p-nitroorthobenzoate the catalytic coefficient of chloroacetic acid correlates fairly well with σ, but with a small value of ρ.

Because O–H bond making and C–O bond breaking are both important, we should not expect to see clear and simple substituent effects, although inductively electron-releasing groups should always speed reaction by assisting both O–H bond making and C–O bond breaking.

The solvent deuterium isotope effect for the hydronium ion catalyzed reaction and the observation of general acid catalysis will depend upon the extent of H–O bond making in the transition state. If the proton is transferred completely to oxygen in the transition state the reaction will be faster in D_2O than in H_2O, whether or not there is a pre-equilibrium proton transfer, or concerted C–O bond breaking. Similarly the observation of general acid catalysis depends upon the extent of proton transfer. If the Brønsted exponent $\alpha \simeq 1$, the hydronium ion will be far and away the most effective catalyst, and we will not observe any general acid catalysis.[1] (One should consider general acid catalysis on an operational rather than a theoretical basis, *e.g.*, solvolysis of methyl orthobenzoate is catalyzed by chloroacetic acid in aqueous methanol,[14] whereas that of ethyl orthobenzoate is not catalyzed by acetic acid in aqueous dioxane,[5a] and in any event Eigen has recently shown how the experimental value of α can depend upon the pK values of the catalysts.[21]) The relative importance of bond making and bond breaking will depend upon the structure of the ortho ester, the nature of the catalyzing acid, and their environment.

The value of the entropy of activation is often used to distinguish between hydronium ion catalyzed A-1 and A-2 mechanisms,[26] but it is unlikely to be of much help in distinguishing between a conventional A-1 mechanism of hydrolysis of an ortho ester and one involving rate-limiting proton transfer to oxygen. In both reactions the proton is almost wholly transferred to the substrate, and in any event there is a broad spectrum of values of the entropy of activation which is regarded as characteristic of an A-1 mechanism. The values of the entropy of activation which are zero or positive for the hydronium ion catalyzed hydrolysis are therefore reasonable in terms of the proposed mechanism.

(26) L. L. Schaleger and F. A. Long in "Advances in Physical Organic Chemistry," Vol. 1, V. Gold, Ed., Academic Press, Inc., New York, N. Y., 1963, p. 1.

Fluorothiocarbonyl Compounds.[1] I. Preparation of Thio Ketones, Thioacyl Halides, and Thio Esters

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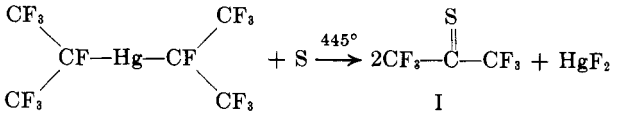
General methods for preparing fluoro thio ketones, fluorothioacyl halides, and fluoro thio esters are described. Reaction of perfluoro-*sec*-alkyl mercurials with sulfur leads to perfluoro thio ketones. For example, hexafluorothioacetone is obtained by passing bis(perfluoroisopropyl)mercury through the vapors of boiling sulfur. This thio ketone dimerizes spontaneously to tetrakis(trifluoromethyl)-1,3-dithietane. Pyrolysis of the dimer regenerates the fluoro thio ketone. Perfluoro thio ketones are also obtainable by reaction of perfluoro-*sec*-alkyl iodide with phosphorus pentasulfide at 550°. A third synthesis is photolytic reduction of a bis(perfluoro-*sec*-alkyl) disulfide to a mercaptan followed by dehydrofluorination with sodium fluoride. Perfluorothioacyl fluorides and chlorides, including trifluorothioacetyl fluoride and chloride, can be synthesized by similar methods. Certain members of this class can also be obtained from fluoro olefins and sulfur. The simplest fluoro thio acid fluoride, thiocarbonyl fluoride, is easily made by pyrolysis of the dithietane formed by fluorination of thiophosgene dimer. In addition, the preparation of fluoro thio esters by reaction of fluorothioacyl halides with thiols and a description of several special thio ester syntheses are given.

In earlier communications,[1] we have reported briefly on our investigation of the chemistry of perfluorothiocarbonyl compounds. In the course of this investigation, we have devised a number of approaches to the preparation of these compounds. Many of these approaches represent new synthetic methods that are generally applicable to the preparation of a large variety of fluorine-containing thiocarbonyl compounds, including thio ketones, thioacyl halides, and thio esters.

Fluoro Thio Ketones.—Hexafluorothioacetone has been prepared in 60% yield by the reaction of bis(perfluoroisopropyl)mercury[2] with refluxing sulfur vapor. The thio ketone is a deep blue compound boiling at 8°. It was identified by its mass spectrum, which showed a parent ion of m/e 182, and by its fluorine n.m.r. spectrum, which consisted of a single unsplit peak.

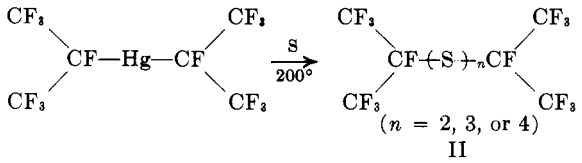


The reaction of perfluoromercurials with boiling sulfur appears to have wide applicability, and we have used it to prepare 4H-perfluorobutane-2-thione and 4-chloroperfluorobutane-2-thione from bis(4H-octafluoro-2-butyl)mercury and bis(4-chlorooctafluoro-2-butyl)mercury, respectively.

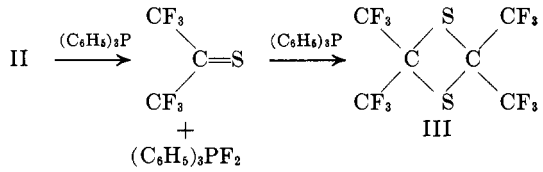
If bis(perfluoroisopropyl)mercury comes into contact with sulfur at lower temperatures, the reaction takes a different course. At 200°, a mixture of perfluoroisopropyl di- and polysulfides is formed. The disulfides

(1) Part of the work included in this series of papers was reported in a Communication to the Editor [W. J. Middleton, E. G. Howard, and W. H. Sharkey, *J. Am. Chem. Soc.*, **83**, 2589 (1961)] and later at the 140th Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961.

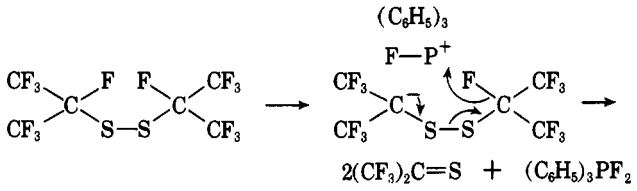
(2) P. E. Aldrich, E. G. Howard, W. J. Linn, W. J. Middleton, and W. H. Sharkey, *J. Org. Chem.*, **28**, 184 (1963).



can be defluorinated by triphenylphosphine to give the dimer of hexafluorothioacetone, 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane (III).

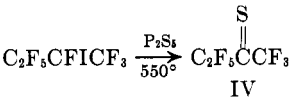


It is probable that hexafluorothioacetone is formed first and then dimerizes in the presence of excess triphenylphosphine, a known dimerization catalyst. It is rather remarkable that triphenylphosphine removes fluorine instead of sulfur from the di- and polysulfides. This reaction may involve nucleophilic attack of fluorine by phosphorus followed by elimination of a carbanion and decomposition of the carbanion.

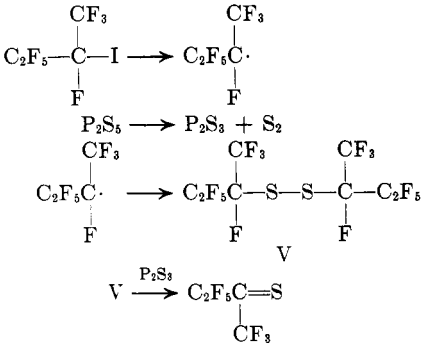


The same reaction takes place with tri- and tetrasulfides, but in these cases it is necessary to use excess triphenylphosphine, which removes extra sulfur as $(C_6H_5)_3P{=}S$.

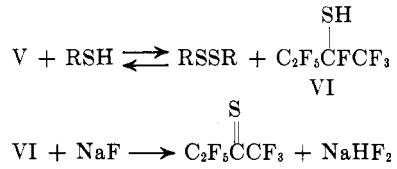
Another route to perfluoro thio ketones is sulfurization of secondary perfluoroalkyl iodides with refluxing phosphorus pentasulfide. By this means, 2-iodoperfluorobutane is converted to perfluorobutane-2-thione (IV) in yields as high as 90%. This sulfurization ap-



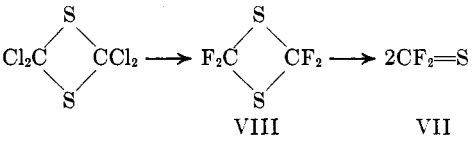
pears to be analogous to the high-temperature oxidation of perfluoroalkyl derivatives to acid fluorides in the presence of nitrogen dioxide as reported by Severson and Brice.[3] These authors proposed that perfluoroalkyl iodides decompose thermally to perfluoroalkyl radicals, which then react with other species present. In our case, the radical could react with sulfur to form sulfides from which fluorine could be removed by phosphorus. Possible steps are the following.



At lower temperatures, sulfur reacts with 2-iodoperfluorobutane to form the disulfide V. Reduction of the disulfide can be accomplished by ultraviolet irradiation in the presence of a higher-boiling thiol and the new thiol (VI) so obtained can be converted to a thio ketone by dehydrofluorination with sodium fluoride.[4]

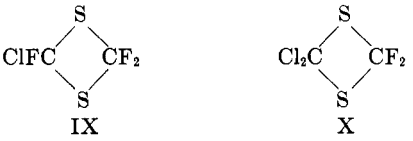


Fluoro Thio Acid Fluorides.—The simplest fluorothio acid fluoride, thiocarbonyl fluoride (VII), which has been mentioned several times in the literature,[5] can be prepared very conveniently in high purity by a three-step process based on thiophosgene. The first step is conversion of thiophosgene to its dimer.[6] Fluorination of the dimer with antimony trifluoride gives 2,2,4,4-tetrafluoro-1,3-dithietane (VIII), pyrolysis of



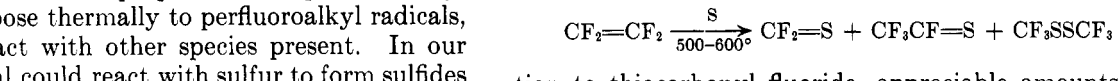
which at 475–500° leads to thiocarbonyl fluoride in nearly quantitative yield. Material prepared in this way, after redistillation in a low-temperature column, is free of all measurable impurities other than about 15–25 p.p.m. of carbonyl sulfide.

In the fluorination step, small amounts of the chlorofluorodithietanes, IX and X, are formed in addition to



VIII. Upon pyrolysis at 450°, IX is cleaved to a mixture of thiocarbonyl chlorofluoride and thiocarbonyl fluoride. These compounds are separable by distillation. The chlorofluoride is a bright yellow gas boiling at 7°, and thiocarbonyl fluoride is a colorless gas boiling at −54°. Compound X on pyrolysis yields thiocarbonyl fluoride and thiophosgene.

Thiocarbonyl fluoride can also be obtained from tetrafluoroethylene by reaction with sulfur. In addi-



tion to thiocarbonyl fluoride, appreciable amounts of trifluorothioacetyl fluoride and bis(trifluoromethyl)-disulfide are formed. The composition of the product mixture is importantly affected by reaction conditions. It is of interest that Martin[7] has reported that trifluorothioacetyl fluoride is the major product when tetrafluoroethylene undergoes reaction with sulfur vapor over a bed of activated charcoal.

(3) W. A. Severson and T. J. Brice, *J. Am. Chem. Soc.*, **80**, 2313 (1958).

(4) J. F. Harris and F. W. Stace [*ibid.*, **85**, 749 (1963)] have prepared hydrogen-containing thioacyl fluorides by the dehydrofluorination of α-fluorothiols with sodium fluoride.

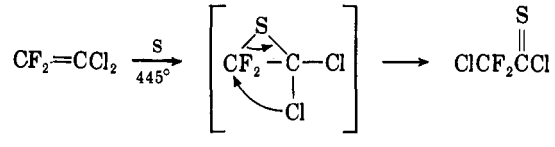
(5) W. Sundermeyer and W. Meise, *Z. Anorg. Allgem. Chem.*, **317**, 334 (1962). Earlier references to thiocarbonyl fluoride are tabulated in this paper.

(6) A. Schonberg and A. Stephenson, *Ber.*, **66B**, 567 (1933).

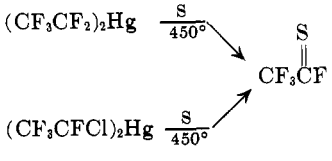
(7) K. V. Martin, U. S. Patent 3,048,629 (1962).

In contrast to the above, chloro- and bromofluoroethylenes react with sulfur in the absence of a catalyst to give high yields of fluorothioacetyl halides. An example of this remarkable reaction is the passage of chlorotrifluoroethylene through boiling sulfur to obtain chlorodifluorothioacetyl fluoride. The product we obtained has a boiling point of 23°, which differs considerably from the value reported in the literature.[8] The fluorine n.m.r. spectrum of this compound consisted of a low-field triplet and a high-field doublet in a ratio of 1:2, as would be expected. The occurrence of peaks at low field in the fluorine n.m.r. spectrum for F attached to C=S appears to be general for thio acid fluorides. Such low-field peaks have been observed for all of the thio acid fluorides prepared in this study.

Bromotrifluoroethylene also reacts with boiling sulfur, and the product is bromodifluorothioacetyl fluoride. The mechanism of this reaction has not been studied, but it may involve the formation of an episulfide that rearranges by migration of a chlorine or bromine atom. Such a scheme is supported by the behavior of 1,1-dichloro-2,2-difluoroethylene, which reacts with sulfur to give chlorodifluorothioacetyl chloride.



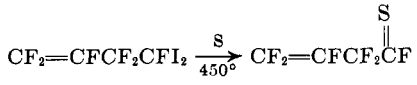
The reaction of perfluoroalkyl mercurials with sulfur is applicable to syntheses of thio acid fluorides. Perfluorothioacetyl fluoride can be obtained from both bis(perfluoroethyl)mercury and bis(1-chloroperfluoroethyl)mercury. Bis(1,1-dichloroperfluoroethyl)mercury



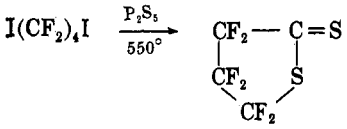
reacts with sulfur at 450° to give trifluorothioacetyl chloride.

Reaction of phosphorus pentasulfide with perfluoroalkyl iodides is also applicable to synthesis of acid fluorides. Thus, another way of synthesizing perfluorothioacetyl fluoride is by reaction of perfluoroethyl iodide with phosphorus pentasulfide at 550° Under the same conditions, 1-iodoperfluoropropane is converted to perfluorothiopropionyl fluoride.

A special case is 4,4-diiodoperfluoro-1-butene, with which sulfur reacts principally at the site of the iodine atoms.

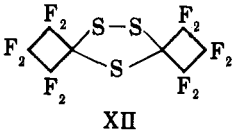


Fluoro Thio Esters.—Another special case is the reaction of 1,4-diiodoperfluorobutane with phosphorus pentasulfide to form the dithio lactone XI, a purple-red liquid.

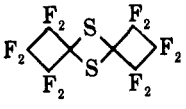


XI

XI can also be obtained by heating perfluorocyclobutanone[9] with phosphorus pentasulfide at 550° and by pyrolysis of the trithiane XII[10] that is obtained in admixture with the dithietane XIII when hexafluorocyclobutanone is heated with phosphorus pentasulfide under milder conditions.

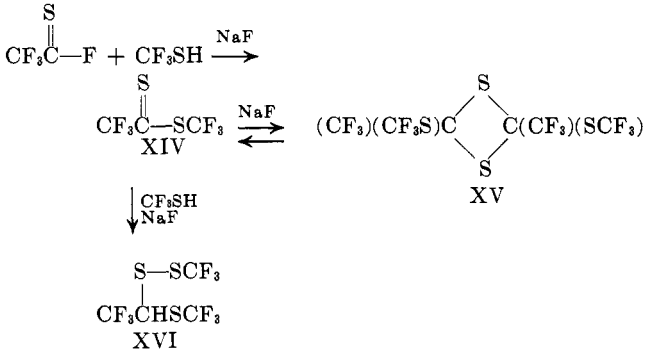


XII



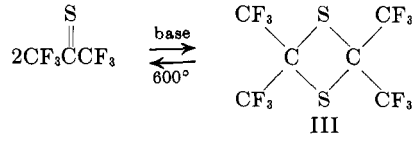
XIII

A general route to alkyl fluoro dithio esters is reaction of fluorothioacyl fluorides with thiols in the presence of sodium fluoride. Ethyl trifluorodithioacetate[11] and phenyl trifluorodithioacetate are readily prepared in this way. The preparation of trifluoromethyl dithio esters is much more complicated as is illustrated.



Sodium fluoride, which is needed to remove hydrogen fluoride, catalyzes the dimerization of the dithio ester XIV almost as fast as it is formed. Sodium fluoride also catalyzes addition of CF_3SH to the dithio ester to form XVI. The dithio ester is best obtained by pyrolysis of the dimer XV at 600°.

Reactions of Fluorothiocarbonyls.—Hexafluorothioacetone, in contrast to previously reported thio ketones,[12] is not oxidized by atmospheric oxygen and, in contrast to fluoro ketones, does not react with water in the absence of a catalyst. It does dimerize very readily to 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane either on standing several hours at room temperature or upon distillation at atmospheric pressure or upon treatment with a trace of a basic catalyst, such



III

(8) N. N. Yarovenko, S. P. Motornyi, L. I. Kirenskaya, A. S. Vasilyeva, *J. Gen. Chem. USSR* (Eng. Transl.), **27**, 2301 (1957). A boiling temperature of 36° is given for chlorodifluorothioacetyl fluoride that was prepared by the action of tin on 2-chlorotetrafluoroethanesulfenyl chloride.

(9) D. C. England, *J. Am. Chem. Soc.*, **83**, 2205 (1961).

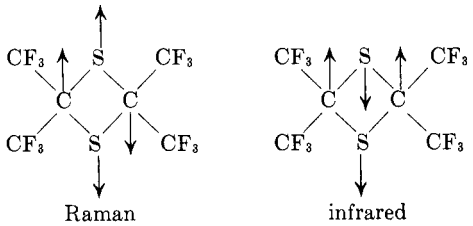
(10) D. C. England, unpublished results. These compounds were prepared by the reaction of perfluorocyclobutanone with phosphorus pentasulfide at 210°.

(11) Shortly after our initial communication on thiocarbonyl compounds in which we described ethyl trifluorothioacetate as an active dienophile, H. C. Brown and R. Pater [*J. Org. Chem.*, **27**, 2858 (1962)] reported a synthesis of this compound by reaction of hydrogen sulfide with the hydrochloride of ethyl trifluoroacetylthioimidate.

(12) E. Campaigne, *Chem. Rev.*, **32**, 1 (1946).

as pyridine, dimethylformamide, or triphenylphosphine. Surprisingly, such mild bases as acetone and ether are very good dimerization catalysts. Dimerization rate is greatly retarded at low temperatures as the monomer has a half-life of several months if purified by distillation at reduced pressure and stored at −78°.

The 1,3-dithietane structure has been assigned to the dimer on the basis of spectral evidence, molecular weight determinations, and chemical behavior. The mass spectrum shows a parent ion at *m/e* 364. Additional proof that the compound is a dimer is shown by its cryoscopic molecular weight in benzene, which is 372. The fluorine n.m.r. spectrum consists of a single band with no splitting. These data can only be rationalized by assigning a 1,3- or 1,2-dithietane structure. From a comparison of the infrared and Raman spectra of the dimer, we have concluded that it is a 1,3-dithietane and is planar.[13] If attention is restricted to those bands associated with vibrations in the ring, which occur at low frequencies, then there should be no bands common to the Raman and infrared for the centrosymmetric 1,3-dithietane molecule. For the 1,2-dithietane, all bands in the Raman should also appear in the infrared. Comparison of the spectra shows only four bands common to the Raman and infrared. These are 20.6–20.4, 10.7, 8.23–8.30, and 7.64–7.60 μ. The highest frequency bands, 8.23–8.30 and 7.64–7.70 μ, can be dismissed as being C–F stretching frequencies that are the same for either structure. The 20.4-μ band is so weak in the infrared that it ordinarily would not be reported. Forbidden transitions occasionally occur, and this may be such a case. The 10.7-μ band is strong in the infrared but weak in the Raman. It could be the result of vibrations of the type shown.

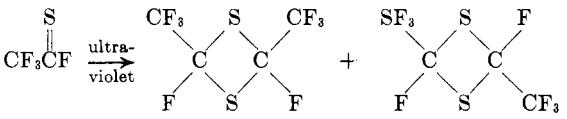


The first does not change symmetry and would be active in the Raman. The second would be active in the infrared. It is possible that both could absorb at the same frequency. The nonconcurrence of most of the many bands in each spectrum and the rationalization of the two bands in common lead to the assignment of the 1,3-dithietane structure to the dimer.

Pyrolysis of the dimer at 600° causes cleavage of the ring to regenerate hexafluorothioacetone quantitatively. Though the dimer has unusual thermal stability, as is indicated by the high pyrolysis temperature, and is stable to acids, it is very susceptible to attack by bases. Reaction with sodium methoxide in methanol proceeds very rapidly to give dimethyl α-methylthio-α-methoxymalonate.[14]

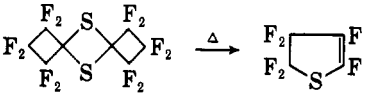
Perfluorobutanethione (IV) dimerizes to a 1,3-dithietane so rapidly that it cannot be distilled at atmospheric pressure. In this case, the dithietane also can be cleaved at high temperatures to regenerate the thio ketone. Perfluorobutanethione can be purified by v.p.c. or by distillation at subatmospheric pressures and low temperatures.

Easy dimerization to dithietanes is also characteristic of 4-hydro- and 4-chloroperfluorobutanethiones. Trifluorothioacetyl fluoride does not dimerize spontaneously. However, if irradiated with ultraviolet light at temperatures below 0°, it is converted to a mixture of *cis*- and *trans*-2,4-difluoro-2,4-bis(trifluoromethyl)-1,3-dithietane. The *cis* and *trans* isomers are formed



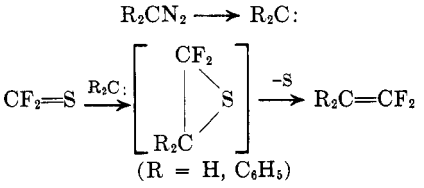
in approximately equal amounts, as is determined by gas chromatographic and F^{19} n.m.r. spectral analyses. These dithietanes, in contrast to the dimer of hexafluorothioacetone, do not react with aqueous or alcoholic alkali at room temperature. Other thio acid halides also dimerize to dithietanes upon ultraviolet irradiation. These include trifluorothioacetyl chloride and chloro- and bromodifluorothioacetyl fluorides. Chlorodifluorothioacetyl chloride dimerizes spontaneously at room temperature.

XIII is a dithietane that does not cleave to a fluorothiocarbonyl compound. Instead, it rearranges, when heated, to a perfluorodihydrothiophene.



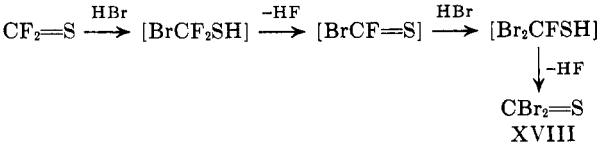
XIII XVII

Although thiocarbonyl fluoride does not dimerize under the conditions we have described for thio ketones and thioacetyl fluorides, it does undergo certain other addition reactions, including addition of carbenes. For example, diazomethane and diphenyldiazomethane

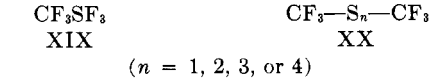


react to form thiiranes. The thiiranes are unstable and immediately eliminate sulfur.

Hydrogen bromide also adds to thiocarbonyl fluoride. The product is thiocarbonyl bromide (XVIII), a previously unreported compound. The reaction probably involves mercaptan intermediates that eliminate hydrogen fluoride.



Such fluorinating agents as iodine pentafluoride and sulfur tetrafluoride convert thiocarbonyl fluoride to trifluoromethylsulfur trifluoride (XIX) and bis(trifluoromethyl) mono and polysulfides (XX), respec-

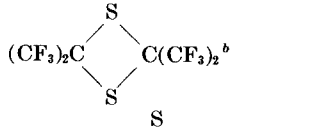
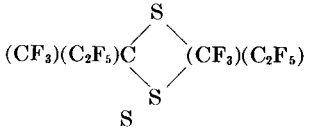
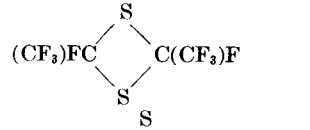
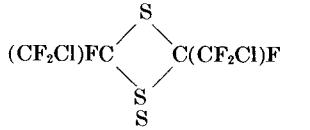
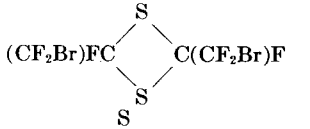
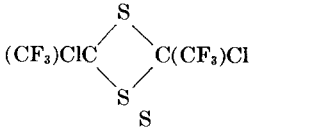
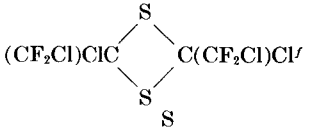
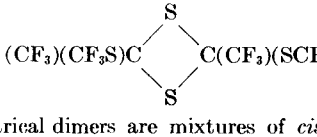


(13) We are indebted to Professor R. C. Lord of the Massachusetts Institute of Technology for this analysis of symmetry considerations. See J. R. Durig and R. C. Lord, *Spectrochim. Acta*, **19**, 769 (1963).

(14) Dr. A. L. Barney of this laboratory carried out this reaction.

Table I

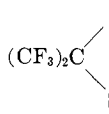
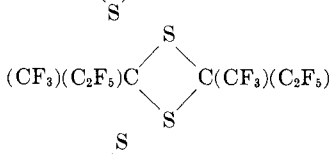
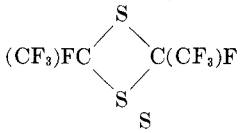
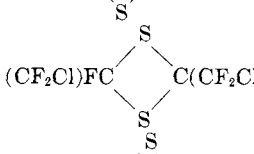
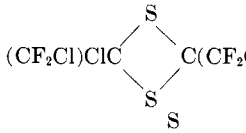
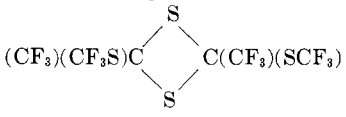
Dimers of Thiocarbonyl Compounds

Monomer	Dimer: Structure	Formula[a]	Yield, %	B.p., °C.	$n^{25}D$	Carbon, % Calcd.	Carbon, % Found	Fluorine, % Calcd.	Fluorine, % Found	Sulfur, % Calcd.	Sulfur, % Found
CF_3CSCF_3		$C_6F_{12}S_2$	100	110	1.3357	19.79	19.64	62.61	62.36	17.61	17.52
$C_2F_5CSCF_3$		$C_8F_{16}S_2$	100	142–144	1.3479	20.70	20.42	65.49	65.31	13.81	13.30
CF_3CCSF		$C_4F_8S_2$	60	73	1.3378	18.19	18.27	57.54	57.81	24.27	24.37
CF_2ClCSF		$C_4Cl_2F_6S_2$[c]	83	137	1.4127	16.17	16.68	38.24	38.34	21.58	21.88
CF_2BrCSF		$C_4Br_2F_6S_2$	58	40–41 (3 mm.)	1.4572	41.41[d]	41.09[d]	29.53	29.62	17.13	16.79
CF_3CSCl		$C_4Cl_2F_6S_2$[e]	93	66–68 (25 mm.)	1.4162	16.17	16.50	38.37	38.33	21.65	20.93
$CF_2ClCSCl$		$C_4Cl_4F_4S_2$[g]	45[h]	76 (9 mm.)	1.4852	14.6	14.65	23.0	23.19	19.4	19.6
CF_3CSSCF_3		$C_6F_{12}S_4$	100	55–56 (10 mm.)	1.3391	16.82	17.27	53.23	53.72	29.04	30.03

[a] All unsymmetrical dimers are mixtures of *cis* and *trans* isomers. [b] M.p. 23.6°. [c] *Anal.* Calcd. for Cl: 23.87. Found: 23.80. [d] *Anal.* Calcd. for Br. [e] *Anal.* Calcd. for Cl: 23.87. Found: 23.84. [f] This compound was prepared by C. L. Dickinson of this laboratory. [g] *Anal.* Calcd. for Cl: 43.0. Found: 43.0. [h] Cumulative yield for preparation of monomer and its dimerization. The dimerization yield is probably quantitative.

TABLE II

PREPARATION OF THIOCARBONYL COMPOUNDS BY PYROLYSIS OF DITHIETANES

Dithietane	Pyrolysis[a] temp., °C	Thiocarbonyl compound	B.p., °C.	Yield, %
	600	CF_3CSCF_3	8	92
	550	$C_2F_5CSCF_3$	*ca.* 0 (200 mm.)	60
	475	CF_3CSF	−21	90
	475	CF_2ClCSF	22–23	95
	600 (1.0 mm.)	$CF_2ClCSCl$	*ca.* −10 (20 mm.), n^{25}_D 1.4465	81
	600 (0.1 mm.)	CF_3CSSCF_3	*ca.* 0 (50 mm.)	74

[a] The pyrolysis was carried out at atmospheric pressure unless otherwise noted.

tively. These same fluorination products are obtained when 2,2,4,4-tetrafluoro-1,3-dithietane is substituted for thiocarbonyl fluoride.

Experimental[15]

Hexafluorothioacetone (I).—Bis(perfluoroisopropyl)mercury, 108 g. (0.2 mole), was added dropwise over a period of 2 hr. to a flask fitted with an air condenser and containing 150 g. of sulfur heated under reflux. A slow stream of nitrogen was passed through the reaction mixture during addition, and effluent gases that passed through the air condenser were condensed in a trap cooled by a solid carbon dioxide–acetone mixture. The condensate was a deep blue liquid that was rapidly distilled at reduced pressure to give 22 g. (60%) of hexafluorothioacetone,[16] b.p. −20° (200 mm.). The ketone could be distilled at atmospheric pressure, b.p. 8°, but under these conditions many of the thio ketones dimerized.

The F^{19} n.m.r. spectrum of hexafluorothioacetone showed a single unsplit resonance line at +68.0 p.p.m. from the resonance of trichlorofluoromethane used as an internal standard. The infrared spectrum of solid hexafluorothioacetone consisted of strong absorption between 7.5 and 9 and sharp bands at 10.7 and 13.15 μ. The mass spectrum shows a parent ion at *m/e* 182.

Anal. Calcd. for C_3F_6S: F, 62.61. Found: F, 62.50.

Bis(perfluoroisopropyl) Polysulfides (II).—A 400-ml. stainless steel bomb containing 156 g. (0.29 moles) of bis(perfluoroisopropyl)mercury and 32 g. (1 mole) of sulfur was heated at 220° for 12 hr. Distillation of the product gave 30.5 g. of bis(perfluoroisopropyl) disulfide, b.p. 121–123°, 39.5 g. of bis(perfluoroisopropyl) trisulfide, b.p. 150–155°, and 12.7 g. of bis(perfluoroisopropyl) tetrasulfide, b.p. 180–186°.

Anal. Calcd. for $C_6F_{14}S_2$ (disulfide): C, 17.9; S, 15.9. Found: C, 17.9; S, 15.3.

Anal. Calcd. for $C_6F_{14}S_3$ (trisulfide): C, 16.6; S, 22.1. Found: C, 17.0; S, 22.1.

Anal. Calcd. for $C_6F_{14}S_4$ (tetrasulfide): C, 15.4; S, 27.4. Found: C, 15.3; S, 26.8.

2,2,4,4-Tetrakis(trifluoromethyl)-1,3-dithietane. A. From Hexafluorothioacetone.—Upon storage near its boiling point for several days, the thio ketone slowly dimerized to give a quantitative yield of 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane, b.p. 110°. Analyses are given in Table I. Raman bands occurred at 7.64, 8.23, 9.75, 13.15, 17.65, 20.6, 23.8, and 28.2 μ. Infrared bands occurred at 7.60, 7.97, 8.30, 10.70, 13.35, 14.27, 17.87, 18.50, 26.1, 27.0, 30.1, and 33.0 μ. The F^{19} n.m.r. spectrum showed a singlet at +7.57 p.p.m.

B. From Bis(perfluoroisopropyl) Disulfide.—A solution of 10 g. (0.038 mole) of triphenylphosphine in 15 ml. of acetone was added dropwise with stirring to 10.05 g. (0.025 mole) of bis(perfluoroisopropyl) disulfide cooled in ice. The reaction mixture was distilled to dryness under vacuum and the distillate was drowned in water. The organic layer was separated, dried over silica gel, and distilled to give 5.0 g. of 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane.

Reaction of Triphenylphosphine with Bis(perfluoropropyl) Disulfide.—Bis(perfluoropropyl) disulfide (20.1 g., 0.05 mole), was added dropwise with stirring to a solution of 24.7 g. (0.1 mole) of triphenylphosphine in 50 ml. of acetone. The precipitate that formed after a few minutes was collected on a filter and washed with cold acetone. There was obtained 20.3 g. (0.065 mole) of triphenylphosphine difluoride as white needles, m.p. 144–146°.

Anal. Calcd. for $C_{18}H_{15}F_2P$: C, 71.99; H, 5.04; F, 12.66; P, 10.32. Found: C, 71.46; H, 4.95; F, 12.12; P, 10.69.

The filtrate was mixed with water, and a viscous yellow oil with a sharp odor separated. Analysis indicated this oil to be a polymer of perfluorothiopropionyl fluoride.

Anal. Calcd. for $(C_3F_6S)_n$: C, 19.79; F, 62.61; S, 17.61. Found: C, 19.23; F, 62.12; S, 17.14.

Pyrolysis of 1,3-Dithietanes.—Cleavage of dithietanes to thiocarbonyl compounds at high temperatures has been applied to the cases listed in Table II. The procedure for preparing hexafluorothioacetone from its dimer (III) was used in all of these preparations except that pyrolysis temperatures and pressures were varied to fit individual cases. 2,2,4,4-Tetrakis(trifluoromethyl)-1,3-dithietane (50 ml., 88 g.) was added dropwise over 5 hr. to an unpacked platinum tube 0.5 in. in diameter and 20 in. long inclined at a 30° angle and heated at 600° over a 12-in. section. During this addition, nitrogen at the rate of about 100 ml./minute was passed through the tube. Effluent gases were condensed in a trap cooled with a solid carbon dioxide–acetone

(15) Fluorine n.m.r. spectra were obtained with a Varian Associates high-resolution n.m.r. spectrometer operating at 56.4 Mc./sec. Spectra were calibrated in terms of displacement in parts per million (p.p.m.) from the F^{19} resonance of 1,2-difluoro-1,1,2,2-tetrachloroethane used as an external standard, except where otherwise noted. Negative frequency displacements are for resonances occurring at lower field than the references. Boiling points and melting points are uncorrected.

(16) E. G. Howard and W. J. Middleton, U. S. Patent 2,970,173 (1961).

mixture, and the condensate was rapidly distilled at reduced pressure to give 49 ml. (81 g., 92%) of hexafluorothioacetone as a deep blue liquid boiling at about −20° (200 mm.).

Synthesis of Fluoro Thio Ketones.—The procedure used to prepare hexafluorothioacetone from bis(perfluoroisopropyl)mercury was used to convert bis(4H-octafluoro-2-butyl)mercury to 4H-heptafluorobutane-2-thione. The thio ketone, a deep blue compound boiling at −27° (20 mm.), was obtained in 30% yield. Similarly, bis(4-chlorooctafluoro-2-butyl)mercury was converted to 4-chloroheptafluorobutane-2-thione, b.p. −19° (18 mm.).

Perfluorobutanethione (IV).—A 300-ml. flask was charged with 50 g. of phosphorus pentasulfide and flushed with nitrogen, which was continuously passed through the flask at a rate of 2 ml./sec. throughout the preparation. The flask was heated strongly to cause the phosphorus pentasulfide to reflux (520°) a few inches up in air condenser, and then 2-iodoperfluorobutane[17] (24 g., 0.069 mole) was added dropwise over a period of 15 min. There was obtained 15 g. (92%) of perfluorobutanethione as a deep blue liquid. A sample was purified by means of gas chromatography at room temperature on a column of silicone oil (Dow-Corning DC 200) on firebrick. The F^{19} n.m.r. spectrum of the above product (IV) showed the presence of three kinds of fluorine in the ratio of 3:3:2.

Anal. Calcd. for C_4F_6S: C, 20.70; F, 65.49; S, 13.81. Found: C, 20.76; F, 64.85; S, 13.56.

Perfluorothioacetyl Fluoride.—In a 500-ml. round-bottom flask equipped with an apparatus for adding a solid, a nitrogen inlet tube, and an air condenser leading to a trap cooled by solid carbon dioxide was placed 100 g. of powdered sulfur. The sulfur was heated to vigorous reflux, and 50 g. (0.115 mole) of solid bis(1-chlorotetrafluoroethyl)mercury was added in 1-2-g. portions over a period of 30 min. The condensate in a trap was distilled to give 20.5 g. (67%) of perfluorothioacetyl fluoride[18a] as a yellow liquid, b.p. −22°. The F^{19} n.m.r. spectrum showed a quartet (J = 10 c.p.s.) centered at −120.9 p.p.m. of relative area 1 and a doublet (J = 10 c.p.s.) centered at +7.66 p.p.m. of relative area 3. Perfluorothioacetyl fluoride contained bands at 4.83, 4.87, 7.40, 8.05, 8.45, 9.48, 9.53, 12.98, 13.08, and 13.38 μ in its infrared spectrum.

Bis(perfluoroethyl)mercury can be substituted for bis(1-chlorotetrafluoroethyl)mercury to obtain perfluorothioacetyl fluoride in yields comparable with that above. When perfluorothioacetyl fluoride was sealed in a glass tube for 1 week, it polymerized to a white, elastic solid.

Anal. Calcd. for $(C_4F_6S_2)_n$: C, 18.19; F, 57.54; S, 24.27. Found: C, 18.37; F, 57.41; S, 24.31.

Perfluorothioacetyl Chloride.—The above procedure was used to treat bis(1,1-dichlorotrifluoroethyl)mercury with sulfur. The product was perfluorothioacetyl chloride,[18b] which was obtained in 37% yield, as a bright red liquid boiling at 28–29°.

Anal. Calcd. for C_2ClF_3S: C, 16.17; Cl, 23.87; F, 38.37; S, 21.58. Found: C, 16.11; Cl, 24.79; F, 38.37; S, 21.65.

Other Fluorothiocarbonyl Compounds from Phosphorus Pentasulfide and Iodides.—Addition of gaseous perfluoroethyl iodide to refluxing phosphorus pentasulfide gave perfluorothioacetyl fluoride, b.p. −21°, in 45% yield. Similarly, gaseous perfluoropropyl iodide lead to a perfluoropropionyl fluoride, b.p. 9°, in 55% yield.

Anal. Calcd. for C_3F_6S: F, 62.61. Found: F, 62.73.

Perfluorothio-3-butenoyl Fluoride.—Sulfur (40 g., 1.25 moles) was placed in the bottom of an upright U tube 1 in. in diameter and 12 in. high. To one end of the tube a dropping funnel was connected and to the other end a trap cooled by solid carbon dioxide and acetone. A slow stream of nitrogen was passed through the tube, and the sulfur was heated until vapors refluxed about 4 in. up to the arms of the tube. 4,4-Diiodoperfluoro-1-butene,[19] 6.2 g. (0.015 mole), was then added dropwise over a period of 30 min. The liquid that condensed in the trap was distilled to give 2.04 g. (70%) of a bright yellow liquid, b.p. 45–46°.

Anal. Calcd. for C_4F_6S: C, 24.75; F, 58.73; S, 16.52. Found: C, 24.63; F, 58.58; S, 16.82.

Perfluorodithiobutyrolactone (XI).—Hexafluorocyclobutanone (26.5 g., 0.15 mole) was added in a saturated nitrogen stream, obtained by bubbling nitrogen through the liquid ketone, to a 300-ml. flask containing 100 g. of phosphorus pentasulfide heated to reflux (520°). The addition required 18 min. The effluent gases were condensed in a trap cooled wth a mixture of solid carbon dioxide and acetone. The condensate contained two layers. The upper layer 4.5 ml., was carbon disulfide. The lower layer, 10.5 ml., was fractionated to give 3.2 g. (0.014 mole, 9.5%) of perfluorodithiobutyrolactone, b.p. 53–56° (170 mm.), $n^{25}D$ 1.4267, as a purple-red oil. Its F^{19} n.m.r. spectrum confirmed the presence of equal amounts of three kinds of fluorine.

Anal. Calcd. for $C_4F_6S_2$: S, 28.3. Found: S, 28.1.

The dithio lactone was also prepared by adding 1,4-diiodohexafluorobutane dropwise to refluxing phosphorus pentasulfide in the manner described for preparation of perfluorobutanethione. The yield of dithiolactone by this method was 25%.

Pyrolysis of Perfluoro-5,10-dithiodispiro[3.1.3.1]decane.—A 2.5-cm. quartz tube packed for a length of 25 cm. with quartz rings was heated to 600°, and 22 g. of perfluoro-5,10-dithiodispiro[3.1.3.1]decane (XIII) was added dropwise through the tube at 2-mm. pressure. The addition required about 1 hr. The exhaust gases were condensed in a trap cooled by a mixture of acetone and solid carbon dioxide. The condensate was distilled to give 11.2 g. of perfluoro-2,3-dihydrothiophene (XVII), b.p. 50.5°, $n^{25}D$ 1.3483.

Anal. Calcd. for C_4F_6S: C, 24.75; F, 58.73; S, 16.52. Found: C, 25.11; F, 58.72; S, 16.10.

Perfluoro-5,10,11-trithio[3.1.3.2]undecane (XII), 42 g. (0.1 mole), was pyrolyzed in a similar manner to give 31.4 g. of perfluoro-2,3-dihydrothiophene and 5.1 g. of perfluorodithiobutyrolactone (XI), b.p. 93–95°.

Anal. Calcd. for $C_4F_6S_2$: C, 21.24; F, 50.51; S, 28.35. Found: C, 21.04; F, 50.01; S, 28.62.

Dimers of Thiocarbonyl Compounds (See Table I).—The dimers of hexafluoroacetone, perfluorobutane-2-thione, chlorodifluorothioacetyl chloride, and trifluoromethyl trifluorothioacetate all formed spontaneously in quantitative yield when the monomeric thiocarbonyl compound was stored at room temperature for a few days. The other thiocarbonyl compounds listed in Table I were dimerized by irradiation with ultraviolet light. The irradiation procedure is illustrated by the preparation of 2,4-bis(chlorodifluoromethyl)-2,4-difluoro-1,3-dithietane.[20] A solution of 38 g. of chlorodifluorothioacetyl fluoride in 25 ml. of dichlorodifluoromethane contained in a quartz reaction vessel was irradiated with ultraviolet light[21] for 3 hr. The dichlorodifluoromethane was evaporated and the residue was distilled to give 31.3 g. of 2,4-bis(chlorodifluoromethyl)-2,4-difluoro-1,3-dithietane as a colorless oil, b.p. 44° (23 mm.) and 137° (760 mm.), $n^{25}D$ 1.4127.

Spectral data are given in Table III.

TABLE III

SPECTRAL DATA FOR THIOCARBONYL COMPOUNDS

Compound	$\lambda_{max}^{cyclohexane}$, m$\mu$	ϵ
CF_3CSCF_3	580	12.7
	318	14.0
	313	14.4
	308	13.6
$CF_2ClCSCl$	510	11.5
CF_2ClCSF	425	31.8
$CF_3CS_2CF_3$	532	11.5
CF_3SCSCl	468	10.7
CF_3SCSF	394	24.6
$CF_3SCSSCF_3$	497	16.5
$CF_2ClCSC_6H_5$	518	26

Methanolysis of 2,2,4,4-Tetrakis(trifluoromethyl)-1,3-dithietane.—2,2,4,4-Tetrakis(trifluoromethyl)-1,3-dithietane, 36.5 g. (0.1 mole), was added dropwise to a stirred solution of 65 g. (1.2 mole) of sodium methoxide in 300 ml. of methyl alcohol. The reaction was exothermic and was cooled to keep the temperature between 40 and 50°. After the addition, the reaction mixture was refluxed for 4 hr. and cooled. The precipitated sodium fluoride was removed by filtration; the filtrate was acidified with

(17) M. Hauptschein, M. Braid, and F. E. Lawler, *J. Am. Chem. Soc.*, **79**, 2549 (1957).

(18) (a) W. J. Middleton, U. S. Patent 3,069,395 (1962); (b) W. J. Middleton, U. S. Patent 3,113,936 (1963).

(19) J. D. Park, R. Seffl, J. R. Lacher, *J. Am. Chem. Soc.*, **78**, 59 (1956).

(20) W. J. Middleton, U. S. Patent 3,117,977 (1964).

(21) The ultraviolet source consisted of a helix-shaped (4 × 2.5 in.), low-pressure mercury lamp constructed of 37-mm. quartz tubing and powered by a 5000-v. 600-mamp. transformer. The lamp was slipped over the quartz reaction tube so that its radiation impinged primarily upon the liquid portion of the reaction mixture.

TABLE IV

FLUOROALKYL MERCAPTANS FROM REDUCTION OF DISULFIDES

Disulfide	Reducing agent	Time of irradiation, days	Mercaptan	B.p., °C.	Yield, %
$(CF_3CF_2S)_2$	$H(CF_2)_4CH_2SH$	4	CF_3CF_2SH	−5	30
$(CF_3CF_2CF_2S)_2$	$H(CF_2)_4CH_2SH$	3	$CF_3CF_2CF_2SH$[a]	26	21
$(CF_2ClCF_2S)_2$	C_6H_5SH	4	CF_2ClCF_2SH[b]	33	6
$[CF_3CF_2CF(CF_3)S]_2$	$H(CF_2)_4CH_2SH$	5	$CF_3CF_2CFSHCF_3$	53	3

[a] *Anal.* Calcd. for C_3HF_7S: C, 17.83; H, 0.05; F, 65.81; S, 15.86. Found: C, 17.53; H, 0.85; F, 65.57; S, 15.83. [b] *Anal.* Calcd. for C_2HClF_4S: C, 14.25; H, 0.60; Cl, 21.04; F, 45.09; S, 19.02. Found: C, 14.29; H, 0.93; Cl, 20.91; F, 44.81; S, 19.00.

10% hydrochloric acid, and poured into water. The aqueous mixture was extracted with ether, and the ether extract was dried over calcium chloride. Distillation gave 8.0 g. of dimethyl α-methylthio-α-methoxymalonate as a colorless liquid, b.p. 45–50° (1 mm.), that solidified to a colorless solid, m.p. 50°, upon cooling. The infrared and n.m.r. spectra are consistent with this structure.

Anal. Calcd. for $C_7H_{12}O_5S$: C, 40.37; H, 5.82; S, 15.41. Found: C, 40.47; H, 6.27; S, 15.40.

Reaction of Fluoro Olefins with Sulfur. A. Bromodifluorothioacetyl Fluoride.—A 500-ml., round-bottom flask having two wide bore necks 8 in. long and containing 200 g. of sulfur was heated strongly until sulfur vapors refluxed about 4 in. up the necks. A slow stream (about 200 ml./min.) of bromotrifluoroethylene was passed into one of the necks, and the gases that passed out of the other neck were condensed in a trap cooled by an acetone solid carbon dioxide mixture. A total of 180 g. (0.97 mole) of bromotrifluoroethylene was passed through the sulfur vapors in this manner. The condensate weighed 200 g. Distillation gave 177 g. (82%) of bromodifluorothioacetyl fluoride as a bright yellow liquid, b.p. 41–42°. The F^{19} n.m.r. spectrum showed a doublet of relative area 2 and a triplet at lower field of relative area 1.

Anal. Calcd. for C_2BrF_3S: Br, 41.41; F, 29.53; S, 17.13. Found: Br, 41.33; F, 29.58; S, 17.18.

B. Chlorodifluorothioacetyl Fluoride.—Use of chlorotrifluoroethylene in the above procedure gave a 77% yield of chlorodifluorothioacetyl fluoride as a bright yellow liquid, b.p. 23°.

Anal. Calcd. for C_2ClF_3S: Cl, 23.87; F, 38.37. Found: Cl, 23.91; F, 38.49.

C. Chlorodifluorothioacetyl Chloride.[22]—This compound, b.p. −10° (20 mm.), $n^{25}D$ 1.4465, was obtained as a deep red liquid in 70% yield by passing 1,1-dichloro-2,2-difluoroethylene through sulfur vapor. Chlorodifluorothioacetyl chloride dimerized spontaneously. Pure monomer was obtained by thermal cracking of the dimer (see Table I).

Anal. Calcd. for $C_2Cl_2F_2S$: C, 14.56; Cl, 42.98; F, 23.02; S, 19.40. Found: C, 14.71; Cl, 43.12; F, 23.02; S, 19.37.

Fluoroalkyl Mercaptans.—The four fluoroalkyl mercaptans shown in Table IV were prepared by photolytic reduction of the corresponding disulfide with a miscible mercaptan. In a typical preparation, a solution of 30.2 g. (0.1 mole) of pentafluoroethyl disulfide in 62 g. of 2,2,3,3,4,4,5,5-octafluoropentanethiol was irradiated with ultraviolet light[21] for 4 days while a slow stream of nitrogen passed through the reaction mixture. The effluent gases were condensed in a trap cooled with a mixture of acetone and solid carbon dioxide. Trap contents were distilled to give 9.1 g. (0.06 mole, 30%) of pentafluoroethanethiol, b.p. −4°, as a colorless liquid. This material became yellow on storage in glass after a few days.

These mercaptans were quantitatively dehydrofluorinated with sodium fluoride, as was illustrated by the preparation of trifluorothioacetyl fluoride. Pentafluoroethanethiol, 6 g., was slowly vaporized in a stream of nitrogen and passed through a column at 25° containing 50 g. of sodium fluoride pellets packed in a 0.5-in.-diameter glass tube. The effluent gases were condensed in a trap cooled to −78°. The yellow condensate was distilled to give 5.0 g. of perfluorothioacetyl fluoride as a bright yellow liquid, b.p. −21°.

2,4-Bis(trifluoromethyl)-2,4-bis(trifluoromethylthio)-1,3-dithietane.—A Carius tube containing 20 g. of sodium fluoride pellets, 15 ml. (22.5 g., 0.17 mole) of perfluorothioacetyl fluoride, and 15 ml. of perfluoromethanethiol was allowed to remain at room temperature for 1 week. The tube was cooled and opened, and the liquid portion was distilled to give 14.3 g. of colorless trifluoromethyl 2,2,2-trifluoro-1-trifluoromethylthioethyl disulfide (XVI),[23] b.p. 57–80° (78 mm.), $n^{25}D$ 1.3753, and 10.9 g. of colorless 2,4-bis(trifluoromethyl)-2,4-bis(trifluoromethylthio)-1,3-dithietane (XV). The F^{19} n.m.r. spectrum of the dithietane showed a pair of quartets (J = 8 c.p.s.) of equal area at +9.22 (for C–CF_3) and −27.54 p.p.m. (for S–CF_3), and a slightly less intense pair of quartets (J = 7 c.p.s.) at +8.42 (for C–CF_3) and −27.18 p.p.m. (for S–CF_3), indicating that a mixture of the *cis* and *trans* forms was present. Additional characterization data are given in Table I.

Ethyl Trifluorodithioacetate.—Trifluorothioacetyl fluoride, 19.3 g. (0.15 mole), was slowly distilled into a stirred suspension of 12.6 g. (0.3 mole) of powdered sodium fluoride in 31 g. (0.5 mole) of ethyl mercaptan. Unchanged trifluorothioacetyl fluoride was returned to the reaction mixture by means of an acetone–solid carbon dioxide cooled reflux condenser. The temperature of the reaction mixture was maintained below 10° by an ice bath. After the addition, the mixture was warmed to room temperature and filtered. The filtrate was distilled to give 24.9 g. (96% yield) of ethyl trifluorodithioacetate as a red-orange liquid, b.p. 134°, $n^{25}D$ 1.4798.

Anal. Calcd. for $C_4H_5F_3S_2$: F, 32.72; S, 36.81. Found: F, 32.69; S, 37.19.

Phenyl Chlorodifluorodithioacetate.—A deep red oil, b.p. 85–86° (1.5 mm.), $n^{25}D$ 1.5876, was obtained in 95% yield by reaction of chlorodifluorothioacetyl fluoride with benzenethiol.

Anal. Calcd. for $C_8H_5ClF_2S_2$: C, 40.25; H, 2.13; Cl, 14.83; F, 15.90; S, 26.86. Found: C, 40.29; H, 2.52; Cl, 14.73. F, 16.11; S, 27.31.

Ethyl Chlorodifluorodithioacetate.—This compound was obtained in 95% yield as a bright red oil, b.p. 51–52° (5 mm.), by reaction of ethanethiol with chlorodifluorothioacetyl fluoride.

Anal. Calcd. for $C_4H_5ClF_2S$: C, 25.70; H, 2.64; S, 33.60. Found: C, 25.20; H, 2.79; S, 33.73.

Methyl Trifluorothionacetate.—Methanol and trifluorothioacetyl fluoride were allowed to react to give trifluorothionacetate in 80% yield as a bright yellow oil, b.p. 67°, $n^{25}D$ 1.3711.

Anal. Calcd. for $C_3H_3F_3OS$: C, 25.00; H, 2.08; F, 39.55; S, 22.24. Found: C, 25.08; H, 2.33; F, 39.42; S, 22.28.

2,2,4,4-Tetrafluoro-1,3-dithietane (VIII).—A mixture of 108 g. (0.47 mole) of thiophosgene dimer,[6] 179 g. (1.0 mole) of antimony trifluoride, and 250 ml. of dry tetramethylene sulfone was stirred and heated at 90–100° for 2 hr. The volatile products that formed during the heating period were condensed in a trap cooled with ice. The orange condensate (66 g.) was distilled through an 18-in. spinning-band column to give 45.6 g. (60% yield) of slightly impure 2,2,4,4-tetrafluoro-1,3-dithietane[24] as a light yellow liquid, b.p. 47–48°; 7.8 g. of thiophosgene, b.p. 73–76°; and 5.7 g. of 2-chloro-2,4,4-trifluoro-1,3-dithietane (IX) as a colorless oil, b.p. 89–90°, $n^{25}D$ 1.4501.

Anal. Calcd. for $C_2ClF_3S_2$: Cl, 19.63; S, 35.50. Found: Cl, 19.68; S, 35.62.

The tetrafluorodithietane was further purified by vigorous shaking with 25 ml. of 10% sodium hydroxide and 5 ml. of 30% hydrogen peroxide until the yellow color disappeared. The lower layer was separated, dried over silica gel, and distilled to give 40.8 g. of colorless 2,2,4,4-tetrafluoro-1,3-dithietane, b.p. 48°, m.p. −6°, $n^{25}D$ 1.3908, d^{20}_4 1.6036.

Anal. Calcd. for $C_2F_4S_2$: C, 14.63; F, 46.30; S, 39.06; mol. wt., 164. Found: C, 14.73; F, 46.60; S, 39.16; mol. wt. (cryoscopic in benzene), 164.

(22) We are indebted to Dr. C. L. Dickinson of this laboratory for this experiment.

(23) W. J. Middleton and W. H. Sharkey, *J. Org. Chem.*, **30**, 1384 (1965).

(24) W. J. Middleton, U. S. Patent 2,980,695 (1961).

The major absorption bands in the gas phase infrared spectrum, in decreasing intensity, are 9.24, 8.95, and 10.35 μ. The F^{19} n.m.r. spectrum contains a single unsplit line at -1.77 p.p.m.

2,2-Dichloro-4,4-difluoro-1,3-dithietane (X).—2,2-Dichloro-4,4-difluoro-1,3-dithietane (X), b.p. 130°, $n^{25}D$ 1.5048, was obtained by distilling the combined higher boiling residues from several preparations of tetrafluorodithietane. The F^{19} n.m.r. spectrum contained a single unsplit resonance line.

Anal. Calcd. for $C_2Cl_2F_2S_2$: C, 12.19; Cl, 35.99; F, 19.28; S, 32.54. Found: C, 12.55; Cl, 36.07; F, 19.18; S, 32.86.

Thiocarbonyl Fuoride.—Tetrafluoro-1,3-dithietane, 40 g. (0.24 mole), was added dropwise over a period of 2 hr. through a platinum tube, 0.5 in. in diameter and 25 in. long, inclined at an angle of 30° and heated to 475–500° over a length of 12 in. A slow stream of helium (20 ml./min.) was passed through the tube during pyrolysis. The effluent gases were condensed in successive traps, cooled by a mixture of acetone and carbon dioxide and liquid nitrogen, respectively. The material in the traps was combined and distilled through a 16-in. column packed with "Hastelloy" helices. There was obtained 36 g. (90% yield) of thiocarbonyl fluoride as a colorless liquid boiling at $-54°$. The F^{19} n.m.r. spectrum contained a single unsplit band at -107.8 p.p.m.[25] The mass spectrum was consistent for the $CF_2{=}S$ structure.

Thiocarbonyl Chlorofluoride.—2-Chloro-2,4,4-trifluoro-1,3-dithietane, 60 g., was added dropwise over a period of 3 hr. to a platinum tube 0.5 in. in diameter, inclined at an angle of 30°, and heated to 400° over a length of 12 in. A stream of helium, 20 ml./min., was passed through the tube during the pyrolysis. The effluent gases were condensed in a trap cooled by liquid nitrogen, and the condensate was transferred to a low-temperature still and fractionated. There was obtained 25.0 g. (91% yield) of thiocarbonyl fluoride, b.p. -54 to $-53°$, and 22 g. (67% yield) of bright yellow thiocarbonyl chlorofluoride, b.p. 6–7°. The thiocarbonyl chlorofluoride was identified by its F^{19} n.m.r. spectrum, which contains a single unsplit line at -161.8 p.p.m., and its mass spectrum.

Fluorination Reactions. A. Sulfur Tetrafluoride and Thiocarbonyl Fluoride.—Thiocarbonyl fluoride (14 g., 0.17 mole) was heated in a "Hastelloy C" shaker tube with 18 g. (0.168 mole) of sulfur tetrafluoride for 4 hr. at 200°. The tube was cooled and the gaseous products bled from the tube. Distillation through a low-temperature still gave 1.3 g. of $(CF_3)_2S$, b.p. -20 to $-18°$, identified by comparison of its F^{19} n.m.r. spectrum with that of an authentic sample.[26]

The liquid products on distillation yielded CF_3SSCF_3, b.p. 34–35°, totaling 1.6 g., and CF_3SSSCF_3, b.p. 84–85°, $n^{25}D$ 1.3971, totaling 10.0 g.

B. Sulfur Tetrafluoride and Tetrafluorodithietane.—Tetrafluorodithietane (30 g., 0.183 mole) and 20 g. of sulfur tetrafluoride were heated in a "Hastelloy C" shaker tube for 2 hr. at 150° and 3 hr. at 250°. Distillation of the gaseous products through a low-temperature still yielded only a small amount of $(CF_3)_2S$. The liquid products were filtered to remove small particles of sulfur and distilled to give 4.32 g. of CF_3SSCF_3, b.p. 33–35°; 4.30 g. of CF_3SSSCF_3, b.p. 83–85°; and 2.86 g. of material having b.p. 129–132°, $n^{25}D$ 1.4542. This last fraction was shown by mass spectrometry to consist of 83% $CF_3S_4CF_3$.[27]

C. Thiocarbonyl Fluoride and Iodine Pentafluoride.—Iodine pentafluoride (20 g., 0.09 mole) and thiocarbonyl fluoride (9 g., 0.11 mole) were heated in a stainless steel shaker tube at 150° for 6 hr. The gaseous product was vented through a trap cooled in solid carbon dioxide, and the condensate was distilled to give 11.2 g. (65%) of CF_3SF_3, b.p. -8 to $-6°$.

D. Tetrafluorodithietane and Iodine Pentafluoride.—Tetrafluorodithietane (100 g., 0.62 mole) and iodine pentafluoride (225 g., 1.01 moles) were heated in a stainless steel shaker tube 4 hr. at 150° for 6 hr. at 200°. The gaseous products were collected by venting the tube through a trap cooled in solid carbon dioxide. Distillation through a low-temperature column gave 104 g. (55%) of CF_3SF_3, b.p. -8 to $-6°$. Analysis by mass spectrometry showed the principal impurity to be silicon tetrafluoride (0.8%).

E. Tetrafluorodithietane and Iodine Pentafluoride at 125°.—Tetrafluorodithietane (20 g., 0.122 mole) and iodine pentafluoride (22.2 g., 0.1 mole) were heated in a stainless steel shaker tube at 125° for 6 hr. The liquid product was filtered to remove iodine and distilled to give 10.8 g. of product, b.p. 32–33.5°. Analysis by mass spectrometry indicated the presence of CF_3SSCF_3 (85%) and $CF_2(SF_3)_2$[28] (12%), with lesser amounts of carbon disulfide, air, and silicon tetrafluoride.

1,1-Difluoro-2,2-diphenylethylene.—Diphenyldiazomethane[29] (19.4 g., 0.1 mole) was dissolved in 150 ml. of petroleum ether (b.p. 30–75°), and gaseous thiocarbonyl fluoride was bubbled into the solution until the purple color of the diazo compound had faded. A solid totaling 4.19 g., m.p. 170–173°, was collected by filtration. Two recrystallizations from ethanol (Darco) gave coarse white needles, m.p. 177–178°. This material was identified as tetraphenylethylene sulfide,[30] m.p. 175°, by its infrared spectrum, its ultraviolet spectrum, and its pyrolysis[30] to tetraphenylethylene and sulfur when heated to 200°. This represented a 23% conversion from diphenyldiazomethane.

The petroleum ether filtrate from above was concentrated and on standing overnight deposited amorphous sulfur. Distillation of the supernatant oil yielded 1,1-difluoro-2,2-diphenylethylene[31] totaling 9.83 g. (45% conversion based on diphenyldiazomethane), b.p. 74–76° (0.55 mm.), $n^{25}D$ 1.5618, identified by its infrared, ultraviolet, and F^{19} resonance spectra, as well as by its cleavage with potassium permanganate to benzophenone.

Reaction of Thiocarbonyl Fluoride with Diazomethane.—Gaseous thiocarbonyl fluoride was added with stirring to an ethereal solution of diazomethane[32] (5.9 g. in 100 ml.), cooled to $-30°$. The yellow diazomethane color rapidly faded. The clear solution was warmed to 0–10°, whereupon a gas was rapidly evolved with concomitant precipitation of amorphous sulfur. The evolved gases (8.2 g.) were condensed in a trap cooled with liquid nitrogen. Analysis by mass spectroscopy indicated the condensate consisted of 86% vinylidene fluoride (53% conversion based upon diazomethane), 6% carbonyl sulfide, 7% carbon disulfide, and 1% silicon tetrafluoride.

1,1-Difluoro-2,2-bis(*p*-chlorophenyl)ethylene.—A solution of 26.4 g. (0.1 mole) of bis(*p*-chlorophenyl)diazomethane[33] in 200 ml. of petroleum ether was cooled to 0° while thiocarbonyl fluoride was bubbled in until the purple diazomethane color faded. The solid which formed was collected on a filter and totaled 5.0 g., m.p. 220–230°. Recrystallization from acetone yielded fine light yellow needles, m.p. 223–226°. Analytical data confirmed that the structure was tetrakis(*p*-chlorophenyl)-ethylene sulfide.

Anal. Calcd. for $C_{26}H_{16}Cl_4S$: C, 62.17; H, 3.21; Cl, 28.23; S, 6.40; mol. wt., 502. Found: C, 62.11; H, 3.26; Cl, 28.10; S, 6.22; mol. wt., 493.

The petroleum ether filtrate from above was concentrated and distilled to give 9.8 g. of 1,1-difluoro-2,2-bis(*p*-chlorophenyl)-ethylene (34% conversion based on the diazomethane), b.p. 143–145° (0.3 mm.), $n^{25}D$ 1.5730. The infrared spectrum showed strong absorption at 5.83 μ for the $=CF_2$ stretching.

Anal. Calcd. for $C_{14}H_8Cl_2F_2$: C, 58.98; H, 3.13; F, 14.71. Found: C, 59.21; H, 2.98; F, 14.58.

Thiocarbonyl Bromide.—Anhydrous hydrogen bromide (18 g., 0.225 mole) and thiocarbonyl fluoride (15 g., 0.184 mole) were condensed in a Hastelloy-lined shaker tube. The tube was then heated at 150° for 4 hr. After venting, the liquid product recovered from the tube was distilled through a spinning-band column. The reaction mixture was complicated, but a fraction, b.p. 142–144°, $n^{25}D$ 1.6015, was obtained. This was a heavy orange-red liquid which was found to be thiocarbonyl bromide by its analysis and mass spectrometer pattern.

Anal. Calcd. for $CSBr_2$: C, 4.62; S, 14.99; mol. wt., 204. Found: C, 4.77; 4.71; S, 14.61, 14.87; mol. wt. (cryoscopic in benzene), 201.

Thiocarbonyl bromide is quite unstable. A sample analyzed after standing 2 weeks in a clear glass vial consisted of 97%

(25) A. J. Downs and E. A. V. Ebsworth, *J. Chem. Soc.*, 3516 (1960); A. J. Downs, *ibid.*, 3516 (1962). These authors report a resonance for CF_2S obtained by decomposition of SiH_3SCF_3 of -40.5 ± 3 p.p.m. from CCl_3F as a standard. This value corresponds to -108 p.p.m. relative to 1,2-difluoro-1,1,2,2-tetrachloroethane.

(26) R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 3219 (1953); 3871 (1955).

(27) R. N. Hazeldine and J. M. Kidd [*ibid.*, 3219 (1953); 3871 (1955)] reported b.p. 135° and $n^{20}D$ 1.4608 for this tetrasulfide.

(28) A. F. Clifford, H. K. El-Shamy, H. J. Emeleus, and R. N. Hazeldine, *ibid.*, 2372 (1953).

(29) H. Staudinger, E. Anthes, and F. Pfenninger, *Ber.*, **49**, 1932 (1916).

(30) H. Staudinger and J. Siegwart, *Helv. Chim. Acta*, **3**, 833 (1920).

(31) A. L. Dittman and J. M. Wrightson, U. S. Patent 2,705,706 (1955).

(32) F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 165.

(33) L. I. Smith and K. L. Howard, ref. 32, Coll. Vol. III, 1955, p. 351.

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.

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

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.

Fluorothiocarbonyl Compounds. II.[1] Reactions of Hexafluorothioacetone

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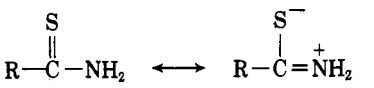
Study of the chemistry of hexafluorothioacetone has shown that it is very reactive with nucleophilic reagents. An example is sodium bisulfite, which adds to give Bunte salts in a manner opposite to that normally expected. Such reverse additions also take place with mercaptans, in which case disulfides 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



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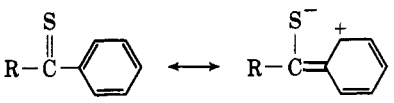

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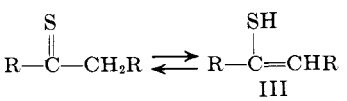
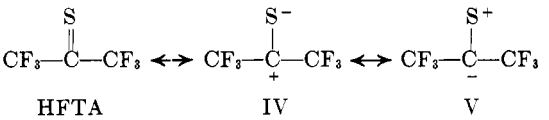
ketones are in equilibrium with enolic forms, such as III. In addition, many of the reported thio ketones



III

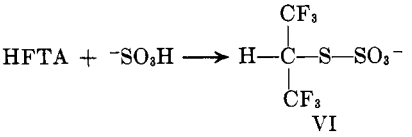
are difficult to prepare in monomeric form and are unstable to air. The synthesis of fluoro thio ketones[1] has provided compounds that do not possess these complicating factors and, of these, hexafluorothioacetone (HFTA) is an ideal model for a study of C=S reactivity. HFTA has its own peculiarity, however, which is the strong electron-withdrawing power of the two trifluoromethyl groups. This electron withdrawal is manifested by high reactivity toward nucleophilic



HFTA IV V

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.

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



VI

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.

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

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