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# CHEMISTRY OF PENTAFLUOROSULFANYL COMPOUNDS

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## I. Introduction

Fluorinated compounds containing five- and six-coordinate sulfur are of considerable interest. They include those with sulfur as the central atom surrounded by five or six ligands as well as many with six-coordinate sulfur as a functional group, such as pentafluorosulfanyl, $SF_5$. Compounds in which this group is present are of special interest because they often possess the advantageous properties of the parent compound, $SF_6$, among which are a high group electronegativity, large steric bulk, a nonfunctional hexacoordinate stereochemistry, and high thermal and hydrolytic stability. These properties are manifested in various potential applications such as their use as solvents for polymers, as perfluorinated blood substitutes, as surface active agents, as fumigants, and as thermally and chemically stable systems (*1*). This chapter gives the reader a broad picture of the synthesis and chemistry of the various classes of pentafluorosulfanyl compounds, many of which are the subject of much ongoing research.

## II. Pentafluorosulfanyl Halides

The two compounds of this class that are known, $SF_5Cl$ and to a lesser extent $SF_5Br$, are important intermediates in the preparation of derivatives that contain the $SF_5$ group. The chloro derivative, $SF_5Cl$, was first prepared in 1960 (*2*) as a minor product of the reaction between $SCl_2$ and HF-free $F_2$ diluted with nitrogen at −10°C. Other methods of preparation include chlorination of $S_2F_{10}$ (*3*), electrolysis of an $SCl_2/HF$ mixture (*4*), reaction of ClF with $SF_4$ (*5, 6*) and KSCN (*7*), and reaction of chlorine, CsF, and $SF_4$ (*8*). High yields are obtained as shown below (*9, 10*):

$$SF_4 + ClF \xrightarrow[25^\circ C,\ 0.5\ hr]{CsF} SF_5Cl\ (92\%).$$

A mixture of $S_2F_{10}$ and $Br_2$ at 140–150°C results in the formation of $SF_5Br$ (*11, 12*). An alternate method is the reaction of $SF_4$ with BrF (or a mixture of $BrF_5$ and $Br_2$) at 90–100°C (*13*).

It is reported that $SF_5Cl$ (m.p., −64°C; b.p., −21°C) is stable up to ca. 400°C in inert vessels, but decomposes at substantially lower temperature in the presence of Cu/Hg or in ultraviolet light. It is not hydrolyzed by water or aqueous acids, but is rapidly decomposed by aqueous alkali (*14*):

$$SF_5Cl + 7OH^- \longrightarrow SO_4^{2-} + 5F^- + Cl^- + H^+ + 3H_2O.$$

The bromo derivative, $SF_5Br$ (m.p., −78°C; b.p., 31°C), is less stable thermally, with decomposition starting at 150°C. The products of the thermal decomposition of $SF_5X$ (X = Cl, Br) are $SF_6$, $SF_4$, and $X_2$. The products of UV photolysis of $SF_5Br$ are $SF_6$, $SF_4$, $S_2F_{10}$, and $Br_2$ (*15*). The vacuum-UV photolysis of $SF_5Br$ in an Ar matrix at 8 K provides a convenient method of generating BrF (*16*).

The vapor-phase Raman spectrum of $SF_5Cl$ (*17*), the argon-matrix Raman and infrared spectra of $SF_5Cl$ and $SF_5Br$ (*18*), and the vapor-phase infrared and liquid-phase Raman spectra of $SF_5Br$ (*19*), as well as photoelectron diffraction (*20*) and microwave spectra of $SF_5Cl$ (*21*) and $SF_5Br$ (*22*) have been reported. The ionization potential of $SF_5$ (9.65 eV) has been measured by photoionization mass spectrometry of $SF_5Cl$ (*23*).

Phosphorus(III) compounds are oxidatively fluorinated by $SF_5Cl$; e.g., $C_6H_5PCl_2$, $(C_6H_5)_2PCl$, and $CH_3PCl_2$ form the fluorophosphoranes $C_6H_5PF_4$, $(C_6H_5)_2PF_3$, and $CH_3PF_4$, respectively (*24*). Reaction of $SF_5Cl$ with methylamine yields $CH_3N{=}SF_2$ (*25*). The first known metal–pentafluorosulfanyl complex, $\{PtCl(SF_5)[P(C_6H_5)_3]_2\}$ is synthesized by the reaction of *trans*-stilbenebis(triphenylphosphine)platinum(O) with $SF_5Cl$ in benzene (*26*).

Under photochemical conditions $SF_5Cl$ can be reacted with some simple substrates. For example, with $H_2$ it gives $S_2F_{10}$ (*27*); with $O_2$, the products are $SF_5OOSF_5$ and $SF_5OSF_5$ (*28*); and with $N_2F_4$, $SF_5NF_2$ is obtained (*29*). The ability of $SF_5X$ to form the stable $SF_5\cdot$ radical is an important feature of its chemistry.

In some instances, fluorination takes place with breakdown of the $SF_5$ group. Fluorination occurs in the gas-phase photochemical reaction between $SF_5Cl$ and $SO_2$, which gives $SOF_2$, $SO_2F_2$, $SO_2Cl_2$, $S_2F_{10}$, $SF_5OSO_2F$, and $SF_5OSF_5$ (*30*). Similarly, the photochemical reaction with CO yields COClF, $COF_2$, $SF_6$, $S_2F_{10}$, $SF_4$, and COS (*31*).

When $SF_5Cl$ reacts with trimethylsilylcyanide, $(CH_3)_3SiCN$, at −10°C, a white sublimable solid, $S(CN)_2$ (*32*), is formed. On reaction of $SF_5Cl$ with $(CF_3)_2NCN$ under photolytic conditions, $(CF_3)_2NC(Cl){=}NSF_5$ is obtained (*33*), and with $(CF_3)_2NCF_2N(Cl)CF_3$, $(CF_3)_2NCF_2N(SF_5)CF_3$ is produced in 50% yield. This product is characterized by spectral (IR, NMR, mass) data (*34*).

The fluorine atoms of $SF_5X$ are substituted in reactions with nucleophiles such as dimethylaminotrimethylsilane, $(CH_3)_2NSi(CH_3)_3$, and lithium hexafluoropropylidenimine, $LiN{=}C(CF_3)_2$; e.g., $SF_5X$ with $(CH_3)_2NSi(CH_3)_3$ at −78°C gives $(CH_3)_2NSF_4X$ (*35, 36*). The equivalence of four fluorine atoms in equatorial positions is supported by $^{19}F$ NMR of the products (*35*). The replacement of F rather than Cl or Br in $SF_5X$ is probably favored because of the higher SiF bond energy.

The reaction of $LiN{=}C(CF_3)_2$ with $SF_5X$ leads to stepwise replacement of fluorine with concomitant fluoride ion migration as shown (*37–39*):

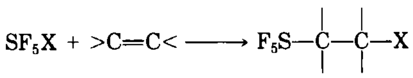
$$SF_5X + LiN{=}C(CF_3)_2 \longrightarrow SF_3X[{=}NCF(CF_3)_2] + LiF$$
$$SF_3X[{=}NCF(CF_3)_2] + LiN{=}C(CF_3)_2 \longrightarrow SFX[{=}NCF(CF_3)_2]_2 + LiF.$$

Both $SF_5Cl$ and $SF_5Br$ react with unsaturated organic compounds. There are numerous examples of the addition of an $SF_5$ group and a halogen atom across a C=C, C=O, C≡C, or C≡N bond, although under certain conditions fluorination also occurs. The photochemical reactions of $SF_5Cl$ with olefins have been studied in detail and are believed to involve a chain reaction as shown below (*40*).

$$SF_5Cl \xrightarrow{h\nu} SF_5\cdot + Cl\cdot$$
$$SF_5\cdot + CH_2{=}CH_2 \longrightarrow SF_5CH_2CH_2\cdot$$
$$Cl\cdot + CH_2{=}CH_2 \longrightarrow ClCH_2CH_2\cdot$$
$$SF_5CH_2CH_2\cdot + SF_5Cl \longrightarrow SF_5CH_2CH_2Cl + SF_5\cdot$$
$$ClCH_2CH_2\cdot + SF_5Cl \longrightarrow ClCH_2CH_2Cl + SF_5\cdot$$
$$SF_5\cdot + SF_5\cdot \longrightarrow S_2F_{10}$$

Similar reactions take place with other olefins (propene, cyclohexene, butadiene, and vinyl chloride). These reactions may also be initiated thermally (90–100°C). Some polymerization is observed. In fact, it is found that with isobutene and styrene only polymerization occurs (*41*). With less reactive fluoroolefins, addition of $SF_5Cl$ takes place only under photolytic conditions or by using a radical initiator such as benzoyl peroxide. Trifluoro-, tetrafluoro-, and chlorotrifluoroethylene as well as hexafluoropropylene give mainly 2-chloropolyfluoroalkylsulfur pentafluoride. With excess fluoroolefin, telomers of the type $SF_5(CF_2)_nCl$ are obtained (*42–44*). Acrylic acid derivatives, $CH_2{=}CHR$ (R = $CO_2Me$, CN), react with $SF_5Cl$ in Freon-113 at 120°C to give 32–42% $SF_5CH_2CHClR$ (*45*).

Addition of $SF_5X$ (X = Cl, Br) to olefins gives rise to a variety of pentafluorosulfanylalkanes (*46*).



$$SF_5X + {>}C{=}C{<} \longrightarrow F_5S{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}X$$

$>C{=}C<$ = $CH_2{=}CF_2$, $CFCl{=}CF_2$ (*47*), $CFH{=}CF_2$ (*43, 47, 48, 49*), $CH_2{=}CH_2$ (*40*),

$CH_3OCF{=}CF_2$ (*50*), $CHF{=}CHF$ (*51*), $(CH_3)_3SiCH{=}CH_2$ (*52*),

$CH_2{=}CFCl$, $CH_2{=}CHCF_3$, $CHF{=}CHCl$, $CHF{=}CFCl$ (*53*),

$CF_2{=}CHCl$ (*54*),

X = Cl (*40, 43, 48, 49, 50, 52*), X = Br (*47, 51, 52, 54*)

As shown, the reactions of $SF_5Br$ with olefins are the same as those described for $SF_5Cl$, but, in general, take place under milder conditions in keeping with the greater reactivity of the bromo compound. Thus, $C_2H_4$ and $SF_5Br$ give $SF_5CH_2CH_2Br$ at room temperature and addition to the halogenated olefins, $CH_2{=}CHF$, $CH_2{=}CF_2$, $CHF{=}CF_2$, and $CClF{=}CF_2$, occurs without irradiation or use of a catalyst (*47, 51*).

Fluorinated polymers are formed when $SF_5Br$ reacts with the appropriate fluoroolefins at 90 ± 5°C and autogenous pressures of up to 90 atm for periods of 4 days to 2 weeks (*53*).

$$SF_5Br \begin{array}{lll} + CH_2{=}CHF \text{ (excess)} & \longrightarrow & SF_5(CH_2CHF)_{10}Br \\ + CH_2{=}CF_2 & \longrightarrow & SF_5(CH_2CF_2)_8Br \\ + CFH{=}CF_2 & \longrightarrow & SF_5(CFHCF_2)_{30}Br_{0.7} \\ + CF_2{=}CF_2 & \longrightarrow & SF_5(CF_2CF_2)_{16}Br_{0.3} \end{array}$$

With $C_2H_4$, no polymer is obtained. In addition to the above polymers, the adducts $SF_5RBr$ (R = $CH_2CHF$, $CH_2CF_2$, $CFHCF_2$, $CF_2CF_2$, $CH_2CFCl$, $CH_2CHCF_3$, $CHFCHCl$, $CHFCFCl$, $CF_2CClH$) are also formed (*53, 54*). The monomeric adducts, with the exception of $SF_5CF_2$-$CF_2Br$, are reported (*47*). Polymers and telomers containing $SF_5$ are found in the patent literature (*55*) and elsewhere (*56*).

The reaction between $SF_5X$ and acetylene is similar to that with olefins (*57, 58*). The addition product $SF_5CH{=}CHX$ can be converted to $SF_5C{\equiv}CH$ [X = Cl (11%) (*57*), X = Br (~50%) (*58*)]. Reactions between $CH_3C{\equiv}CH$ or $CF_3C{\equiv}CH$ and $SF_5Br$ give $SF_5CH{=}C(CH_3)Br$ in 30% yield (b.p., 109 ± 1°C) and $SF_5CH{=}C(CF_3)Br$ in 58% yield (b.p., 93 ± 1°C), respectively. The products are clear, colorless, hydrolytically stable liquids and are identified from their IR, NMR, and mass spectra (*59*). The reaction of $SF_5Cl$ with $CH_3C{\equiv}COR$ gives an 85% yield of ethylidenesulfur tetrafluoride, $CH_3CH{=}SF_4$ (*60*). A trigonal bipyramidal structure is proposed based on NMR studies.

The addition of $SF_5Cl$ to a $C{=}O$ group occurs less readily than addition to $C{=}C$ bonds. With ketene the product of reaction at 25°C in a pressure vessel is $SF_5CH_2C(O)Cl$. This acid chloride is a useful precursor to the strong acid $SF_5CH_2COOH$ (*45*).

Addition of $SF_5Cl$ to the $—C{\equiv}N$ functionality is a reaction of considerable preparative significance (*8*).

$$\begin{array}{lll} & + \ ClCN & \longrightarrow SF_5N{=}CCl_2 \\ SF_5Cl & + \ CF_3CN & \longrightarrow SF_5N{=}C(CF_3)Cl \\ & + \ C_3F_7CN & \longrightarrow SF_5N{=}C(C_3F_7)Cl \end{array}$$

It is possible to fluorinate the products using NaF in tetramethylene sulfone. The compound thus obtained from $SF_5N{=}CCl_2$, i.e., $SF_5N{=}CF_2$, forms a mercurial, $Hg[NCF_3(SF_5)]_2$, with $HgF_2$, and on heating isomerizes to $SF_4{=}NCF_3$. With $(C_2N_2)$ two molecules of $SF_5Cl$ add to give $SF_5N{=}C(Cl)C(Cl){=}NSF_5$. With methylamine $SF_5Cl$ gives $CH_3\text{-}N{=}SF_2$ (*61*). Irradiation of a mixture of $SF_5Cl$ and $(CF_3)_2NCl$ gives $SF_5N(CF_3)_2$ (*62*). When $SF_5Br$ reacts with pentafluorosulfanyl(fluorosulfuryl)ketene $F_5S(SO_2F)C{=}C{=}O$, only BrF addition takes place, to give $F_5SCBr(SO_2F)C(O)F$ (*63*). Sulfur tetrafluoride is the other product.

Pentafluorothiophenyllithium readily attacks $SF_5Br$ at −78°C to form bis(pentafluorophenyl)trisulfane and bis(pentafluorophenyl)disulfane (*64*). However, in its reaction with $SF_5Cl$, $C_6F_5SCl$ is produced in addition to the di- and trisulfanes (*64*). Regardless of the molar ratio of the reactants, these are the only products obtained. Similar behavior is observed in the nucleophilic reactions of trifluoromethylthiolithium. Reaction of $SF_5X$ ($X = Cl, Br$) with $C_6F_5Li$ forms an unstable intermediate, $(C_6F_5)_2SXF$, which is hydrolyzed to $(C_6F_5)_2SO$. The mechanism for the formation of the compounds isolated is suggested (*64*).

## III. Pentafluorosulfanyl Hypohalites, $SF_5OX$

### A. $SF_5OF$

The first of these compounds to be isolated was $SF_5OF$, formed in low yield by fluorination of $SO_2$ or $SOF_2$ with $F_2$ at 200°C using $AgF_2$ as a catalyst (*65*). It is also obtained in >90% yield by the reaction of $F_2$ with $SOF_4$ at 25°C in the presence of CsF in a static system (*66*, *67*). The salt $CsOSF_5$ is believed to be an intermediate, analogous to the report that the salt $CsOCF_3$ is an intermediate in the reaction between $F_2$ and $COF_2$ in the presence of CsF (*68*). Pentafluorosulfanyl hypofluorite is also obtained in the reaction between $CsOSF_5$ and $FSO_2OF$ at 100°C (*69*).

Although $SF_5OF$ (b.p., −55.1°C) is thermally stable to about 200°C, at higher temperatures it decomposes to $SF_6$ and $O_2$ (*70*). Photolysis gives a low yield of the peroxide, $(SF_5)_2O_2$, which is consistent with cleavage of the O–F bond on irradiation. That this bond also breaks upon thermolysis is indicated by the formation of $SF_5ONF_2$ when the compound is heated with $N_2F_4$ (*71–73*). When $SF_5OF$ is reacted with $SO_2$ in the liquid phase, $SF_6$, $SO_2F_2$, $SO_3$, and $SF_5OSO_2F$ are formed (*74*). With $SF_4$ it gives $SF_5OSF_5$, $SF_5OOSF_5$, and $SF_5OSF_4OSF_5$. A similar reaction in the presence of $O_2$ gives $SF_5OSF_4OOSF_5$ and $SF_5OSF_4OOSF_4OSF_5$ as additional products. These new products react with benzene to give $C_6H_5OSF_4OSF_5$. The reaction of $CF_3OF$ with $SF_4$ gives $CF_3OSF_5$ as the only product. Trifluoromethyl hypofluorite, sulfur(IV) fluoride, and oxygen react to give $CF_3OSF_4OSF_5$, $CF_3OSF_4OOSF_5$, and a compound believed to be $CF_3OSF_4OOSF_4OCF_3$. A reaction mechanism is proposed (*74*).

Other reactions of $SF_5OF$ that have been investigated include reactions with CO at 165°C to form $COF_2$ and $SOF_4$ and those with $CCl_4$ in UV light, giving $COF_2$, $Cl_2$, and $SF_5OSF_5$ (*75*). With $NO_2$, $SOF_4$ and $NO_2F$ are formed (*75*). Photolytic reaction of $SF_5OF$ with oxalyl chloride gives $F_5SOC(O)F$ (*76*).

Pentafluorosulfanyl hypofluorite adds readily to a number of alkenes to give only one product, containing the components $SF_5O$ and F (*77, 78*). Because of its facile synthesis, some use is made of $SF_5OF$ in electrophilic fluorination (*79*). The gas-phase structure of $SF_5OF$ is reported (*80*).

## B. $SF_5OCl$

This hypochlorite is considerably less stable than the hypofluorite. The hypobromite and hypoiodite have not been prepared. Pentafluorosulfanyl hypochlorite is synthesized from ClF and $SOF_4$ in the presence of CsF at −20°C (*81, 82*).

Pentafluorosulfanyl hypochlorite (b.p., 8.9°C) is thermally stable up to about 20°C, at which temperature it decomposes to $SOF_4$ and ClF. Upon photolysis, the peroxide $(SF_5)_2O_2$ is formed in high yield (*83–85*) via cleavage of the O–Cl bond. The yield of the peroxide is much greater than that observed when $SF_5OF$ is irradiated. Photolysis of $SF_5OCl$ with $N_2F_4$ (*84*) and CO (*86*) gives $SF_5ONF_2$ and $SF_5OC(O)Cl$, respectively.

Because of the partial positive charge associated with chlorine in the hypochlorite, $SF_5OCl$ reacts readily with molecules containing negative chlorine. Seppelt exploited this property (*87*) and reacted $SF_5OCl$ with HCl at −95°C to obtain the unstable pentafluoroorthosulfuric acid, $SF_5OH$, which decomposes via elimination of HF at −60°C. Although the decomposition of $CF_3OH$ is thermodynamically more favored, its greater stability is attributed to a longer intramolecular H–F distance compared with that in $SF_5OH$ (*88, 89*).

A low-temperature addition reaction occurs between $SF_5OCl$ and symmetric fluoroolefins to form pentafluorosulfanylalkyl ethers in nearly quantitative yields (*78, 90–92*). It is found that with unsymmetrical olefins the chlorine atom of the hypochlorite most often bonds to the olefinic carbon atom with higher electron density. The reactions of $SF_5OCl$ and $SF_5OF$ with fluorinated ethylenes are used to prepare new $SF_5O$-substituted fluorocarbons in 44–77% yield (*93*).

$$SF_5OCl + CF_2{=}CFH \longrightarrow \underset{(44\%)}{SF_5OCF_2CFHCl}$$

$$SF_5OCl + CF_2{=}CFCl \longrightarrow \underset{(50\%)}{SF_5OCFClCF_2Cl}$$

$$SF_5OCl + CF_2{=}CFBr \longrightarrow SF_5OCFBrCF_2Cl + \underset{(77\%)}{SF_5OCF_2CFBrCl}$$

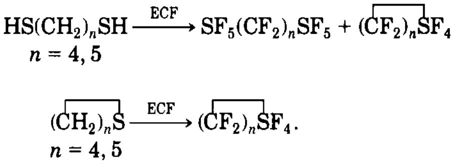
The compounds are characterized by $^{19}F$ and $^{1}H$ NMR, IR, and Raman spectral studies. Compounds of the type $SF_5OR_f$ are thermally very stable. They do not yield the perfluorovinyl derivative, $SF_5OCF{=}CF_2$, on dehalogenation as is the case when $CF_3OCF{=}CF_2$ is formed from $CF_3OCFClCF_2Cl$ (*94*).

At room temperature, $SF_5OCl$ adds quantitatively to $C_3F_7NC$ to give $C_3F_7N{=}C(Cl)OSF_5$. The IR, NMR, and mass spectra are compatible with the structure (*95*).

## IV. Pentafluorosulfanylalkanes, Alkenes, and Alkynes

Several perfluoroalkylpentafluorosulfur(VI) compounds, $R_fSF_5$ ($R_f$ = $CF_3$, $C_2F_5$, n-$C_3F_7$, i-$C_3F_7$, n-$C_4F_9$, sec.-$C_4F_9$, n-$C_5F_{11}$, i-$C_5F_{11}$), are reported. When $CF_2ClSCl$ is passed over $AgF_2$ at 60–70°C with a residence time of 10 min, a 30% yield of $SF_5CF_3$, together with $CF_2ClSF_3$ (40%) and $CF_3SF_3$ (30%), is obtained (*96*). Fluorination of $CF_3SSCF_3$ with $CoF_3$ provides $SF_5CF_3$ in high yield (*97*). The reaction of $C_2F_5SSC_2F_5$ with ClF at 25°C (10 hr) yields $SF_5C_2F_5$ (17.1%). When $R_fSCl$ ($R_f$ = $C_2F_5$, n-$C_3F_7$, n-$C_4F_9$) is treated with ClF at 25°C (10 hr) small amounts of $R_fSF_5$ are formed (*98*). The physical properties and spectral data (IR, $^{19}F$ NMR, and mass) are reported (*96, 98, 99*), as is the gas-phase electron diffraction structure of $SF_5CF_3$ (*100*).

Electrofluorination of alkane thiols in AHF leads to variable yields of perfluoroalkylpentafluorosulfur(VI) compounds (*101, 102*). Dithiols and sulfides also yield $SF_5R_f$. Dithiols give both cyclic and acyclic sulfur(VI) derivatives (*103*), e.g.,



$$HS(CH_2)_nSH \xrightarrow{ECF} SF_5(CF_2)_nSF_5 + \overline{(CF_2)_nSF_4} \quad n = 4, 5$$

$$\overline{(CH_2)_nS} \xrightarrow{ECF} \overline{(CF_2)_nSF_4}. \quad n = 4, 5$$

Electrochemical fluorination of sulfur dissolved in $CS_2$ in the presence of chlorine gives several products, including $SF_5CF_3$, $SF_5CF_2SF_5$, and $CF_2ClSF_5$ (*104*). The reaction of elemental fluorine with branched alkyl mercaptans or sulfides gives $SF_5$ organofluorine compounds (*105*).

$$(CH_3)_3CCH_2SH \xrightarrow[-120°C \text{ to room temperature}]{F_2/He} SF_5CF_2C(CF_3)_3$$

$$(CH_3)_3CSH \xrightarrow[-120°C \text{ to room temperature}]{F_2/He} SF_5CF_2C(CF_3)_2F$$

$$(CH_3)_3CSC(CH_3)_3 \xrightarrow[-120°C \text{ to room temperature}]{F_2/He} SF_5CF_2C(CF_3)_2F + C(CF_3)_3F$$

$$(CH_3)_2HCSCH(CH_3)_2 \xrightarrow[-120°C \text{ to room temperature}]{F_2/He} SF_5CF_2CF_2CF_3$$

Direct fluorination of $CS_2$ with $F_2$ diluted with He at −120°C (3 days), followed by warming to −80°C (3 days), gives a 15% yield of $(SF_5)_2CF_2$ (*106, 107*). The IR spectrum of this product is in agreement with that provided earlier (*108*). The gas-phase structure of $(SF_5)_2CF_2$ is reported (*109*).

The compound $SF_5CH_3$ can be obtained from $SF_5CH_2COOAg$ by the following sequence of reactions.

$$SF_5CH_2COOAg + X_2 \xrightarrow{\Delta} SF_5CH_2X$$

$X_2 = Br_2$ (*110, 111*), $I_2$ (*112*)

$$SF_5CH_2X \xrightarrow{Zn/HCl} SF_5CH_3$$

Similarly, $SF_5CH_2F$ (*113*) and $SF_5CHF_2$ (*114*) are also formed. The parent acid is obtained by the reaction of $SF_5Cl$ with the ketene, $CH_2{=}C{=}O$, followed by hydrolysis of the resulting acid chloride (*110–112*).

$$SF_5Cl + CH_2{=}C{=}O \longrightarrow SF_5CH_2C(O)Cl \xrightarrow{H_2O} SF_5CH_2COOH$$

The silver salt, $SF_5CH_2COOAg$, is formed by reacting the acid with silver carbonate (*50, 111, 112*).

When $SF_5CH_2Br$ is lithiated at −110°C, LiF is lost on warming to leave the remarkably stable methylene sulfur tetrafluoride, $CH_2{=}SF_4$ (*111*). It is also synthesized by the reaction of $O{=}C(Cl)CH_2SF_5$ with $[Mn(CO)_5]^-$ (*115, 116*).

Pentafluorosulfanylalkanes are also obtained by saturation of $SF_5$-containing olefins. Dehydrohalogenation of $SF_5$-alkanes results in the formation of $SF_5$-alkenes, which can be converted to additional $SF_5$-alkanes.

$$SF_5CHFCF_2X \xrightarrow[\text{reflux}]{\text{KOH}} SF_5CF{=}CF_2 \ (\mathit{43, 47})$$

$$(X = Br, Cl)$$

$$SF_5CHFCHFBr \xrightarrow[\text{reflux}]{\text{KOH}} SF_5CF{=}CHF \ (\mathit{51})$$

A variety of materials add across the double bond in the resulting vinyl-$SF_5$ compounds (*117*), e.g.,

$$SF_5CH{=}CH_2 + SF_5Br \xrightarrow[8\ \text{hr}]{70^\circ\text{C}} SF_5CHBrCH_2SF_5.$$

Attempts to dehydrobrominate this bis-$SF_5$ compound result in the loss of $SF_4$ and HF to give $SF_5CBr{=}CH_2$.

Indirect "HF" addition (via KF-formamide) to pentafluorosulfur olefins yields hydrylpentafluorosulfur-F-alkanes.

$$SF_5CX{=}CF_2 + HF \longrightarrow SF_5CH(X)CF_3$$

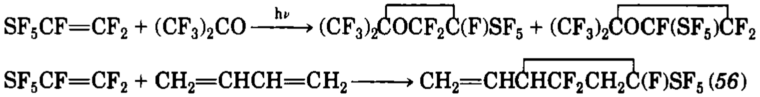
$$X = H, F, CF_3 \ (\mathit{118})$$

Reaction of $SF_5CF{=}CF_2$ with a mixture of $I_2$ and $IF_5$ gives $SF_5CFICF_3$ (*119*). The presence of H in the hydrylpentafluorosulfur-F-alkanes provides a site to introduce additional functional groups (*120*). Reaction of $SF_5CHXCF_3$ with $S_2O_6F_2$ gives the corresponding fluorosulfate (*118, 121*). Similarly $(CF_3)_2CHSF_5$ with $S_2O_6F_2$ at 80°C (25 hr) forms $(CF_3)_2$-$C(OSO_2F)SF_5$ (66% yield) (*118*). Both $(CF_3)_2NO$ and $Cl_2$ add as well.

$$SF_5CH{=}CHX + Y \longrightarrow SF_5CHYCHXY$$

$$X = H, Y = (CF_3)_2NO;\ X = CH_3, Y = Cl_2 \ (\mathit{121})$$

In some cases, cyclization occurs (*122*).



(*56*)

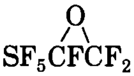
Trifluoroethenylpentafluorosulfur(VI), $SF_5CF{=}CF_2$, is obtained in 80% yield by debromination of $SF_5CFBrCF_2Br$ with Cu at 188°C (0.5 hr, 3 Torr). Irradiation of $SF_5CFBrCF_2Br$ in a silica tube in the presence of mercury gives $SF_5CF{=}CF_2$ in 67% yield (*56*). Trifluoroethenylpentafluorosulfur(VI) is stable in air up to 300°C. It decomposes at 380°C, giving $SF_4$ and unidentified fluorocarbons (*56*). In perfluorobutylamine $SF_5CF{=}CF_2$ reacts with $O_3^-$ or $O_2$ at 25°C (12 hr) to give, respectively, 72 or 52% yields of $FC(O)CF_2OSF_5$, as well as $CF_3Cl$, $SOF_2$, $SO_2F_2$, and $(SF_5)_2O$. The IR and $^{19}F$ NMR spectra of $FC(O)CF_2OSF_5$ are reported (*123*). When $SF_5CF{=}CF_2$ reacts with $NaOCH_3$ in $CH_3OH$ at 60°C (20 hr), $SF_5CHFCF_2OCH_3$ is formed (90% yield; b.p., 73.4°C) (*56*). In aqueous solution in the presence of $K_2S_2O_8$–$Na_2SO_3$, copolymerization of $CF_2{=}CFSF_5$ with $CH_2{=}CF_2$ at 85°C (20 hr) gives $[(CH_2CF_2)_x$-$CF_2CF(SF_5)]_n$ [68% yield; $\nu$ SF = 867 (vs, br) $cm^{-1}$] (*56*). With KF and formamide, $CF_3CHFSF_5$ is obtained (86% yield; b.p., 26.9°C) (*118*). Under similar conditions $SF_5C(CF_3){=}CF_2$ gives a 91% yield of $(CF_3)_2$-$CHSF_5$ (b.p., 52.2°C) (*118*). The former is obtained in ~60% yield by shaking $CF_3CH(SF_5)CF_2Cl$ with excess KOH at 20°C for 1 hr. The $SF_5$ monomer, 2-chloro-3-(pentafluorosulfur)tetrafluoropropene [$SF_5CF_2$-$C(Cl)CF_2$], is prepared in 20% yield by the addition of $SF_5Cl$ to $CF_2{=}C{=}CF_2$ in a metal vessel at 100°C (*124*).

A mixture of AgF in acetonitrile reacts with excess $SF_5CF{=}CF_2$ in ≥2:1 molar ratio at 25°C and with stirring to yield $AgCF(CF_3)SF_5$ that is isolated as the acetonitrile solvate. The solvate is stable up to 50°C. Thermolysis at 80–90°C gives $CF_3CF(SF_5)CF(SF_5)CF_3$ as the major product. Other products include $C_2F_5CF(CF_3)SF_5$, $SF_4$, $S_2F_{10}$, $SOF_2$, $CF_3CF{=}CFCF_3$, and Ag. The solvate reacts with HX (X = Cl, Br, OH) at 20°C (1 hr) to give $CF_3CHFSF_5$ and traces of $CF_3CF(SF_5)CF$-$(SF_5)CF_3$. With $CH_3I$ at 20°C (12 hr), $SOF_2$, $SiF_4$, and $CF_3CHFSF_5$ are formed (*125*). Bromination of $AgCF(CF_3)SF_5$ with dry $Br_2$ over the temperature range from −196 to 20°C (12 hr) gives $CF_3CFBrSF_5$ (45% yield; b.p., 57.2°C) and $(CF_3CFSF_5)_2$. The latter compound is unstable and decomposes to $S_2F_{10}$ and $CF_3CF{=}CFCF_3$ at 100°C (*125*). The IR, $^{19}F$ NMR, and mass spectral data of $CF_3CF(SF_5)CF(SF_5)CF_3$ are reported (*125*).

A mixture of $SF_5CF{=}CF_2$ and $Br_2$ at 20°C (20 days) in the dark gives only traces of $CF_2BrCFBrSF_5$. Yields of ~91% of $CF_2BrCFBrSF_5$ are obtained on UV irradiation of the same mixture for 20 hr in a silica tube. The photochemical reaction between $SF_5CF{=}CF_2$ and HBr also give $CF_2BrCFBrSF_5$ in 17.5% yield. An equilibrium mixture of $SF_5CF{=}CF_2$, $Cl_2$, and $Br_2$ in $CH_2Cl_2$ gives a mixture of $CF_2BrCFClSF_5$ (9.5%), $CF_2ClCFClSF_5$ (1%), $CF_2ClCFBrSF_5$ (6.5%), and $CF_2BrCFBrSF_5$ (62%). The same reaction at 80°C (22 hr) gives $CF_2BrCFClSF_5$ (13%), $CF_2ClCFClSF_5$ (1%), $CF_2ClCFBrSF_5$ (15%), and $CF_2BrCFBrSF_5$ (51%) (*56*). Spectral data ($^{19}F$ NMR) for $CF_2BrCFBrSF_5$, $CF_2BrCFClSF_5$, and $CF_2ClCFBrSF_5$ are available (*99*).

Irradiation (UV) of a mixture of $SF_5CF{=}CF_2$ and $CF_3I$ in a sealed silica tube gives a 9% yield of $CF_3CF_2CFISF_5$ (*56*). An equimolar mixture of $S_2F_{10}$ and $ICF_2CF_2I$ when pressurized with $CF_2{=}CF_2$ (150 psi) and heated to 150°C for 4 hr yields $ICF_2CF_2SF_5$ (*126*). Heating the mixture to 150°C with intermittent injection of $CF_2{=}CF_2$ leads to the formation of a product mixture, which on distillation gives three main fractions identified as $SF_5CF_2CF_2I$, $SF_5(CF_2CF_2)_2I$, and $SF_5(CF_2CF_2)_3I$. The mass spectrum of the residue shows parent ions corresponding to $SF_5(CF_2CF_2)_nI$, $n = 4$–$9$. With slow warming, a mixture of $S_2F_{10}$, $I_2$, and $C_2F_4$ (pressurized) (from 20 to 150°C) gives a violet liquid with an estimated molecular composition of $SF_5CF_2CF_2I$ (34%), $SF_5(CF_2CF_2)_2I$ (35%), $SF_5(CF_2CF_2)_3I$ (14%), $SF_5(CF_2CF_2)_4I$ (5%), and $SF_5(CF_2CF_2)_5I$ (2%) (*125, 126*). An interesting reaction involving iodo-$SF_5$ alkanes is oxidative fluorination by $ClF_3$ (*127*).

$$\underset{(n = 2, 4)}{SF_5(CF_2)_nI} + ClF_3 \longrightarrow SF_5(CF_2)_nIF_4$$

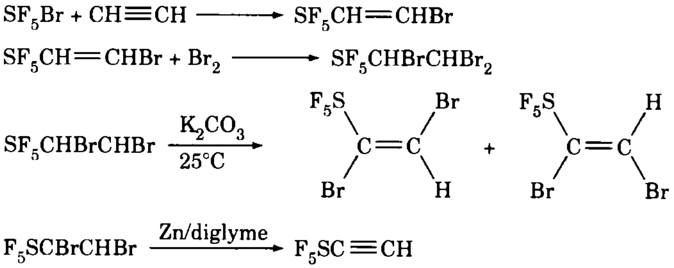
With NaOCl, $SF_5CF{=}CF_2$, in Freon-113 and in the presence of a phase-transfer catalyst $[N(n\text{-}C_8H_{17})_3CH_3{}^+Cl^-]$, forms the epoxide  $SF_5\overset{O}{\overbrace{CFCF_2}}$ (*128*). The epoxide is decomposed by ether and reacts with CsF to give primarily $SF_4$ and $CF_3C(O)F$.

Carbonyl fluoride reacts with $SF_5CF{=}CF_2$ in the presence of CsF and acetonitrile to give $SF_5CF(CF_3)C(O)F$, which reacts further with $NH_3$, $CH_3OH$, and $H_2O$ to give, respectively, $SF_5CF(CF_3)C(O)NH_2$, $SF_5CF(CF_3)C(O)OCH_3$, and $SF_5CF(CF_3)C(O)OH$ (*129*). On dehydration with $P_4O_{10}$, the amide, $SF_5CF(CF_3)C(O)NH_2$, gives the nitrile $SF_5CF(CF_3)CN$. All of these compounds, with the exception of the amide, are colorless, stable liquids. The amide is a stable, white solid (m.p., 32–34°C).

Trialkylphosphites react with F-alkenes, e.g., $CF_3CR'{=}CF_2$, to give the phosphonates, $CF_3CR'{=}CFP(O)(OR)_2$ (R = Et, $^iPr$; R′ = F, $CF_3$), and alkyl fluorides (RF) via an Arbuzov-type reaction (*130*). The use of trimethylsilylphosphites, $(RO)_2POSiMe_3$ (R = Et, $SiMe_3$), is advantageous because of their greater nucleophilicity and the ease of formation of trimethylsilylfluoride (*131*). Trimethylsilylphosphites react with $SF_5CF{=}CF_2$ to give alkenylphosphonates $SF_5CF{=}CFP(O)(OR)_2$ (R = Et, $SiMe_3$) (*132*). Only (E) isomers are formed. These compounds are colorless, moisture-sensitive liquids.

The $SF_5$-substituted iodoperfluoroalkene, $SF_5CF{=}CFI(E)$, is obtained in 24% yield (*133*) via the reaction of trimethylphosphine, iodine, and $SF_5CF{=}CF_2$. It is a colorless liquid and is characterized by spectral data (*133*).

The substituted acetylene, $SF_5C{\equiv}CH$, is obtained in 11% yield from the reaction of $SF_5Cl$ with acetylene (*134*). It is also formed in ~9% yield in a four-step synthesis from the reaction of $SF_5Br$ with $C_2H_2$ (*135*).



This $SF_5$-acetylene can also be obtained in ~50% yield by dehydrobromination of $SF_5CH{=}CHBr$ (*135*). The gas-phase electron diffraction structure of $SF_5C{\equiv}CH$ is reported (*136*). In the $^1H$ NMR spectrum, the acetylenic proton resonates at a more shielded position and appears as a pentet with $J_{F-H}$ = 3 Hz (*134*). This suggests that it couples significantly only with the four equatorial S–F atoms and not the axial S–F atom. Of particular interest are comparative $^{19}F$ NMR spectral studies of $F_5SC{\equiv}CH$ and other saturated hydrocarbons/fluorocarbons containing the $SF_5$ group (*137*).

Pentafluorosulfanyl acetylene is a useful starting reagent for the synthesis of a variety of $SF_5$ derivatives of saturated ethers, vinyl ethers, pyrazoles, cyclic alkenes, and alkyl-substituted phenyl-sulfur pentafluorides (*134*). It is also used for the preparation of a number of $F_5S$-containing alkenes and alkynes (*138, 139*).

$$SF_5Br \begin{cases} + SF_5C{\equiv}CH \xrightarrow[3\,hr]{110^\circ C} SF_5CBr{=}C(H)SF_5 \xrightarrow{KOH} F_5SC{\equiv}CSF_5 \\ + RC{\equiv}CH \longrightarrow F_5SCH{=}C(Br)R \xrightarrow{KOH} F_5SC{\equiv}CR \\ \quad (R = CH_3, CF_3) \end{cases}$$

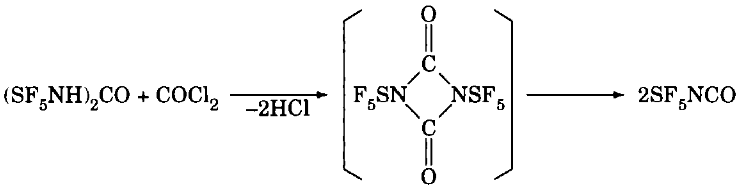
Mono- and bis(pentafluorosulfur)diacetylenes, $F_5SC{\equiv}C{-}C{\equiv}CH$ and $F_5SC{\equiv}C{-}C{\equiv}CSF_5$, are obtained by the addition of $F_5SBr$ to diacetylene followed by dehydrobromination. These monomers yield interesting polymers (*140*). A variety of uses are proposed for several of these pentafluorosulfur-containing alkanes and alkenes, e.g., as dielectric insulators (*122, 141*), elastomer precursors (*142*), blood substitutes (*143*), fumigants (*144*), and insecticides (*145*).

## V. Sulfur Isocyanate Pentafluoride and Sulfur Isothiocyanate Pentafluoride

Pentafluorosulfanyl isocyanate, $SF_5NCO$ and $SF_5NCS$, were first reported in 1964 by Tullock *et al.* (*8*). They are obtained from the reaction of pentafluorosulfanyl(trifluoromethyl)amine with benzoic acid and thiobenzoic acid, respectively. An alternative preparative method of $F_5SNCS$ involves thiolysis of $F_5SN{=}CCl_2$ with $H_2S$ in the presence of NaF.

$$F_5SN{=}CCl_2 + H_2S \xrightarrow{NaF} F_5SN{=}C{=}S$$

Hydrolysis of $SF_5N{=}CCl_2$ gives only traces of $SF_5NCO$. Another route for the preparation of $SF_5NCO$ is found in the reaction of $NSF_3$, $COF_2$, and AHF (*146*). Reaction of *N,N'*-bis(pentafluorosulfanyl)urea, $(SF_5\text{-}NH)_2CO$, with a slight excess of $COF_2$ at 100°C (12 hr) gives essentially pure $SF_5NCO$ (*147*). When $COCl_2$ is used instead of $COF_2$, the reaction proceeds much less cleanly. Nevertheless, the infrared spectrum of the product mixture suggests that the reaction proceeds through the formation of an intermediate cyclic compound, which is not isolated.



With *N,N'*-bis(trifluoromethyl)urea, the corresponding cyclic intermediate has been isolated and characterized (*148*). The preparation and purification of $SF_5NCO$ are greatly simplified by first preparing $SF_5\text{-}NHC(O)F$ from an equimolar reaction mixture of $NSF_3$, $COF_2$, and AHF (*149*), followed by dehydrofluorination (*150, 151*).

Although reaction of $SF_5NH_2$ with $COF_2$ gives $SF_5NCO$ in good yield

(*146*), the analogous reaction of $SF_5NH_2$ with either CSClF or $CSCl_2$ fails to produce more than 1–2% of $SF_5NCS$ (*150*). Two methods that often produce isothiocyanates in high yield involve the reactions of iminodichloromethanes with either $Na_2S$ or $P_2S_5$ (*152*). Reaction of dichloro(pentafluorosulfanylimino)methane with $P_2S_5$ in refluxing toluene gives $SF_5NCS$ in 70% yield (*150*). It is also obtained in ~40% yield when $SF_5N{=}CCl_2$ reacts with triphenylphosphine in benzonitrile for 1 day (*153*).

Both $F_5SN{=}C{=}O$ (b.p., 5–5.5°C) and $SF_5N{=}C{=}S$ (b.p., 47–48°C) are well characterized by their elemental analyses and IR, $^{19}F$, and $^{13}C$ NMR spectral studies (*8, 146, 150*). The gas-phase structure of $SF_5NCO$ obtained by electron diffraction and microwave spectroscopy is reported (*154*).

The isocyanate, $SF_5NCO$, is easily hydrolyzed to $SF_5NH_2$ and $CO_2$, whereas $SF_5NCS$ is hydrolytically very stable. Both compounds undergo addition reactions with substrates containing easily replaceable hydrogen atoms, i.e., alcohols, thiols, and amines. With alcohols (thiols) the isocyanate and isothiocyanate give urethanes and thiourethanes, respectively.

$$SF_5NCO + ROH \longrightarrow SF_5NHC(O)OR$$

$$R = CH_3, CH_2CH_2C(O)C(O)CNHSF_5, C_6H_5, 4\text{-}C_6H_4C(O)C(O)CNHSF_5,$$
$$4\text{-}C_6H_4OH\ (\mathit{150}),\ C_6H_5CH_2\ (\mathit{8})$$

$$SF_5NCS + CH_3OH \longrightarrow SF_5NHC(S)OCH_3$$

$$SF_5NCO + RSH \longrightarrow SF_5NHC(O)SR$$
$$R = CH_3, C_6H_5\ (\mathit{150})$$

$$SF_5NCS + CH_3SH \longrightarrow SF_5NHC(S)SCH_3$$

The urethanes are stable indefinitely in aqueous solution, but are decomposed by aqueous alkali. The dithiourethanes are, however, unstable and decompose readily at room temperature. With $PCl_5$ the urethane $SF_5NHC(O)CH_3$ gives $SF_5NCO$ as the major product (*155*), whereas the fluorosulfonylurethanes give the corresponding sulfonylchloroimines (*156*). The thiourethanes, $SF_5NHC(O)SR$, give $SF_5NCO$ as well as the imine (*155*). The crystal structure of $SF_5NHC(O)SCH_3$ is reported (*157*).

On treatment of $SF_5NCO$ with polynitroalcohols, carbamates are produced. They are potentially energetic and have densities of ~2 g/cm$^3$ (*158*).

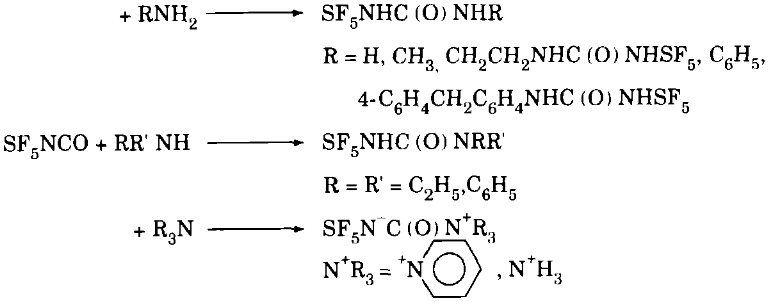
$$SF_5NCO + R(NO_2)_nCH_2OH \longrightarrow SF_5NHCO_2CH_2R(NO_2)_n$$

Such carbamates can be further nitrated, e.g., *N*-pentafluorosulfanyl-3,3,3-trinitropropyl carbamate is nitrated with trifluoroacetyl nitrate [a mixture of $(CF_3CO)_2O$ + 100% $HNO_3$] to produce *N*-pentafluorosulfanyl-*N*-nitro-3,3,3-trinitropropyl carbamate in 43% yield (*159*).

$$SF_5NHCO_2CH_2CH_2C(NO_2)_3 \xrightarrow{(CF_3CO)_2O + HNO_3} SF_5N(NO_2)CO_2CH_2CH_2C(NO_2)_3$$

These nitro compounds, which have a pentafluorosulfanyl group attached, exhibit increased density, decreased shock sensitivity, and good thermal stability and release considerable energy upon detonation (*160*).

Pentafluorosulfanyl isocyanate reacts with ammonia and primary, secondary, and tertiary amines to form a variety of substituted ureas (*150*).



The thioisocyanate, $SF_5NCS$, reacts with aniline to give $SF_5NHC(S)$-$NHC_6H_5$. The substituted ureas undergo thermal decomposition. The zwitterionic derivatives, $SF_5N^-C(O)N^+R_3$, are far less stable thermally than the analogous fluorosulfonyl derivatives (*161*). The reaction of $SF_5NCO$ with triphenylphosphine gives some evidence for a zwitterionic compound, but the compound could not be isolated (*161*). On the other hand, fluorosulfonyl isocyanate does react with tertiary phosphines, producing the corresponding adducts in high yield (*162*). The IR, NMR, and mass spectral data for these substituted ureas are reported (*150*).

Dimethylsulfoxide, aldehydes, and formamides react with $SF_5NCO$ to give imines and amidines (*147, 150*).

$$+ (CH_3)_2SO \xrightarrow{-CO_2} SF_5N{=}S(CH_3)_2$$

$$+ RC(O)H \xrightarrow{-CO_2} SF_5N{=}C(H)R$$

$$SF_5NCO \qquad (R = C_6H_5, 4\text{-}C_6H_4CH_3, 4\text{-}C_6H_4OCH_3)$$

$$\begin{array}{ll} & + \mathrm{RR'NC(O)H} \xrightarrow{-\mathrm{CO_2}} \mathrm{SF_5N{=}C(H)NRR'} \\ \mathrm{SF_5NCO} & \qquad\qquad (\mathrm{R = R' = CH_3; R = CH_3, R' = C_6H_5}) \\ & + \mathrm{(CH_3)_2NC(O)CH_3} \xrightarrow{-\mathrm{CO_2}} \mathrm{SF_5N{=}C(CH_3)N(CH_3)_2} \end{array}$$

Certain electron-deficient isocyanates are known to react with organic carbonyls and sulfoxides to yield the corresponding imines (*163–165*).

With acetylacetone, $SF_5NCO$ gives the *N*-(pentafluorosulfanyl) amide of diacetoacetic acid, which enolizes to give two enolic products in $CDCl_3$. In $(CD_3)_2SO$, however, only one enolic form and a keto form is observed. The structures of these tautomers are supported by $^1H$, $^{19}F$, and $^{13}C$ NMR spectroscopy (*150*).

Analogous reactions with both chloro- and fluorosulfonyl isocyanates are also reported (*166*). Reactions of $SF_5NCO$ with trimethylorthoformate, $HC(OMe)_3$, give $SF_5NHC(O)C(OMe)_3$ and $SF_5N(CH_3)C(O)OMe$ (*150*). The formation of the latter probably takes place via the same mechanism as has been proposed for a similar reaction with chlorosulfonyl isocyanate (*167*).

When $SF_5N(SiMe_3)C(O)OMe$ is reacted with CsF in the presence of 18-crown-6, $Cs(18\text{-crown-}6)_2[SF_5NC(O)OMe]$ is formed. Decomposition occurs to give $[Cs(18\text{-crown-}6)_2][SF_5]$, which is characterized by single-crystal X-ray analysis. The $SF_5$ anion is described as naked $SF_5$; i.e., the distance between $Cs^+$ and $SF_4{-}F$ is $>7$ Å (*167b*).

At 60–80°C, $SF_5NCO$ reacts with $PCl_5$ to give $SF_5N{=}CCl_2$ (*147*). The product is identified by comparison of spectral data obtained with those reported earlier (*8*).

Amides containing $SF_5$ form when $SF_5NCO$ reacts with carboxylic acids (*148*). The reaction is believed to pass through a mixed acid anhydride intermediate that loses $CO_2$ to give the corresponding *N*-pentafluorosulfanyl amide in good yield. No reaction is observed with carboxylic acids having electron-deficient carboxylate groups.

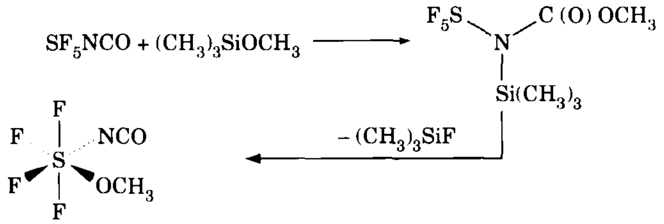
$$\mathrm{SF_5NCO + RCOOH \longrightarrow [SF_5NHC(O)OC(O)R] \xrightarrow{-CO_2} SF_5NHC(O)R}$$

$$\mathrm{R = CH_3\ (98\%);\ CH{=}CH_2\ (35\%)}$$

With (dimethylamino)triethylsilane, fluorine loss occurs via formation of $(CH_3)_3SiF$ (*168*).

$$\mathrm{SF_5NCO + (CH_3)_3SiN(C_2H_5)_2 \xrightarrow[-196\ \mathrm{to}\ -30^\circ C]{\text{isopentane}} SF_4{=}NC(O)N(C_2H_5)_2}$$

On reaction with trimethyl(methoxy)silane, *cis*-$CH_3OSF_4NCO$ is formed (*169*). The reaction appears to proceed as shown below, with subsequent intramolecular migration of the methoxy group.

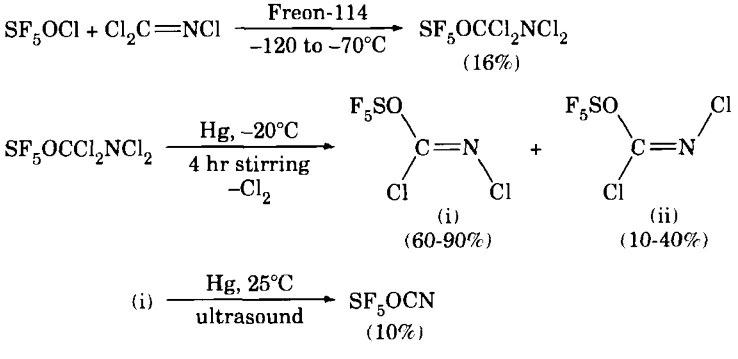


On further reaction with methanol, the methoxy compound gives a urethane derivative.

$$cis\text{-}CH_3OSF_4NCO + CH_3OH \longrightarrow cis\text{-}CH_3OSF_4NHC(O)OCH_3$$

## VI. Sulfur Cyanate Pentafluoride, $SF_5OCN$

Seppelt *et al.* (*170*) reported the first synthesis of $SF_5OCN$ by the sequence of reactions below.



The identification of isomers i and ii is made on the basis of NMR data (*170*). Only isomer i undergoes further chlorine elimination in the presence of mercury to afford the desired product in 10% yield. Isomer ii under similar conditions decomposes to give $SOF_4$ and ClCN. The IR and $^{14}N$ NMR spectra (*170, 172*) are used to differentiate between $SF_5$ cyanate and $SF_5$ isocyanate.

The cyanate, $SF_5OCN$ (b.p., 5°C; m.p., −60°C), undergoes rearrangement at high temperature to give $SF_5N{=}C{=}O$. The IR, Raman, $^{19}F$ and $^{14}N$ NMR, and mass spectral data for $SF_5OCN$ are reported (*170*). Its geometric structure has been determined by gas-phase electron diffraction spectroscopy (*173*) and the results have been compared with the gas-phase structure of $SF_5NCO$ (*154*). *Ab initio* calculations (*173*) are consistent with the experimental geometries of both isomers.

## VII. Sulfur Cyanide Pentafluoride, $SF_5CN$

The synthesis of $SF_5CN$ by fluorination of methyl thiocyanate, $CH_3SCN$, was first claimed in 1959 (*174*), but the claim was in error. The actual product isolated was the isomer $CF_3N{=}SF_2$ (*175*). Various other attempts to synthesize $SF_5CN$, such as by reaction of $(FCN)_3$ with $SF_4$ in the presence of CsF (*176*), the photolytic reaction between $S_2F_{10}$ and $(CN)_2$ (*11*), and metathesis between $CsSF_5$ and BrCN (*177*), failed. It was presumed that $SF_5CN$, if formed, isomerized to $CF_3N{=}SF_2$ (*177*).

The first successful synthesis of $SF_5CN$ (5% yield) by fluorination of $(SCN)_2$ in $FCl_2CCF_2Cl$ with elemental fluorine diluted with $N_2$ (1 : 10) at −20°C is reported by Lösking and Willner (*178*). It is a stable, colorless gas at room temperature (b.p., −25°C). It does not isomerize as suggested in the earlier literature (*177*). It does not decompose even on pyrolysis at 350°C. The IR and $^{19}F$ NMR spectral data and molecular weight data are consistent with the structure (*178*). The molecular structures obtained by gas-phase electron diffraction and microwave spectroscopy concur (*179*).

## VIII. Sulfur Isocyanide Pentafluoride, $SF_5NC$

The preparation of $SF_5NC$ in about 5% yield by the following sequence of reactions is reported by Thrasher (*180*).

$$SF_5N{=}CCl_2 + 3HF \longrightarrow SF_5NHCF_3 + 2HCl$$

$$SF_5NHCF_3 + BBr_3 \xrightarrow[-HBr]{} SF_5N(CF_3)BBr_2$$

$$SF_5N(CF_3)BBr_2 \xrightarrow[-BF3]{} SF_5N{=}CBr_2$$

$$SF_5N{=}CBr_2 \xrightarrow[-MgBr_2]{Mg/THF} SF_5NC$$

A similar sequence of reactions gives $CF_3NC$ in 65–90% yield (*181*). Reaction of $SF_5N{=}CBr_2$ with lithium alkyls/aryls also produces $SF_5NC$ in low yield (~5%) (*180*). However, $SF_5N{=}CCl_2$ under similar reaction conditions produces only traces of the isocyanide. Pentafluorosulfanyl isocyanide is a colorless gas and slowly isomerizes to $SF_5CN$ at ambient temperature. The IR and $^{19}F$ NMR spectral data of $SF_5NC$ are reported (*180*).

## IX. Pentafluorosulfanylamine and Other Derivatives

Pentafluorosulfanylamine is prepared in ~34% yield by the addition of AHF to $NSF_3$ (*182*).

$$NSF_3 + 2HF \longrightarrow F_5SNH_2$$

It is a volatile white solid (m.p., 43°C). The vapor pressure is given by the expression $\log P_{mm} = -2096/T + 9.145$. It is soluble in ether even at −78°C. Dissociation into $NSF_3$ and HF increases rapidly with temperature and the presence of moisture. It is stable when stored at −78°C and can be handled in a dry glass vacuum system. In aqueous base, hydrolysis occurs.

$$SF_5NH_2 + 6OH^- \longrightarrow SO_3NH^- + 5F^- + 3H_2O$$

Some important reactions of $SF_5NH_2$ are summarized below.

$$\begin{array}{lllll}
 & + SF_4 & \longrightarrow & SF_5N{=}SF_2 & (\mathit{183, 184}) \\
 & + SOF_4 & \longrightarrow & SF_5N{=}SOF_2 & (\mathit{185}) \\
 & + F_2 & \longrightarrow & SF_5NF_2 & (\mathit{186}) \\
SF_5NH_2 & + COF_2 & \longrightarrow & SF_5NCO & (\mathit{146}) \\
 & + SCl_2 & \longrightarrow & SF_5N{=}SCl_2 & (\mathit{187, 188}) \\
 & + PCl_5 & \longrightarrow & SF_5N{=}PCl_3 & (\mathit{147}) \\
 & + SOCl_2 + Cl_2 & \longrightarrow & SF_5N{=}SCl_2 & (\mathit{189})
\end{array}$$

With $BF_3$ and $PF_5$, $SF_5NH_2$ forms 1 : 1 adducts (*183*). Reaction occurs at room temperature between $SF_5NH_2$ and various acid chlorides and fluorides containing electron-deficient carbonyl groups to produce *N*-pentafluorosulfanyl amides, $F_5SNHC(O)R$ (R = F, $CF_3$, $CH_3$) (*149*). The reaction of $SF_5NCO$ with certain carboxylic acids at room temperature provides an alternate route for the preparation of amides, $SF_5$-

$NHC(O)R$ (*149*). Malonic acid reacts with $SF_5NCO$ at 60°C to give both the amide acid, $SF_5NHC(O)CH_2COOH$, and the diamide, $SF_5NHC(O)CH_2C(O)NHSF_5$ (*149*). This diamide is also obtained from the reaction of $SF_5NH_2$ with carbon suboxide (*149*).

$$2SF_5NH_2 + C_3O_2 \longrightarrow SF_5NHC(O)CH_2C(O)NHSF_5$$

In water, $SF_5NHC(O)F$ gives the urea derivative, $(SF_5NH)_2CO$ (*190*). Reaction of the amide $SF_5NHC(O)R$ with $PCl_5$ gives the corresponding pentafluorosulfanylimines.

$$SF_5NHC(O)R + PCl_5 \xrightarrow[CCl_4]{60\text{–}100°C} SF_5N{=}C(Cl)R + POCl_3 + HCl$$

Similar reactions are employed for the synthesis of chlorimines from amides (*191*) and *N*-fluorosulfonylimines (*192, 193*). Acylation of $SF_5NH_2$ with oxalyl chloride produces the corresponding diamide; $SF_5NHC(O)C(O)NHSF_5$, in 78% yield, whereas acylation by fluorosuccinyl chloride yields both the diamide, $[SF_5NHC(O)CF_2]_2$, and the cyclic succinimide, $SF_5\overline{NC(O)CF_2CF_2C}O$. The identity of all these compounds is confirmed by IR, NMR, and mass spectrometry (*149*). Nucleophiles such as $H_2O$, $NH_3$, and $CH_3OH$ open the ring of the cyclic imide to give products such as $SF_5NHC(O)CF_2CF_2C(O)X$ ($X = OH, NH_2, OCH_3$) (*190*). Mono- and disubstituted products, $SF_5NHC(O)(CF_2)_{3,4}C(O)F$ and $SF_5NHC(O)(CF_2)_{3,4}C(O)NHSF_5$, are formed by the reaction of $SF_5NH_2$ with perfluoroglutaryl chloride and perfluoroadipoyl fluoride, respectively (*190*). The amide acid fluorides are hydrolyzed by atmospheric moisture to the amide acid, $SF_5NHC(O)(CF_2)_{3,4}C(O)OH$. The amide, $SF_5NHC(O)NHSF_5$ (*146*), reacts with $PCl_5$ to produce the carbodiimide, $SF_5N{=}C{=}NSF_5$ (*149*). The latter is also obtained by the reaction of $SF_5NH_2$ with $SF_5N{=}CCl_2$ (*147*).

### X. Pentafluorosulfanyl *N*,*N*-Dichloroamine, $SF_5NCl_2$

Chlorine monofluoride reacts with $NSF_3$ at −78°C to give $SF_5NCl_2$ in 25–32% yield (*194, 195*). It is also prepared by the reaction of $Cl_2$ with $NSF_3$ in the presence of $HgF_2$ (*196*).

$$NSF_3 + ClF \xrightarrow{-78°C} F_5SNCl_2$$

$$NSF_3 + 2Cl_2 \xrightarrow{HgF_2} F_5SNCl_2$$

Pentafluorosulfanyl *N,N*-dichloroamine is a light yellow volatile liquid [b.p., 64°C (extrapolated; m.p., −120°C]. It is sensitive to mechanical shock and is thermally unstable at 80°C, giving $SF_5Cl$, $N_2$, and $Cl_2$. It is hydrolyzed slowly to give $SF_5N(H)Cl$ and finally $SF_5NH_2$. It reacts slowly with mercury, producing $NSF_3$. It reacts with $PCl_3$ and $Se_2Cl_2$ or Se at low temperature to give $SF_5N{=}PCl_3$ and $SF_5N{=}SeCl_2$, respectively, in >80% yield (*197*). On warming to room temperature, $SF_5N{=}PCl_3$ decomposes, giving $PF_5$, $Cl_2$, and $(NSCl)_n$. By comparison, $SF_5N{=}SeCl_2$ decomposes to give $NSF_3$, $SeF_4$, and $SeCl_4$. The dichloroamine reacts with $SCl_2$ or $S_2Cl_2$ to give $SF_5N{=}SCl_2$, which is also unstable. With $SF_5N{=}SCl_2$, $SF_5NCl_2$ reacts to give $SF_5N{=}S{=}NSF_5$ (*198*).

$$F_5SNCl_2 + Cl_2S{=}NSF_5 \longrightarrow 2Cl_2 + SF_5N{=}S{=}N{-}SF_5$$

With HCl, $SF_5NCl_2$ forms an adduct, $SF_5NH_2{\cdot}HCl$, which decomposes giving $NSF_3$, HF, and HCl. Analogous reactions of anhydrous HCl with $R_fNCl_2$ are well known (*199–201*).

## XI. Pentafluorosulfanyl *N,N*-Difluoramine, $SF_5NF_2$

In 1963 three groups reported the synthesis of $SF_5NF_2$ (*29, 202, 203*). The best preparative method is the UV irradiation of $SF_4$ or $SF_5Cl$ with $N_2F_4$. It is a colorless gas (b.p., −17.5°C) and can be stored in steel cylinders at room temperature. It slowly decomposes on heating to $SF_4$ and $NF_3$. The IR, NMR, and mass spectral data (*29, 202*) and the gas-phase structure are reported (*204*).

## XII. Pentafluorosulfanyl Perfluoroalkylamines, $SF_5N(H)R_f$

A 75% yield of $SF_5N(H)CF_3$ is obtained by the reaction of AHF with perfluoroazomethine, $SF_5N{=}CF_2$ (*8*). Reaction of $SF_5N{=}CCl_2$ and HF also gives the same product.

$$SF_5N{=}CF_2 + HF \longrightarrow SF_5N(H)CF_3$$

This amine is a thermally stable liquid (b.p., 28.5–31°C). Although it does not attack glass, it is completely hydrolyzed by aqueous alkali. Its IR, NMR, and mass spectral data are reported (*8*).

The higher homologue, $SF_5N(H)C_2F_5$, is obtained as one of the products during the reaction of HF with $SF_5N{=}C(Cl)CF_3$ (*8*). It is a stable liquid (b.p., 45.5–47°C). The reaction of HF with $SF_5N{=}C(Cl)C_3F_7$ does not give $SF_5N(H)C_4F_9$, but rather $SF_5N{=}CFC_3F_7$ (62% yield), which apparently results from the rapid loss of HF by $SF_5N(H)C_4F_9$.

## XIII. $SF_5N(CF_3)_2$

Dobbie (*208*) reported the preparation of $SF_5N(CF_3)_2$ (~10% yield) by prolonged irradiation of a mixture of $SF_5Cl/SF_4$ and $(CF_3)_2NCl$. It is a stable compound (b.p., 33°C) and is unaffected by acid or alkali at room temperature. The compound $SF_5N(CF_3)C_2F_5$ is also reported (*209*).

## XIV. $SF_5N(X)CF_3$ (X = F, Cl, Br, I)

The fluorination of sulfur difluoride imides gives $SF_5N(F)R_f$.

$$R_fN{=}SF_2 + 2F_2 \longrightarrow R_fN(F)SF_5$$

$$R_f = CF_3, C_2F_5, SO_2F$$

When $R_f = CF_3$ or $C_2F_5$, CsF is used as a catalyst (*205*), but when $R_f = SO_2F$, the presence of CsF is not necessary (*206*). Roberts (*207*) suggests $CF_3N(F)SF_5$ as the probable structure for the product of fluorination of methyl thiocyanate with elemental fluorine, although the actual workers (*174*) proposed the alternate structure, $SF_5CF_2NF_2$.

The reaction between $SF_5N{=}CCl_2$ and $HgF_2$ gives the mercurial, $Hg[N(CF_3)SF_5]_2$, in almost quantitative yield (*8, 210*).

$$2SF_5N{=}CCl_2 \xrightarrow[150^\circ C]{HgF_2} \underset{(99\%)}{Hg[N(CF_3)SF_5]_2}$$

Reactions of the mercurial with halogens or interhalogens lead to the formation of a series of pentafluorosulfanyl *N*-halo(trifluoromethyl) amines, $SF_5N(X)CF_3$ (X = F, Br, Cl, I) (*210*).

$$\mathrm{Hg[N(CF_3)SF_5]_2}\left\{\begin{array}{l}\xrightarrow[-\mathrm{HgF_2}]{2\mathrm{F_2}} \mathrm{2SF_5N(F)CF_3}\ \ (54\%)\\[1ex] \xrightarrow[-\mathrm{HgCl_2}]{2\mathrm{Cl_2}} \mathrm{2SF_5N(Cl)CF_3}\ \ (98\%)\\[1ex] \xrightarrow[-\mathrm{HgBr_2}]{2\mathrm{Br_2}} \mathrm{2SF_5N(Br)CF_3}\ \ (80\%)\\[1ex] \xrightarrow{2\mathrm{ICl}} \mathrm{2SF_5N(I)CF_3}\ \ \text{(unstable)}\end{array}\right.$$

When a mixture of $SF_5NHCF_3$, $AgF_2$, and $Cl_2$ is heated, $SF_5N(Cl)CF_3$ is obtained (*8*). The *N*-fluoro derivative is also reported from the direct fluorination of both $CF_3N{=}SF_2$ (*205*) and $SF_5N{=}CF_2$ (*211*). Halogens do not react with the mercurial $Hg[N(SF_5)_2]_2$ (*212*) or $Hg[N(SO_2CF_3)_2]$ (*213*). Instead, these *N*-haloamines are formed either by alternate methods (*214, 215*) or with polar halogenides such as $BrOSO_2F$ (*213*). On the other hand, all of the *N*-halobis(trifluoromethyl)amines with the exception of *N*-fluoro derivatives are obtained from the reaction of $Hg[N(CF_3)_2]_2$ with halogens (*216*). Mews (*212*) has attributed the lack of reactivity of $Hg[N(SF_5)_2]_2$ with halogens to greater N–X bond polarity in the *N*-haloamines, which would result from the greater group electronegativity of $N(SF_5)_2$ (3.2–3.45) compared with $(CF_3)_2N$ (2.85–3.0). It is also possible that the greater steric bulk of the $SF_5$ groups lowers the reactivity of this mercurial compound relative to $Hg[N(CF_3)_2]_2$. The spectroscopic data [IR, NMR, mass] of the *N*-halo derivatives are reported (*210*).

Methyl iodide reacts with the mercurial $Hg[N(CF_3)SF_5]_2$ to give an *N*-methyl derivative in 33% yield.

$$\mathrm{Hg[N(CF_3)SF_5] + 2CH_3I \longrightarrow 2SF_5N(CH_3)CF_3 + HgI_2}$$

It is a clear liquid and is identified by spectral analysis (*210*).

The *N*-bromoamine, $SF_5N(Br)CF_3$, adds to the alkenes $C_2H_4$ and $C_3F_6$ to give $SF_5N(CF_3)CH_2CH_2Br$ (85%) and the mixture of isomers $SF_5N(CF_3)CF_2CF(Br)CF_3$ and $SF_5N(CF_3)CF(CF_3)CF_2Br$ (53%), respectively. These formulations are supported by spectral analysis (*210*). Similarly, the *N*-chloroamine, $SF_5N(Cl)CF_3$, also reacts with $C_2H_4$ and $C_2F_4$, giving $SF_5N(CF_3)CH_2CH_2Cl$ (88% yield; b.p., 100°C) and $SF_5N(CF_3)CF_2CF_2Cl$ (52%). Both are colorless liquids and are characterized from their spectroscopic (IR, NMR, and mass) data (*217*). The preparation and characterization of $CF_3N(SF_5)TeF_5$ are also reported (*218*).

## XV. $SF_5N(Cl)R_f$ ($R_f$ = $C_2F_5$, n-$C_3F_7$, n-$C_4F_9$)

The pentafluorosulfanyl *N*-chloroperfluoroalkylamines, $SF_5N(Cl)R_f$ ($R_f = C_2F_5$, n-$C_3F_7$, n-$C_4F_9$), are prepared (*217*) by the reaction of chlorine monofluoride with fluorimines, $SF_5N{=}C(F)R_f$. The latter are obtained by the reaction of $SF_5Cl$ with nitriles (*8, 217*).

$$SF_5N{=}C(F)R_f + ClF \longrightarrow SF_5N(Cl)CF_2R_f$$

$$R_f = C_2F_5\ (87\%);\ C_3F_7\ (89\%);\ \text{n-}C_4F_9\ (64\%)$$

The *N*-chloroamines, $SF_5N(Cl)C_2F_5$ and $SF_5N(Cl)C_4F_9$, react with $C_2H_4$ to give $SF_5N(C_2F_5)CH_2CH_2Cl$ and $SF_5N(C_4F_9)CH_2CH_2Cl$, respectively.

## XVI. Bis(pentafluorosulfanyl)perfluoroalkylamines

The tertiary amine bis(pentafluorosulfanyl)trifluoromethylamine, $(SF_5)_2NCF_3$, is formed in over 90% yield from the gas-phase UV photolysis of $SF_5N(Cl)CF_3$ (*210*).

$$2SF_5N(Cl)CF_3 \xrightarrow{h\nu} (SF_5)_2NCF_3 + 0.5CF_3N{=}NCF_3 + Cl_2$$

A small amount of hydrazine, $SF_5(CF_3)NN(CF_3)SF_5$, is also produced in the reaction (*8*). The tertiary amine, $(SF_5)_2NCF_3$, is a liquid (b.p., 72–74°C) and is characterized by IR, NMR, and mass spectroscopy (*210*).

The tertiary amines bis(pentafluorosulfanyl)perfluoroethylamine and bis(pentafluorosulfanyl)perfluoropropylamine are prepared by the following sequence of reactions (*217*).

$$SF_5Cl + R_fCN \xrightarrow{h\nu} SF_5N{=}C(Cl)R_f$$

$$SF_5N{=}C(Cl)R_f + 0.5HgF_2 \xrightarrow{150^\circ C} SF_5N{=}C(F)R_f + 0.5HgCl_2$$

$$SF_5N{=}C(F)R_f + ClF \xrightarrow[-78^\circ C]{-196^\circ C} SF_5N(Cl)CF_2R_f$$

$$2SF_5N(Cl)CF_2R_f \xrightarrow{h\nu} (SF_5)_2NCF_2R_f + Cl_2 + 0.5R_fCF_2N{=}NCF_2R_f$$

$$R_f = CF_3, C_2F_5$$

The yields of $(SF_5)_2NC_2F_5$ and $(SF_5)_2NC_3F_7$ are 58 and 8%, respectively (*217*). The overall yield decreases with the increased chain length of the perfluoroalkyl group. This decreased yield is attributed to $\beta$-elimination of a perfluoroalkyl radical from the perfluoroalkyl chain

$$2SF_5N(Cl)CF_2R_f \longrightarrow 2SF_5N{=}CF_2 + R_f\cdot + Cl\cdot$$

Analogous $\beta$-eliminations during photolysis of perfluoro-*N*-chloramines have been observed by Shreeve *et al.* (*219, 220*). Addition of ClF to unsaturated systems such as N=S (*221, 222*) and N=C (219, 223, 224) is known to produce highly fluorinated *N*-chloramines. The spectroscopic data (IR, NMR, and mass) of $(SF_5)_2NC_2F_5$ and $(SF_5)_2NC_3F_7$ are reported (*217*).

## XVII. Tris(pentafluorosulfanyl)amine, $(SF_5)_3N$

$(SF_5)_3N$ is obtained in over 90% yield by the UV photolysis of $(SF_5)_2$-NCl (*217, 225*). These $SF_5$-containing tertiary amines are likely to find commercial applications.

## XVIII. Bis(pentafluorosulfanyl)bis(trifluoromethyl)hydrazine, $SF_5(CF_3)NN(CF_3)SF_5$

The hydrazine $SF_5(CF_3)NN(CF_3)SF_5$ is obtained in 62% yield by the reaction of $AgF_2$ with $F_5SN(H)CF_3$ at 100°C (*8*).

$$2SF_5N(H)CF_3 + 2AgF_2 \longrightarrow SF_5(CF_3)NN(CF_3)SF_5 + 2AgF + 2HF$$

A similar reaction with $(CF_3)_2NH$ is described (*226*). A small amount of $SF_5(CF_3)NN(CF_3)SF_5$ is obtained during the photolysis of $SF_5N(Cl)CF_3$ (*210*). A hydrolytically stable liquid, $SF_5(CF_3)NN(CF_3)SF_5$, boils at 103–104°C. It is not attacked by aqueous alkali at 100°C. It reacts with chlorine to give the chloramine $ClN(SF_5)(CF_3)$, which adds to perfluoropropylene in a fashion similar to that of $BrN(CF_3)_2$ (*227*).

## XIX. Tetrakis(pentafluorosulfanyl)hydrazine, $(SF_5)_2NN(SF_5)_2$

The preparation of $(SF_5)_2NN(SF_5)_2$ (a white solid; m.p., 44.5–46°C) is claimed from the UV photolysis of $SF_5NCl_2$ and $SF_5Cl$ (*228*). However, it was later demonstrated that the white solid is $(SF_5)_3N$ (*225*).

## XX. Bis(pentafluorosulfanyl)amine, $(SF_5)_2NH$

When $NSF_3$ is fluorinated at low temperature with elemental fluorine, *N*-(pentafluorosulfanyl)iminosulfur tetrafluoride is formed in ~50% yield (*229*).

$$3NSF_3 + 3F_2 \xrightarrow[-20^\circ C]{-196^\circ C \text{ to}} SF_5N{=}SF_4 + SF_6 + N_2$$

It is a stable, colorless liquid (b.p., 49°C; m.p., $<-100^\circ C$). It can be heated without decomposition in metal or Kel-F vessels.

The $NSF_4$ group in $SF_5NSF_4$ functions both as a fluoride ion donor and as a fluoride ion acceptor, e.g.,

$$SF_5NSF_4 + AsF_5 \xrightarrow[-50 \text{ to } -20^\circ C]{SO_2ClF} F_5SNSF_3{}^+AsF_6{}^-$$

$$SF_5NSF_4 + CsF \xrightarrow[14 \text{ days}]{20^\circ C} Cs^+[N(SF_5)_2]^-.$$

The anion $[N(SF_5)_2]^-$ is a precursor to bis(pentafluorosulfanyl)amines.

Bis(pentafluorosulfanyl)amine is prepared in quantitative yield by the addition of hydrogen fluoride to $SF_5NSF_4$ (*214*). It is a colorless liquid that boils at 60.4°C, and it is stable in glass at room temperature. At elevated temperatures in the presence of alkali metal fluorides, it loses HF and forms $SF_5NSF_4$. It is a weak acid, which with large cations forms stable salts such as $Ph_4P^+N(SF_5)_2{}^-$ (*229*).

## XXI. $(SF_5)_2NX$ (X = F, Cl)

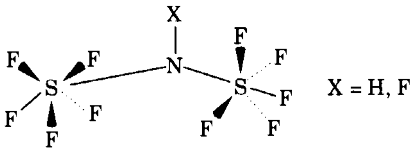
*N*-fluoro- and *N*-chlorobis(pentafluorosulfanyl)amines are obtained in 91 and 87% yields from the corresponding cesium salt (*214*).

$$CsN(SF_5)_2 + F_2 \longrightarrow FN(SF_5)_2 + CsF$$

$$CsN(SF_5)_2 + ClF \longrightarrow ClN(SF_5)_2 + CsF$$

The *N*-fluoroamine boils at 51.6°C, and $ClN(SF_5)_2$ boils at 78°C. They are both stable, colorless liquids at room temperature. The *N*-chloroamine reacts readily with substrates having negative halide ions ($Cl^-$, $Br^-$). Because the two $SF_5$ groups are magnetically nonequivalent, the $^{19}F$ NMR spectra of these amines are quite complex. The structure below, consisting of a planar $S_2NX$ framework with large SNS angles

(134.8° ± 1° and 138.3° ± 1°) is proposed for $(SF_5)_2NH$ and $FN(SF_5)_2$ based on electron diffraction studies (*214*). The SN distances increase with increasing electronegativity of the substituents (*230*).



## XXII. *N*-Pentafluorosulfanyl Haloimines, $F_5SN{=}CX_2$ (X = Cl, F)

### A. $SF_5N{=}CCl_2$

*N*-Pentafluorosulfanyl chloroimine, $SF_5N{=}CCl_2$, was first synthesized in 30% yield by Tullock *et al.* (*8*) from the photolytically induced reaction of $SF_5Cl$ with ClCN. Other derivatives are obtained by the irradiation of $SF_5Cl$ and $R_fCN$.

$$SF_5Cl + R_fCN \xrightarrow{h\nu} SF_5N{=}C(Cl)R_f$$

$$R_f = Cl,\ CF_3,\ C_2F_5$$

The reaction of $SF_5NCO$ with $PCl_5$ at 60–80°C also gives $SF_5N{=}CCl_2$ (b.p., 86–88°C) (*147*), which can be stored in glass at room temperature without decomposition and is moderately resistant to hydrolysis. Aqueous alkali degrades $SF_5N{=}CCl_2$ quickly. Both carbon–chlorine bonds in $SF_5N{=}CCl_2$ are readily cleaved when this compound is reacted with excess sodium methoxide (*231*).

$$SF_5N{=}CCl_2 + 2NaOCH_3 \longrightarrow \underset{(88\%)}{SF_5N{=}C(OCH_3)_2}$$

When $SF_5N{=}CCl_2$ and $NaOCH_3$ react in a 1 : 1 molar ratio, a mixture of $SF_5N{=}C(Cl)OCH_3$ and $SF_5N{=}C(OCH_3)_2$ is obtained. The analogous N-fluorosulfuryl derivative, $FSO_2N{=}C(Cl)OCH_3$, is obtained by the reaction of $FSO_2NHC(O)OCH_3$ with $PCl_5$ (*232*). The reaction of $SF_5N{=}CCl_2$ with $NaOC_6H_5$ carried out in a 1 : 2 molar ratio for 48 hr gives $SF_5N{=}C(Cl)OC_6H_5$ in 17% yield and $SF_5N{=}C(OC_6H_5)_2$ in 31% yield. These reactions are representative of a general method for the synthesis of imidates (*233, 234*).

On treatment with two molar equivalents of diethylamine (the second molar equivalent being used as an HCl scavenger), $SF_5N{=}CCl_2$ gives the monosubstituted derivative $SF_5N{=}C(Cl)N(C_2H_5)_2$ in 88% yield. This chloroformamidine reacts only slowly with additional diethylamine or other nucleophilic reagents (*231*).

$$\begin{array}{lll} & + 2HN(C_2H_5)_2 \xrightarrow{\text{11 days}} & SF_5N{=}C[N(C_2H_5)_2]_2 \\ & & \quad (12\%) \\ SF_5N{=}C(Cl)N(C_2H_5)_2 & + NaOCH_3 \xrightarrow{\text{3 days}} & SF_5N{=}C(OCH_3)N(C_2H_5)_2 \\ & & \quad (19\%) \\ & + C_6H_5Li \xrightarrow{\text{12 days}} & SF_5N{=}C(C_6H_5)N(C_2H_5)_2 \\ & & \quad (41\%) \end{array}$$

The compounds $SF_5N{=}C(CF_3)N(C_2H_5)_2$ and $SF_5N{=}C(CH_3)N(C_2H_5)_2$ are also synthesized by reacting excess diethylamine with the corresponding chlorimines (*231*). Many *N*-fluorosulfonyl derivatives have been reported by Roesky and coworkers (*192, 235–237*). The IR, NMR ($^1H$, $^{19}F$, $^{13}C$), and mass spectral data for the pentafluorosulfanylimine derivatives are recorded (*231*).

The compounds $SF_5N{=}C(Cl)N(C_2H_5)_2$ and $SF_5N{=}C(Cl)OCH_3$ are very stable toward hydrolysis. In contrast, the *N*-fluorosulfonyl derivatives are prone to hydrolysis (*235*).

When $SF_5N{=}CCl_2$ is reacted with $P_2S_5$, $SF_5N{=}C{=}S$ is obtained in 70% yield (*150*). With excess $HgF_2$, $SF_5N{=}CCl_2$ forms the mercurial $Hg[N(CF_3)(SF_5)]_2$ (*210*). With a 1:1 molar ratio of $HgF_2$ at 150°C, $SF_5N{=}C(Cl)R_f$ is fluorinated to $SF_5N{=}C(F)R_f$ (*218*). This mercurial is a useful precursor for the preparation of $SF_5$-containing tertiary amines.

$$2SF_5N{=}CCl_2 + 3HgF_2 \xrightarrow{150^\circ C} Hg[N(CF_3)(SF_5)]_2 + 2HgCl_2$$

At room temperature $SF_5N{=}CCl_2$ reacts with $TMSNMe_2$ to give $SF_5N{=}C(NMe_2)_2$ in good yield (*238*). With $Me_3SiNMe_2$, $SF_5N{=}CCl_2$ gives a 66% yield of $SF_5N{=}C[N(CH_3)_2]_2$ at room temperature (*239*). The metathesis reactions of $SF_5N{=}C(Cl)R_f$ with $NaN_3$ produce azido compounds that are valuable precursors to a family of asymmetric carbodiimides (*240*), viz.,

$$SF_5N{=}C(Cl)R_f + NaN_3 \longrightarrow SF_5N{=}C(N_3)R_f \xrightarrow{\Delta} SF_5N{=}C{=}NR_f.$$

$$R_f = CF_3,\ C_2F_5,\ CF_2NF_2$$

In the presence of CsF and with $CH_3CN$ as a solvent, $SF_5N{=}C(Cl)C_2F_5$ reacts with $TMSC_6F_5$ and $TMSCF_3$ at room temperature to give $SF_5N{=}C(C_6F_5)C_2F_5$ and $SF_5N{=}C(CF_3)C_2F_5$, respectively (*238*). Reaction of $SF_5N{=}C(Cl)C_2F_5$ with $CH_3I$ in the presence of AgF and $CH_3CN$ at room temperature gives $SF_5N(CH_3)C_3F_7$ along with $SF_5N{=}C(F)C_2F_5$ (*238*). No solvent or CsF is necessary for the reaction of $TMSNMe_2$ with $SF_5N{=}C(Cl)C_2F_5$ to give $SF_5N{=}C(NMe_2)C_2F_5$.

## B. $SF_5N{=}CF_2$

*N*-Pentafluorosulfanyl fluoroimine is obtained in 80% yield when $SF_5N{=}CCl_2$ is reacted with NaF in tetramethylene sulfone (*8*).

$$SF_5N{=}CCl_2 + 2NaF \longrightarrow SF_5N{=}CF_2$$

This fluoroimine (b.p., 11–13°C) dimerizes in the presence of pyridine below room temperature to $SF_5N{=}CFN(CF_3)SF_5$. The dimer is also formed when $SF_5N{=}CF_2$ is heated to 225°C in the presence of KF. In addition to the monomer and the dimer, an isomer of $SF_5N{=}CF_2$, i.e., $F_4S{=}NCF_3$, formed on heating the amine, $SF_5NHCF_3$ (obtained in 75% yield by the addition of AHF to $SF_5N{=}CF_2$), and KF to 225°C. The isomer is believed to be a slightly distorted trigonal bipyramid with the $NCF_3$ moiety at an equatorial position (*8*).

On treatment with $CF_3OOH$, $SF_5N{=}CF_2$ gives the peroxyamine, $SF_5N(H)CF_2OOCF_3$, in 79% yield (b.p., 77.3°C) (*241*). Dehydrofluorination of this amine with NaF gives the perfluorooxaziridine, $F_5S\overline{NCF_2O}$ (*241*), in 83% yield. A minor product of the reaction, $SF_5N(CF_3)C(O)F$, is obtained in ~8% yield.

$$SF_5N{=}CF_2 + CF_3OOH \longrightarrow SF_5N(H)CF_2OOCF_3$$

$$SF_5N(H)CF_2OOCF_3 + NaF \longrightarrow SF_5\overline{NCF_2O} + COF_2 + NaF{\cdot}HF$$

A glass is formed by $SF_5\overline{NCF_2O}$ (b.p., 14.9°C) at −195°C. In the case of $CF_3\overline{NCF_2O}$, nucleophiles (e.g., $F^-$) readily and exclusively attack nitrogen (*242*), whereas nucleophiles attack $SF_5\overline{NCF_2O}$ less readily and at both the carbon and nitrogen atoms (*241*).

With $CF_3CH_2OLi$, $SF_5N{=}CF_2$ gives $SF_5N{=}C(OCH_2CF_3)_2$ in 75% yield (*34*). With $CH_3I$ in the presence of CsF in $CH_3CN$ at room temperature, $SF_5N(CH_3)CF_3$ is synthesized (*238*).

## XXIII. Pentafluorosulfanyliminodihalosulfanes, $SF_5N{=}SX_2$ (X = F, Cl)

### A. $SF_5N{=}SF_2$

Pentafluorosulfanyliminodifluorosulfane, $SF_5N{=}SF_2$, was synthesized in 1965 from the fluorination of $S_4N_4$ (*243*) and also from the reaction of $SF_4$ and $NSF_3$ using a $BF_3$ catalyst (*184*). However, the best yields of $SF_5N{=}SF_2$ are obtained from the reaction of $SF_5NH_2$ with $SF_4$ in the presence of anhydrous hydrofluoric acid (*183*). It is a clear, colorless liquid that boils at 38°C. The chemical shifts of the fluorine resonances in the $^{19}F$ NMR spectrum in various solvents and the effect of the solvent polarity on the chemical shifts are described (*244*). It is not easily hydrolyzed by water at room temperature; however, alkaline hydrolysis is facile (*184*).

$$SF_5N{=}SF_2 + 10OH^- \longrightarrow SO_3NH_2^- + 7F^- + SO_3^{2-} + 4H_2O$$

Reacting elemental fluorine with $SF_5N{=}SF_2$ gives $(SF_5N{=})_2SF_2$ in 16% yield (*183*). No reaction occurs between $AgF_2$ and $SF_5N{=}SF_2$. Photolytic fluorination of $SF_5N{=}SF_2$ takes place to form $SF_5N(F)SF_4N(F)SF_5$ (*245*). Reactions of $SF_5N{=}SF_2$ with sodium alkoxides and aryloxides produce both the mono- and the disubstituted derivatives, $SF_5N{=}S(F)OR$ and $SF_5N{=}S(OR)_2$ (*246*).

$$SF_5N{=}SF_2 + RONa \xrightarrow{-} SF_5N{=}S(F)OR \xrightarrow{RONa} SF_5N{=}S(OR)_2$$

$$R = CH_3,\ CH_2CH{=}CH_2,\ C_6H_5,\ p\text{-}C_6H_4NO_2,\ p\text{-}C_6H_4Br,\ p\text{-}C_6H_4CN$$

Similarly, Abe and Shreeve (*247*) react $C_2F_5N{=}SF_2$ with $NaOCH_3$, but isolate only the disubstituted derivative, $C_2F_5N{=}S(OCH_3)_2$. Silylamines react readily with $SF_5N{=}SF_2$ to give both $SF_5N{=}S(F)NR_2$ and $SF_5N{=}S(NR_2)_2$ (*188*).

### B. $SF_5N{=}SCl_2$

Pentafluorosulfanyliminodichlorosulfane, $SF_5N{=}SCl_2$, was first synthesized in 90% yield (*248*) by reacting $SF_5NH_2$ with $SCl_2$. However, all subsequent attempts to repeat this reaction result in less than a 10% yield of $SF_5N{=}SCl_2$. When $Cl_2$ is present, $SF_5NH_2$ reacts with $SCl_2$ at room temperature over 6 hr to give a 40% yield of $SF_5N{=}SCl_2$ (*189*). This compound is extremely hygroscopic. The reaction between $SF_5N{=}SF_2$ and $PCl_5$ also gives $SF_5N{=}SCl_2$ in 75% yield (*147, 188*).

Chlorination of [(perfluoroalkyl)imino]difluorosulfanes with various chlorinating agents, e.g., $AlCl_3$ (*249*), $PCl_5$ (*250*), and $SiCl_4$ (*251*), is reported in the literature.

The reaction between $TiCl_4$ and $SF_5N{=}SF_2$ is almost instantaneous and gives better than an 89% yield of $SF_5N{=}SCl_2$. A small quantity of the mixed halide derivative, $SF_5N{=}SClF$, is also isolated (*189*). The reaction between $SnCl_4$ and $SF_5N{=}SF_2$ is slower than the reaction with $TiCl_4$, but the same product is formed. The reaction of $SnCl_4$ with $SF_5N{=}SF_2$ in the presence of trimethylsilane enhances the yield of $SF_5NSCl_2$. Antimony(V) chloride reacts very slowly at 100°C with $SF_5N{=}SF_2$ to give $SF_5N{=}SCl_2$. A small quantity of $SF_5NSFCl$ is obtained in this reaction also (*189*).

In the reaction of $SF_5N{=}SF_2$ with $PCl_5$ (*147, 188*), $AlCl_3$ (*147*), $SiCl_4$ (*147*), $SbCl_5$, $SnCl_4$, or $TiCl_4$ (*189*), there appears to be a correlation between the yield and the ability of the chlorinating agent to expand its coordination sphere as well as the relative Lewis acidity of the chlorinating agent. Titanium(IV) chloride has available inner *d*-orbitals with which it can expand its coordination sphere, as well as a relatively high Lewis acidity. In addition, the Ti–F bond strength is very high (139.7 Kcal/mol). These factors may account for the high yield of $SF_5N{=}SCl_2$ from the reaction of $SF_5N{=}SF_2$ with $TiCl_4$.

The synthesis of $SF_5N{=}S(F)NSF_2$ is reported (*252*) from the reaction of $SF_5N{=}SCl_2$ with $Hg(NSF_2)_2$. This pentafluorosulfanyliminosulfane derivative loses NSF, presumably through an intramolecular fluoride ion transfer, to give $SF_5N{=}SF_2$.

The reaction of $SF_5N{=}SCl_2$ with AgNCO produces the diisocyanate, $SF_5N{=}S(NCO)_2$, in 28% yield (*246*). This diisocyanate is also obtained from the reaction of $SF_5N{=}SCl_2$ with KOCN in liquid $SO_2$ (*246*). The diisocyanate is a yellow, nonvolatile liquid that slowly deepens in color on standing at room temperature and becomes more viscous and less volatile, suggestive of polymerization. The diisocyanate, $C_2F_5N{=}S(NCO)_2$, synthesized by Abe and Shreeve (*247*) is also reported to be unstable at 25°C and is characterized only by IR and $^{19}F$ NMR spectroscopy. The IR, NMR, and mass spectra of $SF_5N{=}S(NCO)_2$ are reported (*246*).

The low-temperature reaction of $SF_5N{=}SCl_2$ and $Ag_2O$ in nitrobenzene gives $SF_5N{=}S{=}O$ in ~15% yield (*246*). Formation of the same product by the same reactants in $MeNO_2$ also occurs (*198*). However, $SF_5N{=}S{=}O$ is reported to be converted to $SF_5N{=}S{=}NSF_5$, which is also obtained by the reaction of $SF_5N{=}SCl_2$ with $SF_5NH_2$ (*147*). The compound $SF_5N{=}S{=}O$ has previously been proposed as an intermediate in both the reaction of $SF_5N{=}SF_2$ with water, leading to $SF_5NH_2$

and $SO_2$ (*147, 183*), and the reaction of $SF_5NH_2$ with $SOCl_2$, leading to the formation of $SF_5N{=}SCl_2$ and $SF_5N{=}SClF$ (*189*). In the presence of CsF, $SF_5N{=}S{=}O$ reacts with $Cl_2$ to give $SF_5N{=}S(O)ClF$. With CsF or $PCl_5$, $SF_5N{=}S(O)ClF$ gives $SF_5N{=}S(O)F_2$ or $SF_5N{=}S(O)Cl_2$, respectively (*198*). With $(Me_2N)_3S^+Me_3SiF_2^-$, $SF_5N{=}S{=}O$ gives $TAS^+SF_5NS(O)F^-$ (*253*). The anion is identified by its $^{19}F$ NMR spectrum. Formation of other similar compounds (*253*) are represented by the general equation,

$$R_fN{=}S{=}O + TAS^+F^- \longrightarrow TAS^+R_fN{=}S(O)F^-$$

$$R_f = CF_3,\ C_2F_5,\ (CF_3)_2CF;\ TAS{=}(Me_2N)_3S.$$

The fluorosulfuryl analog, $FSO_2N{=}S{=}O$, gives $TAS^+FSO_2NS(O)F^-$ (*253*).

## XXIV. Pentafluorosulfanyl-β-sultones and Sulfonic Acids

The family of fluoroalkyl sulfonic acids are some of the strongest protonic acids known. These acids or their derivatives are known to have wide chemical applications. There are several methods available for their preparation (*254–258*). The utility of any of these methods in producing an $SF_5$-containing sulfonic acid or its derivatives has not been demonstrated.

Sulfur trioxide reacts with fluoroolefins, producing β-sultones (*256*). At least two β-sultones containing the $SF_5$ group are well characterized and will be described here, along with their utility in preparing the desired sulfonic acids or their derivatives. The reader is referred to a review by Gard (*259*) on β-fluorosultones.

### A. $F_5S\overline{CFCF_2OS}O_2$

The pentafluorosulfur β-sultone, 2-hydroxyl-1-(pentafluoro-$\lambda^6$-sulfanyl)-1,2,2-trifluoroethanesulfonic acid sultone (I), is prepared in 58% yield by reacting $SF_5CF{=}CF_2$ with distilled $SO_3$ at 100°C (*260*).

$$SF_5CF{=}CF_2 + SO_3 \longrightarrow F_5S{-}\underset{O_2S-}{CF}{-}\underset{O}{CF_2}$$

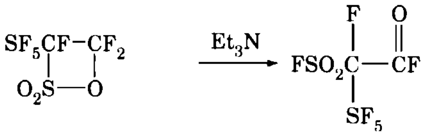
(I)

It is a colorless, stable liquid that boils at 88°C. On treatment with a base, either $Ca(OH)_2$ or NaOH, the corresponding calcium or sodium hydryl(pentafluoro-$\lambda^6$-sulfanyl)fluoromethanesulfonate is produced.

$$\mathrm{I}\begin{cases} + Ca(OH)_2 \longrightarrow Ca(SF_5CFHSO_3)_2 + CaF_2 + CaCO_3 + H_2O \\ + NaOH \longrightarrow Na(SF_5CFHSO_3) + NaF + Na_2CO_3 + H_2O \end{cases}$$

The calcium or sodium salt with 100% $H_2SO_4$ gives over a 60% yield of a $SF_5$-containing sulfonic acid, hydryl(pentafluorosulfur-$\lambda^6$-sulfanyl)-trifluoromethanesulfonic acid, $SF_5CFHSO_3H$. It is a colorless, stable liquid, boiling at 89–90°C.

Treatment of I with a catalytic amount of triethylamine causes a quantitative rearrangement to 2-(fluorosulfonyl)-2-(pentafluoro-$\lambda^6$-sulfanyl)-2-fluoroacetyl fluoride. A mechanism for the formation and rearrangement reaction is described (*260*).



On hydrolysis, I gives hydryl(pentafluoro-$\lambda^6$-sulfanyl)fluoromethanesulfonyl fluoride.

$$I + H_2O \longrightarrow F_5SCFHSO_2F + CO_2 + HF$$

Spectral data (IR, $^{19}F$ NMR, and mass) for the compounds described are recorded (*259*).

Static fluorination of $F_5SCFHSO_2F$ under mild conditions and in the presence of sodium fluoride gives $F_5SCF_2SO_2F$ (b.p., 51 ± 1°C) in 57% yield (*261*). Basic hydrolysis of $F_5SCF_2SO_2F$ gives the corresponding stable sulfonate salt, which, on distillation with concentrated sulfuric acid, gives the corresponding sulfonic acid in 39% yield (b.p., 35 ± 1°C).

$$2F_5SCF_2SO_2F + 2M(OH)_2 \longrightarrow 2M(F_5SCF_2SO_3)_2 + MF_2 + H_2O$$

$$M = Ca, Ba$$

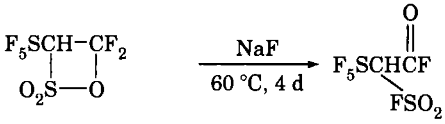
$$M(F_5SCF_2SO_3)_2 + H_2SO_4(aq) \longrightarrow 2F_5SCF_2SO_3H\cdot 2.5H_2O + MSO_4$$

$F_5SCF_2SO_2F$ with $CF_3CH_2OLi$ gives the sulfonate ester in 68% yield.

$$F_5SCF_2SO_2F + CH_3CH_2OLi \longrightarrow F_5SCF_2SO_2OCH_2CF_3 + LiF$$

## B. $F_5SCHCF_2OSO_2$

The fluorosultone $F_5SCHCF_2OSO_2$ is prepared by the reaction of $F_5SCH{=}CF_2$ with $SO_3$ under autogeneous pressure at 100°C in 58% yield (*262*). It is a white crystalline solid [m.p., 47–48°C; b.p., 108–111°C (600 mm)] that exhibits a vapor pressure of 9 Torr at 22°C. The rearranged isomer, $F_5SCH(SO_2F)COF$, is obtained as a clear liquid in 58% yield (b.p., 115–117°C) when the fluorosultone is heated to ~60°C for 4 days.



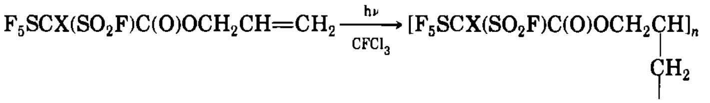
In the presence of water, $F_5S\,CHCF_2OSO_2$ undergoes rearrangement, followed by a concerted hydrolysis–decarboxylation reaction to give $F_5SCH_2SO_2F$ in 51% yield (b.p., 110–111°C). The $F_5S$-sulfonyl fluoride with aqueous sodium hydroxide gives the corresponding sodium sulfonate salt in solution, which, when treated with gaseous hydrogen chloride, produces the white solid, $SF_5$-containing sulfonic acid, $F_5SCH_2$-$SO_3H{\cdot}H_2O$, in 22% yield (m.p., 97 ± 1°C) (*262*).

Pentafluorosulfanyl esters, i.e., $F_5SCX(SO_2F)C(O)OR$ [R = $CH_3CH_2$, $(CF_3)_2CH$ (*262*), $(CH_3)_2CH$ (*263*), $CH_2{=}CHCH_2$; X = F/H) (*264*), are obtained by using the corresponding sultone with the respective alcohol in the presence of sodium fluoride.

$$F_5SCXCF_2OSO_2 + ROH + NaF \longrightarrow F_5SCX(SO_2F)C(O)OR + NaHF_2$$

Fluorinated monomers and polymers containing a fluorosulfonyl group are prepared and characterized via the reaction of the $\beta$-fluorosultones $F_5SCFCF_2OSO_2$ and $F_5SCHCF_2OSO_2$ with allyl alcohol (*264*). A polyester containing both $SF_5$ and $FSO_2$ groups is obtained by UV photolysis of the monomer.

$$F_5SCXCF_2OSO_2 + CH_2{=}CHCH_2OH \xrightarrow{NaF} F_5SCX(SO_2F)C(O)OCH_2CH{=}CH_2$$
$$(X = F, H)$$



$$F_5SCX(SO_2F)C(O)OCH_2CH{=}CH_2 \xrightarrow[CFCl_3]{h\nu} [F_5SCX(SO_2F)C(O)OCH_2\underset{\underset{|}{CH_2}}{\underset{|}{C}}H]_n$$

The monomer is obtained in 70% yield and is a stable water-like liquid (b.p., 103 ± 1°C).

The diester $[F_5SCF(SO_2F)C(O)OCH_2CF_2]_2CF_2$ is prepared [79% yield; b.p., 152°C (15 mm)] from the reaction between $HOCH_2(CF_2)_3$-$CH_2OH$ and the sultone $F_5S\overline{CFCF_2OS}O_2$ (*265*). Mechanistically, the sodium fluoride, the alcohol, or both serve as a catalyst for the rearrangement of the sultone (*265, 266*). The esters formed in this fashion are stable in the presence of $F^-$ ion at ambient or higher temperatures. The spectral data (IR; $^1H$, $^{19}F$, and $^{13}C$ NMR; and mass) for these esters and the crystal structure of the sultone $F_5S\overline{CHCF_2OS}O_2$ are given (*267*).

Heating of the ester $F_5SCH(SO_2F)C(O)OCH(CH_3)_2$ with $P_4O_{10}$ results in the formation of a ketene (*263*).

$$F_5SCH(SO_2F)C(O)OCH(CH_3)_2 \xrightarrow[P_4O_{10}]{\Delta} F_5SC(SO_2F){=}C{=}O$$

The same ketene is also prepared by NaF-catalyzed rearrangement of the sultone, $F_5S\overline{CHCF_2OS}O_2$, followed by treatment with $BF_3{\cdot}NEt_3$ (*259*).

$$F_5S\overline{CHCF_2OS}O_2 + F_3B{\cdot}NEt_3 \longrightarrow F_4S{=}\overline{CCF_2OS}O_2 + F_5SC(SO_2F){=}C{=}O + HNET_3{\cdot}BF_4$$

Several additional β-fluorosultone derivatives are obtained from $F_4S{=}\overline{CCF_2OS}O_2$ (*268*).

$$\begin{array}{lll} & + \text{ClF}\ (CF_3OCl) \longrightarrow & F_5S\overline{CClCF_2OS}O_2 + (COF_2) \\ F_4S{=}\overline{CCF_2OS}O_2 & + \text{HF} \longrightarrow & F_5S\overline{CHCF_2OS}O_2 \\ & + \text{HCl} \longrightarrow & SF_4Cl\overline{CHCF_2OS}O_2 \end{array}$$

With CsF or $CsOCF_3$, the stable cesium salt $Cs^+[SF_5C(SO_2F)COF]^-$ is formed (*259*). The reactions of the ketene, $F_5SC(SO_2F){=}C{=}O$, with electrophilic ($SO_3$) and nucleophilic (MF, $NaN_3$, $[(CH_3)_2N]_2C{=}O$) reagents are also described (*63*).

$$F_5SC(SO_2F){=}C{=}O + SO_3 \longrightarrow F_4S{=}C(SO_2F)_2 + CO_2$$

$$SF_5C(SO_2F){=}C{=}O + CsF \longrightarrow Cs^+[F_5SC(SO_2F)C(O)F]^-$$

The formation of the following compounds via halogenation of the cesium salt is also reported (*63*): $F_5SC(SO_2F)XC(O)F$ (X = Br, Cl), $F_5SC(SO_2F)ClC(O)Cl$, and $F_5SCBr_2SO_2F$. Reaction of $F_5SC(SO_2F)XC(O)F$ (X = Br, Cl) with water gives $F_5SCHXSO_2F$. With ethylene, $F_5SC(SO_2F)BrC(O)F$ yields $F_5SCH(SO_2F)CH_2CH_2Br$ (*63*).

The $SF_5$-containing ketene, $F_5SCH{=}C{=}O$, is obtained in 70% yield from the dehydration of pentafluoro-$\lambda^6$-sulfanylacetic acid (*269*).

$$F_5SCH_2COOH \xrightarrow{P_4O_{10}} F_5SCH{=}C{=}O$$

The ketene is a colorless liquid that boils at 47°C. A molecular ion peak is observed in the mass spectrum. The IR and NMR ($^{19}F$ and $^1H$) spectra for this compound are reported (*18*). The ketene dimerizes on heating and isomerizes at reduced pressure in the presence of glass.

$$F_5SCH{=}C{=}O \xrightarrow[270\text{–}290^\circ C]{\text{glass}} F_4S{=}CHC(O)F$$

The $F_5S$-containing ketene undergoes typical addition/elimination reactions with HCl, $H_2O$, EtOH, $Br_2$, etc. (*269*).

Treatment of $SF_5CXHCY_2Br$ (X,Y = H,F) with sodium sulfite affords the salt $SF_5CHXCY_2SO_3Na$, which when reacted with aqueous hydrochloric acid gives the acid/acid hydrate (*270*). Two acid hydrates, $SF_5CHFCF_2SO_3H \cdot H_2O$ and $SF_5CH_2CF_2SO_3H \cdot H_2O$, as well as anhydrous $SF_5CH_2CH_2SO_3H$, are prepared by this method.

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