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## The Free Radical Addition of Hydrogen Sulfide to Fluoroethylenes

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Radiation-induced free radical addition of hydrogen sulfide to several fluoroethylenes to give fluorinated ethane-thiols has been studied. The direction of addition to unsymmetrical ethylenes is consistent with previously studied radical additions to such olefins, assuming that the  $\cdot\text{SH}$  is the adding or chain-carrying species. The thiols with fluorines on the carbon containing the SH group were found to readily undergo dehydrofluorination yielding thiocarbonyl compounds.

Although free radical additions of a variety of substances,<sup>1</sup> including thiols,<sup>2</sup> to fluoroolefins have been studied, there has apparently been very little study of the addition of hydrogen sulfide to fluoroolefins. This paper presents the results of a study of the X-ray initiated free radical addition of hydrogen sulfide to tetrafluoroethylene, chlorotrifluoroethylene, trifluoroethylene, 1,1-difluoroethylene, trifluorovinyl methyl ether,

bromotrifluoroethylene and vinyl fluoride. During the preparation of this paper, a report<sup>3</sup> of the ultraviolet radiation-initiated addition of hydrogen sulfide to tetrafluoroethylene and chlorotrifluoroethylene appeared.

### Results

The results of the reaction with each olefin are presented below. The experimental details and the

TABLE I  
X-RAY INITIATED ADDITION OF HYDROGEN SULFIDE TO FLUOROOLEFINS

Olefin (moles)	H <sub>2</sub> S, moles	Dose rate, rads/min.	Time, hours	G Yield	Products (% yield)
CF <sub>2</sub> =CF <sub>2</sub> (0.3)	(1.03)	10,000-15,000	3	..	HCF <sub>2</sub> CF <sub>2</sub> SH (60)
ClCF=CF <sub>2</sub> (1.29)	(3.06)	10,000	4	..	HCICFCF <sub>2</sub> SH (60)
CF <sub>2</sub> =CFH (0.27)	(0.45)	13,000	..	810	HCF <sub>2</sub> CFHSH (85) H <sub>2</sub> CFCF <sub>2</sub> SH (15) } (27)
CF <sub>2</sub> =CH <sub>2</sub> (0.156)	(0.625)	16,000	2.75	1300	HCF <sub>2</sub> CH <sub>2</sub> SH (69)
CF <sub>2</sub> =CH <sub>2</sub> (2.14)	(4.34)	10,000-12,000	4	..	HCF <sub>2</sub> CH <sub>2</sub> SH (62) (HCF <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> S (19)
BrCF=CF <sub>2</sub> (0.07)	(0.15)	16,000	3	110	HBrCFCF <sub>2</sub> SH (8)
CH <sub>2</sub> =CHF (1.09)	(1.82)	~8,000	3	~600	FCH <sub>2</sub> CH <sub>2</sub> SH (10) + polymer
CH <sub>3</sub> OCF=CF <sub>2</sub> (0.075)	(0.30)	{ 3,300 6,600	{ 0.5 0.5	8000	CH <sub>3</sub> OCFHCF <sub>2</sub> SH (67)

TABLE II  
NEW COMPOUNDS

Compound	B.p., °C. (mm.)	n <sub>D</sub> <sup>20</sup>	t, °C.	Formula	—Chlorine, %—		—Fluorine, %—		—Sulfur, %—		Infrared (SH freq.), μ
					Calcd.	Found	Calcd.	Found	Calcd.	Found	
HCF <sub>2</sub> CF <sub>2</sub> SH	25-27			C <sub>2</sub> H <sub>2</sub> F <sub>4</sub> S			56.7	56.6	23.9	24.2	
HCF <sub>2</sub> CF <sub>2</sub> SCI	57-59	1.3610	25	C <sub>2</sub> HClF <sub>3</sub> S	21.1	21.1	45.1	45.5	19.0	19.6	
HCICFCF <sub>2</sub> SH	66-67	1.3791	25	C <sub>2</sub> H <sub>2</sub> ClF <sub>3</sub> S	23.6	23.8	37.9	37.6	21.3	21.0	3.86
HCICFCF	56-57	1.4182	25	C <sub>2</sub> HClF <sub>2</sub> S	27.2	27.3	29.1	29.5	24.5	24.6	
HCICFCF <sub>2</sub> SCI	98	1.4153	25	C <sub>2</sub> HCl <sub>2</sub> F <sub>3</sub> S	38.3	38.3	30.8	31.2	17.4	17.1	
(HCICFCF <sub>2</sub> ) <sub>2</sub> S	74 (62)	1.3897	25	C <sub>4</sub> H <sub>2</sub> Cl <sub>2</sub> F <sub>6</sub> S	26.5	26.4			12.0	12.1	
(HCICFCF <sub>2</sub> ) <sub>2</sub> S <sub>2</sub>	71-72 (12)	1.4329	25	C <sub>4</sub> H <sub>2</sub> Cl <sub>2</sub> F <sub>2</sub> S <sub>2</sub>	23.7	24.5	38.1	38.0	21.4	21.2	
HCF <sub>2</sub> CFHSH	20-22 (100)			C <sub>2</sub> H <sub>3</sub> F <sub>3</sub> S			49.0	48.4	27.6	28.1	3.85
HCF <sub>2</sub> CH <sub>2</sub> SH	64	1.3920	24	C <sub>2</sub> H <sub>4</sub> F <sub>2</sub> S			38.7	39.0	32.7	32.8	
(HCF <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> S	51-54 (20)	1.3938-									
		1.3944	24	C <sub>4</sub> H <sub>6</sub> F <sub>4</sub> S			46.9	46.5	19.8	19.9	
(HCF <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> S <sub>2</sub>	84 (21)	1.4465	24	C <sub>4</sub> H <sub>6</sub> F <sub>4</sub> S <sub>2</sub>			39.1	39.9	33.0	34.1	
HBrCFCF <sub>2</sub> SH	42-46 (150)			C <sub>2</sub> H <sub>2</sub> Br <sub>2</sub> F <sub>3</sub> S	41.0	41.0	29.3	29.3			3.85
FCH <sub>2</sub> CH <sub>2</sub> SH	35-36 (206)	1.4284	25								
CH <sub>3</sub> OCFHCF <sub>2</sub> SH	14-16 (17)	1.3733	25	C <sub>3</sub> H <sub>5</sub> F <sub>3</sub> OS			39.0	38.1	21.9	21.3	3.85
(CH <sub>3</sub> OCFHCF <sub>2</sub> ) <sub>2</sub> S	65-66 (1.5)	1.3778	25	C <sub>6</sub> H <sub>8</sub> O <sub>2</sub> F <sub>2</sub> S			44.1	44.2	12.4	12.8	
HCICFCF <sub>2</sub> SCF <sub>2</sub> CFHOCH <sub>3</sub>	57-60 (0.8)	1.3827	25	C <sub>6</sub> H <sub>5</sub> ClF <sub>6</sub> OS			43.4	43.4	12.2	12.1	
HCICFCF <sub>2</sub> SCFHCF <sub>2</sub> H	51-53 (34)	1.3750									
		1.3759	25	C <sub>4</sub> H <sub>3</sub> ClF <sub>6</sub> S	15.2	15.2	49.0	48.9			
HCF <sub>2</sub> CF <sub>2</sub> SCFHCF <sub>2</sub> H	104-105	1.3383	25	C <sub>4</sub> H <sub>3</sub> F <sub>5</sub> S			61.5	61.2	14.8	14.7	

(1) R. N. Haszeldine, *et al.*, *J. Chem. Soc.*, 1592, 3559, 3565 (1953); 923, 3747 (1954); 3005 (1955); 61 (1956); 2193, 2800 (1957).

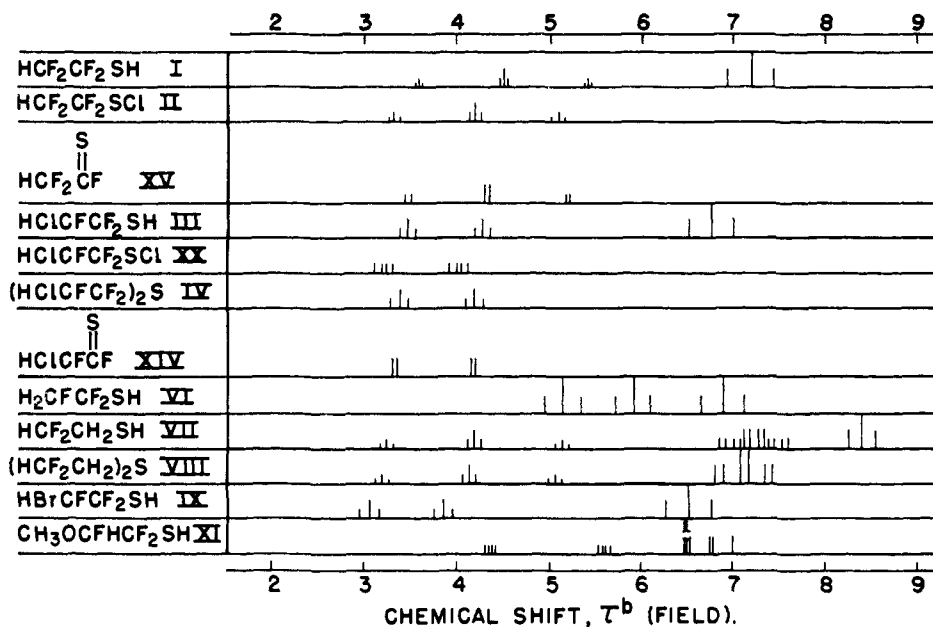
(2) (a) J. F. Harris, Jr., and F. W. Stacey, *J. Am. Chem. Soc.*, **83**, 840 (1961); (b) W. T. Miller, U. S. Patent 2,864,867 (1958) [C. A., **53**, 9058 (1959)]; (c) W. E. Hanford, U. S. Patent 2,443,003 (1948) [C. A., **42**, 6841 (1948)]; (d) E. K. Ellingboe, U. S. Patent 2,439,203 (1948) [C. A., **42**, 5046 (1948)].

properties of the adducts and related compounds are given in Tables I and II.

**Tetrafluoroethylene.**—When a mixture of hydrogen sulfide and tetrafluoroethylene (3:1 mole ratio) con-

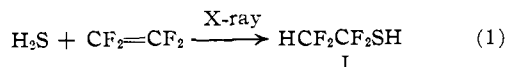
(3) A. V. Fokin, A. A. Skladnev and I. L. Knunyants, *Proc. Acad. Sci. U.S.S.R., Chem. Sect. (Eng. Transl.)*, **198**, 597 (1961).

TABLE III  
PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA AT 60 Mc.<sup>a</sup>



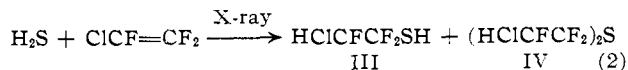
<sup>a</sup> Proton spectra were obtained with an A-60 nuclear magnetic resonance spectrophotometer manufactured by Varian Associates, Palo Alto, Calif. Intensities are represented by relative line heights. <sup>b</sup> The standard, tetramethylsilane, was external.

tained in a stainless steel pressure vessel was irradiated with X-rays, 1,1,2,2-tetrafluoroethanethiol was obtained in yields up to 60% (eq. 1). Some higher-boiling



material was also obtained from which no single compound was isolated. The proton nuclear magnetic resonance (n.m.r.) pattern (Table III) of the thiol contains a triplet ( $\tau$  7.18,  $J$  15.2 c.p.s.) assigned to the SH hydrogen and another widely split triplet ( $\tau$  4.52,  $J$  54.3 c.p.s.) corresponding to the  $\text{CF}_2\text{H}$  hydrogen. That this is the correct assignment is confirmed by the fact that when the thiol is converted to the sulfenyl chloride II,  $\text{HCF}_2\text{CF}_2\text{SCl}$ , the triplet at  $\tau$  7.18 disappears and the widely split triplet (now centered at  $\tau$  4.20,  $J$  54 c.p.s.) remains. Of course, there can be no ambiguity in the structure of this thiol, but analysis of its n.m.r. spectrum provides a reference for determining the structures of the 1:1 adducts obtained from unsymmetrical olefins discussed below.

**Chlorotrifluoroethylene.**—The X-ray irradiation of a mixture of chlorotrifluoroethylene and excess hydrogen sulfide resulted in the formation of 2-chloro-1,1,2-trifluoroethanethiol (III) in yields of up to 60% and some higher-boiling material from which was isolated bis-(2-chloro-1,1,2-trifluoroethyl) sulfide (IV). The



structure of the thiol was indicated by the proton n.m.r. pattern which consists of a doublet ( $\tau$  3.89,  $J$  49 c.p.s.) and a triplet ( $\tau$  6.76,  $J$  14 c.p.s.). This latter resonance, which disappears on conversion of the thiol to the sulfenyl chloride XX, was assigned to the SH hydrogen, and since it is primarily split to a triplet, it is certain that the SH group is on the  $\text{CF}_2$  group and not on the  $\text{CFCl}$ . Confirmation of this assignment lies in the fact that in both the thiol and sulfenyl chloride, the other resonance ( $\text{CFH}$ ) is primarily a doublet.<sup>4</sup> The proton n.m.r. pat-

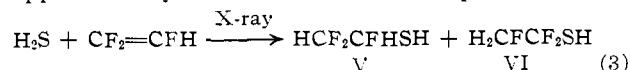
(4) Fokin, Skladnev and Knunyants (ref. 3) concluded on the basis of chemical evidence that the structure of the 1:1 adduct which they ob-

tern of the 2:1 adduct consists of a single resonance ( $\tau$  3.89) initially split to a doublet ( $J$  49 c.p.s.), thus substantiating structure IV. The elements of a widely split triplet ( $\tau$  3.94,  $J$  56 c.p.s.) which may be due to the presence (<3%) of an isomer containing a  $\text{CF}_2\text{H}$  group (*i.e.*,  $\text{HCF}_2\text{CFCISCF}_2\text{-CFHCl}$  or  $(\text{HCF}_2\text{CFCl})_2\text{S}$ ) were also evident in this spectrum. No such triplet was discernible in the patterns of either the thiol or the sulfenyl chloride.<sup>5</sup>

Small amounts of III were obtained by ultraviolet irradiation of refluxing mixtures of hydrogen sulfide and chlorotrifluoroethylene contained in quartz tubes. Sulfur was formed early in these experiments making the mixture essentially opaque, so that conversions to adduct were consequently very small. Several attempts to achieve the addition by the use of peroxide and azo catalysts gave only traces

of the 1:1 adduct; generally the starting materials were recovered almost quantitatively.

**Trifluoroethylene.**—Examination of the proton and fluorine n.m.r. patterns of the 1:1 adduct fraction obtained from the X-ray irradiation of a mixture of hydrogen sulfide and trifluoroethylene indicated the presence of both possible 1:1 adducts (V and VI) in a ratio of approximately 85:15. The lesser component was con-



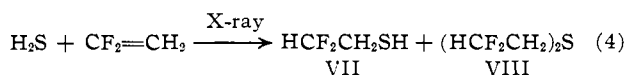
centrated in the lower-boiling portion of the fraction and was not obtained pure by distillation. Samples of the major component were obtained essentially free of contamination by the other isomer. In the proton n.m.r. pattern of the major isomer there is a resonance ( $\tau$  7.32) in the region expected for the SH hydrogen, which is initially split to a doublet ( $J$  11 c.p.s.) and then split again to doublets ( $J \cong 2$  c.p.s.). This is consistent with structure V and inconsistent with VI in which the SH hydrogen should be split to a triplet or a pair of doublets with nearly the same  $J$ -values. There is considerable overlap of the resonances corresponding to the other two hydrogen atoms.<sup>6</sup> The fluorine pattern confirms the assignment. It consists of two resonances in a ratio of approximately 2:1, both of which are initially doublets. The  $\text{CF}_2$  doublet ( $J$  55 c.p.s.) is split to doublets three times again, while the  $\text{CF}$  doublet ( $J$  45 c.p.s.) is split to triplets ( $J$  18 c.p.s.) and then to doublets twice (Fig. 1). The proton pattern of the lower-boiling portion of the 1:1 adduct contains, in addition to the peaks characteristic of V, a triplet ( $\tau$  6.89,  $J$  13 c.p.s.) as expected for the SH in structure VI. There is also a pair of triplets ( $\tau$  5.54,  $J$  46 c.p.s., tained from the ultraviolet-initiated addition of hydrogen sulfide to chlorotrifluoroethylene was III.

(5) In ref. 3, it is indicated that telomeric thiols of the type  $\text{H}(\text{CX}_2\text{CX}_2)_n\text{-SH}$  were obtained in the ultraviolet catalyzed reactions of  $\text{H}_2\text{S}$  with tetrafluoroethylene and chlorotrifluoroethylene, although no characterization of these products was offered. In the present work, in which the ratio of olefin to hydrogen sulfide was generally much lower than those employed in ref. 3, no such materials were isolated.

(6) In view of the complicated splitting pattern no attempt was made to reproduce this spectrum in Table III.

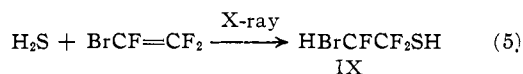
$J_2$  12 c.p.s.) consistent with the  $\text{CH}_2$  in VI. After the distillation of the 1:1 adduct fraction from the reaction mixture there remained a considerable quantity of viscous, presumably polymeric, product which would not distill. It was not determined whether this material arose as a result of the distillation or was truly a product of the irradiation itself. In view of this, the stated composition of the 1:1 adduct fraction must be considered somewhat tenuous.

**1,1-Difluoroethylene.**—The X-ray irradiation of a 2:1 mole ratio mixture of hydrogen sulfide and 1,1-difluoroethylene resulted in the formation of 2,2-difluoroethanethiol (VII) and the corresponding sulfide

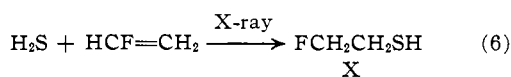


VIII. The proton n.m.r. pattern of the thiol consists of three resonances (itself indicative of VII rather than the alternative isomer which should contain only two resonances), one of which is a widely split triplet ( $\tau$  4.19,  $J$  56 c.p.s.) characteristic of the  $\text{CF}_2\text{H}$  group. The fluorine pattern, consisting of a single resonance split to a doublet ( $J$  55 c.p.s.) and triplets ( $J$  15 c.p.s.) in that order, confirms the assignment. The proton spectrum of the 2:1 adduct consists of two resonances with the splitting pattern expected for structure VIII. There is no evidence in these patterns for the alternative isomers.

**Bromotrifluoroethylene.**—The X-ray irradiation of a mixture comprising a 3:1 mole ratio of hydrogen sulfide and bromotrifluoroethylene gave a small yield of a 1:1 adduct. The proton n.m.r. pattern of this adduct contains a triplet ( $\tau$  6.53,  $J$  14 c.p.s.) corresponding to the SH hydrogen and a doublet ( $\tau$  3.47,  $J$  48 c.p.s.) split to triplets ( $J$  13 c.p.s.) for the other hydrogen atom. On the basis of this pattern, structure IX was assigned.



**Vinyl Fluoride.**—From the X-ray irradiation of a mixture of hydrogen sulfide and vinyl fluoride, a single



1:1 adduct was isolated which according to the proton and fluorine n.m.r. spectra possessed structure X. Thus, in the proton spectrum there are three resonances in a 2:2:1 ratio, indicative of structure X.<sup>6</sup> The alternative structure should have three resonances in a 3:1:1 ratio. The resonance at lowest field ( $\tau$  5.59) is initially a doublet ( $J$  47 c.p.s.) split to triplets ( $J$  6.2 c.p.s.) and was assigned to the  $\text{CH}_2\text{F}$  group. The mid-field resonance is split in a complicated manner and not readily interpreted in terms of simple first-order splitting rules. The high-field resonance ( $\tau$  8.39) is roughly a triplet ( $J \cong 9$  c.p.s.) and was assigned to the SH hydrogen. There are no resonances which could be assigned to the alternative structure. The fluorine pattern contains a single resonance split to triplets ( $J_1$  50 c.p.s.,  $J_2$  21 c.p.s.). Since there was considerable decomposition during the distillation, it cannot be said unequivocally that none of the other possible isomer was formed. The properties of X correspond closely with those reported for the product obtained from the ultraviolet-initiated addition of thiolacetic acid to vinyl fluoride followed by hydrolysis (eq. 7).<sup>7</sup>

(7) E. K. Ellingboe, U. S. Patent 2,439,203 [C. A., **42**, 5046 (1948)].

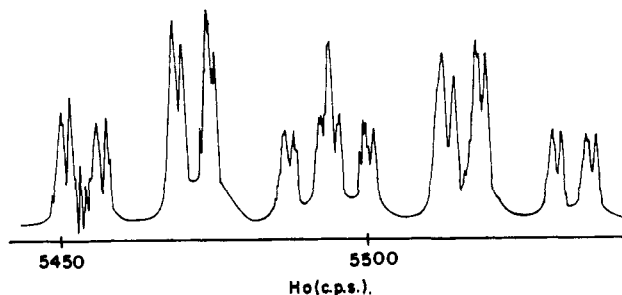
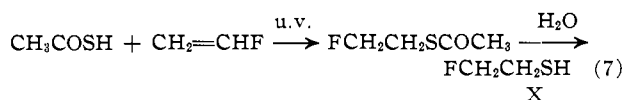
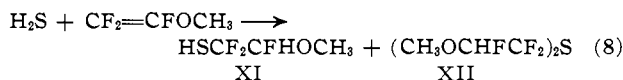


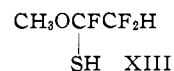
Fig. 1.—High resolution trace of the CF resonance in  $\text{HCF}_2\text{-CFHS}$  (V).



**Trifluorovinyl Methyl Ether.**—The ultraviolet or X-ray-initiated addition of hydrogen sulfide to trifluorovinyl methyl ether yielded a mixture of a 1:1 and a 2:1 adduct. The structure of the 1:1 adduct



was assigned on the basis of the proton n.m.r. spectrum which consists of three major resonances corresponding to the CH, the  $\text{OCH}_3$  and the SH protons. The CH resonance is initially a doublet ( $\tau$  4.91,  $J$  64 c.p.s.) split to doublets twice again ( $J$  4 and 3 c.p.s.). This splitting pattern is consistent with the CH in XI and would be inconsistent with the alternative structure. The SH resonance ( $\tau$  6.78) is clearly a pair of overlapping doublets also consistent with XI. The elements of a broad triplet ( $\tau$  4.12,  $J$  55 c.p.s.), indicative of a  $\text{CF}_2\text{H}$  group, and an additional unsplit methoxyl resonance were observed in the spectrum. These resonances indicate that there could be as much as 5% of the alternative isomer XIII present, although no peak clearly attributable to the other SH group



was observed. If the contaminant is indeed XIII, it seems likely that it arises from a concurrent ionic mechanism since in a previous study of a radical thiol addition to this olefin a single isomer was formed.<sup>2a,8</sup>

## Discussion

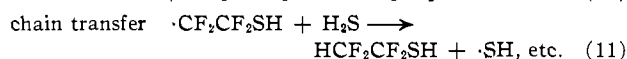
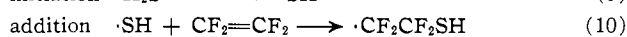
Although X-ray irradiation was used almost exclusively as the means of initiation in this work, it is not necessarily to be concluded that this is the method of choice. In the one case where a comparison was made, *i.e.*, the addition to chlorotrifluoroethylene, it was found that X-ray initiation was superior to the use of benzoyl peroxide or  $\alpha, \alpha'$ -azo-bisisobutyronitrile at 80° with no solvent, or ultraviolet irradiation of the reactants at reflux ( $\sim -40$  to  $-50^\circ$ ). On the other hand, Fokin, *et al.*,<sup>3</sup> indicate that ultraviolet irradiation of these same reactants in sealed tubes at room temperature and above is highly satisfactory. In our hands, X-ray irradiation and ultraviolet irradiation at reflux seemed of comparable effectiveness for achieving the addition to methyl trifluorovinyl ether. An advantage in using X-rays in these additions is that the highly

(8) In previous studies of radical additions of hydrogen sulfide to vinyl ethers, formation of  $\alpha$ -mercaptoethyl ethers was observed in addition to the expected  $\beta$ -mercaptoethyl ethers, the relative proportions depending upon the structure of the ether. The formation of the  $\alpha$ -isomers was attributed to competing ionic reactions: M. F. Shostakovskii, E. N. Prilezhaeva and E. S. Shapiro, *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. (Eng. Transl.)*, 235, 245 (1954); *ibid.*, 653 (1955).

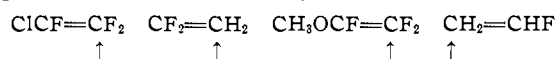
volatile and toxic reactants can be contained in stainless steel pressure vessels.

The reactions in all cases are no doubt free-radical chain reactions. The *G*-values calculated for the X-ray-initiated experiments indicate that in most cases the kinetic chain length is quite large. Although the quantum yield was not measured, the ultraviolet-initiated reaction with trifluorovinyl methyl ether was noted to be extremely fast, just a few minutes of irradiation being sufficient to convert 0.1 mole of reactants to product.<sup>9</sup>

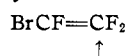
The generally accepted mechanism<sup>10</sup> for radical addition of hydrogen sulfide to olefins involves a sequence of steps represented in eq. 9-11 for the addition to tetrafluoroethylene



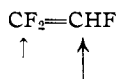
In this scheme the SH radical is the adding or chain-carrying species, and the orientation of the final product in cases involving unsymmetrical olefins is determined by which of the doubly bonded carbon atoms is attacked by the SH radical in eq. 10. In previous studies of radical addition to unsymmetrical olefins, the orientations found can most generally be correlated by assuming that the adding radical adds to give the more stable of the two possible intermediate radicals and that the major or exclusive product results from chain transfer by this radical with the addendum.<sup>1,2a</sup> The orientation found in the 1:1 H<sub>2</sub>S adducts from chlorotrifluoroethylene, 1,1-difluoroethylene, vinyl fluoride and methyl trifluorovinyl ether are consistent with previous studies of radical additions to these same olefins; in each case the adding radical attacks the carbon indicated by the arrows. There have apparently been no reports of radical additions of unsymmetrical reagents to bromotrifluoroethylene. However, it would



be predicted on the basis of intermediate radical stabilities that attack should occur at the CF<sub>2</sub> group, as indeed it apparently does in the instant case. In



the reaction with trifluoroethylene both isomers were obtained, indicating attack by the SH radical at both the CHF and CF<sub>2</sub> group of the olefin, the major attack occurring at the CHF. Again, this is consistent with



previously studied radical additions (HBr, CF<sub>3</sub>I, CF<sub>3</sub>SH and CH<sub>3</sub>SH) to trifluoroethylene in which both isomers also were obtained, the major one resulting from attack by the adding species at the CFH in each case.

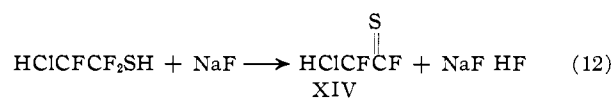
The thiols obtained in these studies vary in their properties depending upon the number of fluorine atoms on the carbon containing the SH group. Those with two fluorine atoms, *i.e.*, HCF<sub>2</sub>CF<sub>2</sub>SH, HCICFCF<sub>2</sub>SH and CH<sub>3</sub>OCFHCFC<sub>2</sub>SH, can be kept at -20° for several weeks, but at room temperature gross decomposition

(9) A very fast radical chain addition of trifluoromethanesulfonyl chloride to this olefin has also been observed: J. F. Harris, Jr., *J. Am. Chem. Soc.*, **84**, 3148 (1962).

(10) (a) F. W. Stacey and J. F. Harris, Jr., "Organic Reactions," Vol. 13, John Wiley and Sons, Inc., New York, N. Y., in press; (b) H. L. Goering, D. I. Relyea and D. W. Larsen, *J. Am. Chem. Soc.*, **78**, 348 (1956).

was apparent after just a day or so. This is in contrast to trifluoromethanethiol which is apparently stable for several months at room temperature. The one thiol prepared in this study with a single fluorine atom on the α-carbon, *i.e.*, HCF<sub>2</sub>CFHSH (V), is even less stable than those with two fluorine atoms. Plastic bottles containing this material ruptured after a day or so at room temperature or after several days at -20°. 2,2-Difluoroethanethiol, with no α-fluorines, is stable indefinitely and appears to be much like ethanethiol in characteristics, including odor. The odors of the other thiols are very acrid and strong but entirely different from those of the corresponding aliphatic thiols.

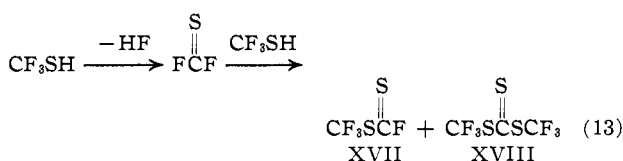
The nature of the decomposition of the thiols with α-fluorines was not investigated, but it is probably related to the great ease with which the elements of hydrogen fluoride can be removed to give thiocarbonyl compounds. For example, simply passing 1,1,2-trifluoro-2-chloroethanethiol in the vapor phase diluted with nitrogen through a tube packed with sodium fluoride pellets resulted in the formation of chloro-fluorothioacetyl fluoride (XIV) in good yield.<sup>11</sup> Similar treatment of 2-H-tetrafluoroethanethiol and 2-H-2-



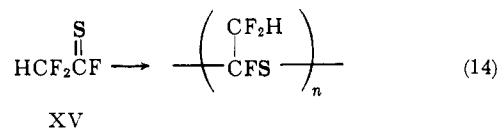
methoxytrifluoroethanethiol led to the thioacyl fluorides XV and XVI, respectively. These reactions are



reminiscent of the previously reported<sup>12</sup> dehydrofluorination of trifluoromethanethiol, which gives bis-(trifluoromethyl)-trithiocarbonate (XVIII) and (trifluoromethylthio)-fluorothioformate (XVII), presumably through thiocarbonyl difluoride as intermediate.



The thioacyl fluorides are characterized by their yellow color ( $\lambda_{\text{max}}$  2,200 and 4,100 Å.) and by the extremely low field position of the thioacyl fluoride n.m.r. absorption (at -7000 to -7100 c.p.s. (56.4 Mc.) with respect to *sym*-difluorotetrachloroethane). They also polymerize easily, often spontaneously below room temperature. The polymerization of difluorothioacetyl fluoride at room temperature can be followed



by either proton or fluorine n.m.r. spectroscopy. Figure 2 shows the proton pattern of a sample in the midst of polymerization, the resonance of the hydrogen atoms in the polymer appearing as a broad triplet in

(11) Two other fluorinated thioacetyl fluorides have been reported:  $\begin{array}{c} \text{S} \\ \parallel \\ \text{CF}_3\text{CF} \end{array}$  [E. G. Howard, W. H. Sharkey and W. J. Middleton, *J. Am. Chem. Soc.*, **83**, 2589 (1961)] and  $\begin{array}{c} \text{S} \\ \parallel \\ \text{CICF}_2\text{CF} \end{array}$  [N. N. Yarovenko, S. P. Motorny, L. I. Kirenskaya and A. S. Vasilyeva, *J. Gen. Chem. U.S.S.R.* (Eng. Transl.), **27**, 2301 (1957)].

(12) (a) E. H. Man, U. S. Patent 2,820,807 (1958) [C. A., **52**, 11900 (1958)]; (b) R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 3871 (1955).

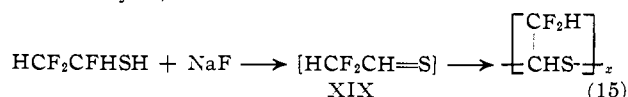
TABLE IV  
 FLUORINE<sup>19</sup> NUCLEAR MAGNETIC RESONANCE DATA (56.4 Mc.)<sup>a</sup>

Compound <sup>b</sup>	CF <sub>2</sub>	CF
H-CF <sub>2</sub> -CF <sub>2</sub> -SH (1) (a) (b) (2)	(a) +3394; J <sup>2</sup> <sub>a-1</sub> 55, J <sup>3</sup> <sub>a-b</sub> 6 (b) +920; J <sup>2</sup> <sub>b-2</sub> 15, J <sup>2</sup> <sub>b-1</sub> 2.4	
H-CF <sub>2</sub> -CF <sub>2</sub> -SCl (1) (a) (b)	(a) +3717; J <sup>2</sup> <sub>a-1</sub> 52, J <sup>3</sup> <sub>a-b</sub> 8 (b) +1734; J <sup>2</sup> <sub>b-1</sub> 3.2	
H-CF <sub>2</sub> -C(=S)-F (1) (a) (b)	(a) +2911; J <sup>2</sup> <sub>a-1</sub> 53	(b) -7070; J <sup>3</sup> <sub>b-a</sub> 31; J <sup>2</sup> <sub>b-1</sub> 2.2
H-CFCl-CF <sub>2</sub> -SH (1) (a) (b) (2)	(b) +618 <sup>c</sup>	(a) +4487; J <sup>2</sup> <sub>a-1</sub> 51, J <sup>3</sup> <sub>a-b</sub> 16 <sup>d</sup>
H-CFCl-C(=S)-SCl (1) (a) (b) (c)	(b) +1375; J <sup>2</sup> <sub>b-o</sub> 227, J <sup>2</sup> <sub>b-1</sub> 5.8 (c) +1451; J <sup>2</sup> <sub>a-o</sub> 17, J <sup>2</sup> <sub>c-1</sub> 7.8	(a) +4575; J <sup>2</sup> <sub>a-1</sub> 48, J <sup>2</sup> <sub>a-b</sub> 17
H-CFCIC-F (1) (a) (b)		(a) +3804; J <sup>2</sup> <sub>a-1</sub> 50 (b) -7027; J <sup>2</sup> <sub>a-b</sub> 50, J <sup>2</sup> <sub>b-1</sub> 3.6
H-CF <sub>2</sub> -HCF-SH (1) (a) (2) (b) (3)	(a) +3495; J <sup>2</sup> <sub>a-1</sub> 55	(b) +5494; J <sup>2</sup> <sub>b-2</sub> 45, J <sup>3</sup> <sub>b-a</sub> 18
H-CF <sub>2</sub> -CH <sub>2</sub> -SH (1) (a) (2) (3)	(a) +2768; J <sup>2</sup> <sub>a-1</sub> 55, J <sup>3</sup> <sub>a-2</sub> 15	
HBrCF-CF <sub>2</sub> -SH (1) (a) (b) (2)	(b) +520	(a) +4660; J <sup>2</sup> <sub>a-1</sub> 50, J <sup>3</sup> <sub>a-b</sub> 20
F-CH <sub>2</sub> -CH <sub>2</sub> -SH (a) (1) (2)		(a) +8180; J <sup>3</sup> <sub>a-1</sub> 50, J <sup>3</sup> <sub>a-2</sub> 21

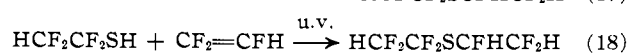
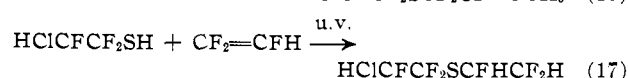
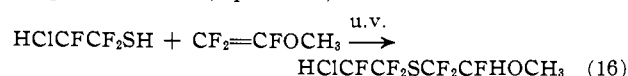
<sup>a</sup> Spectra were obtained by means of a high resolution nuclear magnetic resonance spectrometer and associated electromagnet, both manufactured by Varian Associates, Palo Alto, Calif., operating at approximately 14,100 gauss. The resonances are presented in tabular form since the scale required for graphic representation would not allow the splitting patterns to be shown. <sup>b</sup> Each different fluorine atom is labeled (a), (b) or (c), and similarly the hydrogen atoms are labeled (1), (2) or (3). The number following the letter is the position of the center of the resonance in cycles per second displaced from the resonance of *sym*-1,2-difluorotetrachloroethane as an external standard. The coupling constants, represented by *J*, are given in cycles per second. The superscripts represent the multiplicity of the splitting (*i.e.*, *J*<sup>2</sup> corresponds to a doublet and *J*<sup>3</sup> to a triplet) and the subscripts indicate the coupled nuclei to which the *J*-value applies. <sup>c</sup> This resonance contains at least 10 lines indicating that the fluorine atoms are not equivalent. <sup>d</sup> In view of the non-equivalence of the fluorine atoms in the CF<sub>2</sub> group, this apparent triplet splitting is no doubt due to overlapping doublets. <sup>e</sup> The CF<sub>2</sub> resonance for this compound is a typical weak-strong-strong-weak pattern indicating non-equivalence of the two fluorine atoms. They are thus designated separately in the formula. The chemical shifts given for these fluorines are the frequencies corresponding to the strong components and are thus not exactly the true chemical shifts.

contrast to the resonance of the protons of the remaining monomer which comprise a sharp triplet as expected.

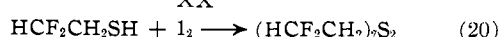
When 1,2,2-trifluoroethanethiol (V) was submitted to the dehydrofluorination procedure described above, no volatile product was obtained, but a polymeric material was found deposited on the sodium fluoride pellets. Apparently difluorothioacetaldehyde (XIX) formed and immediately polymerized on the sodium fluoride (eq. 15). In some of the experiments, a fleeting purple color, possibly due to the monomeric thioaldehyde, was noted on the sodium fluoride.



In other reactions, these fluorinated thiols exhibit typical thiol behavior. For example, under the influence of ultraviolet radiation, they add to olefins to give sulfides (eq. 16-18). Chlorine converts them



to a mixture of sulfonyl chloride (XX) and disulfide (eq. 19), and oxidation to disulfides can be accomplished with iodine (eq. 20).



## Experimental

I. X-Ray-initiated Addition of Hydrogen Sulfide to Fluoroolefins.—All of these reactions were carried out in the same manner. The results are presented in Table I. The details of a typical experiment involving reaction of hydrogen sulfide with 1,1-difluoroethylene follow.

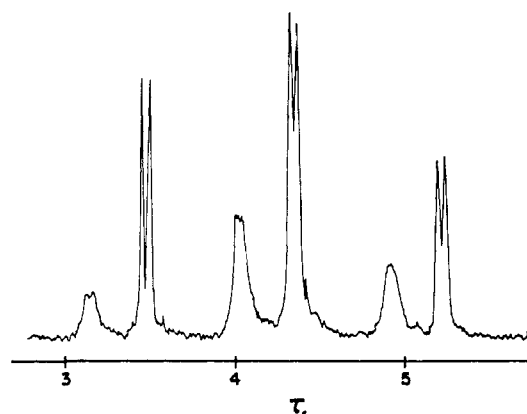


Fig. 2.—Proton n.m.r. spectrum of a sample of difluorothioacetyl fluoride undergoing polymerization.

A mixture of 10 g. (0.156 mole) of 1,1-difluoroethylene and 20 g. (0.625 mole) of hydrogen sulfide was put in a 100-ml. stainless-steel pressure vessel and irradiated with X-rays for 2.75 hours at an average dose rate of about 16,000 rads/minute.<sup>13</sup> The volatiles were bled off, and the residue was distilled through a small spinning-band still to give 10.5 g. (69%) of 2,2-difluoroethanethiol distilling at 66°. The properties and analytical data for this compound are listed in Table II.

(13) The X-rays were generated by impinging 3 Mv. electrons from a Van de Graaff accelerator on a water-cooled gold target mounted beneath the window of the electron tube. Dose rates were determined by ferrous sulfate dosimetry.

II. Ultraviolet-initiated Addition of Hydrogen Sulfide to Methyl Trifluorovinyl Ether.—A mixture of 30 ml. of methyl trifluorovinyl ether and an equal volume of liquid hydrogen sulfide in a quartz reactor fitted with a Dry Ice condenser was irradiated by the procedure described in ref. 2a. Just a few minutes of irradiation was required to complete the reaction as evidenced by the slowing down of the reflux rate. After evaporation of the excess volatiles, there remained 37.82 g. of residue. Distillation of a portion (26.7 g.) of this through a helix-packed, low-temperature still gave 6 g. of 2-methoxy-1,1,2-trifluoroethanethiol distilling at 8–10° (8 mm.). The remainder of the reaction mixture was treated similarly, and the residues from these two portions were combined and distilled at 1.3 mm. pressure. There was thus obtained 15.02 g. of a 2:1 adduct, presumably of structure XII, distilling at 65–66° (1.5 mm.).

III. Preparation of Sulfonyl Chlorides. A. 2-Chloro-1,1,2-trifluoroethanesulfonyl Chloride.—Chlorine gas (dried by bubbling through concd. sulfuric acid) was passed through a refluxing solution of 20 g. (0.133 mole) of 2-chloro-1,1,2-trifluoroethanethiol in 50 ml. of dichloromethane for a period of 2.5 hours. Upon distillation of the reaction mixture through a small Vigreux still, there was obtained 11.3 g. (46%) of 2-chloro-1,1,2-trifluoroethanesulfonyl chloride distilling at 95–98° and 7.5 g. (38%) of bis-(2-chloro-1,1,2-trifluoroethyl) disulfide distilling at 67–72° (12 mm.) (mostly at 71–72° (12 mm.)).

B. 2-H-Tetrafluoroethanesulfonyl Chloride.—Chlorine was passed through 20.4 g. (0.152 mole) of 2-H-tetrafluoroethanethiol contained in a flask fitted with a Dry Ice-acetone-cooled condenser until there was a considerable excess of chlorine present as indicated by the rate of reflux. Upon distillation of the mixture there was obtained 17.1 g. (67%) of 2-H-tetrafluoroethanesulfonyl chloride distilling at 57–59°.

IV. Dehydrofluorination of Thiols with  $\alpha$ -Fluorine Atoms. A. 2-Chloro-1,1,2-trifluoroethanethiol.—Eight grams (0.053 mole) of 2-chloro-1,1,2-trifluoroethanethiol was placed in a small side-arm flask fitted with a nitrogen capillary extending through the side-arm to the bottom of the flask. The flask was then connected *via* glass to a horizontal Pyrex tube (0.5 × 12 in.) packed nearly full with sodium fluoride pellets (1/8 in.) which was connected through two Dry Ice-acetone cooled traps to a vacuum line. The system was evacuated to about 300 mm. and the nitrogen turned on. In 0.5 hour, the thiol was completely vaporized. The trap contents (5.2 g., 75%) were warmed to room temperature and then distilled. There was obtained 4.3 g. (62%) of chlorofluorothioacetyl fluoride as a bright yellow liquid distilling at 56–57°.

On standing for a few days, even at about 0°, samples of chlorofluorothioacetyl fluoride thickened and eventually became solid.

B. 2-H-Tetrafluoroethanethiol.—2-H-Tetrafluoroethanethiol (9.9 g., 0.074 mole) was treated in exactly the same way as described in IVA except that the flask containing the thiol was cooled in a bath maintained at –35 to –40° to control the rate of vaporization of the thiol. Upon transfer by vaporization of the trap contents to another Dry Ice-cooled trap there was obtained 5.0 g. (59%) of difluorothioacetyl fluoride, which distilled through a low-temperature still at 14–16°. Owing to its low boiling point and its tendency to polymerize, this material was not analyzed satisfactorily. Its identity was established, however, by its fluorine n.m.r. spectrum (Table IV) which contained a low field acyl fluoride peak, and by analysis of the solid polymer which formed even on storage at –80°.

*Anal.* Calcd. for (HCF<sub>2</sub>CFS)<sub>2</sub>: C, 21.0; H, 0.9; F, 50.0; S, 28.1. Found: C, 21.6; H, 1.3; F, 49.4; S, 28.2.

C. 2-Methoxy-1,1,2-trifluoroethanethiol.—2-Methoxy-1,1,2-trifluoroethanethiol (8.0 ml.) was treated as described in IVA except that the system was evacuated to about 1 mm. pressure. The orange-yellow trap contents (5.0 g.) distilled at –13 to –11° (0.9 mm.). At –80° this material thickened and became less colored (indicative of polymerization). At room temperature the material thickened, darkened, and evolved gas. An examination of the fluorine n.m.r. pattern revealed two resonances, one of which was a doublet in the thioacyl fluoride region and the other a pair of doublets. Because of the instability of this material, no elemental analyses were attempted.

D. 1,2,2-Trifluoroethanethiol.—1,2,2-Trifluoroethanethiol (8.5 g., 0.073 mole) was passed through a sodium fluoride packed tube exactly as described in IVA. About 1 g. of liquid condensed in a trap, and an examination of the fluorine n.m.r. indicated that this was primarily the starting thiol. The column packing was extracted twice with 200-ml. portions of ether, and the resulting solution filtered and evaporated. There remained 3.2 g. of a sticky semi-solid low-molecular weight polymer of difluorothioacetaldehyde.

*Anal.* Calcd. for (C<sub>2</sub>H<sub>2</sub>F<sub>3</sub>S)<sub>2</sub>: C, 25.0; H, 2.2; F, 39.5; S, 33.3. Found: C, 24.3; H, 2.3; F, 39.5; S, 32.6.

The fluorine n.m.r. pattern of an ether solution of the polymer contained one resonance which was a doublet.

V. Ultraviolet-initiated Addition of Fluorinated Thiols to Olefins. A. Addition of 2-Chloro-1,1,2-trifluoroethanethiol to Trifluoroethylene.—A mixture of 42 g. (0.279 mole) of 2-chloro-1,1,2-trifluoroethanethiol and 27 g. (0.329 mole) of trifluoroethylene was irradiated according to the procedure described in II for 2 hours. Upon distillation of the reaction mixture, there was obtained 53.0 g. (82%) of 2-chloro-1,1,2-trifluoroethyl 1,2,2-trifluoroethyl sulfide distilling at 51° (36 mm.) to 53° (34 mm.).

B. Addition of 2-H-Tetrafluoroethanethiol to Trifluoroethylene.—A mixture of 18 g. (0.134 mole) of 2-H-tetrafluoroethanethiol and 15 g. (0.185 mole) of trifluoroethylene was irradiated for 18 hours. Upon distillation of the reaction mixture through a small spinning-band still there was obtained 20.3 g. (70%) of 2-H-tetrafluoroethyl 1,2,2-trifluoroethyl sulfide distilling at 104–105°.

C. Addition of 2-Chloro-1,1,2-trifluoroethanethiol to Methyl Trifluorovinyl Ether.—A mixture of 3 g. of 2-chloro-1,1,2-trifluoroethanethiol and 3 ml. of methyl trifluorovinyl ether was irradiated for 12 minutes. Upon distillation of the reaction mixture there was obtained 1.70 g. of 2-chloro-1,1,2-trifluoroethyl 2-methoxy-1,1,2-trifluoroethyl sulfide distilling at 57–60° (8.0 mm.).

VI. Oxidation of 2,2-Difluoroethanethiol.—A solution of 35 g. of iodine and 30 g. of potassium iodide in 100 ml. of water was added slowly to a stirred suspension of 25 g. (0.255 mole) of 2,2-difluoroethanethiol in 50 ml. of water. When the iodine was in slight excess, aqueous sodium thiosulfate solution was added until the color was dissipated. The solution was then extracted twice with 75-ml. portions of ether. The extracts were shaken once with aqueous sodium thiosulfate, once with water, dried over anhydrous magnesium sulfate and distilled. There was obtained 21.2 g. (85%) of bis-(2,2-difluoroethyl) disulfide distilling at 84° (21 mm.).