

a much better accelerator than tetramethylurea, and even better than N-methylpyrrolidone, the most active of the saturated amides so far discovered. This expectation arose from the hypothesis² that selective solvation of sodium ion by amides primarily involves a region of high electron density in the π -orbital surrounding the amide oxygen atom. The planar geometry of N,N'-dimethylethyleneurea, with consequent maximum overlap of the p-orbitals of the sp^2 -hybridized N, C and O atoms, presents an ideal situation for producing a relatively high order of negative charge around the oxygen atom. The observation that N,N'-dimethylethyleneurea is twice as effective in accelerating the alkylation reaction as its acyclic analog tetramethylurea accords with expectation. That it is only slightly better than N-methyl-2-pyrrolidone indicates that the second nitrogen lone pair is not equal to the first in contributing to the π -orbital electron density of the oxygen atom.

Although it is an effective catalyst, DMSO, like THF but unlike DMF, increases its participation with increasing concentration. DMSO has already been found¹ to differ from DMF in that its presence resulted in a measurable increase in activation enthalpy of the alkylation reaction. In view of their differing geometries (DMF is predominantly planar at room temperature and DMSO is pyramidal) and probable differing modes of electron delocalization (DMF uses a $p\pi$ -orbital while DMSO very likely uses a $d\pi$ -orbital²), the

discovery of differences in their behavior as cation solvators is not surprising.

One more conclusion can be derived from the present work. Previously,¹ a mechanism for solvent acceleration was proposed involving specific solvation of the cation by the effective additive with resulting dissociation of the high molecular weight ion pair aggregate shown to be present in benzene solution. Production of a low molecular weight solvated species would then result in the observed acceleration of alkylation rate. The extent of acceleration would depend on the intrinsic cation-solvating capacity of the additive and on its concentration, since these two factors would determine the position of the equilibrium between ion pair aggregate and reactive solvated species. The present work shows that with increasing concentrations of two very effective additives (DMF and DMSO) no rate maximum is achieved. This means that, if the proposed mechanism is correct, some high molecular weight aggregate must still be present even in nearly pure DMF and DMSO, at the concentrations (*ca.* 0.1 *M*) of sodio-derivative employed. This appears, *a priori*, to be rather unlikely. Appropriate physical measurements should settle the question, and these are being planned.

Acknowledgments.—The author is indebted to Mr. Paul Sanders and Miss J. Szyszkowska for the statistical analyses and to Mr. N. F. Ryan for technical assistance.

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The Free Radical Addition of Trifluoromethanethiol to Fluoroolefins

By JOHN F. HARRIS, JR., AND F. W. STACEY

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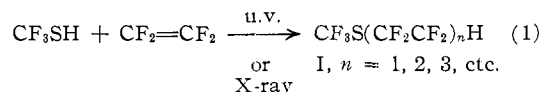
Trifluoromethanethiol adds readily to terminal fluoroolefins under the influence of X-rays or ultraviolet radiation. The addition to hexafluoropropylene gives both possible 1:1 adducts in nearly equal amounts, in contrast to previously studied radical additions to this olefin which have been reported to give only one product.

Introduction.—Although considerable work has been reported on the free radical addition of a variety of substances to fluoroolefins,¹ there appears to be very little in the literature about the free radical addition of thiols to fluoroolefins. Apparently, the only reports concern the benzoyl peroxide-initiated addition of thiophenol to perfluoro-1,5-hexadiene^{2a} and the addition of ethanethiol to tetrafluoroethylene with the same initiator.^{2b} The structures of the products were not determined. The free radical addition of thiols to hydrocarbon olefins is well known.³ There have been a few reports of the base-catalyzed addition of thiols to fluoroolefins.^{2a,4} Apparently, there is

no report of the addition of a fluorinated thiol to a fluoroolefin.

Results.—We have found that the addition of thiols and more particularly trifluoromethanethiol to tetrafluoroethylene, chlorotrifluoroethylene, trifluoroethylene, hexafluoropropylene, 1,1-difluoroethylene and trifluorovinyl methyl ether (all *terminal* fluoroolefins) proceeds smoothly under the influence of ultraviolet radiation or X-rays. With two olefins, hexafluoropropene and trifluoroethylene, both possible 1:1 adducts were obtained. The results are summarized in equations 1–10.

Tetrafluoroethylene



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

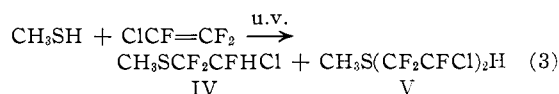
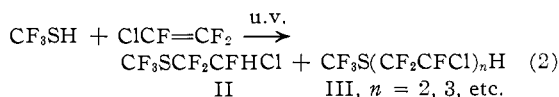
(2) (a) W. T. Miller, U. S. Patent 2,864,867 (1958); (b) W. E. Hanford, U. S. Patent 2,443,003 (1948).

(3) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 313–326.

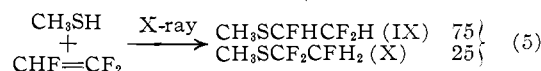
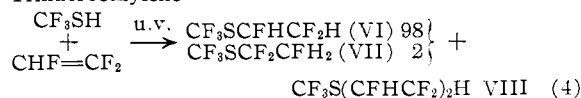
(4) (a) I. L. Knunyants and A. V. Fokin, *Bull. acad. sci. USSR Div. Chem. Sci. (Eng. Trans.)*, 279 (1952); (b) I. L. Knunyants,

A. I. Shechotikhin and A. V. Fokin, *ibid.*, 255 (1953); (c) K. E. Rapp, *et al.*, *J. Am. Chem. Soc.*, **72**, 3642 (1950).

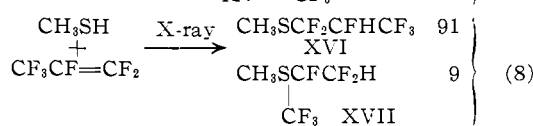
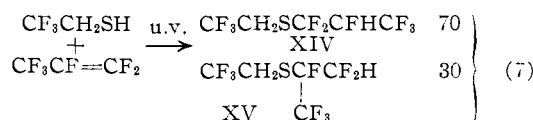
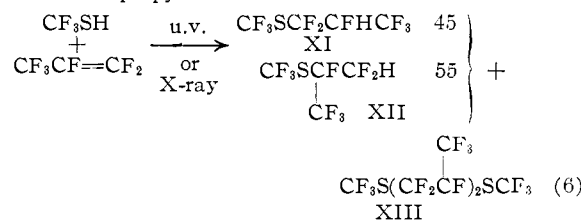
Chlorotrifluoroethylene



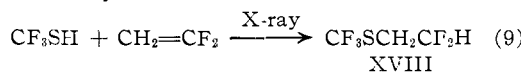
Trifluoroethylene



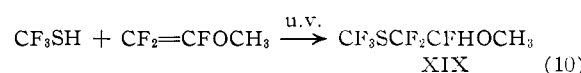
Hexafluoropropylene



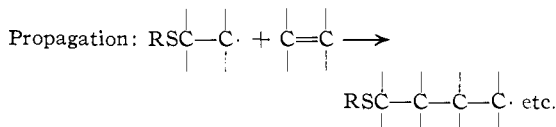
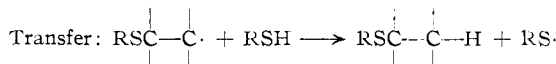
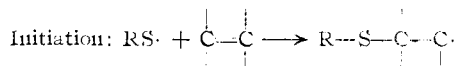
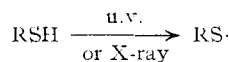
1,1-Difluoroethylene



Trifluorovinyl methyl ether



By contrast, little or no adduct was formed on ultraviolet irradiation of a mixture of trifluoromethanethiol and perfluoro-2-butene, an *internally* unsaturated fluoroolefin. All of the reactions reported herein can be conveniently represented by the conventional radical chain type process



Reaction conditions and results of each experiment are presented in Table II. The physical properties and analytical data for the products are re-

ported in Table III. The proton nuclear magnetic resonance patterns of the products are contained in Table IV.

Discussion.—Several factors have been considered as determining the direction of radical additions to olefins. Among these are steric factors, polar factors⁵ and the stability of the intermediate radicals. Based on studies of the ultraviolet-catalyzed addition of hydrogen bromide and of trifluoromethyl iodide to a series of olefins (mostly fluoroolefins), Haszeldine and co-workers⁶ concluded that polar effects and steric effects are of minor importance and that the direction of addition is determined primarily by the relative stabilities of the intermediate radicals. Thus, the product formed is that resulting from the more stable of the two possible intermediate radicals. In this scheme, the expected order (tert. > sec. > primary) of radical stability obtains.⁷ In Haszeldine's hands, this concept of intermediate radical stability provided an adequate correlation of nearly all the additions studied. The lone anomalous case was 2-H-pentafluoropropylene to which trifluoromethyl iodide and hydrogen bromide added in opposite directions.⁸

Figure 1 summarizes the results obtained in the present study with respect to the direction of addition of thiyl radicals to the unsymmetrical fluoroolefins.

$\text{CF}_3\text{S}\cdot$	$\text{CF}_3\text{CF}=\text{CF}_2$ (55) (45)	$\text{CHF}=\text{CF}_2$ (98) (2)	$\text{CF}_2=\text{CH}_2$ (0) (100)
	$\text{CF}_2=\text{CFCI}$ (100) (0)	$\text{CF}_2=\text{CFOCH}_3$ (100) (0)	
$\text{CF}_3\text{CH}_2\text{S}\cdot$	$\text{CF}_3\text{CF}=\text{CF}_2$ (30) (70)		
$\text{CH}_3\text{S}\cdot$	$\text{CF}_3\text{CF}=\text{CF}_2$ (9) (91)	$\text{CHF}=\text{CF}_2$ (75) (25)	

Fig. 1.

Most of the radical addition reactions of thiols to fluoroolefins reported here can be correlated on the basis of the intermediate radical stability postulates of Haszeldine and co-workers. Thus, in all

TABLE I

RSH R =	ISOMER DISTRIBUTION IN THIOL ADDITIONS TO HEXAFLUOROPROPYLENE	
	RSCF ₂ CFHCF ₃ (A), %	RSC(CF ₃)FCF ₂ H (B), %
CF ₃	45	55
CF ₃ CH ₂	70	30
CH ₃	91	9

(5) W. A. Waters, "Chemistry of Free Radicals," 2nd ed., Oxford University Press, 1948, pp. 182-183, suggested that radicals are electrophilic by nature and accordingly should add to the carbon atom of the double bond with the highest electron density. This scheme assumes that the polarization of the double bond is the same in radical additions as in ionic additions.

(6) R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 2193 (1957), and previous papers.

(7) The designations "tertiary," "secondary" and "primary" are determined solely by the number of atoms or groups other than hydrogen on the carbon atom bearing the odd electron, and do not necessarily refer to the carbon skeleton. Substituents differ in their stabilizing ability, e.g., H < F < Cl, CF₃, RO, etc., and thus a primary or secondary radical may actually be more stable than a particular secondary or tertiary one in certain cases (R. N. Haszeldine and E. R. Steele, *J. Chem. Soc.*, 2193 (1957)).

(8) R. N. Haszeldine and B. R. Steele, *ibid.*, 3005 (1955).

TABLE II
 ADDITION OF THIOLS TO FLUOROOLEFINS

Olefin, g., mole	Thiol, g., mole	Initiator	Time	Products Isolated	Yield, %
CF ₂ =CF ₂ , 40, 0.4	CF ₃ SH, 19, 0.186	X-rays, 8000 ^a	3.5 hr.	CF ₃ SCF ₂ CF ₂ H CF ₃ S(CF ₂ CF ₂) ₂ H CF ₃ S(CF ₂ CF ₂) ₃ H	30 14 5
CF ₂ =CF ₂ , 37, 0.37	CF ₃ SH, 53.3, 0.52	X-rays, ~8000 ^a	3.0 hr.	CF ₃ SCF ₂ CF ₂ H CF ₃ S(CF ₂ CF ₂) ₂ H CF ₃ S(CF ₂ CF ₂) ₃ H	53 17.3 3.6
CF ₂ =CF ₂ , 10, 0.1	CF ₃ SH, 15, 0.15	U.v.	7 days	CF ₃ SCF ₂ CF ₂ H	49
CF ₂ =CFCl, 40, 0.343	CF ₃ SH, 20, 0.196	U.v.	2 days	CF ₃ SCF ₂ CFCIH CF ₃ S(CF ₂ CFCI) ₂ H CF ₃ S(CF ₂ CFCI) ₃ H	62 20 3
CF ₂ =CFCl, 95, 0.822	CH ₃ SH, 23, 0.478	U.v.	2.5 hr.	CH ₃ SCF ₂ CFCIH CH ₃ S(CF ₂ CFCI) ₂ H	84 4.5
CF ₂ =CFH, 50, 0.61	CF ₃ SH, 76, 0.745	U.v.	1.25 hr.	CF ₃ SCHFCF ₂ H CF ₃ SCF ₂ CFH ₂ CF ₃ S(CFHCF ₂) ₂ H	83 Trace 3.5 ^b
CF ₂ =CFH, 27, 0.33	CF ₃ SH, 53, 0.52	X-ray, 16,000 ^a	3 hr.	CF ₃ SCHFCF ₂ H	64
CF ₂ =CFH, 21, 0.25	CH ₃ SH, 40, 0.83	X-ray, 13,000 ^a	4 hr.	CH ₃ SCHFCF ₂ H (75) CH ₃ SCF ₂ CFH ₂ (25)	60
CF ₃ CF=CF ₂ , 60, 0.40	CF ₃ SH, 15, 0.147	U.v.	4 days	CF ₃ SCF ₂ CFHCF ₃ (45) CF ₃ SC(CF ₃)FCF ₂ H (55)	56
CF ₃ CF=CF ₂ , 37, 0.247	CF ₃ SH, 34.0, 0.333	U.v.	40 hr.	CF ₃ S(CF ₂ C(CF ₃)F) ₂ SCF ₃ CF ₃ SCF ₂ CFHCF ₃ (43) CF ₃ SC(CF ₃)FCF ₂ H (57)	13 ^c 73
CF ₃ CF=CF ₂ , 14.5, 0.097	CF ₃ SH, 10.5, 0.103	X-ray, 40,000 ^a	6 hr.	CF ₃ SCF ₂ CFHCF ₃ (47) CF ₃ SC(CF ₃)FCF ₂ H (53)	57
CF ₃ CF=CF ₂ , 56, 0.373	CF ₃ CH ₂ SH, 17, 0.146	U.v.	3 days	CF ₃ CH ₂ SCF ₂ CFHCF ₃ (70) CF ₃ CH ₂ SC(CF ₃)FCF ₂ H (30)	65
CF ₃ CF=CF ₂ , 56, 0.36	CH ₃ SH, 48.0, 1.00	X-ray, 20,000- 40,000 ^a	5.5 hr.	CH ₃ SCF ₂ CFHCF ₃ (91) CH ₃ SC(CF ₃)FCF ₂ H (9)	11
CF ₂ =CH ₂ , 14, 0.218	CF ₃ SH, 27, 0.265	X-ray, 16,000 ^a	3 hr.	CF ₃ SCH ₂ CF ₂ H	72
CF ₂ =CFOCH ₃ , 30, 0.268	CF ₃ SH, 25, 0.245	U.v.	15 min.	CF ₃ SCF ₂ CFHOCH ₃	71

^a Rad./min. ^b Crude.

 TABLE III
 THIOL-FLUOROOLEFIN ADDUCTS

Compound	B.p., °C. (mm.)	nd ^a	Formula	Carbon, %		Hydrogen, %		Fluorine, %		Sulfur, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
CF ₃ SCF ₂ CF ₂ H	33		C ₃ HF ₇ S					65.8	65.4	15.9	15.9
CF ₃ S(CF ₂ CF ₂) ₂ H	84		C ₆ HF ₁₁ S					69.1	69.1	10.6	10.4
CF ₃ S(CF ₂ CF ₂) ₃ H	127-129	1.3008	C ₇ HF ₁₅ S							8.0	7.8
CF ₃ SCF ₂ CFCIH	66-67	1.3339- 1.3341	C ₃ HClF ₆ S	16.5	16.7	0.5	0.6	52.1	52.3		
CF ₃ S(CF ₂ CFCI) ₂ H	145-146	1.3627	C ₅ HCl ₂ F ₆ S	17.9	18.1	.3	.5	51.0	51.3	9.6	9.5
CF ₃ S(CF ₂ CFCI) ₃ H	87-90 (11)	1.3791	C ₇ HCl ₃ F ₁₂ S	18.6	19.1	.2	.4	50.4	50.1	7.1	7.4
CH ₃ SCF ₂ CFHCl	51 (98)	1.4024	C ₃ H ₄ ClF ₃ S					34.6	34.8	21.6 ^d	21.6 ^d
CH ₃ S(CF ₂ CFCI) ₂ H	57 (7)	1.4061	C ₅ H ₄ Cl ₂ F ₆ S					40.6	39.8	25.2 ^d	24.9 ^d
CF ₃ SCHFCF ₂ H	52	1.3112- 1.3119	C ₃ H ₂ F ₆ S					61.9	62.1	17.4	17.3
CF ₃ S(CFHICF ₂) ₂ H	100-102	1.3213	C ₅ H ₃ F ₉ S					64.3	64.0	12.0	12.2
CH ₃ SCHFCF ₂ H	^b	1.3889 ^e	C ₃ H ₃ F ₃ S					43.9	44.2	24.6	24.5
CH ₃ SCF ₂ CFH ₂	^c	1.3779 ^e	C ₃ H ₃ F ₃ S					43.9	44.4	24.6	24.5
CF ₃ SCF ₂ CFHCF ₃	53-54		C ₄ HF ₉ S					67.9	68.1	12.7	12.7
CF ₃ SC(CF ₃)FCF ₂ H	55		C ₄ HF ₉ S					67.9	67.8	12.7	13.0
CF ₃ S(C(CF ₃)FCF ₂) ₂ SCF ₃	156-159	1.3314 ^f	C ₈ F ₁₈ S ₂					68.0	68.2	12.8	12.1
CF ₃ CH ₂ SCF ₂ CFHCF ₃	105	1.3208 ^f	C ₆ H ₃ F ₉ S					64.3	63.9	12.0	12.5
CF ₃ CH ₂ SC(CF ₃)FCF ₂ H	98	1.3220 ^f	C ₅ H ₂ F ₆ S					64.3	64.8	12.0	12.0
CH ₃ SCF ₂ CFHCF ₃ 91% CH ₃ SC(CF ₃)FCF ₂ H 9% ^g	84.5-86	1.3400- 1.3393	C ₄ H ₄ F ₆ S					57.5	57.1	16.2	16.5
CF ₃ SCH ₂ CF ₂ H	58	1.3270	C ₃ H ₃ F ₆ S	21.7	22.0	1.8	2.0	57.2	57.3	19.3	19.4
CF ₃ SCF ₂ CFHOCH ₃	102	1.3303- 1.3307	C ₄ H ₄ F ₆ OS	22.4	22.7	1.9	2.0	53.2	53.1	15.0	15.3

^a Temperature was 25° C. unless otherwise indicated. containing 80-90% of it distilled at 39-42° (85 mm.)

^b A boiling point on the pure isomer was not obtained. A fraction

containing 80-90% of it distilled at 30-32.5° (85 mm.)

^c A boiling point on the pure isomer was not obtained. A fraction

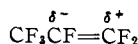
containing 80-90% of it distilled at 30-32.5° (85 mm.)

^d Chlorine, % 23°. ^f 24°.

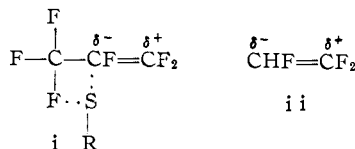
those cases where a single 1:1 adduct is obtained (*i.e.*, the additions to chlorotrifluoroethylene, vinylidene fluoride and trifluorovinyl methyl ether) the products are those deriving from the predicted more stable intermediate radicals. These products are also the ones which would be predicted on the basis of steric considerations. However, in those cases where both possible adducts are obtained (*viz.*, thiol additions to hexafluoropropylene and trifluoroethylene) it appears that other effects must be considered. For example, in the additions to hexafluoropropylene there is a large variation in the isomer distribution depending upon the thiol employed (Table I).

Similarly, in the two additions to trifluoroethylene, there is a large difference in the isomer distribution between methanethiol (75:25) and trifluoromethanethiol (98:2).⁹ It is thus apparent that the ratio of isomers found is strongly dependent upon the nature of the adding radical.

We would like to point out that in the thiol additions to hexafluoropropylene it is possible to make a correlation between the product distribution and the *relative* electrophilicities of the thiyl radicals. Although no quantitative electrophilicity data seem to be available, consideration of the comparative inductive effects of the CF₃, CF₃CH₂ and the CH₃ groups leads to the conclusion that the relative electrophilicities of the three thiyl radicals involved in these reactions would be in the order CF₃S· > CF₃CH₂S· > CH₃S·. This is the same as the order of occurrence of isomer B (Table I), the formation of which requires the attachment of the radical to the negatively¹⁰ polarized carbon of the double bond



This formation of isomer B (the less favored isomer on steric grounds and on the basis of Haszeldine's intermediate radical stability concept) may also be assisted by the negative screen afforded by the adjacent trifluoromethyl group. Thus, in the transition state, interaction of the thiyl radical with (1) the relatively negative carbon of the double bond, and (2) the fluorine atoms on the CF₃ group may be envisioned as *i*. Both of these effects would be expected to favor formation of isomer B, and would be expected to be stronger with more highly electrophilic radicals.



The isomer ratios obtained in the additions of trifluoromethanethiol and methanethiol to trifluoroethylene can also be correlated with the relative electrophilicities of the thiyl radicals. The more electrophilic CF₃S radical should be more inclined than the CH₃S radical to attack the negative carbon of trifluoroethylene, *ii* thus further

(9) Haszeldine and Steele, *J. Chem. Soc.*, 2800 (1957), have reported less drastic differences in isomer distribution for the additions to trifluoroethylene of HBr (ratio 58:42) and of CF₃I (ratio 80:20).

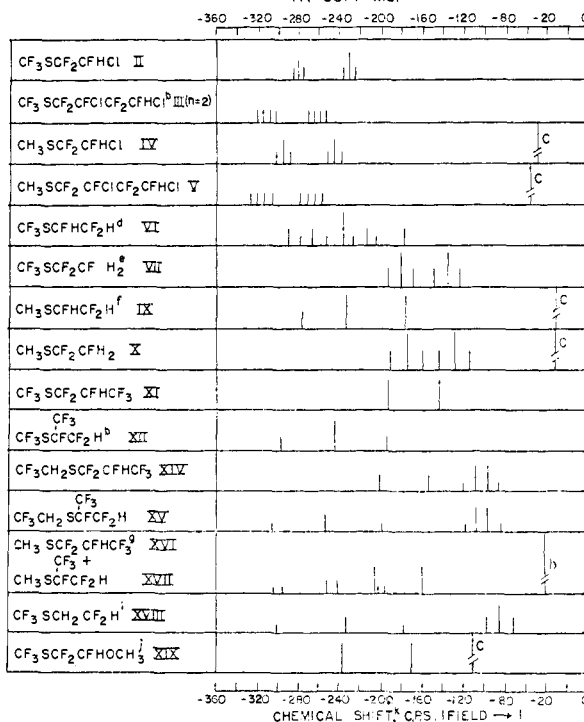
(10) It is assumed here that the polarization of hexafluoropropylene is the same in radical additions as it is in ionic additions.

favoring the isomer which in this case is favored on the basis of intermediate radical stability.¹¹

The difference in electrophilicity among radicals is probably not great enough to be of importance in free radical additions generally; in fact, in the reaction of chlorotrifluoroethylene with trifluoromethanethiol none of the isomer favored on the basis of the electrophilic trifluoromethylthiyl radical adding to the more negative carbon was detected. However, in the light of the present results, it is tempting to speculate that in situations where the steric requirements and the stabilities of the intermediate radicals do not differ greatly for the two possible directions of addition, the product (or product mixture) may be determined by the electronic character of the incoming radical.

Identification of Products.—In those cases where two isomers were obtained, relative proportions were estimated from gas chromatograms and from nuclear magnetic resonance patterns, and pure samples of each were obtained by preparative scale gas chromatography. All of the structure assignments were made on the basis of studies of the proton nuclear magnetic resonance patterns (Table IV).

TABLE IV
PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA
AT 56.4 MC.^a



^a 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 9,395 gauss. The scale of peak heights in the table varies from one spectrum to another in the interest of legibility. ^b Each component of this pattern was further split to a doublet. ^c This resonance is for the methyl group. If it were drawn

(11) It can be argued that these results with trifluoroethylene can be related to steric factors, since the CF₃S radical should experience more difficulty than the CH₃S· in approaching the CF₃ group. However, in view of our findings with hexafluoropropylene-thiol additions, we do not consider that the steric factor is predominant.

to scale, it would be several times its indicated height. ^d Each component of the pair of triplets is split to a doublet. Each component of the large triplet is split to a doublet. ^e This pattern was obtained from a sample which contained about 15% of the designated compound. The remainder of the sample was the other isomer (previous pattern), and thus the observed pattern of this sample also contained the resonances of the previous pattern. ^f The resonances at -177 and -232 c.p.s. are clearly the doublet due to the hydrogen on the CF. The resonance at -277 c.p.s. is the left-hand member of the triplet due to the hydrogen on the CF₂. The other two components of this triplet are hidden by the doublet resonances at -177 and -232 c.p.s. The exact frequencies of these components of the triplet could not be determined, and no attempt has been made to show them on the graph. ^g There was considerable overlap of the doublet resonance at -204 c.p.s. and the triplet components at -194 and -202 c.p.s. ^h The resonance at -41 c.p.s. includes the methyl resonances of both isomers. ⁱ Each component of the broad triplet (CH) is further split to a triplet. Each component of the other triplet (CH₂) is further split to a doublet. ^j Each component of the doublet is further split to a triplet. ^k Spectra were measured in terms of displacement in cycles per second (c.p.s.) from the proton resonance of acetone. Negative frequency displacements indicate resonances occurring at lower field relative to the reference.

The resonance of the methenyl hydrogen atom in each of the compounds II, IV, XI, XIV, XVI and XIX is initially a doublet and thus consistent with the structures as written. This splitting would not be consistent with the other possible structures.

In the 2:1 telomers from chlorotrifluoroethylene with trifluoromethanethiol (III) and methanethiol (V), the methenyl hydrogen resonance is also a doublet. This, combined with the structure determined for the 1:1 adducts (II and IV), supports the structures as written.

The resonance of the methenyl hydrogen atom in compounds XII, XV, XVII and XVIII is initially a triplet, thus consistent with the structures as written. These patterns would be inconsistent with the alternative structures.

The patterns of the 1:1 adducts from trifluoroethylene and trifluoromethanethiol (VI and VII) allow an unambiguous assignment since one pattern shows the presence of 2 kinds of hydrogen (VI) and the other shows only one kind (VII). The observed splittings are consistent with this assignment. Similar considerations obtain in the assignment of structure to the trifluoroethylene-methanethiol adducts IX and X.

Experimental

I. Reactions of Thiols with Fluoroolefins. A. Ultra-violet Radiation Initiated Reactions. 1. Atmospheric Pressure.—All of these reactions were carried out in approximately the same manner. The reactor consisted of a vertical quartz tube (2" × 10") 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 (4" × 2.5") low pressure mercury lamp constructed of 37 mm. quartz tubing and powered by a 5000 volt 60 milli-amp 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 reaction of trifluoromethanethiol with chlorotrifluoroethylene are given.

Dry nitrogen was passed through the assembled apparatus for several minutes, and then both the condenser and trap were filled with coolant. Twenty grams (0.196 mole) of trifluoromethanethiol and 40 g. (0.343 mole) of chlorotrifluoroethylene 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 2 days and then distilled through a small spinning band still. There was obtained 26.6 g. (62%) of the 1:1 adduct (b.p. 66-67°), 17.3 g. (20%) of the 2:1 adduct (b.p. 142-144°) and 7.9 g. (3%) of the 3:1 adduct (b.p. 80-90° (11 mm.)). Higher boiling material was obtained which did not fractionate cleanly, but which probably consisted of higher telomers (4:1, 5:1 etc.).

2. Sealed Pyrex Tube.—In view of the low boiling point of tetrafluoroethylene, the ultraviolet-induced reaction of this olefin with trifluoromethanethiol was carried out in a sealed tube.

A mixture of 10 g. (0.10 mole) of tetrafluoroethylene and 15 g. (0.15 mole) of trifluoromethanethiol was condensed into a thick walled Pyrex Carius tube cooled in liquid nitrogen. The tube was evacuated and sealed. The reaction mixture was then irradiated for a period of 7 days with a General Electric H85-C3 lamp placed at a distance of 1 inch from the part of the tube containing the liquid portion of the reaction mixture. Upon distillation of the reaction mixture, there was obtained 10.0 g. (49%) of trifluoromethyl 1,1,2,2-tetrafluoroethyl sulfide (b.p. 26-31°). There remained a residue of 4.4 g. which presumably consisted of the higher telomers (2:1, 3:1, etc.).

B. X-Ray Initiated Reactions.—All of these reactions were carried out in the same manner. The details of a typical experiment involving reaction of trifluoromethanethiol with 1,1-difluoroethylene follow:

A mixture of 27 g. (0.275 mole) of trifluoromethanethiol and 14 g. (0.218 mole) of 1,1-difluoroethylene was put into a 100-ml. stainless steel cylinder. The mixture was irradiated with X-rays for 3 hours at an average dose rate of approximately 16,000 rads/minute.¹² Volatiles were bled off and the residue (30 g.) was distilled through a small spinning band still. There was obtained 26 g. (72%) of trifluoromethyl 2,2-difluoroethyl sulfide distilling at 55-58° (mostly 58°, *n*_D²⁰ 1.3270-1.3276).

II. Gas Chromatography Experiments.¹³ A. Hexafluoropropylene-Thiol Adducts.—The 1:1 adduct fractions were examined with a Perkin-Elmer Fractometer 154-B. The column was constructed from a 6' × 0.25" piece of copper tubing and packed with a mixture consisting of 20% of the diglyceride of ω-trifluoroheptanoic acid¹⁴ and 40-60 mesh Columapak. The details of the analyses are shown in Table V.

TABLE V

Reaction product	Column temp., °C.	Pre-heater temp., °C.	Helium flow rate, ml./min.	Back press., lb.	Retention time, min.
CF ₃ SH—	40	55	40	5	XII 5.35
CF ₂ =CFCF ₃					XI 6.7
CF ₃ CH ₂ SH—	79	100	80		XV 5.2
CF ₂ =CFCF ₃					XIV 8.3
CH ₃ SH—	41		100	50	XVII 11.0
CF ₂ =CFCF ₃					XVI 14.6

The isomers XI and XII were separated with a 6' × 0.75" column packed with 25% of the diglyceride of ω-trifluoroheptanoic acid on firebrick. The temperature was 40° and the helium flow rate was 600 ml./minute. Samples of 0.4 ml. were used and the appropriate fractions were collected in traps cooled with Dry Ice.

Separation of XIV and XV was accomplished with the same equipment as described for the separation of XI and XII. The temperature was 75° and the helium flow rate was 1100 ml./minute.

(12) 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.

(13) We are indebted to Mrs. A. B. Richmond and Mr. J. W. Robson of this Laboratory for most of the gas chromatography experiments.

(14) Prepared from ω-trifluoroheptanoic acid and glycerol by Dr. C. M. Langkammerer of this Laboratory; *n*_D²⁰ 1.4040. *Anal.* Calcd. for C₁₅H₂₂F₆O₂: C, 43.4; H, 5.6; F, 28.8. Found: C, 45.4; H, 5.0; F, 27.7.

B. Trifluoroethylene-Methanethiol Adducts.—These isomers (IX and X) were separated with a $13' \times 0.75''$ column packed with a 3:7 mixture of Dow Corning Silicone 200 (50 centistokes) and 48-65 mesh fire brick. The column temperature was 80-90°.

Starting Materials.—2,2,2-Trifluoroethanethiol was prepared by the reductive thiolation of trifluoroacetaldehyde hydrate as described by Harris and Sheppard.¹⁵

(15) J. F. Harris, Jr., and W. A. Sheppard, *J. Org. Chem.*, **26**, in press (1961).

[CONTRIBUTION FROM THE ORGANIC CHEMICALS DIVISION, MONSANTO CHEMICAL CO., ST. LOUIS, MO.]

Ozone Oxidation of Nucleophilic Substances. I. Tertiary Phosphite Esters¹

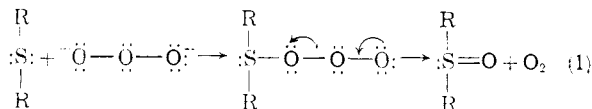
BY QUENTIN E. THOMPSON

RECEIVED JUNE 20, 1960

Triaryl and trialkyl phosphites were oxidized rapidly and quantitatively to the corresponding phosphates by ozone. Trialkyl phosphites showed exact 1:1 proportions at high ester dilution, but in concentrated solution two moles was oxidized by one mole of ozone. Similar 2:1 proportions were observed in all cases with triaryl phosphites provided ozone was added to the phosphite at temperatures above -5°. At -70°, ozone and triaryl phosphites formed 1:1 adducts. The n.m.r. spectrum of the P³¹ nucleus in (PhO)₃P-O₃ showed a shift of $+63 \pm 1$ p.p.m. indicating probable pentacovalency. The cyclic structure III has been tentatively assigned. Treatment of the adduct with excess trialkyl phosphite gave one mole of triaryl phosphate and essentially two moles of trialkyl phosphite. Dimethyl sulfide and tributylphosphine were similarly oxidized. Utilization of more than one of the oxygen atoms in ozone was also observed upon addition of ozone to phosphines or dialkyl sulfides in concentrated solution.

The importance of ozone as a carbon-carbon double bond reagent has overshadowed its role as an oxidizing agent for other organic functional groups although nucleophilic substances such as organic amines, sulfides and phosphines are known to undergo facile ozone oxidation. Unselective oxidative decomposition of primary amines by ozone has been known for many years.^{2,3} Generally, trialkylamines are converted to the corresponding amine oxides.²⁻⁵ Dialkyl, arylalkyl and some diaryl sulfides are readily oxidized to their corresponding sulfoxides and sulfones.^{4,6-10} Various other sulfur compounds are also oxidized smoothly with ozone.¹⁰ Triphenylphosphine and triphenylarsine have been converted to their respective oxides in high yields.⁴

These reactions have in common as their initial step the electrophilic attack of ozone upon an unshared electron pair of the amine, sulfide, etc. The mechanism presently accepted¹¹ for this type of oxidation is shown as follows for dialkyl sulfides.⁹ To the extent that a 1:1 relationship



occurs this formulation is satisfactory. When substantial deviation from this ratio is observed, *i.e.*, when more than one atom of oxygen per ozone molecule is placed upon the substrate, the adequacy of the present scheme comes under question.

(1) A preliminary report of some of this work has appeared in *Chemistry & Industry*, 121 (1959).

(2) W. Strecker and H. Thienemann, *Ber.*, **53**, 2096 (1920).

(3) W. Strecker and M. Baltes, *ibid.*, **54**, 2693 (1921).

(4) L. Horner, H. Schaefer and W. Ludwig, *ibid.*, **91**, 75 (1958).

(5) A. Maggiolo and S. Niegowski, *Advances in Chem. Ser.*, **21**, 202 (1959).

(6) H. Böhme and H. Fischer, *Ber.*, **75**, 1310 (1942); A. Meuwisen and H. Gebhardt, *ibid.*, **70**, 796 (1937).

(7) C. C. Price and O. H. Bullitt, *J. Org. Chem.*, **12**, 238 (1947).

(8) H. Boer and E. C. Kooyman, *Anal. Chim. Acta*, **5**, 550 (1951).

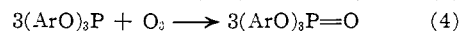
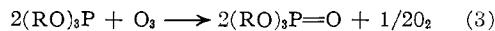
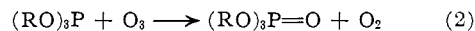
(9) A. Maggiolo and E. A. Blair, *Advances in Chem. Ser.*, **21**, 200 (1959).

(10) D. Barnard, *J. Chem. Soc.*, 4547 (1957).

(11) F. S. Bailey, *Chem. Revs.*, **58**, 925 (1958).

In the case of sulfides, serious discrepancies are to be noted in ozone reaction proportions between the observation of Maggiolo⁹ and Horner⁴ on the one hand and Barnard¹⁰ and Boer and Kooyman⁸ on the other. The former have, under their experimental conditions, observed the 1:1 ratio upon which the simple mechanism 1 was based. The latter workers, and in particular Barnard,¹⁰ have observed that significantly less ozone is required to effect the R₂S → R₂SO₂ transformation than the two moles required by 1. These discrepancies can now be accounted for as a result of observations made in this Laboratory while investigating the ozone oxidation of another class of nucleophilic compounds, namely, tertiary phosphite esters.¹²

Both triaryl and trialkyl phosphites were found to be rapidly and quantitatively oxidized to their corresponding phosphates under mild conditions. Unexpectedly, one, two or, in certain special cases with triaryl phosphites, essentially all three of the oxygen atoms of ozone could be utilized depending on experimental factors. Thus, the over-all proportions could in the various cases correspond to equations (2), (3) and (4)



When the lower trialkylphosphites (R = CH₃, *iso*-C₃H₇ and *n*-C₄H₉) were oxidized in the conventional manner by addition of an ozone-oxygen stream to a cold solution of the phosphite, uptake of ozone was rapid. Absorption ceased abruptly at the end of the reaction. Ozone consumption for the various oxidations amounted to 65-95 mole per cent. of that required on a 1:1 stoichiometric basis. It was apparent from these experiments that the proportions varied between 1:1 and 2:1 depending on the concentration of the

(12) Oxidations of tertiary phosphites to their corresponding phosphates have been effected by a variety of other oxidizing agents; *cf.* J. R. Cox and F. H. Westheimer, *J. Am. Chem. Soc.*, **80**, 5441 (1958), and references cited therein.