Synthesis of Halogenated Dialkyl Sulfides

ROSS C. TERRELL, THOMAS UCCIARDI, AND JAMES F. VITCHA

Central Research Laboratories, Air Reduction Company, Inc., Murray Hill, New Jersey

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A series of halogenated dialkyl sulfides has been synthesized. The chlorination, fluorination, dehydrohalogenation, and acid cleavage of some of these sulfides have also been studied.

The base-catalyzed reaction of mercaptans with gaseous fluoro olefins under pressure as well as dehydrofluorination, chlorination, and other reactions of the sulfides formed have been reported.[1]

None of the reported reactions, however, has yielded alkyl sulfides **1** having a completely halogenated ethyl group. The synthesis of some compounds of this type

$$RSCF_2CX_3$$

1, R = alkyl; X = halogen

(Table I) together with some other reactions of halogenated sulfides are the subject of this paper. Two methods (A and B) were used to synthesize alkyl pentahaloethyl sulfides **1**.

$$RSH + CF_2{=}CX_2 \xrightarrow{\text{base}} \underset{\mathbf{2}}{RSCF_2CX_2H} \xrightarrow[\text{DMOS}]{\text{KOH}}$$

$$\underset{\mathbf{3}}{RSCF{=}CX_2} \xrightarrow{X_2} \underset{\mathbf{4}}{RSCFXCX_3} \xrightarrow[SbF_5]{SbF_3} RSCF_2CX_3 \quad (A)$$

X = halogen

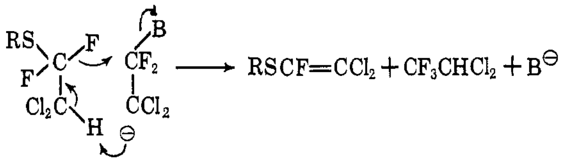
$$CF_3CH_2OTs + RSNa \xrightarrow{\text{DMSO}} CF_3CH_2SR \xrightarrow{SO_2Cl_2}$$

$$CF_3CCl_2SR \xrightarrow[SbF_5]{SbF_3} CF_3CF_2SR \quad (B)$$

Discussion

Reaction of Mercaptans with Fluoro Olefins.—The published method[1] for the synthesis of fluoroalkyl sulfides was found to be both inconvenient and hazardous[2] and a better method has been developed. It has been found that the reaction proceeds readily even at temperatures below 0° and can be carried out by bubbling the fluoro olefin into the mercaptan in the presence of a basic catalyst. Sodium hydroxide, sodium methoxide, and Triton B were used and were equally effective. This method works well for the olefins, trifluorochloroethylene, trifluorobromoethylene, and *unsym*-difluorodichloroethylene, but not for trifluoroethylene. Methyl, ethyl, propyl, isopropyl, and 2,2,2-trifluoroethyl mercaptans gave equally good results. The olefin can also be generated *in situ*[3] by using a haloethane such as 1,1,2-trifluoro-2-chloroethane and a slightly larger than stoichiometric quantity of sodium mercaptide. Reactions were uncomplicated except in the case of 1,1-difluoro-2,2-dichloroethylene where the exothermic reaction with methyl mercaptan at temperatures above 50° gave a mixture of saturated and unsaturated sulfides plus the hydrogen fluoride addition product of the olefin. This unusual reaction, which is base catalyzed and takes place without evolution of free hydrogen fluoride, can be formulated as an intramolecular, base-catalyzed transfer of hydrogen fluoride from the sulfide to the olefin.[4]

$$B^{\ominus} + CF_2{=}CCl_2 \rightleftarrows BCF_2CCl_2^{\ominus} \xrightarrow{RSCF_2CHCl_2}$$



Dehydrohalogenation of Sulfides.—The dehydrohalogenation of fluoro sulfides using potassium hydroxide in mineral oil has been reported.[1] This method has been found to require long heating and often to yield mixtures of products. Dehydrofluorination with powdered potassium hydroxide in dimethyl sulfoxide has been found to be a better method. Reaction in this solvent is rapid, exothermic,[5] and usually complete in about 10 min.

The vinyl sulfides formed were less stable than the saturated sulfides and sometimes decomposed on long standing at room temperature. The sulfides are, however, more stable than the corresponding oxygen compounds.[6] Vinyl sulfides **3** were quantitatively halogenated with either bromine or chlorine. Sulfuryl chloride gave the same product as chlorine, in addition to mixtures of products resulting from some α-chlorination.[7]

Fluorination of Chloro and Bromo Sulfides.—Fluorination of bromo and chloro sulfides **4**, using an excess of antimony trifluoride and a catalytic amount of antimony pentafluoride, gave substitution of only the α-chlorine or bromine. In none of the reactions were any other halogens replaced. The reaction was sometimes difficult, requiring a large excess of antimony trifluoride and long heating. Structure proof of the fluorinated sulfides **4** and **5** was done by cleavage to thio esters with concentrated sulfuric acid.[8] The thio esters were identified by conversion to known anilides.

Chlorination of Methyl-1,1,2-trifluoro-2-chloroethyl Sulfide with Chlorine and Sulfuryl Chloride.—The chlo-

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[1] (a) I. L. Knuyants and A. V. Fokin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 261 (1952); (b) I. L. Knuyants, A. I. Shchekotikhin, and A. V. Fokin, *ibid.*, 282 (1953); (c) K. E. Rapp, R. L. Pruett, J. T. Barr, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., *J. Am. Chem. Soc.*, **72**, 3642 (1950); (d) *ibid.*, **74**, 749 (1952).

[2] A violent exothermic reaction resulted when methyl mercaptan, trifluorochloroethylene, and a catalytic amount of Triton B were mixed at −78° as described in ref. 1c.

[3] P. Tarrant and J. A. Young, *J. Am. Chem. Soc.*, **75**, 932 (1953).

[4] The reason that this reaction occurs with this olefin and not the others used may be due to its unusually high solubility in the reaction mixture. It has been found that the product, $CH_3SCF_2CHCl_2$, will dissolve more than three times its own weight of $CF_2{=}CCl_2$ (b.p. 18°) at temperatures above 50°.

[5] The exothermic reaction is easily controlled if the potassium hydroxide is added slowly to a solution of the sulfide in dimethyl sulfoxide. If the sulfide is added to the base in dimethyl sulfoxide, a violent uncontrollable reaction often takes place.

[6] R. S. Corley, J. Lal, and M. W. Kane, *J. Am. Chem. Soc.*, **78**, 3489 (1956).

[7] C. Price and S. Oae, "Sulfur Bonding," The Ronald Press Co., New York, N. Y., 1962, p. 59.

[8] Attempted cleavage of α,α-difluoro sulfides using aluminum chloride has been reported to yield only tars. See ref. 1c and 1d.

TABLE I

Compound	B.p., °C. (mm.)	$n^{20}D$	Yield, %[a]	% C		% H		% F	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
$CHCl_2SCF_2CHFCl$	78 (50)	1.4507	15[b]	15.45	15.7	0.86	0.96	45.6	43.5[c]
$CH_3SCF_2CFClBr$	44 (20)	1.4511	50	14.80	14.87	1.23	1.31	23.4	23.3
$CH_3SCFBrCFClBr$	65 (3)	1.5300	96	11.85	11.82	0.99	0.91	...	...
$CH_3SCF{=}CCl_2$	44 (20)	1.5070	90	22.5	22.7	1.88	1.89	11.85	12.5
$CH_3SCF{=}CFCl$[d]	96.5	1.4454	80	24.8	24.85	2.08	2.15	...	...
CH_2ClSCF_2CHFCl	52 (18)	1.4414	65	18.1	18.47	1.51	1.50	28.6	28.4
$CF_3CCl_2SCH_3$	52 (100)	1.4233	50	18.1	18.02	1.51	1.54	35.6	34.8[c]
$CH_3SCF_2CFCl_2$	45 (50)	1.4196	35	18.1	18.75	1.51	1.65	28.6	28.2
$CH_3SCF_2CCl_3$	58 (20)	...	15	...	...	...	...	50.4	49.5[c]
$CH_3SCFClCFCl_2$	77 (50)	1.4684	75	16.7	16.68	1.4	1.41	17.65	17.66
$CF_3CF_2SCH_3$	36.5	1.3130	30	21.6	21.34	1.8	1.84	57.0	56.6
$CH_3SCFClCCl_3$	78 (7)	1.5144	90	15.5	15.64	1.29	1.33	8.4	8.23
CH_3SCF_2CHFBr	52 (50)	1.4375	75	17.22	17.33	1.91	1.87	...	...
$CH_3SCF_2CHCl_2$	47 (20)	1.4530	80	20.0	20.6	2.22	2.33	38.8	38.2[c]
$CH_3SCH_2CF_3$	67	1.3658	50	27.69	27.73	3.84	3.87	...	...
$CH_3SCF_2CH_2Cl$	44 (43)	1.4310	50	24.6	25.14	3.41	3.61	26.0	25.1
$CF_3CH_2SCF_2CHFCl$	60 (100)	1.3662	50	20.7	20.5	1.29	1.34	...	...
$CH_3CH_2SCF_2CHFBr$	58 (50)	1.4393	75	21.62	21.45	2.70	2.64	...	...
$CH_3S\overset{O}{\overset{\Vert}{C}}CHFCl$	65 (50)	1.4748	50	25.2	25.09	2.8	2.68	...	...
$CH_3CH_2SCF_2CHCl_2$	49 (10)	1.4525	80	24.80	24.55	3.09	3.19	19.6	19.4
$CF_3CH_2SCH_2CH_2OH$	82 (14)	1.4193	45	...	...	...	...	35.3	35.4
$CH_3CH_2SCH_2CF_3$	90	1.3778	50	33.33	33.65	4.85	4.76	...	...
$CH_3CH_2CH_2SCF_2CHFCl$	71 (50)	1.4179	55	31.2	32.0	4.19	4.18	29.6	29.68
$CH_3CH_2CH_2SCF_2CHCl_2$	57 (6)	1.4600	70	28.8	29.2	3.84	3.87	18.3	17.7
$(CH_3)_2CHSCF_2CHFCl$	58 (45)	1.4120	50	31.2	31.46	4.19	3.86	29.6	29.85
$(CH_3)_2CHSCF_2CHCl_2$	42 (5)	1.4518	50	28.8	29.04	3.84	3.88	18.3	18.22

[a] All yields are for fractionally distilled products. Purity was routinely confirmed by vapor phase chromatography. [b] 50% of the monochloro product, CH_2ClSCF_2CHFCl, was obtained from the same reaction. [c] Per cent chlorine. [d] Reference 1b gives b.p. 88–89°, $n^{20}D$ 1.4390. These figures are apparently incorrect.

rination of halogenated sulfides has been reported to yield only cleavage products resulting from splitting of the carbon–sulfur bonds.[1] A careful study of the photochlorination of methyl 1,1,2-trifluoro-2-chloroethyl sulfide has shown that two chlorination products are formed prior to degradation of the molecule.

$$CH_3SCF_2CHFCl \xrightarrow[\text{light}]{Cl_2} \underset{6}{CH_2ClSCF_2CHFCl} \longrightarrow \underset{7}{CHCl_2SCF_2CHFCl} \longrightarrow \text{degradation products}$$

After addition of 1 mole of chlorine, the crude chlorination mixture contained about 90% of the monochlorinated product **6**. Further chlorination was very slow giving a mixture of mono- **6** and dichloro sulfide **7** together with sulfur chlorides and other cleavage products. No higher chlorination products and no products resulting from replacement of the β-hydrogen were found in any of the reactions. When the chlorination was done by refluxing with excess sulfuryl chloride, only the mono chloro sulfide **6** was formed.[7]

Attempted fluorination of these chlorination products using antimony trifluoride and antimony pentafluoride gave only tars and decomposition products.

Preparation and Reactions of Alkyl 2,2,2-Trifluoroethyl Sulfides.—The reaction of the tosylate of 2,2,2-trifluoroethanol with the sodium salts of methyl, ethyl, or 2-hydroxyethyl mercaptan in dimethyl sulfoxide gave the expected thio ethers.

Methyl 2,2,2-trifluoroethyl sulfide was chlorinated by refluxing with excess sulfuryl chloride to yield only methyl 1,1-dichloro-2,2,2-trifluoroethyl sulfide. Structure of this compound was determined by cleavage with concentrated sulfuric acid followed by reaction with aniline to yield the anilide of trifluoroacetic acid. The 1,1-dichloroethyl sulfide is the expected product based on the proposed mechanism for the ionic chlorination of sulfides with sulfuryl chloride.[7] Fluorination of methyl 1,1-dichloro-2,2,2-trifluoroethyl sulfide with excess antimony trifluoride and a catalytic amount of antimony pentafluoride gave methyl pentafluoroethyl sulfide.

Experimental Section

Melting points were taken on a Fisher-Johns melting point block and are uncorrected. N.m.r. spectra were recorded with a Varian A-60 n.m.r. spectrometer using tetramethylsilane as an internal standard and carbon tetrachloride as solvent.[9a] All starting materials were purchased with the exception of 2,2,2-trifluoroethyl mercaptan which was prepared by the method of Harris and Sheppard,[9b] and the tosylate of trifluoroethanol which was supplied by The Trubek Laboratories, East Rutherford, N. J.

Addition of Mercaptans to Fluoro Olefins.—The same method was used for all reactions and is illustrated for the reaction of methyl mercaptan with trifluorochloroethylene.

Methyl mercaptan (146 g., 3 moles) and sodium methoxide (20 ml. of a 4 *N* solution) were charged to a reactor fitted with a fritted gas inlet tube, a thermometer, and a Dry Ice condenser. Trifluorochloroethylene was then added *via* the gas inlet tube at such a rate that only a slight reflux of the reaction mixture was maintained. The reaction started at about 5° and was about

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(9) (a) These spectra were determined by Dr. Martin Vogel of Rutgers University, New Brunswick, N. J. (b) J. F. Harris and W. A. Sheppard, *J. Org. Chem.*, **26**, 354 (1961).

70° at the end of the addition when the temperature dropped rapidly.[10]

The product was washed with water, dried, and fractionated to yield pure methyl 1,1,2-trifluoro-2-chloroethyl sulfide: 435 g., 90%, b.p. 105°, $n^{20}\text{D}$ 1.4045; lit.[1] b.p. 104°, $n^{20}\text{D}$ 1.4083.

Methyl 1,1-Difluoro-2-chloroethyl Sulfide.—To a solution of sodium (25 g., 1 g.-atom) in absolute methanol (125 ml.) was added methyl mercaptan (60 g., 1.25 moles) and 1,1-difluoro-1,2-dichloroethane (135 g., 1 mole). The reaction was refluxed for 4 hr., water was added, and the product was separated, dried, and fractionally distilled.[11]

Dehydrohalogenation Reactions.—Dehydrofluorination reactions were done as described for methyl 1,1,2-trifluoro-2-chloroethyl sulfide.

Powdered potassium hydroxide (160 g., 2.5 moles) was added slowly, with stirring, to a solution of methyl 1,1,2-trifluoro-2-chloroethyl sulfide (327 g., 2 moles) in dimethyl sulfoxide (160 g.). (*Caution!* Do not add the sulfide to the base.[5]) The crude product was distilled directly from the reaction mixture,[12] dried, and redistilled.

Halogenation of Vinyl Sulfides.—Vinyl sulfides were halogenated by addition of a stoichiometric amount of bromine or chlorine with cooling followed by distillation. Chlorination was also done by refluxing with an excess of sulfuryl chloride, but was less satisfactory since mixtures of products were sometimes obtained.

Chlorination of Methyl 1,1,2-Trifluoro-2-chloroethyl Sulfide. A. Chlorine.—Chlorine gas was bubbled through a fritted-glass inlet tube into methyl 1,1,2-trifluoro-2-chloroethyl sulfide with illumination from a 250-w. incandescent lamp. The reaction started at about 60° and the temperature rose during the reaction to 150° with no external heat other than that from the lamp. The amount of chlorine reacted was estimated by titration of the hydrogen chloride evolved. After addition of about 1 mole of chlorine, the reaction mixture contained 90% chloromethyl 1,1,2-trifluoro-2-chloroethyl sulfide and, after addition of about 1.4 moles of chlorine, 57% monochloromethyl sulfide and 36% dichloromethyl 1,1,2-trifluoro-2-chloroethyl sulfide plus small amounts of unidentified compounds. At this point the reaction became very slow, and, since there was some cleavage of the molecule to sulfur chlorides and other decomposition products, the reaction was stopped. The mono- and dichloromethyl sulfides were isolated by fractional distillation and the structures were confirmed by determination of the n.m.r. spectra.[9a]

B. Sulfuryl Chloride.—A mixture of methyl 1,1,2-trifluoro-2-chloroethyl sulfide (164 g., 1 mole) and sulfuryl chloride (268 g., 2 moles) was refluxed for 20 hr. and the crude product (151 g., b.p. 51–55°) was distilled through a short Vigreux column. Redistillation gave pure monochloromethyl sulfide identical with that prepared by photochlorination. There were no higher chlorination products formed in this reaction.

Ethyl 2,2,2-Trifluoroethyl Sulfide.—All reactions of sodium mercaptides with 2,2,2-trifluoroethyl tosylate were done in the same manner as described for the preparation of ethyl 2,2,2-trifluoroethyl sulfide.

To a solution of ethyl mercaptan (62 g., 1 mole) and potassium hydroxide (70 g., 1.1 moles) in water (200 ml.) was added a solution of 2,2,2-trifluoroethyl tosylate (254 g., 1 mole) in dimethyl sulfoxide (200 ml.). The crude product was distilled directly[12] from the reaction mixture, dried, and fractionally distilled.

Methyl 1,1-Dichloro-2,2,2-trifluoroethyl Sulfide.—A mixture of methyl 2,2,2-trifluoroethyl sulfide (242 g., 1.86 moles) and sulfuryl chloride (750 g., 5.6 moles) was refluxed for 10 hr. Excess sulfuryl chloride (90 g.) was distilled out and the crude product was distilled under reduced pressure, 285 g. (77%), b.p. 57° (100 mm.). This crude product was washed with dilute sodium carbonate, dried, and fractionally distilled.

Fluorination of Chloro and Bromo Sulfides.—All fluorination reactions were done in the same way and as described for the fluorination of methyl 1,2,2-trichloro-1,2-difluoroethyl sulfide.

A mixture of methyl 1,2,2-trichloro-1,2-difluoroethyl sulfide (180 g., 0.83 mole), antimony trifluoride (90 g., 0.5 mole), and antimony pentafluoride (4 g.) was heated at 130° with stirring for 15 min. The product was isolated by distillation from the reaction mixture or was decanted from the cooled, solidified antimony salts and distilled. The crude acidic product was treated with quinoline to remove acids and traces of antimony and fractionally distilled.

Cleavage of Sulfides with Concentrated Sulfuric Acid.—Methyl 1,1,2-trifluoro-2-chloroethyl sulfide (55 g.) was dissolved slowly, with cooling, in concentrated sulfuric acid (100 g.). After 10 min. the reaction was poured onto ice and the precipitated thio ester was separated and fractionally distilled. When this ester was refluxed for 2 hr. with excess aniline, methyl mercaptan was evolved. Addition of hydrochloric acid dissolved the excess aniline and precipitated the anilide of chlorofluoroacetic acid which was recrystallized from methanol–water, m.p. 84–85°, lit.[13] m.p. 84–85°. These reactions were used for structure proof of three other thio ethers (Table II) and were done in the same way except that the acid was heated in order to dissolve the sulfide, and the intermediate thio esters were not distilled.

Table II

Sulfide	M.p. of anilide, °C. Obsd.	Lit.
$CF_3CCl_2SCH_3$	88–89	$CF_3\overset{O}{\overset{\|}{C}}NHPh$, 89–90[a]
$CFCl_2CF_2SCH_3$	75–76	$CFCl_2\overset{O}{\overset{\|}{C}}NHPh$, 72–73[b]
$CFClBrCF_2SCH_3$	97	$CFClBr\overset{O}{\overset{\|}{C}}NHPh$, 98–98.3[c]

[a] R. Reed, Jr., *J. Am. Chem. Soc.*, **78**, 801 (1956). [b] Reference 13. [c] Reference 6.

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[10] When the olefin used was 1,1-dichloro-2,2-difluoroethylene, it was necessary to cool the reaction to maintain the temperature below 50° to avoid vinyl sulfide formation. In addition, there was no definition temperature drop at the end of the reaction and it was possible to add a large excess of olefin.

[11] Although this product could be isolated without difficulty, it tended to decompose on long standing at room temperature. In one case the decomposition burst a glass bottle. Fragments of the bottle showed evidence of etching from hydrogen fluoride.

[12] Higher boiling products were isolated by precipitation with water after heating the reaction mixture at 100° for 1 hr.

[13] W. T. Miller, *J. Am. Chem. Soc.*, **78**, 2793 (1956).