SULFUR–NITROGEN–FLUORINE COMPOUNDS

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I. Introduction

Since the preparation of the first pure sulfur–nitrogen–fluorine compounds, NSF, NSF_3, and $S_4N_4F_4$, in 1955 (*105–107*) this field has developed very rapidly. The chemistry of these compounds has been the subject of several reviews (*67–69*, *72*, *76*) and has also been covered more or less fully in reviews on sulfur–fluorine (*23*, *134*, *196*, *236*, *252*, *276*) and sulfur–nitrogen chemistry (*12–15*, *115*, *207*). The spate of recent publications has, however, rendered these earlier summaries incomplete. The present article covers developments up to the middle of 1970, with the main emphasis on recent work. Compounds with other halogens are considered only insofar as they are of interest in this context. The earlier division into acyclic and cyclic compounds has been retained, as has been the classification in terms of the various oxidation numbers of sulfur. An attempt has been made, starting from NSF and NSF_3, to point out the general relationships in the chemistry of sulfur–nitrogen–fluorine compounds.

II. Acyclic Compounds

A. Sulfur(+2)–Nitrogen–Fluorine Compounds

Amino derivatives of sulfur difluoride (*142*, *245*) are as yet unknown, but compounds of the type $R_2N{-}S{-}X$ with X = Cl can be prepared (see Fig. 1). The only known sulfur(+2)–nitrogen–fluorine compound is trifluoromethyl thiodifluoramine, $CF_3{-}S{-}NF_2$ (*256*). It is quite unstable,

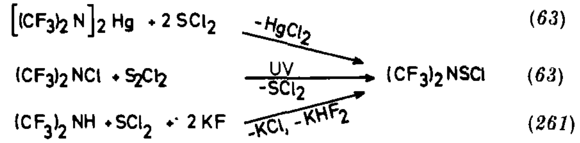


FIG. 1. Preparation of $(CF_3)_2NSCl$.

$$CF_3SSCF_3 + N_2F_4 \xrightarrow[\text{electric discharge}]{\text{UV}} 2CF_3SNF_2 \tag{1}$$

decomposing rapidly at room temperature. When the above reaction is carried out thermally, trifluoromethyl sulfur difluoride imide, CF_3NSF_2, results (*256*):

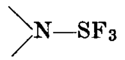
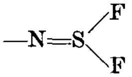
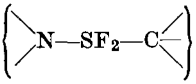
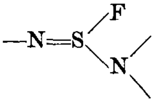
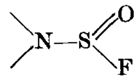
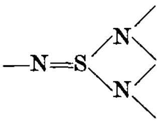
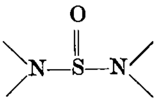
$$CF_3S{-}S{-}CF_3 + N_2F_4 \xrightarrow{225^\circ} 2CF_3{-}N{=}SF_2 \tag{2}$$

B. SULFUR(+4)–NITROGEN–FLUORINE COMPOUNDS

In keeping with the higher coordination number of sulfur, the preparative possibilities in this case are much greater than for S(+2). Table I shows the types of compounds so far obtained, and also some types of fluorine-free derivatives which stem from N–S–F compounds. The chemistry of these compounds is shown in Fig. 2. Starting from NSF, almost all the above types may be synthesized. Whereas in the case of sulfur(+6) additions to the N≡S triple bond of NSF_3 yield pentafluorosulfanylamines, R_2NSF_5, with a single sulfur–nitrogen bond, as the stable end products (*30*, *34*, *35*), these additions with thiazyl fluoride

TABLE I

TYPES OF COMPOUNDS WITH SULFUR IN THE +4 OXIDATION STATE

—	—		—	—
—			—	—
—N≡S—F				F—N=S=O
	—N=S=N—			
				R—N=S=O

lead to sulfur difluoride imides, R–N=SF_2, with a sulfur–nitrogen double bond (*238*). So far it has not proved possible to bring about extensive

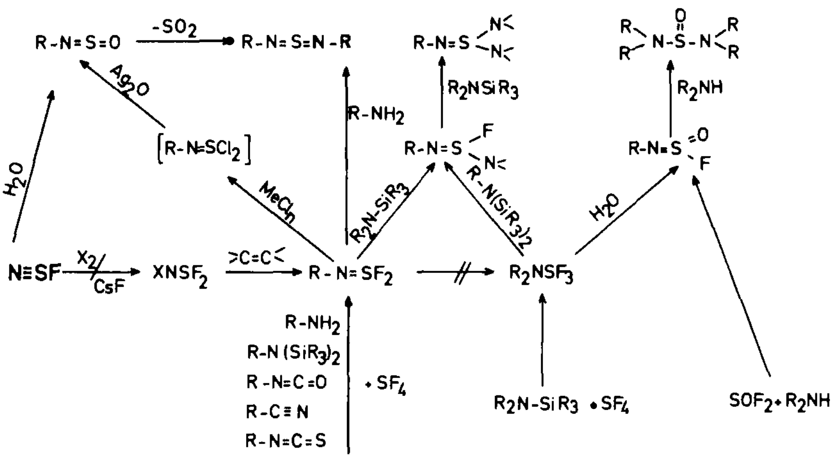


FIG. 2. Chemistry of S-N-F compounds.

addition to the aminosulfur trifluorides, R_2NSF_3; the corresponding reactions lead to cleavage of the N–S bond or to addition with simultaneous oxidation of the sulfur.

1. Thiazyl Fluoride, N≡S–F

Several methods for preparing NSF are given in the literature.

(*a*) Fluorination of substances which contain S–N bonds. The starting material is S_4N_4; AgF_2 (*97*, *99*), CoF_3 (*97*), and HgF_2 (*93*) may be used as fluorinating agents. Fluorination with SeF_4, F_2 (*37*), and SF_4

$$S_4N_4 + 4HgF_2 \xrightarrow[\text{reflux}]{CCl_4} 4NSF + 2Hg_2F_2 \qquad (3)$$

(*37*, *70*) has also been described; IF_5 and SbF_5 first yield the adducts $(NSF)_4 \cdot S_4N_4$ or $S_4N_4(SbF_5)_4$ which give NSF when they are decomposed thermally (*37*).

(*b*) Reaction of SF_4 with ammonia (*37*, *39*, *70*, *114*)

$$SF_4 + 4NH_3 \xrightarrow[\text{streaming}]{20°} NSF + 3NH_4F \qquad (4)$$

$$S + 4AgF_2 \xrightarrow[CCl_4]{+NH_3} NSF + 3HF + 4AgF \qquad (5)$$

(*c*) Reaction of NF_3 with sulfur or metal sulfides.

$$NF_3 + 3S \xrightarrow{350^\circ\text{–}400^\circ} NSF + SSF_2 \qquad (\mathit{75}) \tag{6}$$

$$MoS_2 + NF_3 \xrightarrow{280^\circ} NSF + MoF_3 \qquad (\mathit{111}) \tag{7}$$

The mechanism of the last two reactions has not been elucidated, but it may resemble the rearrangement of $CF_3S\text{–}NF_2$ to $CF_3\text{–}N{=}SF_2$. The compound $S{=}N\text{–}F$, which would be expected as an intermediate in this mechanism, has, however, not been observed so far. Formation of NSF in the flash photolysis of NF_3 with COS and CS_2 has also been reported (*168*).

These reactions yield NSF, mixed with many side products, which are often difficult to separate. Yields are small, reaching a maximum of 20%, except for reaction (6), for which 30% has been reported.

(*d*) Decomposition of compounds which already contain the N–S–F group has also been proposed for the preparation of thiazyl fluoride in addition to the methods described above.

$$S_4N_4F_4 \xrightarrow[\text{reflux}]{CCl_4} 4NSF \qquad (\mathit{97}) \tag{8}$$

$$COFNSF_2 \xrightarrow[CsF]{20^\circ} COF_2 + NSF \qquad (\mathit{33, 238}) \tag{9}$$

$$Hg(NSF_2)_2 \xrightarrow[\text{high vacuum}]{110^\circ} HgF_2 + 2NSF \qquad (\mathit{90}) \tag{10}$$

The last route is particularly suitable for the preparation of larger quantities of NSF, as the reaction is almost quantitative and yields no other volatile products.

The structure of thiazyl fluoride (Fig. 3) has been determined from IR, NMR, and microwave spectra (*146*). The results do not agree with the structure proposed earlier on the basis of electron diffraction studies (*99*, *232*). The N–S force constant f_{NS}, calculated from microwave and infrared data, has a value of 10.7 mdyne/Å (*44*, *176*, *195*), from which a bond order of 2.4 may be deduced (*251*). For NSCl, which has a similar structure, $f_{NS} = 10.0$ mdyne/Å, while the bond order $N_{NS} = 2.2$ (*180*). This dependence on the electronegativity of ligands bonded to sulfur supports the idea of $p_\pi\text{–}d_\pi$ bonding between nitrogen and sulfur.

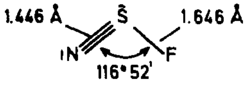


FIG. 3. Structure of thiazyl fluoride (*146*).

Other data include enthalpy of formation: ΔH_f° (NSF, gas) $= +41 \pm 2$ kcal/mole (*186*); dissociation energy: $D(\mathrm{N{\equiv}S}) = 71 \pm 5$ kcal/mole (*186*); dipole moment: 1.902 D (*44*). The NMR (*195*) and electronic spectra (*11*) have also been recorded.

Thiazyl fluoride (m.p. −89°C; b.p. 0.4°C) is a pale yellow liquid which is sensitive to moisture and cannot be stored at room temperature without decomposition. Trimerization occurs in the liquid state [Eq. (11)], while S_4N_4 and $S_3N_2F_2$ are formed in the gas phase at reduced pressure (*108*, *112*). The structure F–S–N=S=N–S–F has been suggested for the last of these compounds. Since, however, X-ray investigations have shown the chlorine analog $S_3N_2Cl_2$ (e.g., *143*) to have a ring structure (*277*), confirmation of the structure of $S_3N_2F_2$ would be of interest.

$$3\mathrm{NSF} \xrightarrow{20^\circ} \mathrm{N_3S_3F_3} \qquad (93) \qquad (11)$$

Because of its instability, NSF is somewhat difficult to handle, and accordingly only a few of its reactions are known. Its hydrolysis has been studied in detail (*222*) and yields thionyl imide, HNSO, in the first stage (*97*). This is cleaved hydrolytically to hydroxyl-amine and sulfoxylic acid, the latter then decomposing via $S_2O_3^{2-}$ to HSO_3^- and S. The HSO_3^- ion reacts with residual sulfoxylic acid to form tri- and hexathionate, both of which may be isolated as their tetraphenylphosphonium salts. Other known reactions of NSF are shown in Fig. 4. The first reaction in Fig. 4 serves for making thiazyl trifluoride on a preparative scale. The last two reactions illustrate the transformation of thiazyl fluoride into the sulfur difluoride imides, which are discussed in the next section.

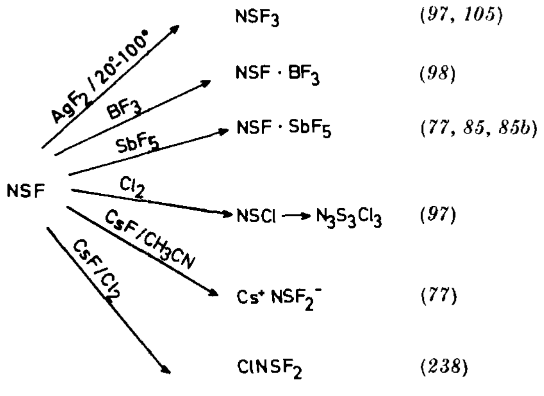


FIG. 4. Reactions of NSF.

2. *Sulfur Difluoride Imides* $RN{=}SF_2$

a. Halosulfur Difluoride Imides. The simplest sulfur difluoride imides are the N-halogen compounds, $XNSF_2$, where X may be F, Cl, Br, or I. They are best prepared by the reaction of $Hg(NSF_2)_2$ with halogens, while $ClNSF_2$ (*238*) is also formed from NSF, CsF, and chlorine. The mercurial is the first metallosulfur difluoride imide to be established and may be obtained from $OCFNSF_2$ and HgF_2 (*90*).

$$HgF_2 + 2OCFNSF_2 \longrightarrow Hg(NSF_2)_2 + 2COF_2 \qquad (12)$$

As we mentioned above, $Hg(NSF_2)_2$ may be decomposed in vacuum to NSF and HgF_2. The halides may be prepared under the conditions shown in Fig. 5. The chloro compound, $ClNSF_2$ is the most stable and does not decompose below 100°. The iodine analog $INSF_2$ is much less stable, and its existence has been established only on the basis of the IR spectrum. $FNSF_2$ is the isomer of NSF_3, which will be described later. Its yield in the reaction shown in Fig. 5 is small in contrast to $ClNSF_2$ and $BrNSF_2$, for which the reactions are almost quantitative.

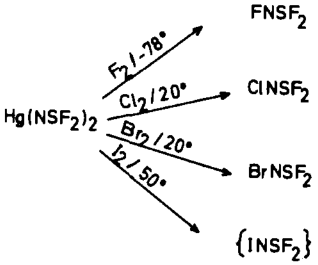


FIG. 5. *N*-Halogenosulfur difluoride imides (*90*, *91*).

As was reported recently, $ClNSF_2$ and $BrNSF_2$ are formed from *N*-halogenohexamethyldisilazanes and SF_4 according to Eq. (13) (*248*).

$$X{-}N[Si(CH_3)_3]_2 + SF_4 \longrightarrow X{-}N{=}SF_2 + 2(CH_3)_3SiF \qquad (13)$$

Nothing can be said about the preparative value of this method as yields are not recorded, but the separation of *N*-halogenosulfur difluoride imides from the R_3SiF produced in the reaction is likely to be difficult, and indeed may be possible only by the use of gas chromatography. The structure of $Hg(NSF_2)_2$ has been determined by X-ray analysis (*150*); that of $ClNSF_2$ is based on electron diffraction (*130*) (Fig. 6). The short S–N distance of 1.439 Å in $Hg(NSF_2)_2$ is striking and is comparable with the corresponding distances of 1.416 Å in gaseous NSF_3 and 1.446 Å in NSF. It corresponds with a bond order of 2.4. The marked involvement of the lone electron pair of the nitrogen atom in the S–N bond will explain the unusually large value of 131° for the angle at the nitrogen atom. The Hg–N distance corresponds with a single bond ($r_{\mathrm{Hg}} = 1.30$ Å; $r_{\mathrm{N}} = 0.70$ Å).

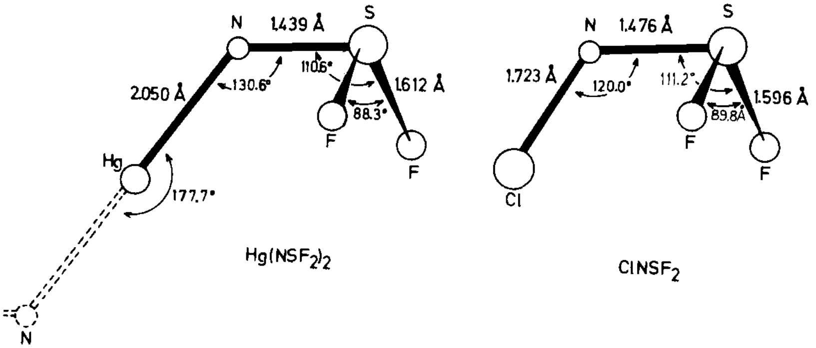
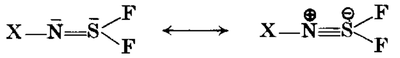


FIG. 6. Structures of $Hg(NSF_2)_2$ and $ClNSF_2$.

The structure of $ClNSF_2$ resembles that of $Hg(NSF_2)_2$. The S–N distance (1.480 Å) is somewhat greater and corresponds with a bond order of 2.0. The participation of the lone pair of electrons on nitrogen in the S–N bond must consequently be less and, as a result, the bond angle at nitrogen is smaller (120.3°). The bonding relationships may be represented by the two canonical structures shown, the bond being

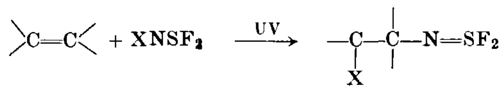


$$X{-}\bar{N}{=}\bar{S}{<}^{F}_{F} \longleftrightarrow X{-}\overset{\oplus}{N}{\equiv}\overset{\ominus}{S}{<}^{F}_{F}$$

(I) (II)

further strengthened by p_π–d_π overlap. This weights structure (II) relative to (I) (*178*).

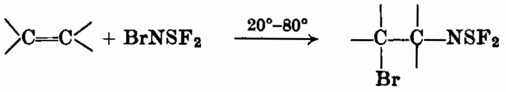
Organosulfur difluoride imides are accessible through the *N*-halogenosulfur difluoride imides. Addition to a C=C double bond takes place both by irradiation with $ClNSF_2$ or $BrNSF_2$ and also by thermal addition (in the case of $BrNSF_2$) (*172–174*).



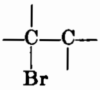
$$>C{=}C< + XNSF_2 \xrightarrow{UV} -\underset{X}{\overset{|}{\underset{|}{C}}}-\overset{|}{\underset{|}{C}}-N{=}SF_2 \qquad (14)$$

The reactions occur by a radical mechanism, the initial attack on the C=C bond being by the NSF_2 radical. The mechanism for the thermal addition has not yet been elucidated, although in this case the polarity

($\overset{\delta+}{X}$–$\overset{\delta-}{NSF_2}$) should be involved (*172, 174*) [the electronegativity of the NSF_2 group has been determined as 3.3 (*101*)].

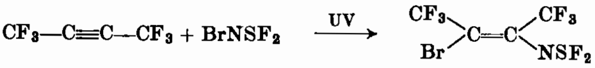


$$\mathrm{>C{=}C< + BrNSF_2 \xrightarrow{20^\circ\text{–}80^\circ} -\underset{Br}{\overset{|}{C}}-\overset{|}{\underset{|}{C}}-NSF_2} \qquad (15)$$



$\mathrm{-\underset{Br}{\overset{|}{C}}-\underset{|}{C}-}$ = $CF_2Br–CF_2$, $CF_2Br–CH_2$, $CH_2Br–CF_2$, $CFClBr–CF_2$, $CF_2Br–CHF$, $CHFBr–CF_2$

Addition to a triple bond has so far been observed in only one instance (*174a*).



$$\mathrm{CF_3{-}C{\equiv}C{-}CF_3 + BrNSF_2 \xrightarrow{UV} (CF_3)(Br)C{=}C(CF_3)(NSF_2)} \qquad (16)$$

(both isomers)

b. Further Sulfur Difluoride Imides $R–N{=}SF_2$. Almost all methods for preparing sulfur difluoride imides apart from those involving the halogen compounds depend on the reaction of sulfur tetrafluoride with nitrogen-containing compounds such as the following.

(1) Primary amines or perfluoroimines:

$$\mathrm{RNH_2 + SF_4 \xrightarrow{-2HF} R{-}N{=}SF_2} \qquad (17)$$

R = CH_3 (*41, 43*); C_6F_5 (*78*); $(CF_3)_2CF$ (*81*)

$$\mathrm{(CF_3)_2C{=}NH + SF_4 \xrightarrow[-HF]{20^\circ/CsF} (CF_3)_2CF{-}NSF_2} \quad (81) \qquad (18)$$

Substitution of all the fluorine atoms usually takes place with the strongly basic organic amines, whereas with inorganic amines the sulfur difluoride imide stage may be realized.

$$\mathrm{R{-}N{=}SF_2 + RNH_2 \xrightarrow{-2HF} R{-}N{=}S{=}N{-}R} \qquad (19)$$

R = C_6H_5 (*50*); CH_3 (*41, 43*); C_6F_5–, *p* Cl-C_6H_4– (*192*)

(2) *N*-silylated primary amines:

$$\mathrm{R{-}N(SiMe_3)_2 + SF_4 \longrightarrow R{-}N{=}SF_2 + 2Me_3SiF} \qquad (20)$$

R = CH_3, C_2H_5 (*54*)

This reaction takes place less vigorously than that with the unsubstituted amines, so that the desired $R–NSF_2$ compounds are, in the main, obtained in good yields.

(3) Cyanates:

$$\mathrm{R{-}N{=}C{=}O + SF_4 \xrightarrow{100^\circ\text{–}150^\circ} RN{=}SF_2 + COF_2} \qquad (21)$$

R = C_6H_5 (*253, 254*)

(4) Cyanides:

$$R{-}C{\equiv}N + SF_4 \xrightarrow{160^\circ\text{–}350^\circ} R{-}CF_2{-}N{=}SF_2 \qquad (22)$$

$R = C_6H_5{-}, CF_3{-}$ (*253, 254*),
$CH_2F{-}, (CH_3)_3C{-}, N{\equiv}C{-}$ (*253*),
$C_2F_5{-}$ (*58*)

The last two reactions can only be used if the expected products are thermally stable.

The compound CF_3NSF_2 is produced in the reaction of a large number of nitrogen-containing organic compounds with SF_4 (*71, 126, 166, 254*). It was first made by fluorinating methyl isocyanate (*6*), although the structure was not correctly assigned. It can now be obtained on a preparative scale by a method which does not involve the use of SF_4 (*254, 260*).

$$MeSCN + 3Cl_2 + 5NaF \xrightarrow{235^\circ} CF_3N{=}SF_2 + MeCl + 5NaCl \qquad (23)$$

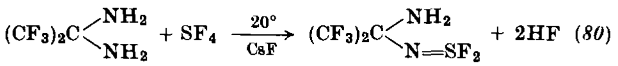
Me = alkali metal

It is not known if this reaction also takes place through SF_4 formed in the chlorination and subsequent fluorination of sulfur.

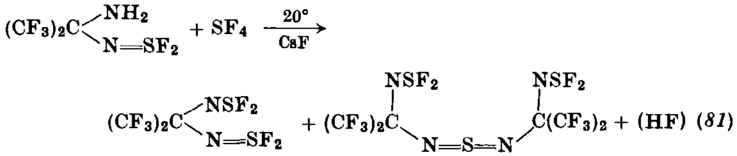
A series of interesting organosulfur difluoride imides has been synthesized with the aid of reactions (17)–(22).

$$(CN)_2 + SF_4 \xrightarrow{350^\circ} N{\equiv}C{-}CF_2{-}N{=}SF_2 \xrightarrow{+SF_4} ({-}CF_2{-}NSF_2)_2 \ (\textit{254}) \qquad (24)$$

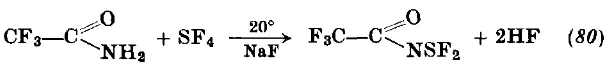
$$C_3N_3F_2NH_2 + SF_4 \xrightarrow[CsF]{110^\circ} C_3N_3F_2{-}NSF_2 \ (\textit{215}) \qquad (25)$$



$$(CF_3)_2C\Big\langle\begin{matrix}NH_2\\NH_2\end{matrix} + SF_4 \xrightarrow[CsF]{20^\circ} (CF_3)_2C\Big\langle\begin{matrix}NH_2\\N{=}SF_2\end{matrix} + 2HF \ (\textit{80}) \qquad (26)$$



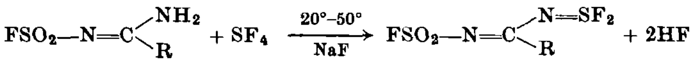
$$(CF_3)_2C\Big\langle\begin{matrix}NH_2\\N{=}SF_2\end{matrix} + SF_4 \xrightarrow[CsF]{20^\circ}$$
$$(CF_3)_2C\Big\langle\begin{matrix}NSF_2\\N{=}SF_2\end{matrix} + (CF_3)_2\overset{\displaystyle NSF_2}{\overset{|}{C}}{-}N{=}S{=}N{-}\overset{\displaystyle NSF_2}{\overset{|}{C}}(CF_3)_2 + (HF)\ (\textit{81}) \qquad (27)$$



$$CF_3{-}C\Big\langle\begin{matrix}{=}O\\NH_2\end{matrix} + SF_4 \xrightarrow[NaF]{20^\circ} F_3C{-}C\Big\langle\begin{matrix}{=}O\\NSF_2\end{matrix} + 2HF \ (\textit{80}) \qquad (28)$$

$$N{\equiv}C{-}NSF_2 + SF_4 \xrightarrow[NaF]{40^\circ} F_2S{=}N{-}CF_2{-}N{=}SF_2 \ (\textit{71}) \qquad (29)$$

$$N{\equiv}C{-}N{=}SOF_2 + SF_4 \xrightarrow{130^\circ} F_2S{=}N{-}CF_2{-}N{=}SOF_2 \ (\textit{78}) \qquad (30)$$



$$FSO_2{-}N{=}C\Big\langle\begin{matrix}NH_2\\R\end{matrix} + SF_4 \xrightarrow[NaF]{20^\circ\text{–}50^\circ} FSO_2{-}N{=}C\Big\langle\begin{matrix}N{=}SF_2\\R\end{matrix} + 2HF \qquad (31)$$

$R = CH_3, CF_3$ (*219*)

Examples are also known where the sulfur difluoride imide group is bonded to the organic residue through a nitrogen or sulfur bridge.

$$\mathrm{(CF_3)_2C{=}N{-}NH_2 + SF_4 \xrightarrow[CsF]{0^\circ\text{–}20^\circ} (CF_3)_2C{=}N{-}N{=}SF_2 + 2HF} \quad (\mathit{81}) \qquad (32)$$

$$\mathrm{CF_3SO_2NH_2 + SF_4 \xrightarrow[NaF]{20^\circ} CF_3SO_2N{=}SF_2 + 2HF} \quad (\mathit{229}) \qquad (33)$$

$$\mathrm{CF_3{-}S{-}NH_2 + SF_4 \xrightarrow[NaF]{20^\circ} CF_3{-}S{-}N{=}SF_2 + 2HF} \quad (\mathit{128, 129}) \qquad (34)$$

Purely inorganic members of the series, other than the *N*-halogeno- and metallosulfur difluoride imides, are:

$$\mathrm{OPF_2{-}NH_2 + SF_4 \xrightarrow[NaF]{40^\circ} OPF_2{-}N{=}SF_2 + 2HF} \quad (\mathit{101}) \qquad (35)$$

$$\mathrm{P_3N_3F_5NH_2 + SF_4 \xrightarrow[NaF]{90^\circ} P_3N_3F_5{-}N{=}SF_2 + 2HF} \quad (\mathit{183}) \qquad (36)$$

$$\mathrm{SF_5NH_2 + SF_4 \xrightarrow{20^\circ} SF_5NSF_2 + 2HF} \quad (\mathit{36}) \qquad (37)$$

$$\mathrm{ClSO_2NH_2 + SF_4 \xrightarrow[NaF]{50^\circ\text{–}60^\circ} ClSO_2N{=}SF_2 + 2HF} \quad (\mathit{19}) \qquad (38)$$

$$\mathrm{FSO_2NH_2 + SF_4 \xrightarrow[NaF]{20^\circ} FSO_2N{=}SF_2 + 2HF} \quad (\mathit{100}) \qquad (39)$$

SF_5NSF_2 was also observed in the fluorination of S_4N_4 with elemental fluorine (*38*).

The compound FSO_2NSF_2 is further formed in the reaction of SF_4 with $FSO_2N{=}C{=}O$ (*19, 227*), $HOSO_2NH_2$, and $SO_2(NH_2)_2$ (*19*). When the reaction with sulfamide is carried out at room temperature, *N*,*N*′-sulfonylbis(sulfur difluoride imide) may be isolated.

$$\mathrm{H_2N{-}SO_2{-}NH_2 + 2\,SF_4 \xrightarrow[NaF]{20^\circ} F_2S{=}N{-}SO_2{-}N{=}SF_2 + 4\,HF} \quad (\mathit{218}) \qquad (40)$$

If the isocyanate group in reaction (21) is bonded to silicon or phosphorus, cleavage of the Si–N or P–N bond takes place with formation of *N*-fluoroformylsulfur difluoride imide, $COFNSF_2$. Small quantities of

$$\mathrm{Si(NCO)_4 + 4\,SF_4 \xrightarrow{20^\circ\text{–}100^\circ} SiF_4 + 4\,COFNSF_2} \quad (\mathit{32}) \qquad (41)$$

$$\mathrm{POF_2(NCO) + SF_4 \xrightarrow{20^\circ} POF_3 + COFNSF_2} \quad (\mathit{19}) \qquad (42)$$

$COFNSF_2$ also result from the reaction of SF_4 with $POF(NCO)_2$, $PO(NCO)_3$ (*32*), and CH_3SO_2NCO (*32*). The reaction with urea gives a 60% yield.

$$H_2N—CO—NH_2 + 2\,SF_4 \xrightarrow[NaF]{75°} FCO—NSF_2 + 4\,HF + NSF \quad (19) \qquad (43)$$

The next higher acyl sulfur difluoride imide, CF_3CONSF_2, is formed from trifluoroacetamide and SF_4 *(80)*. *N*-Fluoroformylsulfurdifluorideimide is, as the reactions in Fig. 7 show, an important starting material in sulfur–nitrogen–fluorine chemistry. Analogous reactions can be carried out with CF_3CONSF_2 *(80)*.

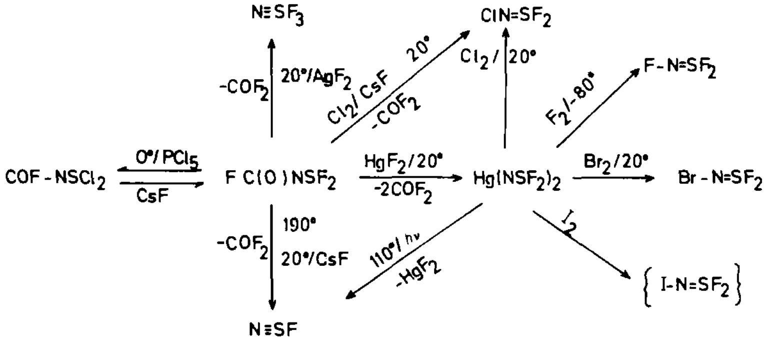


FIG. 7. Reactions of $COFNSF_2$.

c. Pseudohalogenosulfur Difluoride Imides. The only known *N*-pseudohalogenosulfur difluoride imide is *N*-cyanosulfur difluoride imide,

$$H_2N—CN + SF_4 \xrightarrow[NaF]{40°} N{\equiv}C—NSF_2 + 2\,HF \quad (71) \qquad (44)$$

$$R_3Si—N{=}C{=}N—SiR_3 + SF_4 \longrightarrow N{\equiv}C—NSF_2 + 2\,R_3SiF \quad (258) \qquad (45)$$

$NC–NSF_2$. In reaction (44) further interaction with SF_4 gives $CF_2(NSF_2)_2$.

d. Reactions of the Sulfur Difluoride Imides. The following are the main reaction possibilities: (*i*) cleavage of the R–N bond, (*ii*) addition to the N=S bond, (*iii*) change in the oxidation number of sulfur, and (*iv*) replacement of the fluorine atoms of the $-NSF_2$ by other groups.

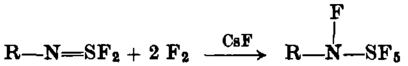
i. Reactions of this type have been described for the acyl- and *N*-halogenosulfur difluoride imides, but other reactions involving transfer of the $-NSF_2$ group are unknown. On the other hand, alkyl groups may be chlorinated and carbonyl groups converted to CF_2 groups by SF_4.

$$CH_3N{=}SF_2 + Cl_2 \xrightarrow[-HCl]{} CH_2ClNSF_2 + CHCl_2NSF_2 + CF_3NSCl_2 \quad (53) \qquad (46)$$

$$\mathrm{R{-}C(O){-}N{=}SF_2 + SF_4 \xrightarrow[90^\circ/NaF]{150^\circ} R{-}CF_2{-}NSF_2 + SOF_2} \qquad (47)$$

R = F (*73*), CF_3 (*80*)

ii. Examples in the literature show that additions to the N=S bond



$$\mathrm{R{-}N{=}SF_2 + 2\,F_2 \xrightarrow{CsF} R{-}\overset{\displaystyle F}{\overset{|}{N}}{-}SF_5} \qquad (48)$$

R = CF_3, C_2F_5 (*164*), FSO_2 (*202*)

result in simultaneous oxidation of sulfur. Photochemical fluorination with N_2F_4 leads to cleavage of the C–N bond and oxidation of sulfur (*59*).

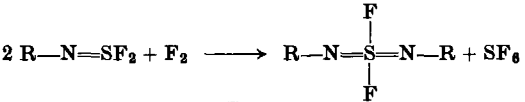
$$\mathrm{R_f{-}N{=}SF_2 + \tfrac{3}{2}N_2F_4 \xrightarrow{UV} R_f{-}F + SF_5NF_2 + \tfrac{3}{2}N_2} \qquad (49)$$

($R_f = CF_3, C_2F_5, C_3F_7$)

iii. Oxidation of sulfur with retention of the N=S double bond has so far been observed only in the irradiation of R_f–NSF_2 with OF_2 (*174c*).

$$\mathrm{R_f{-}N{=}SF_2 + OF_2 \xrightarrow{UV} R_f{-}N{=}SOF_2} + \text{cleavage products} \qquad (50)$$

The uncatalyzed reaction with fluorine results in oxidation of the sulfur and cleavage of the N=S double bond to form sulfur(VI) difluoride diimides.



$$\mathrm{2\,R{-}N{=}SF_2 + F_2 \longrightarrow R{-}N{=}\overset{\displaystyle F}{\underset{\displaystyle F}{S}}{=}N{-}R + SF_6} \qquad (51)$$

R = CF_3, C_2F_5 (*164*), SF_5 (*36*)

iv. Exchange of the fluorine atoms for other groups has been most fully studied. With $AlCl_3$, PCl_5, and $SiCl_4$ transformation to sulfur dichloride takes place.

$$\mathrm{3\,R{-}N{=}SF_2 + 2\,AlCl_3 \xrightarrow{nitromethane} 3\,R{-}N{=}SCl_2 + 2\,AlF_3} \quad (160) \qquad (52)$$

R = CF_3, C_2F_5

$$\mathrm{5\,COFNSF_2 + 2\,PCl_5 \xrightarrow{0^\circ} 5\,COFNSCl_2 + 2\,PF_5} \quad (230) \qquad (53)$$

[likewise CF_3-C(O)- (*80*); $(CF_3)_2CF$- (*132*);
CF_2Cl-CF_2 (*174*); C_6F_5 (*82*)]

$$\mathrm{2\,F_2S{=}N{-}CF_2{-}N{=}SOF_2 + SiCl_4 \longrightarrow 2\,Cl_2S{=}N{-}CF_2{-}N{=}SOF_2 + SiF_4} \quad (82) \qquad (54)$$

The reverse of the above reaction, involving the transformation of sulfur dichloride imides, which are often readily accessible in other ways (reaction of amines with $SOCl_2$ [e.g., (*199*)] or SCl_2 or of sulfinylimides with PCl_5 [e.g. (*175*, *197*)] has been successfully carried out in only a few instances. Hydrogen fluoride produces cleavage of the N=S bond according to reaction (55).

$$ClSO_2N{=}SCl_2 + 5\,HF \longrightarrow FSO_2NH_2 + SF_4 + 3\,HCl \quad (\mathit{199}) \tag{55}$$

NaF leads to NSF.

$$ClSO_2NSCl_2 + NaF \xrightarrow[100°\text{–}120°]{TMSO} ClSO_2F + NSF \quad (\mathit{199}) \tag{56}$$

Only in the reaction of R–C(O)$NSCl_2$ with Cl_2 in presence of CsF did formation of the sulfur difluoride imide occur in place of the expected

$$R{-}C(O)NSCl_2 + 2CsF \xrightarrow[20°]{Cl_2} R{-}C(O){-}NSF_2 + 2CsCl \tag{57}$$

$$R = F\ (\mathit{92});\ CF_3\ (\mathit{132})$$

formation of $ClNSCl_2$. Fluorination of $SF_5N{=}SCl_2$, prepared from pentafluorosulfanylamine and SCl_2, also gives the sulfur difluoride imide (*31*).

$$SF_5N{=}SCl_2 + 2AgF_2 \longrightarrow SF_5{-}NSF_2 + AgCl + \tfrac{1}{2}Cl_2 \tag{58}$$

Other groups may also be introduced instead of chlorine (*254*), as shown in Fig. 8.

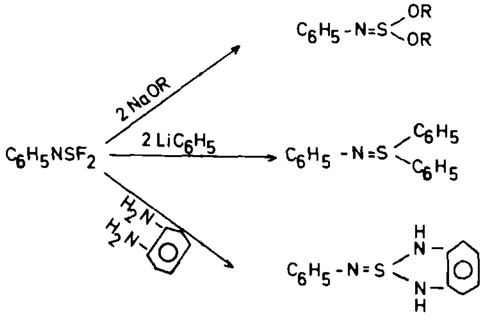


FIG. 8. Reactions of $C_6H_5NSF_2$ (*254*).

As has already been pointed out, reaction of sulfur difluoride imides with primary amines [cf. Eq. (17)] and sometimes also with *N*-silylated amines, gives sulfur diimides [for the chemistry of these compounds, see ref. (*151*)]. Sulfur diimides which are substituted by thio groups or halogens on the nitrogen atom can be prepared in this way.

$$\mathrm{CF_3{-}SNH_2 + CF_3SNSF_2 \xrightarrow{NaF} CF_3{-}S{-}N{=}S{=}N{-}S{-}CF_3}$$ (*128, 129*) (59)

$$\mathrm{XNSF_2 + X[N(SiR_3)]_2 \xrightarrow[CFCl_2CFCl_2]{0^\circ} X{-}N{=}S{=}N{-}X + 2R_3SiF}$$ (*248*) (60)

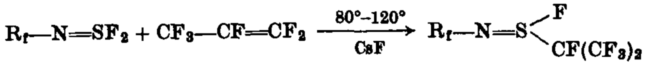
$\mathrm{X = Br, I}$ [or $\mathrm{SF_4 + 2XN(SiR_3)_2}$]

Using the reaction principle of Eq. (19), asymmetrically substituted products are also accessible (*174b*).

$$\mathrm{R{-}N{=}SF_2 + R'N(SiR_3)_2 \xrightarrow{0^\circ} R{-}N{=}S{=}N{-}R' + 2R_3SiF}$$ (61)

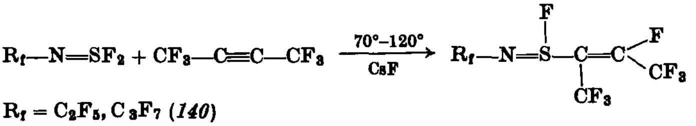
$\mathrm{R = CF_2ClCF_2;\ R' = CH_3}$

S-Perfluoroalkyl-substituted derivatives are formed by addition of $\mathrm{R_f{-}N{=}SF_2}$ to the double bond of perfluoroalkenes and the triple bond of perfluoroalkines in presence of CsF.



$$\mathrm{R_f{-}N{=}SF_2 + CF_3{-}CF{=}CF_2 \xrightarrow[CsF]{80^\circ-120^\circ} R_f{-}N{=}S(F)CF(CF_3)_2}$$ (62)

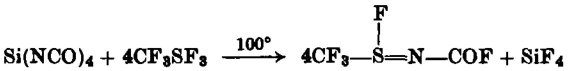
$\mathrm{R_f = CF_3, C_2F_5, C_3F_7{-}}$ (*58*)



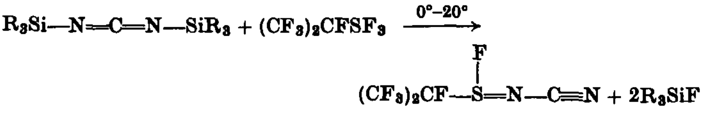
$$\mathrm{R_f{-}N{=}SF_2 + CF_3{-}C{\equiv}C{-}CF_3 \xrightarrow[CsF]{70^\circ-120^\circ} R_f{-}N{=}S(F){-}C(CF_3){=}C(F)CF_3}$$ (63)

$\mathrm{R_f = C_2F_5, C_3F_7}$ (*140*)

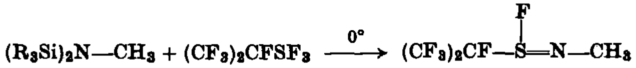
Cyclic products probably are also formed, although their structures have not as yet been fully established (*57*). A second route to *S*-perfluoroalkyl sulfur monofluoride imides is through perfluoroalkyl sulfur trifluorides, which can be transformed into the corresponding compounds as in the reaction with $\mathrm{SF_4}$.



$$\mathrm{Si(NCO)_4 + 4CF_3SF_3 \xrightarrow{100^\circ} 4CF_3{-}S(F){=}N{-}COF + SiF_4}$$ (*60*) (64)



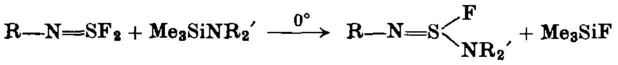
$$\mathrm{R_3Si{-}N{=}C{=}N{-}SiR_3 + (CF_3)_2CFSF_3 \xrightarrow{0^\circ-20^\circ} (CF_3)_2CF{-}S(F){=}N{-}C{\equiv}N + 2R_3SiF}$$ (*171*) (65)



$$\mathrm{(R_3Si)_2N{-}CH_3 + (CF_3)_2CFSF_3 \xrightarrow{0^\circ} (CF_3)_2CF{-}S(F){=}N{-}CH_3}$$ (*171*) (66)

e. S-Dialkylaminomonofluoroimides, $\mathrm{R{-}N{=}S{<}^{F}_{N{<}}}$. Representatives of this class of compound, in which a nitrogen–sulfur single and double bond are adjacent, may be synthesized by the two following routes.

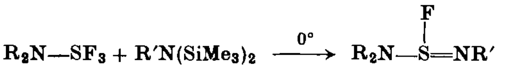
i. From sulfur difluoride imides and *N*-silylated secondary amines.



$$R{-}N{=}SF_2 + Me_3SiNR_2' \xrightarrow{0^\circ} R{-}N{=}S\begin{matrix}F\\NR_2'\end{matrix} + Me_3SiF \quad (67)$$

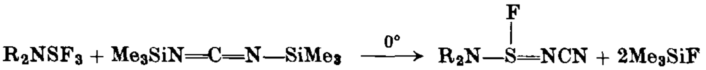
$R = CF_2Cl{-}CF_2$, $R' = CH_3$ $R = CFCl_2{-}CF_2$, $R' = C_2H_5$ (*174*)

ii. From aminosulfur trifluorides and *N*-silylated primary amines.



$$R_2N{-}SF_3 + R'N(SiMe_3)_2 \xrightarrow{0^\circ} R_2N{-}\overset{\displaystyle F}{\overset{|}{S}}{=}NR' \quad (135) \quad (68)$$

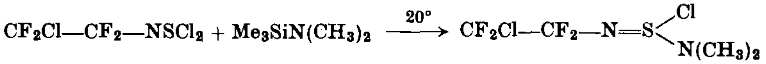
$R = CH_3, C_2H_5$; $R' = CF_3{-}CO$



$$R_2NSF_3 + Me_3SiN{=}C{=}N{-}SiMe_3 \xrightarrow{0^\circ} R_2N{-}\overset{\displaystyle F}{\overset{|}{S}}{=}NCN + 2Me_3SiF \quad (133) \quad (69)$$

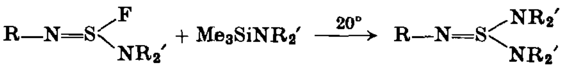
$R = CH_3, C_2H_5$

Reactions of sulfur dichloride imides and sulfur difluoride imides are analogous (*174b*).



$$CF_2Cl{-}CF_2{-}NSCl_2 + Me_3SiN(CH_3)_2 \xrightarrow{20^\circ} CF_2Cl{-}CF_2{-}N{=}S\begin{matrix}Cl\\N(CH_3)_2\end{matrix} \quad (70)$$

Whereas the fluorine derivatives are already quite unstable, the chlorine compounds may not be distilled without decomposition. With excess of Me_3SiNR_2', two fluorine atoms are replaced [cf. Fig. 8] (*174b*):



$$R{-}N{=}S\begin{matrix}F\\NR_2'\end{matrix} + Me_3SiNR_2' \xrightarrow{20^\circ} R{-}N{=}S\begin{matrix}NR_2'\\NR_2'\end{matrix} \quad (71)$$

$R = CF_2Cl$, $R' = CH_3$

3. *Aminosulfur Trifluorides*, R_2NSF_3

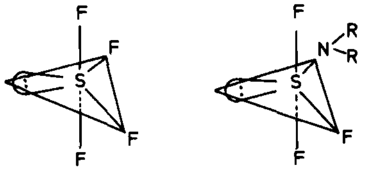
Aminosulfur trifluorides result from the cleavage of the Si–N bond in *N*-silylated primary amines by reaction with SF_4.

$$Me_3SiNR_2 + SF_4 \xrightarrow{20^\circ} R_2N{-}SF_3 + Me_3SiF \quad (72)$$

$R = CH_3$ (*54, 55*), C_2H_5 (*133*)

Direct reaction of SF_4 with the unsilylated amines gives no definite products.

NMR investigations show that the structure of aminosulfur trifluoride is derived from that of SF_4 by replacement of one fluorine atom by the dialkylamino group. The compounds are as clear as water and are very highly reactive liquids which decompose rapidly in glass vessels at room temperatures. They may be used as preparative reagents in much the same way as SF_4 [compare Eqs. (68) and (69)].



SF_4 R_2NSF_3

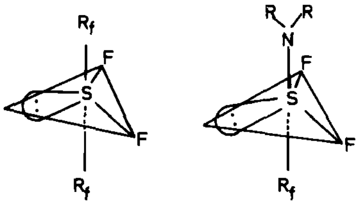
FIG. 9. Structures of SF_4 and R_2NSF_3.

So far it has not proved possible to substitute a further fluorine atom by a simple, directly bonded nitrogen-containing radical, although by a reaction analogous to that in Eq. (72), and using perfluoroalkyl sulfur trifluorides, the first disubstituted nitrogen-containing derivatives of sulfur tetrafluoride have been made (*170*).

$$R_f\text{—}SF_3 + Me_3SiNR_2 \xrightarrow{0°} R_f\text{—}SF_2\text{—}NR_2 + Me_3SiF \qquad (73)$$

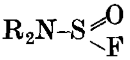
$$R_f = (CF_3)_2CF;\ R = CH_3,\ C_2H_5$$

As with compounds of the type $(R_f)_2SF_2$ (*233*), NMR investigations gave no clear indication of the structure. The magnetic equivalence of the two CF_3 or R groups supports a trans configuration for the amino and R_f groups, but this could also arise from intramolecular exchange effects (*233*) (Fig. 10).



$(R_f)_2SF_2$ $R_f\text{-}SF_2\text{-}NR_2$

FIG. 10. Proposed structures of $(R_f)_2SF_2$ and $R_f\text{–}SF_2\text{–}NR_2$.



4. *Fluorosulfinic Acid Amide* $R_2N\text{–}S\begin{smallmatrix}\nearrow O\\ \searrow F\end{smallmatrix}$

Fluorosulfinic acid amides, which are formed in the hydrolysis of aminosulfur trifluorides, also result from the reaction of SOF_2 with secondary amines (*119*) or their *N*-silyl compounds (*21a*) according to Fig. 11.

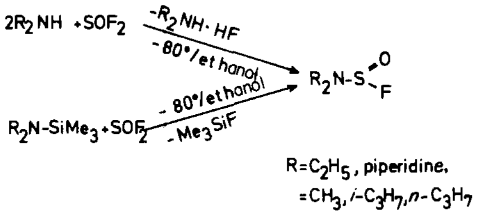


FIG. 11. Preparation of R_2NSOF (*21a, 119, 174c*).

These compounds are colorless and highly reactive liquids which decompose slowly at room temperature. With excess of amine and at higher temperatures exchange of the second fluorine atom also occurs, leading to $(R_2N)_2SO$.

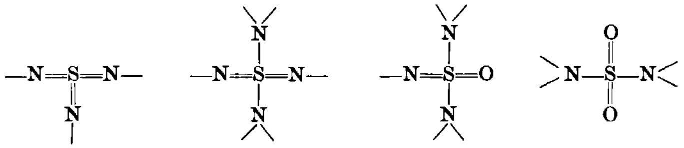
5. *N-Fluorosulfinylimine*, F–N=SO

The compound F–NSO results in low yield in the reaction of trimethylsilyl sulfinylamine, Me_3SiNSO, with fluorine. It tends to explode and has not been closely investigated.

$$Me_3SiNSO + F_2 \xrightarrow{-80°/CFCl_3} Me_3SiF + FNSO \quad (266) \qquad (74)$$

C. SULFUR(+6)–NITROGEN–FLUORINE COMPOUNDS

Table II summarizes the types of compound in which sulfur has the oxidation number +6. In addition, fluorine-free derivatives with the following groupings can be prepared.



The first nitrogen–sulfur(+6)–fluorine compound to be recognized was thiazyl trifluoride, $N{\equiv}SF_3$ (*105*); the first oxygen-sulfur(+6)–nitrogen–fluorine compound being FSO_2NR_2 (*64, 137, 243a*). The same role is played by NSF_3 for the sulfur(+6) compounds as by N=SF for those of sulfur(+4). Starting from thiazyl trifluoride it is possible to synthesize almost every type of compound shown in Table II (see Fig. 12).

TABLE II

TYPES OF COMPOUNDS WITH SULFUR IN THE +6 OXIDATION STATE

—	—	$>N{-}SF_5$	—	—	—
—	$-N{=}SF_4$	$\{>N{-}SF_4{-}R\}$	—	$>N{-}\overset{O}{\overset{\Vert}{S}}F_3$	—
$N{\equiv}SF_3$	—				—
$N{\equiv}SF_2{-}N<$	$-N{=}SF_2{=}N-$		$-N{=}\overset{F}{\underset{F}{S}}{=}O$		—
	$-N{=}\overset{>N}{\underset{F}{S}}{=}N-$		$-N{=}\overset{>N}{\underset{F}{S}}{=}O$		$>N{-}SO_2F$

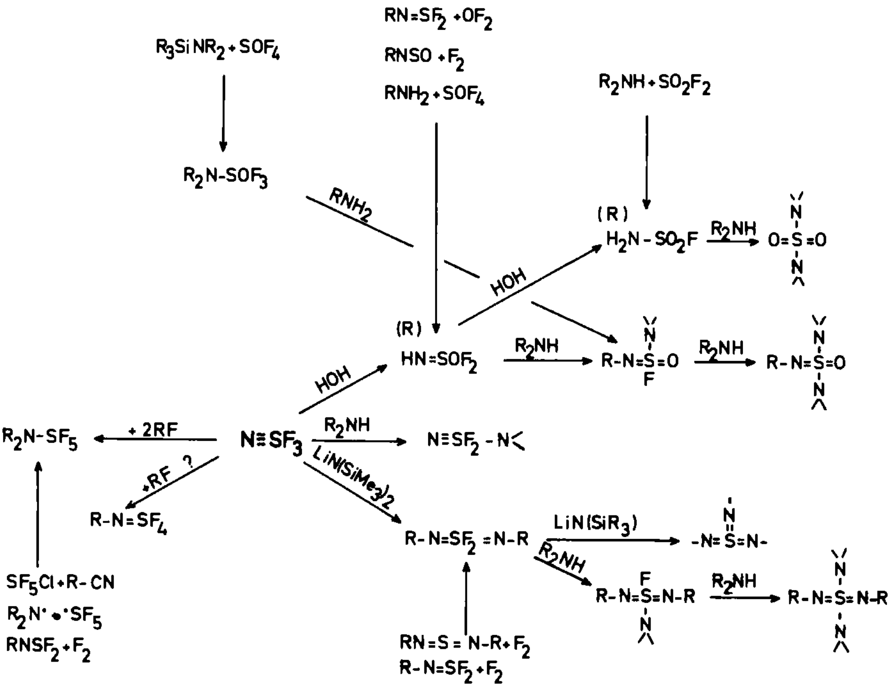


FIG. 12. Chemistry of N–S(+6)–F compounds.

1. *Thiazyl Trifluoride*, NSF_3

Two routes are available for the preparation of NSF_3: (*a*) fluorination of S–N compounds with sulfur in the +4 oxidation state (or lower), using AgF_2 (Fig. 13)

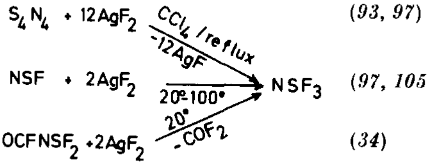


FIG. 13. Preparation of NSF_3.

and (*b*) reaction of S(+6)–F compounds with excess of ammonia:

$$S_2F_{10} + NH_3 \xrightarrow{150^\circ} N{\equiv}SF_3 + SF_4 + 3HF \quad (\mathit{40, 42}) \qquad (75)$$

The second method is not employed in preparative work because of the high toxicity of S_2F_{10} and the low yield.

The structure of NSF_3 (Fig. 14) has been determined from the IR, NMR, and microwave spectra (*145*) and, as a first approximation, can be regarded as derived from that of SF_6 ($d_{SF} = 1.56$) by replacing three fluorine atoms with one triply bonded nitrogen. The very short S≡N distance of 1.416Å corresponds with a bond order of 2.7 (*95*), with the N–S bond strengthened as a result of $p_\pi(N)$–$d_\pi(S)$ overlap (*72*). A calorimetric determination of the enthalpy of formation gave ΔH_f° (NSF_3, gas) = −85 kcal/mole. The dissociation energy $D_{N\equiv S} = 93 \pm 2$ kcal/mole [by combination with mass spectrometric appearance potentials (*186*)].

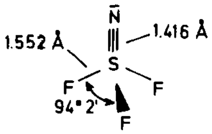


FIG. 14. Structure of NSF_3 (*145*).

Force constants (*181, 194, 195*) and thermodynamic functions (*181, 194*) have been calculated from the IR (*195*) and Raman spectra (*181*). The NMR (*195*) and electronic spectra (*181*) have been recorded, as have critical data (*93*).

Thiazyl trifluoride (m.p. −72.6° ± 0.5°, b.p. −27.1° ± 0.1°), unlike NSF, is very stable both thermally and chemically. It resists hydrolysis by dilute acids and reacts with metallic sodium only at 300°C. Decomposition in glass vessels sets in at 500° (*97*). Because of this stability the use of NSF_3 (mixed with SF_6) as a dielectric has been suggested (*62*).

The reactions of NSF_3 may be divided into:

(*a*) Adduct formation with Lewis acids, e.g., BF_3. The product dissociates in the gas phase into its components. Support for the formation of an adduct comes from the IR spectrum (−180°). The sharp

$$N{\equiv}SF_3 + BF_3 \xrightarrow{<0^\circ} F_3B{-}NSF_3 \quad (97, 98, 179) \qquad (76)$$

increase in the ν_{SN} frequency by about 200 cm^{-1} can be interpreted as due to a change in the N≡S bond order from 2.7 in NSF_3 to 2.9 in the adduct. Antimony pentafluoride also forms the adduct, $NSF_3 \cdot SbF_5$ (*85*), although its structure has not yet been investigated.

(*b*) Exchange of the fluorine atoms while retaining the S≡N bond.

$$N{\equiv}SF_3 + 2R_2NH \xrightarrow[\text{ether}]{20^\circ} N{\equiv}SF_2{-}NR_2 + R_2NH \cdot HF \qquad (77)$$

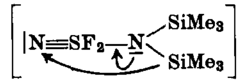
$R = C_2H_5$ (*94*), piperidine (*84*)

$$N{\equiv}SF_3 + ROH + (CH_3)_3N \xrightarrow{0^\circ\text{–}20^\circ} N{\equiv}SF_2{-}OR + (CH_3)_3N \cdot HF \qquad (78)$$

$R = C_6H_5$ (*84*)

(*c*) Exchange of the fluorine atoms and rearrangement of the products.

$$N{\equiv}SF_3 + LiN(SiMe_3)_2 \xrightarrow[-LiF]{0^\circ\text{–}20^\circ}$$



$$\left[|N{\equiv}SF_2{-}N(SiMe_3)_2 \right] \longrightarrow Me_3Si{-}N{=}SF_2{=}N{-}SiMe_3 \quad (109) \qquad (79)$$

Reaction with a further molecule of $LiN(SiMe_3)_2$ results in the splitting off of the remaining two fluorine atoms and the formation of the aza analog of sulfur trioxide (*109*).

(79a)

Tris(trimethylsilylimido)sulfur, $S(=NSiMe_3)_3$, is the first known derivative of sulfur triimide. It is also the only compound known to date in which sulfur has an oxidation number of +6 and a coordination number of 3 and which is also a monomer at room temperature.

The hydrolysis of $N{\equiv}SF_3$ is a reaction of the same type. In earlier investigations (*97*) only the end products ($H_2NSO_3^-$ and F^-) could be identified, but now isolation of the intermediates has enabled the mechanism to be elucidated (Fig. 15).

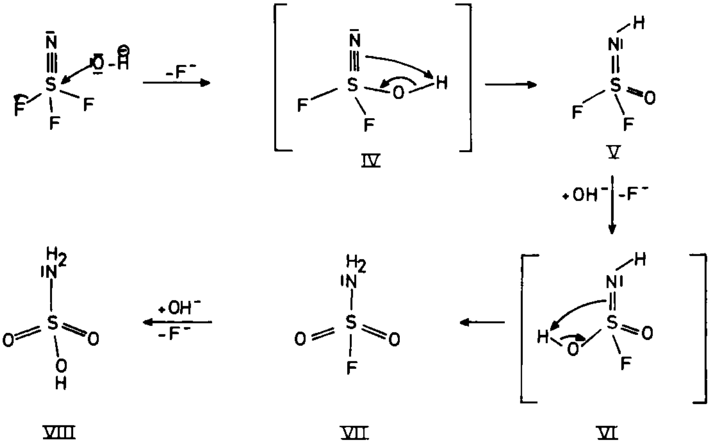


FIG. 15. Mechanism for the hydrolysis of NSF_3 (*223*).

While the intermediates IV and VI rearrange rapidly, sulfur oxide difluoride imide can be isolated in the form of its tetraphenylphosphonium salt. It was not possible to detect fluorosulfonyl amide, but *N*-substituted derivatives have been observed in the hydrolysis of other sulfur oxide difluoride imides (*210*, *213*, *228*) [cf. Eq. (108)].

(*d*) Additions to the N≡S triple bond.

$$N{\equiv}SF_3 + 2HF \xrightarrow{20^\circ} SF_5NH_2 \quad (\mathit{30}) \qquad (80)$$

$$N{\equiv}SF_3 + 2ClF \xrightarrow{-78^\circ} SF_5{-}NCl_2 \quad (\mathit{35}) \qquad (81)$$

$$N{\equiv}SF_3 + SF_4 \xrightarrow[BF_3]{180^\circ} SF_5{-}NSF_2 \quad (\mathit{34}) \qquad (82)$$

The monoaddition products were not isolated; whether the IR bands also observed in the reaction represented by Eq. (81) can be assigned to a compound $Cl{-}N{=}SF_4$ has yet to be clarified (*34*).

Boron trichloride reacts with NSF_3 by a mechanism which is not yet understood, forming the interesting ionic compound $[N(SCl)_2]^+[BCl_4]^-$

$$2N{\equiv}SF_3 + 3BCl_3 \xrightarrow{20^\circ} [N(SCl)_2]^+[BCl_4]^- + \tfrac{1}{2}N_2 + \tfrac{3}{2}Cl_2 + 2BF_3 \quad (\mathit{86}) \qquad (83)$$

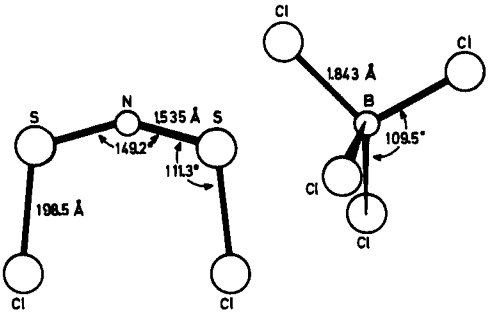


FIG. 16. Structure of $[N(SCl)_2]^+[BCl_4]^-$ (*86*).

(*86*) Fig. 16. Reaction probably takes place through adduct formation followed by F–Cl exchange on sulfur and reduction of NSF_3 to NSCl. This is supported by other methods for the synthesis of this compound.

$$S_3N_3Cl_3 + 3BCl_3 + 3SCl_2 \longrightarrow [N(SCl)_2]^+[BCl_4]^- \quad (110) \qquad (84)$$

$$S_3N_2Cl_2 + Cl_2 + BCl_3 \longrightarrow [N(SCl)_2]^+[BCl_4]^- \quad (110) \qquad (85)$$

The corresponding salts with $[AlCl_4]^-$ and $[SbCl_6]^-$ also exist (*110*).

2. Sulfur Tetrafluoride Imides, $R{-}N{=}SF_4$

The only representative of this class of compounds is $CF_3N{=}SF_4$, a secondary product in the fluorination of $SF_5{-}N{=}CCl_2$ with NaF (*263*) or in the dehydrofluorination of $SF_5{-}NHCF_3$ with KF.

$$Cl_2C{=}N{-}SF_5 + 2NaF \xrightarrow[TMSO]{60°-160°} \underset{(85\%)}{F_2C{=}N{-}SF_5} + \underset{(15\%)}{CF_3N{=}SF_4} \qquad (86)$$

NMR investigations at −80°C indicate a trigonal bipyramidal structure (*182*) analogous to that of the isostructural $O{=}SF_4$ (Fig. 17).

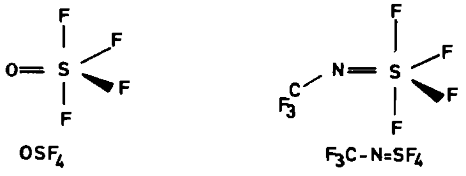


FIG. 17. Structures of OSF_4 and $CF_3{-}N{=}SF_4$.

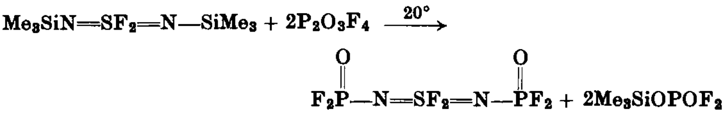
3. *Bisimidosulfur Difluorides*, R–N=SF$_2$=NR

Two methods for preparing bisimidosulfur difluorides have already been given [Eqs. (51) and(79)]. A third possibility is the fluorination of

$$FSO_2{-}N{=}S{=}N{-}SO_2F + F_2 \xrightarrow{UV} FSO_2{-}N{=}SF_2{=}N{-}SO_2F \quad (211) \qquad (87)$$

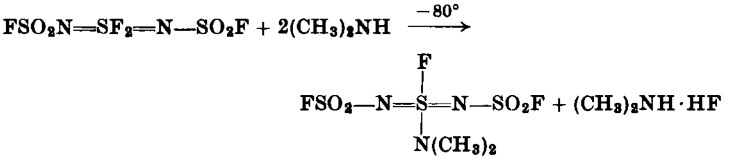
$$CF_3SO_2{-}N{=}S{=}N{-}SO_2F + F_2 \xrightarrow{UV} CF_3SO_2{-}N{=}SF_2{=}N{-}SO_2{-}CF_3 \quad (228) \qquad (88)$$

sulfur diimides. How general these methods are has not yet been tested, but R$_3$Si–N=SF$_2$=N–SiR$_3$ has proved to be a valuable starting material for the preparation of further bisimidosulfur difluorides, e.g.,



$$Me_3SiN{=}SF_2{=}N{-}SiMe_3 + 2P_2O_3F_4 \xrightarrow{20°} F_2\overset{\overset{O}{\|}}{P}{-}N{=}SF_2{=}N{-}\overset{\overset{O}{\|}}{P}F_2 + 2Me_3SiOPOF_2 \quad (268) \qquad (89)$$

Only a single fluorine atom in bis(*N*-fluorosulfonyl)imido sulfur difluoride may be replaced by reaction with amines. At higher temperatures and



$$FSO_2N{=}SF_2{=}N{-}SO_2F + 2(CH_3)_2NH \xrightarrow{-80°} FSO_2{-}N{=}\underset{\underset{N(CH_3)_2}{|}}{\overset{\overset{F}{|}}{S}}{=}N{-}SO_2F + (CH_3)_2NH{\cdot}HF \quad (212) \qquad (90)$$

with excess of amines the aza analog of the sulfuric acid esters result (Fig. 18). Exchange of only one fluorine atom of the –N=SF$_2$=N– group

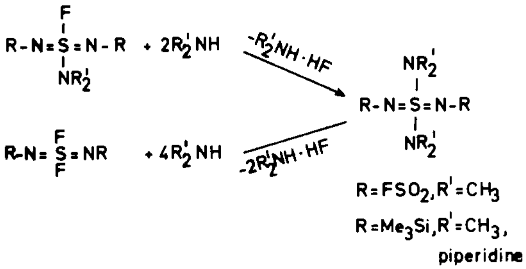
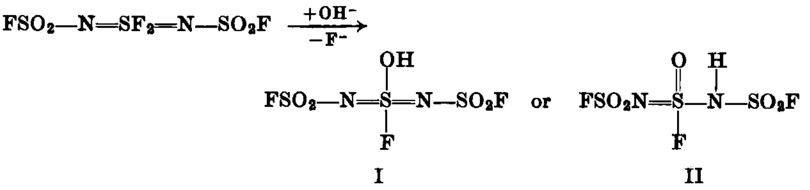


FIG. 18. Preparation of the aza analog of sulfuric acid ester.

can also be brought about by careful hydrolysis (*228*). The product is separated as the tetraphenylphosphonium salt, structure (II) being the most likely of the two possible tautomeric forms shown. There are no structural studies on bisimidosulfur difluorides, but NMR investigations on sulfur



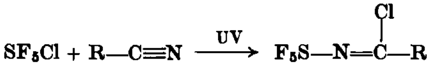
$$FSO_2{-}N{=}SF_2{=}N{-}SO_2F \xrightarrow[-F^-]{+OH^-} \underset{I}{FSO_2{-}N{=}\overset{OH}{\underset{F}{S}}{=}N{-}SO_2F} \text{ or } \underset{II}{FSO_2N{=}\overset{O}{\underset{F}{S}}{-}\overset{H}{N}{-}SO_2F} \qquad (91)$$

tetrafluoride imides in comparison with SOF_4 suggest a close relationship between the $-N{=}SF_2{=}N-$ group and SO_2F_2. The chemistry of organic derivatives of the type $-N{=}S(alk)_2{=}N-$ and $-N{=}S(alk)_2{=}O$ has been discussed recently (*255*).

4. *Pentafluorosulfanyl–Nitrogen Compounds*, $R_2N{-}SF_5$

Synthetic routes to the pentafluorosulfanyl–nitrogen compounds are shown below.

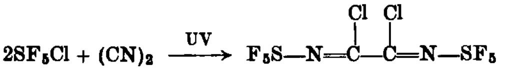
(*a*) Addition of SF_5Cl to a C≡N triple bond.



$$SF_5Cl + R{-}C{\equiv}N \xrightarrow{UV} F_5S{-}N{=}\overset{Cl}{C}{-}R \quad (262, 263) \qquad (92)$$

$R = Cl, CF_3, C_3F_7$

There is addition to both CN groups in dicyanogen.



$$2SF_5Cl + (CN)_2 \xrightarrow{UV} F_5S{-}N{=}\overset{Cl}{C}{-}\overset{Cl}{C}{=}N{-}SF_5 \quad (263) \qquad (93)$$

As can be seen from Fig. 19, the pentafluorosulfanylazomethines are suitable starting materials for the preparation of a large number of further SF_5–N derivatives (*156*, *262*, *263*).

(*b*) Addition of HF, SF_4, and ClF to the triple bond in NSF_3 (*30*, *34*, *35*) according to Eqs. (80), (81), and (82). This route has already been described. It can be used in the preparation of SF_5NH_2, from which further F_5S–N-derivatives can be made (Fig. 20) (*31*, *36*).

(*c*) Combination of SF_5 and NF_2 radicals gives pentafluorosulfanyl difluoramine, $F_5S{-}NF_2$ (Fig. 21). This also results from the reaction between sulfur and N_2F_4 (*155*, *157*), and a very good yield is obtained when $R_f{-}N{=}SF_2$ is irradiated with N_2F_4 (*59*). It has a boiling point of −17.6° and is moderately stable chemically, being resistant to attack by dilute aqueous acids and bases at room temperature. Cleavage to SF_5Cl and HNF_2 occurs with HCl at 100°C and there is a reaction with SO_2 at 150°C in which FSO_2NF_2 and SF_4 are produced (*20*).

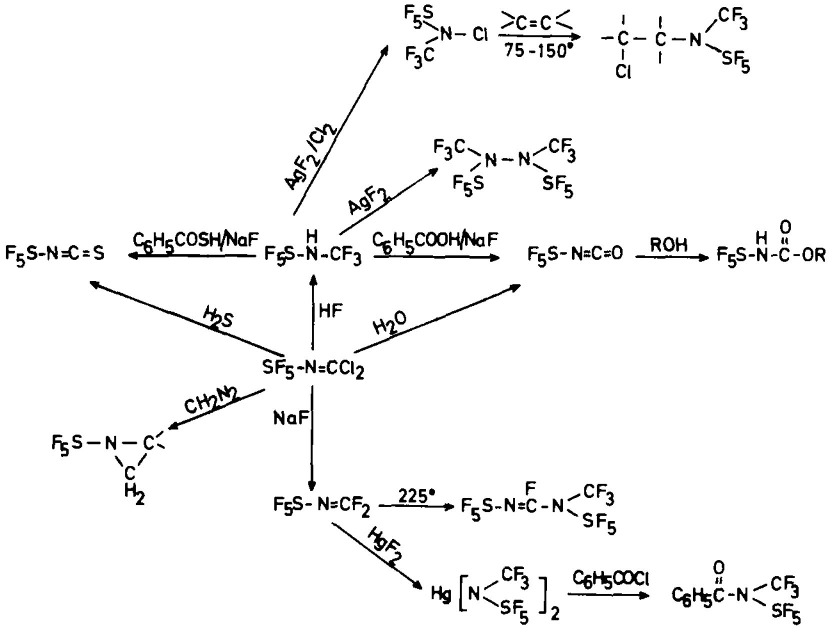


Fig. 19. Reactions of pentafluorosulfanylazomethines.

The compound $(CF_3)_2N–SF_5$ can be made in a reaction analogous to that used for SF_5NF_2 (*56*).

$$(CF_3)_2NCl + SF_5Cl(SF_4) \xrightarrow[-Cl_2]{UV} (CF_3)_2N—SF_5 \quad (56) \qquad (94)$$

(*d*) *N*-Monosubstituted derivatives of $SF_5–NF_2$ are formed in low yields in the fluorination of sulfur difluoride imides (*164, 202*) [cf. Eq. (48)].

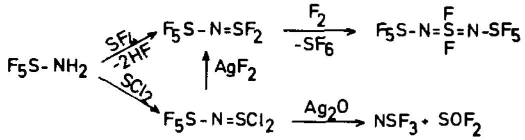


Fig. 20. Reactions of $F_5S–NH_2$.

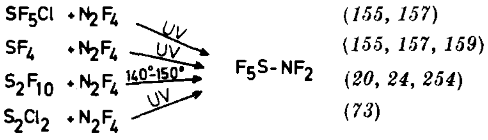


Fig. 21. Preparation of $F_5S–NF_2$.

The SF_5–N groups is reasonably stable to chemical attack and attempts to substitute fluorine in these SF_5 compounds have so far been unsuccessful. Two tetrafluorosulfanylamino compounds are, however, known ($CF_3OSF_4NF_2$ and $CF_3SF_4NF_2$), and their preparation is similar to that of SF_5NF_2.

$$CF_3SF_3 + N_2F_4 \xrightarrow{UV} CF_3SF_4{-}NF_2 \quad (157) \qquad (95)$$

$$CF_3OF + SF_4 + N_2F_4 \xrightarrow{20^\circ} CF_3O{-}SF_4{-}NF_2 \quad (61) \qquad (96)$$

NMR spectra show that the structure of the pentafluorosulfanyl amines is derived from that of SF_6 by replacing an axial fluorine atom by an amino group. In $CF_3OSF_4NF_2$ the two substituents are in the cis position as in bisoxygen-substituted sulfur(+6) tetrafluorides, whereas in CF_3–SF_4–NF_2 they occupy axial trans sites, this arrangement being analogous to that in bisperfluoroalkyl-substituted derivatives (Fig. 22).

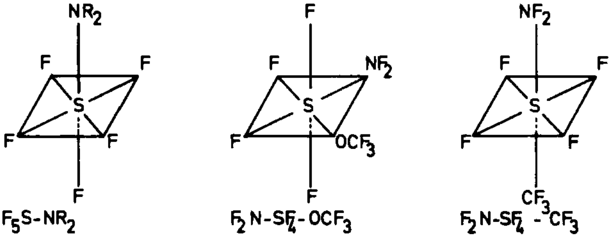


FIG. 22. Structures of pentafluorosulfanylamines and tetrafluorosulfur(+6) amino derivatives.

5. *Sulfur Oxide Difluoride Imides*, R–N=SOF_2

The free acid $HNSOF_2$ corresponding with the $[NSOF_2]^-$ ion, which is formed in the hydrolysis of NSF_3, can be prepared by reaction of NH_3 with SOF_4 in ether (*51*, *188*). Distillation gives an azeotrope from which ether is removed with BF_3. Gaseous NH_3 and SOF_4 give a mixture of NH_4F and $[NH_4]^+[NSOF_2]^-$. Attempts to separate these two products by sublimation lead to polymerization to sulfur oxide fluoride imide $(NSOF)_n$ (*246*).

$$\begin{tikzcd} NH_3 + SOF_4 \arrow[r, "20^\circ", "flow"'] & NH_4F + [NH_4]^+[NSOF_2]^- \arrow[d] \\ & (NSOF)_n + NH_4F \end{tikzcd} \qquad (97)$$

The same polymeric product is observed in the dehydrofluorination of $HNSO_2F$ with CsF or in the reaction of NH_3 with SOF_4 in nonpolar solvents (*188*). The rubbery $(NSOF)_n$ is comparable with the corresponding polymers of phosphonitrilic fluoride $(PNF_2)_n$ which is isoelectronic. The sulfur atoms, like those of phosphorus, have a tetrahedral environment. The sulfanuryl fluoride is more resistant to hydrolysis than the phosphorus compound.

Known sulfur oxide difluoride imides are almost exclusively formed by reaction of OSF_4 with nitrogen-containing compounds. These reactions take place in a manner analogous to those of SF_4, though, because of the lower reactivity of SOF_4, higher temperatures are necessary. This is often a disadvantage when the products are easily decomposed by heat, but catalysts such as NaF, CsF, or BF_3 can sometimes be used to lower the reaction temperature. Some of the synthetic routes leading to sulfur difluoride imides cannot be applied here (e.g., the reaction with cyanates) or are successful only in isolated instances (e.g., with cyanides).

Sulfur oxide difluoride imides, $RNSOF_2$, have up till now been made by the following methods.

(*a*) Reaction of primary amines with OSF_4.

$$3R{-}NH_2 + OSF_4 \xrightarrow{-40°/+100°} R{-}N{=}SOF_2 + 2RNH_2{\cdot}HF \qquad (98)$$

R = CH_3–, C_6H_5–, *p*-HO–C_6H_4–, *m*-H_2N–C_6H_4–, *m*-O_2N–C_6H_4–,
HOOC–$(CH_2)_5$–, *p*- and *m*-$F_2S(O){=}N{-}C_6H_4$– (*51, 52*) C_6F_5 (*79*),
CF_3S– (*127*)

Purely inorganic members of this family can also be made by this method

$$FSO_2NH_2 + OSF_4 \xrightarrow[NaF]{130°} FSO_2N{=}SOF_2 + 2HF \quad (101) \qquad (99)$$

$$POF_2NH_2 + OSF_4 \xrightarrow[NaF]{100°\text{–}120°} POF_2{-}N{=}SOF_2 \quad (103) \qquad (100)$$

(*b*) By cleavage of Si–N compounds.

$$(R_3Si)_3N + SOF_4 \xrightarrow{70°} R_3SiN{=}SOF_2 + 2R_3SiF \quad (104) \qquad (101)$$

$$R_3SiN{=}C{=}N{-}SiR_3 + OSF_4 \xrightarrow{60°\text{–}110°} N{\equiv}C{-}NSOF_2 + 2R_3SiF \quad (74, 165) \qquad (102)$$

$$Si(NCO)_4 + 4OSF_4 \xrightarrow[BF_3]{235°\text{–}240°} 4COF{-}NSOF_2 + SiF_4 \quad (238) \qquad (103)$$

Two methods have also been published recently which avoid the use of OSF_4.

(*d*) Fluorination of sulfinylimides.

$$RSO_2N{=}S{=}O + F_2 \xrightarrow{UV} RSO_2N{=}SOF_2 \qquad (104)$$

$R = F$ (*213*), CH_3 (*210*), CF_3 (*228*)

(*e*) Oxidation of perhaloalkyl sulfur difluoride imides with OF_2 [cf. Equation (50)].

The compounds obtained by method (*b*) serve as starting materials for the preparation of further-$NSOF_2$ derivatives, the Si–N bond in $R_3SiNSOF_2$, for example, being cleaved by $P_2O_3F_4$.

$$R_3SiNSOF_2 + P_2O_3F_4 \xrightarrow{20^\circ} POF_2{-}N{=}SOF_2 + R_3SiOPOF_2 \quad (\mathit{104}) \qquad (105)$$

N-Cyanosulfuroxide difluoride imide reacts with OSF_4 and SF_4 (Fig. 23). Just as in the case of $COFNSF_2$, the corresponding *N*-halogeno compounds are made by starting from *N*-fluoroformylsulfur oxide difluoride imide (*238*) (Fig. 24). Reaction takes place in all probability via the ionic compound $Cs^+NSOF_2^-$ (*238*). At 130°–150° HgF_2 gives $O{=}C(NSOF_2)_2$ (*88*):

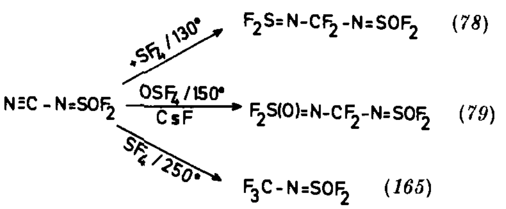


FIG. 23. Reactions of N≡C–NSOF₂.

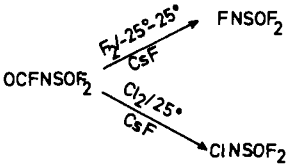


FIG. 24. Preparation of XNSOF₂ compounds (*238*).

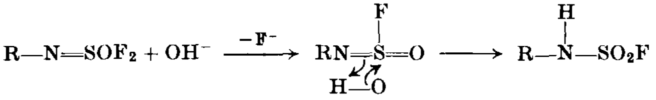
$$HgF_2 + 2COFNSOF_2 \xrightarrow{130^\circ-150^\circ} O{=}C(NSOF_2)_2 + COF_2 + HgF_2 \quad (\mathit{88}) \qquad (106)$$

Chlorination of the residue of this reaction yields $ClNSOF_2$, though the mercurial $Hg(NSOF_2)_2$, which would be expected from this reaction, has not yet been isolated in a pure form.

Addition to double bonds takes place with $ClNSOF_2$ as it does with *N*-halogenosulfur difluoride imides [Eq. (14)].

$$ClNSOF_2 + CF_2{=}CF_2 \xrightarrow{UV} CF_2Cl{-}CF_2{-}NSOF_2 \quad (89) \qquad (107)$$

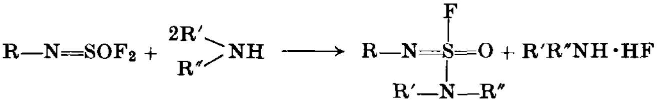
Organosulfur oxide difluoride imides are colorless compounds with considerable chemical stability. They are hydrolyzed only slowly by water or dilute acids, but attack is more rapid with dilute alkalis.



$$R{-}N{=}SOF_2 + OH^- \xrightarrow{-F^-} RN{=}\overset{\displaystyle F}{\underset{\displaystyle H{-}O}{S}}{=}O \longrightarrow R{-}\overset{\displaystyle H}{N}{-}SO_2F \qquad (108)$$

R = FSO_2 (*213*), CH_3SO_2- (*210*), CF_3SO_2 (*228*)

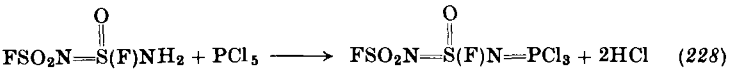
The *N*-substituted fluorosulfonylamines formed in this reaction can be isolated as their difficultly soluble tetraphenylphosphonium salts (cf. the reaction mechanism for the hydrolysis of NSF_3, Fig. 15). Further hydrolysis leads to SO_4^{2-} and F^- ions and the corresponding amine. At low temperatures, amines bring about the exchange of a single fluorine atom, giving an *S*-dialkylaminosulfur oxide monofluorides.



$$R{-}N{=}SOF_2 + 2\,{R' \atop R''}{>}NH \longrightarrow R{-}N{=}\overset{\displaystyle F}{\underset{\displaystyle R'{-}N{-}R''}{S}}{=}O + R'R''NH\cdot HF \qquad (109)$$

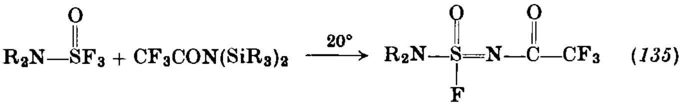
R = C_6H_5, R′, R″ = piperidine; R = HOOC–CH_2,
R′ = H, R″ = CH_2COOH (*52*); R = FSO_2, R′ = R″ = H, CH_3, C_2H_5; R′ = H,
R″ = CH_3 (*213*); R = CF_3SO_2, R′ = R″ = CH_3 (*238*)

The NH_2 group of $FSO_2{-}N{=}\overset{O}{\overset{\|}{S}}(F)NH_2$ is a site for further reactions.



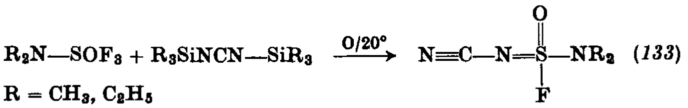
$$FSO_2N{=}\overset{\displaystyle O}{\overset{\|}{S}}(F)NH_2 + PCl_5 \longrightarrow FSO_2N{=}\overset{\displaystyle O}{\overset{\|}{S}}(F)N{=}PCl_3 + 2HCl \quad (228) \qquad (110)$$

It is possible to get *S*-dialkylaminosulfur oxide monofluoride imides by reaction of dialkylaminosulfur oxide trifluorides with primary amines or their *N*-silylated derivatives.



$$R_2N{-}\overset{\displaystyle O}{\overset{\|}{S}}F_3 + CF_3CON(SiR_3)_2 \xrightarrow{20°} R_2N{-}\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle F}{S}}}{=}N{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CF_3 \quad (135) \qquad (111)$$

R = CH_3, C_2H_5



$$R_2N{-}SOF_3 + R_3SiNCN{-}SiR_3 \xrightarrow{0/20^\circ} N{\equiv}C{-}N{=}\overset{\overset{\Large O}{\|}}{\underset{\underset{\Large F}{|}}{S}}{-}NR_2 \ (133) \qquad (112)$$
$$R = CH_3,\ C_2H_5$$

In some cases exchange of the last fluorine atom is possible at higher temperatures (Fig. 25). So far sulfur oxide dichloride imides have not

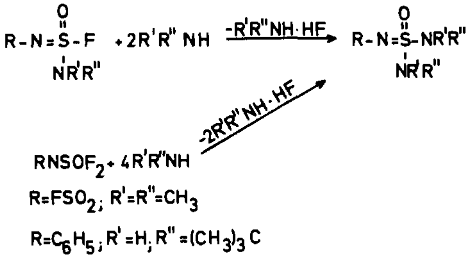
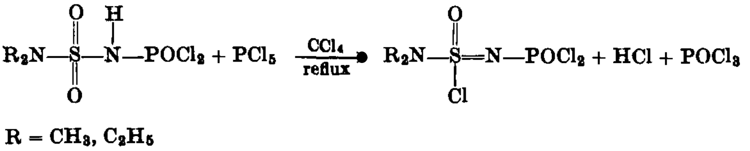


FIG. 25. Preparation of *S*,*S*-(dialkylamino)sulfur(+6) oxide imides (*52*, *212*).

been made. The first two amino derivatives of this class of compounds were synthesized in the interesting reaction shown below (*208*).



$$R_2N{-}\overset{\overset{\Large O}{\|}}{\underset{\underset{\Large O}{\|}}{S}}{-}\overset{\overset{\Large H}{|}}{N}{-}POCl_2 + PCl_5 \xrightarrow[\text{reflux}]{CCl_4} R_2N{-}\overset{\overset{\Large O}{\|}}{\underset{\underset{\Large Cl}{|}}{S}}{=}N{-}POCl_2 + HCl + POCl_3 \qquad (113)$$
$$R = CH_3,\ C_2H_5$$

6. *Aminosulfur Oxide Trifluorides*, $R_2N{-}SOF_3$

As with the corresponding $R_2N{-}SF_3$ compounds, the aminosulfur oxide trifluorides are obtainable only by reaction of *N*-silylated secondary amines with OSF_4.

$$R_2N{-}SiMe_3 + OSF_4 \xrightarrow{20^\circ} R_2N{-}SOF_3 + Me_3SiF \qquad (114)$$
$$R = CH_3\ (83),\ C_2H_5\ (133)$$

These are extraordinarily reactive colorless liquids and the structure can be shown by NMR investigations to be derived from that of OSF_4 by substitution of one equatorial fluorine atom by an dialkylamino group (Fig. 26). Their reactions have already been discussed [Eqs. (111) and (112)].

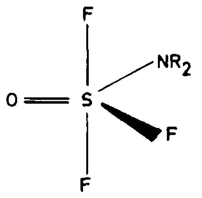
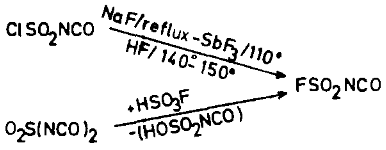


FIG. 26. Proposed structure of R_2NSOF_3.

7. *Fluorosulfonyl–Nitrogen Compounds*, FSO_2–NR_2

Starting from fluorosulfonyl isocyanate, FSO_2NCO, fluorosulfonyl amide, FSO_2NH_2, and imido disulfuryl fluoride, $HN(SO_2F)_2$, an almost bewildering number of fluorosulfonyl–nitrogen compounds may be derived.

a. Preparation and Reactions of FSO_2NCO. Several methods have been developed for this synthesis. It is best to start from the technical product $ClSO_2NCO$, which is fluorinated as shown in Fig. 27. Characteristic of the chemistry of fluorosulfonyl isocyanate (Fig. 28) is the high



(*131, 144, 227, 267*)

(*1, 4*)

FIG. 27. Preparation of $FSO_2N{=}C{=}O$.

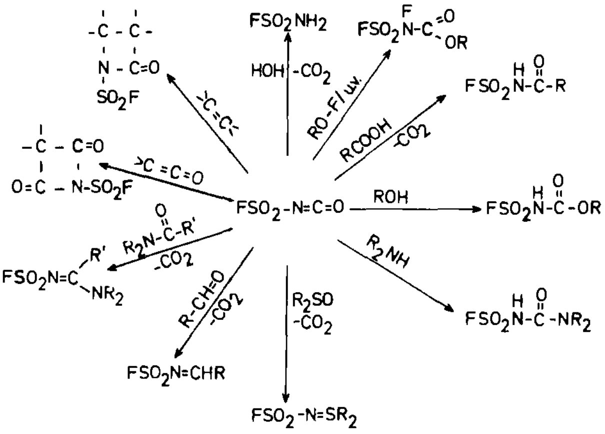


FIG. 28. Chemistry of FSO_2NCO.

reactivity of the -N=C=O group. The S–F bond is cleaved only with some difficulty and survives most reactions.

Reactions of FSO_2NCO with olefins (*122*), ketenes (*125*), amides (*124*), aldehydes (*121*, *123*), ortho esters (*17*), and CH-acidic compounds (*18*) have been reviewed recently (*120*) and will not be considered here in detail.

Addition of alcohols and primary or secondary amines to the C=N double bond takes place as shown in Fig. 29, the products being formed

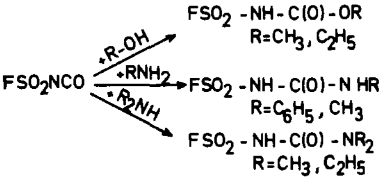


FIG. 29. Addition reactions of FSO_2NCO (*227*, *231*).

in good yield. With fluorosulfonylamide, bisfluorosulfonylamidourea results (*227*).

$$FSO_2N{=}C{=}O + FSO_2NH_2 \longrightarrow FSO_2{-}NH{-}C(O){-}NH{-}SO_2F \quad (227) \quad (115)$$

Recently the addition of fluorine and hypofluorites to the double bond has also been reported (*184*) (Fig. 30). When acids are added to the

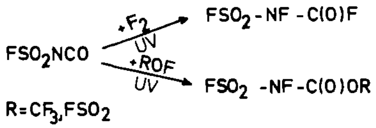
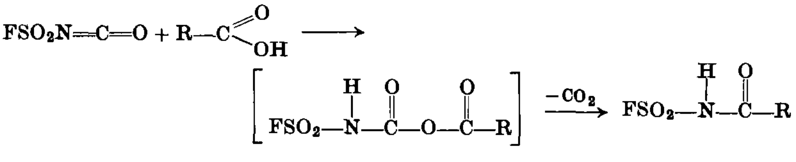


FIG. 30. Photolytic additions to FSO_2NCO (*184*).

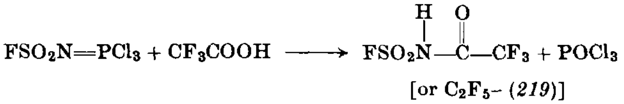
isocyanate group, decarboxylation takes place and *N*-fluorosulfonyl–substituted acid amides result.



$$FSO_2N{=}C{=}O + R{-}C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OH} \longrightarrow \left[FSO_2{-}\overset{H}{\underset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}R\right] \xrightarrow{-CO_2} FSO_2{-}\overset{H}{\underset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}R \quad (116)$$

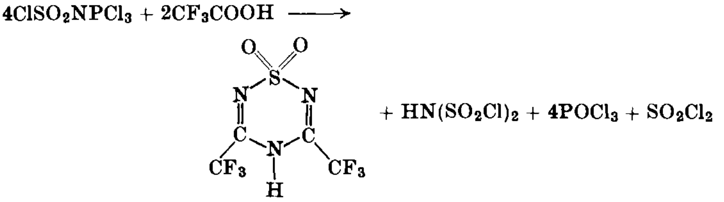
$R = CH_3$, CH_2Cl, $CHCl_2$, CCl_3 (*217*), CH_2F (*221*)

Reaction depends on the p*K* value of the acid. There is no reaction with CF_3COOH even after boiling for days, though the desired CF_3 derivative can be prepared by cleavage of trichlorophosphazosulfonyl fluoride (*221*).



$$FSO_2N{=}PCl_3 + CF_3COOH \longrightarrow FSO_2\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}CF_3 + POCl_3 \qquad (117)$$
$$[\text{or } C_2F_5\text{- } (\mathit{219})]$$

A parallel reaction with $ClSO_2NPCl_3$ gives a cyclic product (*206*).



$4ClSO_2NPCl_3 + 2CF_3COOH \longrightarrow$ … $+ HN(SO_2Cl)_2 + 4POCl_3 + SO_2Cl_2$ (*206*) (118)

In the reaction of dimethylsulfoxide with FSO_2NCO, CO_2 is split off:

$$FSO_2{-}N{=}C{=}O + (CH_3)_2S{=}O \longrightarrow FSO_2N{=}S(CH_3)_2 \quad (\mathit{227}) \qquad (119)$$

If the addition product of FSO_2NCO having the formula $FSO_2\overset{H}{N}\text{-}C(O)R$ (OR, NR_2) is treated with PCl_5, $POCl_3$ is eliminated and the corresponding *N*-methylenesulfonyl fluoride amide is formed (Fig. 31). Exchange

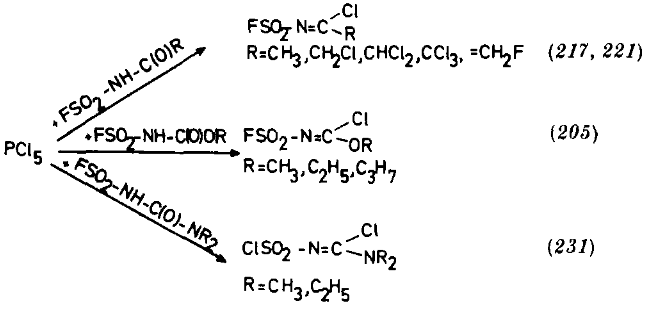


Fig. 31. Preparation of *N*-methylenesulfonyl fluoride amides.

of chlorine atoms bonded to carbon gives rise to a further series of fluorosulfonyl–nitrogen compounds (*219*, *221*, *231*). Figure 32 shows as

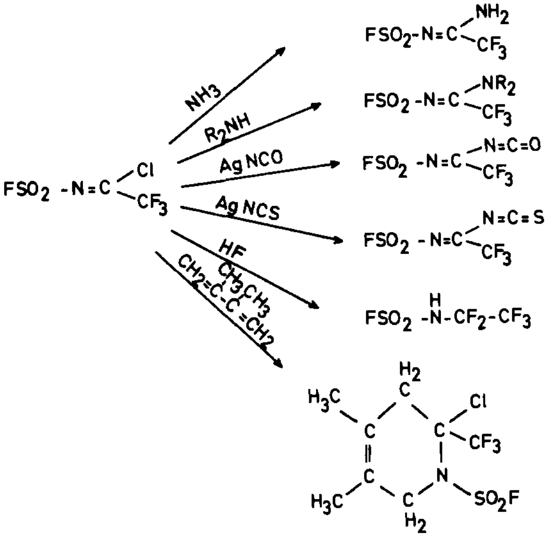
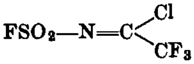


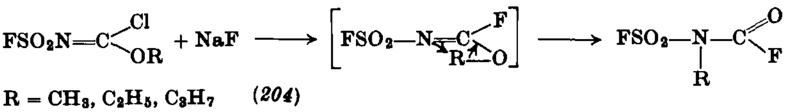
FIG. 32. Reactions of $FSO_2{-}N{=}C\begin{smallmatrix}Cl\\ CF_3\end{smallmatrix}$ (*219*, *221*).

an example the reactions of



$$FSO_2{-}N{=}C\begin{smallmatrix}Cl\\ CF_3\end{smallmatrix}$$

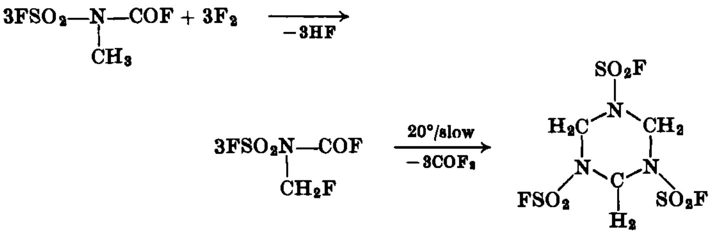
Rearrangements are found to occur when fluorosulfonyl isocyanide alkoxides are fluorinated with NaF.



(120)

R = CH_3, C_2H_5, C_3H_7 (*204*)

Reaction of the methyl compound with elementary fluorine gives the trifluorosulfonyltriazine (*219*).



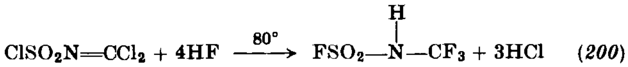
(*219*) (121)

N-Dichloromethylenesulfonyl fluoride amide is produced when PCl_5 reacts with $ClSO_2NCO$ and the product is then fluorinated with SbF_3Cl_2.

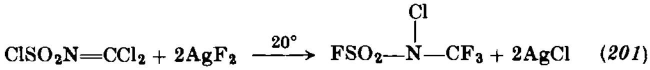
$$ClSO_2N{=}C{=}O + PCl_5 \xrightarrow{210^\circ} ClSO_2N{=}CCl_2 + POCl_3 \quad (\mathit{214}) \qquad (122)$$

$$ClSO_2N{=}CCl_2 + SbF_3Cl_2 \xrightarrow{60^\circ\text{–}85^\circ} FSO_2N{=}CCl_2 \quad (\mathit{214}) \qquad (123)$$

Either HF or AgF_2 will also fluorinate the CCl_2 group.



$$ClSO_2N{=}CCl_2 + 4HF \xrightarrow{80^\circ} FSO_2{-}\overset{\displaystyle H}{\overset{|}{N}}{-}CF_3 + 3HCl \quad (\mathit{200}) \qquad (124)$$



$$ClSO_2N{=}CCl_2 + 2AgF_2 \xrightarrow{20^\circ} FSO_2{-}\overset{\displaystyle Cl}{\overset{|}{N}}{-}CF_3 + 2AgCl \quad (\mathit{201}) \qquad (125)$$

b. Preparation and Reactions of FSO_2NH_2 *and* FSO_2NR_2. Apart from the preparation of FSO_2NH_2 by hydrolysis of FSO_2NCO (Fig. 33), the methods shown in Fig. 34 are also available.

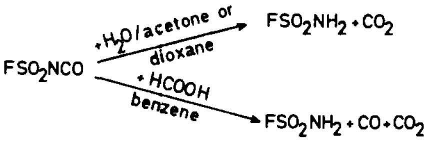


FIG. 33. Preparation of FSO_2NH_2 by hydrolysis of FSO_2NCO (*144, 197*).

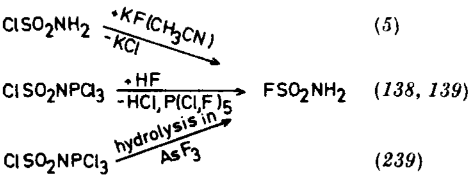


FIG. 34. Preparation of FSO_2NH_2.

Direct reaction of SO_2F_2 or SO_2FCl with ammonia gives sulfamide in good yield (*149*), but when secondary amines are used, *N*,*N*-dialkyl- or diarylfluorosulfonyl amides result.

$$3R_2NH + SO_2F_2 \longrightarrow FSO_2NR_2 + R_2NH{\cdot}HF \qquad (126)$$

R = alkyl (*64, 226*), aryl (*193*)

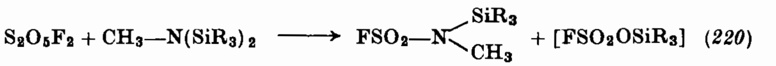
The *N*,*N*-disubstituted derivatives of FSO_2NH_2 are also produced by the following reactions.

$$R_2NSO_2Cl + KF \xrightarrow{H_2O} R_2NSO_2F + KCl \quad (\mathit{243a})$$

$$R_2NSO_2Cl + SbF_3Cl_2 \xrightarrow[\text{reflux}]{C_6H_6} R_2NSO_2F + Sb(F, Cl)_5 \quad (\mathit{137}) \qquad (127)$$

$$S_2O_5F_2 + R_2NH \longrightarrow R_2NSO_2F + [R_2NH_2][FSO_3] \quad (\mathit{2}) \qquad (128)$$

$$S_2O_5F_2 + R_3SiNCNSiR_3 \longrightarrow FSO_2{-}N{=}C{=}N{-}SiR_3 + [FSO_2OSiR_3] \quad (\mathit{220}) \qquad (129)$$



$$S_2O_5F_2 + CH_3{-}N(SiR_3)_2 \longrightarrow FSO_2{-}N\begin{smallmatrix} SiR_3 \\ CH_3 \end{smallmatrix} + [FSO_2OSiR_3] \quad (\mathit{220}) \qquad (130)$$

If ammonia replaces R_2NH in (*128*), fluorosulfonyl amide can also be isolated. Starting from FSO_2NH_2, numerous other fluorosulfonyl–nitrogen compounds can be prepared, as is shown in Fig. 35.

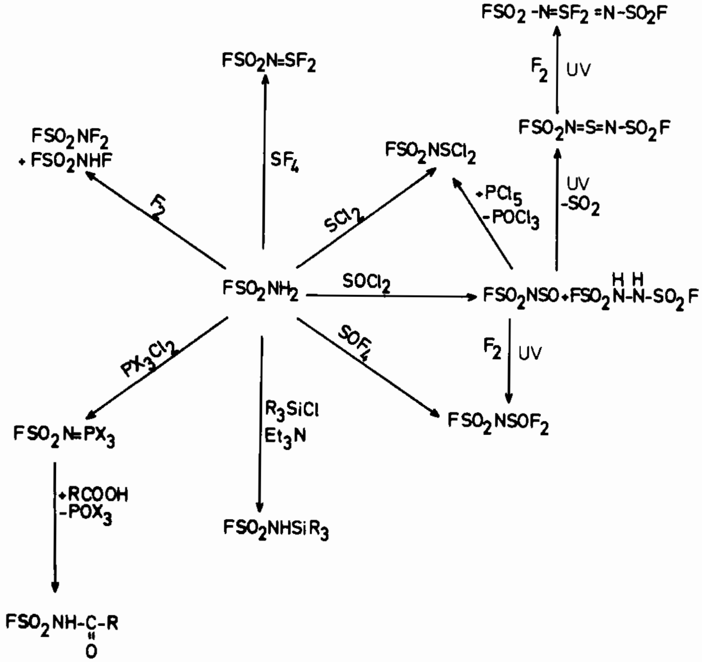


Fig. 35. Chemistry of FSO_2NH_2.

Reaction with elementary fluorine leads to *N*-fluorosulfonyl difluoramine and, in addition, FSO_2NHF, which is the first known derivative of HNF_2.

$$FSO_2NH_2 + F_2 \xrightarrow{-HF} FSO_2NHF + FSO_2NF_2 \quad (\mathit{202}) \qquad (131)$$

The latter of these two compounds is already known as a product of the photochemical or thermal reaction between N_2F_4 and SO_2.

$$N_2F_4 + SO_2 \xrightarrow[100^\circ]{UV} FSO_2\text{–}NF_2 + \tfrac{1}{2}N_2F_2 \quad \textit{(22, 242)} \qquad (132)$$

Whereas FSO_2NF_2 is very stable, $H_2N\text{–}SO_2\text{–}NF_2$, which results in the fluorination of sulfamide in aqueous solution, cannot be isolated in a pure state.

$$H_2N\text{—}SO_2\text{—}NH_2 + 2F_2 \xrightarrow{-2HF} H_2N\text{—}SO_2\text{—}NF_2 \quad \textit{(275)} \qquad (133)$$

Fluorosulfonyl amide reacts with halides of phosphorus and sulfur forming P=N– or S=N–SO_2F derivatives.

$$FSO_2NH_2 + PCl_5 \longrightarrow FSO_2N{=}PCl_3 \quad \textit{(148, 239)} \qquad (134)$$

$$FSO_2NH_2 + PF_3Cl_2 \longrightarrow FSO_2N{=}PF_3 \quad \textit{(161, 225)} \qquad (135)$$

Chlorine–fluorine exchange in the –N=PF_3 group takes place in presence of excess of PF_3Cl_2.

$$2FSO_2N{=}PF_3 + PF_3Cl_2 \longrightarrow 2FSO_2\text{—}N{=}PF_2Cl + PF_5 \quad \textit{(225)} \qquad (136)$$

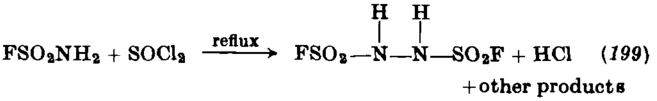
From the chlorine analog, $ClSO_2NH_2$, chlorosulfonyl derivatives are isolated by reactions corresponding with those shown in Eqs. (135) and (136) (*224*). Organophosphorus-substituted fluorosulfonylphosphazo compounds can be made in the same way, although $FSO_2N{=}PBr_3$ is accessible only through FSO_2NSO.

$$FSO_2NH_2 + 3C_6H_5PF_4 + 2[CH_3]_3N \longrightarrow$$
$$FSO_2N{=}PF_2C_6H_5 + 2[(CH_3)_3NH][C_6H_5PF_5] \quad \textit{(209)} \qquad (137)$$

$$FSO_2NSO + PBr_5 \longrightarrow FSO_2N{=}PBr_3 + SOBr_2 \quad \textit{(203)} \qquad (138)$$

Reaction of FSO_2NH_2 with SF_4 (*100*), SCl_2 (*197*), and SOF_4 (*101*) yields *N*-fluorosulfonylsulfur difluoride, dichloride or oxide difluoride imides, the reactions of which have already been discussed. The product with thionyl chloride is FSO_2NSO, but, if $SOCl_2$ and FSO_2NH_2 are heated under reflux, *N*,*N*-hydrazodisulfonyl difluoride is formed.

$$FSO_2NH_2 + SOCl_2 \longrightarrow FSO_2NSO + 2HCl \quad \textit{(197)} \qquad (139)$$



$$FSO_2NH_2 + SOCl_2 \xrightarrow{\text{reflux}} FSO_2\text{—}\overset{H}{\underset{|}{N}}\text{—}\overset{H}{\underset{|}{N}}\text{—}SO_2F + HCl \quad \textit{(199)} \qquad (140)$$
$$+\text{other products}$$

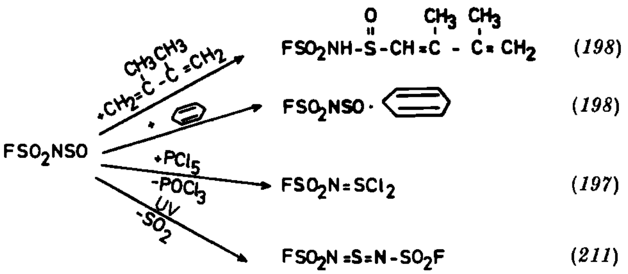


FIG. 36. Reactions of FSO$_2$NSO.

Some further reactions carried out with FSO$_2$NSO are shown in Fig. 36 [cf. also Eq. (104)]. One proton in FSO$_2$NH$_2$ can be replaced by a silyl group (*198*).

$$FSO_2NH_2 + R_3SiCl + Et_3N \longrightarrow FSO_2NH—SiR_3 + Et_3N \cdot HCl \quad (198) \quad (141)$$

Cleavage of Kirsanov products with fluorosulfonic acid also leads to *N*-monosubstituted derivatives of FSO$_2$NH$_2$, e.g.,

$$C_3N_3F_2N{=}PCl_3 + FSO_3H \longrightarrow C_3N_3F_2—NH—SO_2F + POCl_3 \quad (216) \quad (142)$$

As might be expected, the azide FSO$_2$N$_3$, the preparation of which is shown below, is explosive, and has so far found no use in preparative work.

$$S_2O_5F_2 + NaN_3 \xrightarrow{CH_3NO_2} FSO_2N_3 + NaSO_3F \quad (234) \quad (143)$$

$$SO_2F_2 + LiN_3 \xrightarrow{DMF} FSO_2N_3 + LiF \quad (250) \quad (144)$$

c. Preparation and Reaction of Imidobissulfuric Acid Fluoride, HN(SO$_2$F)$_2$. The various preparative routes to HN(SO$_2$F)$_2$ are shown in Fig. 37. When FSO$_2$N=PCl$_3$ is cleaved with HOSO$_2$F, an azeotrope with POCl$_3$ results (*234*), so that it is impossible to prepare pure HN(SO$_2$F)$_2$ in this way. Its formation by hydrolyzing FSO$_2$NSOF$_2$ has

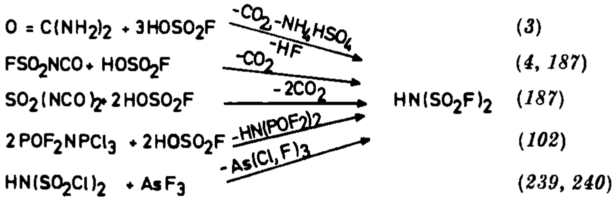


FIG. 37. Preparation of HN(SO$_2$F)$_2$.

already been referred to in Eq. (108). Metal oxides or carbonates give the corresponding $HN(SO_2F)_2$ salts (Fig. 38). The silver salt reacts with

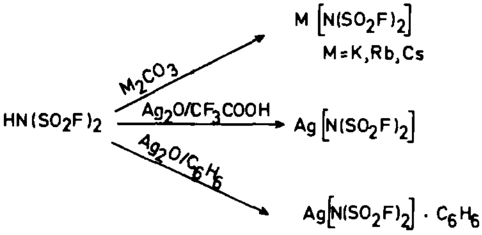


FIG. 38. Reactions of $HN(SO_2F)_2$ (*235*).

alkyl iodides forming the corresponding *N*-alkyl derivatives, while chlorine gives $ClN(SO_2F)_2$. The fluorine derivative is synthesized by

$$Ag[N(SO_2F)_2]\cdot C_6H_6 + RI \longrightarrow R\text{—}N(SO_2F)_2 + AgI + C_6H_6 \qquad (145)$$

$R = CH_3, C_2H_5$ (*235*)

$$Ag[N(SO_2F)_2] + Cl_2 \longrightarrow ClN(SO_2F)_2 + AgCl \quad (237) \qquad (146)$$

$$HN(SO_2F)_2 + F_2 \longrightarrow FN(SO_2F) + HF \quad (162, 240) \qquad (147)$$

direct fluorination of imido bissulfuric acid fluoride. The N–Cl bond in the *N*-chloro compound is readily cleaved and this leads to the following reactions (Fig. 39).

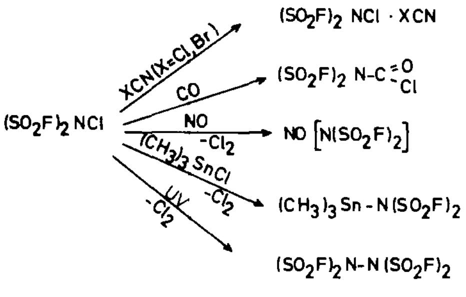
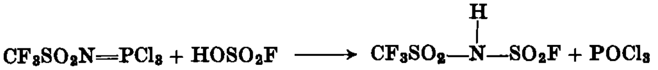


FIG. 39. Reactions of $ClN(SO_2F)_2$ (*237*).

Finally, tris(fluorosulfonyl)hydroxylamine can be produced by the interesting cleavage of $S_2O_6F_2$ with $CsN(SO_2F)_2$ (*241*).

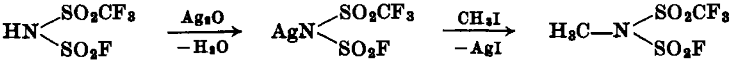
$$CsN(SO_2F)_2 + S_2O_6F_2 \longrightarrow CsOSO_2F + (FSO_2)_2N\text{—}O\text{—}SO_2F \qquad (148)$$

S-Monoalkylated derivatives of $HN(SO_2F)_2$ are obtained by either of two methods: (*a*) by hydrolysis of sulfur oxide difluoride imides [cf. Eq. (108)] or (*b*) from alkylsulfonylphosphazo compounds and fluorosulfonic acid (*220a*).



$$CF_3SO_2N{=}PCl_3 + HOSO_2F \longrightarrow CF_3SO_2{-}\overset{H}{\overset{|}{N}}{-}SO_2F + POCl_3 \qquad (149)$$

They undergo reactions analogous to those of $HN(SO_2F)_2$ (*220a*).



$$HN{<}\begin{smallmatrix}SO_2CF_3\\ SO_2F\end{smallmatrix} \xrightarrow[-H_2O]{Ag_2O} AgN{<}\begin{smallmatrix}SO_2CF_3\\ SO_2F\end{smallmatrix} \xrightarrow[-AgI]{CH_3I} H_3C{-}N{<}\begin{smallmatrix}SO_2CF_3\\ SO_2F\end{smallmatrix} \qquad (150)$$

The interesting *O*-difluoramine-sulfur compounds FSO_2ONF_2 (*163*, *163a*) and SF_5ONF_2 (*135b*, *235a*) will not be discussed since they contain no S–N bond.

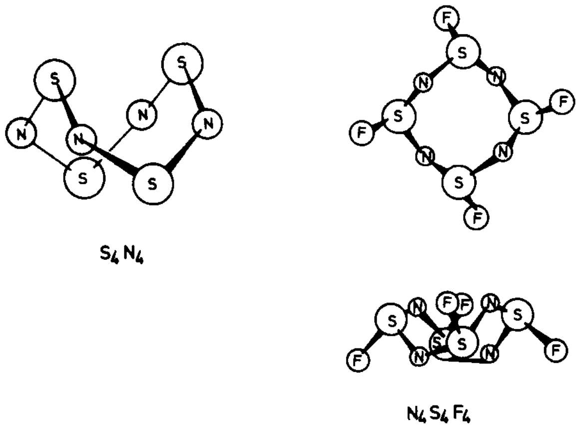
III. Cyclic Compounds

In contrast to the numerous acyclic sulfur–nitrogen–fluorine compounds already described, only a few cyclic compounds with 8-, 7-, or 6-membered rings are known.

1. *Tetrathiazyl Tetrafluoride*, $S_4N_4F_4$

This is the only cyclic compound in this group to have an 8-membered ring structure. Attempts to synthesize it from simple molecules, e.g., by polymerization of NSF, have so far been in vain. This particular reaction always yields trithiazyl trifluoride, $N_3S_3F_3$, with a 6-membered ring. Synthesis of $N_4S_4F_4$ is successful only with the aid of S_4N_4, which has a preformed 8-membered ring. When it is fluorinated in carbon tetrachloride solution with silver difluoride, colorless crystals of $N_4S_4F_4$ separate. The structure has been established by X-ray analysis (*271*, *273*). Fluorine is bonded to sulfur and the conformation of the cage structure of the 8-membered ring of S_4N_4 changes to the compact wavy 8-membered ring of $N_4S_4F_4$ (Fig. 40). In order to understand this change in structure it is first necessary to consider the geometrical and electronic structure of S_4N_4 (*21*, *46–49*). X-Ray analysis (*29*, *158*, *249*) (Fig. 40) shows the molecule to have one direct S–N distance of 1.62 Å (1.60–1.63 Å), corresponding with a bond order of 1.2 (*95*). The distance between two sulfur atoms which are not bonded through nitrogen is 2.58 Å, which

$$S_4N_4 + 4AgF_2 \xrightarrow{CCl_4} N_4S_4F_4 + 4AgF \qquad (151)$$



S_4N_4

$N_4S_4F_4$

FIG. 40. Structures of S_4N_4 and $N_4S_4F_4$.

is significantly less than the sum of the van der Waals radii of 3.7 Å (*191*) and somewhat greater than the distance of 2.04 Å for a single bond (*259*). The S–N–S, N–S–N, and N–N–S bond angles are 113°, 105°, and 90°, respectively. Several attempts have been made to explain these parameters as by the limiting mesomeric forms shown in Fig. 41.

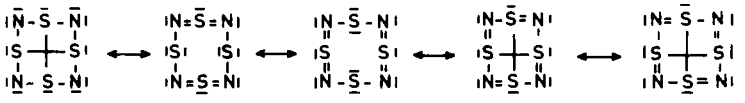


FIG. 41. Limiting mesomeric forms of S_4N_4.

According to Craig *et al.* (*46–49*), the single S–N distance justifies the assumption of p_π–d_π bonds in the 8-membered ring of S_4N_4. This is supported by measurements of the electron spin resonance in sulfur nitride ions (*26*, *27*). It must not, however, be forgotten in this connection that the aromatic character of the ring is only poorly developed. This follows not only from the low S–N bond order of 1.2 (*95*), but also from HMO calculations (*264*, *265*), which show that there is relatively little tendency for the *d* orbital of sulfur to participate in p_π–d_π overlapping. It is assumed from geometrical considerations that interaction between the sulfur atoms is by means of a π bond (*153*). The same result comes from HMO calculations which also give a bond order value of 0.4 for the S–S bond (neglecting the *d* orbitals of the sulfur atom). The π bond is a direct consequence of the N–S···S angle of 90°.

Fluorination of S_4N_4 changes the geometrical structure of S_4N_4 (Fig. 40) as well as its electronic structure (Fig. 42). The ^{19}F NMR spectrum of $N_4S_4F_4$ (which melts at 153° and decomposes above 128°) shows a single peak at −35 ppm($CFCl_3$ as external standard), which indicates that the fluorine atoms in the molecule are structurally equivalent. Dielectric measurements show the dipole moment to be zero; the charges are uniformly distributed over the molecule. X-Ray analysis shows that the wavy $N_4S_4F_4$ ring has two different S–N distances of 1.660 and 1.540 Å (*271*, *273*) with bond orders of 1.7 and 1.1, respectively, indicating localized π bonding. The strongly electronegative fluorine atoms favor promotion of electrons into sulfur *d* orbitals which become contracted. This makes a better overlap of the orbitals possible. Simultaneously the sulfur electrons become more firmly held, which operates against delocalization. The opening up of the S–N–S bond angle from 113° in S_4N_4 to 124° in $N_4S_4F_4$ indicates that the lone pair of electrons on nitrogen is contributing to the S–N bond of $N_4S_4F_4$.

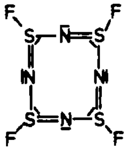


FIG. 42. Electronic structure of $N_4S_4F_4$.

The compound $N_4S_4F_4$ is somewhat soluble in carbon tetrachloride (3.448 gm/liter at 20°). It decomposes slowly in moist air and is hydrolyzed quantitatively by warm alkali according to the equation

$$N_4S_4F_4 + 12H_2O \longrightarrow 4NH_4F + 4H_2SO_3 \qquad (152)$$

Decomposition to NSF takes place when it is heated to 250°, but, as was mentioned in describing the reactions of NSF, polymerization of the latter yields $N_3S_3F_3$ and not $N_4S_4F_4$.

As a Lewis base, $N_4S_4F_4$ forms an adduct with BF_3. The green solid $N_4S_4F_4 \cdot BF_3$ (*87*) is produced from gaseous BF_3 and solid, colorless $N_4S_4F_4$. It decomposes in dry nitrogen at room temperature after some hours. More prolonged reaction of BF_3, for example, at 20° for 1 day, results in ring cleavage, the product being the unstable adduct $NSF \cdot BF_3$, which has already been described. In this instance, the behavior of $N_4S_4F_4$ differs from that of $N_3S_3F_3$, as will be seen later (*85*).

Attempts to replace fluorine atoms in $N_4S_4F_4$ by chlorine with the aid of chlorides such as $SiCl_4$, PCl_5, or $(CH_3)_3SiCl$ were unsuccessful; in each case $N_3S_3Cl_3$ was formed and not $N_4S_4Cl_4$ (*85a*). The latter probably occurs an intermediate of low stability during the chlorination of S_4N_4. When a mixture of oxygen and nitrogen dioxide is passed over $N_4S_4F_4$ at 120° (*85a*), trisulfur dinitrogen dioxide, $S_3N_2O_2$, is formed in addition to SO_2, SOF_2, and a little SO_3 (*116*). A further oxide, trisulfur dinitrogen pentoxide, $S_3N_2O_5$ (*117*), is obtained by reaction of $N_4S_4F_4$ with SO_3 at 200° (*85a*).

2. *Trithiazyl Trifluoride*

This may be prepared in two ways: (*a*) by polymerization of NSF or (*b*), directly by fluorination of a suspension of $N_3S_3Cl_3$ in carbon tetrachloride with AgF_2 at room temperature. The colorless, highly refractive crystals of $N_3S_3F_3$, which are appreciably volatile at room temperature, are readily soluble in carbon tetrachloride and benzene (*244*). They are stable in absence of air, although they decompose and become black in moist air. Hydrolysis by cold dilute sodium hydroxide

$$N_3S_3F_3 + 9H_2O \longrightarrow 3NH_4F + 3H_2SO_3 \qquad (153)$$

is quantitative. The oxidation number of sulfur is +4, as in $N_4S_4F_4$, and fluorine must be bonded to sulfur.

The structure of trithiazyl trifluoride has not yet been determined by X-ray analysis, so that the data for comparison with $N_4S_4F_4$ are lacking. In spite of this, however, some conclusions as to possible structures may be drawn. As in the case of $N_4S_4F_4$, the trimer shows only one signal in the ^{19}F NMR spectrum at –44.1 ppm [$CFCl_3$ external standard (*220b*)]. From this it can be concluded that all the fluorine atoms in $N_3S_3F_3$ are in equivalent positions. The value is close to that for $N_4S_4F_4$ (–35 ppm) and the electronic structures of the two compounds are likely to be similar.

We can now consider the structure of $N_3S_3Cl_3$, from which $N_3S_3F_3$ is prepared (cf. Fig. 43), and which is itself prepared by chlorinating a suspension of S_4N_4 in carbon tetrachloride. X-Ray analysis (*274*) shows the $N_3S_3Cl_3$ molecule to have a chair form with the three chlorine atoms in axial positions. In contrast to $N_4S_4F_4$, there is only a single direct S–N distance of 1.605 Å, corresponding with a bond order of 1.4 (*95*), and indicative of delocalized p_π–d_π bonding in the ring. The $N_3S_3Cl_3$ molecule is deformed; thus the distance of the nitrogen atoms from a plane containing the sulfur atoms is 0.225 Å for N-1 and 0.126 Å for N-2. The S–Cl distances of 2.084 and 2.150 Å are also not equal. The relatively large S–N–S angle of 123.9° suggests that the lone pair of electrons on nitrogen is participating in the S–N bond.

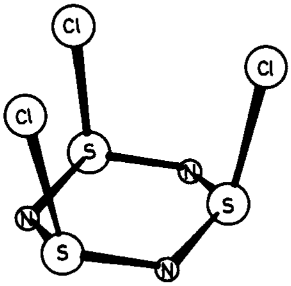


FIG. 43. Structure of $N_3S_3Cl_3$.

It would be expected that the structure of $N_3S_3F_3$ would be similar to that of $N_3S_3Cl_3$. ^{19}F NMR measurements show all the fluorine atoms in $N_3S_3F_3$ to be equivalent. This, however, would be possible only if they were situated in an axial position on one side of the ring, as in $N_3S_3Cl_3$. It could also be concluded from the NMR data that, because of the similarity in the chemical shifts for $N_3S_3F_3$ and $N_4S_4F_4$, there would be different S–N distances in the N_3S_3 ring of $N_3S_3F_3$, i.e., localized π bonding.

Like $N_4S_4F_4$, the trimer also acts as a Lewis base and forms a colorless solid $N_3S_3F_3 \cdot BF_3$ with BF_3, probably with electron donation by a single nitrogen atom in the ring. The adduct is unaffected by excess of BF_3 and is stable to about 60°. It thus differs considerably in stability from the corresponding derivative of $N_4S_4F_4$ (*85*).

The hydrolysis mechanism for $N_3S_3F_3$ may be closely related to that of NSF. If a little water is added to $N_3S_3F_3$ in a glass vessel, the gaseous compounds NSF, HNSO, SO_2, and SiF_4 can be detected (*96*). The reaction scheme in Fig. 44 has been proposed. The first step may be

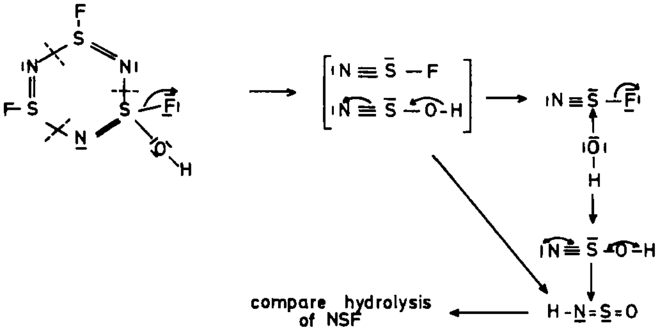


FIG. 44. Hydrolysis of $N_3S_3F_3$.

considered as involving nucleophilic attack by OH^- ions on the sulfur atom of $N_3S_3F_3$. Ring cleavage leads to NSF and HNSO, the latter being formed by further hydrolysis of NSF. Hydrolysis then follows the same route as was described for NSF, with formation of H_2NOH and $S(OH)_2$, which interact through amidosulfinic acid, H_2NSO_2H, to give SO_2 and NH_3. Subsequent reactions yield sulfur, $S_2O_3^{2-}$, and polythionate ions. Formation of SOF_2 may possibly be explained by a side reaction of NSF with HF and subsequent hydrolysis.

3. *Trithiazyl Trifluoride Trioxide (Sulfanuric Fluoride)*, $N_3S_3O_3F_3$

This was first prepared by reaction of potassium fluoride with α-$N_3S_3O_3Cl_3$ (*147*) in carbon tetrachloride at 145° (*247*). Direct synthesis from $HNSOF_2$ has not yet proved possible, although recently $N_3S_3O_3F_3$ was obtained in small amounts by a direct route involving heating $OCFNSOF_2$ with cesium fluoride (*88*). The product from the fluorination of $N_3S_3O_3Cl_3$ was separated into two isomers by gas chromatography. These were shown by their ^{19}F NMR spectra to be *cis*- and *trans*-$N_3S_3O_3F_3$. The *cis* compound (m.p. 17.4°) gave only one signal at -70.9 ppm ($CFCl_3$ as internal standard), whereas the trans isomer gave the multiplet characteristic of an AB_2 compound (-71.9, -71.4 ppm: $J_{AB} = \pm 21.6$ Hz). Since the unique fluorine atom in *trans*-$N_3S_3O_3F_3$ is less shielded from the influence of solvents than the other two fluorine atoms, the sulfur–nitrogen ring of the molecule should be nonplanar, as in the case of $N_3S_3O_3Cl_3$ (*9*, *247*). It may therefore be assumed that *cis*-$N_3S_3O_3F_3$ is structurally similar to α-$N_3S_3O_3Cl_3$ (Fig. 45), the structure of which has been elucidated by X-ray analysis (*9*, *136*, *272*), and which is comparable with that of $N_3S_3Cl_3$ (cf. Fig. 7).

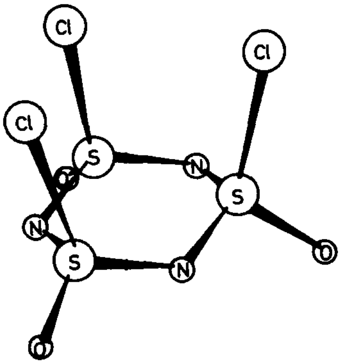


FIG. 45. Structure of α-$N_3S_3O_3Cl_3$.

The $N_3S_3O_3Cl_3$ molecule forms a chair-shaped ring in which two nitrogen atoms lie 0.244 Å outside a plane containing the sulfur atoms, the distance for the third being 0.262 Å. There is only one direct S–N distance of 1.57 Å in the ring, corresponding with a bond order of 1.5 (*95*), so that delocalized p_π–d_π bonding can be assumed. The shorter S–N distance compared with that in $N_3S_3Cl_3$ results from polarization of sulfur by oxygen and from the absence of a lone pair of electrons on sulfur. The chlorine atoms are all on one side of the molecule in axial positions, with the oxygen atoms in equatorial positions. The S–O bond (1.407 Å) has some double-bond character; S_3O_9, which is isosteric with $N_3S_3O_3Cl_3$, has a similar structure. Whether the fluorine analog $N_3S_3O_3F_3$ has localized or delocalized bond can only be determined by further experiments.

The chemical properties of $N_3S_3O_3F_3$ are noteworthy. The compound may be passed through a nickel tube at 350° almost without decomposition. Liquid hydrogen fluoride under pressure is without reaction at 150°; however, boiling caustic soda solution brings about hydrolysis to amidosulfonate and ammonia (*247*).

a. Substitution Products of $N_3S_3O_3F_3$. According to a preliminary communication (*247*), substitution of fluorine atoms in $N_3S_3O_3F_3$ is readily achieved by NH_3 and primary or secondary amines. Details, however, are not available. It has been shown recently (*8*) that diethylamine and *n*-octylamine react to give $N_3S_3O_3F[N(C_2H_5)_2]_2$ and $N_3S_3O_3F[n\text{-}C_8H_{17}NH]_2$.

Various reactions give substitution products which occur as isomers (*177*). Thus, phenyllithium in ether at −70° reacts as follows:

$$\begin{tikzcd}
N_3S_3O_3F_3 + LiC_6H_5 \arrow[r, "-70^\circ", "\text{ether}"'] \arrow[dr] & N_3S_3O_3F_2(C_6H_5) \quad (\text{m.p. } 95^\circ) \\
& N_3S_3O_3F(C_6H_5)_2 \quad (\text{m.p. } 119^\circ)
\end{tikzcd} \qquad (154)$$

The disubstituted product $N_3S_3O_3F(C_6H_5)_2$ can also be made by fluorinating $N_3S_3O_3Cl(C_6H_5)_2$ with NaF in acetonitrile (*169*). The m.p. (107°) is, however, different from that of the other preparation (119°) and isomers may be present. Complete substitution of the fluorine can be achieved only by a Friedel–Crafts reaction with benzene and aluminum chloride.

$$N_3S_3O_3F_3 + 3C_6H_6 \xrightarrow{AlCl_3} \underset{(\text{m.p. } 148^\circ,\ 177^\circ)}{N_3S_3O_3(C_6H_5)_3} \qquad (155)$$

Further disubstituted compounds were prepared with morpholine, 2,6-dimethylmorpholine, piperidine, and pyrrolidine, e.g.,

$$N_3S_3O_3F_3 + 2HNC_4H_8 \xrightarrow{-2HF} \underset{\text{(m.p. 127°, 148°)}}{N_3S_3O_3F(NC_4H_8)_2} \tag{156}$$

The S–N rings in these compounds are nonplanar and an indication of possible structures comes from the ^{19}F NMR spectra (*25*). In the derivatives described above two different chemical shifts are found for the fluorine atoms, one at –72 to –73, the other at –77 to –78 ppm ($CFCl_3$ as internal standard). The first value is attributed by the authors to an axial position of the fluorine atom (derived from the value of –72.8 ppm for *cis*-$N_3S_3O_3F_3$) and the other to an equatorial position. On this basis, $N_3S_3O_3F_2(C_6H_5)_2$ has both F atoms in the equatorial position (–77.2 ppm), while in $N_3S_3O_3F(C_6H_5)_2$ the F atom is in an axial position (–72 ppm). The infrared spectra of the compounds are similar to one another and correspond to those of α- and β-$N_3S_3O_3Cl_3$. Exact assignment of the observed frequencies to specific structural groups is, however, difficult, as no corresponding data are available for the sulfanuric chlorides or fluorides.

4. *Trithiazyl Difluoride Chloride Oxide*, $N_3S_3F_2ClO$

This is accessible through fluorination of $N_3S_3Cl_3O$ (*243*). The latter is a colorless crystalline solid, m.p. 110°, obtained from $S_3N_2O_2$ and liquid

$$3S_3N_2O_2 + 5Cl_2 \longrightarrow 2S_3N_3Cl_3O + 2SOCl_2 + SO_2 \tag{157}$$

chlorine with loss of $SOCl_2$ and SO_2. A ring structure is assumed as it is oxidized by SO_3 to the cyclic compound $N_3S_3Cl_3O_3$. Only one peak is observed in the gas chromatogram, so that only a single compound is present. It is converted by silver difluoride in carbon tetrachloride to $N_3S_3F_2ClO$, for which a ring structure is also likely (Fig. 46). A single

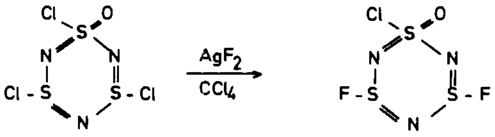


FIG. 46. Preparation of $N_3S_3F_2ClO$.

peak at –35.2 ppm is observed in the ^{19}F NMR spectrum ($CFCl_3$ as standard), and this corresponds with that of $N_4S_4F_4$. Nothing can be said about the bonding relationships in $N_3S_3F_2ClO$, the first sulfur–nitrogen ring compound with different halogen substituents. The existence of this compound does, however, show that combinations between S–N ring systems in which sulfur has variable oxidation numbers is possible.

5. *Thiotrithiazyl Fluoride,* $[N_4S_3]^+F^-$, *and Fluorosulfonate,* $[S_4N_3]^+SO_3F^-$

Thiotrithiazyl fluoride is formed in the reaction of anhydrous hydrogen fluoride with $[S_4N_3]^+Cl^-$ at 80°–100° as yellow-brown crystals of the composition $[S_4N_3]^+F^- \cdot 1.5HF$ (*113*). The residual 1.5HF cannot be removed by heating without decomposing the compound. The infrared spectra of the fluoride and the starting material $[S_4N_3]^+Cl^-$ are very similar. Molecular weight determinations also show that both compounds dissociate into two univalent ions (*16*, *113*), which is an indication of their saltlike character. This had previously been assumed for $[S_4N_3]^+Cl^-$ because of the ready exchange of chlorine for other anionic groups, e.g., NO_3^- or HSO_4^-. Thiotrithiazyl fluorosulfonate has also been prepared recently by reaction of $[S_4N_3]^+Cl^-$ with fluorosulfonic acid (*189*). The

$$S_4N_3^+Cl^- + HSO_3F - S_4N_3^+SO_3F^- + HCl \qquad (158)$$

structural formula proposed for the $[S_4N_3]^+$ ion (Fig. 47) (*118*) has been established by X-ray analysis of $[S_4N_3]^+NO_3^-$ (*45*, *152*, *269*, *270*). In the

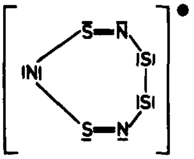


FIG. 47. Structural formula of $S_4N_3^+$.

planar 7-membered ring there are alternating S–N bonds and one S–S bond (Fig. 48). The S–N distances are all almost equal, varying from 1.49 to 1.58 Å (*45*) and the average value of 1.55 Å leads to a bond order of 1.6. The S–S distance of 2.06 Å is very near to that for a single bond (2.08 Å). It is possible to suppose that there is very delocalized π bonding between the S–N bonds, but not between the two sulfur atoms. The bond angles at the nitrogen atoms are striking. They are controlled by the planar arrangement and have very high values (S(1)–N(2)–S(4), 153.3°;

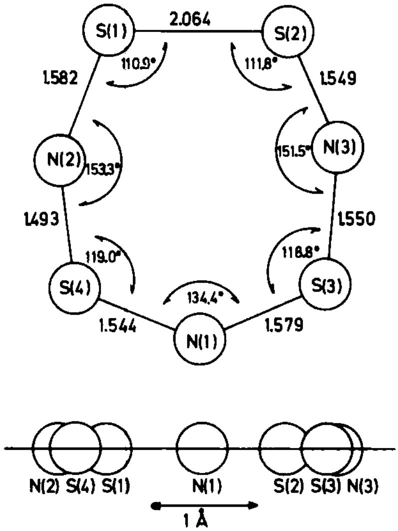


FIG. 48. Structure of the $[S_4N_3]^+$ ring (*45*).

S(2)–N(3)–S(3), 151.5°; S(3)–N(1)–S(4), 134.4°). Some publications on the electronic structure of the $[S_4N_3]^+$ cation have also appeared (*7*, *28*, *65*, *141*, *154*).

IV. Bonding Relationships of the S–N Group

In order to characterize the S–N bond in sulfur–nitrogen compounds various attempts have been made to establish a relationship between the S–N bond distance (d_{SN}) and the bond order (N_{SN}). The resulting linear dependence (*10*, *28*, *66*, *67*) of d_{SN} and N_{SN} can, however, only be considered as an approximation. The values of N_{SN} found for the larger S–N distances are certainly too high. Since reliable values for the force constant f_{SN} and for d_{SN} are available for some S–N compounds, including NSF and NSF_3, a relationship between f_{NS} and d_{NS} has been established which takes the form $f_{NS} = 145d_{NS}^{-7.00}$ (cf. Fig. 48). Table III shows force constants and bond distances for some SN compounds. Here force constants have been deduced from measured bond distances or, conversely, bond distances from known force constants for the relationship given above. The values of the bond order calculated from force constants are also included. From the curve it is also possible to

TABLE III

FORCE CONSTANTS, SN DISTANCES, AND BOND ORDER OF SULFUR–NITROGEN COMPOUNDS *(95)*[a]

Compound	r_{NS} [Å]	f_{NS} [mdyne/Å]	N_{NS}
NSF_3	1.416	12.55	2.7
NSF	1.446	10.71	2.4
NSCl	(1.46)	10.02	2.2
HNSO	(1.50)	8.3	1.9
$S_4N_4F_4$	1.54	(6.9)	1.7
$S_4N_3^+$	1.55	(6.6)	1.6
α-$S_3N_3O_3Cl_3$	1.564	(6.2)	1.5
$S_3N_3Cl_3$	1.605	(5.3)	1.4
S_4N_4	1.63	(4.6)	1.2
$S_4N_4F_4$	1.66	(4.1)	1.1
$S_4N_4H_4$	1.67	(3.9)	1.1
NH_2SO_3H	1.73	3.1	0.8

[a] Numbers in parentheses are calculated values.

determine f_{SN} values and the corresponding bond orders for cyclic compounds for which d_{SN} values are known (Fig. 49).

The following example shows that the equation given above relating f_{NS} and d_{NS} is more satisfactory than the linear relationship. The ^{14}N

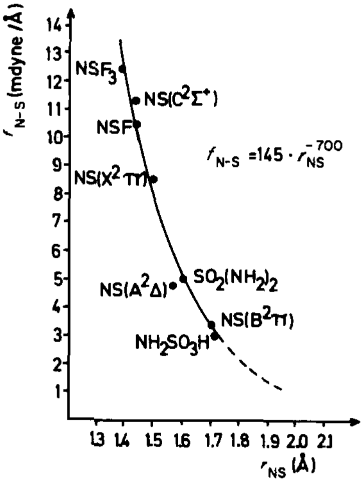


FIG. 49. Force constant, f_{NS}, as a function of the SN distance, d_{NS}.

chemical shift for S_4N_4 has a value of 485 ± 20 ppm, which is near to the value for an S–N single bond (530 to 540 ppm), whereas the ^{14}N shift for $[S_4N_3]^+$ lies at 235 ppm (*167*). The measured value is too high if the S–N bond order of 1.5 is assumed for S_4N_4 based on the linear relationship) (*10*, *28*, *67*). If, however, a value of 1.2 for S_4N_4 is taken from Table III, the ^{14}N shift compared with that of $S_4N_3^+$ falls into place. The bond orders determined here may be compared with bond energies determined experimentally. Some values are noted in Table IV. They do not show the expected trend and apparently the range of error in data obtained by the various methods is too large [cf. also (*185*)].

TABLE IV

NS Bond Order, N_{SN}, and NS Bond Energy, d_{NS}[a]

	NSF_3	NS^+	NSF	$NCNSF_2$	$(FSO_2)_2NF$	FSO_2NF_2	F_5SNF_2
$d_{(NS)}$	93 (*186*)	122.5 (*185*)	71 (*186*)	75 (*95*)	48 (*190*)	39 (*190*)	32 (*190*)
N_{SN}	2.7	2.6 (*85b*)	2.4	2.2	—	—	—

[a] Numbers in parentheses are reference citations.

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