Tetrafluorothiirane

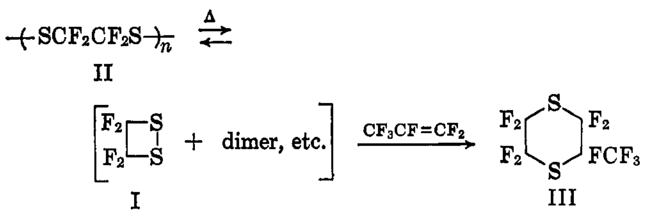
W. R. BRASEN, H. N. CRIPPS, C. G. BOTTOMLEY, M. W. FARLOW, AND C. G. KRESPAN

Contribution No. 1064 from the Central Research Department, Experimental Station,
E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware 19898

Received July 30, 1965

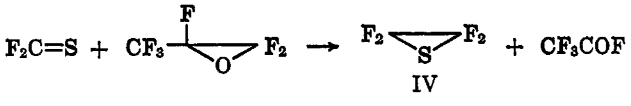
Pure tetrafluorothiirane has good stability to heat and ultraviolet light. Free-radical attack occurs at sulfur with ring opening. The radical intermediate so formed can participate efficiently in chain reactions by adding to an olefin, attacking another molecule of tetrafluorothiirane, or abstracting hydrogen from a substrate. Ring opening is also induced by nucleophiles, but by attack on carbon rather than sulfur. This can result in cycloaddition reactions with unsaturated molecules such as ketones or formation of thioacetic acid derivatives with stronger bases. Aluminum chloride, a powerful electrophile, causes unusual isomerization and condensation reactions.

Completely fluorinated monosulfides, both cyclic[1] and acyclic,[2] are characteristically unreactive toward reagents of any type. Most fluorinated disulfides are also relatively stable to heat, acids, and electrophilic radicals,[2-4] though quite sensitive to basic reagents. A notable exception is tetrafluoro-1,2-dithietane (I), which at 25° exists only briefly.[5] Its spontaneous polymerization can be easily reversed above 250°, thereby providing an example of a saturated fluorinated disulfide with a thermally labile S–S bond. The dithietane I and similar pyrolysis products of the polydisulfide II are reactive toward olefinic bonds; thermal decomposition of II in the presence of hexafluoropropene resulted in trapping of the transient species as 2-trifluoromethylheptafluoro-1,4-dithiane (III). Similar reactions with bis(trifluoromethyl) disulfide and hexafluoropropene or tetrafluoroethylene were unsuccessful.

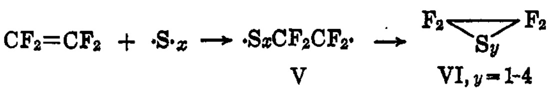


Before the present studies on tetrafluorothiirane, no perfluorinated monosulfide with reactivity approaching that of disulfides I and II was known.

Synthesis.—The most useful laboratory preparation of tetrafluorothiirane found in this study was the reaction of thiocarbonyl fluoride with hexafluoropropene epoxide. Above 170°, the fluoro epoxide served as an apparent source of CF_2:, which added to CF_2S to form the thiirane IV. Close control of conditions proved necessary to obtain 30–40% yields reproducibly. The episulfide of hexafluoropropene was prepared similarly using trifluorothioacetyl fluoride as the thiocarbonyl reactant.

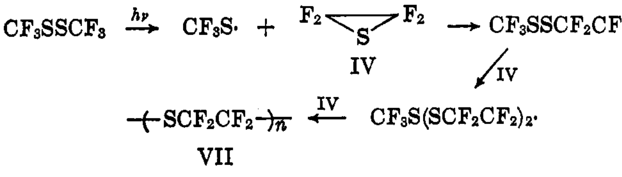


Reaction of sulfur with tetrafluoroethylene in the vapor phase was also found to produce tetrafluorothiirane (IV). However, yields were about 2%, and IV was obtained as part of a difficultly separable mixture containing carbon disulfide and octafluorocyclobutane. Although an investigation of widely varied conditions showed that at low conversions it was possible to increase the yield of IV, the amounts formed were still small. These observations and earlier results on this reaction[5] are in accord with the intervention of diradical V as an intermediate common to thiirane IV and the cyclic polysulfides VI (y = 2–4). Selection of the site of intermolecular attack of the fluororadical end on atoms along the sulfur chain will be influenced mainly by steric requirements for the reaction, less by the value of X (which tends to be >4), and still less by other easily controlled variables.



Reactivity.—Tetrafluorothiirane (IV), b.p. −10.5° after purification by gas chromatography, can be handled and stored without difficulty. Its stability is such that thermal decomposition is slow at <200°, and photodecomposition is also slow.

Ultraviolet irradiation in the presence of an initiator such as bis(trifluoromethyl) disulfide, however, results in an extraordinary polymerization to the ring-opened structure VII. Clearly radical attack on a ring atom occurs, and evidence from a related reaction (see below) indicates that sulfur with its unshared electrons is the point of attack[6] in the initiation and propagation steps.



The good thermal stability (to ~300°) and resistance to base (unaffected by hot aqueous base and monoamines), as well as the high crystallinity of the polymer, show it to be the poly(monosulfide) VII. Since the product formed is regular and molecular weight is high, occurrence of other ring-opening and chain-transfer reactions is unlikely.

Chlorine or fluoroalkylsulfenyl chlorides can also be used as photoactivated initiators with thiirane IV. Molecular weights of products have been lower in these

---

[1] C. G. Krespan and C. M. Langkammerer, *J. Org. Chem.*, **27**, 3584 (1962).

[2] G. A. R. Brandt, H. J. Emeleus, and R. N. Haszeldine, *J. Chem. Soc.*, 2198 (1952).

[3] M. Hauptschein and A. V. Grosse, *J. Am. Chem. Soc.*, **73**, 5461 (1951).

[4] R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 3219 (1953).

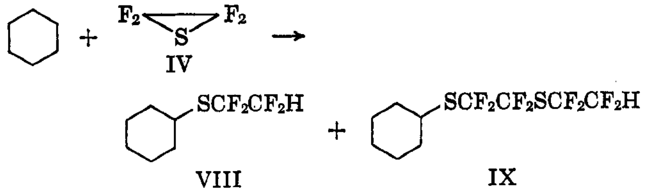
[5] C. G. Krespan and W. R. Brasen, *J. Org. Chem.*, **27**, 3995 (1962).

[6] J. F. Harris, Jr. [*J. Am. Chem. Soc.*, **84**, 3148 (1962)] reported convincing evidence for radical attack on the sulfur atom in CF_3SCl as well as on chlorine.

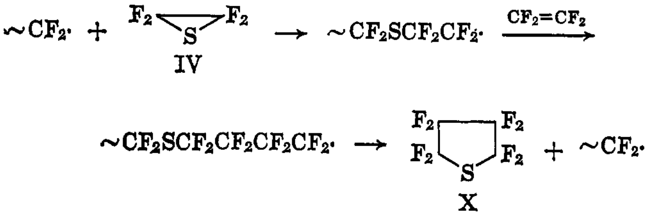
cases, almost certainly because chain transfer is more efficient with the chlorinated materials. In fact, preparation of 2-chlorotetrafluoroethylsulfenyl chloride is easily accomplished by irradiating IV with an excess of chlorine. Sulfenyl bromide was not obtained by heating IV and bromine; if formed, this unstable intermediate reverted to bromine and bis(2-bromotetrafluoroethyl) disulfide, the products isolated.

Not only do radical initiators induce homopolymerization, but radical copolymerization of the thiirane with monomers such as ethylene and propylene proceeds easily to give 1:1 compositions. The tendency toward alternation has been frequently encountered before,[7] but never with a saturated reactant so unlikely to be polarizable or to participate in resonance (electron transfer) in the transition state.

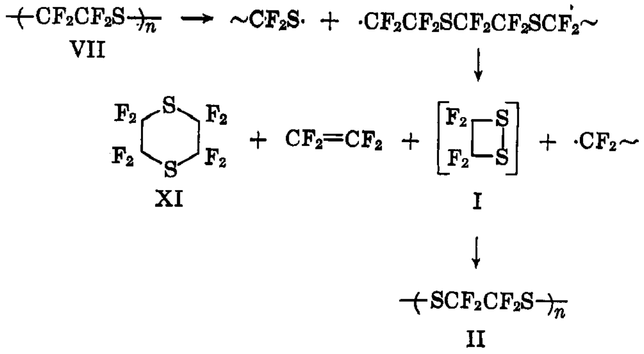
Radical-initiated reaction of tetrafluorothiirane with cyclohexane led to low molecular weight adducts because of a relatively efficient chain-transfer step. Identification of the principal adducts as cyclohexyl tetrafluoroethyl sulfide (VIII) and the 2:1 telomer IX of similar structure confirms the sulfur atom as the site of attack by cyclohexyl radical. Since other types of radicals are more electrophilic than alkyl radicals[8,9] and attack of a radical on saturated carbon rather than on a peripheral atom is rare, it is probable that radicals in general attack the thiirane at sulfur.



Another unusual example of radical attack on sulfur in a perfluorinated monosulfide was encountered during copolymerizations of IV with tetrafluoroethylene. A sizeable proportion of octafluorothiolane (X) was formed by a radical-chain mechanism which is best explained by intramolecular attack of a radical end on sulfide sulfur in the chain. Essentially no reaction occurred in the absence of a free-radical source.

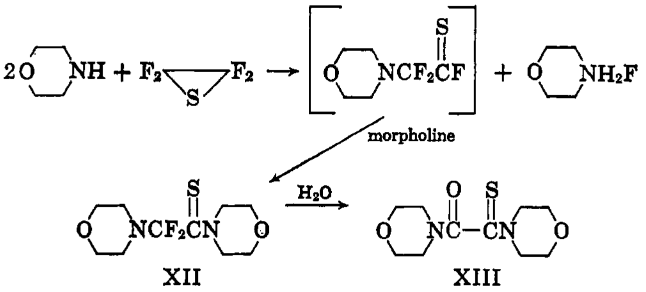


Perhaps because of the much higher temperatures involved, pyrolysis of poly(tetrafluorothiirane) (VII) took a very different course. Once a C–S bond in VII had undergone homolysis, the fluorocarbon radical end gave intramolecular attack on sulfide sulfur to form octafluoro-1,4-dithiane (XI) to only a minor extent. The major reaction was elimination of tetrafluoroethylene as well as of dithietane I, as indication that I is relatively stable at elevated temperatures.

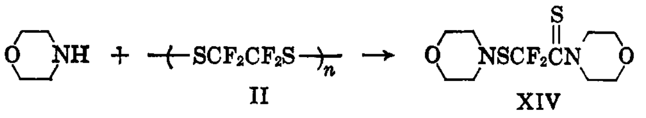


These reactions provide further support for the postulated structures of the polymers involved.

Unlike most perfluorinated sulfides, IV is easily attacked by base. Amines attack the thiirane IV at a carbon atom rather than at sulfur, as shown by the formation of C–N bonds in products XII and XIII from morpholine. Nucleophilic attack on a saturated carbon atom in a completely fluorinated compound is unusual because of shielding by the negative fluorine atoms. Therefore, the high reactivity observed in the present instance must be ascribed to the greatly modified sp^3 bonding of carbon in the strained ring.



Under much more strenuous conditions, polymer VII (the acyclic form of IV) and dithiane XI (larger ring than IV) are both stable. It is also noteworthy that reaction of morpholine with poly(tetra-1,2-dithietane) (II), unlike reaction with IV, occurred with the expected[2] attack on sulfur to give sulfenamide XIV. The surprisingly consistent direction of cleavage of the S–S bonds led to a fair yield of XIV and provided further support for structure II.[5]



A similar type of cleavage occurred with tetrafluoro-1,2,3,4-tetrathiane (XV) to give the two expected products, XVI and XVII (see Chart I).

Reaction of thiirane IV with diphenyl sulfoxide as the base gave disulfide XVIII *via* an oxidation–reduction after the initial attack on carbon of the thiirane.

IV could also be added 1,3 to the multiple bonds of only modestly basic groups. An example is the cycloadduct XIX with benzophenone in which the negative oxygen is again bonded to carbon.

Although most of the electrophilic reagents tested, including BF$_3$, were without effect on thiirane IV, AlCl$_3$ apparently induced a rearrangement of IV to trifluorothioacetyl fluoride (XX), and then caused dimerization of XX to the dithio ester XXI, and subsequently caused XXI to cyclodimerize to XXII. This

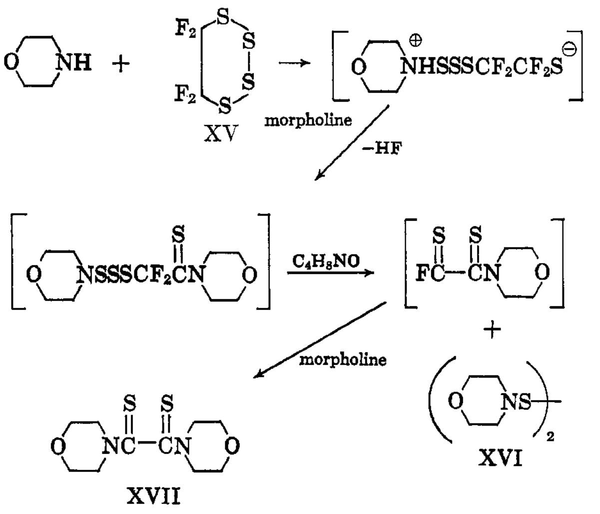
---

[7] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 132.

[8] G. A. Russell and R. C. Williamson, Jr., *J. Am. Chem. Soc.*, **86**, 2357 (1964).

[9] I. M. Whittemore, A. P. Stefani, and M. Szwarc, *ibid.*, **84**, 3799 (1962).

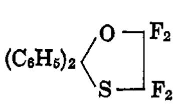
CHART I



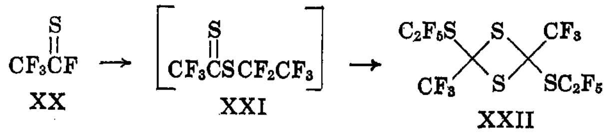
interpretation is borne out by the separate conversion of the thio acid fluoride to XXII by $AlCl_3$. Thiocarbonyl fluoride, on the other hand, stopped at the thio ester stage with $AlCl_3$, giving bis(trifluoromethyl) trithiocarbonate rather than its dimer.

$FC(=O)CF_2SSCF_2C(=O)F$

XVIII



XIX



Experimental Section[10]

Tetrafluorothiirane (IV).[11] **A. From Thiocarbonyl Fluoride**[12]—Into a 1-l. Hastelloy rocker bomb cooled to −80° was condensed 175 g. (1.9 moles) of thiocarbonyl fluoride[13] (containing 11% chlorodifluoromethane) and 240 g. (1.25 moles) of hexafluoropropene epoxide (containing 13% hexafluoropropene).[11,14] After having been pressured to 30 p.s.i. with hydrogen chloride, the bomb was heated to 175° and maintained at that temperature for 8 hr. (Note: Restricted loading density, careful temperature control, and a small amount of HCl are essential for reproducible results. Below 170° little reaction occurs, while above 180° large quantities of high-boiling materials tend to form.) That portion of the reaction product volatile at room temperature, 393 g., was distilled through a 60-cm. low-temperature still. As determined by analytical gas chromatography, the first fraction, 300 g., b.p. −62 to −20°, consisted of chlorodifluoromethane (b.p. −62°), trifluoroacetyl fluoride (b.p. −59°) thiocarbonyl fluoride (b.p. −54°), hexafluoropropene epoxide (b.p. −29°), and hexafluoropropene (b.p. −22°). The second fraction, 84 g., b.p. −20 to −0°, was tetrafluorothiirane (b.p. −10.5°) with octafluorocyclobutane (b.p. −6°) as the major impurity. The pot residue weighed 9 g. Final purification was achieved by preparative gas chromatography, using a 38 ft. × 1.5 in. column packed with 25–48 mesh firebrick impregnated with 200-cstoke Silicone 200 Oil with helium as a carrier gas Thus 65 g. (39%) of colorless tetrafluorothiirane of >99% purity was obtained at longer retention time than octafluorocyclobutane.

Anal. Calcd. for C_2F_4S: F, 57.54; S, 24.28; mol. wt., 132. Found: F, 57.57, 58.08; S, 24.28; mol. wt., 130 (gas density).

The episulfide has a melting point of −120.8° and a freezing point of −120.6°. Density at −80° is about 1.65–1.7. The F^{19} n.m.r. spectrum consisted of a single resonance at +31.7 p.p.m. The infrared spectrum consisted of four principal bands at 6.86, 8.51, 9.30, and 12.0 μ; that at 6.86 μ is apparently associated with the heterocyclic ring.

B. From Sulfur and Tetrafluoroethylene.—The reactor was a 1-l. flask with a central exit neck 1 ft. long (25-mm. diameter) and a gas inlet tube (8 mm. diameter). The exit tube was connected with a goose neck to an air-cooled receiver which led in turn to an ice-cooled trap and two traps cooled to −80°.

Two pounds of sulfur was placed in the reactor and heated overnight at gentle reflux (*ca.* 445°) under a slow stream of nitrogen. The central neck was wrapped with asbestos, and heating was continued while the nitrogen was replaced with a slow stream of tetrafluoroethylene. After a few minutes, the cyclic polysulfides began to distil, and the tetrafluoroethylene flow was increased to 1.5 moles/hr. After 6 hr., the sulfur was practically exhausted and the reaction was stopped. The products were 1395 g. of cyclic polysulfides[5] in the air-cooled receiver, 225 g. of volatiles in the Dry Ice traps, and about 115 g. of nonvolatile residue in the reactor. The volatile products were shown to be composed largely of unreacted tetrafluoroethylene, thiocarbonyl fluoride, trifluorothioacetyl fluoride, octafluorocyclobutane, carbon disulfide, and tetrafluorothiirane. Careful fractionation of the volatiles gave 27 g. (2%) of crude tetrafluorothiirane, which was further purified by gas chromatography (see above).

Photolysis of Tetrafluorothiirane.—A 6-in. Vycor tube (9-mm. o.d.) was charged with 3 g. of tetrafluorothiirane, degassed, and sealed under vacuum. The tube was placed inside a spiral mercury resonance lamp and was irradiated at ambient temperature. After 17 hr., the walls of the tube were coated with a thin layer of polymer, and the tube was inverted and exposed for 6 hr. longer. More polymer formed on the walls of the tube. Analysis of the liquid and gaseous products by gas chromatography showed them to consist mainly of unreacted tetrafluorothiirane. Small amounts of octafluorocyclobutane, thiocarbonyl fluoride, carbon disulfide, octafluorodithiane, and trace amounts of three unknowns were also detected.

Polymerization of Tetrafluorothiirane. A. Light-Catalyzed.—A Pyrex tube (15 mm. o.d., 1 mm. wall thickness, 15.5 in. long) was charged with 23.8 g. of tetrafluorothiirane, 10 ml. of octafluorodithiane, and 12 mg. of bis(trifluoromethyl) disulfide and sealed *in vacuo*. The tube was placed in a horizontal position inside a quartz tube through which tap water was circulated. The tube was slowly rotated (about 1 r.p.m.) and irradiated with an RS sunlamp 12 in. distant. After 24 hr., the tube was opened and poly(tetrafluorothiirane) (VII) was obtained in 99% yield. Scrupulously purified episulfide did not polymerize at all unless the disulfide was added.

Anal. Calcd. for $(C_2F_4S)_n$: C, 18.18; F, 57.54; S, 24.28. Found: C, 18.24, 18.66; F, 57.61, 57.37; S, 24.51, 24.59.

B. N_2F_2 Initiation.—A platinum tube (8 in. long, 0.5 in. diameter) was charged with 12 g. of purified, degassed tetrafluorothiirane and 6 mg. of *trans*-dinitrogen difluoride. After the calculated amount of N_2F_2 was introduced from a small glass loop of known volume, the tube was sealed *in vacuo* at −196°. The sealed tube was placed in a metal pressure vessel and cooled to −80°, and the vessel was closed and pressured with nitrogen to 900–2000 atm. The pressure was kept in this range throughout the polymerization. The vessel was heated over a 2-hr. period to 60°. After 5 hr. at 60°, the temperature was slowly increased to 70° and kept at 70° for 5 hr. The pressure vessel was cooled to −80°, and the platinum tube was removed and cut open with scissors. The poly(tetrafluorothiirane) was obtained as a hard, white, solid plug in nearly 100% conversion. Occasionally, a run failed owing to premature decomposition of the initiator, and then no polymer was formed. In some runs, rapid exothermic polymerization resulted in low molecular weight polymer in poor conversion. The use of an inert medium, octafluorodi-

---

[10] All boiling points and melting points are uncorrected. The fluorine n.m.r. spectra were obtained at 56.4 Mc./sec. with a Varian Associates HR-60 high-resolution spectrometer. Spectra were calibrated in terms of higher field displacement in parts per million (p.p.m.) from the F^{19} resonance of 1,2-difluoro-1,1,2,2-tetrachloroethane as external standard. The H^1 n.m.r. spectra were obtained at 60 Mc./sec. with a Varian Associates A-60 spectrometer and were calibrated in terms of lower field displacement from tetramethylsilane as internal standard.

[11] F. C. McGrew, U. S. Patent 3,136,744 (1964).

[12] We are indebted to Dr. F. C. McGrew for suggesting this experiment based on an earlier observation by Dr. E. P. Moore that hexafluoropropene epoxide serves as a source of CF_2: when heated.

[13] W. J. Middleton, E. G. Howard, and W. H. Sharkey, *J. Am. Chem. Soc.*, **83**, 2589 (1961).

[14] H. H. Biggs and J. L. Warnell, French Patent 1,322,597 (1963).

thiane or hexafluoropropane cyclic dimer, gave high molecular weight polymer, but usually in lower conversion.

C. Properties of Poly(tetrafluorothiirane).—Poly(tetrafluorothiirane) made by either method A and B is a thermoplastic with a crystalline melting point around 175°. Like many fluorocarbon plastics, it has a high melt viscosity (10^5 poises at 300°) but can be readily fabricated at 250° with slight decomposition. The properties of the polymer vary with the thermal treatment of the sample after molding. Quenched films are tough (tensile strength 2500–2900 p.s.i., elongation at break ~100%) and can be repeatedly folded without breaking. Samples annealed by slow cooling after pressing are weak and brittle. If re-pressed and quenched, the annealed samples become tough and flexible. These changes are associated with variations in the crystalline content of the polymer.

Copolymerization of Tetrafluorothiirane and Tetrafloroethylene.—A mixture of 4.2 g. (0.04 mole) of tetrafluoroethylene, 5.3 g. (0.04 mole) of tetrafluorothiirane, 3 ml. of hexafluoropropene cyclic dimer, and 2 mg. of *trans*-dinitrogen difluoride was sealed in a platinum tube at −196°. The sealed tube was placed in a metal pressure vessel which had been precooled to −80°. The pressure vessel was closed and pressured to 100 atm. with nitrogen. The pressure vessel was heated slowly to 50°, and after 3 hr. at 50° it was heated to 55° and kept there for 3 hr. The platinum tube was cooled to −80° and opened. The volatile products were transferred to a cold trap at −80° leaving a solid white polymer (4.1 g., 43%). Octafluorothiolane (2.5 g., 26%) was isolated from the volatile products by preparative gas chromatography and was identified by comparison of its infrared spectrum with that of authentic material and by a molecular weight determination.

Anal. Calcd. for C_4F_8S: mol. wt., 232.1. Found: mol. wt., 235.5 (gas density).

The sulfur analysis (S, 9.66%) indicated that the polymer contained tetrafluorothiirane and tetrafluoroethylene in a mole ratio of 0.52. Differential thermal analysis and thermogravimetric analysis suggested that the product was copolymer containing some homopolymer of tetrafluorothiirane.[15]

When 1.7 g. (0.017 mole) of tetrafluoroethylene and 5.9 g. (0.045 mole) of tetrafluorothiirane were used in an otherwise identical experiment, the yield of octafluorothiolane was 29% (1.2 g.) based on tetrafluoroethylene charged, and the polymer (2.68 g., 35%) contained tetrafluorothiirane and tetrafluoroethylene in a mole ratio of 1.05 based on the sulfur content (14%).

Octafluorothiolane was also formed when tetrafluorothiirane and tetrafluoroethylene were copolymerized with benzoyl peroxide (25–100°, 100 atm., platinum tube) and with bis(trifluoromethyl) disulfide (8°, autogenous pressure, Pyrex tube irradiated with ultraviolet light).

Telomerization of Tetrafluorothiirane with Cyclohexane.—A cylindrical quartz reactor (1-in. diameter, 1 ft. long) equipped with a Dry Ice cooled condenser was flushed with dry nitrogen and charged with 42 g. (0.5 mole) of anhydrous nitrogen-saturated cyclohexane, 6.6 g. (0.05 mole) of tetrafluorothiirane, and 0.06 g. of bis(trifluoromethyl) disulfide. The reactants were exposed to radiation from a General Electric H85A3/UV lamp at 6 in. for 7.5 hr. Gentle reflux occurred during the early stages of the reaction but stopped near the end. Cyclohexane and unreacted tetrafluorothiirane (2.5 g., 38%) were removed by distillation at atmospheric pressure. The residue (5.7 g.) was combined with the residue (12.5 g.) from a similar experiment on twice the scale and distilled through a 6-in. Vigreux still. A fraction (8.8 g.) boiling at 82–90° (25–18 mm.) was primarily cyclohexyl 1,1,2,2-tetrafluoroethyl sulfide (VIII). Pure sulfide (5.2 g., 26% yield, 16% conversion), b.p. 73–74° (22 mm.), $n^{25}{}_D$ 1.4231, was obtained when this fraction was put through a 4-ft. Prepko gas chromatographic column (25% Fluorosilicone FS1265, 150°, He flow 665 cc./min.) in eight equal injections.

Anal. Calcd. for $C_8H_{12}F_4S$: F, 35.14; S, 14.83; mol. wt., 216.2. Found: F, 35.44, 35.23; S, 14.62, 14.87; mol. wt. 217 (cryoscopic in benzene).

The H^1 n.m.r. spectrum consisted of a triplet (relative intensity 1) centered at +5.82 p.p.m. for CF_2H (J_{H-F} = 55 c.p.s.) split into triplets (J_{H-F} = 3.5 c.p.s.). The hydrogen on the carbon bearing the sulfur group gave a diffuse multiplet (relative intensity 1) centered at 3.42 p.p.m. The remaining hydrogen atoms on the cyclohexane ring appeared as a broad peak (relative intensity 10) centered at 1.52 p.p.m. with considerable splitting. The F^{19} n.m.r. spectrum had a doublet centered at +65.5 p.p.m. for CF_2H (J_{H-F} = 55 c.p.s.) further split into triplets (J_{F-F} = 10 c.p.s.) by the adjacent CF_2. The latter difluoromethylene group gave rise to a triplet centered at +24.1 p.p.m. (J_{F-F} = 10 c.p.s.), each part of which was split into doublets (J_{H-F} = 3.5 c.p.s.) by the hydrogen on the adjacent carbon.

Preparative gas chromatography of the residue (1.5 g.) gave 0.3 g. (2% yield, 1% conversion) of 1-cyclohexyl-1,4-dithia-2,2,3,3,5,5,6,6-octafluorohexane (IX), still containing impurity.

Anal. Calcd. for $C_{10}H_{12}F_8S_2$: F, 43.64; S, 18.41: mol. wt., 348.3. Found: F, 44.12; S, 17.84; mol. wt., 375 (cryoscopic in benzene).

The H^1 n.m.r. spectrum was identical with that of cyclohexyl 1,1,2,2-tetrafluoroethyl sulfide except that the hydrogen on the tetrafluoroethyl group appeared as a triplet centered at 60.2 p.p.m. (J_{F-H} = 54 c.p.s.) which was split into triplets (J_{F-H} = 3.5 c.p.s.)

The F^{19} n.m.r. spectrum consisted of four complex peaks of equal intensity. Fluorine atoms in the CF_2H group appeared as a doublet (J_{H-F} = 52 c.p.s.) centered at +66 p.p.m. with each part split further into at least eight peaks. The adjacent CF_2 groups gave rise to a broad complex peak centered at +22 p.p.m. The other four fluorines appeared as two triplets centered at +18.4 and +14.7 p.p.m. (J_{F-F} = 10.5 c.p.s.).

Copolymerization of Tetrafluorothiirane and Propylene.—A dry test tube equipped with serum stopper was charged with 1.6 g. (0.012 mole) of tetrafluorothiirane and 1.6 g. (0.038 mole) of propylene at −80°. The mixture was cooled to −196° and evacuated. The apparatus was pressured to about 10 mm. with dry nitrogen and allowed to warm to −80°. After three such treatments, the apparatus was kept at −80°, and polymerization was initiated by injecting 0.25 ml. (6×10^{-4} mole/ml.) of ethyl diethylboron peroxide ($Et_2B-OOEt$) in hexane and 0.15 ml. (20×10^{-4} mole/ml.) of triethylboron in hexane.[16] After 96 hr., a quantitative conversion to clear syrupy polymer was obtained. The crude polymer was dissolved in xylene and precipitated by pouring into methanol. The solid polymer (0.6 g., 28%) analyzed for a 1:1 copolymer of tetrafluorothiirane and propylene.

Anal. Calcd. for $(C_5H_6F_4S)_n$: S, 18.41. Found: S, 18.46.

In a different procedure, a platinum tube was charged with 3 g. of tetrafluorothiirane, 0.9 g. of propylene, and 3 mg. of *trans*-dinitrogen difluoride and sealed *in vacuo* at −196°. The tube was placed in a pressure vessel and heated slowly to 70° under 80-atm. pressure. After 8 hr., the tube was opened and 1.76 g. (44.5%) of a clear, solid polymer was obtained. The sulfur analysis (found: S, 19.4) indicated that the copolymer had 1.3 moles of tetrafluorothiirane/mole of propylene.

Pyrolysis of Poly(tetrafluorothiirane).—Two grams of the polymer was placed in a platinum tube which was then evacuated to 1 μ through a liquid nitrogen trap. The tube was heated to 350 ± 2° in an aluminum block, and the gases evolved were collected in the cold trap. As the pyrolysis proceeded, a white solid and a yellow solid collected in the trap. After 16.5 hr., the poly(tetrafluorothiirane) was nearly all decomposed. The trap contents consisted of a liquid (A) (0.1 g.), a mixture of yellow and white solids (B) (0.7 g.), and a gaseous product (C) (1.1 g.). By infrared and gas chromatographic analyses the gaseous product was shown to be tetrafluoroethylene and the liquid product was shown to be 96.5% octafluorodithiane and 0.3% octafluorothiolane, with a trace of 2-trifluoromethyl-2,4,4,5,5-pentafluoro-1,3-dithiolane and three unknowns (approximately 3% of the total). The mixture of solids was warmed to room temperature, and the yellow color slowly disappeared. Analysis indicated the white solid to be poly(tetrafluoro-1,2-dithietane).

Anal. Calcd. for $(C_2F_4S_2)_n$: S, 39.07. Found: S, 39.31.

The structure was confirmed as $-(SCF_2CF_2S)-_n$ by reaction with morpholine to form $(OC_4H_8N-)-SCF_2CS(NC_4H_8O)$ (see below).

Pyrolysis of Tetrafluorothiirane.—Pyrolysis of tetrafluorothiirane was studied by passing a sample through a preheater on a gas chromatographic apparatus. The preheater was constructed of 8-mm. Pyrex tubing with a central thermocouple well of 5-mm. Pyrex tubing. The preheater exit led to a gas chromatographic column constructed of 0.25-in. copper tubing (12 ft. long) packed with 30% of Silicone DC-200 Oil on firebrick. The remainder of the gas chromatographic unit was of conventional design with thermal conductivity detectors.

---

(15) We thank Drs. W. E. Garrison and J. Chiu for these observations.

(16) We thank Dr. J. Bruce for supplying this initiator and directions for its use. A paper describing this initiator system is in preparation.

When 1 ml. of gaseous episulfide was injected into the preheater at temperatures below 300° at a contact time of about 10 sec., there was no detectable decomposition. A small amount of decomposition occurred when the temperature was raised to 320°. At 375° the pyrolysate contained 87% unreacted episulfide, 5% tetrafluoroethylene, and 8% CF_2S. A trace of CF_3CSF was also detected. At 430° the pyrolysate was 11% episulfide, 49% CF_2S, 30% tetrafluoroethylene, and 10% of an unknown.

Dithiobis(difluoroglycolyl Fluoride) (XVIII).—A mixture of 20.0 g. (0.10 mole) of diphenyl sulfoxide and 11.0 g. (0.083 mole) of tetrafluorothiirane was sealed under vacuum in a 100-ml., heavy-walled glass tube. After 20 days at room temperature, the tube was cooled and opened and the bis(acid fluoride), 10.1 g. (93%), was volatilized under vacuum. Distillation through a 6-in. Vigreux column gave a colorless liquid, b.p. 53–54° (78 mm.). The infrared spectrum showed strong absorption at 5.4 μ (COF). The F^{19} n.m.r. spectrum contained two sets of peaks, a doublet at +19.3 p.p.m. (CF_2) and a triplet at −84.2 p.p.m. (COF).

Anal. Calcd. for $C_4H_6O_2S_2$: C, 18.61; F, 44.16; S, 24.84. Found: C, 18.80; F, 43.92; S, 24.06.

The high-boiling residue from the reaction slowly deposited white crystals. These crystals were isolated by filtration and washed with petroleum ether (b.p. 38–54°) under nitrogen. The infrared spectrum showed marked differences from diphenyl sulfoxide, and the F^{19} n.m.r. spectrum of the material contained a single peak at −51.9 p.p.m. which was 600 cycles broad. Hydrolysis of a sample gave diphenyl sulfoxide. These data suggest the unknown is diphenylsulfur difluoride. Removal of the petroleum ether from the filtrates above gave the theoretical amount of diphenyl sulfide, identified by comparison of its infrared spectrum with that of an authentic sample.

Diethyl Dithiobis(difluoroglycolate).—To 25 ml. of cold absolute ethanol was added dropwise 6.8 g. (0.026 mole) of dithiobis-(difluoroglycolyl fluoride). Distillation of the reaction mixture gave 6.2 g. (78%) of the ester as a colorless oil, b.p. 74° (0.25 mm.), $n^{25}\mathrm{D}$ 1.4350. Strong absorption occurred in the infrared spectrum at 5.6 μ (C=O), and the F^{19} n.m.r. spectrum contained a single sharp peak at +16.4 p.p.m.

Anal. Calcd. for $C_8H_{10}F_4O_4S_2$: C, 30.98; H, 3.25; F, 24.50. S, 20.67; mol. wt., 310. Found: C, 31.56; H, 3.52; F, 24.75; S, 20.67; mol. wt., 299, 312 (freezing point in benzene).

2,2-Diphenyl-4,4,5,5-tetrafluoro-1,3-oxathiolane (XIX).—A mixture of 6.0 g. (0.033 mole) of benzophenone and 4.6 g. (0.025 mole) of tetrafluorothiirane was sealed under vacuum in a 25-ml., heavy-walled glass tube and heated at 100° for 6 hr. The tube was cooled and opened, and the liquid residue was diluted with petroleum ether. On cooling to 0°, a precipitate of white needles formed. Removal of the solid by filtration gave 1.83 g. of the oxathiolane, m.p. 41–43°. On concentration of the filtrate, a second crop of 1.37 g. (total yield 31%) was obtained, m.p. 34–38°. Recrystallization from petroleum ether gave crystals, m.p. 44–45°. The F^{19} n.m.r. spectrum consisted of two triplets, one centered at +14.7 p.p.m. and the other centered at +19.3 p.p.m. (J = 6 c.p.s.).

Anal. Calcd. for $C_{15}H_{10}F_4OS$: C, 57.31; H, 3.21; F, 24.11; S, 10.20. Found: C, 57.57; H, 3.14; F, 24.23; S, 9.77.

Hydrolysis of 0.80 g. of the oxathiolane was carried out in 100 ml. of ethanol containing 10 ml. of water and 4 ml. of concentrated hydrochloric acid. This mixture was refluxed for 3 hr., the ethanol was evaporated on a steam bath, and the residue was extracted with petroleum ether. Removal of the petroleum ether left 0.57 g. of a pale yellow semisolid shown to be chiefly benzophenone by infrared analysis and by conversion to a 2,4-DNP (2,4-dinitrophenylhydrazone) derivative identical with authentic benzophenone 2,4-DNP.

Addition of Trifluorothioacetyl Fluoride.—A mixture of 5.6 g. g. (0.043 mole) of trifluorothioacetyl fluoride and 3.0 g. (0.023 mole) of tetrafluorothiirane was heated for 10 hr. at 225° in a Carius tube. The gaseous products were bled off and the liquid residue (2.25 g.) was put through a preparative gas chromatograph (27 ft. long, 3/8-in. o.d. copper tube packed with 25% Silicone 200 Oil on firebrick, temperature 85°). 2-Trifluoromethyl-2,4,4,5,5-pentafluoro-1,3-dithiolane was obtained in 16% yield and identified by comparison of its infrared spectrum with that of an authentic sample.[1] No reaction occurred at 150° for 10 hr.

2,4-Bis(pentafluoroethylmercapto)-2,4-bis(trifluoromethyl-1,3-dithietane (XXII). A. From Tetrafluorothiirane.—A mixture of 16.2 g. (0.12 mole) of tetrafluorothiirane and 0.5 g. of aluminum chloride was sealed under vacuum in a 100-ml., heavy-walled glass tube. After 5 hr. at 25°, the liquid portion was deep red. After 7 days the tube was cooled and opened, and the contents were removed at reduced pressure (~1 mm.). The bulk of the product, 13.7 g., condensed in a trap cooled in ice, while a more volatile fraction, 2.0 ml., was collected in a liquid nitrogen trap. Distillation of the main fraction gave 10.5 g. (64%) of the dithietane as a colorless liquid, b.p. 76.5° (18 mm.), $n^{24}\mathrm{D}$ 1.3811.

Anal. Calcd. for $C_8F_{16}S_4$: C, 18.19; F, 57.38; S, 24.47; mol. wt., 528. Found: C, 18.36; F, 56.25; S, 24.94; mol. wt., 573, 589 (freezing point in benzene).

Gas chromatography demonstrated the presence of both *cis* and *trans* isomers in substantial amounts. The F^{19} n.m.r. spectrum contained a triplet at +9.93 p.p.m. and a quartet at +24.6 p.p.m., assignable to the perfluoroethyl groups of one isomer, and a triplet at +10.7 p.p.m. and a quartet at +23.8 p.p.m., assignable to the perfluoroethyl groups of the other isomer. For the ethyl groups of both isomers, J = 25 c.p.s. Because the isomers were present in unequal amounts, identification of the triplet–quartet pairs was apparent by relative intensities. The trifluoromethyl groups of both isomers appeared as a single peak at +18.0 p.p.m.

B. From Trifluorothioacetyl Fluoride.—Reaction of 15 g. of trifluorothioacetyl fluoride with 1 g. of aluminum chloride was carried out as described above. Work-up provided 7.5 g. (50%) of the 1,3-dithietane.

N-(Trifluorothioacetyl)morpholine.—A solution of 1.0 g. (0.0019 mole) of 2,4-bis(pentafluoroethylmercapto)-2,4-bis(trifluoromethyl)-1,3-dithietane in 10 ml. of ether was treated dropwise with 2.0 g. of morpholine in 10 ml. of ether. The yellow solution was evaporated, and the residue was triturated with water, leaving 1.4 g. (93%) of the yellow thioamide, m.p. 36.5–37.0°. Recrystallization from petroleum ether gave yellow plates, m.p. 42.0–42.5°. The F^{19} n.m.r. spectrum consisted of a single peak at +6.10 p.p.m.

Anal. Calcd. for $C_6H_8F_3NOS$: C, 36.18; H, 4.05; F, 28.62; N, 7.03; S, 16.09. Found: C, 36.56; H, 4.05; F, 28.39; N, 6.73; S, 15.81.

Trimerization of Thiocarbonyl Fluoride.—A mixture of 21 g. (0.23 mole) of thiocarbonyl fluoride (90% pure) and 1.0 g. of aluminum chloride was sealed under vacuum in a 100-ml., heavy-walled glass tube and allowed to stand at room temperature 7 days. The tube was cooled and opened, and the contents were removed under reduced pressure (~1 mm.). The main portion of the product, 12.7 g. of a deep red liquid, condensed in a Dry Ice cooled trap, while a more volatile fraction, 5.2 ml., condensed in a liquid nitrogen cooled trap. Distillation of the red liquid gave 8.9 g. (47%) of bis(trifluoromethyl)trithiocarbonate as a red liquid, $n^{25.5}\mathrm{D}$ 1.4454, b.p. 106.5°.[17]

Halogenation of Tetrafluorothiirane. A. Chlorination.—A mixture of 2.6 g. (0.02 mole) of tetrafluorothiirane and 1.5 g. (0.02 mole) of chlorine was sealed in a Pyrex tube and irradiated overnight with a low-pressure mercury lamp. Distillation of the resulting mixture gave 2.2 g. (54%) of 2-chlorotetrafluoroethanesulfenyl chloride, b.p. 70°, identified by comparison with an authentic sample.[18] Similar reactions with excess tetrafluorothiirane gave telomers. These oils were not degraded to lower molecular weight by aqueous base, indicating the free-radical polymerization has given predominantly the monosulfide structure.

B. Bromination.—A mixture of 5.0 g. (0.031 mole) of bromine and 3.9 g. (0.03 mole) of tetrafluorothiirane was sealed under vacuum in a 25-ml., heavy-walled, glass polymer tube, and the tube was heated 6 hr. at 100°. The tube was cooled and opened, and the liquid product was distilled twice through an 18-in. spinning-band column, giving 4.7 g. (74%) of bis(2-bromotetrafluoroethyl) disulfide as a colorless oil, b.p. 68–69° (22 mm.), $n^{26}\mathrm{D}$ 1.4276.

Anal. Calcd. for $C_4Br_2F_8S_2$: C, 11.33; Br, 37.70; F, 35.85; S, 15.12. Found: C, 11.72; Br, 37.30; F, 35.18; S, 13.83.

The F^{19} n.m.r. spectrum consisted of two triplets centered at −3.72 p.p.m. (CF_2Br) and +20.9 p.p.m. (CF_2S).

C. Iodination.—Little reaction occurred between iodine and tetrafluorothiirane at temperatures below 100°. A reaction conducted at 250° yielded a gross mixture of products.

---

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

(18) A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, p. 344.

Degradation Studies with Amines. A. Poly(tetrafluorothiirane).—The polymeric monosulfide was essentially unaffected by a refluxing mixture of dimethylformamide and *p*-toluidine, and was stable to hot aqueous base as well as to hot concentrated nitric acid. However, the difunctional amine, ethylenediamine, degraded it completely on heating for 4 hr.

B. Tetrafluorothiirane.—To a stirred solution of 4.5 g. (0.034 mole) of tetrafluorothiirane in 75 ml. of ether at 0° under dry nitrogen was added 11.6 g. (0.14 mole) of morpholine in 100 ml. of ether. After 0.5 hr. at 0°, the solution was filtered to remove precipitated morpholine hydrofluoride. Solvent was evaporated, leaving oily crystals which showed strong absorption in the infrared (Nujol) at 6.7 μ (NC=S) and a single peak at +9.92 p.p.m. in the F^{19} n.m.r. spectrum (in $CHCl_3$). The spectral data support a fluorinated thio amide structure, XII. On standing in moist air, the yellow crystals rapidly hydrolyzed to N,N′-monothiooxalyldimorpholine (XIII), m.p. 170.0–172.0° (from benzene).

Anal. Calcd. for $C_{10}H_{16}N_2O_3S$: C, 49.15; H, 6.60; N, 11.47. S, 13.13. Found: C, 49.51; H, 6.49; N, 12.07; S, 12.92.

The monothiooxamide has strong absorption in the infrared (Nujol) at 6.1 (NC=O) and 6.7 μ (NC=S).

C. Poly(tetrafluoro-1,2-dithietane).—To a suspension of 4.92 g. (0.03 g.-mole) of $-\!\!(CF_2CF_2SS)\!\!-_n$ in 100 ml. of methanol was added 20 g. (0.23 mole) of morpholine. No noticeable evolution of heat occurred. The mixture was heated to dissolve all of the solid, then cooled to 0° to give a white precipitate. This solid was recrystallized from methylene chloride–ethanol to give 0.9 g. (12% yield) of N,N′-dithiooxalyldimorpholine, XVII), m.p. 267–268°, identified by comparison with a known sample (see below). Dilution of the filtrate from the reaction mixture with water gave 3.8 g. (43% yield) of N,N′-(S-morpholino)-mercaptodifluorothioacetylmorpholine (XIV), m.p. 122–126°. Recrystalllization from methanol gave pale yellow crystals, m.p. 124–128°. The infrared spectrum had the expected bands at 3.35, 3.45, and 3.50 μ (saturated C–H) and at 6.65 μ (NC=S).

Anal. Calcd. for $C_{10}H_{16}F_2N_2O_2S_2$: C, 40.25; H, 5.41; F, 12.74; N, 9.39; S, 21.49; mol. wt., 298. Found: C, 40.88; H, 5.47; F, 12.13; N, 9.16; S, 22.76; mol. wt., 292, 281 (ebullioscopic).

D. Tetrafluoro-1,2,3,4-tetrathiane or Its Polymer.—To 6.84 g. (0.03 mole) of tetrafluoro-1,2,3,4-tetrathiane[5] and 100 ml. of methanol was added a solution of 31.3 g. (0.36 mole) of morpholin in 50 ml. of methanol. (Note: The tetrathiane polymerizes when mixed with methanol, so a suspension of the polytetrasulfide gives the same result.) The addition was carried out with cooling in an ice bath over 0.5 hr. A white crystalline solid precipitated during the reaction and was isolated by filtration. Recrystallization from methylene chloride–ethanol gave 7.0 g. (90% yield) of N,N′-dithiooxalyldimorpholine (XVII), m.p. 269–270°.

Anal. Calcd. for $C_{10}H_{16}N_2O_2S_2$: C, 46.12; H, 6.19; N, 10.76; S, 24.63; mol. wt., 260. Found: C, 46.25; H, 6.30; N, 10.76; S, 24.92; mol. wt., 256, 248 (ebullioscopic).

Dilution of the filtrate from the reaction mixture with water caused precipitate of a white solid. Recrystallization of this solid from methanol gave 3.2 g. (42% yield) of dimorpholine disulfide, (XVI), m.p. 126–128°.

Anal. Calcd. for $C_8H_{16}N_2O_2S_2$: C, 40.64; H, 6.82; S, 27.12; mol. wt., 236. Found: C, 41.41; H, 6.64; S, 27.12; mol. wt., 237, 230 (ebullioscopic).

Dithiooxamides were similarly prepared from methylamine, *p*-toluidine, piperazine, and N-methylaniline.

2-Trifluoromethylheptafluoro-1,4-dithiane (III).—A mixture of 48 g. (1.5 g.-atoms) of sulfur, 35 g. (0.35 mole) of tetrafluoroethylene, 53 g. (0.35 mole) of hexafluoropropene, and 50 ml. of carbon disulfide was heated under autogenous pressure at 150° for 2 hr., then at 300° for 10 hr. The liquid portion of the product was cooled to −80°, and the lower layer was separated and distilled. There was thus obtained 3.6 g. (8% yield based on tetrafluoroethylene) of octafluoro-1,4-dithiane and 12.3 g. (11% yield based on tetrafluoroethylene) of a colorless oil, b.p. 100–101°, $n^{26}D$ 1.3496.

Anal. Calcd. for $C_5F_{10}S_2$: F, 60.48; S, 20.41. Found: F, 60.60; S, 20.14.

The infrared spectrum contained no absorption in the double bond region. N.m.r. indicated fluorinated groups compatible with the substituted dithiane by having resonances at +4.77 (CF_3) and +7.40 p.p.m. (CF), both with fine structure, and a complex set of broadly split resonances, suggestive of AB patterns, in the 10–40 p.p.m. region (CF_2).

Somewhat better yields were attained by preparing $-\!\!(CF_2CF_2SS)\!\!-_n$[5] directly from equimolar amounts of tetrafluoro-1,2,3,4-tetrathiane and tetrafluoroethylene at 150° in the presence of excess hexafluoropropene and carbon disusfide, then causing the polydisulfide to react with hexafluoropropene by raising the temperature. Excessive amounts of octafluoro-1,4-dithiane are difficult to remove by simple distillation, but can be eliminated by azeotropic distillation with added carbon disulfide.

2-Trifluoromethyl-2,3,3-trifluorothiirane.—A mixture of 50.6 g. (0.38 mole) of trifluorothioacetyl fluoride and 81 g. (0.50 mole) of hexafluoropropene epoxide (93% pure) was heated for 6 hr. at 175° in a metal tube under autogeneous pressure. The reaction mixture was purified on a preparative gas chromatographic column to give 29.5 g. (42.5%) of the thiirane, b.p. 14°.

Anal. Calcd. for C_3F_6S: F, 62.60; S, 17.61; mol. wt., 182. Found: F, 62.74, 62.90; S, 17.44, 17.72; mol. wt., 184 (gas density).

The ultraviolet spectrum has a λ_{max} of 234 mμ (ϵ 142). The infrared spectrum has strong absorption bands at 7.15, 7.56, 8.04, 8.22, 8.42, 8.88, 10.04, 12.26, and 13.51 μ. The F^{19} n.m.r. spectrum contained three resonances in the ratio 3:2:1 corresponding to CF_3 at +8.06, CF_2 at +4.26, and CF at +10.68 p.p.m. Each resonance exhibited complex splitting which could not be resolved.