PREPARATION AND REACTIONS OF PERFLUOROHALOGENOORGANOSULFENYL HALIDES*

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I. Introduction

Perfluorohalogenoorganosulfenyl halides are, like thiols, mercaptides, and thioketones, key compounds for the synthesis of new perfluorohalogenoorganomercapto derivatives. The high reactivity of the S—X bond (X = Cl, Br) toward electrophilic as well as nucleophilic reagents causes them to be highly valued starting materials for the synthesis of new derivatives. The chemistry of the not very stable sulfenyl fluorides has

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* English translation by Dr. N. Welcman, Department of Chemistry, Technion-Israel, Institute of Technology, Haifa, Israel.

hardly been investigated. However, the easily accessible and relatively stable sulfenyl chlorides have been studied extensively (*42*, *105*, *106*, *109*).

Particularly worth mentioning is the application of sulfenyl compounds in plant preservation. Of primary importance in this respect are the reactions of sulfenyl chlorides with secondary amines, which, with proper choice of the starting materials, lead to compounds with good fungicidal properties. The reactions of $(CH_3)_2NSO_2N(C_6H_5)H$, $(CH_3)_2NSO_2N(p\text{-}CH_3\text{—}C_6H_4)NH$ (*107*), phthalimide (*10*, *108*), and other secondary amines with the sulfenyl chlorides, $CFCl_2SCl$ (*107*) and $(CF_3S)_2$ CClSCl (*108*), furnish sulfenyl amides of great effectiveness.

II. Perfluorohalogenoorganosulfenyl Fluorides

A. PREPARATION

Evidence for the existence of this type of compound appeared only in 1967. Seel, Gombler, and Budenz (*145*) reacted trihalomethanesulfenyl chlorides with active potassium fluoride (prepared through degradation of potassium fluorosulfinate) at 150°C in the gas phase:

$$CF_nCl_{3-n}SCl + KF \longrightarrow CF_nCl_{3-n}SF \quad (n = 0, 1, 2, 3)$$

The products were identified by ^{19}F NMR spectroscopy. The chemical shifts δ (using $CFCl_3$ as an external standard) and spin-spin coupling constants J of liquid fluorides are listed in Table I. Compound CF_3SF could additionally be characterized by means of its infrared [ν(S—F) = 808 cm^{-1}] and mass spectra (among other fragments: CF_3SF^+, CF_3^+, SF^+) (*144*). The liquid product of the reaction between CCl_3SCl and HgF_2 or AgF, formulated in a previous publication (*102*) as CCl_3SF, proved later to be the isomeric $CFCl_2SCl$ (*73*, *99*, *150*).

TABLE I

CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR LIQUID SULFENYL FLUORIDES

Compound	$\delta(R_f)$ (ppm)	δ(SF) (ppm)	J_{F-F}(Hz)
CCl_3SF	—	249	—
$CFCl_2SF$	31 (Doublet)	265 (Doublet)	4.85
CF_2ClSF	45 (Doublet)	297 (Triplet)	6.85
CF_3SF	58 (Doublet)	351 (Quartet)	27

The best method for the preparation of CF_3SF is the reaction of CF_3SCl with HgF_2 in a nickel or platinum apparatus at 130°C, followed by removal of the reaction products by condensation in liquid nitrogen (*144*). Analogous reactions with metal fluorides lead to other sulfenyl fluorides (*102*, *189*):

$$CF_3CF_2CF_2SCl + AgF \xrightarrow[\text{autoclave}]{125°\text{–}160°C/6\ \text{hr}} CF_3CF_2CF_2SF$$

$$NF_2CCl_2SCl + AgF_2 \xrightarrow[\substack{\text{Monel metal}\\ \text{autoclave}}]{25°C/6\text{–}12\ \text{hr}} NF_2CCl_2SF$$

The compound isomeric with perfluoropropane-1-sulfenyl fluoride is formed by the pyrolysis of $[(CF_3)_2CF]_2SF_2$ (*136*):

$$(CF_3)_2CF—SF_2—CF(CF_3)_2 \xrightarrow{200°C} (CF_3)_2CFSF + SF_4 + (CF_3)_2CFCF(CF_3)_2$$

Difluorodifluoroaminomethanesulfenyl fluoride, NF_2CF_2SF, is formed among other products by the fluorination of AgSCN or KSCN (*32*). Perfluorooctanesulfenyl fluoride, $CF_3(CF_2)_7SF$, is obtained by electrolytic fluorination of the appropriate thiol (*152*).

A further reaction of general importance, the cleavage of disulfanes by means of a fluorinating agent, provides in the case of perfluoroaryl disulfanes the sulfenyl fluorides in good yield (*33*):

$$(4\text{-}R_fC_6F_4S)_2 + AgF_2 \xrightarrow[CFCl_2CF_2Cl]{20°C/10\ \text{hr}} 4\text{-}R_fC_6F_4SF \quad (R_f = F, CF_3)$$

B. PROPERTIES

All compounds, except the slightly green $(CF_3)_2CFSF$, are colorless liquids or colorless gases above their boiling points. The sulfenyl fluorides, $CF_nCl_{3-n}SF$ ($n = 0, 1, 2, 3$), are stable for some time in the liquid phase at −50°C and in the gaseous state at low pressures (~10 torr, 20°C). However, even at room temperature a fast isomerization takes place to sulfenyl chlorides containing the appropriately fluorinated trihalomethane:

$$CF_nCl_{3-n}SF \longrightarrow CF_{n+1}Cl_{2-n}SCl \quad (n = 0, 1, 2)$$

The speed of the fluorine–chlorine exchange at the sulfur atom decreases with increasing degree of fluorination at the carbon atom (*145*). Compound CF_3SF does not undergo exchange reactions at all; however, in the liquid phase it exists in equilibrium with the dimeric compound $CF_3SF_2SCF_3$. Both the monomer and the dimer are converted in a matter of a few hours into CF_3SSCF_3 and CF_3SF_3, particularly in the presence of potassium fluoride (*144*):

$$3CF_3SF \longrightarrow CF_3S(F_2)SCF_3 + CF_3SF \longrightarrow CF_3SSCF_3 + CF_3SF_3$$

The CF_3SF reacts with both base (e.g., Mg) and noble metals (e.g., Cu, Hg) to give the metal fluoride and CF_3SSCF_3. Only pure nickel made inert by treatment with SF_4 is somewhat stable toward CF_3SF (*144*).

The dihalodifluoroaminomethanesulfenyl fluorides, NF_2CX_2SF ($X = Cl, F$), are relatively stable substances. The dichloro compound is stable at 20°C toward isomerization and decomposition in metal containers; it reacts with oxygen to give $NF_2CCl_2S(O)F$ (*189*). On heating to 100°C in Pyrex containers, it decomposes to SO_2, $FN{=}CCl_2$, SiF_4 and minor quantities of $NF_2CCl_2S(O)F$. The difluoro compound hydrolyzes in water and bases and also shows oxidizing properties; in alcoholic solution iodine is liberated from an aqueous potassium iodide solution, sulfur being deposited at the same time (*32*).

III. Perfluorohalogenoorganosulfenyl Chlorides

A. PREPARATION

This class of compound has experienced considerable growth of interest in recent years through numerous new publications. Several common approaches for the preparation are discussed in the following.

1. *Fluorination with Metal Fluorides or HF*

The reaction of CCl_3SCl with an alkali metal fluoride (NaF) in a high-boiling polar solvent, e.g., tetramethylenesulfone or acetonitrile, leads in good yield to the important trifluoromethanesulfenyl chloride, CF_3SCl (*158, 159*):

$$CCl_3SCl + NaF \xrightarrow{170°-250°C} CF_3SCl \text{ (47\% yield)}$$

Among the by-products obtained in this reaction are minor quantities of CF_2ClSCl as well as the compounds CF_3SSCF_3 and $CF_3S(O)F$ (resulting from the reaction of CF_3SF_3 and SiO_2); this can be explained only by the intermediate formation of the acid fluoride, CF_3SF (*43*). This compound disproportionates into CF_3SF_3 and CF_3SSCF_3:

$$3CF_3SF \longrightarrow CF_3SF_3 + CF_3SSCF_3$$

This indirect proof of the appearance of CF_3SF leads to the conclusion that fluorination of sulfenyl chlorides of the series $CF_nCl_{3-n}SCl$ ($n = 0, 1, 2$) with alkali metal fluorides follows the mechanism observed in the formation of sulfenyl fluorides: the initial chlorine–fluorine exchange at the sulfur atom is followed by isomerization to the sulfenyl chloride containing the corresponding more highly fluorinated methyl group.

In accord with this mechanism, trichloromethanethiosulfenyl chloride, CCl_3SSCl, cannot be fluorinated under analogous reaction conditions (*44*). Plainly, the isomerization is here impossible on steric grounds because of the additional sulfur atom.

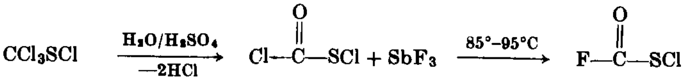
Further, the metal fluorides SbF_3 (with admixture of small quantities of $SbCl_5$), HgF_2, and AgF are also found suitable for the fluorination of sulfenyl halides, e.g.,

$$CF_2ClSCl + SbF_3 \longrightarrow CF_3SCl \text{ (11\% yield) } (187)$$

$$CCl_3SCl, CFCl_2SCl + SbF_3/SbCl_5 \xrightarrow{150°C} CF_2ClSCl \ (43)$$

$$CCl_3SCl + HgF_2 \text{ or } AgF \longrightarrow CFCl_2SCl \ (150)$$

The bifunctional chlorocarbonylsulfenyl chloride, obtainable through partial hydrolysis of trichloromethanesulfenyl chloride (*162*), is fluorinated by SbF_3 at the carbonyl group (*66, 67*):



$$CCl_3SCl \xrightarrow[-2HCl]{H_2O/H_2SO_4} Cl-\overset{\overset{\displaystyle O}{\|}}{C}-SCl + SbF_3 \xrightarrow{85°-95°C} F-\overset{\overset{\displaystyle O}{\|}}{C}-SCl$$

On fluorinating $CCl_3SN(C_2H_5)_2$ (prepared from CCl_3SCl and diethylamine) (*185*), a mixture of the mono- and difluoro compounds is obtained. The following cleavage with HCl provides the corresponding sulfenyl chlorides (*128, 185*):

$$CCl_3SN(C_2H_5)_2 + SbF_3 \longrightarrow CF_nCl_{3-n}SN(C_2H_5)_2 \xrightarrow{HCl} CF_nCl_{3-n}SCl \ (n = 1, 2)$$

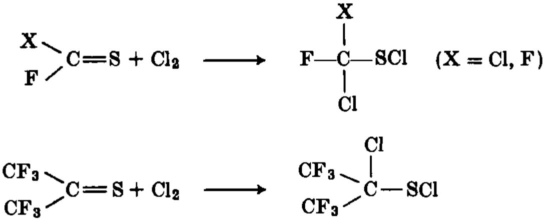
In a direct reaction of the amide with hydrogen fluoride only $CFCl_2SCl$ is obtained (*128*). This points again to an isomerization of the CCl_3SF formed initially. The reaction between CCl_3SCl and an excess of anhydrous hydrogen fluoride leads to the same product (*128*). This reaction is also feasible on a technical scale if the reagents are vigorously mixed and pressure as well as high temperature are applied. Under such conditions small quantities of CF_2ClSCl are also formed (*109*). According to a patented procedure (*141*), gas-phase fluorination with hydrogen fluoride at 180°C in the presence of a chromium oxide–fluoride catalyst [prepared by fluorination of chromium(III) hydroxide] furnishes CF_3SCl in 74% yield.

2. *Addition of Chlorine or Chlorine Monofluoride to the C=S Double Bond of Perhalogenothiocarbonyl Compounds*

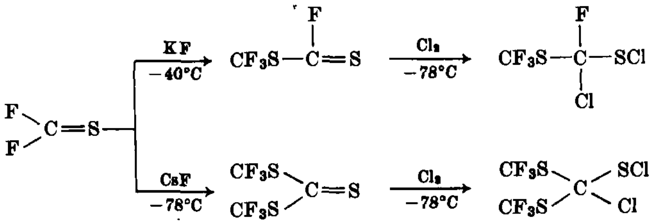
An important and widely applicable method for the synthesis of perfluorohalogenosulfenyl halides is based on the ability of the halogens

(Cl_2, Br_2) and interhalogen compounds (ClF) to add to C═S double bonds.

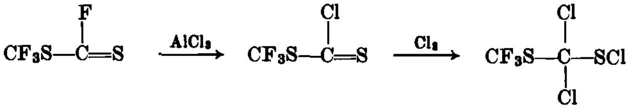
By this method of addition of chlorine to fluorothiocarbonyl chloride, thiocarbonyl difluoride (*109*), or hexafluorothioacetone (*120*), the respective sulfenyl chlorides are obtained:



Analogously, it is possible to react the linear compounds $CF_3SC(X)S$ ($X = F, SCF_3$), obtainable through catalytic dimerization or trimerization, in order to produce new sulfenyl chlorides (*51, 53*):

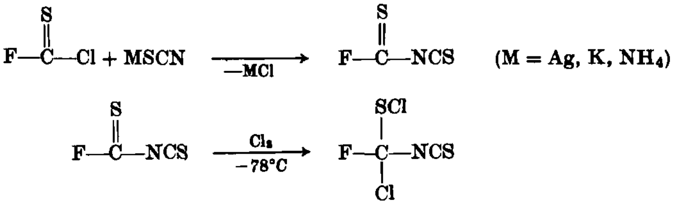


Trifluoromethylthiocarbonyl fluoride can be converted to the chloride by halogen exchange with aluminum trichloride. By chlorine addition this compound furnishes another sulfenyl chloride (*55*):



$$CF_3S{-}\overset{\displaystyle F}{\overset{|}{C}}{=}S \xrightarrow{AlCl_3} CF_3S{-}\overset{\displaystyle Cl}{\overset{|}{C}}{=}S \xrightarrow{Cl_2} CF_3S{-}\underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle Cl}{\overset{|}{C}}}}{-}SCl$$

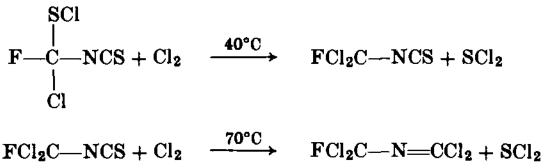
It is worth mentioning that fluorothiocarbonyl isothiocyanate, produced by the reaction of CSFCl with metal thiocyanates (*52*), combines with chlorine quantitatively at low temperatures at the C═S double bond, without suffering an attack on the isothiocyanate group (*21*):



$$F{-}\overset{\displaystyle S}{\overset{\|}{C}}{-}Cl + MSCN \xrightarrow[-MCl]{} F{-}\overset{\displaystyle S}{\overset{\|}{C}}{-}NCS \quad (M = Ag, K, NH_4)$$

$$F{-}\overset{\displaystyle S}{\overset{\|}{C}}{-}NCS \xrightarrow[-78°C]{Cl_2} F{-}\underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle SCl}{\overset{|}{C}}}}{-}NCS$$

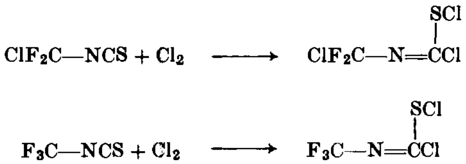
Only at elevated temperatures is the isothiocyanate group also attacked by further addition of chlorine with simultaneous elimination of sulfur dichloride. It is thus converted into the isocyanide dichloride group, without isolation of an intermediate:



$$F\text{—}\overset{\overset{\textstyle SCl}{|}}{\underset{\underset{\textstyle Cl}{|}}{C}}\text{—}NCS + Cl_2 \xrightarrow{40°C} FCl_2C\text{—}NCS + SCl_2$$

$$FCl_2C\text{—}NCS + Cl_2 \xrightarrow{70°C} FCl_2C\text{—}N{=}CCl_2 + SCl_2$$

The more highly fluorinated isothiocyanates, F_2ClC—NCS and F_3C—NCS, even at 80°C with chlorine yield only the iminochloromethanesulfenyl chlorides *(21)*:

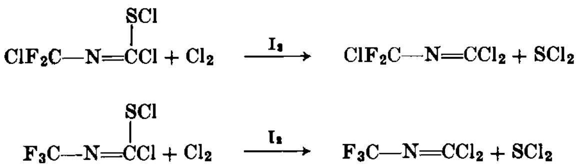


$$ClF_2C\text{—}NCS + Cl_2 \longrightarrow ClF_2C\text{—}N{=}\overset{\overset{\textstyle SCl}{|}}{C}Cl$$

$$F_3C\text{—}NCS + Cl_2 \longrightarrow F_3C\text{—}N{=}\overset{\overset{\textstyle SCl}{|}}{C}Cl$$

It may be assumed, therefore, that highly electronegative groups, such as CF_2Cl or CF_3, stabilize the imino compounds. Similar observations were made with aliphatic and aromatic iminochloromethanesulfenyl chlorides; the former are very unstable, but the latter are stable to some degree *(190)*.

In the presence of catalytic quantities of iodine, chlorination again proceeds further to the isocyanide dichlorides *(21)*:



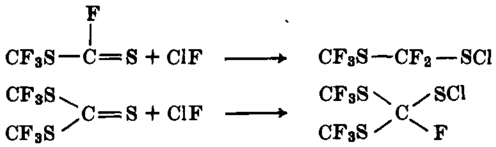
$$ClF_2C\text{—}N{=}\overset{\overset{\textstyle SCl}{|}}{C}Cl + Cl_2 \xrightarrow{I_2} ClF_2C\text{—}N{=}CCl_2 + SCl_2$$

$$F_3C\text{—}N{=}\overset{\overset{\textstyle SCl}{|}}{C}Cl + Cl_2 \xrightarrow{I_2} F_3C\text{—}N{=}CCl_2 + SCl_2$$

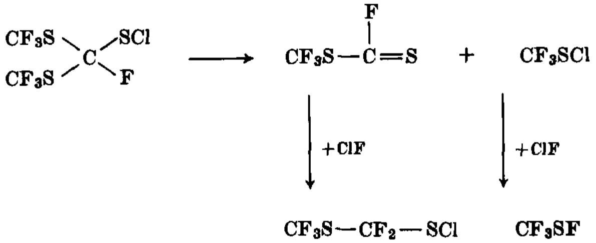
Chlorine monofluoride combines smoothly with thiocarbonyl compounds. For instance, the sulfenyl chlorides of the series CF_nCl_{3-n}-SCl ($n = 1, 2, 3$), which were already prepared by other methods, are obtained in good yield:

$$Cl_nF_{2-n}C{=}S + ClF \longrightarrow Cl_nF_{3-n}CSCl \quad (n = 0, 1, 2)\ \textit{(20)}$$

Addition of ClF to the dimeric and trimeric thiocarbonyl difluoride furnishes sulfenyl chlorides which were not accessible for a long time *(20)*:



In the latter reaction, rather large quantities of the disulfane, $(CF_3S)_2$-$CFSSCF_3$, are formed, as well as the decomposition products $CF_3SC(S)F$, CF_3SCl, and CF_3SCF_2SCl. Formation of these compounds is probably due to decomposition of the $(CF_3S)_2CFSCl$ initially formed to $CF_3SC(S)F$ and to CF_3SCl and the subsequent reactions with excess of ClF:



The relatively stable sulfenyl fluoride eventually combines in a competing reaction with unreacted $(CF_3S)_2C{=}S$ to give $(CF_3S)_2C(F)SSCF_3$.

3. *Chlorolysis of Perfluorohalogenoorganodisulfanes*

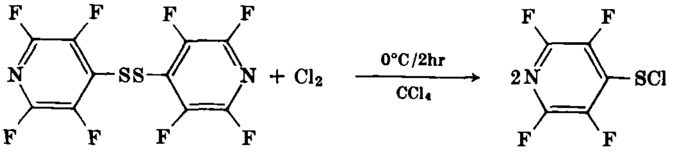
Chlorolysis of the corresponding disulfanes is a favorable procedure for the preparation of aliphatic, aromatic, and heterocyclic sulfenyl chlorides under not too demanding conditions [low temperature; mild chlorinating agents, such as SO_2Cl_2 (*14*) or CH_3SCl_3 (*15*)]. Perfluorinated sulfenyl chlorides can also be prepared by this procedure in special cases: a mixture of CF_3SSCF_3 and chlorine reacts in a Pyrex Carius tube under UV irradiation to form sulfenyl chloride in an equilibrium reaction (*84*):

$$CF_3SSCF_3 + Cl_2 \xrightleftharpoons{h\nu} 2CF_3SCl \quad \text{(about 50\% yield)}$$

The chlorination of $C_6F_5SSC_6F_5$ in an inert solvent furnishes the perfluorobenzene sulfenyl chloride (*137*):

$$C_6F_5SSC_6F_5 + Cl_2 \xrightarrow[CCl_4]{20°C/2\ hr} 2C_6F_5SCl$$

By passing an HCl-free stream of chlorine into a cooled solution of bis(2,3,5,6-tetrafluoropyridyl)disulfane, the sulfenyl chloride is obtained in 73% yield (*6*):



By the use of higher temperatures as well as by partial UV irradiation, it is possible to cleave the longer-chain disulfanes, e.g.,

$$\mathrm{CF_3CF_2CF_2SSCF_2CF_2CF_3 + Cl_2 \xrightarrow[25^\circ-130^\circ C]{h\nu} 2CF_3CF_2CF_2SCl} \quad (102)$$

$$\mathrm{CF_2ClCF_2SSCF_2CF_2Cl + Cl_2 \xrightarrow{80^\circ-90^\circ C} 2CF_2ClCF_2SCl} \quad (100)$$

$$\mathrm{(CF_3)_2CFSSCF(CF_3)_2 + Cl_2 \xrightarrow[reflux]{h\nu} 2(CF_3)_2CFSCl} \quad (3)$$

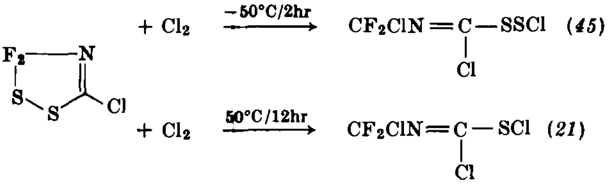
$$\mathrm{(CF_2ClCCl_2CF_2CFCl)_2S_2 + Cl_2 \xrightarrow{150^\circ-200^\circ C} 2CF_2ClCCl_2CF_2CFClSCl} \quad (88)$$

$$\mathrm{[(CF_3)_2CF(CF_2)_4]_2S_2 + Cl_2 \xrightarrow{150^\circ C} 2(CF_3)_2CF(CF_2)_4SCl} \quad (74)$$

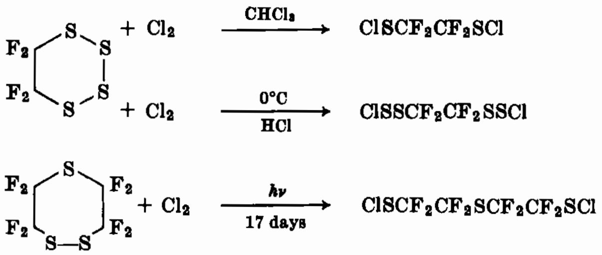
$$\mathrm{(CF_2ClCFCl)_2S_{\mathit{x}} + Cl_2 \xrightarrow{120^\circ C/7\ hr} 2CF_2ClCFClSCl} \quad (x = 2, 3) \quad (5)$$

On heating the sulfane mixture $[C_4F_9CF(CF_3)_2]_2S_n$ (average sulfur chain length $n = 2.5$) with chlorine for 125 hr at 105°C, the perfluorohexane-2-sulfenyl chloride is formed in appreciable yield (*86*, *127*). The patent literature (*5*, *19*, *87–89*, *127*) abounds with long-chain sulfenyl chlorides prepared according to this latter procedure, but physical data are lacking.

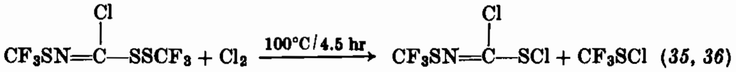
Cyclic disulfanes also undergo cleavage reactions. 5,5-Difluoro-3-chloro-1,2,4-dithiazole reacts with chlorine to give various sulfenyl chlorides depending on temperature:



Bifunctional sulfenyl chlorides are obtained in the reaction of 5,5,6,6-tetrafluoro-1,2,3,4-tetrathiane or perfluoro-1,2,5-trithiepane (*104*):

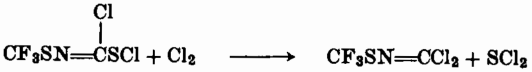


Cleavage with chlorine can also lead to the formation of fragments of different size, e.g.,



$$CF_3SN{=}C(Cl){-}SSCF_3 + Cl_2 \xrightarrow{100°C/4.5\ hr} CF_3SN{=}C(Cl){-}SCl + CF_3SCl \quad (35, 36)$$

To some extent this reaction is followed by one yielding an isocyanide dichloride:

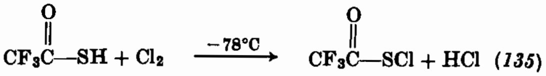


$$CF_3SN{=}C(Cl)SCl + Cl_2 \longrightarrow CF_3SN{=}CCl_2 + SCl_2$$

4. *Reactions of Perfluorohalogenoorganothiols or -mercaptides with Chlorine*

Chlorination of thiols serves for the preparation of temperature-sensitive sulfenyl halides, since the main reaction products are easily separated from the side products by fractional condensation, e.g.,

$$C_6F_5SH + Cl_2 \xrightarrow[CCl_4]{-10°C} C_6F_5SCl + HCl \quad (124,\ 137)$$



$$CF_3C(=O){-}SH + Cl_2 \xrightarrow{-78°C} CF_3C(=O){-}SCl + HCl \quad (135)$$

The reactions take place in several steps (*115*). First, the thiol is chlorinated to the appropriate sulfenyl chloride; then the latter reacts further with additional thiol to give the disulfane; finally, chlorolysis of the disulfane takes place.

A similar reaction occurs when heavy metal mercaptides are cleaved with chlorine, e.g.,

$$\left.\begin{array}{l} AgSCF_3 \\ \\ Hg(SCF_3)_2 \end{array}\right\} + 2Cl_2 \xrightarrow{-22°C} 2CF_3SCl + \left\{\begin{array}{l} AgCl \\ \\ HgCl_2 \end{array}\right. \quad (29, 84)$$

$$\left.\begin{array}{l} Pb(SC_6F_5)_2 \\ \\ Hg(SC_6F_5)_2 \end{array}\right\} + 2Cl_2 \xrightarrow[CCl_4]{0°C} 2C_6F_5SCl + \left\{\begin{array}{l} PbCl_2 \\ \\ HgCl_2 \end{array}\right. \quad (124, 137)$$

5. *Photolytically Initiated Addition of Sulfur Chlorides to Perfluorohalogenoolefins*

Addition of sulfur chlorides to perfluoroolefins furnishes a series of interesting sulfenyl chlorides (*100*):

$$CF_2{=}CF_2 + SCl_2 \xrightarrow{100°\text{–}110°C/5\ hr} CF_2ClCF_2SCl + CF_2ClCF_2SSCl$$

$$CF_2{=}CF_2 + S_2Cl_2 \xrightarrow{100°\text{–}120°C/6\ hr}$$

$$CF_2ClCF_2SCl + (ClCF_2CF_2)_2S + (ClCF_2CF_2S)_2 + (ClCF_2CF_2S)_2S$$

The reaction with SCl_2 can be effected advantageously under UV irradiation in the presence of phosphorus trichloride (*127*), e.g.,

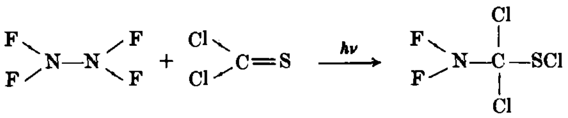
$$CF_3CF{=}CF_2 + SCl_2 \xrightarrow[5\%\ PCl_3]{h\nu/45°\text{–}50°C} CF_3CFClCF_2SCl \text{ or } CF_3C(CF_2Cl)FSCl$$

$$CFCl{=}CF_2 + SCl_2 \xrightarrow[5\%\ PCl_3]{h\nu/45\text{–}50°C} CF_2ClCFClSCl \text{ or } CFCl_2CF_2SCl$$

The mixture of isomers formed in any of these reactions could not be separated.

6. *Other Reactions*

Photolysis of a mixture of N_2F_4 and thiophosgene results in a remarkable addition; from a mixture of several compounds dichlorodifluoroaminomethanesulfenyl chloride can be separated (*188*):



Finally, it should be mentioned that in the meantime the series of the chlorodithioperfluorohalogenomethanes, $CF_nCl_{3-n}SSCl$ ($n = 1, 2, 3$), has been completed, although by very different means: $CFCl_2SSCl$, together with $CFCl_2SCl$ and S_2Cl_2, can be obtained by chlorination of bis(fluorodichloro)methane polysulfides, $CFCl_2S_nCFCl_2$ ($n > 2$) (*119*). The polysulfides are produced by warming $CFCl_2SCl$ with sulfur, or, alternatively, as side products in the industrial synthesis of $CFCl_2SCl$ from CCl_3SCl and HF (*109*). Compound $CF_2ClSSCl$ is formed in an attempt to fluorinate the isocyanide dichloride $F_2ClCSSN{=}CCl_2$; the isocyanide dichloride is an addition product of thiocarbonyl difluoride and $ClSN{=}CCl_2$ (*35*, *36*):

$$F_2C{=}S + ClSN{=}CCl_2 \xrightarrow[30\ hr]{h\nu} F_2ClCSSN{=}CCl_2 \xrightarrow[110°C]{SbF_3/TMS} CF_2ClSSCl + ClCN$$

The mechanism of this reaction is unknown. Compound CF_3SSCl can be prepared in 93% yield by splitting the disulfanes, R_2NSSCF_3 ($R = CH_3$, C_2H_5), that are obtained from *N*,*N*-dialkylaminosulfenyl chloride and $Hg(SCF_3)_2$, with hydrogen chloride (*16*):

$$R_2NSSCF_3 + 2HCl \xrightarrow{20°C} CF_3SSCl + R_2NH \cdot HCl$$

B. PROPERTIES

The sulfenyl chlorides are yellow or slightly yellow colored liquids, with the exception of C_3F_7SCl, which is orange (*102*) and $ClSCF_2CF_2SCF_2CF_2SCl$, which is colorless (*104*). They are air-stable at room temperature. The photolysis by irradiation for 14 days of CF_3SCl in a quartz tube leads to the formation of sulfur, CF_3Cl, S_2Cl_2, SCl_2, and CF_3SSCF_3 (*84*). These compounds are water-stable for several hours at room temperature, but they are decomposed by bases (*85*). They are freely soluble in most organic solvents, but immiscible with water.

Hydrolysis, which has been extensively studied in the case of CF_3SCl (*85*), is more complicated than implied by the equation

$$CF_3SCl + H_2O \longrightarrow CF_3SOH + HCl$$

On shaking CF_3SCl with an excess of water for 3 hr at 20°C, the yellow coloration disappears. After additional shaking for 9 hr, 55–60% CF_3SSCF_3 and COS are obtained as well as CF_3SO_2H. The solution, when made alkaline, also contains fluoride ions, the concentration of which corresponds to a 6% hydrolysis. The formation of the compounds isolated is best interpreted by the equation:

$$3CF_3SCl + 2H_2O \longrightarrow CF_3SSCF_3 + CF_3SO_2H + 3HCl$$

However, on shaking CF_3SCl with water for 12 to 24 hr, starting with too little and gradually increasing the amount of water until a fourfold excess is present, $CF_3SSO_2CF_3$ can also be isolated in an amount equivalent to that of CF_3SSCF_3:

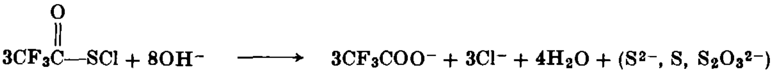
$$4CF_3SCl + 2H_2O \longrightarrow CF_3SSCF_3 + CF_3SO_2SCF_3 + 4HCl$$

The alkaline hydrolysis with a 15% NaOH solution generally proceeds as follows:

$$3CF_3SCl + 4NaOH \longrightarrow CF_3SSCF_3 + CF_3SO_2Na + 3NaCl + 2H_2O$$

If the reaction is run at 70°C, then CF_3SSCF_3 hydrolyzes to sulfur, S^{2-}, F^-, and CO_3^{2-}. At 95°C a complete hydrolysis of CF_3SO_2Na takes place producing CHF_3.

The hydrolysis of CF_3—C(O)SCl proceeds as follows (*159*):



$$3\mathrm{CF_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{—SCl} + 8\mathrm{OH^-} \longrightarrow 3\mathrm{CF_3COO^-} + 3\mathrm{Cl^-} + 4\mathrm{H_2O} + (\mathrm{S^{2-}}, \mathrm{S}, \mathrm{S_2O_3^{2-}})$$

Sulfenyl chlorides can be oxidized by means of chlorine water or hydrogen peroxide to sulfonyl chlorides:

$$\mathrm{RSCl} + 2\mathrm{Cl_2} + 2\mathrm{H_2O} \longrightarrow \mathrm{RSO_2Cl} + 4\mathrm{HCl} \quad [\mathrm{R} = \mathrm{CF_3}\,(85),\ \mathrm{CF_2ClCFCl}\,(5), \mathrm{C_6F_5}\,(134)]$$

$$\mathrm{ClSCF_2CF_2SCl} + 4\mathrm{Cl_2} + 4\mathrm{H_2O} \longrightarrow \mathrm{ClSO_2CF_2CF_2SO_2Cl} + 8\mathrm{HCl} \quad (104)$$

On shaking sulfenyl chlorides with mercury or a solution of potassium iodide, disulfanes are produced:

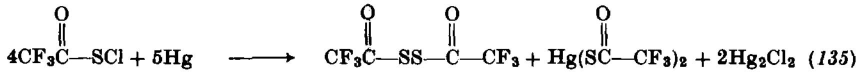
$$2\mathrm{RSCl} + 2\mathrm{KI} \longrightarrow \mathrm{RSSR} + \mathrm{I_2} + 2\mathrm{KCl} \quad [\mathrm{R} = \mathrm{CFCl_2}\,(150),\ \mathrm{CF_2ClCF_2}\,(100)]$$

$$x\mathrm{ClSCF_2CF_2SCF_2CF_2SCl} + 2x\mathrm{KI} \longrightarrow (\mathrm{SCF_2CF_2SCF_2CF_2S})_x + 2x\mathrm{KCl} + x\mathrm{I_2} \quad (104)$$

$$x\mathrm{ClSCF_2CF_2SCl} + 2x\mathrm{KI} \longrightarrow (\mathrm{SCF_2CF_2S})_x + 2x\mathrm{KCl} + x\mathrm{I_2} \quad (104)$$

$$2\mathrm{CF_3SCl} + 2\mathrm{Hg} \longrightarrow \mathrm{CF_3SSCF_3} + \mathrm{Hg_2Cl_2} \quad (84)$$

$$x\mathrm{ClSCF_2CF_2SCl} + 2x\mathrm{Hg} \longrightarrow (\mathrm{SCF_2CF_2S})_x + x\mathrm{Hg_2Cl_2} \quad (104)$$



$$4\mathrm{CF_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{—SCl} + 5\mathrm{Hg} \longrightarrow \mathrm{CF_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{—SS—}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{—CF_3} + \mathrm{Hg(S}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{—CF_3)_2} + 2\mathrm{Hg_2Cl_2} \quad (135)$$

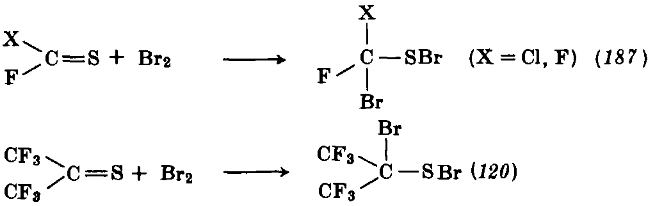
No reaction occurs between CF_3SCl and CO within 8 hr at 100°C. However, on irradiation of a mixture of CF_3SCl and CO with Pyrex-filtered light ($\lambda > 300$ nm), predominantly CF_3SSCF_3 and $COCl_2$ are formed, as well as minor amounts of $CF_3S—C(O)Cl$ (*157*).

Investigations of the halogen exchange between solid AgCl and liquid sulfenyl chlorides of the type $R_1R_2R_3CSCl$ (R_1, R_2, R_3 = F, Cl, CF_3, CF_3S) with the aid of radioactive ^{36}Cl (*12*) indicate that highly electronegative substituents induce polarization of the S—Cl bond and thereby increase the heterolytic reactivity of this bond.

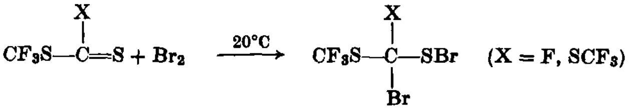
IV. Perfluorohalogenoorganosulfenyl Bromides

Relatively few perfluorohalogenoalkanesulfenyl bromides are presently known. These are orange-to-red colored substances which are prepared with difficulty and are too unstable to arouse interest. Apart from a few specific syntheses they may be obtained by the methods used for the preparation of sulfenyl chlorides.

Thiocarbonyl compounds add bromine to the C=S double bond, e.g.,



Dimeric and trimeric thiocarbonyl fluorides react in the same manner (*53*):



$$CF_3S{-}C(X){=}S + Br_2 \xrightarrow{20°C} CF_3S{-}CXBr{-}SBr \quad (X = F, SCF_3)$$

Compound $(CF_3S)_2CBrSBr$ could not be obtained in the pure state: ^{19}F NMR spectra have shown that in this case an equilibrium reaction takes place, which moves to the right only to the extent of 90%.

A chlorine–bromine exchange in fluorodichloromethanesulfenyl chloride by means of hydrogen bromide provides a route to additional sulfenyl bromides (*109*). After the initial halogen exchange at the sulfur, further addition of hydrogen bromide causes stepwise substitution at the methyl group:

$$CFCl_2{-}SCl \xrightarrow{48\%\ HBr} CFCl_2{-}SBr \xrightarrow{HBr} CFClBr{-}SBr \xrightarrow{HBr} CFBr_2{-}SBr$$

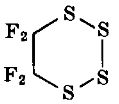
Several methods are available for the synthesis of CF_3SBr. Either CF_2BrSBr is fluorinated at 100°C with antimony trifluoride (*186*) or CF_3SCl is reacted with bromine cyanide over activated carbon at 70°C (*36*). Apart from that it is obtained always contaminated with CF_3SSCF_3 in the reaction between $Hg(SCF_3)_2$ and bromine (*31*) these compounds react at 0°C to give a mixture composed of 55% CF_3SBr and 45% CF_3SSCF_3.

The complete disproportionation of $CF_3S(O)Br$ to CF_3SBr and CF_3SO_2Br can also be regarded as a method for synthesizing CF_3SBr, since it can easily be separated from the sulfonyl bromide (*131*).

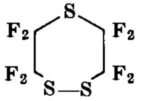
Trifluoroacetylsulfenyl bromide is obtained in a way analogous to that for the corresponding sulfenyl chloride, by bromination of the thiol (*135*):

$$CF_3{-}C(O)SH + Br_2 \longrightarrow CF_3{-}C(O)SBr + HBr$$

Bromine, too, causes the fission of cyclic sulfanes (*104*), e.g.,



$$+ Br_2 \longrightarrow BrSCF_2CF_2SBr$$



$$+ Br_2 \longrightarrow BrSCF_2CF_2SCF_2CF_2SBr$$

Like CF_3SSCl, although in lower yield, CF_3SSBr can be prepared, by fission of the S—N bond in *N*,*N*-dialkylaminotrifluoromethyl disulfanes with HBr (*16*):

$$R_2NSSCF_3 + 2BHr \longrightarrow CF_3SSBr + R_2NH \cdot HBr \quad (R = CH_3, C_2H_5)$$

The decrease in yield can be accounted for by partial decomposition of the quite unstable CF_3SSBr:

$$2CF_3SSBr \longrightarrow CF_3SSCF_3 + S_2Br_2 \quad (\longrightarrow Br_2 + 2S)$$

Bromination of CF_3SSCl with boron tribromide proceeds considerably better:

$$3CF_3SSCl + BBr_3 \longrightarrow 3CF_3SSBr + BCl_3$$

From this reaction CF_3SSBr can be isolated in 65% yield.

V. Reactions of Perfluorohalogenoorganosulfenyl Halides and Related Reactions

A. With Pseudohalides

The reaction of perfluorohalogenoalkanesulfenyl halides with silver pseudohalides leads to a group of compounds capable of undergoing a host of chemical changes. The first substances prepared in this way were the derivatives of trifluoromethanesulfenyl chloride (*28*):

$$CF_3SCl + AgX \longrightarrow CF_3SX + AgCl \quad (X = CN, SCN, SeCN, OCN)$$

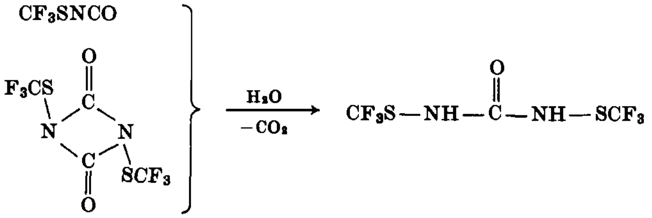
The thiocyanate is stable toward water for some period of time. However, the alkaline hydrolysis, in analogy with normal thiocyanates (*156*), causes rapid decomposition. Intermediates CF_3SH and HNCO are formed through cleavage of the CF_3S—C bond, but whereas the cyanate remains intact, the trifluoromethanethiol hydrolyzes further (*85*):

$$\begin{tikzcd} CF_3SCN \arrow[r, "OH^-(H_2O)"] & CF_3SH + NCO^- \arrow[d, "OH^-(H_2O)"] \\ & F^- + S^{2-} + CO_3^{2-} \end{tikzcd}$$

The thermally unstable CF_3SSCN decomposes readily at room temperature within a few minutes to CF_3SSCF_3 and polythiocyanate (*85*, *116*, *117*). The selenocyanate, on the other hand, is stable up to 300°C and its decomposition at 500°C yields selenium quantitatively. By contrast, phenylsulfenylselenocyanate decomposes readily at 175°C according to the equation:

$$C_6H_5SSeCN \longrightarrow (C_6H_5S)_2 + (CN)_2 + Se_3(CN)_2 + Se$$

The isocyanate has been investigated more intensively than the other pseudohalides (*39*). In its preparation from CF_3SCl and AgOCN, the linear dimeric $(CF_3S)_2NC(O)NCO$ is also formed in 25% yield, besides CF_3SNCO (75%). A cyclic dimer is obtained by heating the monomer to 100°C for several hours. As has been shown in spectroscopic investigations (*24*, *40*), it has the structure of a planar uretidine-1,3-dione ring with *trans*-CF_3S groups. Hydrolysis of CF_3SNCO and of uretidine-1,3-dione furnishes a symmetrically disubstituted urea and carbon dioxide:



By contrast, the linear dimer gives an unsymmetrically substituted urea:

$$(CF_3S)_2NC(O)NCO + H_2O \longrightarrow (CF_3S)_2NC(O)NH_2 + CO_2$$

Hydrolysis of the monomer also furnishes symmetrically disubstituted urea, in constrast to that of CF_3NCO (*7*):

$$CF_3SNCO + H_2O \longrightarrow \langle CF_3S\text{—}NH\text{—}COOH\rangle \xrightarrow{-CO_2}$$

$$\langle CF_3S\text{—}NH_2\rangle \xrightarrow{CF_3SNCO} CF_3S\text{—}NH\text{—}C(O)\text{—}NH\text{—}SCF_3$$

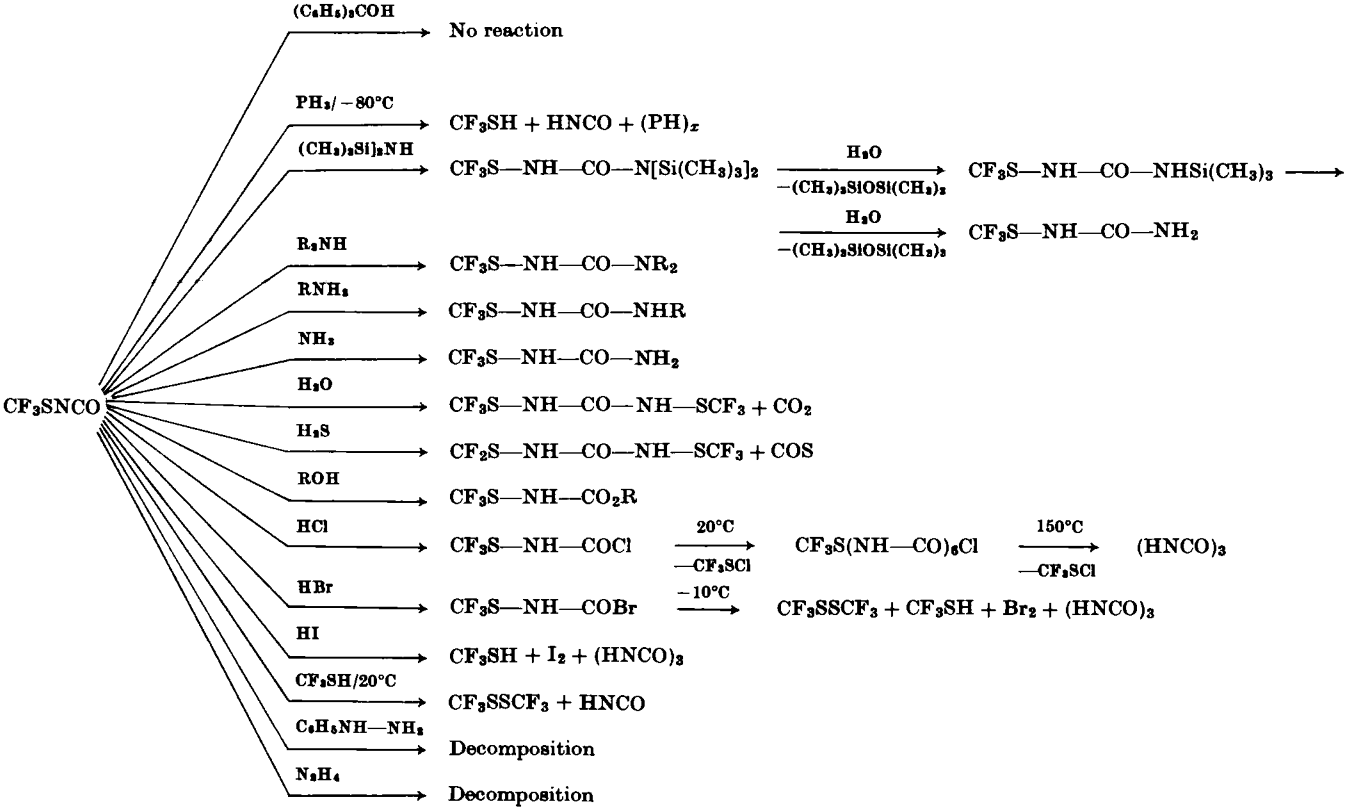
The IR spectra of the CF_3S derivatives of urea, as well as of the deuterated compound, have been discussed at great length (*71*).

In the presence of catalytic quantities of anhydrous sodium acetate, the cyclic trimer, tris(trifluoromethylmercapto) isocyanurate, is obtained at 100°C (*28*, *40*).

Compound CF_3SNCO undergoes further reactions typical of organic isocyanates with hydrogen halides (*41*), amines (*28*), and other species (*39*, *69*), as is shown in Table II.

TABLE II

Reaction of CF_3SNCO with Various Compounds



$$CF_3SNCO \xrightarrow{(C_6H_5)_3COH} \text{No reaction}$$

$$CF_3SNCO \xrightarrow{PH_3/-80°C} CF_3SH + HNCO + (PH)_x$$

$$CF_3SNCO \xrightarrow{(CH_3)_3Si]_2NH} CF_3S—NH—CO—N[Si(CH_3)_3]_2 \xrightarrow[-(CH_3)_3SiOSi(CH_3)_3]{H_2O} CF_3S—NH—CO—NHSi(CH_3)_3 \xrightarrow[-(CH_3)_3SiOSi(CH_3)_3]{H_2O} CF_3S—NH—CO—NH_2$$

$$CF_3SNCO \xrightarrow{R_2NH} CF_3S—NH—CO—NR_2$$

$$CF_3SNCO \xrightarrow{RNH_2} CF_3S—NH—CO—NHR$$

$$CF_3SNCO \xrightarrow{NH_3} CF_3S—NH—CO—NH_2$$

$$CF_3SNCO \xrightarrow{H_2O} CF_3S—NH—CO—NH—SCF_3 + CO_2$$

$$CF_3SNCO \xrightarrow{H_2S} CF_2S—NH—CO—NH—SCF_3 + COS$$

$$CF_3SNCO \xrightarrow{ROH} CF_3S—NH—CO_2R$$

$$CF_3SNCO \xrightarrow{HCl} CF_3S—NH—COCl \xrightarrow[—CF_3SCl]{20°C} CF_3S(NH—CO)_6Cl \xrightarrow[—CF_3SCl]{150°C} (HNCO)_3$$

$$CF_3SNCO \xrightarrow{HBr} CF_3S—NH—COBr \xrightarrow{-10°C} CF_3SSCF_3 + CF_3SH + Br_2 + (HNCO)_3$$

$$CF_3SNCO \xrightarrow{HI} CF_3SH + I_2 + (HNCO)_3$$

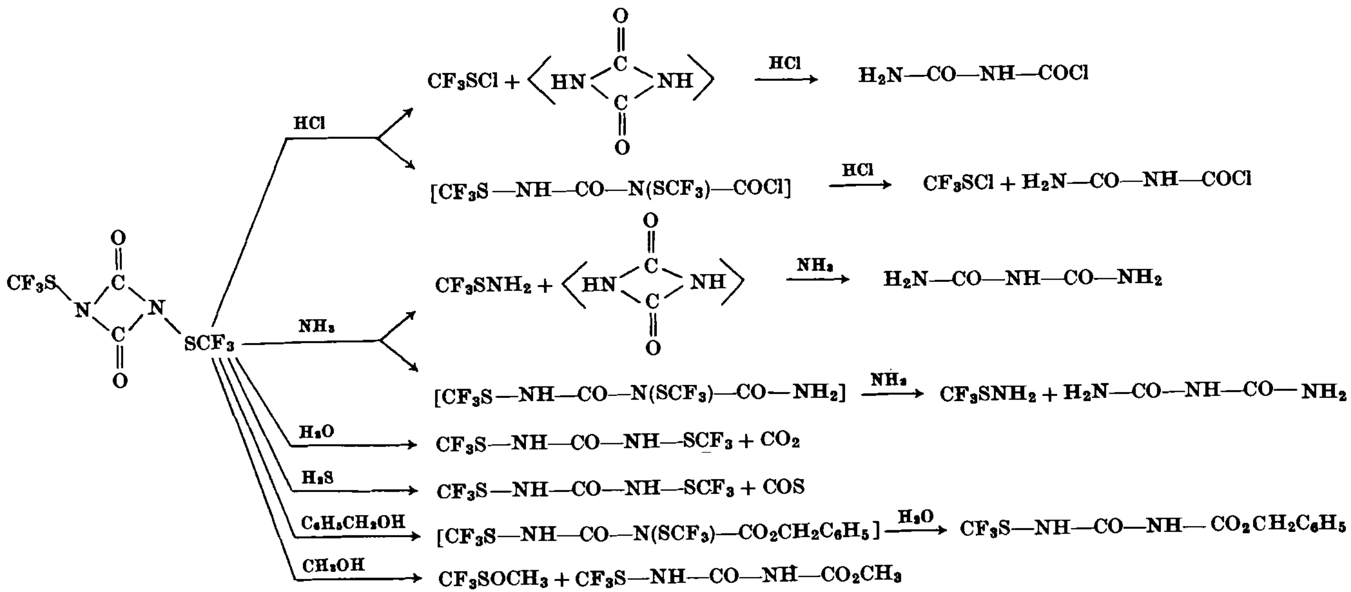
$$CF_3SNCO \xrightarrow{CF_3SH/20°C} CF_3SSCF_3 + HNCO$$

$$CF_3SNCO \xrightarrow{C_6H_5NH—NH_2} \text{Decomposition}$$

$$CF_3SNCO \xrightarrow{N_2H_4} \text{Decomposition}$$

TABLE III

REACTION OF 2,4-BIS(TRIFLUOROMETHYLMERCAPTO)URETIDINE-1,3-DIONE WITH VARIOUS COMPOUNDS



The chemical behavior of the cyclic dimer is quite analogous to that of other uretidine diones (*69*). Some characteristic reactions are summarized in Table III. As can be seen in Table III the mechanism of the reactions with ammonia and hydrogen chloride is not quite clear. The isolated products can be obtained either via a uretidine-dione or via a linear intermediate.

In the reaction of trifluoromethylmercaptosulfenyl chloride with AgNCO the formation of only the monomeric isocyanate is observed (in 87% yield) (*16*):

$$CF_3SSCl + AgNCO \longrightarrow CF_3SSNCO + AgCl$$

The additional sulfur atom seems to reduce the reactivity of the S—Cl bond to nucleophilic attack only to a slight extent. Hydrolysis yields, here too, the symmetrically disubstituted *N*,*N'*-bis(trifluoromethylmercaptosulfenyl) urea:

$$2CF_3SSNCO + H_2O \longrightarrow CF_3SS—NH—CO(O)—NH—SSCF_3 + CO_2$$

Difluorochloro- and fluorodichloromethanesulfenyl chlorides react directly with AgOCN to give the monomeric isocyanates, $CF_2ClSNCO$ and $CFCl_2SNCO$, whereas in benzene solution the corresponding isocyanurates are formed (*61*). Freshly prepared $CF_2ClSNCO$ either trimerizes or dimerizes to a uretidine dione within a month when kept at 20°C.

The sulfenylthiocyanates $CF_2ClSSCN$ and $CFCl_2SSCN$ are formed as monomers in benzene but are very unstable and decompose readily to the disulfane and polythiocyanate:

$$2CF_nCl_{3-n}SSCN \longrightarrow CF_nCl_{3-n}SSCF_nCl_{3-n} + (SCN)_x \qquad (n = 1, 2)$$

Compound $CF_3S—CFCl—SCl$ (*53*) reacts with AgCN, AgSCN, and AgOCN to give the corresponding pseudohalides, which differ only very slightly in their chemical properties from the respective $CFCl_2S$ derivatives. It is noteworthy that $(CF_3S)_2CCl—SCl$ does not react under any circumstances with metal pseudohalides; by contrast, $(CF_3)_2CCl—SCl$ (*120*) yields the compounds $(CF_3)_2CCl—SCN$ and $(CF_3)_2CCl—SSCN$. The sulfenylthiocyanate is remarkably stable: even at 135°C no polythiocyanate separates out.

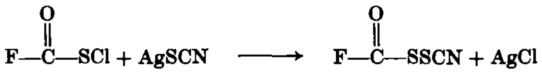
Pentafluorobenzene sulfenyl chloride, C_6F_5SCl, forms a very stable thiocyanate, as well as the compounds C_6F_5SSCN (a yellow polymeric substance of variable composition) and C_6F_5SSeCN (decomposes quantitatively at 50°C), neither of which could be isolated in the pure state at room temperature (*124*).

The isocyanate prepared in benzene solution (*123*, *124*) consists, according to osmometric measurements, of a mixture of the dimer and trimer. It does not react with compounds containing active hydrogen through addition to the N═C double bond, but, instead, through the formation of a sulfenyl halide and cyanuric acid:

$$3\mathrm{C_6F_5SNCO} + 3\mathrm{HX} \longrightarrow 3\mathrm{C_6F_5SX} + (\mathrm{HNCO})_3 \quad (\mathrm{X} = \mathrm{Cl, Br})$$

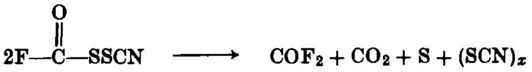
The mass spectrum shows the molecular ion of the monomer only; the $\mathrm{C_6F_5S^+}$ ion is also present in relatively high intensity. These findings suggest that the S—N bond in the polymeric $\mathrm{C_6F_5SNCO}$ is very weak and consequently the compound depolymerizes quite readily.

When reacting fluorocarbonyl sulfenyl chloride with silver pseudohalides (*66*, *67*), it is observed that it reacts only monofunctionally in contrast to the bifunctional chloro compound, e.g.,



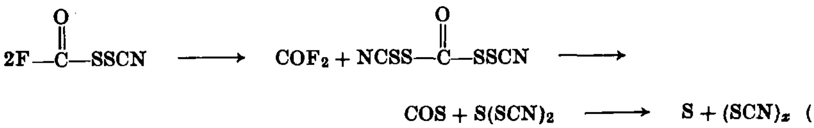
$$\mathrm{F{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}SCl + AgSCN \longrightarrow F{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}SSCN + AgCl}$$

The sulfenyl thiocyanate is unstable and decomposes at 20°C within a few days in a remarkable way:



$$\mathrm{2F{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}SSCN \longrightarrow COF_2 + CO_2 + S + (SCN)_{\mathit{x}}}$$

Presumably $\mathrm{COF_2}$ is split off initially from 2 moles of sulfenylthiocyanate and the remaining decomposition products are formed in additional intermediate steps:



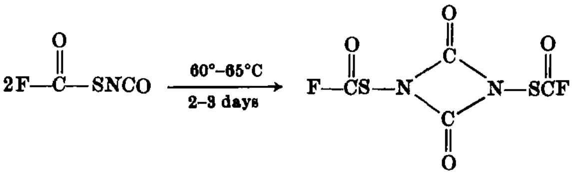
$$\mathrm{2F{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}SSCN \longrightarrow COF_2 + NCSS{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}SSCN \longrightarrow COS + S(SCN)_2 \longrightarrow S + (SCN)_{\mathit{x}}}$$

(*118*)

Of interest is the reaction with silver cyanide: at low temperatures (−80°C) the thiocyanate forms initially and then, as shown by ^{19}F NMR measurements, it undergoes a slow transmutation at 30°C into the isothiocyanate (*67*):

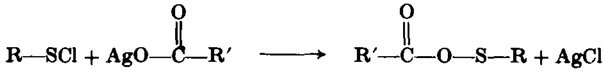
$$\mathrm{F\overset{\overset{\displaystyle O}{\|}}{C}{-}SCN \longrightarrow F\overset{\overset{\displaystyle O}{\|}}{C}{-}NCS}$$

Compound FC(O)SNCO shows the well-known chemical properties of an isocyanate; it also dimerizes to a uretidine dione:



B. WITH SILVER PERFLUOROHALOGENOCARBOXYLATES

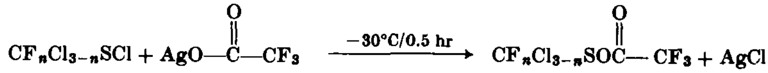
In the reaction of sulfenyl chlorides with silver carboxylates mixed anhydrides are formed; they are known as sulfenyl carboxylates (*90, 130*):



$$R{-}SCl + AgO{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R' \longrightarrow R'{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}S{-}R + AgCl$$

The reaction of sulfenyl chlorides, CF_nCl_{3-n} SCl ($n = 1, 2, 3$) with silver trifluoroacetate furnishes stable halogenated sulfenyl carboxylates of the general formula

$CF_nCl_{3-n}SOC(O)CF_3$ (*62*):



$$CF_nCl_{3-n}SCl + AgO{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CF_3 \xrightarrow{-30°C/0.5\ hr} CF_nCl_{3-n}SO\overset{\overset{\displaystyle O}{\|}}{C}{-}CF_3 + AgCl$$

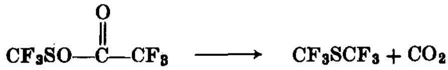
These colorless liquids are stable indefinitely at room temperature.

Trifluoromethanesulfenyl trifluoroacetate decomposes after a short time on irradiation with UV light to the symmetrical anhydrides $[CF_3C(O)]_2O$ and CF_3SOSCF_3; the latter is unstable and disproportionates:

$$2CF_3SOSCF_3 \longrightarrow CF_3SSCF_3 + CF_3SO_2SCF_3 \quad (63)$$

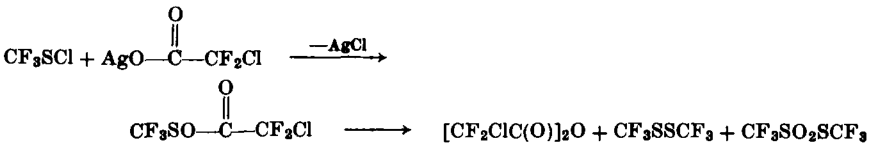
By contrast, $CF_2ClSOC(O)CF_3$, and $CFCl_2SOC(O)CF_3$ decarboxylate after a short UV irradiation with formation of the sulfanes, CF_2ClSCF_3 (*154*) and $CFCl_2SCF_3$ (*62*), respectively.

Thermal decomposition at 170°C (2 days) of $CF_3SOC(O)CF_3$ proceeds also with splitting off of CO_2:



$$CF_3SO{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CF_3 \longrightarrow CF_3SCF_3 + CO_2$$

If a chlorine atom is substituted for a fluorine atom in the acetate, the corresponding sulfenyl carboxylate cannot be isolated; instead, only decomposition products are obtained:



$$CF_3SCl + AgO{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CF_2Cl \xrightarrow{-AgCl}$$
$$CF_3SO{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CF_2Cl \longrightarrow [CF_2ClC(O)]_2O + CF_3SSCF_3 + CF_3SO_2SCF_3$$

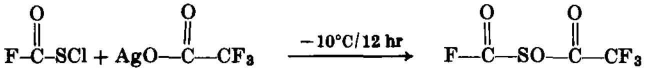
The reaction of CF_3SCl with silver salts of higher perfluorocarboxyacids likewise does not lead to sulfenyl carboxylates, but to the carboxyacid anhydride, CF_3SSCF_3 and $CF_3SO_2SCF_3$ (*62*). However, upon irradiation of the reaction mixture with UV light, without attempting to isolate the sulfenyl carboxylate, the corresponding sulfanes are obtained (*139*):

$$\mathrm{CF_3SCl + CF_3CF_2C(O)OAg \xrightarrow[2\ hr]{h\nu} CF_3SCF_2CF_3 + CO_2}$$
$$(70\%)$$

$$\mathrm{CF_3SCl + CF_3CF_2CF_2C(O)OAg \xrightarrow[4\ hr]{h\nu} CF_3SCF_2CF_2CF_3 + CO_2}$$
$$(50\%)$$

These examples show unmistakably that the substituent at the carboxyl group also influences the stability of the sulfenyl carboxylate.

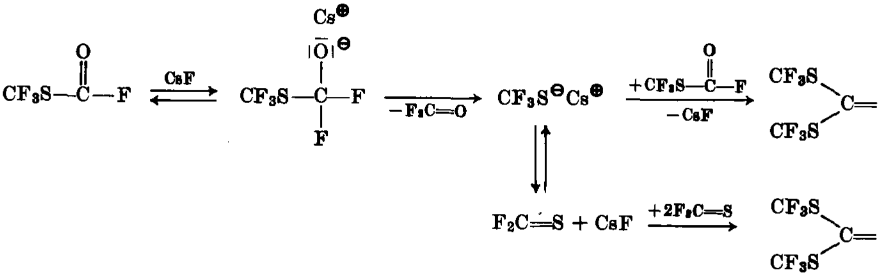
Fluorocarbonylsulfenyl chloride reacts in the following manner with silver trifluoroacetate:



$$\mathrm{F{-}C(O){-}SCl + AgO{-}C(O){-}CF_3 \xrightarrow{-10^\circ C/12\ hr} F{-}C(O){-}SO{-}C(O){-}CF_3}$$ (*48, 68*)

The sulfenyl carboxylate is, on complete exclusion of moisture, a stable, colorless liquid, which on irradiation with UV light decomposes to $FC(O)SCF_3$ and CO_2. The sulfane is a good starting material for the synthesis of additional perfluoro compounds: By means of fluorine–chlorine substitution with BCl_3 (20°C, 2 days), it is possible to obtain $ClC(O)SCF_3$, whose existence previously could be shown only by mass spectrometric study of the products of irradiation of a mixture of CF_3SCl and CO (*157*). As an acid chloride, $ClC(O)SCF_3$ can be esterified with alcohols, but hydrolysis to the free acid fails.

Treatment of $FC(O)SCF_3$ with CsF affords bis(trifluoromethyl)-dithiocarbonate, $(CF_3S)_2CO$, with the evolution of COF_2; $(CF_3S)_2CS$ is also formed as a by-product. The following reaction mechanism explains the formation of the products isolated:

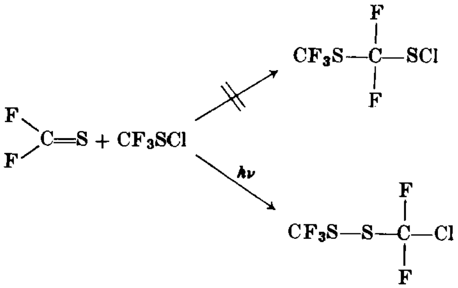


The primary step in this reaction scheme—the addition of alkali metal fluorides to C=O double bonds—was first observed with perfluorocarbonyl fluorides and hexafluoroacetone (*132*).

C. WITH PERFLUOROHALOGENOTHIOKETONES

Addition of halogens or interhalogens to perfluorohalogenothioketones, as already described, represents an important method for the preparation of complex sulfenyl halides.

In an attempt to add sulfenyl halides to the C=S double bond, only the unsymmetrical disulfanes are formed, instead of mercapto-substituted sulfenyl halides (*54*, *56*, 72), e.g.,



This reaction has been carefully studied since the well-known syntheses of perhalogenated disulfanes have always led to symmetric products.

Various factors suggest a free-radical mechanism:

1. Sulfenyl halides do not react with thiocarbonyls unless irradiated with UV light.

2. Compounds such as CF_3SCl decompose when irradiated (*84*):

$$2CF_3SCl \longrightarrow CF_3SSCF_3 + Cl_2 \qquad (50\%)$$

3. There are always products present that are formed through the combination of two R_fS radicals. For example, the reaction of CSF_2 with CF_3SCl proceeds by the following photochemical mechanism (*84*):

$$CF_3S{-}Cl \longrightarrow CF_3S^{\cdot} + {}^{\cdot}Cl \qquad (a)$$

$$CF_3S^{\cdot} + CSF_2 \longrightarrow CF_3S{-}SCF_2^{\cdot} \qquad (b)$$

$$CF_3S{-}SCF_2^{\cdot} + CF_3S{-}Cl \longrightarrow CF_3S{-}SCF_2Cl + CF_3S^{\cdot} \qquad (c)$$

$$Cl^{\cdot} + SCF_2 \longrightarrow ClF_2CS^{\cdot} \qquad (d)$$

$$ClF_2CS^{\cdot} + CF_3S{-}Cl \longrightarrow CF_3S{-}SCF_2Cl + {}^{\cdot}Cl \qquad (e)$$

According to the first reaction, the S—Cl bond is homolytically cleaved. The radicals thus formed react [Eqs. (b) and (d)] to give the precursor of the end product, which is produced according to Eqs. (c) and (e) together with the newly formed radicals of reaction (a). The appearance of the free radicals $CF_3S^{\cdot}$, $Cl^{\cdot}$, and $ClF_2CS^{\cdot}$ is supported by the presence of the by-products $\mathrm{CF_3S{-}SCF_3}$, $\mathrm{CF_2ClS{-}SCF_2Cl}$, and $\mathrm{CF_2ClS{-}Cl}$, as proved unequivocally by the ^{19}F NMR spectrum. The following equations illustrate the method of their formation:

$$\begin{array}{rcl} \mathrm{CF_3S^{\bullet} + {}^{\bullet}SCF_3} & \longrightarrow & \mathrm{CF_3S{-}SCF_3} \\ \mathrm{CF_2ClS^{\bullet} + {}^{\bullet}SCF_2Cl} & \longrightarrow & \mathrm{CF_2ClS{-}SCF_2Cl} \\ \mathrm{Cl^{\bullet} + {}^{\bullet}Cl} & \longrightarrow & \mathrm{Cl_2} \\ \mathrm{CSF_2 + Cl_2} & \longrightarrow & \mathrm{CF_2ClS{-}Cl} \end{array}$$

Since no compound is found of the formula $\mathrm{CF_3S{-}SCF_2Cl}$, it is unlikely that $\mathrm{CF_3S^{\bullet}}$ and $\mathrm{Cl^{\bullet}}$ react according to

$$\begin{array}{lrcl} & \mathrm{CF_3S^{\bullet} + F_2C{=}S} & \longrightarrow & \mathrm{CF_3SCF_2{-}S^{\bullet}} \\ \text{or} & & & \\ & \mathrm{Cl^{\bullet} + F_2C{=}S} & \longrightarrow & \mathrm{{}^{\bullet}CF_2SCl} \end{array}$$

Other disulfanes can be prepared similarly, as summarized in Table IV. The yields are substantially higher when sulfenyl halides of the formula $\mathrm{CF}_n\mathrm{Cl}_{3-n}\mathrm{SX}$ (X = Cl, Br) are reacted. Within a homologous series the

TABLE IV

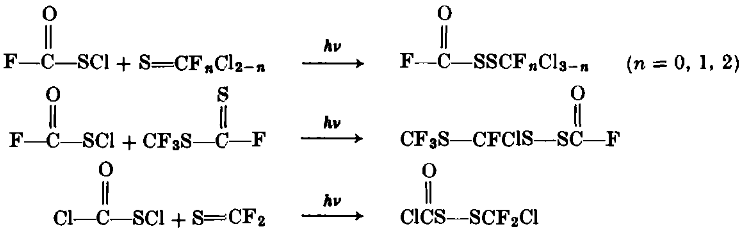
Preparation of Disulfane Compounds

	Starting materials			
Disulfane	Thiocarbonyl compound	Sulfenyl halide	Reaction time (hr)	Yield (%)
$\mathrm{CF_3S{-}SCF_2Cl}$	$\mathrm{CSF_2}$	$\mathrm{CF_3SCl}$	0.3	67
$\mathrm{CF_3S{-}SCFCl_2}$	CSFCl	$\mathrm{CF_3SCl}$	36	56
$\mathrm{CF_2ClS{-}SCFCl_2}$	$\mathrm{CSF_2}$	$\mathrm{CFCl_2SCl}$	20	62
$\mathrm{CF_2BrS{-}SCF_2Br}$	$\mathrm{CSF_2}$	$\mathrm{CF_2BrSBr}$	0.3	100
$\mathrm{CF_2BrS{-}SCBrClF}$	$\mathrm{CSF_2}$	$\mathrm{CFClBrSBr}$	2	78
$\mathrm{CFClBrS{-}SCBrClF}$	CSFCl	$\mathrm{CFClBrSBr}$	6	75
$\mathrm{CF_3S{-}CClFS{-}SCF_3}$	$\mathrm{CF_3SC(S)F}$	$\mathrm{CF_3SCl}$	24	29
$\mathrm{CF_3S{-}CCl_2S{-}SCF_3}$	$\mathrm{CF_3SC(S)Cl}$	$\mathrm{CF_3SCl}$	24	24
$\mathrm{CF_3S{-}CClFS{-}SCF_2Cl}$	$\mathrm{CSF_2}$	$\mathrm{CF_3S{-}CClFSCl}$	16	33
$\mathrm{CF_3S{-}CClFS{-}SCFCl_2}$	CSFCl	$\mathrm{CF_3S{-}CClFSCl}$	22	60.5
$\mathrm{CF_3S{-}CCl_2S{-}SCF_2Cl}$	$\mathrm{CSF_2}$	$\mathrm{CF_3S{-}CCl_2SCl}$	71	32.6
$\mathrm{CF_3S{-}CCl_2S{-}SCFCl_2}^{a}$	CSFCl	$\mathrm{CF_3S{-}CCl_2SCl}$	62	—
$\mathrm{(CF_3)_2{-}CClS{-}SCF_2Cl}$	$\mathrm{CSF_2}$	$\mathrm{(CF_3)_2{-}CClSCl}$	9	25
$\mathrm{(CF_3S)_2{-}CFS{-}SCF_2Cl}$	$\mathrm{CSF_2}$	$\mathrm{(CF_3S)_2{-}CFSCl}$	4	30
$\mathrm{(CF_3S)_2{-}CFS{-}SCFCl_2}$	CSFCl	$\mathrm{(CF_3S)_2{-}CFSCl}$	150	25
$\mathrm{(CF_3S)_2{-}CFS{-}SCCl_3}$	$\mathrm{CSCl_2}$	$\mathrm{(CF_3S)_2{-}CFSCl}$	250	15
$\mathrm{(CF_3S)_2{-}CFS{-}SCFCl{-}SCF_3}$	$\mathrm{CF_3SC(S)F}$	$\mathrm{(CF_3S)_2{-}CFSCl}$	150	25
$\mathrm{(CF_3S)_2{-}CFS{-}SCCl_2{-}SCF_3}$	$\mathrm{CF_3SC(S)Cl}$	$\mathrm{(CF_3S)_2{-}CFSCl}$	150	20

[a] This compound was not obtained in the pure state.

reactions become faster with increasing degree of fluorination of the starting compound.

The same reaction can also be applied to halogenocarbonylsulfenyl chlorides and affords perhalogenated disulfanes with interesting functional groups (*68*):

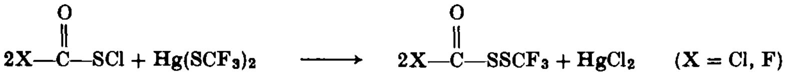


$$\mathrm{F{-}\overset{\overset{O}{\|}}{C}{-}SCl + S{=}CF_nCl_{2-n} \xrightarrow{h\nu} F{-}\overset{\overset{O}{\|}}{C}{-}SSCF_nCl_{3-n}} \quad (n = 0, 1, 2)$$

$$\mathrm{F{-}\overset{\overset{O}{\|}}{C}{-}SCl + CF_3S{-}\overset{\overset{S}{\|}}{C}{-}F \xrightarrow{h\nu} CF_3S{-}CFClS{-}S\overset{\overset{O}{\|}}{C}{-}F}$$

$$\mathrm{Cl{-}\overset{\overset{O}{\|}}{C}{-}SCl + S{=}CF_2 \xrightarrow{h\nu} Cl\overset{\overset{O}{\|}}{C}S{-}SCF_2Cl}$$

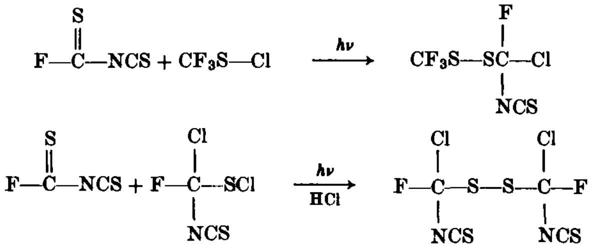
Compound $ClC(O)SSCCl_3$ is obtained from $FC(O)SSCCl_3$ through fluorine–chlorine exchange with BCl_3; $ClC(O)SSCF_3$ and $FC(O)SSCF_3$ are formed as follows:



$$\mathrm{2X{-}\overset{\overset{O}{\|}}{C}{-}SCl + Hg(SCF_3)_2 \longrightarrow 2X{-}\overset{\overset{O}{\|}}{C}{-}SSCF_3 + HgCl_2} \quad (X = Cl, F)$$

In the homologous series $ClC(O)SSCF_nCl_{3-n}$ ($n = 0$–3), compound $ClC(O)SSCFCl_2$ is missing: it cannot be synthesized either directly from $ClC(O)SCl$ and CSFCl nor through halogen exchange in $FC(O)SSCFCl_2$, since in this case the fluorine atom of the halomethyl group is also exchanged (*48*).

The fluorothiocarbonyl isothiocyanates may also be reacted successfully in place of the thiocarbonyl compounds (*21*), e.g.,



$$\mathrm{F{-}\overset{\overset{S}{\|}}{C}{-}NCS + CF_3S{-}Cl \xrightarrow{h\nu} CF_3S{-}S\underset{\underset{NCS}{|}}{\overset{\overset{F}{|}}{C}}{-}Cl}$$

$$\mathrm{F{-}\overset{\overset{S}{\|}}{C}{-}NCS + F{-}\underset{\underset{NCS}{|}}{\overset{\overset{Cl}{|}}{C}}{-}SCl \xrightarrow[HCl]{h\nu} F{-}\underset{\underset{NCS}{|}}{\overset{\overset{Cl}{|}}{C}}{-}S{-}S{-}\underset{\underset{NCS}{|}}{\overset{\overset{Cl}{|}}{C}}{-}F}$$

D. WITH AMMONIA, PRIMARY AND SECONDARY AMINES, AND AMIDES

In the reaction between stoichiometric quantities of CF_3SCl and ammonia in a Carius tube at low temperature the trifluoromethylmercaptoamine is formed (*30*):

$$CF_3SCl + 2NH_3 \xrightarrow{-45°C} CF_3SNH_2 + NH_4Cl$$

This reaction can also be carried out in an autoclave at 10°C (*70*) or, in high yield, by introducing CF_3SCl into liquid ammonia at –80°C (*64, 70*).

The mixed amines, $CF_nCl_{3-n}SNH_2$ ($n = 1, 2$), are synthesized from the corresponding sulfenyl chlorides and ammonia at –60°C with the use of a perhalogenated solvent (*58*):

$$CF_nCl_{3-n}SCl + 2NH_3 \xrightarrow[CCl_3F]{-60°C} CF_nCl_{3-n}SNH_2 + NH_4Cl \qquad (n = 1, 2)$$

The corresponding pentafluorobenzene derivative is obtained by adding the sulfenyl chloride dropwise to a saturated solution of ammonia in diethyl ether (*138*):

$$C_6F_5SCl + 2NH_3 \xrightarrow[ether]{0°C} C_6F_5SNH_2 + NH_4Cl$$

A more complete substitution of the trihalomethylmercaptoamines is achieved most readily at –60°C in *n*-pentane or $CFCl_3$ solution in the presence of pyridine as an HCl acceptor and with an additional mole of sulfenyl chloride (*58*):

$$CF_{3-n}Cl_nSNH_2 + CF_{3-n}Cl_nSCl + C_5H_5N \longrightarrow (CF_{3-n}Cl_nS)_2NH + C_5H_5N\cdot HCl \qquad (n = 0, 1, 2)$$

$$CF_3SNH_2 + CF_nCl_{3-n}SCl + C_5H_5N \longrightarrow CF_3S(CF_nCl_{3-n}S)NH + C_5H_5N\cdot HCl \qquad (n = 0, 1, 2)$$

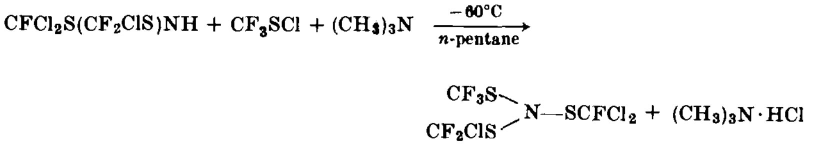
$$CFCl_2SNH_2 + CF_2ClSCl + C_5H_5N \longrightarrow CFCl_2S(CF_2ClS)NH + C_5H_5N\cdot HCl$$

Compound $(C_6F_5S)_2NH$ too, like the monosubstituted amine, is obtained by adding C_6F_5SCl dropwise to a solution of NH_3 in ether (*138*). In this case the concentration of ammonia is kept slightly lower. This compound is also formed as the sole product of the direct reaction of C_6F_5SCl and ammonia in a Carius tube (*123*).

All bis(mercapto)amines can be converted into the corresponding tris(mercapto)amines in the presence of, for example, trimethylamine as HCl acceptor. In this way it is possible to prepare $(C_6F_5S)_3N$ from $(C_6F_5S)_2NH$ and C_6F_5SCl (*138*):

$$(C_6F_5S)_2NH + C_6F_5SCl + (CH_3)_3N \xrightarrow[ether]{34°C} (C_6F_5S)_3N + (CH_3)_3N\cdot HCl$$

A trihalomercaptoamine with three different substituents is formed as follows:



$$CFCl_2S(CF_2ClS)NH + CF_3SCl + (CH_3)_3N \xrightarrow[n\text{-pentane}]{-60°C} (CF_3S)(CF_2ClS)N{-}SCFCl_2 + (CH_3)_3N\cdot HCl \quad (58)$$

For the synthesis of other triply sulfenylated amines, it is best to start with the primary ones:

$$\left.\begin{matrix} CF_3SNH_2 \\ CF_2ClSNH_2 \\ CFCl_2SNH_2 \end{matrix}\right\} + 2CF_nCl_{3-n}SCl + 2(CH_3)_3N \xrightarrow[n\text{-pentane}]{-60°C} \left\{\begin{matrix} CF_3SN(SCF_nCl_{3-n})_2 + 2(CH_3)_3N\cdot HCl \\ CF_2ClSN(SCCl_{3-n}F_n)_2 + 2(CH_3)_3N\cdot HCl \\ CFCl_2SN(SCCl_{3-n}F_n)_2 + 2(CH_3)_3N\cdot HCl \end{matrix}\right.$$

$$(n = 1, 2)$$

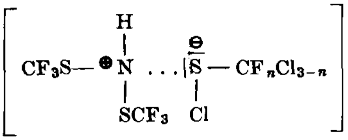
In an attempt to prepare tris(mercapto)amines of the type $(CF_3S)_2NSCF_nCl_{3-n}$ ($n = 0, 1, 2$) from $(CF_3S)_2NH$ and the appropriate sulfenyl chloride, it was observed that, besides the expected bis(trifluoromethylmercapto)derivatives, other products were also formed (*57*):

$$(CF_3S)_2NH + CF_2ClSCl \longrightarrow (CF_3S)_2NSCF_2Cl + CF_3SN(SCF_2Cl)_2 + (CF_3S)_3N$$

$$(CF_3S)_2NH + CFCl_2SCl \longrightarrow (CF_3S_2)NSCFCl_2 + CF_3SN(SCFCl_2)_2 + (CF_3S)_3N$$

$$(CF_3S)_2NH + CCl_3SCl \longrightarrow (CF_3S)_2NSCCl_3 + (CF_3S)_3N$$

A comparison of yields showed that formation of $(CF_3S)_3N$ is favored with growing degree of chlorination of the sulfenyl chlorides, whereas the nucleophilic substitution at the sulfenyl sulfur is reduced by the imide nitrogen. It is, therefore, to be assumed that with increasing content of chlorine, the elimination of CF_3SCl rather than HCl from the intermediate is favored on energetic and steric grounds:



$$\left[CF_3S-\overset{\displaystyle H}{\underset{\displaystyle SCF_3}{\overset{\oplus}{N}}}\cdots\overset{\ominus}{\underset{\displaystyle Cl}{S}}-CF_nCl_{3-n} \right] \quad (n = 0, 1, 2)$$

The CF_3SCl thus formed affords in the competing reaction

$$(CF_3S)_2NH + CF_3SCl \longrightarrow (CF_3S)_3N + HCl$$

tris(trifluoromethylmercapto)amine, whereas the intermediate $(CF_3S)NH(SCF_nCl_{3-n})$ reacts either with $CF_nCl_{3-n}SCl$ to give $CF_3SN(SCF_nCl_{3-n})_2$ or with CF_3SCl to give $(CF_3S)_2NSCF_nCl_{3-n}$.

All amines so far prepared are stable toward humid air; they are also rather insensitive toward hydrolysis, as can be demonstrated by the reaction of CF_3SNH_2 with water (*30*). However, alkaline and acid aqueous solutions completely destroy these molecules. In hydrochloric acid, CF_3SCl and NH_4Cl are formed initially from CF_3SNH_2; CF_3SCl then reacts further:

$$\begin{tikzcd}
3CF_3SNH_2 + 6HCl \arrow[r] & 3CF_3SCl + 3NH_4Cl \arrow[d, "+2H_2O"] \\
 & CF_3SO_2^- + CF_3SSCF_3 + 3Cl^- + 4H^+
\end{tikzcd}$$

The R_fSN compounds react quite readily with hydrogen chloride through fission of the S—N bond; in this reaction the electronegative chlorine moves to the electropositive sulfur and the proton joins the negative nitrogen:

$$R_fSN< + HCl \longrightarrow R_fSCl + HN< \quad (69)$$

Compound CF_3SNH_2 is incompletely decomposed by bases at 20°C to give F^-, CO_3^{2-}, S^{2-}, NH_3, and CHF_3; at 75°C, however, hydrolysis is complete, and the products contain additionally sulfur, but no CHF_3 (*30*). Compound CF_3SNH_2 is not stable towards UV light and the products of irradiation include CF_3SSCF_3, NH_4F, NH_4SCN, and hydrazinium fluoride. It is to be assumed that the initial step of the photolysis is the homolytic fission of CF_3SNH_2 to $CF_3S^\bullet$ and $^\bullet NH_2$.

Compound $C_6F_5SNH_2$ is not very stable and decomposes in a short time:

$$2C_6F_5SNH_2 \longrightarrow (C_6F_5S)_2NH + NH_3 \quad (138)$$

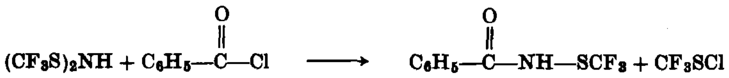
Compound $(CF_3S)_3N$ even if it contains only minor impurities decomposes quantitatively when heated under reflux:

$$2(CF_3S)_3N \longrightarrow 3CF_3SSCF_3 + N_2 \quad (70)$$

Condensation reactions of $(CF_3S)_2NH$ have been thoroughly studied (*57*): with SCl_2 compound $(CF_3S)_2NSN(SCF_3)_2$ is not formed—in analogy with the formation of $(CH_3)_2NSN(CH_3)_2$ from dimethylamine (*11*)—but rather CF_3SCl, among other compounds, is obtained:

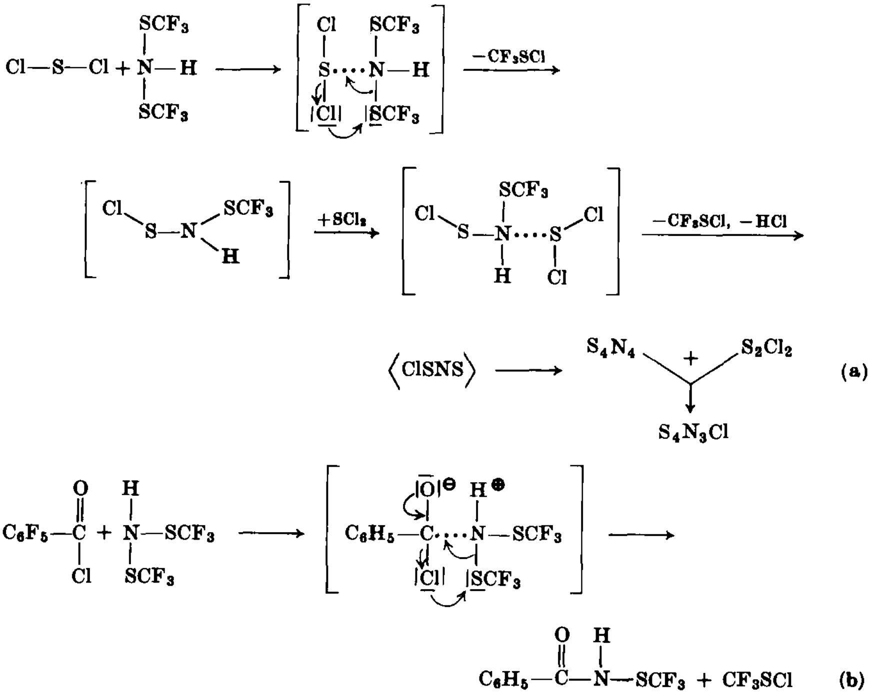
$$3(CF_3S)_2NH + 6SCl_2 \longrightarrow 6CF_3SCl + S_4N_3Cl + HCl$$

The reaction with benzoyl chloride proceeds like a substitution reaction:



$$(CF_3S)_2NH + C_6H_5—\overset{\overset{\displaystyle O}{\|}}{C}—Cl \longrightarrow C_6H_5—\overset{\overset{\displaystyle O}{\|}}{C}—NH—SCF_3 + CF_3SCl$$

In both cases it may be assumed that the electron-withdrawing effect of both CF_3S groups lowers the nucleophilic character of the imide nitrogen to such an extent that it is no longer able to attack—as is the rule with amines—the electrophilic reaction partner (sulfur or carbonyl carbon), but instead forms a weak bond with it. From this intermediate, as is the case with the reactions of $CF_nCl_{3-n}SCl$ ($n = 0, 1, 2$), compound CF_3SCl and the substitution product can be formed as shown in Scheme 1.



SCHEME 1

These same considerations apply to the reaction of $(CF_3S)_3N$ with SCl_2:

$$3(CF_3S)_3N + 6SCl_2 \longrightarrow 9CF_3SCl + S_4N_3Cl + S_2Cl_2$$

The disubstituted amines form with pyridine and trimethylamine 1 : 1 adducts, the stability of which increases with the degree of fluorination (*59*).

Thus, for example, $(CF_3S)_2NH \cdot N(CH_3)_3$ and $(CF_3S)_2NH \cdot NC_5H_5$ are stable and can be distilled without decomposition; similarly $CF_3S(CF_2ClS)_2NH \cdot N(CH_3)_3$ and $(CF_2ClS)_2NH \cdot NC_5H_5$ are also stable. For the higher chlorinated $CF_3S(CFCl_2S)NH$, the pyridine adduct only is stable up to 0°C.

Condensation reactions between perfluorohalogenosulfenyl chlorides and amides as well as primary and secondary amines have been thoroughly investigated. Compounds RNH_2 and $RR'NH$ react with sulfenyl chlorides in the presence of an excess of the amine to give $RN(H)SR_f$ or $RR'NSR_f$, respectively. Amides condense only in the presence of a tertiary amine, such as $(CH_3)_3N$, $(C_2H_5)_3N$, or pyridine. These reactions can be performed in inert organic solvents but afford just as satisfactory yields without any solvent. Substances synthesized up to the present, as well as their physical data and biological activity, have been summarized (*42*).

E. With Arsines, Alcohols, Thioalcohols, Sulfinates, and Carbonyl Compounds

Perfluorohalogenoalkanesulfenyl halides readily undergo condensation reactions with numerous types of compounds; this is due to their polarization $R_fS^{\delta+}—Hal^{\delta-}$ caused by the strong electron-withdrawing action of the fluorine atoms. Thus, the reaction of dimethylarsine with trifluoromethanesulfenyl chloride affords $(CH_3)_2AsSCF_3$, $(CH_3)_2AsCl$, and trifluoromethanethiol:

$$2(CH_3)_2AsH + 2CF_3SCl \longrightarrow (CH_3)_2AsSCF_3 + (CH_3)_2AsCl + CF_3SH + HCl \quad (\mathit{19})$$

Tetramethyldiarsine is cleaved by CF_3SCl at the As—As bond:

$$(CH_3)_2As—As(CH_3)_2 + CF_3SCl \longrightarrow (CH_3)_2AsSCF_3 + (CH_3)_2AsCl$$

Compounds containing As—S bonds react similarly:

$$(CH_3)_2As—SR + CF_3SCl \longrightarrow RS—SCF_3 + (CH_3)_2AsCl \qquad (R = C_2H_5, C_6H_5)$$

The reaction with hydrogen sulfide leads to the formation of trisulfanes (*84*). Condensations with alcohols proceed very smoothly to thioperoxides (*3, 110*):

$$R_fSCl + ROH \longrightarrow R_fSOR + HCl$$

$[R_f = CF_3;\ R = CH_3, C_2H_5, (CH_3)_2CH, CF_3CH_2$
$R_f = CFCl_2;\ R = CH_3OCH_2, CH_3, ClCH_2CH_2, C_4H_9, C_{12}H_{25}, C_6H_5, (CH_3)_3C, 4\text{-}C_6H_4Cl, 2.5\text{-}C_6H_3Cl_2$
$R_f = (CF_3)_2CF;\ R = CH_3]$

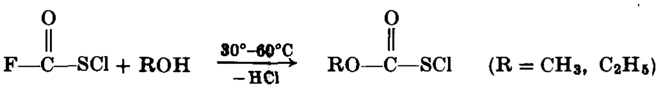
$$2CF_3SCl + HO—CH_2—CH_2—OH \longrightarrow CF_3SO—CH_2—OSCF_3 + 2HCl$$

and those with thiols to disulfanes (*4*, *19*, *84*, *110*, *123*):

$$R_fSCl + RSH \longrightarrow R_fSSR + HCl$$

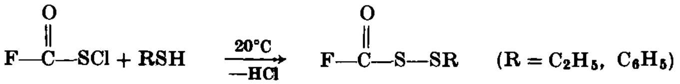
$[R_f = R = CF_3$
$R_f = CF_3;\ R = CH_3, C_2H_5, C_6H_5$
$R_f = C_6F_5;\ R = CH_3, n\text{-}C_4H_9, C_6F_5]$

In all these reactions, HCl acceptors, such as pyridine (*3*) or triethylamine (*110*), are used. In this respect fluorocarbonylsulfenyl chloride behaves quite extraordinarily (*48*): with alcohols it reacts at the fluorocarbonyl group with formation of alkoxycarbonylsulfenyl chlorides.



$$\mathrm{F{-}C({=}O){-}SCl + ROH \xrightarrow[-HCl]{30^\circ\text{–}60^\circ C} RO{-}C({=}O){-}SCl} \qquad (\mathrm{R = CH_3,\ C_2H_5})$$

By contrast, thiols, even in excess, react to furnish exclusively alkyl- or arylhalocarbonyl disulfanes:



$$\mathrm{F{-}C({=}O){-}SCl + RSH \xrightarrow[-HCl]{20^\circ C} F{-}C({=}O){-}S{-}SR} \qquad (\mathrm{R = C_2H_5,\ C_6H_5})$$

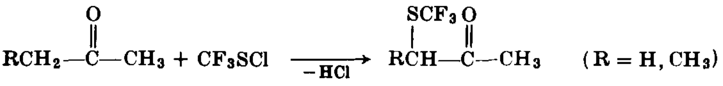
Sulfenyl chlorides react with zincalkyl (or -aryl) sulfinates and also with sodium benzene sulfinate to yield the corresponding esters of thiosulfonic acid (*13*, *111*, *161*):

$$\mathrm{(RSO_2)_2Zn + 2CF_3SCl \longrightarrow 2RSO_2SCF_3 + ZnCl_2}$$
$$\mathrm{C_6H_5SO_2Na + CF_nCl_{3-n}SCl \longrightarrow C_6H_5SO_2SCF_nCl_{3-n}} \qquad (n = 0, 1, 2)$$

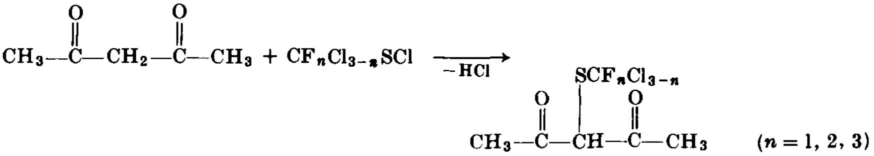
On thermolysis the latter are reduced to thiocarbonyldihalides:

$$\mathrm{C_6H_5SO_2SCF_nCl_{3-n} \xrightarrow{170^\circ\text{–}250^\circ C/1.5\ hr} S{=}CCl_{2-n}F_n} \qquad (n = 0, 1, 2)$$

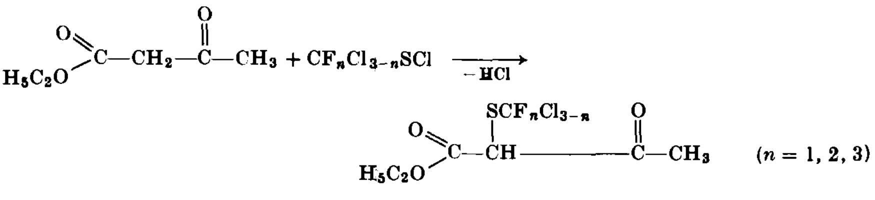
The products of the reactions of perfluorohalogenomethanesulfenyl chlorides with ketones, diketones, and ketoesters are monosubstituted trihalomethylmercapto derivatives, as shown in the following examples (*8*):



$$\mathrm{RCH_2{-}C({=}O){-}CH_3 + CF_3SCl \xrightarrow[-HCl]{} RCH(SCF_3){-}C({=}O){-}CH_3} \qquad (\mathrm{R = H, CH_3})$$

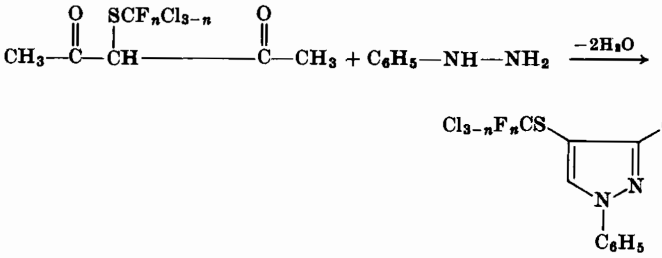


$$\mathrm{CH_3{-}C({=}O){-}CH_2{-}C({=}O){-}CH_3 + CF_nCl_{3-n}SCl \xrightarrow[-HCl]{} CH_3{-}C({=}O){-}CH(SCF_nCl_{3-n}){-}C({=}O){-}CH_3} \qquad (n = 1, 2, 3)$$

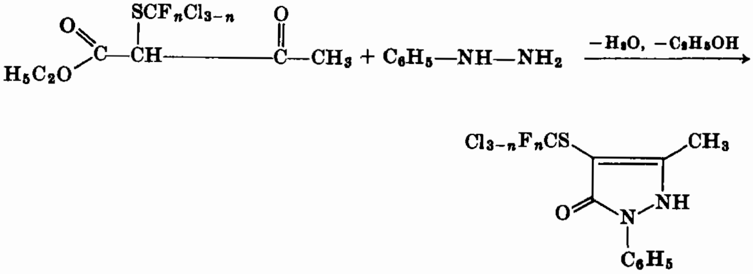


$$\mathrm{H_5C_2O{-}C({=}O){-}CH_2{-}C({=}O){-}CH_3 + CF_nCl_{3-n}SCl \xrightarrow[-HCl]{} H_5C_2O{-}C({=}O){-}CH(SCF_nCl_{3-n}){-}C({=}O){-}CH_3} \qquad (n = 1, 2, 3)$$

The reactivity of the keto group is not influenced by the substitution: the reaction of 3-(trifluoromethylmercapto)-2-butanone with hydroxylamine hydrochloride gives the corresponding oxime in good yield. Cyclization of diketones and keto esters to pyrazole derivatives succeeds by the well-known method using phenylhydrazine:

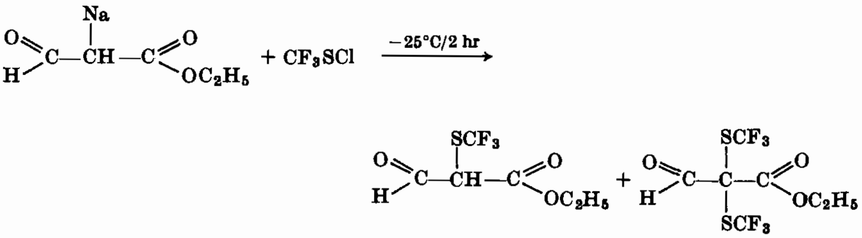


(n = 1, 2, 3)

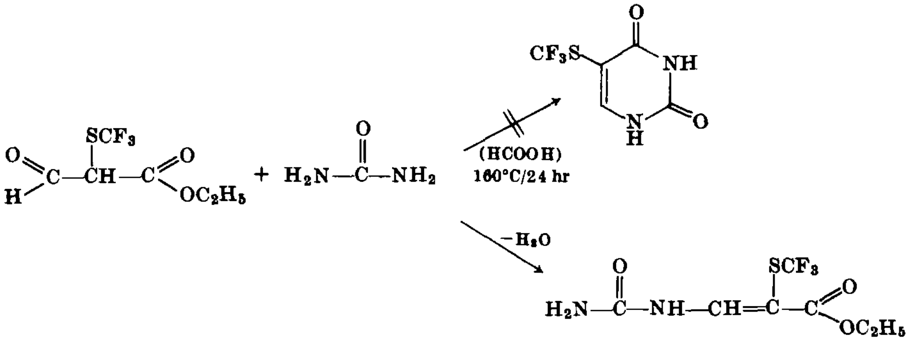


(n = 2, 3)

The 3-oxopropionic acid ethyl ester can be made to react with CF_3SCl by way of metallation; mono- and disubstituted products are formed in this reaction in equal amounts (*49*):



Condensation with urea does not lead in this case, as would be expected, to the uracil derivative with ring closure, because the reaction takes place only at the more reactive aldehyde function:



F. With Alkanes, Alkenes, Alkynes, and Nitriles

Addition reactions of CF_3SCl to olefins and nitriles were intensively studied. It has been shown that these reactions have to be either initiated with UV light or carried out in a strongly polar solvent.

The UV-initiated addition of CF_3SCl to $CHF{=}CF_2$ leads to $CF_3SCFHCF_2Cl$ and CF_3SCF_2CHFCl, the latter being the main product (*76*). The additions of $CFCl{=}CF_2$ (*25*, *76*), $CH_2{=}CHCl$ (*76*), and $CH_2{=}CHC(O)OCH_3$ (*80*) proceed analogously.

Irradiation of a mixture of $CF_2{=}CFX$ ($X = CF_3$, OCH_3) and CF_3SCl affords the main products $CF_3SCFXCF_2Cl$ and CF_3SCF_2CFClX, together with CF_3SSCF_3 and Cl_2. The chlorine thus liberated competes with CF_3SCl in combining with the C=C double bond of the starting materials.

Compound CF_3SCl combines in a polar solvent, e.g., tetramethylenesulfone, at 20° to 25°C with $CH_2{=}CHCl$ to produce $CF_3SCH_2CHCl_2$ in 67% yield (*2*). Analogously, $CF_3SCHClCHCl_2$ is formed in 80% yield from CF_3SCl and $CHCl{=}CHCl$ (*1*). At 80° to 100°C, CF_3SCl reacts with $CH_2{=}CH_2$ in tetramethylenesulfone to give $CF_3SCH_2CH_2Cl$ in 80% yield (*101*).

Under the influence of UV light CF_3SCl can be made to combine with $CF_3SCH{=}CH_2$ to yield $(CF_3S)_2CHCH_2Cl$ and $(CF_3S)_2CHCH_2SCF_3$-(*75*, *79*). Similarly, other sulfenyl chlorides can also be added to C=C double bonds, e.g.,

$$R_fSCl + CH_2{=}CH_2 \longrightarrow R_fSCH_2CH_2Cl$$

$$[R_f = C_2F_5,\ (CF_3)_2CF(CF_2)_4\ (89),\ C_4F_9\ (123)]$$

Sulfenyl chlorides combine also with C≡N triple bonds. The reaction of CF_3SCl with $(CN)_2C{=}C(CN)_2$ in CH_2Cl_2 in the presence of $[(C_2H_5)_4N]Cl$ results in $(CN)_2C{=}C(CN)CCl{=}NSCF_3$ (*82*, *83*). Reactions between R_2NCN and CF_3SCl take a similar course (*65*):

$$R_2NC{\equiv}N + CF_3SCl \longrightarrow R_2N{-}CCl{=}NSCF_3 \qquad (R = CH_3, C_2H_5)$$

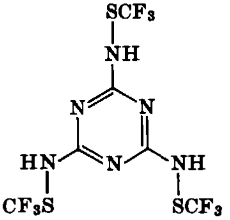
Addition as well as condensation reactions occur with some monosubstituted derivatives:

$$3RNHCN + 4CF_3SCl \longrightarrow 2R(CF_3S)NCCl{=}NSCF_3 + RNHCN\cdot 2HCl$$
$$[R = CH_3, (CH_3)_2CH]$$

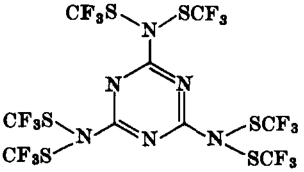
With $(CH_3)_3CN(H)CN$ only the condensation product, $(CH_3)_3CN(SCF_3)$-CN, is formed.

Both addition and substitution are also observed in the reaction of H_2NCN with CF_3SCl. If the reaction is carried out in ether at 0°C, $CF_3SN(H)CCl{=}NSCF_3$, results; however without a solvent and at 20°C, 23% $(CF_3S)_2NCCl{=}NSCF_3$ and 1% $CF_3SN(H)CN$ are additionally formed. The latter can be prepared in better yield (17%) from H_2HCN and $CF_3SN(H)CCl{=}NSCF_3$.

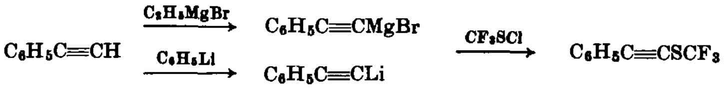
The acidic proton of the amine can be substituted in aqueous acetone by reaction with $AgNO_3$ to give $CF_3SN(Ag)CN$. The silver salt reacts with CF_3SCl to yield hexabis(trifluoromethylmercapto)melamine, which can also be synthesized from $(CF_3S)_2NCCl{=}NSCF_3$ or $CF_3SN(H)CCl{=}NSCF_3$ and amines [$(CH_3)_3N$, pyridine]. Melamine itself reacts with CF_3SCl in acetonitrile and in the presence of pyridine to give



only. Here, too, the hydrogen atoms are acidic and can be substituted with silver nitrate in aqueous acetone to give the trisilver salt. In the reaction with CF_3SCl it affords likewise the compound



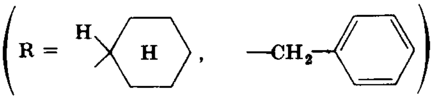
Alkynes react with CF_3SCl only via prior metallation with a Grignard reagent or C_6H_5Li (*81*):



$$C_6H_5C{\equiv}CH \begin{array}{l} \xrightarrow{C_2H_5MgBr} C_6H_5C{\equiv}CMgBr \\ \xrightarrow{C_6H_5Li} C_6H_5C{\equiv}CLi \end{array} \xrightarrow{CF_3SCl} C_6H_5C{\equiv}CSCF_3$$

Under the influence of UV light, condensations between CF_3SCl and hydrocarbons are also possible (*77*, *78*), e.g.,

$$CF_3SCl + RH \xrightarrow{h\nu} CF_3S{-}R + ClR + CF_3SSCF_3 + HCl$$

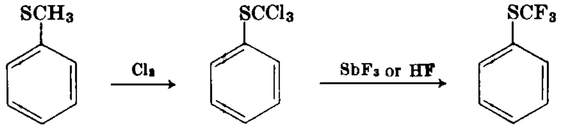


$$CF_3SCl + n\text{-}C_4H_{10} \xrightarrow{h\nu} CF_3SCH_2CH_2CH_2CH_3 + CF_3SCH(CH_3)C_2H_5 + CH_3CHClC_2H_5 + ClCH_2CH_2C_2H_5 + CF_3SSCF_3 + HCl$$

Other sulfenyl chlorides react analogously (*77*).

G. WITH AROMATICS AND HETEROAROMATICS

The introduction of the perfluorohalogenosulfenyl group into aromatic compounds was accomplished long before the preparation of sulfenyl halides. The CF_3S-substituted compounds have been synthesized largely by chlorination of the side chain in arylmethylthioethers followed by chlorine–fluorine exchange. This method was applied for the first time in the synthesis of trifluoromethylmercaptobenzene (*92*, *140*, *172*):

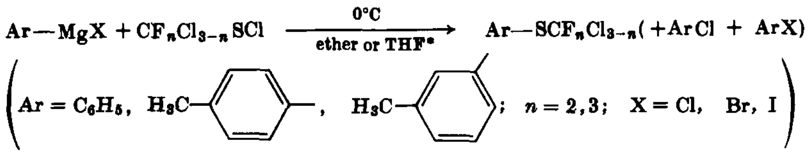


This reaction is also feasible if the benzene ring contains substituents, such as halogens or methyl, carboxyl, and nitro groups.

These compounds can be oxidized without difficulty to the corresponding sulfoxides or sulfones (*92*, *95*, *140*, *142*, *167*, *172*, *176*). On the other hand, the trihalomethylmercapto group is noticeably inert toward chemical changes in the aromatic ring, such as halogenation (*92*), nitration (*174*), reduction of nitro groups, diazotation of amino groups, and hydrolysis of nitrile groups (*172*).

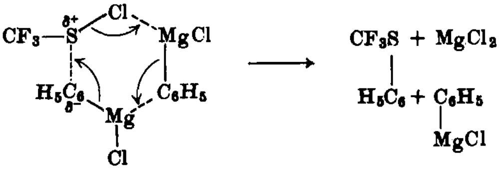
Numerous derivatives play a considerable role as fungicides, insecticides, and pharmaceuticals (*93*, *95*, *125*, *153*) as well as serving as intermediates in the syntheses of dyes (*22*, *94*, *95*, *165*, *166*, *168*, *169*, *171*, *173–175*, *177–182*).

The reaction of aryl magnesium halides with perfluorohalogenosulfenyl chlorides takes place under considerably milder conditions (*47*, *148*):

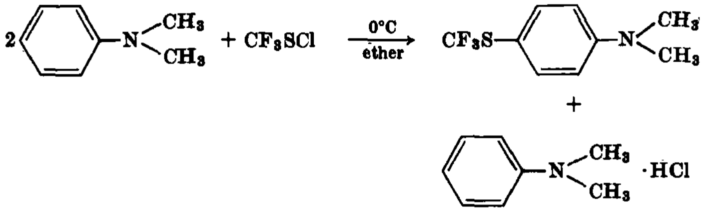


$$\mathrm{Ar{-}MgX + CF_nCl_{3-n}SCl \xrightarrow[\text{ether or THF*}]{0°C} Ar{-}SCF_nCl_{3-n}(+ArCl + ArX)}$$

The perfluorohalogenomethylmercapto compound is formed in about 50% yield, the by-products being aryl halides from the Grignard reagent in 5–15% yield. It is assumed that the reaction follows an S_N2 mechanism with a cyclic intermediate state in analogy with the reaction of Grignard reagents with alkyl halides (*98*, *155*), e.g.,



Aromatic compounds with electron-donor substituents, such as $—N(CH_3)_2$ or —OH, also react with CF_3SCl via direct condensation (*4*, *133*):



(R = H, o-CH_3, m-CH_3, o-OH, m-Cl)

In the case of phenol derivatives, the intermediate formation of sulfenate-esters $ArOSCF_3$, with subsequent rapid conversion to the cyclic substituted product is discussed elsewhere (*3*).

In the presence of Friedel–Crafts catalysts (BF_3, $FeCl_3$, and others), comparatively less reactive compounds, such as benzene (50°C, 2 hr) and toluene (100°C, 4 hr), can be reacted in an autoclave with CF_3SCl to give $C_6H_5—SCF_3$ or a mixture of *m*- and *p*-$CF_3S—C_6H_4CH_3$, respectively. Chloro- and bromobenzene react under more vigorous conditions (200°C, 2 hr) with the formation of a mixture of ortho-, meta-, and para-

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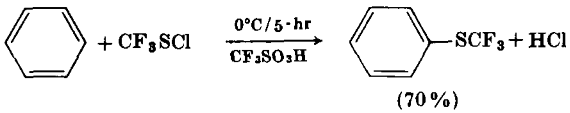
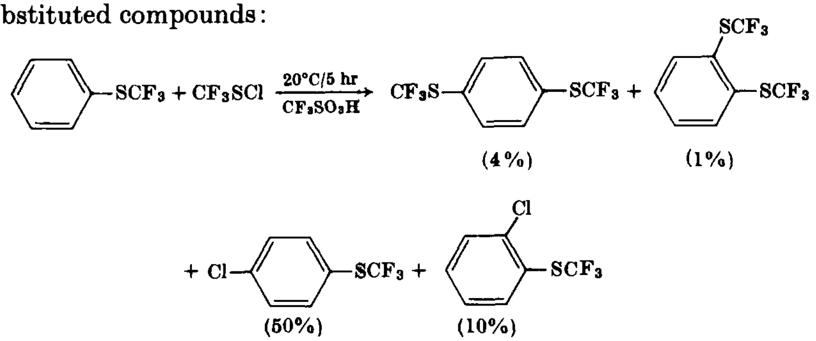
* THF, tetrahydrofuran.

isomers, the catalyst being anhydrous hydrogen fluoride (*4*). Compound C_6F_5SCl reacts with pentafluorobenzene in the presence of SbF_5 to give $C_6F_5SC_6F_5$ in 95% yield (*184*). Trifluoromethane sulfonic acid, introduced by Effenberger and Epple (*27*) for Friedel–Crafts acylations of aromatic compounds, seems to act as a particularly suitable catalyst. It is assumed that the perfluorosulfonic acid–carbonic acid anhydrides initially formed are responsible for the catalytic influence. On addition of 0.1 mole CF_3SO_3H the reaction of benzene with CF_3SCl may be carried out under mild conditions in high yield (*47*):



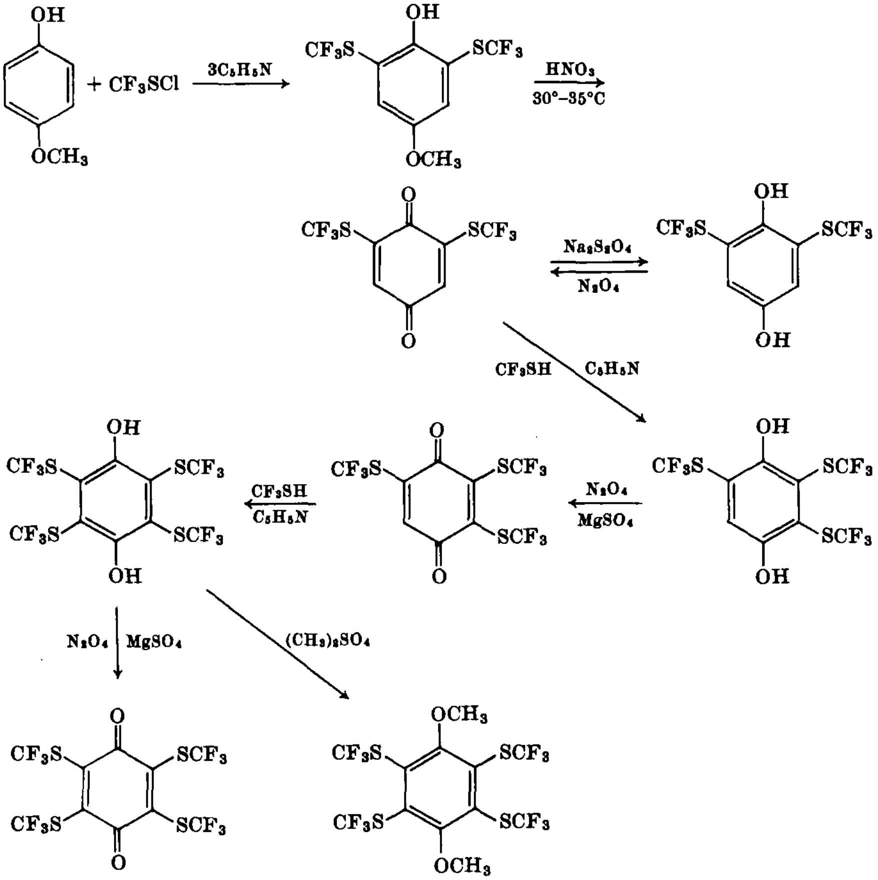
In the reaction of trifluoromethylmercaptobenzene with CF_3SCl in the presence of CF_3SO_3H, chlorine-substituted products are obtained primarily beside small quantities of bis(trifluoromethylmercapto)-substituted compounds:



No investigations have as yet been undertaken to elucidate the mechanism of these reactions, although ordinary electrophilic aromatic substitutions are the most likely. The attacking species is apparently R_fS^+ or an "activated complex" formed through coordination of the perfluorohalogenosulfenyl chloride with a Lewis or a Brønsted acid (*4*).

Hydroquinone reacts with CF_3SCl to afford, not as expected CF_3S-substituted compounds, but chlorohydroquinones instead (*143*). However, carrying out the reaction with 4-methoxyphenol in the presence of a threefold excess of pyridine and an excess of CF_3SCl, 2,6-bis(trifluoromethylmercapto)-4-methoxyphenol is formed in good yield. With concentrated nitric acid it can be oxidatively cleaved to 2,6-bis(trifluoromethylmercapto)-1,4-benzoquinone. This, in turn, reacts with CF_3SH on addition of pyridine to give 2,3,5-tris(trifluoromethylmercapto)hydroquinone, which is converted to the respective quinone by oxidation with N_2O_4 in dichloromethane in the presence of $MgSO_4$.

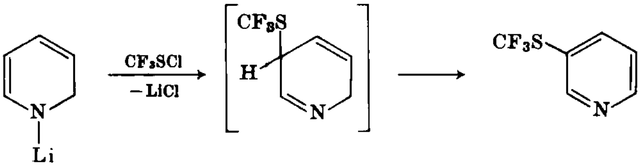
Addition of CF_3SH to this quinone affords the tetra-substituted hydroquinone (*143*) (Scheme 2).



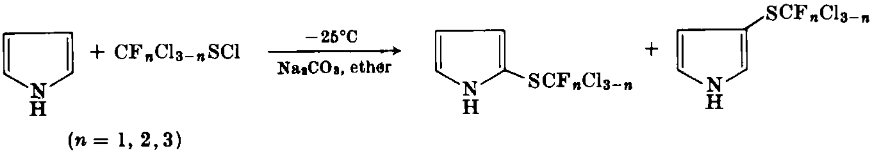
SCHEME 2

Heteroaromatics are subdivided, according to the electron influence of the heteroatom, into π-electron-deficient compounds and compounds with an excess of π electrons on the ring carbon atoms. The typical π-electron-deficient compound pyridine has so far been made to react only in one case: the reaction of lithium tetrakis(*N*-dihydropyridyl)-aluminate (LDPA) (*112–114*), obtainable from pyridine and lithium aluminum hydride, with trifluoromethanesulfenyl chloride in an excess of pyridine affords 3-trifluoromethylmercaptopyridine in low yield (13%) (*60*). This reaction probably occurs through sulfenylation of the 1,2-dihydropyridyl moiety of the LDPA with the formation of a 2,5-

dihydropyridine; this is followed by oxidation to the 3-substituted pyridine (*34*):

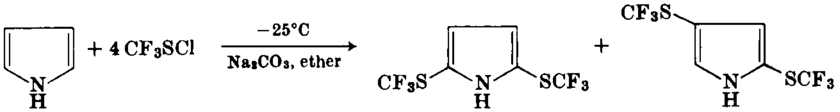


Compounds with excess of π electrons, as for example, pyrrole and thiophene, form a large number of substitution products in their reactions with perfluorohalogenosulfenyl halides (*47*, *60*). Thus pyrrole reacts with an equimolar quantity of a sulfenyl chloride of the series CF_nCl_{3-n}-SCl ($n = 1, 2, 3$) with the formation of a mixture of isomers of monosubstituted compounds:



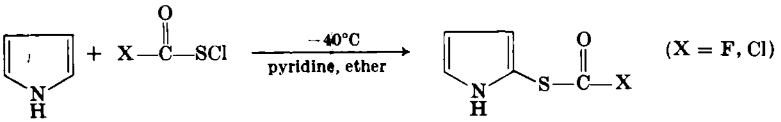
The yields decrease with decreasing degree of fluorination and at the same time the proportion of 2-substituted compounds increases.

An excess of sulfenyl chloride leads to disubstituted products only in the case of CF_3SCl:

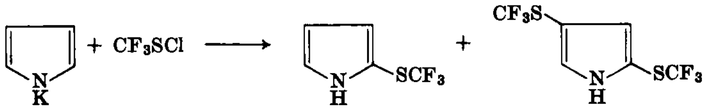


The reaction proceeds quantitatively in the direction shown only with a 1 : 4 excess of the sulfenyl chloride; the reaction in the stoichiometric ratio of 1 : 2 affords a mixture of mono- and disubstituted products.

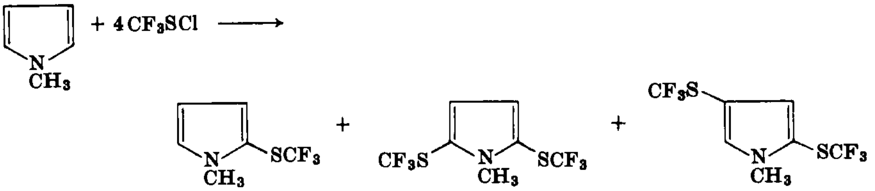
With halogenocarbonylsulfenyl chlorides, 2-substituted compounds are formed exclusively:



Attempts to N-substitute the pyrrole result exclusively in C-substituted products, e.g.,

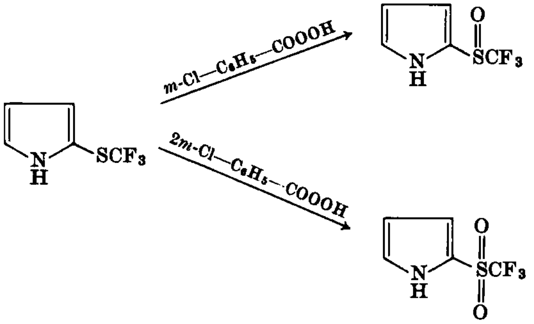


Numerous N-substituted pyrroles undergo at elevated temperatures a conversion to C-substituted compounds. However, an analogous reaction course is not feasible since *N*-methylpyrrole also reacts with CF_3SCl to give C-substituted derivatives:

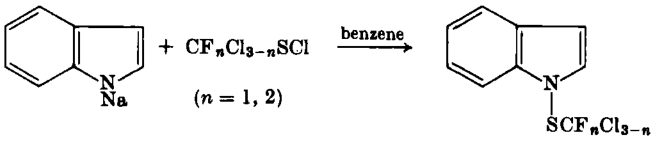


Owing to the extreme sensitivity of the pyrrole to acids, all reactions have to be carried out in high dilution and in presence of an HCl acceptor. The products can be kept for a prolonged period of time only in an extremely purified state.

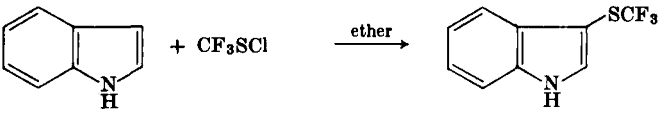
Oxidation to the sulfoxide or sulfone proceeds selectively with the aid of *m*-chloroperbenzoic acid:



Indole and carbazole, which can be regarded theoretically as derivatives of pyrrole through its anellation with one or two benzene rings, show variable behavior toward sulfenyl halides:



(91)



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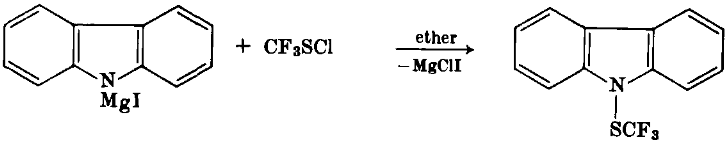
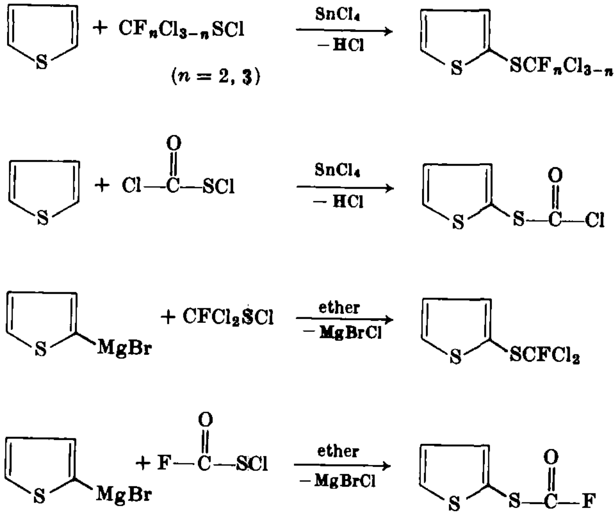


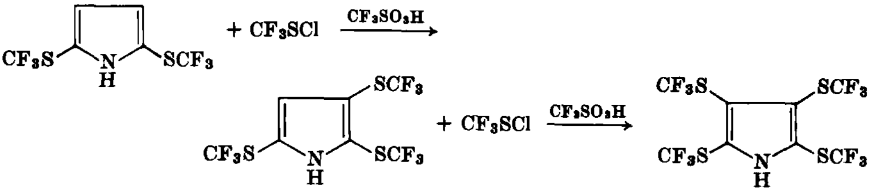
(60)

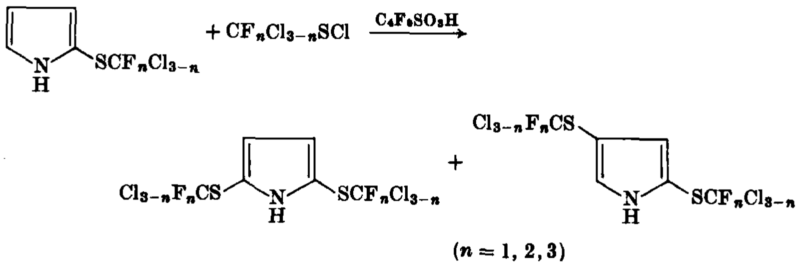
Electrophilic substitutions on thiophene, like those on benzene, can be carried out only in the presence of catalysts. In reactions with sulfenyl halides, $SnCl_4$ proved to be particularly suitable; in the case of the less reactive sulfenyl halides, Grignard reactions lead to the desired products:

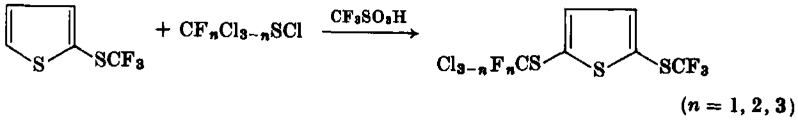


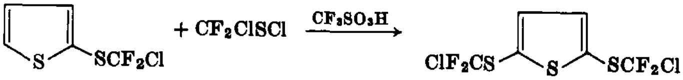
The reaction with fluorocarbonylsulfenyl chloride has to be carried out via the Grignard reagent, since, if $SnCl_4$ is used, a fluorine–chlorine exchange occurs.

The thiophene derivatives are relatively stable in the pure state. The fluorine atoms of the trifluoromethylmercapto group can be quantitatively substituted with chlorine by boron trichloride; with H_2O_2, oxidation to the sulfone takes place. Further substitution is achieved in both cases in the presence of perfluorosulfonic acids:

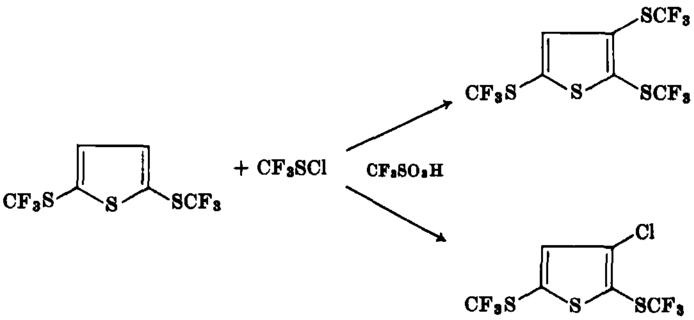




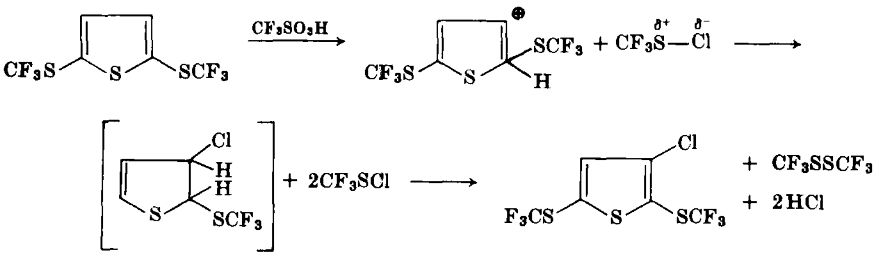




An interesting effect can be observed in the further reaction of 2,5-bis(trifluoromethylmercapto)thiophene with CF_3SCl: beside the small quantities of 2,3,5-tris(trifluoromethylmercapto)thiophene (1%), the main reaction product is 2,5-bis(trifluoromethylmercapto)-3-chlorothiophene:

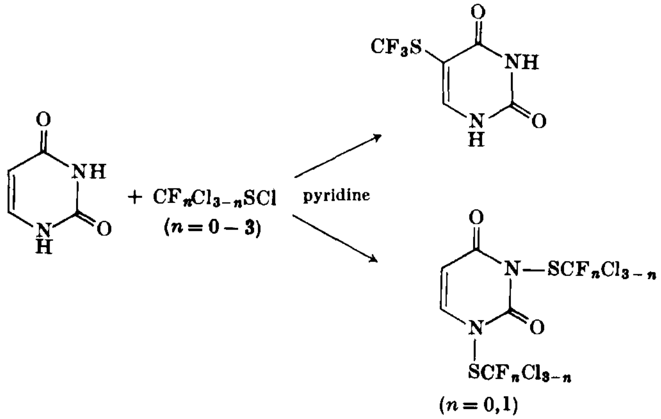


The latter reaction proceeds presumably through protonation of the starting material as follows:



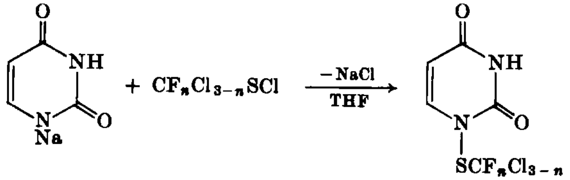
Reactions of uracil and structurally analogous compounds have been thoroughly studied (*49*, *50*). Uracil (2,4-dihydroxypyrimidine), a component of the nucleic acids, can be classified as a heteroaromatic compound only with reserve, since the keto form dominates in the tautomeric equilibrium.

With CF_3SCl and in the presence of pyridine as HCl acceptor, a reaction takes place to give 5-trifluoromethylmercaptouracil. Under identical reaction conditions the sulfenyl halides $CF_nCl_{3-n}SCl$ ($n = 0, 1$) afford dinitrogen-substituted products:



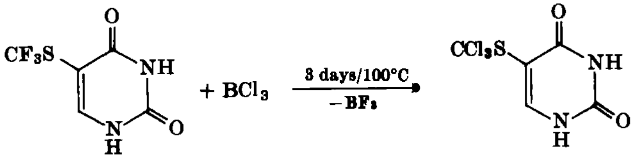
A theoretical interpretation of this different behavior is not yet available. In any case, the most obvious possibility that all sulfenyl halides attack initially at the nitrogen as the most electron abundant site (*160*), and that the CF_3S compound is then converted to the more stable 5-substituted product, is to be disregarded, since 1,3-dimethyluracil, with both nitrogen atoms blocked, gives with CF_3SCl the 5-substituted compounds in high yield.

Mononitrogen-substituted derivatives are obtained from sodium uracil and sulfenyl halides $CF_nCl_{3-n}SCl$ ($n = 0, 1, 2$) (*49*, *96*):

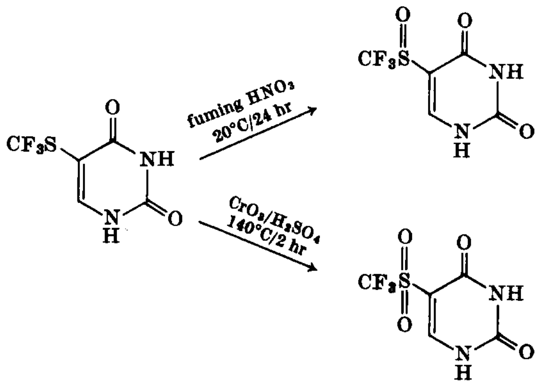


The yield decreases with increasing degree of fluorination of the reactant sulfenyl halides. In the reaction with CF_3SCl, no appreciable quantity of the desired product could be isolated. Although in the mass spectrum of the reaction mixture a peak was observed corresponding to the molecular ion $M^+ = 212$, the position of the substituent could not be unequivocally determined.

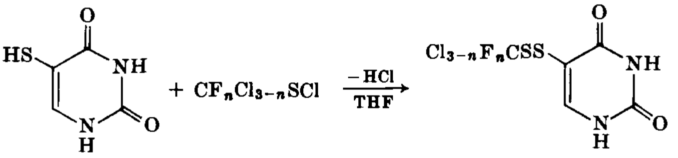
All derivatives, sulfenylated at the nitrogen atom, are stable for a prolonged period of time only at low temperature. 5-Trifluoromethylmercaptouracil is an extraordinarily stable compound. In contrast to 5-bromouracil (*129*), the substituent cannot be exchanged by amines. Nevertheless, a complete fluorine–chlorine exchange can be brought about with the aid of boron trichloride, just as with other aromatic CF_3S compounds (*170*):



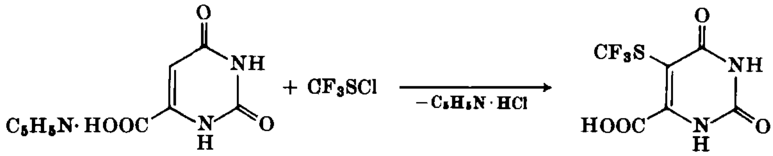
Oxidation to sulfoxide occurs with fuming nitric acid, whereas the sulfone is formed in sulfochromic acid:



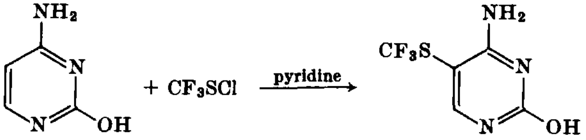
Perhalogenated sulfanes can be obtained by condensation of 5-mercaptouracil with sulfenyl halides, $CF_nCl_{3-n}SCl$ ($n = 1, 2, 3$):



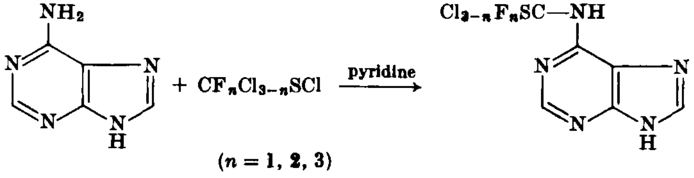
Orotic acid (uracil-6-carboxylic acid), an intermediate in the biosynthesis of uracil, also reacts smoothly with CF_3SCl in pyridine to give the 5-substituted compound. The pyridinium salt initially formed can be easily cleaved with dilute hydrochloric acid:



The nucleic acid building stone, cytosine (4-amino-2-hydroxypyrimidine), again affords, under the same conditions, a 5-substituted product:

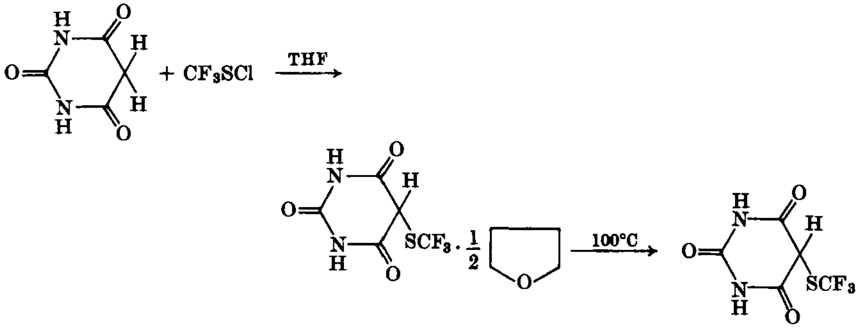


The result is surprising, as with the structurally quite similar adenine (6-aminopurine), N-substitution occurs only at the amino group (*46*):



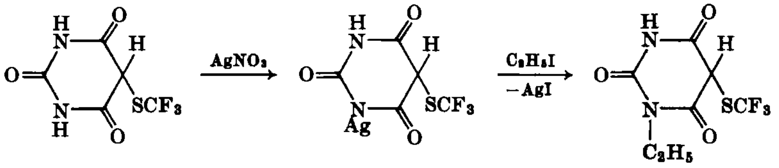
However, NMR studies provide an explanation for the course of this reaction. They show that cytosine exists, at least in polar solvents, in the form of a zwitterion (*103*) and the electrophilic CF_3S group can no longer attack at the positively charged nitrogen.

Barbituric acid, a 2,4,5-trihydroxypyrimidine, which exists in the triketo form, is also able to react with CF_3SCl. Owing to the strong acidity of the methylene group, the reaction can take place in this case without an HCl acceptor as well in a suspension in THF. The 2 : 1 etherate formed initially splits off the solvent quantitatively on heating to 100°C:

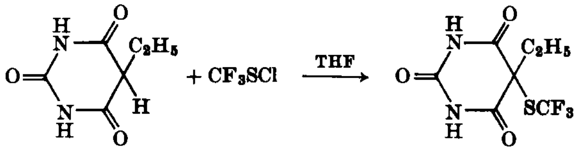


The IR spectrum suggests that the compound exists partly in the enolic form, just like the anhydrous 5-nitrobarbituric acid (*121*).

The proton remaining in the 5-position is evidently very unreactive. Metallation attempts with $AgNO_3$ lead only to the substitution of a nitrogen proton, as can be shown by the following ethylation:

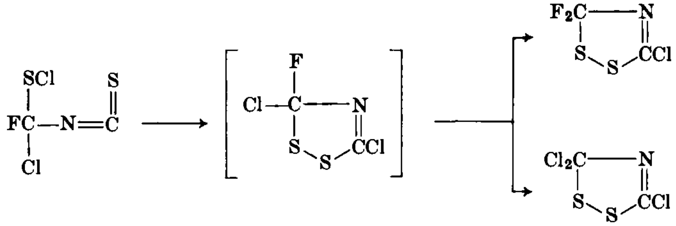


The latter compound differs considerably in its physical properties from the product resulting from a direct reaction of 5-ethylbarbituric acid and CF_3SCl:

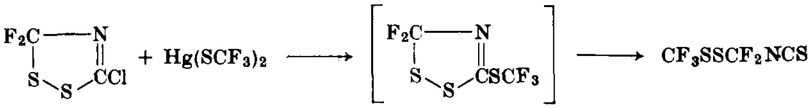


H. Cyclizations, Conversions and Reactions of Sulfenyl Chlorides with Metal Carbonyls

Heating FClC(NCS)SCl with exclusion of moisture (6–8 hr at 70°C) leads to the cyclic compounds 3-chloro-5,5-difluoro- and 3,5,5-trichloro-1,2,4-dithiazole. Presumably this ring-closure reaction takes place through the nonisolated 3,5-dichloro-5-fluoro-1,2,3-dithazole (*20*, *21*):



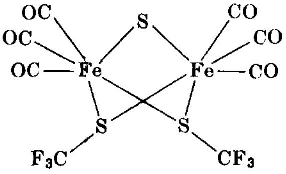
Attempts to react the difluoro-substituted ring with $Hg(SCF_3)_2$ did not lead to displacement of the chlorine by the CF_3S group, but instead CF_3SSCF_2NCS was formed quantitatively *(21)*:



Similar conversions were also observed when an attempt was made to fluorinate the compounds $CF_3SCFClSCl$ or $(CF_3S)_2CClSCl$ with HgF_2 or $HgCl_2$. Here, too, only disulfanes resulted *(20)*:

$$CF_3SC(X)ClSCl \xrightarrow{HgF_2} CF_3SSCCl_2X \quad (X{=}F, CF_3S)$$

Reactions of CF_3SCl with metal carbonyls have been investigated only to a minor extent. A reaction between $Fe(CO)_5$ and CF_3SCl takes place to give in poor yield the following binuclear complex, that exists in two isomeric forms *(37)*:



Reactions of $Mn_2(CO)_{10}$ with CF_3SCl take the following course *(38)*:

$$2Mn_2(CO)_{10} + 4CF_3SCl \longrightarrow Mn_2(CO)_8(SCF_3)_2 + CF_3SSCF_3 + 2MnCl_2 + 12CO$$

VI. Characteristics of Perfluorohalogenoorganomercapto Groups

Characteristic physical data can be attributed to some perfluorohalogenomercapto groups in the large number of compounds synthesized. The most comprehensive data material applies to the following groups: CF_3S—, CF_2ClS—, $CFCl_2S$—, and C_6F_5S—.

Systematic IR spectroscopic studies furnish the following characteristic frequencies for the $CF_nCl_{3-n}S$— ($n = 3, 2, 1$) and C_6F_5S groups:

1. CF_3S group (*122*): $\nu_{as}(C—F) = 1205–1155\ cm^{-1}$; $\nu_s(C—F) = 1135–1095\ cm^{-1}$; $\delta_s(CF_3) = 765–750\ cm^{-1}$; $\delta_{as}(CF_3) = 540–510\ cm^{-1}$; $\nu(C—S) = 495–445\ cm^{-1}$.

2. CF_2ClS group (*61*): $\nu_{as}(C—F) = 1200–1090\ cm^{-1}$; $\nu_s(C—F) = 1090–1050\ cm^{-1}$; $\nu(C—Cl) = 900–850\ cm^{-1}$; $\delta_s(CF_2) = 680–600\ cm^{-1}$; $\delta_{as}(CF_2) = 550–500\ cm^{-1}$; $\nu(C—S) = 480–400\ cm^{-1}$.

3. $CFCl_2S$ group (*61*): $\nu(C—F) = 1055–1020\ cm^{-1}$; $\nu_{as}(C—Cl) = 850–800\ cm^{-1}$; $\nu_s(C—Cl) = 760–670\ cm^{-1}$; $\delta_s(C—F) = 570–520\ cm^{-1}$; $\nu(C—S) = 450–430\ cm^{-1}$.

4. C_6F_5S group* (*9, 10*): 1630 (m) 1510 (vs) cm^{-1}; $\nu(ring) = 1475$ (vs), 1395 (m–s), 1360 (w), 1350 (w), 1270 (w–m), 1125 (m), 1080 (vs), 1055 (w) cm^{-1}; $\nu(C—F) = 970$ (vs), 905 (w) cm^{-1}; $\nu(C—S) = 860$ (vs), 715 (w–m) cm^{-1}. Bands with the intensity (w–m) do not appear in all compounds containing the C_6F_5S group.

The ^{19}F NMR chemical shifts of the $CF_nCl_{3-n}SN$ compounds (*61*) are all observed to be within very narrow limits: for $CF_3SN—$, $\delta = 51 \pm 4$ ppm; for $CF_2ClSN—$, $\delta = 38 \pm 3$ ppm; and for $CFCl_2SN—$, $\delta = 26 \pm 3$ ppm (relative to $CFCl_3$ as standard).

The electronegativity of the CF_3S group derived by different methods is found almost always to be 2.7 on Pauling's scale (*12, 23, 28, 97*). The Hammett–Taft and the Dewar constants obtained from pK_a values or from ^{19}F NMR shifts for CF_3S-substituted benzoic acids, anilines, and phenols or fluorobenzenes show that the CF_3S group has the highest electron affinity of all substituents containing divalent sulfur (*17, 18, 26, 126, 146, 147, 149, 151, 163, 164, 183*).

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* Intensities: weak (w); medium (m); strong (s); very strong (vs).

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