetrafluoroethyl) disulfide is converted into the sulfenyl chloride by treatment with chlorine in an autoclave at 80–90° (*136*):

$$CF_2Cl{\cdot}CF_2{\cdot}S_2{\cdot}CF_2{\cdot}CF_2Cl \xrightarrow{Cl_2} 2CF_2Cl{\cdot}CF_2{\cdot}SCl \qquad (235)$$

This sulfenyl chloride reverts to the parent disulfide on treatment with aqueous potassium iodide, and reacts smoothly with diethylamine to form the sulfenamide. Addition occurs across the double bond of olefins such as cyclohexene and ethylene:

$$C_2H_4 + CF_2Cl{\cdot}CF_2{\cdot}SCl \xrightarrow{95-100°} CF_2Cl{\cdot}CF_2{\cdot}S{\cdot}CH_2{\cdot}CH_2Cl \qquad (236)$$



(237)

A polyfluoroalkyl thiol can also be prepared by reduction of the corresponding disulfide. Thus the reduction of $[CHF_2{\cdot}(CF_2)_5{\cdot}CH_2]_2S_2$ to the thiol $CHF_2{\cdot}[CF_2]_5{\cdot}CH_2{\cdot}SH$ has been achieved by use of lithium aluminium hydride (*72*). Bistrifluoromethyl disulfide is decomposed when treated with hydrogen in the presence of a Raney nickel catalyst at 150° without formation of fluoroform (*25*), so reductive cleavage of the S—S bond appears difficult when it is flanked by CF_2 groups.

(v) *Polyfluoroalkyl sulfones.* Little is known about these. The fluoroalkyl sulfides $CF_3{\cdot}S{\cdot}CH_3$, $CF_2Cl{\cdot}S{\cdot}CH_3$, and $CF_3{\cdot}S{\cdot}CH_2Cl$ are oxidized by chromic oxide in glacial acetic acid to the corresponding sulfones, although pentafluorodimethyl sulfide, $CF_3{\cdot}S{\cdot}CHF_2$, cannot be oxidized by this reagent (*195*). The only perfluoroalkyl sulfone known to the authors, bistrifluoromethyl sulfone, $CF_3{\cdot}SO_2{\cdot}CF_3$, has been prepared in low yield by the electrochemical fluorination of dimethyl sulfone (*114*).

3. Perfluoroalkane Sulfonic Acids

Few of the methods of synthesis of alkane or aryl sulfonic acids can be applied to the preparation of perfluoroalkane sulfonic acids: e.g., the Strecker synthesis fails; bistrifluoromethyl disulfide is inert to concentrated nitric acid up to 115° (cf. alkyl disulfides); fluorohydrocarbons are either inert to fuming sulfuric acid or liberate fluoride ion at high temperatures.

The first polyfluoroalkane sulfonic acid to be described was tetrafluoroethanesulfonic acid, prepared by the addition reaction of sodium bisulfite with tetrafluoroethylene under pressure (*41*). This method has been applied to other fluoroolefins (*149*). Trifluoromethanesulfonic acid was the first perfluorosulfonic acid to be described, and the methods used for its preparation can be applied to higher members of the series.

Trifluoromethanesulfonic acid can be prepared by four routes:

(a) The oxidation of trifluoromethanesulfinic acid (*102*):

$$CF_3{\cdot}SCl \rightarrow CF_3{\cdot}SO_2H \xrightarrow{H_2O_2} CF_3{\cdot}SO_3H; \quad (238)$$

(b) the hydrolysis of the sulfonyl chloride (*102*):

$$CF_3{\cdot}SCl \xrightarrow{Cl_2,\ H_2O} CF_3{\cdot}SO_2Cl \rightarrow CF_3{\cdot}SO_3H; \quad (239)$$

(c) the oxidation of bis(trifluoromethylthio)mercury with hydrogen peroxide (*101*):

$$(CF_3{\cdot}S)_2Hg \xrightarrow{H_2O_2} CF_3{\cdot}SO_3H; \quad (240)$$

(d) the electrochemical fluorination of methanesulfonyl chloride or, better, -fluoride (*30, 81, 82*):

$$CH_3{\cdot}SO_2F \xrightarrow[\text{fluorination}]{\text{electrochemical}} \underset{(96\%)}{CF_3{\cdot}SO_2F} \xrightarrow{Ba(OH)_2} (CF_3{\cdot}SO_3)_2Ba \xrightarrow{H_2SO_4} CF_3{\cdot}SO_3H \quad (241)$$

Homologs of trifluoromethanesulfonic acid can be prepared using method (d) but the yield of sulfonyl fluoride in the fluorination step decreases steadily as the chain length increases (*30, 82*); thus the yield of the acid fluoride $C_8F_{17}{\cdot}SO_2F$ is 25%.

Trifluoromethanesulfonic acid is a colorless, fuming, oily liquid that reacts vigorously with water, chars paper, and acts as a dehydrating agent rather like fuming sulfuric acid. It forms a stable solid hydrate, $H_3O^+CF_3{\cdot}SO_3^-$, which is reconverted to the acid only with difficulty. Trifluoromethanesulfonic acid is one of the strongest monobasic acids known, and in aqueous solution it is completely ionized; a comparison of the extent of ionization of trifluoromethanesulfonic acid in anhydrous acetic acid shows that it is a stronger acid than perchloric acid. It liberates hydrogen chloride from sodium chloride, and silver trifluoromethanesulfonate is soluble in benzene, like other silver salts of strong acids (cf. silver perchlorate).

Well-defined salts can be obtained with organic bases such as aniline, and the sodium and potassium salts have long and useful liquid ranges, since they melt at 248° and 230°, respectively (cf. Na_2SO_4, m.p. 884°; K_2SO_4, m.p. 588°), and are substantially unchanged at 400°. Trifluoromethanesulfonic acid itself is stable to at least 350°, and its aqueous solution can be heated to 275° without decomposition. It shows a marked

TABLE XIX

PHYSICAL PROPERTIES OF POLYFLUOROALKYL DERIVATIVES OF SULFUR

Compound	m.p. (°C)	b.p. (°C/mm Hg)	n_D^t (t, °C)	d_4^t (t, °C)
$CF_3 \cdot SH$	—	−36.7[a]	—	—
$CF_3 \cdot S \cdot HgCl$	124–126	—	—	—
$CF_3 \cdot S \cdot CSF$	—	42.9/762[a]	—	—
$CF_3 \cdot S \cdot NH_2$	−89	46.5[a]	—	—
$CF_3 \cdot S \cdot NHCH_3$	—	47[a]	—	—
$CF_3 \cdot S \cdot N(CH_3)_2$	−92	53[a]	—	—
$CF_3 \cdot S \cdot NHC_6H_5$	—	191[a]	—	—
$CF_3 \cdot S \cdot PCl_2$	—	98[a]	—	—
$CF_3 \cdot S \cdot AsCl_2$	−34	125[a]	—	—
CF_3SCl	—	−0.7[a]	—	—
$CF_3SO_2NH_2$	119	—	—	—
CF_3SO_2F	—	−21.7[a]	—	—
CF_3SO_2Cl	—	32	—	—
CF_3SO_3H	—	162	—	—
$(CF_3)_2S$	—	−22.2[a]	—	—
$CF_3 \cdot S \cdot CH_3$	—	11.5–11.7/750	—	—
$CF_3 \cdot S \cdot CHF_2$	—	0.8–1.3	—	—
$CF_3 \cdot S \cdot CH_2Cl$	—	63.5/740	1.3818 (20)	1.4122 (20)
$CF_2Cl \cdot S \cdot CH_3$	−100.2	56.3/755	1.3926 (20)	1.298 (20)
$CF_2Cl \cdot S \cdot CH_2Cl$	—	105.7/740	1.4408 (20)	1.510 (20)
$(CF_3)_2SO_2$	—	15.6[a]	—	—
$CF_3 \cdot SO_2 \cdot CH_3$	14.0	128.9/737	1.3486 (20)	1.5141 (20)
$CF_3 \cdot SO_2 \cdot CH_2Cl$	−90	139.9/751	1.3859 (20)	1.6533 (20)
$CF_2Cl \cdot SO_2 \cdot CH_3$	21.0–21.6	165.1	1.4050 (20)	1.5685 (20)
$(CF_3 \cdot S)_2Hg$	39–40	3 mm at 55°[b]	—	2.911 (d_0^{25})
$(CF_3 \cdot S)_2Hg$, $P(C_6H_5)_3$	166–168[c]	—	—	—
$(CF_3 \cdot S)_2Hg$, $HCSN(CH_3)_2$	91–92	—	—	—
$(CF_3 \cdot S)_2CS$	—	110	—	—
$(CF_3 \cdot S)_2NH$	−47	73.0[a]	—	—
$(CF_3 \cdot S)_2PCl$	—	115[a]	—	—
$(CF_3 \cdot S)_2AsCl$	−50	128[a]	—	—
$(CF_3 \cdot S)_3P$	−75	~180[a]	—	—
$(CF_3)_2S_2$	—	34.6[a]	—	—
$CF_3 \cdot S_2 \cdot C_2H_5$	—	82.0[a]	—	—
$(CF_3)_2S_3$	—	86.4	1.4023 (20)	—
$(CF_3)_2S_4$	—	135	1.4608 (20)	—
$CF_2Cl \cdot CF_2 \cdot SCl$	—	69.5	1.3890 (20)	1.605 (20)
$CF_2Cl \cdot CF_2 \cdot S \cdot SCl$	—	126	1.4112 (20)	1.674 (20)
$(CF_2Cl \cdot CF_2)_2S$	—	100–102	1.368 (10)	1.662 (10)
$(CF_2Cl \cdot CF_2)_2S_2$	—	139–140	1.3970 (20)	1.685 (20)
$(CF_2Cl \cdot CF_2)_2S_3$	—	50–52/5	1.4340 (20)	1.707 (20)
$(CF_2Cl \cdot CFCl)_2S_3$	—	83–84	1.4888 (29)	—
$(CF_2Cl \cdot CFCl)_2S_4$	—	112–118	1.5217 (29)	—
$C_3F_7 \cdot SH$	—	23.7/759[a]	—	—

TABLE XIX (*Continued*)

Compound	m.p. (°C)	b.p. (°C/mm Hg)	n_D^t (t, °C)	d_4^t (t, °C)
C_3F_7·SF	—	−15 to 0[d]	—	—
C_3F_7·SCl	—	51–51.5	1.3239 (23)	—
$(C_3F_7)_2S$	—	87–90	1.2890 (30)	—
$(C_3F_7)_2S_2$	—	122	1.3222 (26.5)	1.6940 (28)
$(C_3F_7)_2S_3$	—	152.5–153	1.3600 (31)	—
$(CF_3)(C_4F_9)CF$·SCl	—	63.0–63.8/97	1.3237 (26)	—
$[C_4F_9·CF(CF_3)]_2S_2$	—	94/8	1.330 (23)	—
$[C_4F_9·CF(CF_3)]_2S_3$	—	66/<0.1	1.3469 (28.8)	—
$[C_4F_9·CF(CF_3)]_2S_4$	—	~80/<0.1	1.3791 (20)	—
$[C_4F_9·CF(CF_3)]_2S_5$	—	—	1.3975 (19.5)	—
$CHF_2·[CF_2]_5·CH_2·SH$	—	70–71/20	1.3378 (20)	1.6700 (20)
$(CHF_2·[CF_2]_5·CH_2)_2S$	—	159–160/20	1.3370 (20)	1.7822 (20)

[a] Calculated from vapor pressure measurements.
[b] Vapor pressure.
[c] With decomposition.
[d] Distillation range.

resistance to decomposition by aqueous alkali, thus differing from most other trifluoromethyl derivatives of sulfur. It appears, then, that the resistance of trifluoromethyl oxyacids is at a maximum when the hetero atom displays its maximum valence. Pyrolysis of trifluoromethanesulfonic acid in platinum at 650° affords sulfuryl fluoride, carbonyl fluoride, fluoroform, and carbon dioxide (*83*).

The powerful acidity of trifluoromethanesulfonic acid and its homologs provides many useful applications (*83*): thus, trifluoromethanesulfonic anhydride is a good promoter for esterification; alkyl trifluoromethanesulfonates are excellent alkylating agents; the acid itself is an active catalyst in many organic reactions; and the long-chain acids are markedly surface-active and are finding appropriate industrial application in this connection.

The physical properties of the polyfluoroalkyl derivatives of sulfur are listed in Table XIX.

B. Selenium

1. Preparation of Polyfluoroalkyl Selenium Compounds

The only polyfluoroalkyl derivatives of selenium which have been studied in detail are the trifluoromethyl compounds. Early experiments aimed at the preparation of these from carbon diselenide or dimethyl selenide by the electrochemical method failed because decomposition products containing elemental selenium fouled the cell electrodes (*39*). However, the reaction of trifluoroiodomethane with selenium within the

optimum temperature range of 260–285° yields bistrifluoromethyl selenide and bistrifluoromethyl diselenide in the ratio of 4:1, together with traces of bistrifluoromethyl triselenide (*51*):

$$CF_3I + Se \rightarrow CF_3{\cdot}Se{\cdot}CF_3 + CF_3{\cdot}Se_2{\cdot}CF_3 \quad (242)$$

This contrasts with the reaction of trifluoroiodomethane with sulfur, which gives mainly the disulfide with small amounts of the tri- and tetra-sulfides, but no monosulfide (see Section VIII,A,*2*,*a*). Bistrifluoromethyl diselenide can also be prepared by heating together a mixture of selenium and mercuric trifluoroacetate (*203*).

The compounds $CHF_2{\cdot}[CF_2]_5{\cdot}CH_2I$ and $CHF_2{\cdot}[CF_2]_9{\cdot}CH_2I$ react similarly with selenium to give polyfluoroalkyl selenides (*72*):

$$CHF_2{\cdot}[CF_2]_5{\cdot}CH_2I + Se \xrightarrow{260°} (CHF_2{\cdot}[CF_2]_5{\cdot}CH_2)_2Se + (CHF_2{\cdot}[CF_2]_5{\cdot}CH_2)_2Se_2 \quad (243)$$

$$CHF_2{\cdot}[CF_2]_9{\cdot}CH_2I + Se \xrightarrow{260°} (CHF_2{\cdot}[CF_2]_9{\cdot}CH_2)_2Se \quad (244)$$

2. Properties and Reactions of Trifluoromethyl Selenium Compounds (51)

The trifluoromethyl derivatives of selenium are characterized by: (*a*) greater reactivity than the corresponding sulfur compounds, attributed to weaker C—Se and Se—Se bonds; (*b*) an ability to form tetravalent selenium compounds involving halogen, e.g., $CF_3{\cdot}SeCl_3$, not readily formed by the corresponding sulfur compounds; and (*c*) formation of the seleninic acid, $CF_3{\cdot}SeO_2H$, as the most stable oxyacid, in contrast to the sulfonic acid $CF_3{\cdot}SO_3H$. These trends are, in general, in accord with those observed with other derivatives of selenium and sulfur.

Bistrifluoromethyl selenide, $CF_3{\cdot}Se{\cdot}CF_3$, boils at −2°; like its sulfur analog it is resistant to hydrolysis by water or aqueous alkali, although 20% alcoholic potassium hydroxide decomposes it at 100°:

$$CF_3{\cdot}Se{\cdot}CF_3 \xrightarrow{OH^-,\ 100°} CHF_3,\ F^-,\ Se^=,\ CO_3^= \quad (245)$$

It is unaffected by dilute mineral acids, and is inert to concentrated nitric acid in contrast to dimethyl selenide, which is said to be oxidized by the latter reagent to a salt of the selenoxide, $(CH_3)_2Se(OH)NO_3$. Again, unlike the dialkyl selenides, bistrifluoromethyl selenide does not react with mercuric chloride, nor does it form a selenonium compound with methyl iodide. Chlorine reacts slowly with bistrifluoromethyl selenide at room temperature, and rapidly at 150°, to form an equimolar mixture of trifluoromethylselenium trichloride and selenium tetrachloride, together with some chlorotrifluoromethane. Photochemical chlorination using light of wavelength >3000 Å yields trifluoromethylselenium trichloride almost quantitatively; there is no indication of the formation of a stable dichloride, $(CF_3)_2SeCl_2$.

Bistrifluoromethyl diselenide is distinctly more reactive than the mono-

selenide. It is decomposed rapidly by water at 100° with deposition of selenium and, with aqueous alkali, gives fluoride, carbonate, polyselenide ion, and selenium, even below 0°. No fluoroform is produced. The selenol, $CF_3{\cdot}SeH$, and the selenenic acid, $CF_3{\cdot}SeOH$, are possible intermediates which would decompose immediately like their sulfur analogues (see Section (VIII,A,*2*,*b*). The selenol can be synthesized as follows (cf. the preparation of $CF_3{\cdot}SH$, Section VIII,A,*2*,*b*):

$$CF_3{\cdot}Se_2{\cdot}CF_3 + Hg \xrightarrow{\text{ultraviolet light}} (CF_3{\cdot}Se)_2Hg \qquad (246a)$$

$$(CF_3{\cdot}Se)_2Hg \xrightarrow{\text{HCl, 50–100°}} CF_3{\cdot}SeH + (CF_3)_2Se_2 + CF_3{\cdot}Se{\cdot}HgCl \qquad (246b)$$

The mercurial is formed in high yield (96%) from the diselenide and mercury, but the second stage of the synthesis compares unfavorably with the corresponding stage in the preparation of trifluoromethanethiol, and the selenol is obtained in only low yield. The white crystalline intermediate, $CF_3{\cdot}Se{\cdot}HgCl$, can be synthesized separately by reaction of equimolar quantities of bis(trifluoromethylseleno)mercury and mercuric chloride in ether.

Bis(trifluoromethylseleno)mercury is a pale yellow, crystalline solid which sublimes *in vacuo* and is readily soluble in water and organic solvents. It reacts rapidly and quantitatively with bromine or chlorine, with production of the corresponding selenenyl halide, thus:

$$(CF_3{\cdot}Se)_2Hg \begin{cases} \xrightarrow{Br_2} CF_3{\cdot}SeBr + HgBr_2 \\ \xrightarrow{Cl_2} CF_3{\cdot}SeCl + HgCl_2 \end{cases} \qquad (247)$$

These selenenyl halides can also be prepared by the direct, controlled halogenation of bistrifluoromethyl diselenide. Chlorine reacts with the diselenide even at −50°, converting it into the trichloride, $CF_3{\cdot}SeCl_3$, but by use of a limited amount of chlorine, trifluoromethylselenenyl chloride can be obtained:

$$CF_3{\cdot}Se_2{\cdot}CF_3 + Cl_2 \rightarrow 2CF_3{\cdot}SeCl \qquad (248)$$

Trifluoromethylselenenyl bromide can be obtained by bromination of the diselenide at 75°; when a higher reaction temperature is employed (150°) selenium tetrabromide and bromotrifluoromethane are formed. Iodine reacts with bistrifluoromethyl diselenide at temperatures in excess of 160° to yield trifluoroiodomethane.

Trifluoromethylselenenyl chloride is a cherry-red liquid which reacts rapidly and quantitatively with mercury, forming bis(trifluoromethylseleno)mercury. The chlorine is replaced by cyanide when the selenenyl chloride is treated with dry silver cyanide in a sealed tube at temperatures

below 0°C. Trifluoromethylselenocyanate so formed is stable to water, but is decomposed quantitatively by 20% aqueous alkali with formation of fluoride ion. Trifluoromethylselenenyl chloride is hydrolyzed readily by water with formation of bistrifluoromethyl diselenide in amounts which agree with the equation:

$$3CF_3{\cdot}SeCl + 2H_2O \rightarrow CF_3{\cdot}SeO_2H + CF_3{\cdot}Se_2{\cdot}CF_3 + 3HCl \qquad (249)$$

Hydrolysis with 25% aqueous sodium hydroxide decomposes the selenenyl chloride, one-third of the fluorine appearing as fluoroform and two-thirds as fluoride ion. Trifluoromethylselenenyl chloride reacts with ethylene to give the compound $CF_3{\cdot}Se{\cdot}CH_2{\cdot}CH_2Cl$ (*203*).

TABLE XX

PHYSICAL PROPERTIES OF POLYFLUOROALKYL DERIVATIVES OF SELENIUM

Compound	m.p. (°C)	b.p. (°C/mm Hg)	n_D^t (t, °C)	d_4^t (t, °C)
$CF_3{\cdot}SeH$	—	−14.5/758	—	—
$CF_3{\cdot}SeCl$	—	31	1.3930 (14)	1.9899 (14)
$CF_3{\cdot}SeBr$	—	53.5–54.3	—	—
		57	1.4270	2.3567 (24)
$CF_3{\cdot}SeCN$	—	84/758	—	—
		80	1.3875 (22)	1.7912 (22)
$CF_3{\cdot}Se{\cdot}CH_2{\cdot}CH_2Cl$	—	110	1.4355 (14)	1.6910 (14)
$CF_3{\cdot}Se{\cdot}HgCl$	185–190	—	—	—
$CF_3{\cdot}SeCl_3$	88–89	—	—	—
$CF_3{\cdot}SeO_2H$	118.5–119.0	—	—	—
$(CF_3)_2Se$	—	−2	—	—
$(CF_3)_2Se_2$	—	72.5–73.5	—	—
		70	1.4035	2.2031 (18)
$(CF_3{\cdot}Se)_2Hg$	51	—	—	—
$(CHF_2{\cdot}[CF_2]_5{\cdot}CH_2)_2Se$	—	150/10	1.3468 (20)	1.8892 (20)
$(CHF_2{\cdot}[CF_2]_5{\cdot}CH_2)_2Se_2$	—	170–175/10	1.378 (20)	1.979 (20)
$(CHF_2{\cdot}[CF_2]_9{\cdot}CH_2)_2Se$	94–96	170/0.6	—	—

Trifluoromethareseleninic acid, $CF_3{\cdot}SeO_2H$, can be prepared in high yield by the oxidation of bistrifluoromethyl diselenide with concentrated nitric acid; it can also be obtained by exposing trifluoromethylselenium trichloride to moist air. The acid is stable, nondeliquescent, strong and monobasic, and attempts to oxidize it to the selenonic acid, $CF_3{\cdot}SeO_3H$, have so far failed.

The physical properties of the polyfluoroalkyl derivatives of selenium are listed in Table XX.

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