

Gmelin Handbook of Inorganic Chemistry

8th Edition

F Perfluorohalogenoorgano Compounds of Main Group Elements

Supplement Volume 2



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8th Edition

F **Perfluorohalogenoorgano** **Compounds** **of Main Group Elements**

Supplement Volume 3

Compounds with Elements of the Main Group 6
(S^{IV}, S^{VI}, Se, Te) and with I

with 3 illustrations

By Alois Haas

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8th Edition

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Perfluorohalogenoorgano Compounds of Main Group Elements

Part 1

Compounds of Sulfur — 1973

Part 2

Compounds of Sulfur, Selenium, and Tellurium — 1973

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Suppl. Vol. 2

Sulfur(II) Compounds — 1986

Suppl. Vol. 3

Compounds with S^{IV}, S^{VI}, Se, Te and with I — 1987 (present volume)

Preface

This third volume of the Supplement Series supplying the Main Volumes of the series "Perfluorohalogenoorgano Compounds of Main Group Elements", Part 1 to 9, completes the treatment of the compounds of the Main Group VI elements. It covers sulfur(IV) compounds, sulfonic acids, sulfonic anhydrides, and sulfonates, sulfur(VI) oxides, sulfonyl nitrogen compounds, sulfonyl halides, sulfur(VI) halides, and the compounds of selenium and tellurium. It also includes the perfluorohalogenoorgano compounds of iodine in oxidation states higher than one and contains a formula index for the Supplement Volumes 1, 2, and 3. The Supplement Series will be concluded by the description of the nitrogen compounds.

Concept, organization, and selection as to the coverage of the material are the same as in the Main Volumes. Title compounds are newly synthesized ones as well as those compounds already referred to in the Main Volumes and for which new facts have been published.

Conventions as to the presentation of the data are given in the prefaces of the Main Volumes. In contrast to the convention for NMR chemical shifts used previously, chemical shifts downfield from the standard are designated as positive, according to the recommendations of the IUPAC Commission on Molecular Structure and Spectroscopy (Pure and Applied Chemistry 29 [1972] 625/8, 45 [1976] 217/9).

I wish to thank Prof. Dr. Dr. h.c. E. Fluck and his co-workers for their excellent cooperation. I also wish to take the opportunity to express my appreciation to colleagues who assisted me by providing reprints and patents.

Bochum, November 1986

A. Haas

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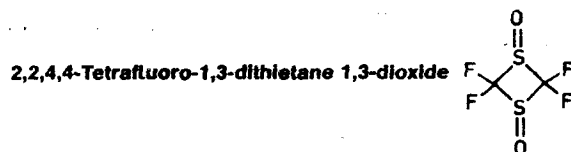
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6 Perfluorohalogenoorgano Compounds of Main Group 6 Elements (Continuation)

6.2.2 Perfluorohalogenoorganosulfur(IV) Compounds

Results of earlier investigations are reported in Part 2, 1973, pp. 50/76.

6.2.2.1 Preparation



Thiocarbonyl difluoride S-oxide $F_2C=S=O$

Thiocarbonyl chloride fluoride S-oxide $FClC=S=O$

The dithietanoxide is prepared in 63% yield by slowly adding 2,2,4,4-tetrafluoro-1,3-dithietane to a solution of trifluoroperoxyacetic acid in CH_2Cl_2 cooled with ice. The temperature of the reaction, which is finished after 2 h, should not exceed $5^\circ C$. On adding the dithietane oxide to trifluoromethaneperoxysulfonic acid (mixture of $(CF_3SO_2)_2O$ and H_2O_2) at $-5^\circ C$ the dithietane dioxide (trans isomer) is obtained in 39% yield after a reaction time of 7 to 8 hours [84]. It also forms in the reaction of tetrafluoro-1,3-dithietane with CrO_3 in fuming HNO_3 [92]. The dithietane dioxide decomposes at $480^\circ C$ and 10^{-2} Torr to give $F_2C=S=O$ (characterized only by its mass spectrum) [84].

MO calculations were carried out for $F_2C=S=O$ and $FClC=S=O$ [60], see p. 13.

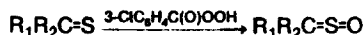
S-Trifluoromethylcarbonochloridodithioate S-oxide $CF_3SC(Cl)=S=O$

S-Trifluoromethylcarbonobromidodithioate S-oxide $CF_3SC(Br)=S=O$

SS,SS-Bis(trifluoromethyl)carbonothiobis(dithioperoxoate) S-oxide $(CF_3SS)_2C=S=O$

Bis(trifluoromethyl)carbonotrithioate S-oxide $(\text{CF}_3\text{S})_2\text{C}=\text{S}=\text{O}$

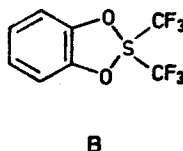
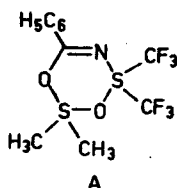
Thiocarbonyl S-oxides are prepared in ether at 0°C according to:



R_1 , R_2 , and % yield in parentheses are given: CF_3S , Cl (64); CF_3S , Br (20); CF_3SS , CF_3SS (37); CF_3S , CF_3S (76) [35].

Bis(trifluoromethyl) sulfoxide $(\text{CF}_3)_2\text{SO}$ **Pentafluoroethyl trifluoromethyl sulfoxide** $\text{C}_2\text{F}_5\text{S}(\text{O})\text{CF}_3$ **Bis(pentafluoroethyl) sulfoxide** $(\text{C}_2\text{F}_5)_2\text{SO}$ ***n*-Pentafluoropropyl trifluoromethyl sulfoxide** $\text{C}_3\text{F}_7\text{S}(\text{O})\text{CF}_3$

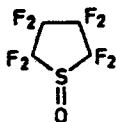
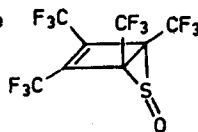
$(\text{CF}_3)_2\text{SO}$ (white solid, colorless liquid) is formed almost quantitatively by hydrolysis or by storage of $(\text{CF}_3)_2\text{SF}_2$ at 20°C (12 h) in glass vessels [1] and in 70% yield from $(\text{CF}_3)_2\text{SF}_2$ and anhydrous HCl at 20°C (24 h) in a Pyrex vessel [61]. Moreover it forms by hydrolysis of the sulfuranes A and B, and by thermolysis of the sulfurane A at 150°C [36], and by the reaction of $(\text{CF}_3)_2\text{S}(\text{OCF}_3)$ with H_2O , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, or $(\text{CF}_3)_2\text{C}(\text{CH}_3)\text{OH}$ [41, 42].



No new methods of preparation (see Pt. 2, p. 50) for $\text{C}_2\text{F}_5\text{S}(\text{O})\text{CF}_3$, $(\text{C}_2\text{F}_5)_2\text{SO}$, or $\text{C}_3\text{F}_7\text{S}(\text{O})\text{CF}_3$ have been reported; for physical properties, see p. 20.

Bis(pentafluorophenyl) sulfoxide $(\text{C}_6\text{F}_5)_2\text{SO}$ **Bis(4-trifluoromethyltetrafluorophenyl) sulfoxide** $(4\text{-CF}_3\text{C}_6\text{F}_4)_2\text{SO}$

Reactions of $4\text{-RC}_6\text{F}_4\text{MgBr}$ ($\text{R} = \text{F}, \text{CF}_3$) with SOCl_2 in ether yield $(\text{C}_6\text{F}_5)_2\text{SO}$ in 78% and $(4\text{-CF}_3\text{C}_6\text{F}_4)_2\text{SO}$ in 88% yield, respectively [2]. $(\text{C}_6\text{F}_5)_2\text{SO}$ is also obtained in 40% yield by the reaction of $\text{C}_6\text{F}_5\text{H}$ and $\text{C}_6\text{F}_5\text{S}(\text{O})\text{F}$ in SO_2 in the presence of SbF_5 at -30°C [3] and in the reaction of $\text{C}_6\text{F}_5\text{Li}$ in ether with *cis*- $\text{SF}_4(\text{OCF}_3)_2$, SF_5Cl , or SF_5Br at -78°C (5 h) in about 50 to 60% yield [40].

Octafluorotetrahydrothiophene 1-oxide**1,2,3,4-Tetrakis(trifluoromethyl)-5-thiabicyclo[2.1.0]pentane S-oxide**

The first compound is formed from $\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{SF}_2$ in contact with glass and by the reaction of the difluoride (1.6-fold excess) with HCl in a Pyrex bulb at 25°C (1 h, 87% yield) [4]. The tetrakis(trifluoromethyl)-substituted Dewar thiophene (see Suppl. Vol. 2, p. 17) is rapidly oxidized by $\text{CF}_3\text{C}(\text{O})\text{OOH}$ to yield the second compound [5].

Trifluoromethanesulfinic acid $\text{CF}_3\text{S}(\text{O})\text{OH}$ and **sulfinates** $\text{MOS}(\text{O})\text{CF}_3$, $\text{M} = \text{Na}, \text{K}, \text{Cs}, \text{Ag}, \frac{1}{2} \text{Zn}$

Trifluoroethenesulfinic acid $\text{CF}_2=\text{CFS}(\text{O})\text{OH}$ and **lithium salt** $\text{LiOS}(\text{O})\text{CF}=\text{CF}_2$

Perfluoroalkanesulfinic acids $\text{R}_1\text{S}(\text{O})\text{OH}$, $\text{R}_1 = (\text{CF}_3)_2\text{CF}, \text{C}_4\text{F}_9, \text{C}_8\text{F}_{17}$

1-Chloro-1,2,2,2-tetrafluoroethanesulfinic acid $\text{CF}_3\text{CFCIS}(\text{O})\text{OH}$

On passing $\text{CF}_3\text{SO}_2\text{F}$ into a vigorously stirred suspension of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ in $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ and refluxing the mixture, $\text{CF}_3\text{S}(\text{O})\text{OH}$ (74% yield) is obtained [71] (see also Pt. 2, p. 50).

Pyrolysis of $\text{C}_6\text{H}_5\text{CH}_2\text{CR}(\text{C}_6\text{H}_5)\text{OS}(\text{O})\text{CF}_3$ at 200°C for $\text{R} = \text{H}$ and at 70°C for $\text{R} = \text{CH}_3$ or of $\text{C}_6\text{H}_5\text{C}(\text{O})\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{OS}(\text{O})\text{CF}_3$ at 160°C yields $\text{CF}_3\text{S}(\text{O})\text{OH}$ [33]. The salts $\text{MOS}(\text{O})\text{CF}_3$ ($\text{M} = \text{Na}, \text{K}, \text{Ag}$) are prepared by neutralizing $\text{CF}_3\text{S}(\text{O})\text{OH}$ with stoichiometric amounts of M_2CO_3 in absolute ethyl alcohol. The yields are 98% for $\text{M} = \text{Na}$, 96% for $\text{M} = \text{K}$, and 81% for $\text{M} = \text{Ag}$ [6]. Another method of preparation of $\text{KOS}(\text{O})\text{CF}_3$ is based on the reaction of *N*-phenacylphenyl trifluoromethanesulfonamide and K_2CO_3 in dry acetone at 25°C (2 d) [63]. $\text{KOS}(\text{O})\text{CF}_3$ is prepared on adding $\text{CF}_3\text{SO}_2\text{Cl}$ over a 10 min period to KI (1:2) stirred in cold acetone [33] and in almost quantitative yields by elimination of CF_3SO_2^- from $\text{C}_6\text{H}_5\text{C}(\text{O})\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{OS}(\text{O})\text{CF}_3$ in CH_3CN with K_2CO_3 at 20°C (36 h) [70]. Reacting $\text{KOS}(\text{O})\text{CF}_3$ with AgNO_3 in CH_3CN at 25°C (2 h) yields quantitatively the silver salt [63].

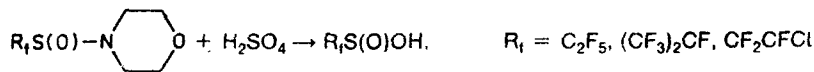
Passing $\text{CF}_3\text{SO}_2\text{F}$ into a suspension of NaN_3 in CH_3OH at 60°C (4 h) followed by stirring the mixture at this temperature for additional 12 h gives $\text{NaOS}(\text{O})\text{CF}_3$ in 93% yield. Addition of a solution of $\text{CF}_3\text{SO}_2\text{N}_3$ in CH_3OH to a stirred suspension of NaN_3 in CH_3OH gives after standing at 20°C for 48 h the salt in 71% yield [69].

$\text{CsOS}(\text{O})\text{CF}_3$ is prepared by heating CsF and the sulfinates $\text{ROS}(\text{O})\text{CF}_3$ with $\text{R} = (\text{CF}_3)_2\text{CH}$ (40°C , 10 h), $\text{R} = \text{CF}_3(\text{CH}_3)_2\text{C}$ (50°C , 10 h), and $\text{R} = (\text{CF}_3)_2\text{CH}_3\text{C}$ (100°C , 10 h). The salt was characterized by its reaction with ClF to give $\text{CF}_3\text{S}(\text{O})\text{Cl}$ only. Similarly $(\text{CF}_3)_2\text{CHOS}(\text{O})\text{CF}_3$ reacts with Ag_2O at 150°C (72 h) to yield $\text{AgOS}(\text{O})\text{CF}_3$ [8]. For preparation of $\text{Zn}[\text{OS}(\text{O})\text{CF}_3]_2$, see Pt. 2, p. 51.

$\text{LiCF}=\text{CF}_2$ reacts with SO_2 in ether to yield after 2 h $\text{LiOS}(\text{O})\text{CF}=\text{CF}_2$. Acidification of the salt with 20% H_2SO_4 gives $\text{CF}_2=\text{CFS}(\text{O})\text{OH}$ in 53% yield [72].

On dropping $C_4F_9SO_2F$ into a solution of $N_2H_4 \cdot H_2O$ in C_2H_5OH the mixture warms up to $60^\circ C$ yielding $C_4F_9S(O)OH$ (93%). Similarly $C_6F_{17}S(O)OH$ is obtained in 93.9% yield from $C_6F_{17}SO_2F$ in ether and $N_2H_4 \cdot H_2O$. In both cases the acids are freed with HCl gas [71].

The sulfinic acids $R_fS(O)H$ with $R_f = C_2F_5$ (84% yield) [87], $(CF_3)_2CF$ (90% yield) [73], and CF_3CFCl (81% yield) [37] are obtained from the corresponding morpholide according to:



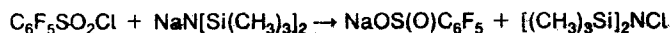
Sodium pentafluorobenzenesulfinate $NaOS(O)C_6F_5$

Lithium pentafluorobenzenesulfinate monohydrate $LiOS(O)C_6F_5 \cdot H_2O$

1,2-Dilithium tetrafluoro-1,2-benzenedisulfinate monohydrate $1,2-[LiOS(O)]_2C_6F_4 \cdot H_2O$

1,4-Dilithium tetrafluoro-1,4-benzenedisulfinate monohydrate $1,4-[LiOS(O)]_2C_6F_4 \cdot H_2O$

The sodium salt is prepared in 92% yield by reacting $C_6F_5SO_2Cl$ with $NaN[Si(CH_3)_3]_2$ in ether at $-30^\circ C$ [83] according to



By passing dry SO_2 into solutions of LiC_6F_5 , of $1,2-Li_2C_6F_4$, or of $1,4-Li_2C_6F_4$ in hexane at $-78^\circ C$ (0.5 to 1 h) the corresponding lithium salts are obtained as monohydrates [7].

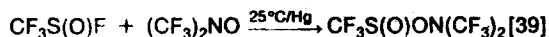
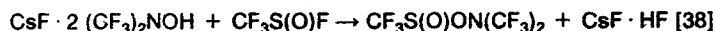
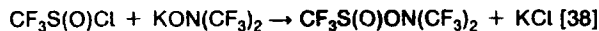
***n*-Nonafluorobutanesulfinic anhydride** $[n-C_4F_9S(O)]_2O$

Nonafluoro-*tert*-butyl trifluoromethanesulfinate $CF_3S(O)OC(CF_3)_3$

O-Trifluoromethylsulfinylbis(trifluoromethyl)hydroxylamine $CF_3S(O)ON(CF_3)_2$

Heating a mixture of $C_4F_9S(O)OH$ and $C_4F_9S(O)Cl$ at $50^\circ C$ (1 h) followed by distillation gives $[n-C_4F_9S(O)]_2O$ (80% yield) [10]. $CF_3S(O)Cl$ reacts with $(CF_3)_3COH \cdot N(CH_3)_3$ at $25^\circ C$ (1 h) in the presence of CsF to give $CF_3S(O)OC(CF_3)_3$ (70% yield) [8], which is also prepared by the reaction of excess $CF_3S(O)Cl$ with $HgCl[OC(CF_3)_3]$ [76].

$CF_3S(O)ON(CF_3)_2$ is synthesized by any of the three following methods:

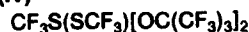


Bis(trifluoromethoxy)bis(trifluoromethyl)sulfur(IV) $(CF_3)_2S(OCF_3)_2$

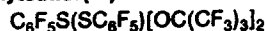
Nonafluoro-*tert*-butoxy(trifluoromethyl)sulfur(IV) oxide $CF_3[(CF_3)_3CO]SO$

Chlorobis(nonafluoro-*tert*-butoxy)trifluoromethylsulfur(IV) $CF_3[(CF_3)_3CO]_2SCl$

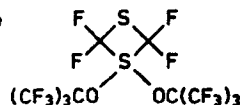
Bis(nonafluoro-*tert*-butoxy)(trifluoromethylsulfanyl)trifluoromethylsulfur(IV)



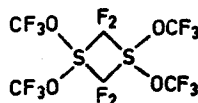
Bis(nonafluoro-*tert*-butoxy)(pentafluorophenylsulfanyl)pentafluorophenylsulfur(IV)



3,3-Bis(nonafluoro-*tert*-butoxy)-2,2,4,4-tetrafluoro-1,3-dithietane



1,1,3,3-Tetrakis(trifluoromethoxy)-2,2,4,4-tetrafluoro-1,3-dithietane



$(\text{CF}_3)_2\text{S}(\text{OCF}_3)_2$ (pale yellow liquid) is obtained by photolysis of a mixture of CF_3SCF_3 and CF_3OCl at 25°C (20 h, Hanovia UV lamp). Under similar conditions 2,2,4,4-tetrafluoro-1,3-dithietane reacts with CF_3OCl forming the 1,1,3,3-tetramethoxydithietane [41, 42].

CF_3SCl and $(\text{CF}_3)_3\text{COCl}$ react at 0°C (5 h) to give $\text{CF}_3[(\text{CF}_3)_3\text{CO}]_2\text{SCl}$ (68% yield). Excess $\text{CF}_3\text{S}(\text{O})\text{Cl}$ reacts with $\text{HgCl}[\text{OC}(\text{CF}_3)_3]$ at 0°C (24 h) to form $\text{CF}_3[(\text{CF}_3)_3\text{CO}]_2\text{SO}$ (95% yield) [76]. When $(\text{CF}_3)_3\text{COCl}$ and CF_3SSCF_3 were co-condensed at -196°C and then warmed to 0°C (72 h) $\text{CF}_3\text{S}(\text{SCF}_3)[\text{OC}(\text{CF}_3)_3]_2$ (colorless liquid) is formed [54, 76]. The reaction with $\text{C}_6\text{F}_5\text{SSC}_6\text{F}_5$ at 0°C (24 h) gave $\text{C}_6\text{F}_5\text{S}(\text{SC}_6\text{F}_5)[\text{OC}(\text{CF}_3)_3]_2$ [54]. Similarly tetrafluoro-1,3-dithietane reacts with $(\text{CF}_3)_3\text{COCl}$ at 0°C (24 h) to form the 3,3-di-*tert*-butoxydithietane in 95% yield [76].

1,3-Bis(trifluoromethyl)-1*H*,3*H*-1,3,2,4-dithiadiazole $\text{F}_3\text{C}-\text{S}-\text{N}=\text{N}-\text{S}-\text{CF}_3$

The compound described in Pt. 1, p. 118, does not exist. The physical data published are identical with those of $(\text{CF}_3\text{S})_2\text{NCH}_2\text{N}(\text{SCF}_3)_2$ [85].

Perfluorohexanesulfinyl azide $\text{C}_6\text{F}_{13}\text{S}(\text{O})\text{N}_3$

Poly(perfluorohexanesulfonylnitrogen) $[\text{C}_6\text{F}_{13}\text{S}(\text{O})\text{N}]_x$

Equimolar quantities of $\text{C}_6\text{F}_5\text{S}(\text{O})\text{Cl}$ and $[(\text{C}_2\text{H}_5)_4\text{N}]\text{N}_3$ reacted in CH_2Cl_2 at -50°C to yield $\text{C}_6\text{F}_{13}\text{S}(\text{O})\text{N}_3$ which was identified by the antisymmetric N_3 stretching of the azide at 2122 cm^{-1} (N_3^- ion: 2006 cm^{-1}). The band decreased to zero intensity in about one minute. When the reaction is carried out at 0°C in CH_2Cl_2 , $(\text{CH}_3)_2\text{CO}$, or CH_3CN as solvents $[\text{C}_6\text{F}_{13}\text{S}(\text{O})\text{N}]_x$ is formed. The oligomer can be prepared in 81% yield from $\text{C}_6\text{F}_{13}\text{S}(\text{O})\text{Cl}$ and NaN_3 at 20°C (60 h, stirring) [26].

Perfluoroalkanesulfinamides $\text{R}_1\text{S}(\text{O})\text{NH}_2$, $\text{R}_1 = \text{CF}_3$, $n\text{-C}_4\text{F}_9$

Pentafluorobenzenesulfinamide $\text{C}_6\text{F}_5\text{S}(\text{O})\text{NH}_2$

A new method of preparation for $\text{CF}_3\text{S}(\text{O})\text{NH}_2$ (see Pt. 2, p. 52) has not been reported. $n\text{-C}_4\text{F}_9\text{S}(\text{O})\text{NH}_2$ is prepared in 71% yield from NH_3 and $n\text{-C}_4\text{F}_9\text{S}(\text{O})\text{Cl}$ in ether [10]. $\text{C}_6\text{F}_5\text{S}(\text{O})\text{NH}_2$

can be synthesized either by oxidation of $C_6F_5SNH_2$ with active MnO_2 in C_6H_6 at $20^\circ C$ (40 h) in 70.5% yield or by ammonolysis of $C_6F_5S(O)Cl$ in ether in 79% yield [9].

N,N'-Bis(trifluoromethylsulfinyl)urea $[CF_3S(O)NH]_2CO$

N'-Trifluoromethylsulfinyl-N-trifluoromethylsulfonylurea $CF_3SO_2NHC(O)NHS(O)CF_3$

The urea derivatives are formed either by refluxing $CF_3S(O)NCO$ with $CF_3S(O)NH_2$ in benzene (95% yield) or by reacting CF_3SO_2NCO with $CF_3S(O)NH_2$ at $0^\circ C$ (93% yield) [6].

N-Sulfinyl-trifluoromethanesulfinamide $CF_3S(O)NSO$

Trifluoromethanesulfinyl isocyanate $CF_3S(O)NCO$

n-Nonafluorobutanesulfinyl isocyanate $n-C_4F_9S(O)NCO$

Equimolar amounts of $SOCl_2$ and $CF_3S(O)NHSi(CH_3)_3$ react at $15^\circ C$ (5 h) to form $CF_3S(O)NSO$ (52% yield) which is also obtained from $CF_3S(O)N[Si(CH_3)_3]_2$ [6]. The two isocyanates are made either by condensing the corresponding sulfinamides $R_fS(O)NH_2$ with $ClSO_2NCO$ at $-80^\circ C$ and then warming the mixture to $100^\circ C$ or by treating $AgNCO$ with $R_fS(O)Cl$ at $60^\circ C$. $CF_3S(O)NCO$ is obtained in 95% and $n-C_4F_9S(O)NCO$ in 92% yield [10].

(Hexafluoroisopropylidene)trifluoromethanesulfinamide $CF_3S(O)N=C(CF_3)_2$

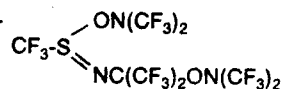
N-(Trichlorophosphoranylidene)trifluoromethanesulfinamide $CF_3S(O)N=PCl_3$

N-(Trichlorophosphoranylidene)-n-nonafluorobutanesulfinamide $n-C_4F_9S(O)N=PCl_3$

$CF_3S(O)F$ reacts with an excess of $LiN=C(CF_3)_2$ during warming from -196 to $+20^\circ C$ (12 h) to give $CF_3S(O)N=C(CF_3)_2$ (73% yield) [28]. It also results from the reaction of $(CF_3)_2C=NH$ with $CF_3S(O)F$ in the presence of CsF . The mixture is kept at $20^\circ C$ (12 h). After removing the volatile substances in vacuum the residue obtained is heated to $120^\circ C$ (10 h) giving $CF_3S(O)N=C(CF_3)_2$ in 23% yield [56].

When stoichiometric amounts of $R_fS(O)NHSi(CH_3)_3$ ($R_f = CF_3, n-C_4F_9$) and PCl_5 in CH_2Cl_2 are refluxed (0.5 h), $CF_3S(O)N=PCl_3$ and $n-C_4F_9S(O)N=PCl_3$ are formed in 52 and 48% yield, respectively [10].

Trifluoromethyl[1-trifluoromethyl-(N,N-bis(trifluoromethyl)aminoxy)-ethylimido][N,N-bis(trifluoromethyl)aminoxy]sulfur(IV)



$CF_3SN=C(CF_3)_2$ reacts with $(CF_3)_2NO$ at $20^\circ C$ (40 h, stirring) to give the sulfur compound [17].

Bis(trifluoromethyl)bis(hexafluoroisopropylideneamido)sulfur(IV) $(CF_3)_2S[N=C(CF_3)_2]_2$

The compound which is formed by ligand exchange of $(CF_3)_2S(OCF_3)_2$ with $LiN=C(CF_3)_2$ is unstable decomposing into CF_3SCF_3 and $[(CF_3)_2C=N]_2$ [42].

N-Trifluoroacetyl-trifluoromethanesulfinimidoyl fluoride $\text{CF}_3\text{S}(\text{F})=\text{NC}(\text{O})\text{CF}_3$

N-Cyano-trifluoromethanesulfinimidoyl fluoride $\text{CF}_3\text{S}(\text{F})=\text{NCN}$

N-Pentafluoroethyl-trifluoromethanesulfinimidoyl fluoride $\text{CF}_3\text{S}(\text{F})=\text{NC}_2\text{F}_5$

N-Heptafluoroisopropyl-trifluoromethanesulfinimidoyl fluoride $\text{CF}_3\text{S}(\text{F})=\text{NCF}(\text{CF}_3)_2$

N-(Heptafluoroisopropyl)-heptafluoro-2-propanesulfinimidoyl fluoride $(\text{CF}_3)_2\text{CFS}(\text{F})=\text{NCF}(\text{CF}_3)_2$

N-Pentafluoroethyl-trifluoromethanesulfinimidoyl chloride $\text{CF}_3\text{S}(\text{Cl})=\text{NC}_2\text{F}_5$

N-Heptafluoroisopropyl-trifluoromethanesulfinimidoyl chloride $\text{CF}_3\text{S}(\text{Cl})=\text{NCF}(\text{CF}_3)_2$

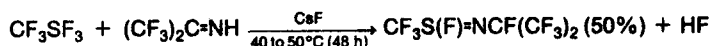
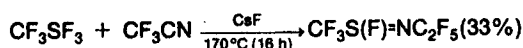
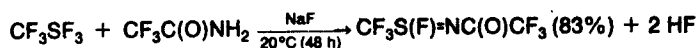
N-Pentafluoroethyl-trifluoromethanesulfinimidoyl isocyanate $\text{CF}_3\text{S}(\text{NCO})=\text{NC}_2\text{F}_5$

N-Heptafluoroisopropyl-trifluoromethanesulfinimidoyl isocyanate $\text{CF}_3\text{S}(\text{NCO})=\text{NCF}(\text{CF}_3)_2$

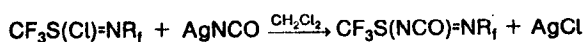
N-Pentafluoroethyl-trifluoromethanesulfinimidoyl isothiocyanate $\text{CF}_3\text{S}(\text{NCS})=\text{NC}_2\text{F}_5$

N-Heptafluoroisopropyl-trifluoromethanesulfinimidoyl isothiocyanate $\text{CF}_3\text{S}(\text{NCS})=\text{NCF}(\text{CF}_3)_2$

The compounds are prepared according to the following equations (yields in parentheses) [55]:

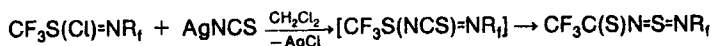


$\text{R}_1 = \text{C}_2\text{F}_5 (81\%), (\text{CF}_3)_2\text{CF} (91\%)$



$\text{R}_1 = \text{C}_2\text{F}_5, (\text{CF}_3)_2\text{CF} (30\%)$

The isothiocyanates are suspected as intermediates in the following metathesis:



Spectroscopic evidence favors the rearranged thiocarbonyl structure rather than the isothiocyanato structure [55].

$\text{CF}_3\text{S}(\text{F})=\text{NCF}(\text{CF}_3)_2$ is formed in the reaction of $(\text{CF}_3)_2\text{C}=\text{NH}$ with $\text{CF}_3\text{S}(\text{O})\text{F}$ and CsF at 20°C (12 h) [55, 56], by the reaction of CF_3SF_3 with $(\text{CF}_3)_2\text{C}=\text{NH}$ [90], and by the fluorination of $\text{CF}_3\text{SN}=\text{C}(\text{CF}_3)_2$ with XeF_2 (stirring for 1 h, cooling by ice) [17]. It is also obtained by condensing $\text{CF}_3\text{CF}=\text{CF}_2$ with $(\text{CF}_3)_2\text{CFN}=\text{SF}_2$ in the presence of CsF at 65°C (24 h). The mixture obtained is purified