Trifluoromethylthioalkanes, -olefins, and -acetylenes

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A variety of poly(trifluoromethylthio) compounds, including tetrakis(trifluoromethylthio)methane, tetrakis(trifluoromethylthio)ethylene, and bis(trifluoromethylthio)acetylene has been synthesized. The ethylene, prepared by pyrolysis of the methane, is easily attacked by nucleophiles, *e.g.*, methoxide and aliphatic amines. The acetylene also reacts with nucleophiles and undergoes free-radical addition reactions.

The chemistry of fluorosulfur compounds has grown rapidly during the past few years; yet relatively few organic compounds containing CF_3S groups have been reported.[1] With the development of convenient preparations of trifluoromethanesulfenyl chloride,[2] bis(trifluoromethylthio)mercury,[3a] and trifluoromethanethiol,[3b] a great number of CF_3S compounds are potentially available. This paper presents the results of a study of the preparation and properties of a variety of trifluoromethylthioalkanes, -olefins, and -acetylenes.

Alkanes.—Several CF_3S-substituted alkanes (I–VI) with varying numbers of CF_3S substituents have been prepared by reactions of bis(trifluoromethylthio)-mercury with the corresponding haloalkanes (eq 1 and Tables I and II).[4] The reactions were generally carried out at atmospheric pressure and at temperatures in the range 100 to 130°, or at reflux in those cases where the haloalkane was relatively low boiling. Usually an excess of the mercury salt was employed. The low melting point (39–40°) and solvent properties of this compound obviated the necessity of an added solvent. The halides employed were generally iodides or bromides. If codistillation of mercury compounds with the product was encountered, the crude reaction mixture was dissolved in trichlorofluoromethane (Freon-11), saturated with anhydrous HCl, and then filtered to remove the precipitated $HgCl_2$ prior to distillation.

$$RX + (CF_3S)_2Hg \longrightarrow RSCF_3 + HgX_2 \qquad (1)$$

$CF_3SC_2H_5$	$CF_3S(CH_2)_nSCF_3$	$(CF_3S)_3CH$
I	II, n = 1, 2, 3, 5	III
$(CF_3S)_4C$	$(CF_3S)_2CHCH_3$	$(CF_3S)_2CHCH_2SCF_3$
IV	V	VI

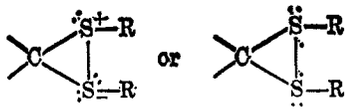
In the reactions with halomethanes, the reactivity increased with the number of halogen substituents. Thus, methylene iodide reacted relatively slowly, several hours at 120° being required to produce a high yield of II (n = 1). Iodoform reacted considerably faster at somewhat lower temperature. Carbon tetrabromide reacted so exothermically at 75° that it was difficult to contain the mixture in the reaction flask, and partial pyrolysis of the product (IV) occurred, resulting in the formation of tetrakis(trifluoromethylthio)-ethylene (eq 2). A less vigorous reaction occurred with dibromodichloromethane, and this reaction proved to be the method of choice for preparing pure IV. Mono-, bis-, and tris(trifluoromethylthio)ethane (I, V, and VI) were analogously prepared but the yield decreased as the number of halogen atoms increased. *sym*-Tetrabromoethane appeared not to have reacted with the mercury salt after 18 hr at 150°.

$$CBr_4 + (CF_3S)_2Hg \longrightarrow \underset{\text{IV}}{C(SCF_3)_4} + \underset{\text{VII}}{(CF_3S)_2C{=}C(SCF_3)_2} \qquad (2)$$

Spectra of Trifluoromethyl Sulfides (Table III).—The infrared spectra are relatively simple and are completely consistent with the structures assigned. For example, the spectrum of $(CF_3S)_4C$ (IV) contains only four strong bands, two at 1157 and 1082 cm^{-1} indicative of CF bonds, a band at 704 cm^{-1} which may be a C–S stretch band, and a band at 758 cm^{-1}. This latter band was observed in the spectra of all of the CF_3S compounds encountered in this study.[5] The spectra of other trifluoromethyl sulfides are tabulated in Table III.

The ultraviolet absorption spectra (Table III) of trifluoromethyl ethyl sulfide (I) and those bis(trifluoromethylthio)alkanes with at least two carbon atoms between the CF_3S groups (II, n = 2,3,5) contain a maximum at 218–219 mμ. The corresponding band in nonfluorinated primary alkyl sulfides occurs at about 210 mμ (with a shoulder at 229 mμ) and has been attributed to the promotion of a nonbonding 3p electron on sulfur to a vacant d orbital.[6]

When there are two CF_3S groups on the same carbon, as in II (n = 1) and V, the maximum is shifted to longer wavelengths (from 219 to 229 mμ) and intensified, but not so much as in the nonfluorinated analogs.[7] This shift to longer wavelengths in the spectra of alkyl mercaptals has been attributed to 3-p–d overlap of the proximate sulfur atoms.[7,8] The higher energy of transition in the fluorinated mercaptals is probably a result



(1) Compounds containing trihalomethylthio groups have been reviewed recently by A. Senning, *Chem. Rev.*, **65**, 385 (1965).

(2) C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **25**, 2016 (1960).

(3) (a) E. H. Man, D. D. Coffman, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 3575 (1959); (b) R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 3219 (1953).

(4) Man, Coffman, and Muetterties[3a] first used this method for the preparation of CF_3S compounds from *t*-butyl chloride, benzyl chloride, allyl chloride, and acetyl chloride. Other trifluoromethyl sulfides have been prepared by addition of CF_3SH to olefins[4a] [J. F. Harris and F. W. Stacey, *J. Am. Chem. Soc.*, **83**, 840 (1961)], by the addition of CF_3SCl to halo olefins[4b] [J. F. Harris, *ibid.*, **84**, 3148 (1962)], and by free-radical reactions of CF_3SCl with hydrocarbons[4c] [J. F. Harris, *J. Org. Chem.*, **31**, 931 (1966)].

(5) This band has been attributed to the C–S stretching frequency as well as to the CF_3 deformation frequency: J. K. Brown, and K. J. Morgan, "Advances in Fluorine Chemistry," Vol. 4, Butterworth, Inc., Washington, D. C., 1965, p 303.

(6) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 476. The hyperconjugating ability of fluoro substituents may contribute to the lower energy of excitation in the trifluoromethyl sulfides: $^-FCF_2{=}S^+R$.

(7) For example, the λ_{max} of $(CH_3S)_2CH_2$ occurs at 235 compared with 210 mμ for $C_2H_5SC_2H_5$: E. A. Fehnel and M. Carmack, *J. Am. Chem. Soc.*, **71**, 84 (1949).

(8) S. Oae, W. Tagaki, and A. Ohno, *Tetrahedron*, **20**, 437 (1964).

TABLE I

REACTIONS OF BIS(TRIFLUOROMETHYLTHIO)MERCURY WITH HALOALKANES

Haloalkane, g (mole)	Quantity of $(CF_3S)_2Hg$, g (mole)	Temp, °C	Time, hr	Product, %
C_2H_5I, 50 (0.32)	130 (0.32)	Reflux	21	$CF_3SC_2H_5$, 78
CH_2I_2, 40 (0.149)	80 (0.199)	120–125	21	$(CF_3S)_2CH_2$, 73
CHI_3, 20 (0.0508)	50 (0.124)	117–121	5	$(CF_3S)_3CH$, 83
CBr_4,[a] 40 (0.121)	200 (0.497)	70–75	Few minutes	$(CF_3S)_4C$, 37 $(CF_3S)_2C{=}C(SCF_3)_2$, 18
CBr_2Cl_2,[b] 15 (0.0618)	100 (0.248)	100	2	$(CF_3S)_4C$, 67
$BrCH_2CH_2Br$, 15 (0.08)	50 (0.124)	Reflux	22.5	$CF_3SCH_2CH_2SCF_3$, 61
Br_2CHCH_3, 18.9 (0.10)	63 (0.157)	Reflux	20	$(CF_3S)_2CHCH_3$, 42
Br_2CHCH_2Br,[b] 20 (0.075)	65 (0.161)	130	16	$(CF_3S)_2CHCH_2SCF_3$, 24
$I(CH_2)_3I$, 50 (0.169)	100 (0.248)	Reflux	3.5	$CF_3S(CH_2)_3SCF_3$, 60
$I(CH_2)_5I$, 25 (0.0772)	50 (0.124)	100–110	1.5	$CF_3S(CH_2)_5SCF_3$, 69

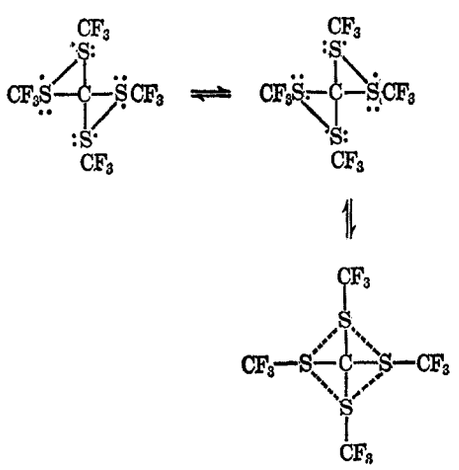
[a] On warming a mixture of CBr_4 and $(CF_3S)_2Hg$, a rapid exothermic reaction occurred during which the temperature of the reaction mixture rose to 130°. [b] In this case the trap contents were dissolved in 100 ml of Freon 11, prior to treatment with anhydrous HCl.

TABLE II

CF_3S-SUBSTITUTED ALKANES PREPARED FROM BIS(TRIFLUOROMETHYLTHIO)MERCURY AND HALOALKANES

Compound	Bp, °C (mm)	$n^{25}D$	Formula	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found	Fluorine, % Calcd	Fluorine, % Found	Sulfur, % Calcd	Sulfur, % Found
$CF_3SC_2H_5$	40	1.3369–1.3373	$C_3H_5F_3S$					43.8	43.6	24.6	24.9
$(CF_3S)_2CH_2$	78	1.3562	$C_3H_2F_6S_2$					52.7	52.4	29.6	29.3
$(CF_3S)_3CH$	106.5	1.3650	$C_4HF_9S_3$					54.1	54.0	30.4	30.0
$(CF_3S)_4C$	47 (10)	1.3980	$C_5F_{12}S_4$	14.4	14.4			54.8	55.2	30.8	31.0
$CF_3SCH_2CH_2SCF_3$	110	1.3738	$C_4H_4F_6S_2$	Identical with the product obtained from the addition of CF_3SH to $CF_3SCH{=}CH_2$							
$CF_3S(CH_2)_3SCF_3$	146	1.3825	$C_5H_6F_6S_2$	24.6	25.1	2.5	2.6	46.7	47.1	26.2	26.2
$CF_3S(CH_2)_5SCF_3$	74 (10)	1.3977	$C_7H_{10}F_6S_2$	30.9	31.2	3.7	3.9	41.9	41.9	23.5	24.1
$(CF_3S)_2CHCH_3$	93	1.3632	$C_4H_4F_6S_2$					49.5	49.8	27.8	27.9
$(CF_3S)_2CHCH_2SCF_3$	63–67 (60)	1.3830	$C_5H_3F_9S_3$	18.2	18.4	0.9	1.3	51.8	51.9		

of the electron-withdrawing effect of the trifluoromethyl groups which makes the 3-p electron pair on the sulfur atom less available for p–d bonding. The maximum in the spectrum of $(CF_3S)_3CH$ occurs at slightly lower wavelength than the maximum in the spectrum of $(CF_3S)_2CH_2$, but it is significantly intensified.[9] In the spectrum of $(CF_3S)_4C$ more intensification occurs and a new band appears at 246 mμ,[10] which may indicate promotion to a p–d orbital emcompassing all four sulfur atoms.



Reactions of Trifluoromethyl Sulfides. Oxidation.—Several of the trifluoromethyl alkyl sulfides were oxidized to the corresponding sulfones (Table IV) with chromium trioxide in glacial acetic acid at 95°.[11]

$$CF_3SCH_2CH_2SCF_3 \xrightarrow[HOAc]{CrO_3} CF_3SO_2CH_2CH_2SO_2CF_3 \qquad (3)$$

The bis(trifluoromethylthio)alkanes II (n = 2, 3, 5) yielded crystalline bissulfones, but from the reaction with II (n = 1), no sulfone was isolated.

Attempted Formation of Salts.—No reaction occurred when trifluoromethyl ethyl sulfide and mercuric chloride were mixed in absolute ethanol. Similarly, no sulfonium salt was obtained when bromine and this sulfide were mixed. This lack of reactivity has been noted previously with other fluoroalkyl sulfides[12] and is no doubt due to the electron-withdrawing capacity of the fluoroalkyl groups which decreases the coordinating ability of the unshared pairs of electrons on the sulfur atom.

Pyrolysis of Tetrakis(trifluoromethylthio)methane.—Tetrakis(trifluoromethylthio)methane (IV) can be distilled at atmospheric pressure without noticeable decomposition; however, after 18 hr at reflux, samples contain small quantities of rather volatile decomposition products. When IV is passed through a packed quartz pyrolysis tube at elevated temperature, two modes of decomposition were observed depending upon the conditions employed. At 400° and 1–1.5 mm, the liquid product was almost entirely bis(trifluoromethyl)-trithiocarbonate (eq 4). There were also present small amounts of bis(trifluoromethyl) sulfide, bis(trifluoro-

(9) This same relationship has been noted in the spectra of $CH_2(SC_2H_5)_2$ and $CH(SC_2H_5)_3$.[5]

(10) The analogous band in the spectrum of tetrakis(methylthio)methane occurs at 244.5 mμ: C. W. N. Cumper, A. Melnikoff, and A. L. Vogel, *J. Chem. Soc., Sect. A*, 242 (1966).

(11) This recipe has been used previously for oxidation of fluoroalkyl sulfides to sulfones: W. E. Truce, G. H. Birum, and E. T. McBee, *J. Am. Chem. Soc.*, **74**, 3594 (1952).

(12) K. E. Rapp, R. L. Pruett, J. T. Barr, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, *ibid.*, **72**, 3642 (1950); **74**, 749 (1952).

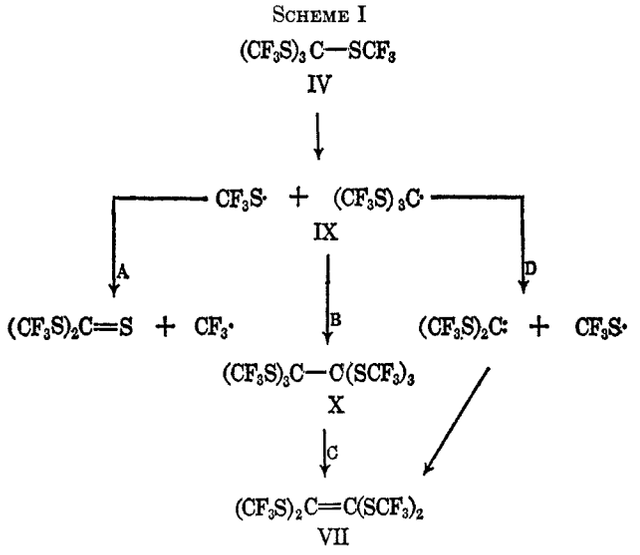
methyl) disulfide, and tetrakis(trifluoromethylthio)-ethylene. At 400° and atmospheric pressure, the major product was tetrakis(trifluoromethylthio)ethylene (eq 5). Considerable quantities of bis(trifluoromethyl)

$$(CF_3S)_4C \xrightarrow{400°} \begin{cases} \xrightarrow{(1\text{ mm})} (CF_3S)_2C{=}S + CF_3SCF_3 & (4) \\ \text{IV} \qquad\qquad \text{VIII} \\ \xrightarrow{(760\text{ mm})} (CF_3S)_2C{=}C(SCF_3)_2 + CF_3SSCF_3 \\ \qquad\qquad \text{VII} \qquad (5) \end{cases}$$

disulfide were also formed. At temperatures of 250–300° and atmospheric pressure, the product contained comparable amounts of both the ethylene and the trithiocarbonate. At 200°, virtually no pyrolysis occurred.

A possible explanation of these results is outlined in Scheme I. Here, IV is initially cleaved to a CF_3S radical and the radical IX, which at low pressures

SCHEME I



eliminates a trifluoromethyl radical *via* pathway A to form the trithiocarbonate. At higher pressures, and consequently higher concentrations of IX, IX dimerizes (pathway B) to form hexakis(trifluoromethylthio)-ethane (X), which at the elevated temperatures loses two CF_3S radicals giving the ethylene VII (pathway C). An alternative formation of the ethylene *via* a carbene (pathway D) seems unlikely. The trithiocarbonate VIII undergoes no change when passed through the pyrolysis tube at 400° and atmospheric pressure and is thus (at least by itself) not an intermediate in the conversion of IV to VII.

Ethylenes. Trifluoromethyl Vinyl Sulfide (XI).—Trifluoromethyl vinyl sulfide (XI) was prepared in two steps beginning with the addition of trifluoromethanesulfenyl chloride to ethylene to give trifluoromethyl 2-chloroethyl sulfide (XII) in 83% yield (eq 6).[13]

$$CF_3SCl + CH_2{=}CH_2 \longrightarrow \underset{\text{XII, 83\%}}{CF_3SCH_2CH_2Cl} \qquad (6)$$

Dehydrochlorination of XII with KOH afforded XI in yields up to 97% (eq 7).

$$CF_3SCH_2CH_2Cl + KOH \longrightarrow \underset{\text{XI, 97\%}}{CF_3SCH{=}CH_2} \qquad (7)$$

(13) XII has also been prepared by the ultraviolet-initiated addition of trifluoromethanethiol to vinyl chloride.[4b]

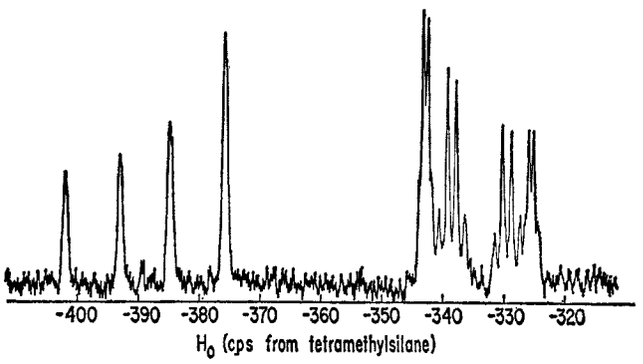


Figure 1.—Observed H^1 nmr spectrum of trifluoromethyl vinyl sulfide in tetramethylsilane at 60 Mc/sec.

Compound XI is a colorless liquid boiling at 22°. The H^1 nmr spectrum consists of a typical ABC pattern (Figure 1). In Table V are tabulated the chemical shifts and coupling constants along with analogous values for methyl vinyl sulfide[14] and ethylene.[15] Several points are of interest. It was previously noted[14] that the β hydrogens in methyl vinyl sulfide occur at somewhat higher field than the protons in ethylene and this has been attributed to a weak conjugative effect.

$$CH_2{=}CHSCH_3 \rightleftharpoons \bar{C}H_2CH{=}\overset{+}{S}CH_3$$

In trifluoromethyl vinyl sulfide the β protons actually occur at lower field than those of ethylene by about 20 cps, indicating a reversal of the conjugative effect and a shift of electron density in the direction of the sulfur atom. This is no doubt a reflection of the strong electron-attracting ability of the CF_3 group attached to sulfur. As in methyl vinyl sulfide, the β protons of trifluoromethyl vinyl sulfide are spin coupled to the substituents on the methyl carbon (in this case fluorine) while the α proton is not. The F^{19} nmr pattern contains a single resonance at +2446 cps with respect to trichlorofluoromethane (internal standard).[16]

Compound XI undergoes a spontaneous addition reaction with chlorine to give XIII (eq 8). Under the influence of ultraviolet irradiation it reacts with bromine to give XIV (eq 9) and with trifluoromethanethiol to give II (n = 2) (eq 10). These latter two reactions are obviously free-radical chain reactions. The structure

$$CF_3SCH{=}CH_2 + Cl_2 \longrightarrow \underset{\text{XIII}}{CF_3SCHClCH_2Cl} \qquad (8)$$

$$CF_3SCH{=}CH_2 + Br_2 \xrightarrow{h\nu} \underset{\text{XIV}}{CF_3SCHBrCH_2Br} \qquad (9)$$

$$CF_3SCH{=}CH_2 + CF_3SH \xrightarrow{h\nu} \underset{\text{II, } n = 2}{CF_3SCH_2CH_2SCF_3} \qquad (10)$$

of the product of reaction 10 was established by its H^1 nmr pattern which consists of a single unsplit methylene resonance at τ 6.82. This pattern is identical with that of the product obtained from the reaction of $(CF_3S)_2Hg$ with 1,2-dibromoethane as described earlier in this paper (Table I).

(14) R. T. Hobgood, Jr., G. S. Reddy, and J. H. Goldstein, *J. Phys. Chem.*, **67**, 110 (1963).

(15) G. S. Reddy and J. H. Goldstein, *J. Am. Chem. Soc.*, **83**, 2045 (1961).

(16) All F^{19} nmr spectra reported in this paper were determined at 56.4 Mc. Solutions of about 10% concentration in trichlorofluoromethane (Freon-11) were used. Chemical shifts are reported in cycles per second (cps) measured from the resonance of the solvent.

TABLE III

INFRARED AND ULTRAVIOLET SPECTRA OF TRIFLUOROMETHYLTHIO COMPOUNDS

A. Alkanes	C—H stretch, cm^{-1}	C—H asym deform, cm^{-1}	C—H sym deform, cm^{-1}	C—F, cm^{-1}	CF_3S, cm^{-1}	Unassigned infrared bands, cm^{-1}	λ_{max}, $m\mu$	ϵ
$CF_3SC_2H_5$	2980 (m) 2940 (m) 2880 (m)	1432 (m) 1457 (s)	1386 (m)	1161 (vs) 1122 (vs) 2240 (w)	754 (s)	1876 (w), 1282 (s), 1244 (m), 1219 (m), 1057 (s), 973 (s), 787 (m), 684 (w), 657 (m)	219	35
$CF_3S(CH_2)_5SCF_3$				1221 (vs) |		219	93
$CF_3S(CH_2)_3SCF_3$	2980 (m) 2900 (w)	1457 (s) 1431 (s)		1048 (vs) 2270 (m)	758 (s)	1878 (m), 1360 (m), 1322 (s), 1276 (s), 1012 (m), 963 (m), 841 (s), 779 (m), 722 (w), 690 (w)	218	102
$CF_3S(CH_2)_2SCF_3$	2950 (w)	1431 (s)		1166 (vs) 1126 (vs) 1102 (vs) 2240 (w) 1091 (vs)	757 (s)	2090 (w), 1863 (w), 1300 (s), 1281 (m), 1227 (s), 1021 (w), 949 (w), 906 (w), 850 (m), 837 (m), 704 (m)	219	143
$CF_3SCH_2SCF_3$	3030 (m) 2975 (w)	1411 (m)		| 1236 (vs) 2240 (m)	757 (s)	1870 (m), 1390 (m), 1309 (m), 1298 (m), 949 (w), 914 (w), 868 (w), 839 (m), 821 (s), 728 (s)	229	311
$(CF_3S)_2CHCH_3$	3000 (m) 2950 (m) 2895 (w)	1455 (s)	1390 (s)	1161 (vs) 1129 (vs) 1102 (vs) 2270 (s)	758 (s)	2500 (w), 2430 (w), 1877 (m), 1662 (m), 1600 (m), 1302 (m-s), 1261 (s), 1215 (s), 1056 (s), 973 (s), 707 (s), 672 (m)	224	224
$(CF_3S)_2CHCH_2SCF_3$	2970 (m)	1420 (m)		1167 (vs) 1133 (vs) 1099 (vs) 2260 (m)	756 (s)	1850 (m), 1728 (w), 1653 (w), 1570 (w), 1296 (m), 1250 (m), 948 (w), 891 (s), 719 (s), 679 (m)		
$(CF_3S)_3CH$	3010 (m)	1301 (m) 1313 (m)		1142 (vs) 1128 (vs) 1091 (vs) 2270 (m)	758 (s)	1898 (w), 1852 (w), 1004 (w), 942 (w), 870 (w), 708 (s), 663 (w)	225	598
$(CF_3S)_4C$				1157 (vs) 1082 (vs) 2270 (m)	758 (s)	1920 (w), 1880 (w), 1849 (w), 1710 (w), 1304 (m), 953 (m), 922 (w), 791 (m), 704 (s)	223 246 (sh)	1620 1040

B. Ethylenes	C=C stretch	C—H stretch	C—H op deform	C—H ip deform	C—F	CF_3S	Unassigned infrared bands	λ_{max}, $m\mu$	ϵ
$CF_3SCH{=}CH_2$	1611 (s)	3110 (m) 3075 (m) 3030 (m)	914 (s) 957 (s) 1839 (s)	1387 (m) 1283 (s)	1177 (vs) 1152 (vs) 1138 (vs) 2275 (m-s)	767 (s) 761 (s) 756 (s)	2345 (m-s), 2295 (m-s), 1901 (s), 1040 (s), 1037 (s), 1029 (s), 733 (s), 728 (s), 722 (s)	209 233	5300 1100
$CF_3SCH{=}CHSCF_3$ (*cis*)	1561 (s)	3080 (m)	691 (s)	1407 (w)	2270 (s) 1170 (vs) 1143 (vs) 1102 (vs)	759 (s)	2860 (w), 1882 (m-s), 1862 (m-s), 1732 (w), 1680 (w), 1304 (s), 902 (m-s), 838 (s), 718 (m-s)	218 234	6520 5970
$CF_3SCH{=}CHSCF_3$ (*trans*)	1554 (s)	3080 (m)	923 (s)	1301 (m-s) and/or 1319 (m-s)	1170 (vs) 1142 (vs) 1103 (vs) 2270 (s)	758 (s)	2090 (w), 1885 (m), 1860 (m), 1690 (m-s), 1403 (w), 841 (m), 801 (s)	223 247	5340 7210

$(CF_3S)_2C{=}CHSCF_3$	1533 (s)	3090 (m)	849 (s)		1146 (vs)	758 (s)			1859 (w–m), 1697 (w–m), 1630 (w–m), 1323 (m), 1303 (m), 1260 (m–s), 909 (s)	258	6040		
		3040 (m)	813 (s)		1098 (vs)								
					2270 (m–s)								
$(CF_3S)_2C{=}C(SCF_3)_2$	1450 (s) (Raman)	...	...	...	1162 (vs)	758 (s) (Raman)			1919 (w), 1850 (w), 1466 (m), 1325 (m), 1299 (m), 962 (s), 853 (s), 710 (w)	282	7580		
					1091 (vs)								
					2270 (m)								
$(CF_3S)_2C{=}C{<}^{F}_{N(C_2H_5)_2}$	1591 (vs)	2990 (m)	C—H asym deform 1463 (s) 1453 (s)	C—H asym deform 1385 (s)	1178 (vs)	725 (s)			1867 (w), 1740 (w), 1652 (s), 1406 (s), 1359 (s), 1296 (m), 1274 (s), 1047 (s), 976 (s), 940 (s), 810 (m), 787 (m), 768 (m), 692 (s)	263	14,300		
		2940 (m)			—								
		2910 (w)			1077 (vs)								
		2880 (w)			2230 (w)								
$(CF_3S)_2C{=}C{<}^{SCF_3}_{Cl}$	1480 (s)	...	...	...	1163 (vs)	758 (s)		C—Cl stretch 727 (w)	1853 (w), 1321 (w), 1298 (m), 976 (s), 871 (s)	271	5940		
					1093 (vs)								
					2270 (m)								
C. Acetylenes	C≡C stretch	C—H stretch	Aromatic C—H		C—F	CF_3S	Unassigned infrared bands						
					1241 (vs)								
$CF_3SC{\equiv}CSCF_3$	2110 (w)	...	...	...	—	758 (s)			2205 (w), 2160 (w), 1932 (w), 1856 (w), 1594 (w), 1323 (m), 1300 (m), 962 (w), 925 (w)				
					1053 (vs)								
					2280 (m)		Aromatic C=C skeletal						
$CF_3SC{\equiv}C$	2180 (m)	3070 (m)	1971 (w)	1882 (w)	1161 (vs)	756 (s)			1380 (w), 1321 (w), 1298 (w), 1279 (w), 1228 (w), 1026 (m), 997 (w), 917 (m), 871 (w), 838 (w)				
			1952 (w)	1808 (w)	1103 (vs)								
			1890 (w)	1757 (w)	2260 (w)								
				1677 (w)									

An ultraviolet-initiated free-radical chain reaction of XI also occurs with CF_3SCl to yield 1,1-bis(trifluoromethylthio)-2-chloroethane (XV) as the major product together with smaller amounts of XIII and VI (eq 11).[17] A gas chromatogram of the crude reaction mixture indicated that some bis(trifluoromethyl)

$$\underset{\text{XI}}{CF_3SCH{=}CH_2} + CF_3SCl \xrightarrow{h\nu} \underset{\text{XV, 43\%}}{(CF_3S)_2CHCH_2Cl} + \underset{\text{XIII, 7\%}}{CF_3SCHClCH_2Cl} + \underset{\text{VI, 9\%}}{(CF_3S)_2CHCH_2SCF_3} + CF_3SSCF_3 \quad (11)$$

disulfide was formed as well as small quantities of several other compounds which were not further investigated. Samples of each of the three major products were isolated by preparative-scale gas chromatography. The structure XV assigned to the predominant product was consistent with the H^1 nmr spectrum (neat) which consists of a doublet (δ = 3.79 ppm from TMS, J = 5.5 cps) and a triplet (δ = 4.73 ppm) in an intensity ratio of 2:1. This spectrum in itself is not sufficient for the assignment since the spectrum of the other possible 1:1 adduct (XVII) would be expected to contain the same features. An authentic sample of XVII was prepared by the chlorination of II (n = 2) (eq 12). The H^1 nmr pattern (neat)

$$\underset{\text{II, } n = 2}{CF_3SCH_2CH_2SCF_3} + Cl_2 \xrightarrow{h\nu} \underset{\text{XVII}}{CF_3SCHClCH_2SCF_3} \quad (12)$$

of XVII also consists of a doublet (δ = 3.31 ppm, J = 7 cps) and a triplet (δ = 5.26 ppm) in a 2:1 intensity ratio, but, as both the chemical shifts and the coupling constant are different from those in the pattern just discussed, it is clear that the major product of eq 11 cannot have structure XVII and must therefore be XV. The structure of 1,1,2-tris(trifluoromethylthio)ethane (VI) was assigned on the basis of the infrared (Table III) and H^1 nmr spectra which were identical with those of VI prepared by the reaction of $(CF_3S)_2Hg$ with 1,1,2-tribromoethane. Similarly, the H^1 nmr pattern of XIII was identical with the pattern of the product of eq 8.

At 200° XI undergoes a reaction with 2,3-dimethylbutadiene to form a 1:1 adduct (eq 13). The Diels–Alder adduct structure (XVIII) was assigned on the basis of the H^1 nmr spectrum which contained no

XI XVIII (13)

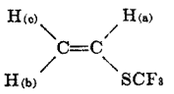
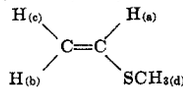
resonances in the vinyl proton region and the infrared spectrum which also indicated the absence of vinyl hydrogens. No C=C stretch band was observed in the infrared spectrum but one was observed at 1670 cm^{-1} in the Raman spectrum. These spectra would be inconsistent with an alternative cyclobutane structure.

(17) Free-radical additions of CF_3SCl to halo olefins have been studied.[4b] The conclusions previously drawn with respect to the mechanism of the addition appear to be entirely applicable in the example reported here.

TABLE IV
TRIFLUOROMETHYL SULFONES

Sulfone	Yield, %	Bp (mm) or mp, °C	$n^{25}D$	Recrystyn solvent	Formula	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found	Fluorine, % Calcd	Fluorine, % Found	Sulfur, % Calcd	Sulfur, % Found
$CF_3SO_2C_2H_5$	60	72 (74)	1.3591	...	$C_3H_5F_3O_2S$					35.2	35.1	19.8	20.3
$CF_3SO_2(CH_2)_2SO_2CF_3$	83	172–174	...	CH_3OH	$C_4H_4F_6O_4S_2$	16.3	16.4	1.4	1.5			21.8	21.7
$CF_3SO_2(CH_2)_3SO_2CF_3$	87	86–87	...	C_2H_5OH	$C_5H_6F_6O_4S_2$	19.5	19.9	2.0	2.0			20.8	20.5
$CF_3SO_2(CH_2)_5SO_2CF_3$	89	61–62	...	C_6H_6 + pentane	$C_7H_{10}F_6O_4S_2$					33.9	34.1	19.1	19.2

TABLE V
H^1 NMR SPECTRUM OF TRIFLUOROMETHYL VINYL SULFIDE (60 Mc/sec)[a]

		
$\omega_a = -385.8$ cps	$\omega_a = -380.7$	$\omega = -317.3$
$\omega_b = -334.1$ cps	$\omega_b = -290.4$	
$\omega_c = -334.0$ cps	$\omega_c = -304.5$	
$J_{ab} = 17$ cps	$J_{ab} = 16.4$	
$J_{ac} = 9$ cps	$J_{ac} = 10.3$	
$J_{bc} \cong 0$	$J_{bc} = -0.3$	
$J_{aF} \cong 0$	$J_{ad} = 0.0$	
$J_{bF} = 0.6$ cps	$J_{bd} = 0.4$	
$J_{cF} = 1.4$ cps	$J_{cd} = 0.2$	

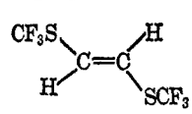
[a] The values listed in this table for $CF_3SCH{=}CH_2$ were estimated from Figure 1.

On storage in pressure vessels at room temperature, XI polymerized to a viscous liquid. Polymerization experiments with azonitrile or peroxide initiators yielded solid polymers which were somewhat elastic.[18]

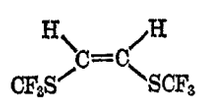
cis- **and** *trans*-**1,2-Bis(trifluoromethylthio)ethylene (XIX).**—Dehydrobromination of bromo-1,2-bis(trifluoromethylthio)ethane (XXa) led to formation of a mixture of the *cis* and *trans* isomers of 1,2-bis(trifluoromethylthio)ethylene (XIX, eq 14). Pure samples of

$$\underset{\text{XXa}}{CF_3S\overset{Br}{\overset{|}{C}}HCH_2SCF_3} + KOH \xrightarrow{EtOH} \underset{\text{XIX (}cis\text{ and }trans\text{)}}{CF_3SCH{=}CHSCF_3} \quad (14)$$

the two isomers were isolated by preparative-scale gas chromatography. The less prevalent isomer was assigned the *trans* structure (XIXa) since its infrared spectrum contains a strong band at 923 cm^{-1} which probably is a *trans*-HC=CH out-of-plane deformation frequency. Appropriately, the spectrum of the other isomer contains a strong band at 691 cm^{-1} which is in the region expected for a *cis*-HC=CH out-of-plane frequency.[19] The H^1 nmr pattern of each isomer contains a single unsplit resonance at τ 3.27.



XIXa



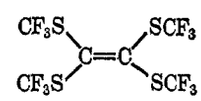
XIXb

Tris(trifluoromethylthio)ethylene (XXb).—Tris compound XXb was prepared by the ultraviolet-initiated addition of trifluoromethanethiol to bis(trifluoromethylthio)acetylene (eq 15). Structure XXb was assigned on

$$CF_3SH + CF_3SC{\equiv}CSCF_3 \xrightarrow{h\nu} \underset{\text{XXb}}{(CF_3S)_2C{=}CHSCF_3} \quad (15)$$

the basis of elemental analysis, the infrared spectrum which contains a strong C=C stretch band at 1533 cm^{-1}, and the H^1 nmr pattern which consists of a single, unsplit resonance in the vinyl proton region at τ 2.13.

Tetrakis(trifluoromethylthio)ethylene (VII).—Compound VII was most conveniently prepared on a large scale by heating a mixture of carbon tetrabromide and bis(trifluoromethylthio)mercury to 100° in an autoclave (eq 2). From these reactions the ethylene was obtained



VII

in 23% yield accompanied by 39% of tetrakis(trifluoromethylthio)methane. Complete separation of the ethylene from the methane was not possible with a 21-in. helix-packed still, but a pure sample of the ethylene was obtained by preparative-scale gas chromatography. Compound VII [bp 71° (25 mm)] is a yellow liquid which freezes at 20.5–21.5° to a colorless solid. The structure was assigned on the basis of elemental analysis, a mass spectrogram which contains the parent ion, the Raman spectrum which contains a strong C=C stretch band at 1450 cm^{-1}, and the fluorine nmr pattern which consists of a single resonance at 2262 cps.[16] The ultraviolet spectrum contains a broad band at 282 mμ (ϵ 7580). It is the foot of this band extending beyond 400 mμ which accounts for the yellow color.

Compound VII does not react with methanol alone, but, upon addition of sodium methoxide, a mildly exothermic reaction leads to the formation of a product to which structure XXI was assigned (eq 16). The H^1 nmr pattern of this product contains resonances at τ 6.58 (CH_3O) and 5.13 (CH) in an intensity ratio of

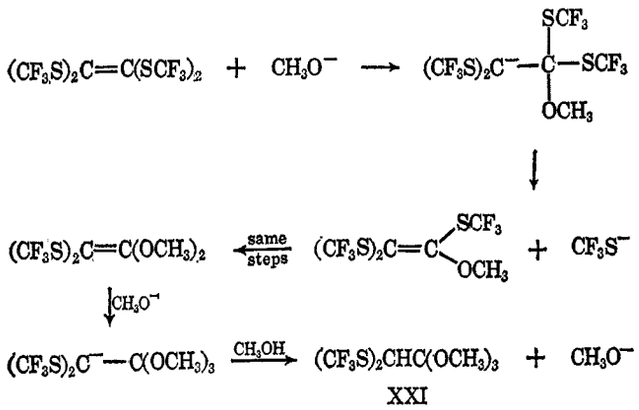
$$(CF_3S)_2C{=}C(SCF_3)_2 + CH_3OH + CH_3ONa \longrightarrow \underset{\text{XXI}}{(CF_3S)_2CHC(OCH_3)_3} \quad (16)$$

9:1. The F^{19} pattern contains a single resonance in the CF_3S region at 2364 cps.[16] These spectra, indicating that the CF_3 groups are identical and that the CH_3 groups are also identical, support structure XXI and would be inconsistent with the alternative isomeric structure in which the CF_3S groups are on different carbon atoms. The infrared spectrum is consistent with structure XXI, but in addition contains peaks indicative of ethylenic and carbonyl impurities. The formation of XXI no doubt involves successive additions of CH_3O^- and eliminations of CF_3S^- as outlined in Scheme II. Intermediates in this process apparently react more readily with methoxide than VII itself, since from a mixture of equimolar amounts of the reactants in methanol, VII was largely recovered.

(18) J. F. Harris, U. S. Patent 3,048,569 (1962); *Chem. Abstr.*, **57**, 16887 (1962).

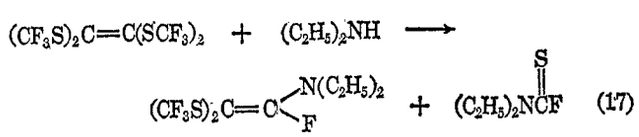
(19) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 48.

SCHEME II



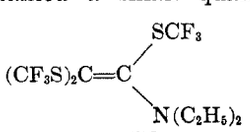
XXI

From the reaction of VII with excess diethylamine (1:4.15 mole ratio) two products were obtained (eq 17). The infrared spectrum of the major product



XXII XXIII (17)

contains a strong band at 1592 cm^{-1} indicating a carbon–carbon double bond. The F^{19} nmr spectrum contains two resonances of about equal intensities in the CF_3S region at 2690 and 2700 cps, and a third, very broad resonance corresponding in intensity to a single fluorine nearby at 2616 cps.[16] The H^1 nmr spectrum contains only a methyl triplet (τ 8.74, J = 7.2 cps) and a methylene quadruplet (τ 6.44) indicating an ethyl group. The methylene quadruplet is further split to doublets (J = 2.5 cps) presumably by the single fluorine. Since there are no vinylic hydrogens in the molecule, the single fluorine must be on the double bond. The resonance of the single fluorine, which is also obviously spin coupled to the CF_3 groups as well as to the CH_2 group, does not show discreet splitting but appears as a very broad peak. This is no doubt due to spin–spin interaction with the nearby nitrogen quadrupole. These spectra together with the elemental analyses are consistent with structure XXII, but isomeric structures in which the CF_3S groups are not on the same carbon atom cannot be ruled out. Evidence for structure XXII, however, was found in a mass spectrogram which, in addition to the parent ion (317) and an ion at 248 (parent less CF_3), contained as the third most abundant species an ion at 145 corresponding to the following fragment: $S{=}C^+{-}SCF_3$. There was also observed a low-intensity ion at 399 indicating that the sample contained a small quantity of XXIV.



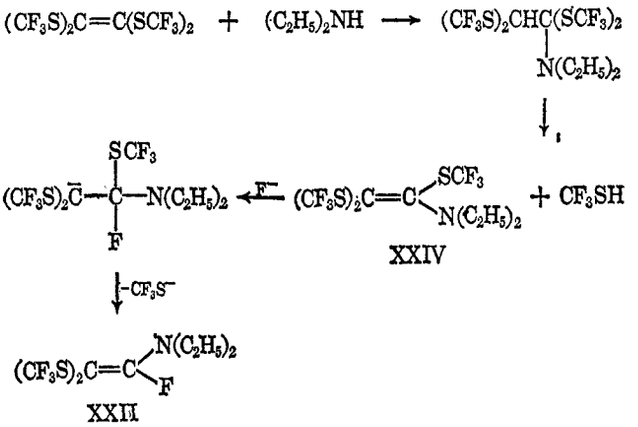
XXIV

The other product was identified as diethylthiocarbamoyl fluoride (XXIII) by comparison of the infrared spectrum with that of an authentic sample.[20]

(20) Diethylthiocarbamoyl fluoride (XXIII) was prepared in this laboratory by Dr. M. Brown by the reaction of CF_2S with diethylamine. This compound has also been reported by N. N. Yarovenko and A. S. Vasileva, *J. Gen. Chem. USSR*, **29**, 3754 (1959).

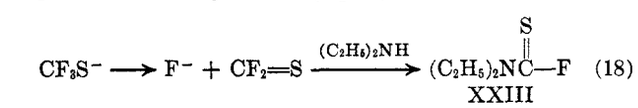
The formation of XXII probably involves initial addition of the amine to VII followed by loss of the elements of CF_3SH to give the ethylene XXIV, evidence for which was found in the mass spectrogram discussed above. Addition of fluoride ion (resulting from the decomposition of the expelled CF_3S group) to XXIV followed by loss of CF_3S^- would account for the production of XXII (Scheme III). Compound XXIII

SCHEME III



XXIV XXII

no doubt arises from further reaction of CF_3S^- or $CF_2{=}S$ with diethylamine (eq 18).



XXIII (18)

Spectra of Ethylenes.—The infrared spectra of the ethylenes contain a strong band in the 1450–1600-cm^{-1} region which can be ascribed to the C=C stretching frequency. As the number of CF_3S groups on the C=C double bond increases, this band exhibits a shift from 1611 cm^{-1} for trifluoromethyl vinyl sulfide[21] to 1450 cm^{-1} (Raman) for tetrakis(trifluoromethylthio)ethylene. The occurrence of a strong C=C stretch band (1554 cm^{-1}) in the spectrum of *trans*-1,2-bis(trifluoromethylthio)ethylene is somewhat surprising since symmetrically substituted *trans*-ethylenes generally exhibit no C=C stretch band in the infrared.[22] The positions of the C—H stretch bands are 15–20 cm^{-1} higher than usually observed for hydrocarbon unsaturates. All of the spectra contain a band in the 760-cm^{-1} region, characteristic of the CF_3S group,[5] as well as very strong C—F bands in the 1100–1200-cm^{-1} region. In addition, there is a medium to strong band at about 2270 cm^{-1} which is probably a C—F overtone.

The ultraviolet spectra of vinyl sulfides have been interpreted as indicating conjugative interaction of the sulfur atom with the C=C function by virtue of the occurrence of maxima at wavelengths longer than those found in the spectra of the related saturated sulfides.[23] In the spectrum of trifluoromethyl vinyl sulfide, a similar shift is observed: 209 and 233 mμ for $CF_3SCH{=}CH_2$ *vs.* 219 mμ for $CF_3SC_2H_5$. As can be

(21) The C=C stretching band for methyl vinyl sulfide occurs at 1587 cm^{-1}: C. C. Price and R. G. Gillis, *J. Am. Chem. Soc.*, **75**, 4750 (1953).

(22) Reference 19, p 38.

(23) For example, the spectrum of methyl vinyl sulfide contains maxima at 230 and 240 mμ (C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press Co., New York, N. Y., 1962, p 34), whereas the maxima of methyl ethyl sulfide are at 210 and 229 mμ (above reference, p 171, Table I).

seen from Table III, there is a progressive shift of the long wavelength maximum to longer wavelengths as the number of CF_3S groups on the carbon–carbon double bond increases.

Acetylenes. Bis(trifluoromethylthio)acetylene (XXV).—Bis(trifluoromethylthio)acetylene (XXV) was prepared in two steps beginning with 1,2-bis(trifluoromethylthio)ethane (II, $n = 2$) (eq 19 and 20).[24] The

$$CF_3SCH_2CH_2SCF_3 + Br_2 \xrightarrow{h\nu} \begin{cases} CF_3SCHBrCH_2SCF_3 \ (44\%) \\ + \\ \left\{ \begin{matrix} CF_3SCHBrCHBrSCF_3 \\ + \\ CF_3SCH_2CBr_2SCF_3 \end{matrix} \right\} (43\%) \end{cases} \quad (19)$$

$$\begin{matrix} CF_3SCHBrCHBrSCF_3 \\ + \\ CF_3SCH_2CBr_2SCF_3 \end{matrix} + KOH \xrightarrow{\Delta} CF_3SC{\equiv}CSCF_3 \quad (20)$$

XXV, 67%

bromination reaction, which was carried out in carbon tetrachloride with a sun lamp as the light source, was a relatively inefficient process, several days of irradiation being required to achieve appreciable conversions. Both a monobromide and a dibromide fraction were always obtained. The H^1 and F^{19} nmr spectra of the dibromide fraction indicated that both possible dibromides were present. The mixture of dibromides was used in the dehydrobromination step.

Compound XXV is a colorless liquid (bp 83°) which slowly darkens on standing. The infrared spectrum contains bands indicative of C—F and SCF_3, and a weak band at 2110 cm^{-1} which may be the C≡C stretch band.[25] The ultraviolet spectrum consists of end absorption with a shoulder at 250 mμ (ε 262).

Compound XXV undergoes free-radical additions, *e.g.*, with trifluoromethanesulfenyl chloride (eq 21) to give a 1:1 adduct (XXVI) and with trifluoromethanethiol as indicated earlier (eq 15). Nucleophilic addi-

$$CF_3SCl + CF_3SC{\equiv}CSCF_3 \xrightarrow{h\nu} (CF_3S)_2C{=}C\begin{matrix} Cl \\ \diagdown \\ \diagup \\ SCF_3 \end{matrix} \quad (21)$$

XXVI

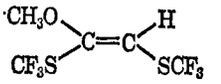
tion reactions also occur readily. For example, a 1:1 adduct was obtained from the sodium methoxide catalyzed reaction of methanol (eq 22). The product was

$$CF_3SC{\equiv}CSCF_3 + CH_3OH \xrightarrow{CH_3ONa} \begin{matrix} CF_3S \\ \diagdown \\ C{=}CHSCF_3 \\ \diagup \\ CH_3O \end{matrix} \quad (22)$$

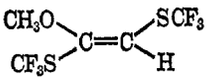
XXVII

clearly an ethylene of structure XXVII according to elemental analysis, and the infrared and ultraviolet spectra. The H^1 nmr spectrum contained two peaks in the vinyl region at τ 3.85 and 4.38 in an intensity ratio of about 2:1, and two peaks in the methoxyl region at 6.11 and 6.22 also in a 2:1 ratio, thus indicating the presence of both the *cis* and *trans* isomers of XXVII.

On the basis of the following arguments, it is believed that the *trans* isomer predominates. Since one would expect that in the *cis* isomer the CH_3O group would



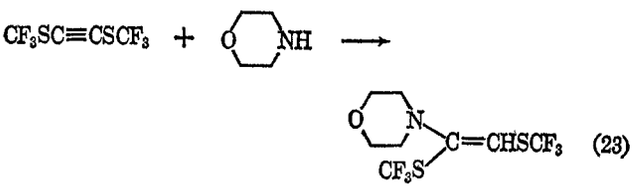
cis XXVII



trans XXVII

exert a greater shielding influence upon the vinyl proton, because of its proximity, than in the *trans* compound, it is predicted that the shift of the vinyl proton resonance to higher field compared to the 1,2-bis(trifluoromethylthio)ethylene without the methoxyl substituent (*i.e.*, structure XIX) would be greater for *cis* XXVII than for *trans* XXVII. The resonances of the vinyl proton for *cis*- and *trans*-1,2-bis(trifluoromethylthio)ethylene (XIX) both occur at τ 3.27. The isomer of XXVII with the vinyl proton resonance at τ 4.38 must therefore be the *cis* isomer, and thus the *trans* isomer predominates in the 2:1 mixture. No studies have been made aimed at establishing the ease with which these isomers interconvert, so at this point it is not possible to say with certainty that the *trans* isomer is the kinetically preferred one.

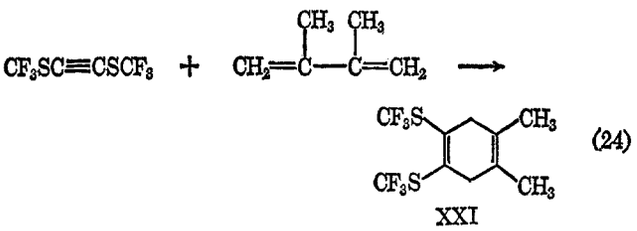
A 1:1 adduct was also obtained from the reaction of XXV with morpholine in ether (eq 23). Here again the H^1 nmr pattern of the product contained two vinyl



XXVIII

proton resonances at τ 3.67 and 4.46 in a ratio of 1:2.3 indicating that both isomers were obtained. From arguments analogous to those given above, it is concluded that the *cis* isomer of XXVIII predominates.

A 1:1 adduct was formed when a mixture of XXV and 2,3-dimethylbutadiene was heated in a sealed tube at 200° (eq 24). The Diels–Alder adduct structure



XXI

XXIX was assigned on the basis of the infrared spectrum, which indicated the absence of vinyl hydrogens.

Phenyl Trifluoromethylthioacetylene (XXX).—This acetylene was prepared in modest yield by the reaction of phenylethynylmagnesium bromide with trifluoromethanesulfenyl chloride (eq 25). The infrared spec-

$$CF_3SCl + C_6H_5C{\equiv}CMgBr \longrightarrow \underset{XXX}{C_6H_5C{\equiv}CSCF_3} \quad (25)$$

(24) Apparently only two symmetrical bis(alkylthio)acetylenes have been reported previously. They are $C_2H_5SC{\equiv}CSC_2H_5$ [H. Baganz and W. Triebsch, *Ber.*, **89**, 895 (1956)] and *t*-$C_4H_9SC{\equiv}CSC_4H_9$-*t* [H. J. Backer, J. Strating, and J. F. A. Hazenberg, *Rec. Trav. Chim.*, **72**, 813 (1953)].

(25) A band in the infrared spectrum of $C_2H_5SC{\equiv}CSC_2H_5$ at 2128 and a band at 2081 cm^{-1} in the Raman spectrum have been attributed to the C≡C stretch by H. Baganz and W. Triebsch, *Ber.*, **89**, 895 (1956). J. R. Nooi and J. F. Arens [*Rec. Trav. Chim.*, **80**, 244 (1961)], however, report finding no band in the C≡C stretch region in the infrared spectrum of this same compound.

trum (Table III) contains a C≡C stretch band at 2180 cm^{-1}.

Experimental Section

1. **Trifluoromethanesulfenyl chloride** was prepared by the reaction of trichloromethanesulfenyl chloride and sodium fluoride in tetramethylene sulfone as described by Tullock and Coffman.[2]

2. **Bis(trifluoromethylthio)mercury** was prepared by the reaction of carbon disulfide and mercuric fluoride at 250° in an autoclave as described by Man, Coffman, and Muetterties.[3a]

3. **Trifluoromethanethiol** was prepared from bis(trifluoromethylthio)mercury in the following manner. Five crude reaction mixtures resulting from reaction of 715 g of mercuric fluoride and 350 g of carbon disulfide[3a] each were combined and filtered to remove the mercuric sulfide. The filtrate was placed in a round-bottomed flask fitted with a cold-water reflux condenser, a paddle stirrer, and a gas inlet tube which extended below the surface of the solution. The condenser was vented through two large Dry Ice cooled traps arranged in series and a calcium chloride filled tube. Anhydrous hydrogen chloride was passed through the solution for several hours. During this time a two-phase mixture of product and CS_2 collected in the traps. The introduction of HCl was continued until the effluent condensate was no longer two phase as indicated by a test with a small, empty Dry Ice cooled trap. The traps containing the thiol–CS_2 mixture were connected to an empty Dry Ice cooled trap and allowed to warm to room temperature, whereupon the thiol condensed in the new trap leaving most of the CS_2 behind. The crude thiol (448 g, 44%) was then distilled through a small Podbielniak still. There was thus obtained 318 g (31% based on HgF_2) of trifluoromethanethiol distilling at −37°.

4. **Reaction of Bis(trifluoromethylthio)mercury with Haloalkanes. A. At Atmospheric Pressure.**—All of these reactions were carried out in approximately the same manner. A description of the reaction with ethyl iodide follows. The details of the other preparations are given in Tables I and II.

A mixture of 50 g (0.320 mole) of ethyl iodide and 130 g (0.320 mole) of bis(trifluoromethylthio)mercury was refluxed for 21 hr. The reaction flask was connected *via* a Dry Ice–acetone cooled trap to a water pump and evacuated until no more material condensed in the trap. Anhydrous hydrogen chloride was passed through the trap contents until the precipitation was complete. After the mixture was filtered to remove the precipitated $HgCl_2$, it was distilled through a small spinning-band still. There was thus obtained 32.4 g (78%) of trifluoromethyl ethyl sulfide distilling at 40°.

B. Reaction with Carbon Tetrabromide in an Autoclave. Preparation of Tetrakis(trifluoromethylthio)ethylene.—A mixture of 330 g (0.819 mole) of bis(trifluoromethylthio)mercury and 120 g (0.362 mole) of carbon tetrabromide was placed in a 1-l. "Hastelloy" autoclave and heated slowly to 100°. After the exothermic reaction was over, the mixture was heated at 100° for 1 hr. Eight such runs were made. The product from each run was stirred with 100 ml of trichlorofluoromethane (Freon-11), the resulting mixture was filtered, and the filtrates were combined and set aside. The combined residues were placed in a large, single-necked flask heated with an oil bath and connected to an oil pump through two Dry Ice cooled traps. The oil bath was heated at 100° and the system was evacuated for 10 hr. The trap contents were combined with the filtrate from above. Anhydrous HCl was passed through the resulting solution until no more precipitation occurred. The mixture was filtered and the filtrate was distilled through a 21-in. helix-packed still. There was thus obtained 424.5 g (39%) of tetrakis(trifluoromethylthio)-methane distilling at 39–39.5° (8 mm), $n^{25}D$ 1.3986–1.4033, and 142.8 g (23%) of tetrakis(trifluoromethylthio)ethylene distilling at 49° (8 mm), $n^{25}D$ 1.4248–1.4258. There was also obtained 19.7 g of an intermediate fraction boiling at 39.5°–48° (8 mm), $n^{25}D$ 1.4096.

A gas chromatogram indicated that the ethylene fraction contained two impurities (one of which was the methane) totaling 12%. A pure sample of the ethylene was obtained by preparative-scale gc [2-ft 25% fluoroalkyl pyromellitate (Zonyl E-T), 100°, He flow rate of 535 ml/min]. The purified ethylene had the following physical properties: bp 71° (25 mm), mp 20.5–21.5° $n^{25}D$ 1.4212. The F^{19} nmr spectrum contained a single resonance at 2262 cps with respect to Cl_3CF as internal standard.[16] The infrared and ultraviolet spectra are given in Table III.

Anal. Calcd for $C_6F_{12}S_4$: C, 16.8; F, 53.3; S, 30.0. Found: C, 17.4; F, 52.9; S, 30.3.

5. **Oxidation of Trifluoromethyl Sulfides.**—A solution of 5 g of the trifluoromethyl sulfide in 20 ml of glacial acetic acid was added during 0.5 hr to a stirred suspension of chromium trioxide (250 g/equivalent of sulfide) in glacial acetic acid (about 10 ml/gram of CrO_3). The temperature was maintained at 25–30°. After the addition was completed, the mixture was heated at 95° for 0.25 hr, cooled to room temperature, and diluted with a large excess of water. If the sulfone crystallized at this point, it was isolated by filtration and purified by recrystallization from an appropriate solvent. If no solid was apparent, the sulfone was removed by four extractions with 50 ml of benzene. The extract was dried over anhydrous magnesium sulfate, filtered, and distilled *in vacuo*. The yields of the sulfones and details of characterization are recorded in Table IV.

6. **Pyrolysis of Tetrakis(trifluoromethylthio)methane. A. At 400° (1–1.5 mm).**—Five grams (0.012 mole) of tetrakis(trifluoromethylthio)methane was introduced dropwise into a vertical quartz column packed with small pieces of quartz tubing, heated at 400°, and evacuated by an oil pump through an acetone–Dry Ice cooled trap and a liquid nitrogen cooled trap. The pressure was maintained at 1–1.5 mm during the addition time of 0.5 hr. Virtually all of the pyrolysate collected in the Dry Ice cooled trap. This deep red material, after having been warmed to room temperature, weighed 2.56 g and was shown by gc (6-ft 10% Apiezon on firebrick, 80°) to consist largely (over 80%) of bis(trifluoromethyl)trithiocarbonate. Small peaks corresponding to tetrakis(trifluoromethylthio)ethylene, bis(trifluoromethyl)disulfide, bis(trifluoromethyl) sulfide, and the starting material were also apparent.

B. At 400° (Atmospheric Pressure).—Five grams of tetrakis(trifluoromethylthio)methane was pyrolyzed in the manner just described except that the system was not evacuated. The Dry Ice trap contents, after having been warmed to room temperature, weighed 1.59 g. A gas chromatogram indicated that the pyrolysate consisted of tetrakis(trifluoromethylthio)ethylene (~70%), bis(trifluoromethyl) disulfide (15%), and bis(trifluoromethyl) sulfide (10%). No peaks corresponding to the trithiocarbonate or the starting material were apparent.

C. At 300° in a Nitrogen Stream.—Twenty-five grams of tetrakis(trifluoromethylthio)methane was pyrolyzed at atmospheric pressure and 300 ° during 1 hr in the manner just described except that a slow stream of nitrogen was passed through the set-up during the pyrolysis. A gas chromatogram indicated that the pyrolysate (17.12 g) consisted of tetrakis(trifluoromethylthio)-ethylene and bis(trifluoromethyl)trithiocarbonate in a ratio of about 3:1. Small quantities of bis(trifluoromethyl) sulfide, disulfide, and the starting material were also apparent.

7. **Addition of Trifluoromethanesulfenyl Chloride to Ethylene.**—A mixture of 60 ml of acetonitrile, 216 g (1.59 moles) of trifluoromethanesulfenyl chloride, and 52 g (1.85 moles) of ethylene contained in a 400-ml pressure vessel was heated slowly to 100° and kept at that temperature for 3 hr. This reaction mixture was combined with two similar mixtures, one derived from 203 g and the other from 165 g of the sulfenyl chloride. The combined reaction mixtures were poured into a large excess of water. The organic layer was extracted once with water, dried over anhydrous magnesium sulfate, and distilled through a large spinning-band still. There was thus obtained 584 g (83%) of trifluoromethyl 2-chloroethyl sulfide distilling at 90–93°. The H^1 nmr pattern is identical with that of the product obtained from the free-radical additon of trifluoromethanethiol to vinyl chloride.[4b]

8. **Dehydrochlorination of Trifluoromethyl 2-Chloroethyl Sulfide.**—A solution of 75 g (0.456 mole) of trifluoromethyl 2-chloroethyl sulfide and 100 ml of absolute ethanol was heated to reflux in a 1-l. flask fitted with a magnetic stirrer, an addition funnel, and a warm-water reflux condenser which was connected to an acetone–Dry Ice cooled trap. A solution of 73 g of potassium hydroxide (85%) in 500 ml of absolute ethyl alcohol was added in a slow stream during about 0.5 hr. The mixture was then refluxed for 1 hr. Distillation of the trap contents through a small spinning-band still gave 53 g (97%) of trifluoromethyl vinyl sulfide distilling at 26–27°. The infrared and ultraviolet spectra are tabulated in Table III.

Anal. Calcd for $C_3H_3F_3S$: F, 44.5; S, 25.0. Found: F, 44.1; S, 25.1.

9. **Addition of Chlorine to Trifluoromethyl Vinyl Sulfide.**—To a solution of 6.0 g (0.0468 mole) of trifluoromethyl vinyl sulfide in 10 ml of trichlorofluoromethane (Freon-11) in a small

TABLE VI

Isomer	Bp, °C	$n^{24}D$	Nmr H^1 (τ), ppm	Nmr F^{19}, cps	Ultraviolet, λ_{max}, mμ (ε)	Sulfur, % Calcd	Sulfur, % Found	Fluorine, % Calcd	Fluorine, % Found
cis	96.5	1.3831	3.27	2392	234 (5980) 218 (6530)	28.1	28.0	50.0	49.8
trans	96.5	1.3892	3.27	2428	247 (7210) 223 (5340)	28.1	28.0	50.0	49.9

quartz tube fitted with a Dry Ice condenser, a gas inlet tube, and a magnetic stirrer was added 2 ml (at −76°) of liquid chlorine. The mixture was irradiated with a sun lamp for a few minutes and then distilled through a small spinning-band still. There was thus obtained 5.07 g (54%) of trifluoromethyl 1,2-dichloroethyl sulfide distilling at 121.5–123°, $n^{25}D$ 1.4203. The H^1 nmr pattern consists of two resonances, one a doublet at τ 6.05 (J = 6 cps) and the other a triplet at 4.55 in an intensity ratio of 2:1.

Anal. Calcd for $C_3H_3Cl_2F_3S$: Cl, 35.6; F, 28.6; S, 16.1. Found: Cl, 36.1; F, 28.5; S, 15.9.

10. Addition of Bromine to Trifluoromethyl Vinyl Sulfide.—To a solution of 20 g (0.156 mole) of trifluoromethyl vinyl sulfide in 50 ml of trichlorofluoromethane was added a solution of 8 ml of bromine in 50 ml of the same solvent during 45 min. The mixture was irradiated with a sun lamp until the bromine color had vanished (a few minutes). Distillation of the reaction mixture through a small spinning-band still gave 39.6 g (87%) of trifluoromethyl 1,2-dibromoethyl sulfide distilling at 42° (7 mm), $n^{24}D$ 1.4812.

Anal. Calcd for $C_3H_3Br_2F_3S$: Br, 55.4; F, 19.8. Found: Br, 55.4; F, 19.9.

11. Addition of Trifluoromethanethiol to Trifluoromethyl Vinyl Sulfide.—A mixture of 53 g (0.414 mole) of trifluoromethyl vinyl sulfide and 50 g (0.49 mole) of trifluoromethanethiol in a quartz tube fitted with a Dry Ice condenser, a magnetic stirrer, and a gas inlet tube was irradiated with a low-pressure mercury resonance lamp for 3 hr as described previously.[4a] Distillation of the reaction mixture through a small spinning-band still gave 77.5 g (82%) of 1,2-bis(trifluoromethylthio)ethane as a colorless liquid distilling at 59° (108 mm), $n^{25}D$ 1.3740. The H^1 nmr pattern consists of a single unsplit resonance at τ 6.82.

Anal. Calcd for $C_4H_4F_6S_2$: F, 49.5; S, 27.8. Found: F 49.8; S, 27.8.

12. Free-Radical Addition of Trifluoromethanesulfenyl Chloride to Trifluoromethyl Vinyl Sulfide.—A mixture of 33 g (0.267 mole) of trifluoromethyl vinyl sulfide and 32 g (0.234 mole) of trifluoromethanesulfenyl chloride was irradiated for 1 hr as described above. Upon distillation through a small spinning-band still, two fractions were collected. Fraction A had bp 126–131°, $n^{25}D$ 1.3995 (18.45 g). Fraction B had bp 131–133°, $n^{25}D$ 1.3942 (16.18 g). Some lower boiling material was obtained which was shown by gas chromatography to contain bis(trifluoromethyl) disulfide and several other unidentified materials in low yield. Examination of fractions A and B by gc (6-ft 20% fluoroalkyl pyromellitate on Columnpak, 81°, He flow rate of 55 ml/min) indicated that each fraction contained the same three major components: 18, 77, and 5% in A, and 0.2, 86, and 14% in B. Samples of each were separated by preparative-scale gc. The material with the lowest retention time (18% of fraction A) was trifluoromethyl 1,2-dichloroethyl sulfide, bp 122°, $n^{25}D$ 1.4213. The H^1 nmr spectrum consists of a doublet at τ 6.05 (J = 6 cps) and a triplet at 4.55 in an intensity ratio of 2:1.

The most abundant component of each fraction was 1,1-bis-(trifluoromethylthio)-2-chloroethane, bp 127–128°, $n^{25}D$ 1.3955. The H^1 nmr spectrum (neat) consists of a doublet at 3.79 ppm from TMS (J = 5.5 cps) and a triplet at 4.73 ppm in an intensity ratio of 2:1.

Anal. Calcd for $C_4H_3ClF_6S_2$: Cl, 13.4; F, 43.0; S, 24.2. Found: Cl, 13.5; F, 42.9; S, 24.5.

The component (14% of fraction B) with the longest retention time was identified as 1,1,2-tris(trifluoromethylthio)ethane, bp 137.5°, $n^{25}D$ 1.3803. The H^1 nmr spectrum consists of a doublet at τ 6.50 (J = 7.3 cps) and a triplet at 5.18 in an intensity ratio of 2:1 and is identical with the spectrum of VI. The infrared spectra (Table III) of thes two materials are also identical.

Anal. Calcd for $C_5H_3F_9S_3$: F, 51.8; S, 29.1. Found: F, 50.8; S, 29.3.

13. Preparation of Chloro-1,2-bis(trifluoromethylthio)ethane by Chlorination of 1,2-Bis(trifluoromethylthio)ethane.—A solution of 25.3 g (0.110 mole) of 1,2-bis(trifluoromethylthio)ethane and 40 ml of fluorotrichloromethane was placed in a flask fitted with gas inlet tube and an acetone–Dry Ice condenser. About 1 ml of liquid chlorine (at −76°) was added from a small graduated trap cooled in Dry Ice, and the refluxing mixture was irradiated with a sun lamp until the yellow color was nearly gone. This procedure was repeated until a total of 5 ml (7.8 g, 0.110 mole) of chlorine had been added. After distillation of the solvent the residue was examined by gc (6-ft 20% diglyceride of ω-trifluorohexanoic acid on Columpak, 82°, He flow rate of 55 ml/mm) and found to contain several compounds, the most abundant being the starting material and the monochloro compound. Upon distillation of the residue through a small spinning-band still, a fraction (4.04 g) was obtained boiling at 60–65° (80 mm) which was shown by gc to contain about 75% of the monochloro compound. A pure sample was separated by preparative-scale gc, bp 129°, $n^{24}D$ 1.3950. The H^1 nmr spectrum (neat) consists of a doublet at 3.31 ppm (J = 7 cps) and a triplet at 5.26 in an intensity ratio of 2:1.

Anal. Calcd for $C_4H_3ClF_6S_2$: F, 43.0; S, 24.2. Found: F, 42.8; S, 23.7.

14. Reaction of Trifluoromethyl Vinyl Sulfide with 2,3-Dimethylbutadiene.—A mixture of 10 ml of trifluoromethyl vinyl sulfide and 10 ml of 2,3-dimethylbutadiene contained in a 100-ml stainless steel autoclave was heated at 200° for 15 hr. Distillation of the reaction mixture gave 9.17 g (about 56%) of 4-trifluoromethylthio-1,2-dimethylcyclohexene distilling at 49–54° (3.75 mm), $n^{25}D$ 1.4470–1.4498. A gas chromatogram indicated that several impurities were present. A pure sample of the product was obtained by preparative-scale gc (4-ft 25% fluoroalkyl pyromellitate (Zonyl E-T) on Gas Chrom R, 125°, He flow rate of 900 ml/min), bp 89° (32 mm), $n^{25}D$ 1.4446.

Anal. Calcd for $C_9H_{13}F_3S$: C, 51.4; H, 6.2; S, 15.3. Found: C, 52.1, 51.9; H, 6.4, 6.4; S, 14.9, 15.0.

15. Dehydrobromination of 1,2-Bis(trifluoromethylthio)bromoethane. Preparation of *cis*- and *trans*-1,2-Bis(trifluoromethylthio)ethylene.—To a solution of 47.5 g (0.154 mole) of 1,2-bis-(trifluoromethylthio)bromoethane (see section 19) in 50 ml of absolute ethanol at 5° was added during 20 min a solution of 10.1 g of 85% potassium hydroxide in 60 ml of absolute ethanol. The temperature was maintained under 30°. The reaction mixture was stirred at room temperature for 0.5 hr and poured into a large excess of ice water. The organic layer was separated, washed twice with water, dried over anhydrous magnesium sulfate, and distilled through a small spinning-band still. There was thus obtained 13.46 g (38.3%) of 1,2-bis(trifluoromethylthio)-ethylene as a clear, colorless liquid distilling at 92–98°, $n^{25}D$ 1.3880–1.3849.

Anal. Calcd for $C_4H_2F_6S_2$: F, 50.0. Found: F, 50.0.

A gas chromatogram (6-ft 25% ethyl ester of Kel-F acid 8114 on Gas Chrom R, 40°, He flow rate of 400 ml/min) indicated the presence of two isomers in a ratio of 75:24. Pure samples of the two isomers were obtained by preparative-scale gc. An analysis of the infrared spectra of the pure isomers (see the Discussion) indicated that the more abundant component was the *cis* isomer. Additional characterization is given in Table VI.

16. Photoinitiated Addition of Trifluoromethanethiol to Bis-(trifluoromethylthio)acetylene. Preparation of Tris(trifluoromethylthio)ethylene.—A mixture of 19.6 g (0.087 mole) of bis-(trifluoromethylthio)acetylene (section 20) and 32 g (0.314 mole) of trifluoromethanethiol contained in a quartz tube fitted with an acetone–Dry Ice condenser was irradiated with a low-pressure mercury resonance lamp as described above for a period of 3 days. Distillation of the reaction mixture through a small spinning-band still gave 11.1 g (39%) of tris(trifluoromethylthio)-ethylene distilling at 42–47.5° (31 mm), $n^{26}D$ 1.4004–1.4013. The H^1 nmr spectrum consists of a single unsplit resnonace at τ 2.13. The infrared and ultraviolet spectra are tabulated in Table III.

Anal. Calcd for $C_5HF_9S_3$: F, 52.0; S, 29.3. Found: F, 51.6; S, 29.8.

17. Reaction of Tetrakis(trifluoromethylthio)ethylene with Methanol and Sodium Methoxide.—A solution of 30 g (0.55 mole) of sodium methoxide in 300 ml of methanol was added dropwise to a stirred solution of 30 g (0.070 mole) of tetrakis(trifluoromethylthio)ethylene in 150 ml of methanol maintained under 35°. The mixture was stirred for 4 hr and then poured into a large excess of water. The organic phase was removed by three extractions with 150 ml of ether. The extracts were dried over anhydrous magnesium sulfate, filtered, and distilled through a small spinning-band still. There was thus obtained 24.46 g (64%) of crude trimethyl bis(trifluoromethylthio)orthoacetate distilling at 64–66.5° (9 mm), $n^{25}D$ 1.3966–1.3998. The H^1 nmr pattern contains two resonances at τ 6.58 (OCH_3) and at 5.13 (CH) in an intensity ratio of 9:1. Neither peak exhibits observable splitting although the CH peak is rather broad. There is also another peak evident at τ 6.0 which is obviously due to an impurity since its proportion varies as the material is fractionated. The F^{19} nmr pattern contains a single, unsplit resonance at 2364 cps.

Anal. Calcd for $C_7H_{10}F_6O_3S_2$: F, 35.6; S, 20.0. Found: F, 35.8; S, 20.0.

18. Reaction of Tetrakis(trifluoromethylthio)ethylene with Diethylamine.—A mixture of 20 g (0.0468 mole) of tetrakis(trifluoromethylthio)ethylene, 20 ml (14.22 g, 0.1944 mole) of diethylamine, and 50 ml of anhydrous ether was stirred at room temperature for 22 hr and then refluxed for 4 hr. After standing at room temperature for 48 hr, the liquid portion was decanted from the mushy solid [probably $(C_2H_5)_2NH\cdot HF$] and distilled, first at atmospheric pressure to remove the ether, and then through a small spinning-band still with an oil pump. Two fractions were obtained. Fraction 1 (3.83 g) had bp 39° (0.5 mm)–41° (0.7 mm), $n^{24}D$ 1.4860–1.4842. Fraction 2 (9.25 g had bp 52–54° (0.9 mm), $n^{25}D$ 1.4347. Examination of fraction 1 by gc (6-ft, 10% butanediol succinate on Chromosorb W, 125°, He flow rate of 70 ml/min) indicated that it was largely (>85%) one compound. Fraction 2 was also almost entirely a single compound. A sample of the main component of each fraction was separated by preparative scale gc.

The main component of fraction 1 was shown by infrared spectroscopy to be N,N-diethylthiocarbamoyl fluoride[20]: bp 53° (1.60 mm), $n^{24}D$ 1.4934; ultraviolet 304 mμ (ϵ 108), 254 mμ (ϵ 18,100).

Anal. Calcd for $C_5H_{10}FNS$: F, 14.1; N, 10.4. Found: F, 14.3; N, 10.5, 10.9.

The main component of fraction 2 was identified as 1,1-bis(trifluoromethylthio)-2-fluoro-2-diethylaminoethylene or an isomer thereof, bp 33° (0.10 mm), $n^{24}D$ 1.4348. The infrared and ultraviolet spectra are tabulated in Table III.

Anal. Calcd for $C_8H_{10}F_7NS_2$: F, 41.9; N, 4.4; S, 20.2. Found: F, 41.2; N, 4.6, 4.7; S, 20.1, 20.2.

19. Bromination of 1,2-Bis(trifluoromethylthio)ethane.—A mixture of 60 g (0.26 mole) of 1,2-bis(trifluoromethylthio)ethane, 34 ml of bromine, and 150 ml of carbon tetrachloride was placed in a 500-ml flask fitted with a Glascol heater and a reflux condenser. The mixture was refluxed and irradiated with a sun lamp for 3 days. Distillation of the reaction mixture through a small spinning-band still gave 35.3 g (44%) of bromo-1,2-bis(trifluoromethylthio)ethane distilling at 75° (77 mm), $n^{25}D$ 1.4226, and 43 g (43%) of dibromo-1,2-bis(trifluoromethylthio)ethane distilling at 59° (7 mm), $n^{25}D$ 1.4599.

Monobromide.—The H^1 nmr pattern contains a doublet at τ 6.37 (J = 7 cps) and a triplet at 4.66 in an intensity ratio of 2:1.

Anal. Calcd for $C_4H_3BrF_6S_2$: Br, 25.8; F, 36.9. Found: Br, 25.9; F, 36.7.

Dibromide.—The H^1 nmr pattern contains two singlets at τ 4.27 and 5.7 in an intensity ratio of 1.13:1. The relative intensities of these peaks vary as the fraction is distilled.

Anal. Calcd for $C_4H_2Br_2F_6S_2$: Br, 41.2; F, 29.4. Found: Br, 41.9; F, 29.4.

20. Dehydrobromination of Dibromo-1,2-bis(trifluoromethylthio)ethane. Preparation of Bis(trifluoromethylthio)acetylene.—One-hundred and fifty-five grams of potassium hydroxide (85%) was placed in a flask fitted with a dropping funnel, a gas inlet tube through which a slow stream of nitrogen passed, an exit tube which led to a Dry Ice cooled trap, and an oil bath. The oil bath was heated to 155° which caused the potassium hydroxide to melt. While the oil bath was maintained at 155°, 49.83 g (0.129 mole) of dibromo-1,2-bis(trifluoromethylthio)ethane was added during about 0.50 hr. Distillation of the trap contents through a small Vigreux still gave 19.3 g (66.5%) of bis(trifluoromethylthio)acetylene distilling at 81–85°, $n^{25}D$ 1,3924–1.3928. Upon redistillation through a small spinning-band still, the product distilled at 83°. The infrared spectrum is tabulated in Table III.

Anal. Calcd for $C_4F_6S_2$: F, 50.3; S, 28.4. Found: F, 50.4; S, 28.4.

21. Photoinitiated Addition of Trifluoromethanesulfenyl Chloride to Bis(trifluoromethylthio)acetylene.—A mixture of 14.8 g (0.0655 mole) of bis(trifluoromethylthio)acetylene and 11 g (0.0805 mole) of trifluoromethanesulfenyl chloride contained in a quartz tube fitted with an acetone–Dry Ice condenser was irradiated with a low-pressure mercury resonance lamp as described above for 18 hr. Distillation of the reaction mixture through a small spinning-band still gave 11.3 g (47.4%) of tris(trifluoromethylthio)chloroethylene distilling at 52–60° (25 mm), $n^{25}D$ 1.4298–1.4308. The ultraviolet and infrared spectra are tabulated in Table III.

Anal. Calcd for $C_5ClF_9S_3$: Cl, 9.8; F, 47.2. Found: Cl, 10.3; F, 47.3.

22. Addition of Methanol to Bis(trifluoromethylthio)acetylene.—A solution of 5.0 g (0.0221 mole) of bis(trifluoromethylthio)acetylene in 55 ml of methanol was added dropwise during 5 min to a stirred solution of 0.25 g (0.0046 mole) of sodium methoxide in 25 ml of methanol. After the mildly exothermic reaction was over and the temperature had returned to room temperature, the mixture was heated on a water bath for 0.25 hr. The mixture was then poured into a large excess of water and the organic phase was removed by two extractions with 25 ml of ether. The ether extracts were dried over anhydrous magnesium sulfate, filtered, and distilled through a microstill. There was thus obtained 3.48 g (61%) of 1,2-bis(trifluoromethylthio)vinyl methyl ether distilling at 73° (115 mm)–77° (117 mm), $n^{25}D$ 1.4007–1.4020. The H^1 nmr pattern contains two resonances in the methoxy region (τ 6.11 and 6.22) and two peaks in the vinyl region (τ 3.85 and 4.38) indicating the presence of both possible isomers in a ratio of about 2:1. The infrared spectrum of this mixture of isomers contains a C=C stretch band at 1613 cm^{-1}. The ultraviolet spectrum contains maxima at 246 mμ (ϵ 5680) and 218 mμ (ϵ 4700).

Anal. Calcd for $C_5H_4F_6OS_2$: C, 23.3; H, 1.6; S, 24.4. Found: C, 23.3; H, 2.2; S, 24.3.

23. Addition of Morpholine to Bis(trifluoromethy'thio)acetylene.—A solution of 2.89 g (0.0332 mole) of morpholine in 30 ml of anhydrous ether was added dropwise to a solution of 7.5 g (0.0332 mole) of bis(trifluoromethylthio)acetylene in 30 ml of ether. The temperature was maintained under 35°. The mixture was stirred for 10 min, heated at reflux briefly, and filtered. Distillation through a small spinning-band still gave 8.68 g (84%) of 1,2-bis(trifluoromethylthio)-N-morpholinoethylene distilling at 40.5–49° (0.05 mm), $n^{25}D$ 1.4550–1.4600. This material became dark and viscous after a few days at room temperature.

The H^1 nmr spectrum contains two resonances in the vinyl proton region (τ 3.67 and 4.46) in a ratio of 1:2.3 in addition to the resonances due to the morpholine group methylene protons. The intensity ratio of the methylene resonances to the vinyl proton resonances is 8:1. The infrared spectrum of this mixture of isomers contains a C=C stretch band at 1546 cm^{-1}. The ultraviolet spectrum contains a maximum at 274 mμ (ϵ 7000).

Anal. Calcd for $C_8H_9NOS_2$: C, 30.7; H, 2.9; F, 36.4; N, 4.5. Found: C, 31.0; H, 3.0; F, 36.2; N, 4.7.

24. Addition of 2,3-Dimethylbutadiene to Bis(trifluoromethylthio)acetylene.—A mixture of 5.0 g (0.0221 mole) of bis(trifluoromethylthio)acetylene and 2.0 g (0.0244 mole) of 2,3-dimethylbutadiene was sealed in a small platinum tube and heated at 150° for 10 hr in a bomb pressured at 1000 atm. Distillation through a small Vigreux still gave 2.32 g (34%) of 1,2-bis(trifluoromethylthio)-4,5-dimethyl-1,4-cyclohexadiene distilling at 43–46° (0.30 mm), $n^{25}D$ 1.4603–1.4610. The infrared spectrum contains CH stretching bands at 2830, 2870, 2930, and 2970 cm^{-1}, but none higher.

Anal. Calcd for $C_{10}H_{10}F_6S_2$: F, 37.0; S, 20.8. Found: F, 35.3; S, 20.4.

25. Preparation of Phenyl(trifluoromethylthio)acetylene.—A solution of ethylmagnesium bromide was prepared in the usual way from 16.7 g (0.153 mole) of ethyl bromide and 4.78 g (0.197

g-atom) of magnesium turnings in 50 ml of anhydrous ether in a flask fitted with a gas inlet tube, a dropping funnel, stirrer, and a Dry Ice–acetone condenser. To this solution, 20 g (0.196 mole) of phenylacetylene in 30 ml of ether was added slowly. After the mixture was cooled to 15–20°, 12 ml (at −76°, 18.8 g, 0.138 mole) of trifluoromethanesulfenyl chloride was added through the gas-addition tube above the surface of the reaction mixture and allowed to reflux into the reaction mixture. This addition required about 1 hr. The reaction mixture was then poured into large volume of ice water containing an excess of hydrochloric acid. The product was removed by two extractions with 100 ml of ether. The ether extracts were washed once with water, dried over anhydrous magnesium sulfate, and rapidly distilled through a small spinning-band still. There was thus obtained 13.77 g (49%) of crude product distilling at 42.5 (1.75 mm)–56° (2.35 mm), $n^{25}D$ 1.5219–1.5509. Upon redistillation of this fraction, 7.20 g (26%) of phenyl (trifluoromethylthio)-acetylene was obtained distilling at 43° (2.4 mm), $n^{25}D$ 1.5198–1.5203. The infrared spectrum is recorded in Table III.

Anal. Calcd for $C_9H_5F_3S$: C, 53.5; H, 2.5; F, 28.2; S, 15.8. Found: C, 53.6; H, 2.6; F, 28.0; S, 15.7.

26. **Nmr Spectra.**—F^{19} nmr spectra (56.4 Mc) were obtained from 10% solutions of the compounds in fluorotrichloromethane (Freon-11) with an A-56/60 nmr spectrometer manufactured by Varian Associates, Palo Alto, Calif. Chemical shifts are reported in cycles per second (cps) measured from the resonance of fluorotrichloromethane as an internal standard.

H^1 nmr spectra (60 Mc) were obtained with an A-60 nmr spectrometer manufactured by Varian Associated, Palo Alto, Calif. Solutions (10%) in CCl_4 containing tetramethylsilane were used except where indicated.

Registry No.—I, 13003-31-1; II (n = 1), 819-67-0; II (n = 2), 674-64-6; II (n = 3), 13003-34-4; II (n = 5), 13003-35-5; III, 691-69-0; IV, 681-87-8; V, 674-43-1; VI, 688-53-9; VII, 13003-40-2; XI, 762-80-1; XIII, 674-36-2; XIV, 13040-44-3; XV, 1542-22-9; XVII, 13003-43-5; XVIII, 13003-44-6; XIXa, 13003-45-7; XIXb, 13003-46-8; XX, 13003-47-9; XXI, 13003-48-0; XXII, 13003-49-1; XXIII, 2266-81-1; XXV, 2069-87-6; XXVI, 13003-52-6; *cis* XXVII, 13003-53-7; *trans* XXVII, 13003-54-8; XXVIII, 13003-55-9; XXIX, 13003-56-0; XXX, 2002-89-3; trifluoromethanethiol, 1493-15-8; bromo-1,2-bis(trifluoromethylthio)ethane, 673-62-1; $CF_3SO_2C_2H_5$, 13003-57-1; $CF_3SO_2(CH_2)_2SO_2CF_3$, 13040-45-4; $CF_3SO_2(CH_2)_3SO_2CF_3$, 13003-58-2; $CF_3SO_2(CH_2)_5SO_2CF_3$, 13003-59-3.

The Thiazolo[2,3-*b*]thiazolium Cation. A New Aromatic System[1]

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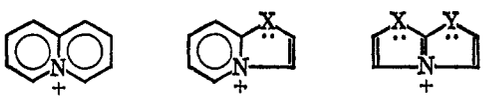
Through cyclization of α-(2-thiazolylthio)aldehydes and ketones, the first simple thiazolo[2,3-*b*]thiazolium salts have been prepared. With a mixture of sulfuric and nitric acids, the 3,5-dimethylthiazolo[2,3-*b*]thiazolium ion undergoes mononitration. With sodium hydroxide, it undergoes ring opening to afford 2-(4-methylthiazol-2-on-3-yl)prop-1-ene-1-thiol.

In an earlier communication,[3] it was pointed out that on the basis of the stability of the quinolizinium ion (1) which may be considered an azonialog[4] of naphthalene, there might exist a whole series of stable azonialogs of well-known bicyclic aromatic heterocyclic systems. To date the thiazolo[3,2-*a*]pyridinium (2, X = S),[3,5,6] the oxazolo[3,2-*a*]pyridinium (2, X = O),[7] and the imidazo[1,2-*a*]pyridinium[8] (2, X = NR) cations have been described. These ions are azonialogs of thianaphthene, benzofuran, and indole, respectively, and each has a 10-π-electron system in a structure formed by the fusion of a five- with a six-membered ring.



1 2 3

It seemed reasonable to expect the existence of stable aromatic cationoid systems having structures like 3 in which there are two, fused five-membered rings and the heteroatoms designated X and Y each have at least one pair of unshared electrons. The present communication describes the first simple[9] thiazolo-[2,3-*b*]thiazolium salts.

By analogy to the synthesis of thiazolo[3,2-*a*]pyridinium salts,[5,6] it would be expected that 2-thiazolyl β-keto sulfides (5) could be cyclized to thiazolothiazolium salts (6). Fortunately, the 2-mercaptothiazoles (4) needed for the preparation of such sulfides are readily available[10,11] by the reaction of α-halo ketones or aldehydes with ammonium dithiocarbamate. Even more fortunate is the earlier observation that ammonium dithiocarbamate can be made to react with 2 moles of an α-halo ketone to afford the required keto sulfide (5, $R_1 = R_3$) directly. The first cyclization attempt was carried out on the known[10] 1-(4-methyl-2-thiazolylthio)propanone (5c). (See Table I.)

Unlike the 1-(2-pyridylthio)propanone, methylthiazolylthiopropanone (5c) did not cyclize readily in concentrated sulfuric acid at room temperature, but on heating for 3 hr at 100° afforded a new salt in 97% yield. The ultraviolet absorption spectrum of the cyclization product showed new maxima at longer wavelengths and the infrared absorption spectrum showed the absence of a carbonyl group. Most convincing evidence that the new product was indeed 6c was afforded by the remarkably simple nmr spec-

(1) A portion of this work was described in a preliminary communication: C. K. Bradsher, D. F. Lohr, Jr., and W. J. Jones, Jr., *Tetrahedron Letters* 1723 (1965).

(2) James B. Duke Fellow, 1964–1966.

(3) C. K. Bradsher and W. F. Lohr, Jr., *Chem. Ind.* (London), 1801 (1964).

(4) The term "azonialog" has been proposed to describe an aromatic compound derived from another by the replacement of a bridgehead carbon atom by a quaternary nitrogen: R. E. Doolittle and C. K. Bradsher, *J. Heterocyclic Chem.*, **2**, 399 (1965).

(5) F. S. Babichev and V. N. Bubnovskaya, *Ukr. Khim. Zh.*, **30**, 848 (1964).

(6) C. K. Bradsher and D. F. Lohr, Jr., *J. Heterocyclic Chem.*, **3**, 27 (1966).

(7) C. K. Bradsher and Mary F. Zinn, *ibid.*, **1**, 219 (1964).

(8) C. K. Bradsher, E. F. Litzinger, Jr., and M. F. Zinn, *ibid.*, **2**, 331 (1965).

(9) G. F. Duffin and J. D. Kendall [U. S. Patent 2,513,923 (1950)] have described a betaine which has the thiazolo[2,3-*b*]thiazolium nucleus.

(10) I. Ubaldini and A. Firoenza, *Gazz. Chim. Ital.*, **73**, 169 (1943).

(11) W. S. Emerson and T. M. Patrick, *J. Org. Chem.*, **13**, 722 (1948).