[CONTRIBUTION NO. 754 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

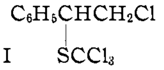
The Free-radical Addition of Trifluoromethanesulfenyl Chloride to Haloölefins[1]

BY JOHN F. HARRIS, JR.

RECEIVED MARCH 2, 1962

A study of the free-radical addition of trifluoromethanesulfenyl chloride to a series of haloölefins has been made. A mechanism based upon the assumption that the chlorine atom is the major adding species is proposed to account for the unusual orientations observed.

The addition of sulfenyl halides to hydrocarbon olefins to give β-haloalkyl sulfides is well known.[2] The evidence thus far obtained indicates that the reaction is an ionic one and that the mechanism involves attack by the electrophilic sulfenium group upon the electron-rich double bond, generally resulting in the predominant (and sometimes exclusive) formation of a single isomer (the Markownikoff isomer).[3] Apparently very little attention has been given to analogous free-radical additions. In virtually the only such study, Prey, Gutschik and Berbalk[4] reported that the ultraviolet or peroxide initiated addition of trichloromethanesulfenyl chloride to styrene results in the formation of I, and pointed out that since the CH_2 group is the usual site of radical attack in the styrene molecule, a chlorine atom from the sulfenyl chloride must be the adding or chain-carrying species. Similar conclusions have been reached in the present study, which was completed before the publication of Prey, Gutschik and Berbalk's results.



I

$$C_6H_5\underset{\displaystyle SCCl_3}{\underset{|}{C}}HCH_2Cl$$

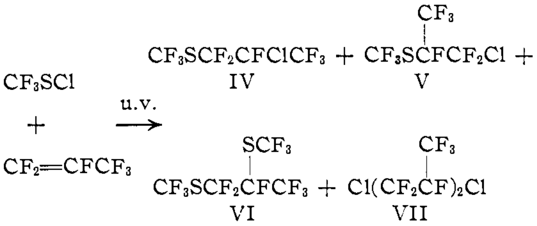
Results

The present paper reports a study which has been made of free-radical additions of trifluoromethanesulfenyl chloride to trifluoroethylene, 1,1-difluoroethylene, chlorotrifluoroethylene, hexafluoropropene, trifluorovinyl methyl ether and vinyl chloride, a group of olefins which does not undergo the ionic addition of sulfenyl halides readily. Initiation was accomplished by ultraviolet radiation, X-rays or with an azonitrile catalyst. The results of the experiments are presented below and collected in Tables I and II.

Trifluoroethylene.—The addition of trifluoromethanesulfenyl chloride to trifluoroethylene gave two 1:1 adducts (II and III), which were separated by preparative scale gas chromatography. The structure of the predominant adduct (III) was assigned on the basis of its identity with respect to boiling point, refractive index and proton and fluorine n.m.r. spectrum to the 1:1 adduct obtained in the addition of trifluoromethanethiol to chlorotrifluoroethylene.[5] The minor adduct must therefore have structure II, and the proton and fluorine n.m.r. patterns (Table III) are consistent with this structure.

$$CF_3SCl + CHF{=}CF_2 \xrightarrow{\text{u.v.}} \underset{\text{II}}{CF_3SCFHCF_2Cl} + \underset{\text{III}}{CF_3SCF_2CFHCl} \quad (1)$$

Hexafluoropropene.—The 1:1 adduct fraction from the addition to hexafluoropropene was shown by examination of the fluorine n.m.r. pattern to contain the two possible 1:1 adducts in a ratio of about 63% IV and 37% V. Although no gas chromatography column was found which would separate the two isomers, assignment of structure was possible on the basis of the fluorine n.m.r. pattern of the mixture. Thus the resonances of the two CF_3 groups on sulfur (−1743 and −1680 c.p.s.) were readily identified and the more intense peak (−1680 c.p.s.) was clearly a triplet, indicating that IV is the more prevalent (63%) isomer. In addition to the 1:1 adducts, considerable quantities of bis-(trifluoromethyl) disulfide, 1,2-bis-(trifluoromethylthio)-hexafluoropropane (VI) and two telomers (VIIa and b) containing two molecules of hexafluoropropene per molecule of chlorine were obtained. These latter three materials were isolated from the higher boiling fractions by preparative scale gas chromatography, and the yield of each, while not accurately determined, was estimated to be about 10%.



$$\begin{matrix} CF_3SCl \\ + \\ CF_2{=}CFCF_3 \end{matrix} \xrightarrow{\text{u.v.}} \begin{matrix} \underset{\text{IV}}{CF_3SCF_2CFClCF_3} + \underset{\text{V}}{CF_3S\overset{\displaystyle CF_3}{\overset{|}{C}}FCF_2Cl} + \\ \underset{\text{VI}}{CF_3SCF_2\overset{\displaystyle SCF_3}{\overset{|}{C}}FCF_3} + \underset{\text{VII}}{Cl(CF_2\overset{\displaystyle CF_3}{\overset{|}{C}}F)_2Cl} \end{matrix} \quad (2)$$

Chlorotrifluoroethylene.—The 1:1 adduct fraction from the addition to chlorotrifluoroethylene was shown by a comparison of the fluorine n.m.r. pattern with that of an authentic sample of trifluoromethyl 1,2-dichlorotrifluoroethyl sulfide (VIII) to contain both 1:1 adducts in ratio of about 78% (VIII): 22% (IX). No gas chromatography column was found which would completely sepa-

$$CF_3SCl + ClCF{=}CF_2 \xrightarrow{\text{u.v.}} \underset{\text{VIII}}{CF_3SCFClCF_2Cl} + \underset{\text{IX}}{CF_3SCF_2CFCl_2} \quad (3)$$

---

(1) Presented before the 140th National Meeting of the American Chemical Society at Chicago, Ill., in September, 1961.

(2) (a) R. Turner and R. Connor, *J. Am. Chem. Soc.*, **69**, 1009 (1947); (b) N. Kharasch and C. M. Buess, *ibid.*, **71**, 2724 (1949); (c) W. L. Orr and N. Kharasch, *ibid.*, **78**, 1201 (1956); *cf.* also "Organic Sulfur Compounds," Vol. I, Edited by N. Kharasch, Pergamon Press, New York, N. Y., 1961, Chapt. 32, pp. 375–396.

(3) In these addition reactions, it is assumed that the polarization of the sulfenyl halide confers positive character to the sulfur atom, *i.e.*, $R\overset{\delta+}{S}\text{–}\overset{\delta-}{Cl}$.

(4) V. Prey, E. Gutschik and H. Berbalk, *Monatsh. Chem.*, **91**, 794 (1960).

(5) J. F. Harris, Jr., and F. W. Stacey, *J. Am. Chem. Soc.*, **83**, 840 (1961).

TABLE I

ULTRAVIOLET INITIATED ADDITION OF TRIFLUOROMETHANESULFENYL CHLORIDE TO HALOÖLEFINS

Olefin, g. (mole)	CF_3SCl, g. (mole)	Method	Time	Products (yield, %)
$CF_2{=}CFH$, 48 (0.585)	80 (0.585)	B	2.75 hr.	CF_3SCF_2CFHCl (III) (50)
				$CF_3SCFHCF_2Cl$ (II) (11)
$CF_2{=}CFCF_3$, 66 (0.44)	50 (0.366)	B	3 days	$CF_3SCF_2CFClCF_3$ (IV) (63) $CF_3SCF(CF_3)CF_2Cl$ (V) (37) } (26.4)
				$CF_3SCF_2CF(CF_3)SCl_3$ (VI) (*ca.* 10)
				$Cl(C_3F_6)_2Cl$ (VIIa and VIIb, roughly 10% each)
				CF_3SSCF_3
$ClCF{=}CF_2$, 96 (0.825)	135 (0.99)	B	26 hr.	$CF_3SCFClCF_2Cl$ (VIII) (42)
				$CF_3SCF_2CFCl_2$ (IX) (12)
$CH_2{=}CHCl$, 10 (0.160)	20 (0.146)	A	16 hr.	$CF_3SCHClCH_2Cl$ (X) (72.7)
				$CF_3SCH_2CHCl_2$ (XI) (4)
$CH_3OCF{=}CF_2$, 20.5 (0.183)	27 (0.198)	B	10 min.	$CH_3OCF(SCF_3)CF_2Cl$ (XII) (16)
				$CH_3OCF(Cl)CF_2SCF_3$ (XIII) (26)
				$CH_3OCF(Cl)CF_2Cl$ (XIV) (31)
				$CH_3OCF(SCF_3)CF_2SCF_3$ (XV) (11)
				CF_3SSCF_3 (31)[a]
$CH_2{=}CF_2$, 11 (0.172)	24 (0.176)	A	9.75 hr.	$CF_3SCF_2CH_2Cl$ (XVI) (40.3)
				$CF_3SCH_2CF_2Cl$ (XVII) (11.2)
				CF_3SSCF_3 (12)

[a] Based on CF_3SCl.

TABLE II

PRODUCTS

Compound	B.p., °C.	n_D (*t*, °C.)	Formula	Chlorine, % Calcd.	Chlorine, % Found	Fluorine, % Calcd.	Fluorine, % Found	Sulfur, % Calcd.	Sulfur, % Found
$CF_3SCFHCF_2Cl$ (II)	54	1.3237 (25)	C_3HClF_6S	16.2	16.2			14.7	14.7
CF_3SCF_2CFHCl (III)	67	1.3334 (25)	C_3HClF_6S	16.2	16.3	52.1	52.3		
$CF_3SCF_2CFClCF_3$ (IV) (63) $CF_3SCF(CF_3)CF_2Cl$ (V) (37)	68–72	1.3143 (25)	C_4ClF_9S			59.6	59.1	11.2	11.5
$CF_3SCF_2CF(CF_3)SCF_3$ (VI)	100	1.3250 (25)	$C_5F_{12}S_2$			64.8	64.3	18.2	17.6
$Cl(C_3F_6)_2Cl$[c] (VIIa)	116	1.3150 (25)	$C_6F_{12}Cl_2$	19.1	18.8	61.4	62.0		
$Cl(C_3F_6)_2Cl$[c] (VIIb)	116	1.3217 (25)	$C_6F_{12}Cl_2$	19.1	19.0	61.4	62.3		
$CF_3SCFClCF_2Cl$ (VIII)	84	1.3560 (24)	$C_3Cl_2F_6S$	28.0	27.7	45.0	45.2	12.7	12.5
$CF_3SCFClCF_2Cl$ (VIII) (78) $CF_3SCF_2CFCl_2$ (IX) (22)	76–82	1.3561 (25)	$C_3Cl_2F_6S$	28.0	28.1	45.0	44.9		
$CF_3SCHClCH_2Cl$ (X)	122	1.4213 (24)	$C_3H_2Cl_2F_3S$	35.6	35.6	28.6	29.1	16.1	16.1
$CF_3SCH_2CHCl_2$ (XI)	115–116	1.4162 (24)	$C_3H_3Cl_2F_3S$	35.6	35.8	28.6	28.2	16.1	16.1
$CF_3SCF(OCH_3)CF_2Cl$ (XII)	105	1.3540 (25)	$C_4H_3ClF_6OS$	14.3	14.6	45.8	45.0		
$CF_3SCF_2CFClOCH_3$ (XIII)	113	1.3528 (24)	$C_4H_3ClF_6OS$			45.8	45.5	12.9	13.0
$CH_3OCFClCF_2Cl$ (XIV)	81	1.3551 (24)	$C_3H_3Cl_2F_3O$	19.7	20.2[a]	1.7	1.8[b]		
$CH_3OCF(SCF_3)CF_2SCF_3$ (XV)	127	1.3531 (25)	$C_5H_3F_9OS_2$			54.4	53.2	20.4	20.4
$CF_3SCF_2CH_2Cl$ (XVI)	79	1.3521 (26.5)	$C_3H_2ClF_5S$	17.7	18.3	47.5	46.9	16.0	16.0
$CF_3SCH_2CF_2Cl$ (XVII)	71	1.3456 (26.5)	$C_3H_2ClF_5S$	17.7	18.2	47.5	46.0	16.0	15.8

[a] Carbon. [b] Hydrogen. [c] Structure not known.

rate the two isomers. Compound VIII was prepared by the chlorination of trifluoromethyl 1,2,2-trifluoroethyl sulfide (eq. 4). There was also a considerable quantity of higher boiling material

$$CF_3SCFHCF_2H + Cl_2 \xrightarrow{u.v.} \underset{\text{VIII}}{CF_3SCFClCF_2Cl} \quad (4)$$

which, according to elemental analysis, was apparently composed largely of $Cl_2/CFCl{=}CF_2$ telomers.

Vinyl Chloride.—From the addition to vinyl chloride the only product actually isolated in pure form was trifluoromethyl 1,2-dichloroethyl sulfide (X). Small amounts (1–6%) of three other products were also detected by gas chromatographic analysis, and by matching retention times with an authentic sample it appears that one of these materials is XI (4%). An authentic sample of

$$CF_3SCl + CH_2{=}CHCl \xrightarrow{u.v.} \underset{\text{X}}{CF_3SCHClCH_2Cl} + \underset{\text{XI}}{CF_3SCH_2CHCl_2} \quad (5)$$

XI was prepared by the ultraviolet-initiated addition of trifluoromethanethiol to 1,1-dichloroethylene (eq. 6). The structure of XI was assigned on the

$$CF_3SH + CH_2{=}CCl_2 \xrightarrow{u.v.} \underset{\text{XI}}{CF_3SCH_2CHCl_2} \quad (6)$$

basis of the proton n.m.r. pattern which consisted of two resonances, a triplet and a doublet, thus excluding the other possible 1:1 adduct which should have only one proton resonance. The proton pattern of X is similar to that of XI (*i.e.*, a triplet and a doublet), but the chemical shifts are different, and thus X is not the same as XI and must therefore have the structure written, *i.e.*, trifluoromethyl 1,2-dichloroethyl sulfide.

TABLE III-A

FLUORINE NUCLEAR MAGNETIC RESONANCE SPECTRA AT 56.4 Mc.[a]

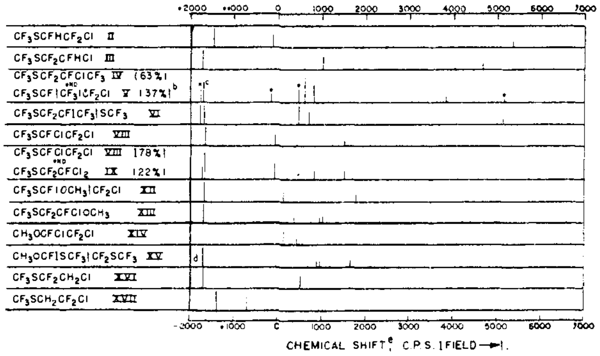
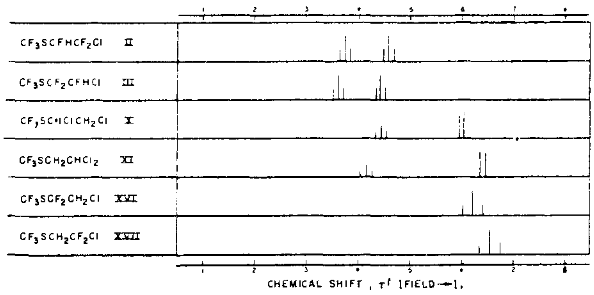


TABLE III-B

PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA AT 60 Mc.[a]



[a] Fluorine spectra were obtained by means of a high resolution n.m.r. spectrometer and associated electromagnet, both manufactured by Varian Associates, Palo Alto, Calif., operating at approximately 9988 gauss. Proton spectra were obtained with an A-60 n.m.r. spectrometer manufactured by Varian Associates, Palo Alto, Calif. Intensities are represented by relative line heights. The chemical shift scale for Table III-A is such that most splittings cannot be shown. [b] The resonances marked with asterisks belong to the 37% component. [c] Split to a triplet. [d] The two CF_3S resonances are so close together (10 c.p.s.) that they appear as a single line here. [e] Spectra are plotted in terms of displacement in cycles per second (c.p.s.) from the fluorine resonance of *sym*-difluorotetrachloroethane as an external standard. [f] $\tau = 10 - \delta$; the standard, tetramethylsilane, was internal.

An addition, presumably ionic, of trifluoromethanesulfenyl chloride to vinyl chloride was also accomplished by heating a mixture of the reactants in acetonitrile at 100°. The conversion to products was not high, and the only product actually isolated (17%) was 2,2-dichloroethyl trifluoromethyl sulfide (XI) (eq. 7). This is the

$$CF_3SCl + CH_2{=}CHCl \xrightarrow[\text{acetonitrile}]{\Delta} \underset{\text{XI}}{CF_3SCH_2CHCl_2} \quad (7)$$

product which one would expect from an ionic addition assuming that in the polarization of the sulfenyl chloride the sulfur is positive relative to the chlorine.

Trifluorovinyl Methyl Ether.—The 1:1 adducts XII and XIII were obtained from the reaction with trifluorovinyl methyl ether.[6] Considerable quantities of bis-(trifluoromethyl) disulfide, the olefin–chlorine addition product (XIV) and the product in which two CF_3S groups became attached to the double bond carbons (XV) were also isolated.

Assignment of structure to the 1:1 adducts was made on the basis of the fluorine n.m.r. patterns of the isolated isomers. In the previously discussed fluorine n.m.r. patterns, the chemical shift of the CF_2 and CF resonances to lower field was larger when the group in question was attached to the Cl than when it was attached to the CF_3S group (*i.e.*, the deshielding effect of Cl is greater than CF_3S). Thus, in compound III the CF_2 (next to CF_3S) is at 1021 c.p.s. whereas in II (next to Cl) it is at −112 c.p.s. Similarly, the CF in III (next to Cl) is at 4672 c.p.s. and in II (next to CF_3S) is at 5364 c.p.s. Also, in the mixed products obtained in this reaction (*i.e.*, XIV, in which both the CF and CF_2 are next to Cl, and XV, in which both the CF and CF_2 are next to CF_3S) the greater deshielding effect of Cl compared with CF_3S upon both the CF (440 c.p.s. in XIV *vs.* 1660 c.p.s. in XV) and the CF_2 (151 c.p.s. in XIV *vs.* 937 c.p.s. in XV) is apparent. Extension of this analogy to the 1:1 adducts obtained in this reaction allows assignment of structure XII to the less prevalent adduct and XIII to the more prevalent one.

$$\left.\begin{matrix} CF_3SCl \\ + \\ CF_2{=}CFOCH_3 \end{matrix}\right\} \xrightarrow{\text{u.v.}}$$
$$\underset{\text{XII}}{CH_3OCF(SCF_3)CF_2Cl} + \underset{\text{XIII}}{CH_3OCFClCF_2SCF_3} + \quad (8)$$
$$\underset{\text{XIV}}{CH_3OCFClCF_2Cl} + \underset{\text{XV}}{CH_3OCF(SCF_3)CF_2SCF_3} +$$
$$CF_3SSCF_3$$

1,1-Difluoroethylene.—From the reaction with 1,1-difluoroethylene the two 1:1 adducts (XVI and XVII) were isolated.[7] By analogy with previously discussed structure assignments, structure XVII (with Cl next to CF_2) was assigned to the isomer (the less prevalent one) with the CF_2 resonance at lower field, and XVI to the isomer with the CF_2 at higher field. Supporting this assignment was the fact that XVI was identical with the major product of the ultraviolet-initiated addition of trifluoromethanethiol to 1,1-difluoro-2-chloroethylene (eq. 10).[8]

$$CF_3SCl + CF_2{=}CH_2 \xrightarrow{\text{u.v.}} \underset{\text{XVI}}{CF_3SCF_2CH_2Cl} + \underset{\text{XVII}}{CF_3SCH_2CF_2Cl} \quad (9)$$

$$CF_3SH + CF_2{=}CHCl \xrightarrow{\text{u.v.}} \underset{\text{XVI}}{CF_3SCF_2CH_2Cl} \quad (10)$$

---

(6) A. Senning and S. O. Lawesson (*Acta Chem. Scand.*, **15**, 1203 (1961)) have reported that the HCl-catalyzed addition of Cl_3CSCl to 2,3-dihydrofuran yields the Markownikoff isomer, *i.e.*, 2-chloro-3-trichloromethylthiotetrahydrofuran.

(7) The addition (presumably ionic) of $ClCF_2CH_2SCl$ to this olefin has been reported to yield the Markownikoff isomer, *i.e.*, $(ClCF_2CH_2)_2S$. I. L. Knunyants and E. G. Vykhovskaya, *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. (Eng. Transl.)*, 769 (1955).

(8) J. F. Harris, unpublished experiments.

TABLE IV

COMPARISON OF COMPOSITION OF 1:1 ADDUCT FRACTIONS FROM FREE RADICAL CF_3SCl AND CF_3SH ADDITION[a,b]

	$CHCl{=}CH_2$		$CF_2{=}CFH$		$CFCl{=}CF_2$		$CF_2{=}CH_2$		$CH_3OCF{=}CF_2$		$CF_2{=}CFCF_3$	
CF_3SCl	95	5	82	18	78	22	78	22	38	62	63	37
CF_3SH	0	100	2	98	0	100	0	100	0	100	45	55

[a] The numbers under each carbon atom represent the % composition of the 1:1 adduct fraction with respect to the orientation of the CF_3S group. [b] All of the thiol addition reactions except the $CF_3SH{-}CH_2{=}CHCl$ reaction are given in ref. 5.

The addition of trifluoromethanesulfenyl chloride to 1,1-difluoroethylene was also accomplished with α,α'-azobis-(isobutyronitrile) (1 mole %) as initiator. The same products in approximately the same ratios as in the ultraviolet-initiated reaction were obtained.

Discussion

Since these reactions can be accomplished not only by ultraviolet irradiation but also by X-ray irradiation and by catalytic amounts of azo-initiators, it seems certain that they are free radical chain reactions. A striking feature of this series of experiments is the formation of both possible 1:1 adducts (Table I) in each case. In previous studies of radical additions to these same olefins, hexafluoropropene[5] and trifluoroethylene[5,9] are the only ones reported to yield both isomers. It is highly unlikely that the formation of both isomers can be attributed to concurrent ionic and radical reactions, since in several cases, *e.g.*, 1,1-difluoroethylene, chlorotrifluoroethylene and vinyl chloride, it was shown that no reaction occurred without radiation or a free radical catalyst.

The orientation of the predominant isomer in most cases is also unusual. A comparison with the corresponding radical–CF_3SH additions[5] (Table IV) shows that the predominant orientation with respect to the CF_3S group in the sulfenyl chloride addition is just opposite to that in the thiol addition in all cases except the methyl trifluorovinyl ether reaction. The radical addition of thiols to olefins has been studied extensively and the generally accepted mechanism involves a chain sequence written in eq. 11–13 for the 1,1-difluoroethylene–trifluoromethanethiol reaction. In this scheme, the CF_3S radical is the adding or chain-carrying species, attacking the CH_2 group

$$\text{Initiation: } CF_3SH \longrightarrow CF_3S\cdot \qquad (11)$$

$$\text{Addition: } CF_3S\cdot + CH_2{=}CF_2 \longrightarrow \underset{\text{XVIII}}{CF_3SCH_2CF_2\cdot} \qquad (12)$$

$$\text{Transfer: } CF_3SCH_2CF_2\cdot + CF_3SH \longrightarrow \underset{\text{XIX}}{CF_3SCH_2CF_2H} + CF_3S\cdot \qquad (13)$$

(the usual site of radical attack in 1,1-difluoroethylene) to give XVIII, and the chain transfer step involves a displacement on hydrogen giving the 1:1 adduct (XIX) and generating a CF_3S radical to carry on the chain. In the predominant product from each of the thiol reactions, excepting that with hexafluoropropene,[10] the CF_3S group is found on the carbon generally attacked by radicals and the orientation is that arising from the predicted more stable of the two possible intermediate radicals; *e.g.*, in the $CF_2{=}CH_2{:}CF_3SH$ reaction, $CF_3SCH_2CF_2\cdot$ is predicted to be more stable than $CF_3SCF_2CH_2\cdot$.

It might be expected that the radical addition of trifluoromethanesulfenyl chloride to olefins would follow an analogous course, for example as in eq. 14–16 (mechanism I) for the addition to 1,1-difluoroethylene. If this were the predominant mechanism, it would be expected that the major 1:1 adduct would be 2-chloro-2,2-difluoroethyl trifluoromethyl sulfide (XVII), which has the same orientation with respect to the CF_3S group

$$\left.\begin{array}{ll} CF_3SCl \longrightarrow CF_3S\cdot + Cl\cdot & (14) \\ CF_3S\cdot + CH_2{=}CF_2 \longrightarrow CF_3SCH_2CF_2\cdot & (15) \\ CF_3SCH_2CF_2\cdot + CF_3SCl \longrightarrow CF_3S\cdot + \underset{\text{XVII}}{CF_3SCH_2CF_2Cl} & (16) \end{array}\right\}\ \begin{array}{c}\text{mechanism}\\ \text{I}\end{array}$$

as the product from the free-radical thiol addition, but in fact this is the minor 1:1 adduct.

The predominance of trifluoromethyl 2-chloro-1,1-difluoroethyl sulfide (XVI) can be rationalized by assuming that the sulfenyl chloride reaction proceeds largely by another chain mechanism (eq. 17 and 18; mechanism II) in which the chlorine atom is the adding species instead of the CF_3S radical, and in which the chain-transfer step comprises a radical displacement on sulfur[11] generating a chlorine atom to carry on the chain. To account for the occurrence of both 1:1 adducts in each reaction, it is assumed that both mechanisms are occurring simultaneously. A consequence of this assumption is that mixed products should also be obtained, *i.e.*, products in which the intermediate radical from mechanism I chain transfers as in mechanism II, and *vice versa* (eq. 19 and 20). In several of the reaction mixtures,

$$\left.\begin{array}{ll} Cl\cdot + CH_2{=}CF_2 \longrightarrow ClCH_2CF_2\cdot & (17) \\ ClCH_2CF_2\cdot + CF_3SCl \longrightarrow ClCH_2CF_2SCF_3 + Cl\cdot & (18) \end{array}\right\}\ \begin{array}{c}\text{mechanism}\\ \text{II}\end{array}$$

$$CF_3S\overset{|}{\underset{|}{C}}\overset{|}{\underset{|}{C}}\cdot + CF_3SCl \longrightarrow CF_3S\overset{|}{\underset{|}{C}}\overset{|}{\underset{|}{C}}SCF_3 + Cl\cdot \qquad (19)$$

$$Cl\overset{|}{\underset{|}{C}}\overset{|}{\underset{|}{C}}\cdot + CF_3SCl \longrightarrow Cl\overset{|}{\underset{|}{C}}\overset{|}{\underset{|}{C}}Cl + CF_3S\cdot \qquad (20)$$

such products were found. For example, in the reaction with hexafluoropropene, VI was isolated, and in the reaction with trifluorovinyl methyl ether, substantial quantities of XIV and XV were isolated. This dual-mechanism interpretation of the olefin–CF_3SCl radical-addition reaction affords an element of consistency in that in all

---

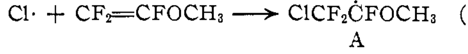
(9) R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 2800 (1957).

(10) In radical additions to hexafluoropropene it might be expected that the adding radical would attack the CF_2 group preferentially, and this has been found to be so in most cases. However, in the ultraviolet-initiated CF_3SH addition, attack occurs at both carbons, predominantly at the CF (ref. 5).

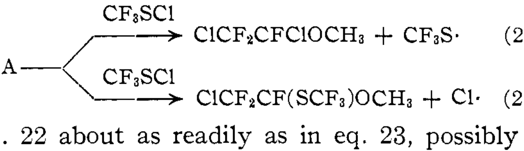
(11) Other examples of radical displacements on sulfur are known, *e.g.*, in the chain transfer by disulfides in vinyl polymerization.

cases, including the analogous thiol additions, the adding radical is required to attack predominantly the same carbon atom of the olefin.[12]

The $CF_3SCl-CF_2{=}CFOCH_3$ reaction needs some special comment. First of all, the kinetic chain must be extremely long since a few minutes of irradiation is sufficient to convert 0.2 mole of reactants to products. Another feature is the relatively high yields of the mixed products XIV (31%) and XV (11%), and bis-trifluoromethyl disulfide (31%). The high yield of XIV (the olefin–chlorine addition product) may indicate that the radical A, resulting from addition of a chlorine atom to the ether (eq. 21) chain transfers as in



$$Cl\cdot + CF_2{=}CFOCH_3 \longrightarrow \underset{A}{ClCF_2\dot{C}FOCH_3} \quad (21)$$



$$A \begin{cases} \xrightarrow{CF_3SCl} ClCF_2CFClOCH_3 + CF_3S\cdot & (22) \\ \xrightarrow{CF_3SCl} ClCF_2CF(SCF_3)OCH_3 + Cl\cdot & (23) \end{cases}$$

eq. 22 about as readily as in eq. 23, possibly because of steric difficulties involved in 23. Increased chain transfer *via* eq. 22 should increase the concentration of CF_3S radicals present in the reaction mixture (compared with the other CF_3SCl–olefin additions reported here) and this is reflected in the relatively high occurrence of bis-trifluoromethyl disulfide and XV. This increase in concentration of CF_3S radicals can also account for the predominance of XIII over XII.

Other interpretations of the results presented in this paper could be entertained; for example, the two adducts could result from attack by a single adding species (*i.e.*, $CF_3S\cdot$ or $Cl\cdot$) at both carbons of the double bond. A strong argument against this contention, as it would pertain to the CF_3S radical, is that in several of the corresponding thiol additions, in which it is certain that the CF_3S radical is the adding species, attack occurs at only one of the carbons. Also, since the predominant CF_3S orientations are opposite in the two reactions, one would be forced to the unlikely conclusion that the adding radical prefers one carbon of the double bond in the sulfenyl chloride reaction and the other carbon in the thiol reaction. The assumption that the two adducts arise from attack by the $Cl\cdot$ at both carbons of the double bond is more reasonable. The predominant orientations with respect to chlorine are consistent with previously studied radical additions. Opposing this argument, however, is the fact that appreciable quantities of mixed products were isolated in several cases. At the present state of our knowledge of radical sulfenyl chloride additions, these mixed products seem best explained by assuming two concurrent mechanisms.

A comparison of radical CF_3SCl additions with radical additions of other types of sulfur compounds is of interest. Hydrogen sulfide,[13] bisulfite ion,[13] sulfonyl halides,[13] thiols[13] and sulfur chloride pentafluoride[14] are known to undergo free-radical chain additions to olefins, and in each case the evidence indicates that the sulfur radical (*i.e.*, $HS\cdot$ from H_2S, $\cdot SO_3^-$ from HSO_3^-, $RSO_2\cdot$ from RSO_2X, $RS\cdot$ from RSH, and $\cdot SF_5$ from SF_5Cl) is the major adding or chain-carrying species. Thus, radical CF_3SCl additions appear to be unique in that the sulfur-containing radical is not the major adding species.

Experimental

I. Ultraviolet-initiated Additions of Trifluoromethanesulfenyl Chloride to Olefins. Method A. (Sealed Pyrex Tube).—All of these reactions were carried out in approximately the same manner. Details for the 1,1-difluoroethylene reaction follow.

A mixture of 24 g. (0.176 mole) of trifluoromethanesulfenyl chloride[15] and 11 g. (0.172 mole) of 1,1-difluoroethylene was sealed in a thick-walled Pyrex Carius tube and irradiated for 9.75 hours with a GE H-87-C3 lamp[16] placed 8 cm. from the liquid portion of the reaction mixture. Upon distillation of the reaction mixture there was obtained 25.65 g. of a fraction boiling at 23–82°, n^{25}_D 1.3495. A study of this fraction by gas chromatography showed the presence of trifluoromethyl 1,1-difluoro-2-chloroethyl sulfide (XVI) (54%), trifluoromethyl 2,2-difluoro-2-chloroethyl sulfide (XVII) (15%), bis-(trifluoromethyl) disulfide (17%) and an unidentified component (14%). Samples of the two 1:1 adducts were separated by prep-scale gas chromatography, and the properties and analyses are given in Table II.

Method B. (Atmospheric Pressure).—All of these reactions were carried out in approximately the same manner. The reactor consisted of a vertical quartz tube (5 × 25 cm.) fitted with a magnetic stirring bar, a gas inlet adapter, and a large acetone–Dry Ice condenser vented through an acetone–Dry Ice cooled trap. The ultraviolet source consisted of a helix-shaped (10 × 6 cm.), low pressure, mercury resonance lamp constructed of 37 mm. quartz tubing and powered by a 5000 volt–60 milliamp. transformer. The lamp was slipped over the quartz reaction tube so that its radiation impinged primarily upon the liquid portion of the reaction mixture. The details of a typical experiment involving the reaction of trifluoromethanesulfenyl chloride with trifluoroethylene follow.

Dry nitrogen was passed through the assembled apparatus for several minutes and then both the condenser and trap were filled with coolant. Trifluoroethylene (48 g., 0.585 mole) and 80 g. (0.585 mole) of trifluoromethanesulfenyl chloride were distilled in. Frosting on the outside of the reactor tube was prevented by allowing a slow stream of methanol to flow down the side of the reactor. The mixture was irradiated for a period of 2.75 hours and then distilled through a small spinning band still. There was obtained 79.35 g. of a fraction boiling at 44–64°, which was shown by gas chromatography to be composed of 80% of trifluoromethyl 2-chloro-1,1,2-trifluoroethyl sulfide (III) and 18% of trifluoromethyl 2-chloro-1,2,2-trifluoroethyl sulfide (II). Pure samples of these materials were obtained by preparative scale gas chromatography.

II. X-Ray-initiated Reaction of Trifluoromethanesulfenyl Chloride with Chlorotrifluoroethylene.—A mixture of 19 g. (0.139 mole) of trifluoromethanesulfenyl chloride and 16 g. (0.137 mole) of chlorotrifluoroethylene contained in a 100-ml. stainless steel pressure vessel was irradiated with X-rays for 4 hours at an average dose rate of approximately 30,000 rads per minute.[17] Upon distillation of the reaction mixture through a small spinning band still there was obtained 11.35 g. (33%) of a 1:1 adduct fraction distilling at 70–82°, n^{25}_D 1.3552. An examination of this material by gas chromatography indicated that it contained approximately the

---

[12] In most previously studied radical additions to unsymmetrical olefins, it has been found that the adding radicals, regardless of their nature, add predominantly to the same carbon of a particular olefin.

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

[14] J. R. Case, N. H. Ray and H. L. Roberts, *J. Chem. Soc.*, 2066, 2070 (1961).

[15] Prepared by the reaction of trichloromethanesulfenyl chloride and sodium fluoride as described by C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **25**, 2016 (1960).

[16] The output of this lamp is roughly 0.7 watt at 2200–2800 Å., 3.7 watts at 2800–3200 Å., 5.1 watts at 3200–4000 Å., and 8.9 watts at 4000–7600 Å.

[17] This experiment was carried out with the same equipment and by the same procedure as the X-ray experiments described in ref. 5.

TABLE V

GAS CHROMATOGRAPHIC ANALYSIS

Reaction mixture	Column packing	Col. temp., °C.	Helium flow rate, ml./min.	Product	Retention time, min.
$CF_2=CFH-CF_3SCl$	20% ethyl ester of Kel-F acid 8114, Columpak, 3.6 m. × 6 mm.	50	60	$CF_3SCFHCF_2Cl$ (II)	5.4
				CF_3SCF_2CFHCl (III)	8.9
$CF_2=CFCF_3-CF_3SCl$ (portion boiling at 100–120°)	20% diglyceride of ω-trifluorohexanoic acid, Columpak, 1.8 m. × 6 mm.	52 (preheater 100°)	80	$CF_3SCF_2CF(CF_3)SCF_3$ (VI)	2.75
				$Cl(C_3F_6)_2Cl$ (VIIa)	4.35
				$Cl(C_3F_6)_2Cl$ (VIIb)	5.35
$CH_2=CHCl-CF_3SCl$	20% diglyceride of ω-trifluorohexanoic acid, Columpak, 3.6 m. × 6 mm.	80	95	Unknown	9.3
				$CF_3SCH_2CHCl_2$ (XI)	9.95
				Unknown	11.4
				$CF_3SCHClCH_2Cl$ (X)	14.1
$CF_2=CFOCH_3-CF_3SCl$	30% D.C. Silicone 200 on firebrick (48–65 mesh), 2.7 m. × 6 mm.	125	40	CF_3SSCF_3	5.4
				$CH_3OCFClCF_2Cl$ (XIV)	13.6
				$CF_3SCF(OCH_3)CF_2Cl$ (XII)	16.9
				$CF_3SCF_2CFClOCH_3$ (XIII)	19.2
				$CF_3SCF_2CF(SCF_3)OCH_3$ (XV)	23.0
$CH_2=CF_2-CF_3SCl$	20% tetrakis-(1H,1H,5H-octafluoropentyl and 1H,1H,7H-dodecafluoroheptyl)-pyromellitate–firebrick, 1.8 m. × 6 mm.	62	34.5	CF_3SSCF_3	2.0
				Unknown	3.85
				$CF_3SCH_2CF_2Cl$ (XVII)	6.5
				$CF_3SCF_2CH_2Cl$ (XVI)	8.4

same ratio of isomers as that obtained in the ultraviolet-initiated experiment.

In an attempt to achieve the addition thermally, a mixture of 15 g. of trifluoromethanesulfenyl chloride, 15 g. of chlorotrifluoroethylene and 25 ml. of methylene chloride was heated at 100° for 6 hours. No product was obtained.

III. **Azonitrile-initiated Addition of Trifluoromethanesulfenyl Chloride to 1,1-Difluoroethylene.**—A mixture of 16 g. (0.117 mole) of trifluoromethanesulfenyl chloride, 7 g. (0.109 mole) of 1,1-difluoroethylene and 0.2 g. (0.00122 mole) of α,α′-azo-bis-(isobutyronitrile) was sealed under vacuum in a Carius tube and heated at 80° for 10 hours. The tube was opened and the contents allowed to warm to room temperature. There remained 18.73 g. of liquid residue. Examination of this residue by gas chromatography showed that it contained the same four compounds observed in the product obtained from the ultraviolet-initiated reaction described under I-A above and in approximately the same proportions.

Another experiment with 18 g. of trifluoromethanesulfenyl chloride and 9 g. of 1,1-difluoroethylene, but no α,α′-azobis-(isobutyronitrile), treated in the manner just described yielded no product.

IV. **The Thermal Reaction of Trifluoromethanesulfenyl Chloride and Vinyl Chloride.**—When these reactants were sealed in a Pyrex Carius tube, but neither irradiated nor heated, no reaction took place. A thermal reaction was achieved as follows. A mixture of 20 g. (0.146 mole) of trifluoromethanesulfenyl chloride, 10 g. (0.160 mole) of vinyl chloride and 25 ml. of acetonitrile was sealed in a Pyrex Carius tube and heated at 100° for 8 hours. The tube contents were distilled until a head temperature of 50° was reached. The distillation was interrupted, and the residue was poured into a large excess of water. The organic layer was separated, dried over anhydrous magnesium sulfate and distilled. There was thus obtained 4.82 g. (17%) of trifluoromethyl 2,2-dichloroethyl sulfide (XI) distilling at 114–115°, $n^{24}D$ 1.4123. A comparison of the proton nuclear magnetic resonance pattern showed that this compound was identical with authentic trifluoromethyl 2,2-dichloroethyl sulfide, prepared by the photochemical addition of trifluoromethanethiol to 1,1-dichloroethylene.

V. **The Ultraviolet-catalyzed Addition of Trifluoromethanethiol to 1,1-Dichloroethylene.**—A mixture of 60 g. (0.62 mole) of 1,1-dichloroethylene and 70 g. (0.685 mole) of trifluoromethanethiol was irradiated according to method B for 41 hours. The reaction mixture was distilled through a small spinning band still. There was obtained 20.71 g. (17%) of trifluoromethyl 2,2-dichloroethyl sulfide (XI) as a clear colorless liquid distilling at 115–116°, $n^{24}D$ 1.4162. There was a considerable quantity of higher boiling material which was not fractionated.

VI. **Ultraviolet-catalyzed Addition of Trifluoromethanethiol to Vinyl Chloride.**—A mixture of 15 g. (0.24 mole) of vinyl chloride and 25 g. (0.245 mole) of trifluoromethanethiol was irradiated according to method B for a period of 0.25 hour. Upon distillation of the reaction mixture through a small spinning band still there was obtained 31.9 g. (78%) of trifluoromethyl 2-chloroethyl sulfide distilling at 94–98° (mostly 98°), $n^{25}D$ 1.3939. The proof of structure of this material is the identity of its proton n.m.r. pattern with that of the 1:1 adduct obtained by the addition of trifluoromethanesulfenyl chloride to ethylene in acetonitrile.

Anal. Calcd. for $C_3H_4ClF_3S$: Cl, 21.6; F, 34.6. Found: Cl, 21.8; F, 34.8.

VII. **The Ultraviolet-catalyzed Chlorination of 1,2,2-Trifluoroethyl Trifluoromethyl Sulfide.**—Trifluoromethyl 1,2,2-trifluoroethyl sulfide[5] (63 g., 0.342 mole) was placed in a flask fitted with a gas inlet tube extending below the liquid surface and a reflux condenser vented through an acetone–Dry Ice cooled trap. While the mixture was being refluxed and irradiated with a GE H-87-C3 lamp placed as close to the flask as possible, chlorine was bubbled through for 5 hours. The accumulated trap contents were returned to the reaction vessel and the chlorination continued for 7 hours. Fractionation of the reaction mixture combined with the trap contents yielded 74 g. of a mixture of starting material and monochlorinated products (b.p. 36–68°), and 5.06 g. (6%) of crude trifluoromethyl 1,2-dichlorotrifluoroethyl sulfide (VIII) distilling at 68–86°, $n^{23}D$ 1.3581. A redistilled sample boiled at 84°, $n^{25}D$ 1.3560.

VIII. **Gas Chromatography Experiments.**—Most of the reaction mixtures were examined with a Perkin–Elmer fractometer 154-B. The details of the analyses are given in Table V. Preparative scale separations were carried out in the usual way, generally with a 1.8 m. × 2 cm. column, packed with the same packing used in the analytical columns.