Precursors and Derivatives of Bis(perfluoroalkyl) Sulfoxides

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The concept that reactivity is vested in *functional groups,* and that the attached aryl or alkyl groups have only a moderating effect, is inherent in much of the systematization of organic chemistry. Thus ketones, carboxylic acids, esters, and the like are recognized as functional classes with characteristic physical and chemical properties more or less regardless of what the rest of the molecule may be.

However, fluorinated derivatives of organic compounds, in which all or at least most of the hydrogens of alkyl or aryl groups are replaced by fluorine atoms, violate the usual rules. Although the molecular weight of C_4F_{10} is four times that of C_4H_{10}, their boiling points are essentially the same. Trifluoroacetic acid, CF_3COOH, is stronger than acetic acid, CH_3COOH, by a factor of 3×10^4. Whereas most ketones are rather unreactive with nucleophiles, perfluoroacetone is so reactive that it even adds water to form a stable hydrate. Such differences are so widespread, and the methods used to synthesize perfluoro compounds are so unlike those used elsewhere in chemistry, that the chemistry of perfluorinated compounds has emerged as a well-recognized field in its own right.

Because the usual chemistry of any functional group is seldom an accurate predictor of what its perfluoro cousins will do, the chemistry of each functional class of perfluoro compounds requires independent investigation. At the time the research now described was started, little was known of the chemistry of perfluoro derivatives of sulfides, sulfoxides, sulfinic acids, and related types.
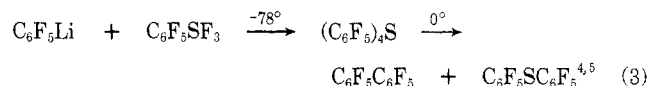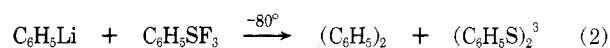
Although there are a variety of techniques available for the synthesis of compounds which contain fluorine, fluorinated sulfur(IV) compounds were, until recently, limited to sulfur tetrafluoride, sulfinyl fluoride, and a few of their derivatives. Electrochemical fluorination (ecf) of organic sulfur compounds has provided a route to many derivatives of sulfur hexafluoride, but rarely are compounds formed in which the oxidation state of the sulfur is less than six. One case where ecf does produce fluorinated sulfur(IV) is the reaction[1]

$$CS_2 \xrightarrow{\text{ecf}} CF_2(SF_3)_2 \qquad (1)$$
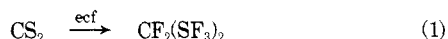
but the yield is only 0.5%. CF_3SF_3 does result from either the direct fluorination (with elemental fluo-
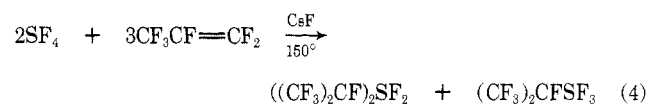
rine) of CS_2[2] or from vapor-phase fluorination of CS_2 with AgF_2,[3] but large amounts of S(VI) products are also obtained.

Fluorination of diaryl disulfides (aryl = C_6H_5, C_6F_5) with a slurry of silver difluoride in 1,1,2-trichlorotrifluoroethane provides a general route to arylsulfur trifluorides[3,4] which are easily hydrolyzed to sulfinic acids. The aryl trifluorides are good fluorinating agents for carbonyl- and carboxyl-containing compounds. Pentafluorobenzenesulfinyl derivatives have slightly lower boiling points than the corresponding phenyl compounds, but markedly better thermal stability and solubility than the phenyl analogs. The difference in stabilities of pentafluorophenyl and phenyl compounds is demonstrated by examining the products formed in reactions 2 and 3. The sulfurane, $(C_6F_5)_4S$, the first with four
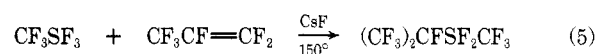
$$C_6H_5Li + C_6H_5SF_3 \xrightarrow{-80°} (C_6H_5)_2 + (C_6H_5S)_2^{3} \qquad (2)$$

$$C_6F_5Li + C_6F_5SF_3 \xrightarrow{-78°} (C_6F_5)_4S \xrightarrow{0°}$$

$$C_6F_5C_6F_5 + C_5F_5SC_6F_5^{4,5} \qquad (3)$$

carbon bonds to sulfur, is readily formed and exists to 0°, while the corresponding phenyl compound does not form.

In 1962, Rosenberg and Muetterties[6] reported the direct synthesis of perfluoroalkylsulfur(IV) fluorides from reaction of a fluoro olefin with either sulfur tetrafluoride or a monosubstituted sulfur(IV) compound, *e.g.*

$$2SF_4 + 3CF_3CF{=}CF_2 \xrightarrow[150°]{C_8F}$$

$$((CF_3)_2CF)_2SF_2 + (CF_3)_2CFSF_3 \qquad (4)$$

or

$$CF_3SF_3 + CF_3CF{=}CF_2 \xrightarrow[150°]{C_8F} (CF_3)_2CFSF_2CF_3 \qquad (5)$$

$((CF_3)_2CF)_2SF_2$ is not attacked by Lewis bases and shows many physical properties that are associated with C_7 and C_8 fluorocarbons. Pyrolysis of this sulfur difluoride gives, among other products, $(CF_3)_2CFSF$, which is one of the few known derivatives of SF_2. Boric oxide and $TiCl_4$ convert the sulfur difluoride to a sulfenic ester, $(CF_3)_2CFSOCF(CF_3)_2$, and a sulfide, $(CF_3)_2CFSCF(CF_3)_2$, respectively.

Phenylsulfur trichloride and benzenesulfinyl chloride are readily prepared according to eq 6, but the

(1) A. F. Clifford, H. K. El-Shamy, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 2372 (1953).
(2) E. A. Tyczkowski and L. A. Bigelow, *J. Amer. Chem. Soc.*, 75, 3523 (1953).
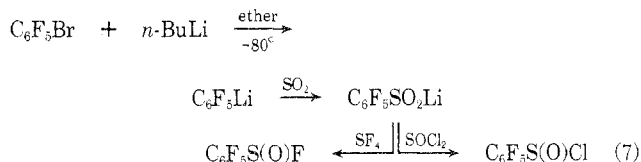(3) W. A. Sheppard, *J. Amer. Chem. Soc.*, 84, 3058 (1962).
(4) W. A. Sheppard, *J. Amer. Chem. Soc.*, 93, 5597 (1971).
(5) W. A. Sheppard and S. S. Foster, *J. Fluorine Chem.*, 2, 53 (1972).
(6) R. M. Rosenberg and E. L. Muetterties, *Inorg. Chem.*, 1, 756 (1962).

$$ArSH \xrightarrow{Cl_2} ArSCl \xrightarrow{Cl_2} ArSCl_3 \xrightarrow{(CH_3CO)_2O} ArSOCl^7 \quad (6)$$

reaction does not proceed under analogous conditions when the aryl group is perfluorophenyl. However, in 1971, Sheppard found that the perfluorobenzenesulfinyl chloride or fluoride was formed *via* the reaction of perfluorophenyllithium with SO_2 and subsequent chlorination or fluorination[4,5]

$$C_6F_5Br \;+\; n\text{-BuLi} \xrightarrow[-80°]{\text{ether}}$$

$$C_6F_5Li \xrightarrow{SO_2} C_6F_5SO_2Li$$

$$C_6F_5S(O)F \xleftarrow{SF_4 \| SOCl_2} C_6F_5S(O)Cl \quad (7)$$

Although the simple alkylsulfinyl fluorides have not been synthesized, the chlorides[8,9] have been studied extensively and their reactions resemble those of other acid chlorides.

Many compounds are known that contain nitrogen–sulfur(IV)–fluorine bonds; the reader is referred to Glemser's excellent review[10] and the references therein for detail. Halogens react with $Hg(NSF)_2$ to form haloimidosulfur difluorides, $XN=SF_2$, which in turn add to olefins to form $RN=SF_2$. Advantage was taken of the formation of the strong $\equiv Si-F$ bond (129 kcal) to form R_2NSF_3 from R_2NSiR_3 and SF_4. The sulfur trifluoride was hydrolyzed to sulfinyl fluoride, $R_2NS(O)F$, which with R_2NH gave $R_2NS(O)NR_2$. Sulfinyl fluorides result also from the reaction of SOF_2 with dialkylamines or (trialkylsilyl)-dialkylamine. Sulfur difluorides are formed *via* a metathetical reaction at 0° between R_fSF_3 and $(CH_3)_3SiNR_2$. The compounds $i\text{-}C_3F_7SF_2NR_2$ (R = CH_3, C_2H_5) appear to exhibit the trans configuration only.

Our initial interest in sulfur(IV) chemistry arose from our desire to synthesize totally fluorinated alkyl sulfoxides and to study the impact of fluorination on their chemistry. In the process of synthesizing these compounds, we uncovered some novel compounds and interesting reactions. This Account describes the precursors and derivatives of bis(perfluoroalkyl) sulfoxides and includes some of their pertinent infrared and nuclear magnetic resonance data.

Perfluoroalkylsulfinyl Halides

By analogy with reaction 4, the CsF-catalyzed reactions between perfluoro olefins and sulfinyl fluoride appeared to offer a good route to sulfoxides. However, under conditions of moderate pressure (18–23 atm) and temperature (150–180°) no sulfoxides were obtained. Only perfluoroalkylsulfinyl fluorides are formed when C_2F_4 or C_3F_6 is used.[11]

Practical synthetic entry into the chemistry of perfluoroalkylsulfur(IV) compounds was developed from an observation of Lawless:[12] he reported trifluoromethylsulfinyl fluoride to be a major product from the action of CF_3SF_3 on glass. The CF_3SF_3 is best

(7) I. B. Douglass and R. V. Norton, *J. Org. Chem.*, **33**, 2104 (1968).
(8) C. R. Russ and I. B. Douglass in "Sulfur in Organic and Inorganic Chemistry," Vol. I, A. Senning, Ed., Marcel Dekker, New York, N. Y., 1971, Chapter 8.
(9) M. L. Kee and I. B. Douglass, *Org. Prop. Proced.*, **2**, 235 (1970).
(10) O. Glemser and R. Mews, *Advan. Inorg. Chem. Radiochem.*, **14**, 333 (1972).
(11) C. T. Ratcliffe and J. M. Shreeve, *J. Amer. Chem. Soc.*, **90**, 5403 (1968).
(12) E. W. Lawless and L. D. Harman, *Inorg. Chem.*, **7**, 391 (1968).

prepared by fluorination of $(CF_3S)_2$ with AgF_2. Traces of moisture are evidently the effective reagent in hydrolysis.

Although we sought more lucrative routes to CF_3SOF, the above method remains the most satisfactory. Typically, this reaction is conducted by condensing about 5 mmol of the CF_3SF_3 into a 1-l. Pyrex vessel followed by the admission of 100 Torr of moist air. Hydrolysis occurs essentially quantitatively in a few hours at 25°.[11]

If an aqueous solution is used, a more complicated series of reactions occurs, including destruction of the CF_3 group. It is unlikely that this solution contains trifluoromethylsulfinic acid.[13,14]

The chemistry of $CF_3S(O)F$ has been studied rather well; this compound and its chloro analog, $CF_3S(O)Cl$, are excellent precursors to $CF_3S(O)$-containing compounds. The thermal stability of $CF_3S(O)F$ was demonstrated by the fact that, when it was heated with N_2F_4 in a nickel vessel at 300° for 2 days, 50% of the unreacted starting materials, in addition to CF_3NF_2 and SOF_2, were recovered.

Although aluminum chloride is useful for replacing S–F groups by S–Cl in many compounds, it is useless for converting $CF_3S(O)F$ to $CF_3S(O)Cl$. However, both hydrogen chloride and hydrogen bromide react readily with $CF_3S(O)F$, and it is of interest to compare these two systems.

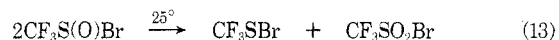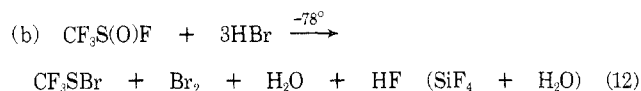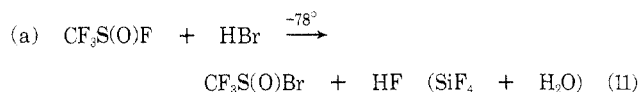(1) With small molar excess of HCl at 25° in Pyrex, $CF_3S(O)Cl$ is formed (eq 8). While this com-

$$CF_3S(O)F + HCl \longrightarrow CF_3S(O)Cl + HF \quad (8)$$
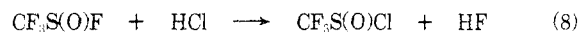
pound is stable when pure, it tends to disproportionate slowly, probably catalyzed by the H_2O formed, if allowed to remain in the reaction mixture.

$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O \quad (9)$$

$$CF_3S(O)Cl \xrightarrow{H_2O} CF_3SO_2Cl + CF_3SCl \quad (10)$$
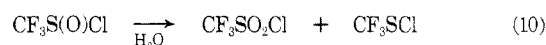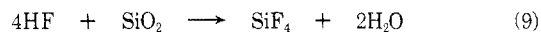
(2) With HBr at −78°, the system is more complex, the products appearing by two different routes (eq 11–13). At 25°, $CF_3S(O)Br$ is unstable with re-

$$(a) \quad CF_3S(O)F + HBr \xrightarrow{-78°}$$

$$CF_3S(O)Br + HF \quad (SiF_4 + H_2O) \quad (11)$$

$$(b) \quad CF_3S(O)F + 3HBr \xrightarrow{-78°}$$

$$CF_3SBr + Br_2 + H_2O + HF \quad (SiF_4 + H_2O) \quad (12)$$

$$2CF_3S(O)Br \xrightarrow{25°} CF_3SBr + CF_3SO_2Br \quad (13)$$

spect to disproportionation, but disproportionation at −78° is sufficiently slow to permit isolation of $CF_3S(O)Br$. The fact that bromine is formed and CF_3SO_2Br is not suggests that CF_3Br is a reaction product and does not result from disproportionation. When the reaction mixture is separated after a brief period at 25°, CF_3SBr is the major sulfur product, with lesser amounts of $CF_3S(O)Br$ and CF_3SO_2Br. The disproportionation of $CF_3S(O)Br$ at 25° can be followed readily by infrared spectroscopy.

Both $CF_3S(O)Br$ and $CF_3S(O)Cl$ may be readily

(13) H. W. Roesky, *Angew. Chem., Int. Ed. Engl.*, **10**, 810 (1971).
(14) R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 2901 (1955).

converted to $CF_3S(O)F$ with NaF at 25°, while CF_3SBr and CF_3SO_2Br are unaffected.

Mixed perfluoro(methylsulfinic-carboxylic) anhydrides of moderate stability were prepared in good yield from reactions of silver salts of carboxylic acids with an excess of $CF_3S(O)Cl$ (to preclude formation of the symmetrical carboxylic acid anhydride which is separated only with much difficulty)[15] (eq 14).

$$CF_3S(O)Cl \ + \ AgOOCR_f \xrightarrow{25°} CF_3S(O)OOCR_f \ + \ AgCl \quad (14)$$

$$R_f = CF_3, C_2F_5, n\text{-}C_3F_7, CH_3$$
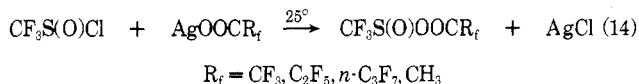
Thermolysis at 100° or photolysis (in Pyrex vessels) of $CF_3S(O)OOCCF_3$ gives CF_3SCF_3, SO_2, COF_2, and $CF_3C(O)OOCCF_3$. Decarboxylation directly to the sulfoxide was not successful; this is in contrast to the effective production of bis(perfluoroalkyl) sulfides from sulfenyl-carboxylic acid anhydrides (see Bis(perfluoroalkyl) Sulfides).

With silver pseudohalides, metathesis occurs readily to form stable compounds which boil at less than 100°[16] (eq 15). The postulated sulfinyl-sulfenyl de-
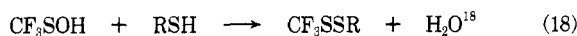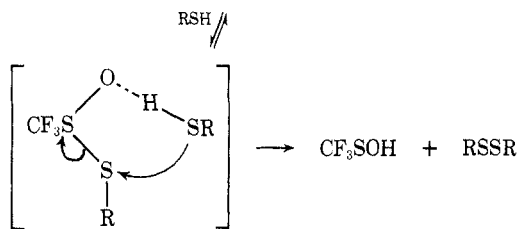
$$CF_3S(O)Cl \ + \ AgX \longrightarrow CF_3S(O)X \ + \ AgCl \quad (15)$$
$$X = CN, NCO$$
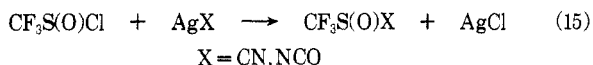
rivative $CF_3S(O)SCF_3$, formed as an unisolable intermediate in the reaction of $CF_3S(O)Cl$ with $Hg(SCF_3)_2$, apparently undergoes disproportionation to disulfide and trifluoromethyl trifluoromethylthiosulfonate.

Stable, partially fluorinated sulfinyl esters resulted from the alcoholysis of trifluoromethylsulfinyl fluoride[17]

$$CF_3S(O)F \ + \ ROH \xrightarrow{-78 \text{ to } 25°} CF_3S(O)OR \quad (16)$$
$$R = CH_3, C_2H_5, CH_2CF_3$$
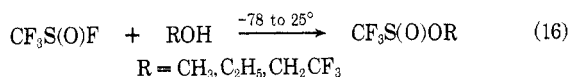
It was not possible to synthesize the thio analogs: a mixture of dilsulfides resulted in every case.

$$CF_3S(O)F \ + \ RSH \longrightarrow CF_3S(O)SR \ + \ HF \quad (17)$$

$$\left[CF_3S \overset{O\cdots H}{\underset{S}{\diagup}} SR \right] \longrightarrow CF_3SOH \ + \ RSSR$$

$$CF_3SOH \ + \ RSH \longrightarrow CF_3SSR \ + \ H_2O^{18} \quad (18)$$

Metathesis of $CF_3S(O)F$ with primary and secondary amines gives mono- and bis(trifluoromethylsulfinamides), $CF_3S(O)NR_2$ and $(CF_3S(O))_2NR$ (R = CH_3, C_2H_5), and ammonia gives $CF_3S(O)NH_2$.[17]
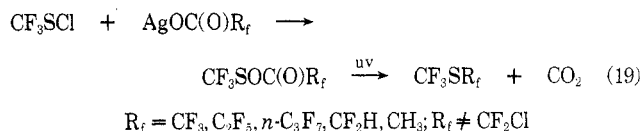
Trifluoromethylsulfinyl fluoride which is a gas at 25° and boils at -1.6° has no tendency to behave as a Lewis acid, say with CsF, which is also the case with SOF_2. However, it does form a white solid with AsF_5 at -78° which dissociates on warming, but no evidence for reaction with BF_3 is found.

Sulfides, Difluorides, and Sulfoxides

Bis(perfluoroalkyl) sulfoxides have not been synthesized by electrochemical fluorination of alkyl sulfoxides.[19,20] Other attempted routes to bis(perfluoroalkyl) sulfoxides were equally unsuccessful: fluorination of bis(perfluoroalkyl) sulfides with metal fluorides,[21] AgF_2, or CoF_3, or with interhalogens to bis(perfluoroalkyl)sulfur difluorides, and oxidation of bis(perfluoroalkyl) sulfides with standard oxidizing agents,[22] e.g., m-chloroperbenzoic acid, NO_2ClO_4, NO_2, or NO_2-O_2.

However, a successful route to these begins with the fluorination of bis(perfluoroalkyl) sulfides and their subsequent oxidation.
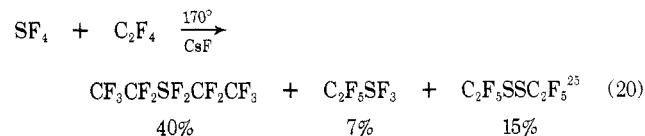
Bis(perfluoroalkyl) Sulfides. Several bis(perfluoroalkyl) sulfides have been prepared recently by the photolysis of perfluoro(sulfenyl-carboxylic) acid anhydrides. Photolysis of $CF_3SOC(O)CF_3$ is far superior to other methods[21,23] for preparing CF_3SCF_3 because it invariably gives quantitative yields.[24] In general, the trifluoromethyl sulfides[25] were prepared as follows.

$$CF_3SCl \ + \ AgOC(O)R_f \longrightarrow$$

$$CF_3SOC(O)R_f \xrightarrow{uv} CF_3SR_f \ + \ CO_2 \quad (19)$$

$$R_f = CF_3, C_2F_5, n\text{-}C_3F_7, CF_2H, CH_3; R_f \neq CF_2Cl$$

When $R_f \neq CF_3$, sulfide formation is accompanied by substantial amounts of $(R_fC(O))_2O$, $CF_3SSO_2CF_3$, and CF_3SSCF_3.

These sulfides are low-boiling compounds which are stable toward glass and mercury and are not hydrolyzed by aqueous base at 100°. CF_3SCF_3 is extremely stable to thermolysis and to chemical reaction with metal fluorides. When CF_3SCF_3 is heated with NO_2, only at temperatures above 450° do CF_4, SO_2, COS, and carbonaceous solids appear as products. However, fluorine attacks it with vigor at 25° to give a series of fluorinated degradation products.

Bis(perfluoroalkyl)sulfur Difluorides. These hydrolytically stable compounds can be obtained readily from reaction of sulfur tetrafluoride with perfluoro olefins or by fluorination of the bis(perfluoroalkyl) sulfides. As shown by Rosenberg and Muetterties,[6] nucleophilic attack on SF_4 by a perfluoroalkyl carbanion formed by interaction of fluoride ion (CsF) and a perfluoro olefin gives sulfur difluorides, e.g.

$$SF_4 \ + \ C_2F_4 \xrightarrow[\text{CsF}]{170°}$$

$$CF_3CF_2SF_2CF_2CF_3 \ + \ C_2F_5SF_3 \ + \ C_2F_5SSC_2F_5{}^{25} \quad (20)$$
$$\qquad 40\% \qquad\qquad\quad 7\% \qquad\qquad 15\%$$

Bis(pentafluoroethyl) disulfide arises from pyrolysis of the sulfur difluoride to form the unstable intermediate, CF_3CF_2SF, which subsequently reacts (eq 21).

(15) D. T. Sauer and J. M. Shreeve, *Inorg. Nucl. Chem. Lett.*, **6**, 501 (1970).

(16) N. Kondo, M.S. Thesis, University of Idaho, 1972.

(17) D. T. Sauer and J. M. Shreeve, *Inorg. Chem.*, **10**, 358 (1971).

(18) G. Tsukamoto, T. Watanabe and I. Utsumi, *Bull. Chem. Soc. Jap.*, **42**, 2566 (1969).

(19) F. W. Hoffman, T. C. Simons, R. B. Beck, H. V. Holler, T. Katz, R. J. Koshar, E. R. Larsen, J. E. Mulvaney, F. E. Rogers, B. Singleton, and R. S. Sparks, *J. Amer. Chem. Soc.*, **79**, 3424 (1957).

(20) H. C. Clark, *Advan. Fluorine Chem.*, **3**, 25 (1963).

(21) E. W. Lawless and L. D. Harman, *J. Inorg. Nucl. Chem.*, **31**, 1541 (1969).

(22) E. W. Lawless and G. J. Hennon, *Tetrahedron Lett.*, 6075 (1968).

(23) K. Sathianandan and J. L. Margrave, *Indian J. Pure Appl. Phys.*, **5**, 464 (1967).

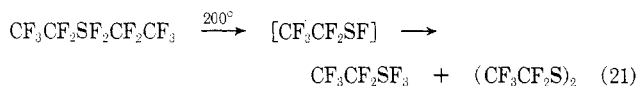(24) A. Haas and D. Y. Oh, *Chem. Ber.*, **102**, 77 (1969).

(25) D. T. Sauer and J. M. Shreeve, *J. Fluorine Chem.*, **1**, 1 (1971).

$$CF_3CF_2SF_2CF_2CF_3 \xrightarrow{200°} [CF_3CF_2SF] \longrightarrow$$

$$CF_3CF_2SF_3 + (CF_3CF_2S)_2 \quad (21)$$

This intermediate is reasonable when one considers the instability of the analogous compound, CF_3SF, in glass, and its tendency to disproportionate to CF_3SF_3 and $(CF_3S)_2$.[11,26] Since $CF_3CF_2SF_3$ is an end product when the $CF_3CF^-_2$-$SF_4$ reaction proceeds in a 1:1 ratio, and also one which can be consumed in a further reaction with additional $CF_3CF_2^-$, it is not possible to establish the route of $(CF_3CF_2S)_2$ formation unequivocably. Formation of $CF_3CF_2SF_3$ in the SF_4 reaction can be minimized by using a 2-3-fold excess of C_2F_4.

Previous attempts to fluorinate bis(perfluoroalkyl) sulfides with AgF_2 or CoF_3 resulted in bond cleavage and oxidation of sulfur to sulfur(VI).[21] With ClF as a fluorinating agent, however, sulfur difluorides in yields greater than 90% can readily be obtained. Unless both of the alkyl groups are totally fluorinated, the yields of sulfur difluorides decrease drastically and complete decomposition occurs in some cases, *e.g.*, with CF_3SCF_2H. It is possible to oxidize the sulfur(IV) difluorides to sulfur(VI) tetrafluorides, $(R_f)_2SF_4$, merely by raising the reaction temperature.

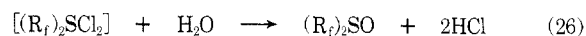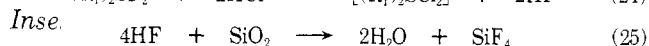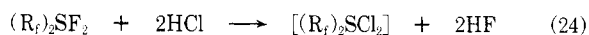$$R_fSF_2R'_f + ClF \xrightarrow{25°} R_fSF_4R'_f \quad (22)$$

$$R_f = R'_f = CF_3 \quad (42\%)$$

$$R_f = CF_3; R'_f = C_2F_5 \quad (13\%)$$
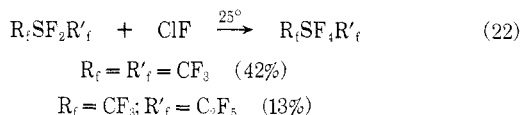
Although $(CF_3)_2SF_4$ had been prepared earlier *via* electrochemical fluorination of $(CH_3)_2S$,[19] only the trans isomer was observed. Based on nmr data, ClF fluorination gives both the cis and trans isomers in the ratio 1:1.6. Comparing this with the cyclic sulfide,[27] tetra(perfluoromethylene) sulfide, at $-40°$ with ClF in a twofold excess, the sulfur difluoride was formed in 74% yield with only a trace of the cyclic sulfur tetrafluoride. If the temperature was raised to 25° and the ClF was present in greater than fourfold excess, tetra(perfluoromethylene)sulfur tetrafluoride formed in 63% yield. The perfluorinated cyclic sulfur difluoride is more stable thermally than the bis(perfluoroalkyl)sulfur difluorides which decompose around 200° to perfluoroalkylsulfenyl fluoride and perfluoroalkylsulfur trifluoride, and upon decomposing gives different products, *viz.*

$$C_4F_9SSC_4F_9 + n\text{-}C_4F_{10} + SF_4 \quad (SOF_2 + SiF_4) \quad (23)$$
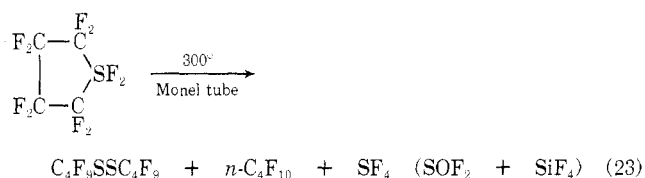
Bis(perfluoroalkyl) Sulfoxides. After $CF_3SF_2CF_3$ had been in contact with yellow HgO at 25° for about a week, 10% was converted to $CF_3S(O)CF_3$.[25] While higher temperatures could increase the rate and extent of this reaction, it was not pursued further since the reaction of anhydrous hydrogen chloride with the bis(perfluoroalkyl)sulfur or tetra(per-

fluoromethylene)sulfur difluorides provides a good preparative route to the respective sulfoxides. For example, $CF_3SF_2CF_3$ reacts with HCl in glass over a 12-hr period to produce the liquid sulfoxide quantitatively,[25] whereas $CF_2CF_2CF_2CF_2SF_2$ in a reaction time of 1 hr gives a 67% yield of the white solid sulfoxide.[27] Reaction rates and yields tend to decrease as the R_f group becomes more complex.

These reactions apparently proceed through a dichloride intermediate, which is readily hydrolyzed by the water generated *in situ* from HF attack on the glass vessel, *e.g.*
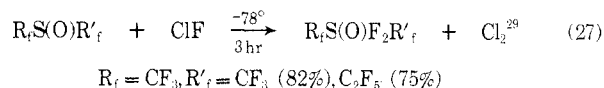
$$(R_f)_2SF_2 + 2HCl \longrightarrow [(R_f)_2SCl_2] + 2HF \quad (24)$$

$$4HF + SiO_2 \longrightarrow 2H_2O + SiF_4 \quad (25)$$

$$[(R_f)_2SCl_2] + H_2O \longrightarrow (R_f)_2SO + 2HCl \quad (26)$$

No attempt was made to isolate this proposed intermediate.[25]

None of the sulfur difluorides reacted with anhydrous NH_3 even at 100°. The hydrolytic stability of all the $>SF_2$ compounds was rather unexpected since such hydrolysis would be thermodynamically favored, and SF_4[28] and the perfluoroalkylsulfur trifluorides[3,11,12] undergo rapid hydrolysis to SOF_2 and $RS(O)F$, respectively, in the presence of trace amounts of water.

Derivatives of Bis(Perfluoroalkyl)sulfur(IV) Compounds

$(R_f)_2S$=O and $CF_2CF_2CF_2CF_2SO$ are readily fluorinated with ClF to give S(VI) oxydifluorides (eq 27). Further fluorination or chlorofluorination of

$$R_fS(O)R'_f + ClF \xrightarrow[3\text{ hr}]{-78°} R_fS(O)F_2R'_f + Cl_2[29] \quad (27)$$

$$R_f = CF_3, R'_f = CF_3 \quad (82\%), C_2F_5 \quad (75\%)$$

$$R_f = C_2F_5; R'_f = C_2F_5 \quad (75\%); R_fR'_f = CF_2CF_2CF_2CF_2- \quad (99\%)[27]$$

these compounds does not occur since additions across a sulfur-oxygen double bond requires a catalyst such as an alkali metal fluoride.[30,31] In contrast to the acyclic compounds, $CF_2CF_2CF_2CF_2S(O)F_2$[27] is extremely reactive to glass and easily hydrolyzed. With water, conversion to the sulfone is quantitative.
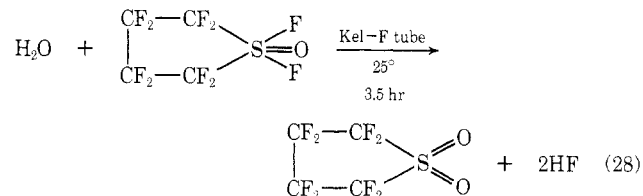
While $(CF_3)_2S(O)F_2$ does not react with HCl,[32] it does interact with perfluorocarboxylic acids to give a variety of products, including perfluoro esters.

(26) F. Seel, W. Gombler, and R. Budenz, *Angew. Chem., Int. Ed. Engl.*, 6, 706 (1967).

(27) T. Abe and J. M. Shreeve, *J. Fluorine Chem.*, in press.

(28) R. E. Dodd, L. A. Woodward, and H. L. Roberts, *Trans. Faraday Soc.*, 52, 1052 (1956).

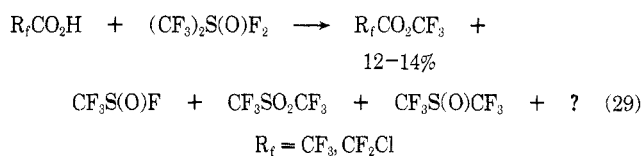(29) D. T. Sauer and J. M. Shreeve, *Z. Anorg. Allg. Chem.*, 385, 113 (1971).

(30) C. J. Schack, R. D. Wilson, J. S. Muirhead, and S. N. Cohz, *J. Amer. Chem. Soc.*, 91, 2902 (1969).

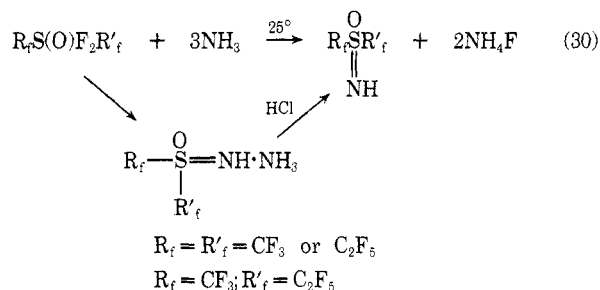(31) J. K. Ruff and M. Lustig, *Inorg. Chem.*, 3, 1422 (1964).

(32) D. T. Sauer, unpublished data, University of Idaho.

$$R_fCO_2H \;+\; (CF_3)_2S(O)F_2 \;\longrightarrow\; R_fCO_2CF_3 \;+\;$$
$$12\text{–}14\%$$
$$CF_3S(O)F \;+\; CF_3SO_2CF_3 \;+\; CF_3S(O)CF_3 \;+\; ? \quad (29)$$
$$R_f = CF_3, CF_2Cl$$

In contrast to the sulfur difluorides, $>SF_2$, the oxydifluorides react smoothly with ammonia[33] to give bis(perfluoroalkyl)sulfur oxyimines quantitatively. In all cases, part of the oxyimine is found as a white sublimable solid, probably $(R_f)_2S(O)NH\cdot NH_3$. This solid is readily converted to the oxyimine when treated with anhydrous hydrogen chloride.

$$R_fS(O)F_2R'_f \;+\; 3NH_3 \xrightarrow{25°} \underset{\underset{NH}{\|}}{R_fSR'_f} \;+\; 2NH_4F \quad (30)$$

$$\underset{\underset{R'_f}{|}}{R_f\!-\!\overset{\overset{O}{\|}}{S}\!=\!NH\cdot NH_3}$$

$$R_f = R'_f = CF_3 \text{ or } C_2F_5$$
$$R_f = CF_3; R'_f = C_2F_5$$

The reactions of bis(perfluoroalkyl)sulfur oxyimines are typified by those of $(CF_3)_2S(O)\!=\!NH$.[33] Although $(CF_3)_2S(O)\!=\!NH$ does not react with labile chlorides neat, in the presence of a base reaction proceeds smoothly at $-20°$.

$$RCl \;+\; (CF_3)_2S(O)NH \xrightarrow[20°]{Et_3N} RN\!=\!S(O)(CF_3)_2 \quad (31)$$
$$R = CF_3S, CN, (CH_3)_3Si$$

$$(CF_3)_2S(O)\!=\!NSi(CH_3)_3 \;+\; HgF_2 \;\longrightarrow\;$$
$$((CF_3)_2S(O)\!=\!N)_2Hg \xrightarrow{CH_3I} (CF_3)_2S(O)\!=\!N\!-\!CH_3 \quad (32)$$
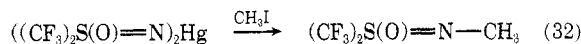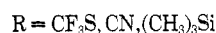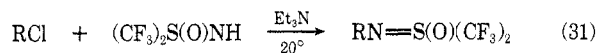
With acid fluorides, NaF promotes the elimination of HF. Although trace amounts of products were observed in the reaction without NaF, the presence of a base greatly enhances the yield. In the absence of NaF, addition of HF across $S\!=\!N$ does not occur.

$$RF \;+\; (CF_3)_2S(O)NH \xrightarrow{NaF} RN\!=\!S(O)(CF_3)_2 \;+\; HF \quad (33)$$
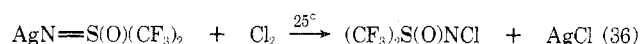$$R = CF_3C(O), CF_3S(O)$$
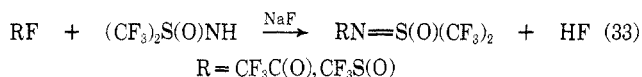
Bis(trifluoromethyl)sulfur oxyimine reacts with silver(I) oxide in benzene solution to form the silver salt $AgN\!=\!S(O)(CF_3)_2$ (eq 34). Reaction of the silver

$$2(CF_3)_2S(O)NH \;+\; Ag_2O \xrightarrow[25°]{benzene}$$
$$2AgN\!=\!S(O)(CF_3)_2 \;+\; H_2O \quad (34)$$
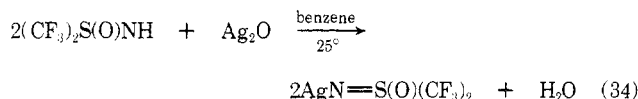
salt with methyl iodide produces N-methylbis(trifluoromethyl)sulfur oxyimine (identical with the product obtained when the parent sulfur oxydifluoride reacts with methylamine) (eq 35); reaction with ele-

$$AgN\!=\!S(O)(CF_3)_2 \;+\; CH_3I \xrightarrow{25°} (CF_3)_2S(O)NCH_3 \;+\; AgI \quad (35)$$
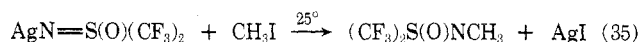
mental chlorine produced the N-chloro derivative (eq 36).

$$AgN\!=\!S(O)(CF_3)_2 \;+\; Cl_2 \xrightarrow{25°} (CF_3)_2S(O)NCl \;+\; AgCl \quad (36)$$
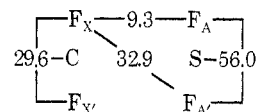
Nuclear Magnetic Resonance Spectra

With the exception of $CF_3SF_2CF_2CF_3$, all of these compounds exhibit first-order nuclear magnetic resonance spectra. The instances of hydrogen and fluorine geminal nonequivalence in S(IV) compounds are of particular interest.

$CF_3S(O)OCH_2CF_3$. In the proton nmr spectrum of $CH_3CH_2OS(O)CF_3$ and $CF_3CH_2OS(O)CF_3$, which are ABM_3X_3 systems, the methylene protons are observed as multiplets centered at δ 4.26 and 4.45, respectively. The protons are magnetically nonequivalent (J_{AB} = 10 and 12.6 Hz for ethyl and 2,2,2-trifluoroethyl, respectively) due to the asymmetric center at the sulfur atom. Comparison of the methylene proton spectrum of $CF_3S(O)N(CH_2CH_3)_2$ with that of the ester $CF_3S(O)OCH_2CF_3$ (CH_3) shows that these protons are now magnetically equivalent, or very nearly so ($J \lesssim 0.2$ Hz), *i.e.*, an $A_2M_3X_3$ system. This change from ABM_3X_3 to $A_2M_3X_3$ is observed also for $FS(O)OCH_2CH_3$ and $FS(O)N(CH_2CH_3)_2$.[34]

The asymmetric center at the sulfur atom is retained in the bis(perfluoroalkyl) sulfoxides which results in the α-methylene fluorine atoms of both the pentafluoroethyl and heptafluoropropyl groups being magnetically nonequivalent, with J_{AB} coupling constants of 242 Hz for $CF_3S(O)CF_2CF_3$ and $CF_3S(O)CF_2CF_2CF_3$ and 228 Hz for $CF_3CF_2S(O)CF_2CF_3$. The fact that $J_{A\text{-}CF_3S} \neq J_{B\text{-}CF_3S}$ is also evidence for magnetic nonequivalence.[25]

Fluorination of the sulfoxides with chlorine monofluoride gave rise to sulfur oxydifluorides, $(R_f)_2S(O)F_2$, where simple first-order spectra were obtained with magnetically equivalent α-methylene fluorines. The presence of $S\!=\!O$ in place of the lone pair does not give rise to a preferred rotamer, but rather free rotation must occur which results in an average of all possible rotamers. However, for $CF_3SF_2CF_2CF_3$, the nmr spectrum of the difluoromethylene group, after decoupling CF_3C and CF_3S, is a basic AA′XX′ pattern where $J_{AX} = J_{A'X'} \neq J_{A'X} = J_{AX'}$. Thus, both the two methylene fluorines and the two sulfur fluorines are magnetically nonequivalent.

A computer analysis of the decoupled spectrum gave rise to the following values for pertinent coupling constants (hertz).

$$\begin{array}{c} \left[\!-F_X\!-\!9.3\!-\!F_A\!-\right] \\ 29.6\!-\!C \quad 32.9 \quad S\!-\!56.0 \\ \left[\!-F_{X'} \qquad F_{A'}\!-\right] \end{array}$$

This is believed to be the first example of magnetic nonequivalence exhibited by vicinal fluorine atoms bonded to sulfur(IV).
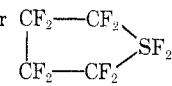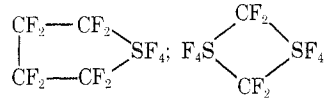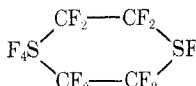
Reestablishment of an asymmetric center occurs when the sulfur oxyimine, $CF_3(C_2F_5)S(O)\!=\!NH$, is formed by reaction of $CF_3(C_2F_5)S(O)F_2$ with ammonia, and thus the fluorine atoms attached to the methylene carbon become magnetically nonequivalent, J_{AB} = 26.3 Hz.

Nuclear magnetic resonance is a very useful tool in confirming the presence of sulfur(II), -(IV), or -(VI) when bonded to a perfluoroalkyl moiety, as is shown

(33) D. T. Sauer and J. M. Shreeve, *Inorg. Chem.*, 11, 238 (1972).

(34) D. H. Brown, K. D. Crosbie, J. I. Darragh, D. S. Ross, and D. W. A. Sharp, *J. Chem. Soc. A*, 914 (1970).

Table I

Type of compound	Group	Range, MHz
CF_3SR_f	CF_3S	35–55
$CF_3S(O)R_f$	$CF_3S(O)$	74–85
$CF_3SO_2R_f$	CF_3SO_2	77–81[a]
$CF_3SF_2R_f$ or CF_2——CF_2 $\diagdown$ SF_2 CF_2——CF_2	SF_2	11–16
	CF_3SF_2	55–58
$CF_3S(O)F_2R_f$	CF_3	63
	SF_2	−55 to −71
trans-$CF_3SF_4CF_3$	CF_3	65
	SF_4	−19
cis-$CF_3SF_4CF_3$ (R_f)	CF_3	64
	SF_{2ax}	−13 to −20
CF_2——CF_2 $\diagdown$ SF_4; F_4S $\diagup$ CF_2 $\diagdown$ SF_4 CF_2——CF_2 $\diagup$ $\diagup$ CF_2 F_4S $\diagup$ CF_2——CF_2 $\diagdown$ SF_4 CF_2——CF_2	SF_{2eq}	−41 to −50

[a] Although this range overlaps that of $CF_3S(O)R_f$, the presence or lack of a strong band due to O==S==O asymmetric stretch within the 1400-1450-cm^{-1} range in the infrared spectrum makes a firm decision possible.

by the rather characteristic resonance ranges for fluorine (see Table I) in similar sulfur compounds (CCl_3F as internal reference).

Infrared Spectra

The gas-phase infrared spectra of these bis(perfluoroalkyl)sulfur compounds are reasonably simple and characteristic. All of the bis(perfluoroalkyl)sulfur difluorides have a characteristic strong band in the range 665–675 cm^{-1} in their infrared spectra. Although earlier workers[23] assigned bands in this region to a C-F mode, complete absence of this band in the corresponding sulfoxides suggests assignment to an S-F stretching mode. Assignment of the S==O bands in the sulfoxides, sulfur oxydifluorides, and sulfur oxyimines is difficult because of the close proximity of C-F asymmetric stretching frequencies.

Halogens or pseudohalogens bonded directly to the sulfur atom have a marked influence on the stretching frequency of the >S==O moiety in sulfinyl compounds by lowering the amount of XYS^+—O^- in relation to XYS==O.[35] The effective electronegativity values of groups X and Y suggested by Kagarise[36] when plotted against >S==O stretching frequencies give a smooth curve.[37] When the electronegativities of the perfluoroalkyl groups of interest in this paper were superimposed on the latter curve, certain bands in the spectra could be assigned to the >S==O stretching frequencies. These bands are usually intense and broad, suggesting >S==O-CF$_3$ band overlap. Some experimental values are given in Table II and plotted in Figure 1. The S-F stretching frequencies for -S(O)F and for >S(O)F$_2$ occur in the 750-(Table II) and 715- (Table III) cm^{-1} range, respectively.

(35) D. Barnard, J. M. Fabian, and H. P. Koch, *J. Chem. Soc.*, 242 (1949).
(36) R. E. Kagarise, *J. Amer. Chem. Soc.*, 77, 1377 (1955).
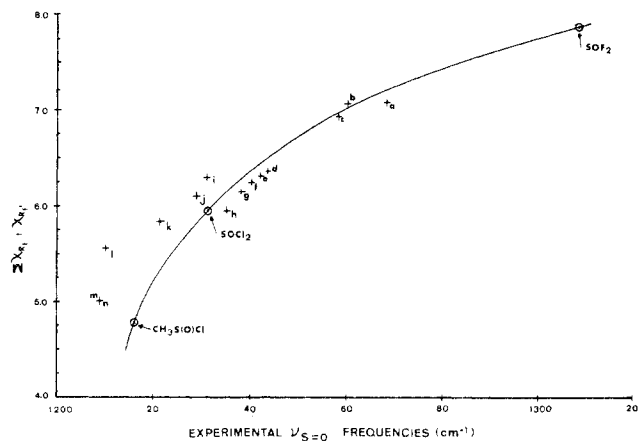(37) H. Szmant and W. Emerson, *J. Amer. Chem. Soc.*, 78, 454 (1956).

Figure 1. Plot of the sum of electronegativities of substituents R_f and R_f' *vs.* the experimental S==O frequencies in the compounds listed in Table I.

Table II
Experimental S==O and S—F Stretching Frequencies for $R_fS(O)R_f'$ (cm^{-1})

	R_f	R_f	$\nu_{S=O}$	ν_{S-F}	R_f	R_f'	$\nu_{S=O}$
	F	F	1308	808, 748	h CF_3	Br	1235
a	CF_3	F	1268	751	Cl	Cl	1231
b	C_2F_5	F	1260	746	i CF_3	n-C_3F_7	1231
c	i-C_3F_7	F	2158	748	j C_2F_5	Cl	1229
d	CF_3	CF_3	1244		k CF_3	OCH_2CF_3	1221
e	CF_3	C_2F_5	1242		CH_3	Cl	1216
f	C_2F_5	C_2F_5	1240		l CF_3	CH_3	1210
g	CF_3	Cl	1238		m CF_3	OCH_3	1209
					n CF_3	OC_2H_5	1209

Table III
Experimental S==O and S—F Stretching Frequencies for $R_fS(O)F_2R_f'$ (cm^{-1})

R_f	R_f'	$\nu_{S=O}$	ν_{S-F}
F	F	1383	928, 821
CF_3	CF_3	1328	715
CF_3	C_2F_5	1318	718
C_2F_5	C_2F_5	1316	718

Table IV
Experimental S==O Stretching Frequencies for $(CF_3)_2S(O)$==NR (cm^{-1})

R	$\nu_{S=O}$	R	$\nu_{S=O}$
CN	1369	$CF_3S(O)$	1339
$CF_3C(O)$	1362	CF_3S	1331
H	1353	Cl	1328

For the case of sulfur-oxygen stretching in sulfur-(VI) compounds, bands have been assigned and appear to follow the trend established for the analogous frequency in the iminosulfur oxydifluoride derivatives (Table IV). Infrared bands at 1199, 1188, and 1165 cm^{-1} are assigned to S==N absorptions in $(CF_3)_2S(O)NH$, $CF_3(C_2F_5)S(O)NH$, and $(C_2F_5)_2S$-$(O)NH$, respectively.