bromine. Another sample irradiated for 3 days with a General Electric RS sun lamp gave bromine in 87% conversion (precipitated as 2,4,6-tribromophenol).

**Reaction of Tetrafluoroethylene with Sulfur.**[34]—A jacketed dropping funnel heated with the vapors of boiling chlorobenzene was affixed to the top of a vertically mounted, heated platinum tube 0.75 in. in diameter and 12 in. long. Provision was also made for a gas inlet between the dropping funnel and the tube. Sodium fluoride pellets (10 g.) supported on a plug of platinum gauze were placed midway between the ends of the tube. To ensure good heat transfer to the reactants, the pellets were covered with a second plug of platinum gauze. The lower end of the platinum tube was attached to a large flask to hold unchanged sulfur, and this flask was connected to a trap cooled by solid carbon dioxide and acetone in which products were collected. The system was purged with nitrogen and the platinum tube heated to 490–525°. Then, molten sulfur was admitted to the tube at a rate of 1 ml./min. along with nitrogen at 0.5 ml./sec. and tetrafluoroethylene at 2.4 ml./sec. The products obtained after addition of approximately 40 g. (0.4 mole) of tetrafluoroethylene were distilled to yield 25 g. boiling at −58 to −49°, which was thiocarbonyl fluoride containing a trace of tetrafluoroethylene; 7 g. boiling at −23 to +2°, which was mainly perfluorothioacetyl fluoride with a trace of some other fluorine-containing material; and 13 g. boiling at 27–29°, which was bis(trifluoromethyl) disulfide.

**Acknowledgment.**—The authors gratefully acknowledge helpful suggestions given by Dr. Morton Brown of this laboratory and Dr. D. M. Marquis of the Jackson Laboratory of the Organic Chemicals Department of E. I. du Pont de Nemours and Company, Wilmington, Delaware.

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[34] D. M. Marquis, U. S. Patent 3,097,236 (1963).

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# Fluorothiocarbonyl Compounds. II.[1] Reactions of Hexafluorothioacetone

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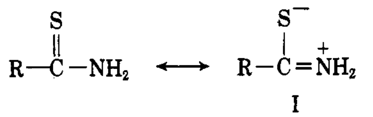
*Received October 28, 1964*

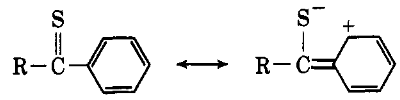
Study of the chemistry of hexafluorothioacetone has shown that it is very reactive with nucleophilic reagents. An example is sodium bisulfite, which adds to give Bunte salts in a manner opposite to that normally expected. Such reverse additions also take place with mercaptans, in which case disulfides are formed. Mercaptans also add in the normal manner to give dithio hemiketals. Unusual methylenephosphoranes are formed by reaction of hexafluorothioacetone with trialkyl phosphites. The exceptional reactivity of this thio ketone also has been demonstrated by reactions with halogens, halogen halides, water, diazo compounds, hydrogen sulfide, and sulfur dioxide.

Reactions involving additions to a true thiocarbonyl group (C=S) have not been studied in detail. One reason for this appears to be the lack of suitable model compounds. Thioureas, thioamides, and even aromatic thio ketones exist to a great extent in such ionic canonical forms as I and II, and most aliphatic thio ketones are in equilibrium with enolic forms, such as III. In addition, many of the reported thio ketones are difficult to prepare in monomeric form and are unstable to air. The synthesis of fluoro thio ketones[1] has provided compounds that do not possess these complicating factors and, of these, hexafluorothioacetone (HFTA) is an ideal model for a study of C=S reactivity. HFTA has its own peculiarity, however, which is the strong electron-withdrawing power of the two trifluoromethyl groups. This electron withdrawal is manifested by high reactivity toward nucleophilic reagents. Because of the easy polarizability of sulfur, many nucleophilic reactions take place by way of transition state V, and these are referred to as reverse additions. However, some nucleophilic reagents react by way of transition state IV, and these are referred to as normal additions.

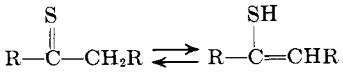


$$\mathrm{R{-}\overset{S}{\overset{\|}{C}}{-}NH_2 \longleftrightarrow R{-}\overset{S^-}{\overset{|}{C}}{=}\overset{+}{N}H_2}$$

I

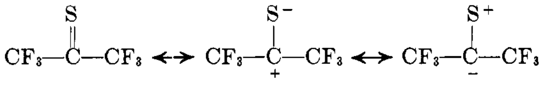


II



$$\mathrm{R{-}\overset{S}{\overset{\|}{C}}{-}CH_2R \rightleftharpoons R{-}\overset{SH}{\overset{|}{C}}{=}CHR}$$

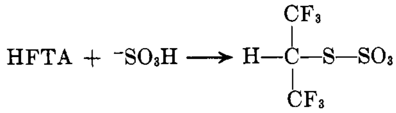
III



$$\mathrm{CF_3{-}\overset{S}{\overset{\|}{C}}{-}CF_3 \longleftrightarrow CF_3{-}\underset{+}{\overset{S^-}{\overset{|}{C}}}{-}CF_3 \longleftrightarrow CF_3{-}\underset{-}{\overset{S^+}{\overset{|}{C}}}{-}CF_3}$$

HFTA IV V

**Reaction of HFTA with Bisulfite Ion.**—The addition of bisulfite ion to HFTA is a striking example of a thiocarbonyl group reacting through the transition state represented by V. Instead of addition to give a salt of an α-mercaptosulfonic acid, HFTA adds bisulfite ion to give a Bunte salt (VI). This reaction occurs rapidly when HFTA is mixed with an aqueous solution of sodium bisulfite at 0°. These adducts were isolated and characterized in the form of water-insoluble, stable, white tetraalkylammonium salts. Absence of SH was shown by infrared and the presence of $C(CF_3)_2H$ was demonstrated by $F^{19}$ n.m.r. and proton n.m.r.



$$\mathrm{HFTA + {}^-SO_3H \longrightarrow H{-}\underset{\underset{CF_3}{|}}{\overset{\overset{CF_3}{|}}{C}}{-}S{-}SO_3^-}$$

VI

Other fluorine-containing thiocarbonyl compounds also react with bisulfite in a reverse manner to give Bunte salts. Examples are the reactions of trifluoromethyl trifluorothioacetate and bis(trifluoromethyl) trithiocarbonate with bisulfite to give products isolated

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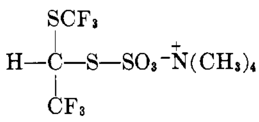
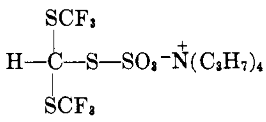
[1] Paper I: W. J. Middleton, E. G. Howard, and W. K. Sharkey, *J. Org. Chem.*, **30**, 1375 (1965).



$$\mathrm{H{-}\overset{\overset{\displaystyle SCF_3}{|}}{\underset{\underset{\displaystyle CF_3}{|}}{C}}{-}S{-}SO_3^{-}\overset{+}{N}(CH_3)_4}$$

VII

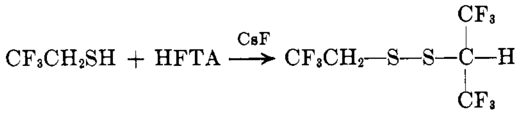


$$\mathrm{H{-}\overset{\overset{\displaystyle SCF_3}{|}}{\underset{\underset{\displaystyle SCF_3}{|}}{C}}{-}S{-}SO_3^{-}\overset{+}{N}(C_3H_7)_4}$$

VIII

as tetraalkylammonium salts VII and VIII, respectively.

**Reactions of HFTA with Mercaptans.**—In its reaction with mercaptans, HFTA behaves in most cases as would be expected if sulfur were positive. For example, addition of 2,2,2-trifluoroethanethiol[2] to HFTA gives the disulfide IX rather than a thio hemiketal.

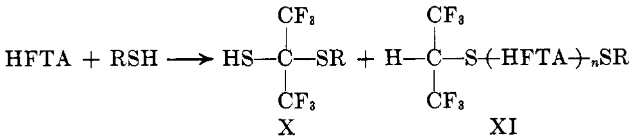


$$\mathrm{CF_3CH_2SH + HFTA \xrightarrow{CsF} CF_3CH_2{-}S{-}S{-}\overset{\overset{\displaystyle CF_3}{|}}{\underset{\underset{\displaystyle CF_3}{|}}{C}}{-}H}$$

IX

It appears likely this addition proceeds by an ionic mechanism rather than a radical mechanism, since no reaction occurs unless cesium fluoride or some other basic catalyst is added.

Mercaptans more basic than trifluoroethyl mercaptan react with HFTA without added catalyst. These reactions appear to give products that are formed by both normal and reverse additions. With methyl and ethyl mercaptan, the major product corresponds to a normal thio hemiketal (X). However, appreciable amounts of two other products, a 2:1 adduct (XI, $n = 1$) and a 3:1 adduct (XI, $n = 2$) were formed. Since these adducts contain no mercaptan groups, as indicated by their infrared and proton n.m.r. spectra, a reverse addition must have occurred as a terminating step in a polymerization reaction.

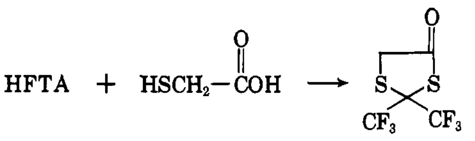


$$\mathrm{HFTA + RSH \longrightarrow HS{-}\overset{\overset{\displaystyle CF_3}{|}}{\underset{\underset{\displaystyle CF_3}{|}}{C}}{-}SR + H{-}\overset{\overset{\displaystyle CF_3}{|}}{\underset{\underset{\displaystyle CF_3}{|}}{C}}{-}S(HFTA)_nSR}$$

X XI

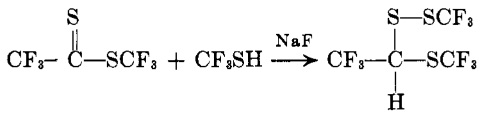
It is interesting to note that exact molecular weight of the reverse addition compounds can be obtained from fluorine n.m.r. data. The doublet characteristic of perfluoroisopropyl identifies the end group. Addition of a second hexafluorothioacetone unit adds a second peak to the spectrum at lower field. When $n = 3$ in compound XI, a third peak is added to the spectrum. Theoretically, the molecular weight of higher derivatives could be obtained by comparing the area of the end group peak with those of the other peaks.

An example of a mercaptan that undergoes normal addition only is mercaptoacetic acid. It reacts with HFTA with loss of water to give the dithiolanone XII.



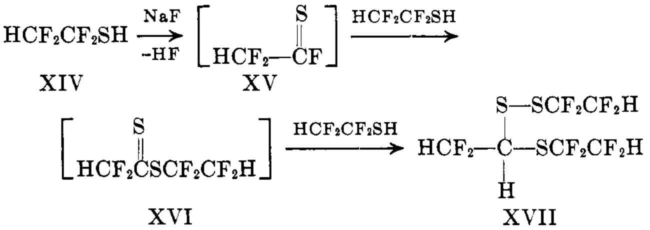
XII

Fluorine-containing dithio esters resemble HFTA in their reaction with acidic mercaptans. Trifluoromethyl trifluorodithioacetate and trifluoromethyl mercaptan in the presence of sodium fluoride catalyst combine to give the reverse adduct XIII. A similar compound (XVII) is formed by treating 1,1,2,2-tetrafluoroethanethiol (XIV) with sodium fluoride. This reaction probably proceeds in several steps, the first being the dehydrofluorination of XIV to give the thio acid fluoride XV, which then reacts with more thiol to give the dithio ester XVI. Reverse addition of XIV to this ester gives the disulfide (XVII), the product actually isolated.



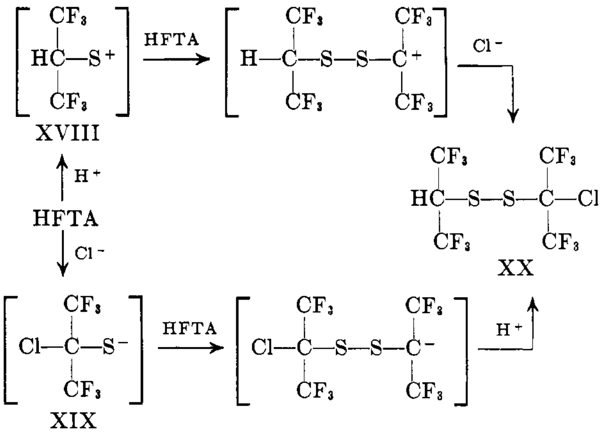
$$\mathrm{CF_3{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}SCF_3 + CF_3SH \xrightarrow{NaF} CF_3{-}\overset{\overset{\displaystyle S{-}SCF_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{-}SCF_3}$$

XIII

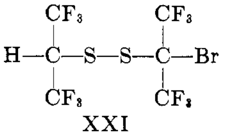


$$\mathrm{\underset{XIV}{HCF_2CF_2SH} \xrightarrow[-HF]{NaF} \underset{XV}{\left[HCF_2{-}\overset{\overset{\displaystyle S}{\|}}{C}F\right]} \xrightarrow{HCF_2CF_2SH} \underset{XVI}{\left[HCF_2\overset{\overset{\displaystyle S}{\|}}{C}SCF_2CF_2H\right]} \xrightarrow{HCF_2CF_2SH} \underset{XVII}{HCF_2{-}\overset{\overset{\displaystyle S{-}SCF_2CF_2H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{-}SCF_2CF_2H}}$$

**Reactions of HFTA with Acids.**—HFTA does not react with either hydrogen chloride or water in the absence of a catalyst. However, HFTA and hydrogen chloride do react in the presence of a small amount of water. The product is a 2:1 adduct (XX) containing a disulfide linkage. The only way formation of a disulfide can be rationalized is by assuming reverse addition. This is true whether the first step is addition of a proton to give XVIII or addition of a chloride ion to give XIX.

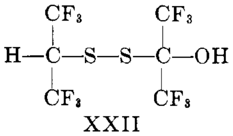


Hydrogen bromide reacts with HFTA in a similar manner to give a disulfide (XXI). An addition product was not obtained from a strong carboxylic acid, trifluoroacetic acid. In this case, the acid appeared to catalyze the addition of water to give the disulfide XXII.



$$\mathrm{H{-}\overset{\overset{\displaystyle CF_3}{|}}{\underset{\underset{\displaystyle CF_3}{|}}{C}}{-}S{-}S{-}\overset{\overset{\displaystyle CF_3}{|}}{\underset{\underset{\displaystyle CF_3}{|}}{C}}{-}Br}$$

XXI



$$\mathrm{H{-}\overset{\overset{\displaystyle CF_3}{|}}{\underset{\underset{\displaystyle CF_3}{|}}{C}}{-}S{-}S{-}\overset{\overset{\displaystyle CF_3}{|}}{\underset{\underset{\displaystyle CF_3}{|}}{C}}{-}OH}$$

XXII

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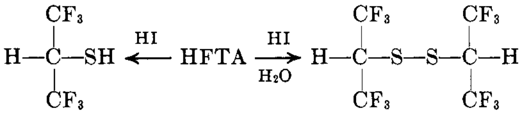
(2) J. F. Harris and W. A. Sheppard, *J. Org. Chem.*, **26**, 354 (1961).

Hydrogen iodide is a special case; it reduces HFTA. Reaction under anhydrous conditions gives the mercaptan XXIII, and use of aqueous hydrogen iodide leads to the disulfide XXIV.

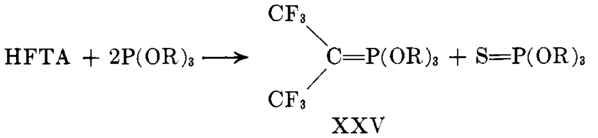


$$\mathrm{H{-}C(CF_3)_2{-}SH} \xleftarrow{\mathrm{HI}} \mathrm{HFTA} \xrightarrow[\mathrm{H_2O}]{\mathrm{HI}} \mathrm{H{-}C(CF_3)_2{-}S{-}S{-}C(CF_3)_2{-}H}$$

XXIII XXIV

These reactions illustrate the great differences in reactivity between sulfur in a thiocarbonyl group and oxygen in a carbonyl group. Characteristic reactions of fluoro ketones are ease of hydration to give *gem*-diols[3] and addition of halogen acids to give $\alpha$-halo alcohols.[4]

**Reactions of HFTA with Trialkyl Phosphites.**—Most organic bases catalyze the dimerization of HFTA, and for this reason it is difficult to examine the reactions of the monomeric thio ketone with such bases as amines. However, with trialkyl phosphites, HFTA reacts smoothly and rapidly to give good yields of trialkoxybis(trifluoromethyl)methylenephosphoranes (XXV).



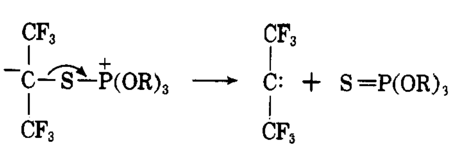
$$\mathrm{HFTA} + 2\mathrm{P(OR)_3} \longrightarrow \mathrm{(CF_3)_2C{=}P(OR)_3} + \mathrm{S{=}P(OR)_3}$$

XXV

($R = CH_3, C_2H_5, CH_3CHCH_3$)

Structures of these phosphoranes were determined by fluorine and proton n.m.r. used in conjunction with elemental analysis. Fluorine shows up as a doublet in the n.m.r. spectrum because it is coupled to the phosphorus. When R is methyl, proton n.m.r. is a doublet, which shows that the protons on all three methyl groups are equivalent and coupled to the phosphorus.

We suggest that the formation of a charged intermediate (XXVI) is the first step in the reaction. If so, loss of a trialkyl thiophosphate molecule from the unstable charged intermediate would give the carbene XXVII. It is visualized the phosphorane is formed by subsequent reaction of the carbene with excess phosphite.

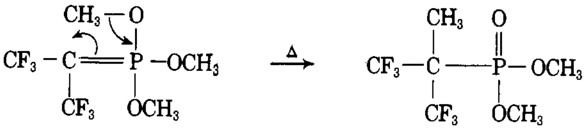


$$^{-}\mathrm{C(CF_3)_2{-}S{-}\overset{+}{P}(OR)_3} \longrightarrow \mathrm{(CF_3)_2C{:}} + \mathrm{S{=}P(OR)_3}$$

XXVI XXVII

The dimer of HFTA, 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane, also reacts with phosphites. to give methylenephosphoranes. It seems likely that the dimer is decomposed to monomeric HFTA by the action of the base, and that it is actually the monomeric thio ketone that reacts with the phosphite.

These methylenephosphoranes are relatively stable, distillable liquids. However, the phosphorane prepared from trimethyl phosphite (XXV, $R = CH_3$) rearranges exothermically when heated to about 180° to give good yields of the phosphonate ester XXVIII.



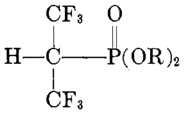
$$\mathrm{(CF_3)_2C{=}P(OCH_3)_3} \xrightarrow{\Delta} \mathrm{CF_3{-}C(CH_3)(CF_3){-}P(O)(OCH_3)_2}$$

XXVIII

The high polarity of the C=P bond is probably the driving force for this rearrangement.

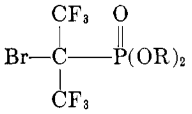
Fluorine and proton n.m.r. offer impressive support for structure XXVIII. Proton spectra show two different kinds of methyl groups in the ratio of 1:2. Each is coupled differently to the phosphorus. Fluorine spectra show one resonance split to doublet by the phosphorus.

The methylenephosphoranes are reactive with electrophilic reagents. They are easily hydrolyzed with aqueous acid and add bromine readily to give esters of phosphonic acids (XXIX and XXX, respectively).



$$\mathrm{H{-}C(CF_3)_2{-}P(O)(OR)_2}$$

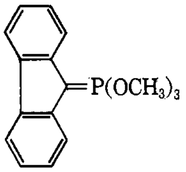
XXIX



$$\mathrm{Br{-}C(CF_3)_2{-}P(O)(OR)_2}$$

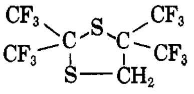
XXX

This phosphite reaction also takes place with thiofluorenone, a nonfluorine-containing thio ketone. The product obtained with trimethyl phosphite is the methylenephosphorane XXXI.

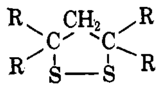


XXXI

**Reactions of HFTA with Diazo Compounds.**—Reaction of HFTA with diazomethane leads to the ring compound, 2,2,5,5-tetrakis(trifluoromethyl)-1,3-dithiolane (XXXII). In addition, lesser amounts of other products involving addition of methylene groups to one or more units of HFTA are formed.



XXXII



XXXIII

The dithiolane XXXII is the product that would result from insertion of a methylene group into the dimer of HFTA, in which the two units of HFTA are arranged in a head-to-tail arrangement. This is different from the reaction of several other thio ketones with diazomethane, which gives dithiolanes of formula XXXIII.[5]

HFTA is analogous to normal ketones in its reaction with substituted diazomethanes. Thiiranes (XXXIV and XXXVI, respectively) are formed by reactions of HFTA with diphenyldiazomethane and ethyl diazoacetate. The ethylene sulfide XXXIV is easily desulfurized by heating at reflux for 15 min. to a high yield of 1,1-bis(trifluoromethyl)-2,2-diphenylethylene (XXXV).

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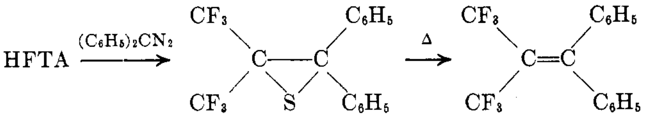
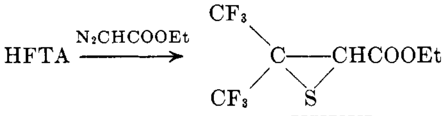
[3] A. L. Henne, J. W. Shepard, and E. J. Young, *J. Am. Chem. Soc.*, **72**, 3577 (1950).

[4] S. Andreades and D. C. England, Abstracts of the 140th Meeting of the American Chemical Society, Chicago, Ill., Sept. 1961, p. 14M; *J. Am. Chem. Soc.*, **83**, 4670 (1961).

[5] A. Schönberg, D. Cernik, and W. Urban, *Ber.*, **64**, 2577 (1931); A. Schönberg, H. Kaltschmitt, and H. Schulten, *ibid.*, **66**, 245 (1933).



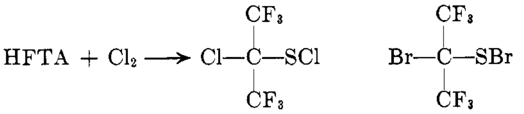
XXXIV XXXV



XXXVI

**High-Temperature Reactions of HFTA.**—Nitric oxide and sulfur dioxide, which do not react with HFTA at low temperatures, oxidize it to hexafluoroacetone at 650°. Oxygen, which is also unreactive at lower temperatures, reacts with HFTA at 650° to give high conversions of carbonyl fluoride and sulfur dioxide. Hydrogen sulfide, which catalyzes dimerization at lower temperatures, reduces HFTA to 1,1,1,3,3,3-hexafluoropropane at 650°.

**Reactions of HFTA with Halogens.**—HFTA reacts with chlorine or bromine to give stable sulfenyl halides (XXXVII and XXXVIII).



XXXVII XXXVIII

## Experimental[6]

**HFTA-Bisulfite Adducts (VI).**—HFTA, 9.1 g. (0.05 mole), was added to a solution of 5.2 g. (0.05 mole) of sodium bisulfite in 25 ml. of water cooled to 0°. The mixture was shaken vigorously until the blue color disappeared. A solution of 15.6 g. (0.05 mole) of tetra-*n*-propylammonium iodide in 100 ml. of water was added, and the white precipitate that formed was collected on a filter and washed with cold water. Recrystallization from alcohol-water gave 18.3 g. (81%) of tetra-*n*-propylammonium S-[bis(trifluoromethyl)methyl]thiosulfate as white prisms, m.p. 123–125°. The $F^{19}$ n.m.r. spectrum in deuteriochloroform showed a doublet at 1.4 p.p.m. The proton n.m.r. spectrum showed a septet ($J$ = 8 c.p.s.) at 4.56 p.p.m. in addition to absorption due to propyl groups. The infrared spectrum showed the absence of a SH group.

*Anal.* Calcd. for $C_{15}H_{29}F_6NO_3S_2$: C, 40.08; H, 6.50; F, 25.36; N, 3.11; S, 14.27. Found: C, 39.52; H, 6.83; F, 25.17; N, 3.31; S, 14.37.

Tetraethylammonium S-[bis(trifluoromethyl)methyl] thiosulfate, m.p. 165–166°, was prepared in 73% yield in a similar manner by reaction of the HFTA–bisulfite adduct with tetraethylammonium iodide. The $F^{19}$ n.m.r. spectrum showed a doublet at −1.4 p.p.m. ($J$ = 8 c.p.s.). The proton n.m.r. spectrum showed a septet at 4.56 ($J$ = 8 c.p.s.), a quartet at 3.32 ($J$ = 7 c.p.s.), and a triplet split to a triplet at 1.34 ($J_{HH}$ = 7 c.p.s., $J_{NH}$ = 2 c.p.s.).

*Anal.* Calcd. for $C_{11}H_{21}F_6NO_3S_2$: C, 33.58; H, 5.38; F, 28.98; N, 3.56; S, 16.30. Found: C, 33.72; H, 5.49; F, 29.21; N, 3.72; S, 16.13.

By using tetramethylammonium chloride in place of tetra-*n*-propylammonium iodide, tetramethylammonium S-[bis(trifluoromethyl)methyl] thiosulfate, m.p. 196–198° dec., was obtained in 57% yield in a similar manner. This salt was recrystallized from water instead of alcohol–water.

*Anal.* Calcd. for $C_7H_{13}F_6NO_3S_2$: C, 24.93; H, 3.88; F, 33.80; N, 4.16; S, 19.01. Found: C, 25.25; H, 4.13; F, 33.91; N, 4.26; S, 18.92.

**Bis(trifluoromethyl) Trithiocarbonate–Bisulfite Adduct (VIII).**—Bis(trifluoromethyl) trithiocarbonate[7] was shaken vigorously with a mixture of 10 ml. of water, 5 ml. of ethyl alcohol, and 3.12 g. (0.03 mole) of sodium bisulfite in a stoppered flask until the red color faded. The solution was filtered, and the filtrate was mixed with a solution of 6.24 g. (0.2 mole) of tetra-*n*-propylammonium iodide in 25 ml. of water. The mixture was cooled and the white precipitate that formed was collected on a filter and recrystallized from alcohol–water. There was obtained 8.8 g. (70%) of tetrapropylammonium S-[bis(trifluoromethylthio)-methyl] thiosulfate as white plates, m.p. 140–143°.

*Anal.* Calcd. for $C_{16}H_{29}F_6NO_3S_4$: C, 35.07; H, 5.69; F, 22.20; N, 2.73; S, 24.91. Found: C, 34.99; H, 6.02; F, 22.34; N, 2.91; S, 25.16.

**Trifluoromethyl Trifluorodithioacetate–Bisulfite Adduct (VII).**—A mixture of 0.2 g. of trifluoromethyl trifluorodithioacetate,[1] 0.2 g. of sodium bisulfite, and 5 ml. of water was shaken at room temperature until the red color disappeared and the mixture became clear. Tetramethylammonium chloride, 1 g., was added, and the resulting solution was cooled. The colorless flakes that separated were collected on a filter and recrystallized from alcohol–water. There was obtained 0.073 g. of tetramethylammonium S-[trifluoromethyl(trifluoromethylthio)methyl] thiosulfate as white plates, m.p. 155° dec., with previous darkening at about 145°. The $F^{19}$ n.m.r. spectrum showed a doublet, and the proton n.m.r. spectrum showed a quartet in addition to a singlet for $N(CH_3)_4^+$.

*Anal.* Calcd. for $C_7H_{13}F_6NO_3S_3$: S, 26.04. Found: S, 25.93.

**Reaction of HFTA with Methyl Mercaptan.**—Methyl mercaptan was slowly distilled into a flask containing 30 g. of HFTA cooled to −78° until the blue color of the thioacetone faded to yellow. The reaction mixture was warmed to room temperature and then distilled. The following fractions were obtained.

Fraction I, 8.2 g., b.p. 55–56°, was the dimer of HFTA.

Fraction II, 18.74 g., b.p. 56–57° (85 mm.), $n^{25}D$ 1.3936, was identified as 1,1,1,3,3,3-hexafluoro-2-methylthio-2-propanethiol (X, R = $CH_3$). The infrared spectrum contained a band at 3.85 $\mu$ for SH. The $F^{19}$ n.m.r. spectrum showed a singlet at +7.06 p.p.m., and the proton n.m.r. showed singlets at 3.90 (area 1) and at 2.45 p.p.m. (area 3).

*Anal.* Calcd. for $C_4H_4F_6S_2$: F, 49.52; S, 27.86. Found: F, 49.45; S, 27.93.

Fraction III, 3.15 g., b.p. 81–83° (22 mm.), $n^{25}D$ 1.4086, was identified as a 2:1 adduct of methyl mercaptan with HFTA (XI, $n$ = 1; R = $CH_3$). The infrared spectrum did not show the presence of SH. The $F^{19}$ n.m.r. spectrum showed a singlet at −2.13 and a doublet at −0.09 p.p.m. ($J$ = 7 c.p.s.). The proton n.m.r. contained a singlet at 2.48 (area 3) and a septet at 4.6 p.p.m. ($J$ = 7 c.p.s.) of area 1.

*Anal.* Calcd. for $C_7H_4F_{12}S_3$: F, 55.32; S, 23.33. Found: F, 55.33; S, 23.33.

Fraction IV, 5.19 g., b.p. 76–77° (1.2 mm.), $n^{25}D$ 1.4098, was identified as a 3:1 adduct of methyl mercaptan with HFTA (XI, $n$ = 2; R = $CH_3$). The infrared spectrum did not show the presence of SH. The $F^{19}$ n.m.r. spectrum showed two singlets at −2.48 and −1.42 and a doublet at +0.09 p.p.m. ($J$ = 7 c.p.s.). The proton n.m.r. spectrum showed a singlet at 2.50 and a doublet at 4.60 p.p.m. ($J$ = 7 c.p.s.), both of equal area.

*Anal.* Calcd. for $C_{10}H_4F_{18}S_4$: F, 57.54; S, 21.58. Found: F, 57.47; S, 21.30.

**Reaction of HFTA with Ethyl Mercaptan.**—HFTA, 25 ml., was added dropwise over a period of 15 min. to 25 ml. of stirred ethyl mercaptan cooled to −78°. The reaction mixture was allowed to warm to room temperature and then distilled. In addition to some HFTA dimer, the following fractions were obtained.

Fraction I, 10.1 g., b.p. 41–42° (19 mm.), $n^{25}D$ 1.3967, was identified as 1,1,1,2,2,2-hexafluoro-2-ethylthio-2-propanethiol (X, R = $C_2H_5$). The infrared spectrum contained a band at 3.9 $\mu$ for SH. The $F^{19}$ n.m.r. spectrum showed a singlet.

*Anal.* Calcd. for $C_5H_6F_6S_2$: C, 24.59; H, 2.48; F, 46.68; S, 26.25. Found: C, 24.91; H, 2.90; F, 47.23; S, 26.44.

Fraction II, 4.3 g., b.p. 48–49° (1.4 mm.), $n^{25}D$ 1.4062, was identified as a 2:1 adduct of HFTA with ethyl mercaptan (XI, $n$ = 1; R = $C_2H_5$). The infrared spectrum did not show the

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[6] Fluorine n.m.r. spectra were obtained with a Varian Associates high-resolution n.m.r. spectrometer and associated electromagnet operating at 56.4 Mc./sec. and approximately 14,000 gauss. Spectra were calibrated in terms of displacement in parts per million from the $F^{19}$ resonance of 1,2-difluoro-1,1,2,2-tetrachloroethane used as an external reference. Proton resonance spectra were obtained with a Varian Associates A-60 spectrometer, and spectra were calibrated in terms of lower field displacement in parts per million from the proton resonance of tetramethylsilane used as an internal reference.

[7] R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 3871 (1955).

presence of SH. The $F^{19}$ n.m.r. spectrum showed a singlet at $-2.13$ and a doublet ($J$ = 7 c.p.s.) at $-0.09$ p.p.m. of equal area. The proton n.m.r. spectrum showed a septet at 4.13 p.p.m. ($J$ = 7 c.p.s.) for $CH(CF_3)_2$.

*Anal.* Calcd. for $C_8H_6F_{12}S_3$: C, 22.54; H, 1.42; F, 53.48; S, 22.56. Found: C, 22.81, H, 1.85; F, 53.76; S, 22.23.

Fraction III, 2.7 g., b.p. 76–77° (1.0 mm.), $n^{25}$D 1.4184, was identified as a 3:1 adduct of HFTA with ethyl mercaptan (XI, $n$ = 2; R = $C_2H_5$). The infrared spectrum did not show the presence of SH. The $F^{19}$ n.m.r. spectrum showed two singlets and a doublet of equal intensity. The proton n.m.r. spectrum showed at septet at 4.13 p.p.m. ($J$ = 7 c.p.s.) for $C(CF_3)_2H$.

*Anal.* Calcd. for $C_{11}H_6F_{18}S_4$: C, 21.71; H, 1.00; F, 56.21; S, 21.08. Found: C, 22.17; H, 1.32; F, 55.93; S, 21.39.

**1,1,1,3,3,3-Hexafluoro-2-ethylthio-2-propanesulfenyl Chloride.**—Chlorine gas was bubbled into a solution of 10 g. of 1,1,1,3,3,3-hexafluoro-2-ethylthio-2-propanethiol in 25 ml. of methylene chloride. Heat of the reaction caused the solution to reflux gently as hydrogen chloride was evolved. After 1 hr., addition of chlorine was stopped, and the reaction mixture was distilled. There was obtained 6.4 g. of 1,1,1,3,3,3-hexafluoro-2-ethylthio-2-propanesulfenyl chloride as a yellow oil, b.p. 41–42° (4.0 mm.), $n^{25}$D 1.4464. The $F^{19}$ n.m.r. spectrum contained a single unsplit resonance line.

*Anal.* Calcd. for $C_5H_5ClF_6S_2$: C, 21.54; H, 1.81; Cl, 12.72; F, 40.91; S, 23.01. Found: C, 21.44; H, 1.85; Cl, 13.36; F, 40.91; S, 22.56.

**Reaction of HFTA with 2,2,2-Trifluoroethanethiol.**—HFTA, 18.2 g. (0.1 mole), was added slowly to a stirred suspension of 0.3 g. of cesium fluoride in 11.6 g. of 2,2,2-trifluoroethanethiol[2] cooled to $-78°$. The blue color faded rapidly as the thio ketone was added. The reaction mixture was distilled to give 11.3 g. of HFTA dimer, b.p. 107–112°, and 3.8 g. of 2,2,2-trifluoro-1-trifluoromethylethyl 2,2,2-trifluoroethyl disulfide (IX) as a colorless oil, b.p. 127–128°, $n^{25}$D 1.3595. Smaller amounts of higher boiling fractions were also present, but they were not cleanly isolated. The $F^{19}$ n.m.r. spectrum of the disulfide contained a doublet ($J$ = 7 c.p.s.) at 0.27 of area 2 and a triplet ($J$ = 9 c.p.s.) at 0.98 p.p.m. of area 1. The proton n.m.r. showed a quartet at 3.43 ($J$ = 10 c.p.s.) and a septet at 3.95 p.p.m. ($J$ = 8 c.p.s.).

*Anal.* Calcd. for $C_5H_3F_9S_2$: C, 20.14; H, 1.01; F, 57.35; S, 21.50. Found: C, 20.40; H, 1.18; F, 57.43; S, 21.96.

**Reaction of HFTA with Mercaptoacetic Acid.**—Mercaptoacetic acid was added dropwise to 18.2 g. (0.1 mole) of HFTA cooled to $-78°$ until the blue color disappeared. The entire reaction mixture solidified. It was melted by allowing it to warm to room temperature and then distilled to give 7.13 g. of HFTA dimer and 10.78 g. of 2,2,-bis(trifluoromethyl)-1,3-dithiolan-4-one (XII) as a colorless liquid, b.p. 58–59° (16 mm.), $n^{25}$D 1.4214. The infrared spectrum contained a band at 5.75 $\mu$ for C=O. The $F^{19}$ n.m.r. spectrum showed a singlet at 3.81 p.p.m., and the proton n.m.r. spectrum showed a singlet at 4.18 p.p.m.

*Anal.* Calcd. for $C_5H_2F_6OS_2$: C, 23.44; H, 0.79; F, 44.50; S, 25.03. Found: C, 23.68; H, 1.16; F, 44.50; S, 25.28.

**Reaction of Trifluoromethyl Trifluorodithioacetate with Trifluoromethanethiol.**—A mixture of 1.0 g. of trifluoromethyl trifluorodithioacetate,[1] 1.0 g. of trifluoromethanethiol,[8] and 1.0 g. of powdered sodium fluoride was sealed in a glass tube and allowed to remain at room temperature for 5 days. The tube was opened, and the remaining liquid was distilled. There was obtained 0.72 g. of trifluoromethyl 2,2,2-trifluoro-1-trifluoromethylthioethyl disulfide (XIII) as a colorless oil, b.p. 118–119°, $n^{25}$D 1.3752. The $F^{19}$ n.m.r. spectrum showed two singlets ($-25.1$ and $-20.4$ p.p.m.) and a doublet ($+2.66$ p.p.m., $J$ = 7 c.p.s.) of equal area. The proton n.m.r. spectrum showed a quartet at 4.74 p.p.m. ($J$ = 7.3 c.p.s.).

*Anal.* Calcd. for $C_4HF_9S$: C, 15.19; H, 0.32; F, 54.07; S, 30.41. Found: C, 15.47; H, 0.87; F, 54.35; S, 30.70.

**Reaction of 1,1,2,2-Tetrafluoroethanethiol with Sodium Fluoride.**—Powdered sodium fluoride, 20 g. (0.5 mole), was added portionwise to a solution of 20 g. (0.167 mole) of 1,1,2,2-tetrafluoroethanethiol[9] in 20 ml. of ether. The suspension was stirred for 2 hr. at room temperature and then filtered. The red filtrate was distilled under reduced pressure to give a small amount of a bright red liquid, b.p. 32° (20 mm.) (probably 1,1,2,2-tetrafluoroethyl difluorodithioacetate), and 10.3 g. of 1,1,2,2-tetrafluoroethyl 2,2-difluoro-1-(1,1,2,2-tetrafluoroethylthio)ethyl disulfide (XVII) as a light pink liquid, b.p. 50–51° (0.8 mm.), $n^{25}$D 1.4151. The infrared and n.m.r. spectra were consistent with this assignment.

*Anal.* Calcd. for $C_6H_4F_{10}S_3$: C, 19.89; H, 1.11; F, 52.45; S, 26.55. Found: C, 20.41; H, 1.39; F, 52.17; S, 26.67.

**Reaction of HFTA with Hydrogen Chloride.**—Acetonitrile, 50 ml., was saturated at 0° with anhydrous hydrogen chloride and then cooled to $-78°$. HFTA, 18.2 g. (0.1 mole), was distilled into the reaction mixture, and then a solution of 10% water in acetonitrile was added dropwise with stirring until the blue color faded. The reaction mixture was warmed to room temperature and poured into 200 ml. of water. The organic layer was separated, washed with 5% sodium bicarbonate and then water, and dried over anhydrous magnesium sulfate. Distillation gave 18.0 g. of 1-chloro-2,2,2-trifluoro-1-trifluoromethylethyl 2,2,2-trifluoro-1-trifluoromethylethyl disulfide (XX) as a colorless liquid, b.p. 67° (48 mm.), $n^{25}$D 1.3598. The $F^{19}$ n.m.r. spectrum showed a doublet at 0.18 ($J$ = 8 c.p.s.) and a singlet at 4.62 p.p.m. of equal area. The proton n.m.r. showed a septet at 3.98 p.p.m. ($J$ = 8 c.p.s.). The infrared spectrum showed no evidence for SH.

*Anal.* Calcd. for $C_6HClF_{12}S_2$: C, 17.99; H, 0.25; Cl, 8.85; F, 56.91; S, 16.04. Found: C, 18.31; H, 0.60; Cl, 8.69, F, 56.06; S, 16.08.

**Reaction of HFTA with Hydrogen Bromide.**—Methyl alcohol, 50 ml., was cooled in an ice bath and anhydrous hydrogen bromide was passed into the alcohol until its volume had increased about 20%. The methanolic hydrogen bromide solution was then cooled to $-78°$, and 18.2 g. (0.1 mole) of HFTA was added dropwise with stirring over a period of 15 min. The solution was poured into 500 ml. of ice–water, and the organic layer was separated, washed with water, and dried over sodium sulfate. Distillation gave 10.39 g. of 1-bromo-2,2,2-trifluoro-1-trifluoromethylethyl 2,2,2-trifluoro-1-trifluoromethylethyl disulfide (XXI as a colorless oil, b.p. 49–50° (13 mm.), $n^{25}$D 1.3752, in addition to some HFTA dimer and residue.

*Anal.* Calcd. for $C_6HBrF_{12}S_2$: Br, 17.96; F, 51.22; S, 14.41. Found: Br, 17.42; F, 51.13; S, 14.40.

**Reaction of HFTA with Aqueous Hydrogen Iodide.**—Fifteen milliliters of 55% aqueous hydrogen iodide was added dropwise to 25 g. of stirred HFTA cooled to $-78°$. After the addition was complete, the reaction mixture was poured into 500 ml. of cold water; 10% aqueous sodium bisulfite was added until the iodine color disappeared. The lower organic layer was separated, washed with water, and dried over calcium chloride. Distillation gave 9.1 g. of bis(2,2,2-trifluoro-1-trifluoromethylethyl) disulfide (XXIV) as a colorless oil, b.p. 124°, $n^{25}$D 1.3380. The $F^{19}$ n.m.r. spectrum contained a doublet at 0.89 p.p.m. ($J$ = 7 c.p.s.), and the proton n.m.r. spectrum contained a septet at 4.02 p.p.m. ($J$ = 7 c.p.s.).

*Anal.* Calcd. for $C_6H_2F_{12}S_2$: F, 62.26; S, 17.51. Found: F, 61.82; S, 17.86.

**Reaction of HFTA with Anhydrous Hydrogen Iodide.**—Anhydrous hydrogen iodide (9 ml., 0.2 mole) was slowly distilled into a flask containing 18.2 g. (0.1 mole) of HFTA cooled to $-78°$. An exothermic reaction ensued, and strong cooling was necessary to keep the reaction under control. The volatile portion of the reaction mixture was removed from the iodine that formed by distillation under reduced pressure. The distillate was shaken with mercury to remove the last traces of iodine and then redistilled. There was obtained 15.5 g. of 2,2,2-trifluoro-1-trifluoromethylethanethiol (XXIII) as a colorless liquid, b.p. 44°. The infrared spectrum indicated the presence of SH at 3.85 and CH at 3.35 $\mu$. The $F^{19}$ n.m.r. spectrum contained a doublet at 3.57 p.p.m. ($J$ = 7 c.p.s.), and the proton n.m.r. spectrum showed a doublet at 2.45 ($J$ = 12 c.p.s.) and a complex multiplet at 3.75 p.p.m.

*Anal.* Calcd. for $C_3H_2F_6S$: C, 20.57; H, 1.10; F, 61.94. Found: C, 20.69; H, 1.47; F, 61.86.

**Reaction of HFTA with Water.**—A mixture of 25 ml. of acetonitrile and 25 ml. of trifluoroacetic acid was cooled to $-10°$ and 18.2 g. (0.1mole) of HFTA was poured into the mixture. A solution of 10% water in acetonitrile was then added dropwise to the stirred reaction mixture until the blue color faded. The reaction mixture was then poured into 200 ml. of water, and the organic layer was separated, washed with water, and dried over magnesium sulfate. Distillation gave 10.2 g. of HFTA dimer and 6.3 g. of 1-hydroxy-2,2,2-trifluoro-1-trifluoromethylethyl 2,2,2-tri-

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(8) E. L. Muetterties, U. S. Patent 2,729,663 (1956).

(9) A. V. Fokin, A. A. Skladnev, and I. L. Knunyants, *Proc. Acad. Sci. USSR, Chem. Sect.* (Eng. Transl.), **138**, 597 (1961).

fluoro-1-trifluoromethylethyl disulfide (XXII) as a colorless liquid, b.p. 60° (38 mm.), $n^{25}D$ 1.3514. The $F^{19}$ n.m.r. spectrum showed a doublet at 0.44 ($J$ = 8 c.p.s.) and a singlet at 14.0 p.p.m. of equal area. The proton n.m.r. spectrum showed a singlet in the range of 4 p.p.m., that shifted with temperature, and a septet at 3.8 p.p.m. ($J$ = 7.5 c.p.s.).

*Anal.* Calcd. for $C_6H_2F_{12}OS_2$: C, 18.83; H, 0.53; F, 59.65; S, 16.78. Found: C, 18.84; H, 0.98; F, 59.06; S, 16.28.

**Reactions of HFTA with Trialkyl Phosphites.**[10]—Trimethyl phosphite, 24.8 g. (0.2 mole), was cooled by an ice bath, and 12.1 g. (0.033 mole) of HFTA dimer was added dropwise with stirring at such a rate that the temperature of the reaction mixture did not rise above 30°. The reaction mixture was distilled at reduced pressure to give 7.1 g. of trimethyl thiophosphate, b.p. 31–32° (0.35 mm.), and 14.4 g. of trimethoxybis(trifluoromethyl)methylenephosphorane (XXV, R = $CH_3$) as a colorless oil, b.p. 61–62° (0.35 mm.), $n^{25}D$ 1.3664. The $F^{19}$ n.m.r. spectrum showed a doublet at −23.3 p.p.m. ($J_{PF}$ = 13 c.p.s.).

*Anal.* Calcd. for $C_6H_9F_6O_3P$: C, 26.28; H, 3.31; P, 11.30; F, 41.59. Found: C, 26.46; H, 3.73; P, 11.79; F, 41.77.

The reaction was repeated using monomeric HFTA in place of the dimer. However, the results were the same, for the first drop of the phosphite caused all of the HFTA to dimerize rapidly.

Triethoxybis(trifluoromethyl)methylenephosphorane (XXV, R = $C_2H_5$), b.p. 74–75° (0.25 mm.), was prepared in a similar manner from HFTA dimer and triethyl phosphite.

*Anal.* Calcd. for $C_9H_{15}F_6O_3P$: C, 34.18; H, 4.78; F, 36.05; P, 9.80. Found: C, 34.32; H, 5.16; F, 35.75; P, 9.94.

Triisopropoxybis(trifluoromethyl)methylenephosphorane, (XXV, R = $i$-$C_3H_7$), b.p. 75–76° (0.05 mm.), $n^{25}D$ 1.3878, was prepared in a similar manner from HFTA dimer and triisopropyl phosphite.

*Anal.* Calcd. for $C_{12}H_{21}F_6O_3P$: C, 40.23; H, 5.92; F, 31.82; P, 8.66. Found: C, 40.55; H, 5.92; F, 31.46; P, 8.82.

**Dimethyl 1,1-Bis(trifluoromethyl)ethylphosphonate (XXVIII).**—Trimethoxybis(trifluoromethyl)methylenephosphorane (20 g.) was heated under reflux for 1 hr. An exothermic reaction occurred at about 180°, and the flask had to be cooled temporarily to prevent flooding the condenser. The reaction mixture was distilled at reduced pressure to give 17.0 g. of dimethyl 1,1-bis(trifluoromethyl)ethylphosphonate as a colorless liquid with a minty odor, b.p. 40–41° (0.8 mm.), $n^{25}D$ 1.3604. The $F^{19}$ n.m.r. spectrum showed a doublet at 0.18 p.p.m. ($J_{PF}$ = 5 c.p.s.), and the proton n.m.r. spectrum showed a doublet ($J_{PH}$ = 16 c.p.s.) at 1.67 of area 1 and a doublet ($J_{PH}$ = 12 c.p.s.) at 3.96 p.p.m. of area 2.

*Anal.* Calcd. for $C_6H_9F_6O_3P$: C, 26.28; H, 3.31; F, 41.59; P, 11.30. Found: C, 26.45; H, 3.47; F, 41.61; P, 11.60.

**Dimethyl 1,1-Bis(trifluoromethyl)ethylphosphonate (XXIX).**—Concentrated hydrochloric acid, 25 ml., was added dropwise to 22 g. (0.08 mole) of trimethoxybis(trifluoromethyl)methylenephosphorane. A vigorous evolution of gas occurred. The reaction mixture was mixed with 50 ml. of water, and the lower organic layer was separated, washed with 50 ml. of water, and dried over silica gel. Distillation gave 10.9 g. of dimethyl 1,1-bis(trifluoromethyl)ethylphosphonate as a colorless oil, b.p. 44° (0.4 mm.). The $F^{19}$ n.m.r. spectrum contained a resonance centered at −6.57 p.p.m. split into doublets by both the hydrogen ($J$ = 7 c.p.s.) and the phosphorus ($J$ = 10 c.p.s.).

*Anal.* Calcd. for $C_5H_7F_6O_3P$: F, 43.83; P, 11.91. Found: F, 43.52; P, 11.87.

**Dimethyl Bromobis(trifluoromethyl)methylphosphonate (XXX).**—A solution of 13.7 g. (0.05 mole) of trimethoxybis(trifluoromethyl)methylenephosphorane in 10 ml. of methylene chloride was cooled to 0°, and 18.0 g. (0.05 mole) of bromine dissolved in 10 ml. of methylene chloride was added dropwise over a period of 10 min. The colorless reaction mixture was distilled to give 12.7 g. of dimethyl bromobis(trifluoromethyl)methylphosphonate as a colorless liquid, b.p. 53–56° (0.5 mm.), thats olidified to a waxy solid, m.p. 52–54°, upon cooling.

*Anal.* Calcd. for $C_5H_6BrF_6O_3P$: Br, 27.46. Found: Br, 27.35.

**Reaction of HFTA Dimer with Tributylphosphine.**—A solution of 36.4 g. (0.1 mole) of HFTA dimer in 50 ml. of ether was cooled to 10° by an ice bath, and 80.8 g. (0.4 mole) of tributylphosphine was added dropwise over a period of 2 hr., keeping the temperature of the reaction mixture below 15°. The black reaction mixture was then distilled under reduced pressure to give 60.3 g. of tributylphosphine difluoride as a colorless liquid, b.p. 76–77° (0.6 mm.), $n^{25}D$ 1.4336. The $F^{19}$ n.m.r. spectrum showed a doublet with other fine structure evident.

*Anal.* Calcd. for $C_{12}H_{27}F_2P$: C, 59.97; H, 11.33; F, 15.82; P, 12.89. Found: C, 59.83; H, 11.21; F, 15.79; P, 13.26.

**Reaction of HFTA with Diazomethane.**—A 1% solution of diazomethane in pentane was added portionwise over a period of 30 min. to a stirred solution of 18.2 g. (0.1 mole) of HFTA in 20 ml. of pentane cooled to −78° until the blue color of the reaction mixture was discharged. The mixture was then rapidly distilled under reduced pressure to give a white residue. This residue was recrystallized from pentane to give 2.7 g. of white plates, m.p. 201°. A deuteriochloroform solution showed a single resonance line in both the $F^{19}$ (−8.78 p.p.m.) and proton (3.26 p.p.m.) n.m.r. spectra. The structure of this compound has not been determined.

*Anal.* Calcd. for $C_{14}H_4F_{24}S_4$: C, 22.23; H, 0.53; F, 60.28; S, 16.95; mol. wt., 756. Found: C, 22.10; H, 0.99; F, 59.90; S, 16.90; mol. wt., 770.

The distillate from this reaction was fractionated to give 5.4 g. of 2,2,5,5-tetrakis(trifluoromethyl)-1,3-dithiolane (XXXII) as a colorless liquid, b.p. 143–144°, $n^{25}D$ 1.3592. The $F^{19}$ n.m.r. spectrum showed two singlets at 2.66 and 3.01 p.p.m. The proton n.m.r. spectrum showed a singlet at 3.93 p.p.m.

*Anal.* Calcd. for $C_7H_2F_{12}S_2$: C, 22.23; H, 0.53; F, 60.28; S, 16.95. Found: C, 22.67; H, 0.80; F, 60.39; S, 16.64.

**Reaction of HFTA with Diphenyldiazomethane.**—A mixture of 19.6 g. (0.1 mole) of benzophenone hydrazone, 22 g. (0.1 mole) of yellow mercuric oxide, and 100 ml. of pentane was stirred for 6 hr. at room temperature. Magnesium sulfate, 20 g., was added, and the suspension was stirred for 20 min. and then filtered. The purple filtrate was transferred to a flask and cooled to −78°. HFTA, 18.2 g. (0.1 mole), was added dropwise to the rapidly stirred solution. A vigorous evolution of gas occurred during the addition. A solid began to separate after about one-third of the HFTA had been added. The reaction mixture was warmed to room temperature and then evaporated to dryness under reduced pressure to give 35 g. of crude product. Recrystallization from pentane gave 27 g. of 2,2-bis(trifluoromethyl)-3,3-diphenyl-1-thiirane (XXXIV) as white needles, m.p. 79–80°. The $F^{19}$ n.m.r. spectrum contained a single unsplit resonance line at −6.81 p.p.m.

*Anal.* Calcd. for $C_{16}H_{10}F_6S$: F, 32.73; S, 9.20; mol. wt., 348.3. Found: F, 32.71; S, 9.29; mol. wt., 354.

**1,1-Bis(trifluoromethyl)-2,2-diphenylethylene (XXXV).**—2,2-Bis(trifluoromethyl)-3,3-diphenyl-1-thiirane, 10 g., was heated under reflux (*ca.* 250°) for 15 min. The yellow reaction mixture was stirred with 2 ml. of mercury to remove the free sulfur and then distilled under reduced pressure to give 8.1 g. of 1,1-bis(trifluoromethyl)-2,2-diphenylethylene as a colorless liquid, b.p. 83–85° (0.8 mm.). This liquid solidified upon standing overnight to give a white solid, m.p. 64–65°. A sample was recrystallized from pentane to give colorless, transparent prisms, m.p. 65°.

*Anal.* Calcd. for $C_{16}H_{10}F_6$: C, 60.76; H, 3.19; F, 36.05. Found: C, 60.73; H, 3.39; F, 36.24.

**Reaction of HFTA and Ethyl Diazoacetate.**—A solution of 22.8 g. (0.2 mole) of ethyl diazoacetate in 40 ml. of pentane was stirred and cooled to −78°. HFTA was added dropwise until a faint blue color persisted. The white solid that separated was collected by filtering the reaction mixture while it was still cold. This solid was recrystallized from ether to give 10.3 g. of 2,2-bis(trifluoromethyl)-3-carbethoxy-1-thiirane (XXXVI) as white needles, m.p. 87–89°. The $F^{19}$ n.m.r. spectrum showed two quadruplets of equal intensity at −10.0 and −8.2 p.p.m. The proton n.m.r. spectrum showed a singlet at 4.52 p.p.m.in addition to absorption due to an ethyl group.

*Anal.* Calcd. for $C_7H_6F_6O_2S$: C, 31.38; H, 2.26; F, 42.51, S, 11.95. Found: C, 31.52; H, 2.02; F, 42.25; S, 12.10.

**2-Chloro-1,1,1,3,3,3-hexafluoro-2-propanesulfenyl Chloride (XXXVII).**—Chlorine, 1.2 ml. (0.025 mole), was condensed into a calibrated tube and cooled to −78°. HFTA, 4.5 g. (0.025 mole), was then distilled into the tube, and the reaction mixture was allowed to remain at −78° for 20 hr., after which time the color had faded. Distillation gave 3.2 g. of 2-chloro-1,1,1,3,3,3-hexafluoro-2-propane sulfenyl chloride, as a bright yellow oil, b.p. 89–90°, $n^{25}D$ 1.3706. The $F^{19}$ n.m.r. spectrum contained a single unsplit resonance line at 6.95 p.p.m.

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(10) W. J. Middleton, U. S. Patent 3,067,233 (1962).

*Anal.* Calcd. for $C_3Cl_2F_6S$: C, 14.24; Cl, 28.02; F, 45.06; S, 12.67. Found: C, 14.61; Cl, 27.77; F, 44.81; S, 13.00.

**2-Bromo-1,1,1,3,3,3-hexafluoro-2-propanesulfenyl Bromide (XXXVIII).**—Bromine, 8.0 g. (0.05 mole), was placed in a flask and cooled to −5° in an ice–salt bath. HFTA, 9.1 g. (0.05 mole), was distilled into the flask, and the reaction mixture was allowed to stand at 0° for 3 hr. and then distilled. There was obtained 14.7 g. (86%) of 2-bromo-1,1,1,3,3,3-hexafluoro-2-propanesulfenyl bromide as an orange-red liquid, b.p. 48–49° (38 mm.), $n^{25}D$ 1.4368. The $F^{19}$ n.m.r. spectrum contained a single unsplit resonance line at 0 p.p.m.

*Anal.* Calcd. for $C_3Br_2F_6S$: C, 10.53; Br, 46.76; F, 33.34; S, 9.36. Found: C, 11.12; Br, 46.67; F, 33.27; S, 9.27.

**Oxidation of HFTA with Nitric Oxide.**—A 2.5-cm. Vycor tube packed for a length of 25 cm. with quartz rings was connected to a trap cooled by Dry Ice–acetone and the tube was heated to 650°. HFTA dimer, 18.2 g. (0.5 mole), was added dropwise through the tube over a period of 2 hr. A slow stream (about 100 ml./min.) of nitric oxide was also passed through the tube along with the dimer. The condensate in the trap was distilled to give 12.9 g. (78%) of a fraction consisting chiefly of hexafluoroacetone, b.p. −26°. Identification was made by comparing the n.m.r. and infrared spectra of this gas with those of an authentic sample of hexafluoroacetone. Sulfur dioxide was also used in place of nitric oxide for this oxidation, but yields were poorer in this case

When oxygen was used in place of the nitric oxide, only sulfur dioxide (82%) was condensed in the trap, indicating the carbon and fluorine portions of HFTA were oxidized to gases not condensed at −78°.

**Reduction of HFTA with Hydrogen Sulfide.**—A 2.5-cm. Vycor tube packed for a length of 25 cm. with quartz rings was connected to a trap cooled by Dry Ice–acetone. The tube was heated to 650°, and 46 g. (0.125 mole) of HFTA dimer was added dropwise over a period of 4 hr. A slow stream of hydrogen sulfide (about 100 ml./min.) was passed through the tube concurrently with the dimer. The condensate in the trap was distilled to give 32 g. of 1,1,1,3,3,3-hexafluoropropane, b.p. −2 to −1°, identified by comparison of its n.m.r. and infrared spectra with those of a known sample.

**Trimethoxyfluoroenylidenephosphorane (XXXI).**—A mixture of 6.3 g. (0.032 mole) of thiofluorenone and 100 ml. of pentane was stirred under nitrogen, and 8.0 g. (0.064 mole) of trimethyl phosphite was added dropwise over a period of 10 min. The green color of the thiofluorenone faded and a yellow solid formed. This solid was collected on a filter under nitrogen and washed with pentane. There was obtained 7.3 g. of trimethoxyfluoroenylidene phosphorane as a yellow powder, m.p. 105–107°. A portion was recrystallized from benzene–hexane and then from hexane to give white needles, m.p. 108°. The infrared spectrum contained bands at 3.3 μ (=CH), at 3.4 and 3.5 μ (saturated CH), in the 6-μ region (aromatic —C=C—), at 7.65 μ (possible P=C), and in the 9-μ region (P—O—C—).

*Anal.* Calcd. for $C_{16}H_{17}O_3P$: C, 66.66; H, 5.95; P, 10.75. Found: C, 66.55; H, 5.92; P, 10.90.

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# Fluorothiocarbonyl Compounds. III.[1] Diels–Alder Reactions

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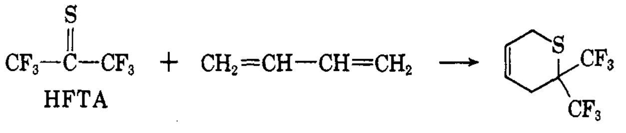
Hexafluorothioacetone is an exceedingly active dienophile in the Diels–Alder reaction. It forms adducts with butadiene, furan, anthracene, and even styrene under very mild conditions. Other thiocarbonyl compounds such as trifluorothioacetyl fluoride, ethyl trifluorodithioacetate, thiocarbonyl fluoride, and thiophosgene are also active dienophiles.

A number of carbonyl compounds, including formaldehyde,[2] chloral,[3] carbonyl cyanide,[4] diethyl mesoxalate,[4] hexafluoroacetone,[5] and hexafluorocyclobutanone,[6] have been shown to function as dienophiles in the Diels–Alder reaction. Among the most active of these are the fluoro ketones.[5,6]

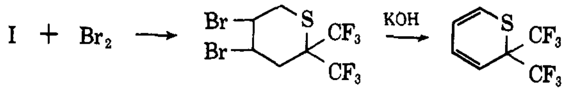
We have found that thiocarbonyl compounds are also active dienophiles, being several orders of magnitude more reactive than the corresponding carbonyl compounds.[7]

**Perfluoro Thio Ketones.**—The most reactive dienophiles of all the thiocarbonyl compounds we have examined are the perfluoro thio ketones, in particular hexafluorothioacetone (HFTA). This thio ketone reacts instantaneously with butadiene at −78° to give high yields of 2,2-bis(trifluoromethyl)-3,6-dihydro-2H-thiopyran (I). This reaction is so fast that it can actually be used to titrate butadiene in an inert solvent, using the appearance of the blue color of the thio ketone as the end point of the titration.



I

The HFTA–butadiene adduct (I) was dehydrogenated in two steps by addition of bromine and elimination of hydrogen bromide to give the thiopyran II. This thiopyran, being a diene itself, reacts with HFTA to form an adduct of uncertain structure. The thiopyran itself appears to be unstable in the monomeric state, for it slowly dimerized over a period of 3 months when stored at room temperature.



II

Hexafluorothioacetone reacts with surprising ease with certain aromatic compounds to form Diels–Alder adducts. It reacts rapidly with furan at −78° and with anthracene at 0° to give adducts III and IV, respectively.

More impressive yet is the reaction of HFTA with styrene and related compounds. Even at −78°, HFTA reacts rapidly and exothermally with styrene to

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[5] J. F. Harris, U. S. Patent 3,136,786 (1964).

[6] D. C. England, *J. Am. Chem. Soc.*, **83**, 2205 (1961).

[7] W. J. Middleton, E. G. Howard, and W. H. Sharkey, *ibid.*, **83**, 2589 (1961).