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## N-, O-, AND S-TRIHALOMETHYL COMPOUNDS

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### I. INTRODUCTION

A number of powerful physiological agents, such as trichloronitromethane (chloropicrin), trichloromethyl chloroformate (diphosgene), and N-trichloromethylthio-1,2,5,6-tetrahydrophthalimide ("Captan") exemplify some of the practical reasons for the persistent interest in N-, O-, and S-trihalomethyl compounds. Since the available information is not easily accessible and in order to stimulate new interest in the pure chemistry and possible metabolic pathways of these compounds, the present review has been prepared in an attempt to cover the literature up to December 31, 1963.

For practical reasons, this review will be restricted to compounds containing identical halogen atoms in the trihalomethyl group (*i.e.*,  $-\text{CF}_3$ ,  $-\text{CCl}_3$ ,  $-\text{CBr}_3$ , and  $-\text{CI}_3$ ), treating "mixed" trihalomethyl compounds (*i.e.*,  $-\text{CCl}_2\text{F}$ , etc.) only as far as they appear as intermediates or by-products. Outside the scope of this review are purely technological aspects, such as minor improvements in manufacturing processes, formulation and field application of pesticides, and analytical procedures (unless they involve basic chemical information). As a consequence of the well-organized review system for fluorine compounds (64, 135, 196, 230, 235,

339, 340, 352, 358), reference to such reviews will be made wherever appropriate. Also the existing reviews on bromine (308) and chlorine (154, 198) compounds should be consulted.

### II. N-TRIHALOMETHYL COMPOUNDS

#### A. N-TRIHALOMETHYLAMINES AND DERIVATIVES

##### 1. N-Trifluoromethylamines and Derivatives

###### a. Preparation and Chemical Properties

When N-methylamines are treated with elemental fluorine or metal fluorides, or electrofluorinated in liquid hydrogen fluoride, all hydrogen atoms are replaced by fluorine. With larger molecules more or less extensive degradation often occurs at the same time (12, 64, 135, 168, 170, 196, 230, 235, 336, 339, 340, 352, 358). Thus one obtains compounds of the type  $\text{CF}_3\text{NRR}'$ ,  $(\text{CF}_3)_2\text{NR}$ ,  $(\text{CF}_3)_3\text{N}$ ,  $\text{CF}_3\text{NF}_2$ , and  $(\text{CF}_3)_2\text{NF}$ , where R and R' designate perfluoroalkyl groups. These N-trifluoromethyl compounds are characterized by extreme chemical inertness and lack of basicity. Typical by-products are hexafluoroazomethane and tetrakis(trifluoromethyl)hydrazine (196). Tertiary N-trifluoromethylamines with unfluorinated alkyl groups are obtained by

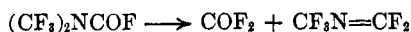
treating tetrasubstituted thiourea derivatives (342) or tetrasubstituted thiuram disulfides (159) with sulfur tetrafluoride.

The fluorination of nitriles and N-methylamides with fluorine is another source for N-trifluoromethyl compounds (9, 40, 196, 306).  $\text{CF}_3\text{NF}_2$  and  $(\text{CF}_3)_2\text{NF}$  are also obtained by treating acetonitrile with nitrogen trifluoride using cobaltic fluoride as a catalyst (94). When cyanuric fluoride was fluorinated with fluorine, the following compounds were isolated (together with cyclic products):  $\text{CF}_3\text{NFCF}_2\text{NF}_2$ ,  $\text{CF}_3\text{NFCF}_2\text{NFCF}_3$ ,  $\text{CF}_3\text{NFCF}_2\text{NFCF}_2\text{NF}_2$ ,  $\text{CF}_3\text{NFCF}=\text{NCF}_3$ , and  $(\text{CF}_3)_2\text{NCF}=\text{NF}$  (201). Analogous results are obtained in the fluorination of 2,4,6-tris(trifluoromethyl)-s-triazine (202).

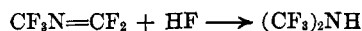
Electrochemical fluorination of carbamic acid derivatives gives products like  $(\text{CF}_3)_2\text{NCOF}$ ,  $\text{O}(\text{CF}_2\text{CF}_2)_2\text{NCOF}$ , and  $(\text{CF}_3)_2\text{NCON}(\text{CF}_3)_2$  (196, 395). From N,N-dimethylcarbonyl chloride,  $(\text{CF}_3)_2\text{NCOF}$  is obtained with  $(\text{CF}_3)_2\text{NCOCl}$  as a by-product (396). Similarly, N,N-dimethylglycine derivatives can be electrofluorinated to  $(\text{CF}_3)_2\text{NCF}_2\text{COF}$  (395). Perfluorinated amides of the type  $\text{CF}_3\text{CON}(\text{CF}_3)_2$  have been obtained (196). N-Trifluoromethylcarbamic acid derivatives are available *via* trifluoromethyl isocyanate, which in turn can be made from hexafluoroazomethane and carbon monoxide at 325° and 650 atm. (71), from trifluoroacetyl chloride and sodium azide (18), from trifluoroacetamide or bis(trifluoroacetyl)imide and argentic fluoride (400), as well as from perfluoro-2-azapropene and water (18, 399) or silica (18).

Thus, ethanolysis of trifluoromethyl isocyanate gives 31% N-trifluoromethylurethan together with 51% bis(trifluoromethyl)amine (18). A great number of alcohols have been treated with trifluoromethyl isocyanate to yield the corresponding urethans (267). Similarly, thiols give rise to the corresponding thiolcarbamic esters (390).

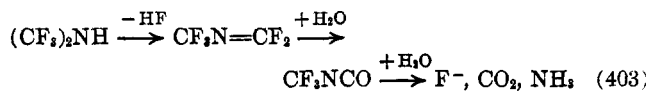
N,N-Bis(trifluoromethyl)carbonyl fluoride may be further fluorinated with argentic fluoride to give  $(\text{CF}_3)_2\text{NF}$  and  $(\text{CF}_3)_2\text{NN}(\text{CF}_3)_2$  (400). Pyrolysis of  $(\text{CF}_3)_2\text{NCOF}$  yields carbonyl fluoride and perfluoro-2-azapropene (196).



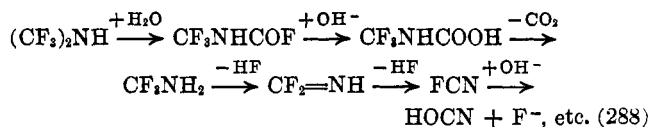
The latter adds hydrogen fluoride to give bis(trifluoromethyl)amine (196).



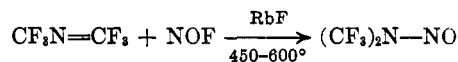
Bis(trifluoromethyl)amine exhibits no basic properties. Thus it neither forms a hydrochloride nor a boron trifluoride adduct. It cannot be acylated with trifluoroacetyl chloride or trifluoroacetic anhydride and can be distilled unchanged from its solution in anhydrous trifluoroacetic acid (403). Two different schemes have been proposed for its hydrolysis



and



With argentic fluoride, bis(trifluoromethyl)amine is converted to  $(\text{CF}_3)_2\text{NF}$  and  $(\text{CF}_3)_2\text{NN}(\text{CF}_3)_2$  (400). Bis(trifluoromethyl)amine can be nitrated with nitric acid in trifluoroacetic acid to the corresponding nitramine, though not nitrosated (403). However, the nitrosamine is available *via* the rubidium fluoride-catalyzed addition of nitrosyl fluoride to perfluoro-2-azapropene at high temperature.



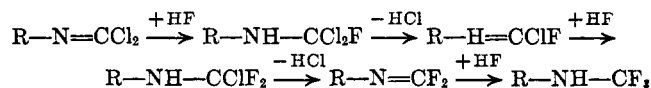
The nitrosamine is a yellow, unstable gas. With peroxytrifluoroacetic acid it can be oxidized to the nitramine (404). Bis(trifluoromethyl)amine can be chlorinated in the presence of sodium fluoride to the N-chloro compound. The N-chloramine reacts with carbon monoxide to yield N,N-bis(trifluoromethyl)carbonyl chloride (364).

Mercuric fluoride adds to perfluoro-2-azapropene to give a mercury derivative of bis(trifluoromethyl)amine.



The mercury amide can be halogenated to the corresponding N-brom- and N-chloramines. N-Bromobis(trifluoromethyl)amine has been added to the double bond of perfluoropropene (403). When the mercury amide is treated with acyl chlorides, the corresponding N,N-bis(trifluoromethyl)amides are obtained (401). It reacts with both nitrosyl chloride and nitryl chloride yielding bis(trifluoromethyl)nitrosamine and bis(trifluoromethyl)nitramine, respectively (237). With sulfur the mercury amide gave, among other products,  $(\text{CF}_3)_2\text{N}-\text{S}-\text{N}(\text{CF}_3)_2$  and  $(\text{CF}_3)_2\text{N}-\text{S}-\text{S}-\text{N}(\text{CF}_3)_2$  (404). N-Sulfides of secondary N-trifluoromethylamines result also from the interaction of isothiocyanates with iodine pentafluoride (354). When treated with acetic anhydride, the sulfides yield N-trifluoromethylamides (354).

An alternative route to secondary trifluoromethylamines is the treatment of N-dichloromethylenamines with hydrogen fluoride.



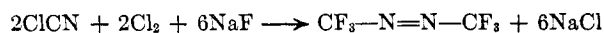
In this manner, N-trifluoromethylaniline and N-trifluoromethyl-p-toluidine were prepared from the corresponding N-dichloromethylene compounds and bis(tri-

fluoromethyl)amine from perchloro-2-azapropene. With excess aniline, only one of the fluorine atoms in N-trifluoromethylaniline is substituted. After hydrolysis, N,N'-diphenylurea is obtained (288). Aromatic N-trifluoromethylamines have been treated with sulfenyl chlorides to yield the corresponding sulfenamides (116).

Perfluoroazomethines of the type  $R_F-N=CF_2$  or  $CF_3N=CFR_F$  which will yield derivatives of secondary N-trifluoromethylamines by addition reactions to the double bond are also obtained by pyrolysis of the appropriate tertiary perfluoroamines (196) or by fluorination of nitriles (40). Perfluoro-2-azapropene is also formed in the reaction between trifluoroacetonitrile and nitrogen trifluoride. Perfluoroazomethines, *i.e.*,  $CF_3N=CF_2$  and  $CF_3CF=NCF_3$ , are obtained from the reaction of perfluoropropene with nitrogen trifluoride at high temperature (94). Perfluoro-2-azapropene can be made in high yield by dehydrofluorination of bis(trifluoromethyl)amine over potassium fluoride at 140–150° (289). It is further formed in the pyrolysis of tetrakis(trifluoromethyl)hydrazine (398). N-Difluoromethylaniline has been made by dehydrofluorination of N-trifluoromethylaniline (289).

At 540° perfluoro-2-azapropene reacts with trifluoromethylsulfur pentafluoride to give perfluorotrimethylamine. With perfluoroethylsulfur pentafluoride the reaction is analogous (196). Perfluoro-2-azapropene has been shown to dimerize when irradiated with ultraviolet light (179, 180) or, at -70 to -50°, in the presence of pyridine (237). For the dimer two alternative structures,  $CF_3-N=CF-N(CF_3)_2$  and  $CF_3-N=CFCF_2NFCF_3$ , have been suggested (179, 180). The dimer, when pyrolyzed at 500°, gives the monomer. With aniline the dimer forms the same products as the monomer (237).

Hexafluoroazomethane, the first N-trifluoromethyl compound to be prepared, has been made from silver cyanide and fluorine, cyanogen iodide and iodine pentafluoride, cyanogen chloride and argentic fluoride (196, 310), ethylenediamine or ethylenimine and fluorine, as well as from hydrogen cyanide and cobaltic fluoride (71). The most satisfactory method seems to be the treatment of cyanogen chloride with chlorine and sodium fluoride (71).

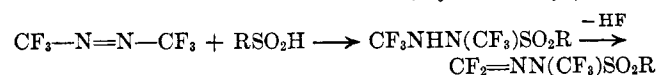
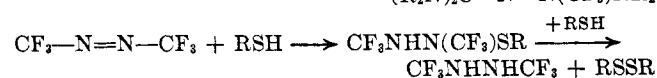
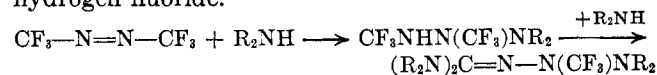


Hexafluoroazomethane has been obtained in the *cis* and the *trans* form (140). N-Trifluoromethylazo compounds of the general formula  $CF_3-N=N-R$  are available from the condensation of trifluoronitrosomethane with primary amines (238). N-Trifluoromethylazo compounds are also obtained by oxidation of the corresponding hydrazo compounds or reduction of the corresponding azoxy compounds (139).

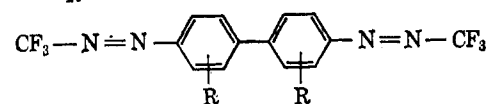
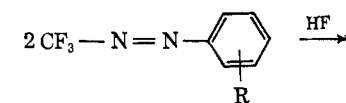
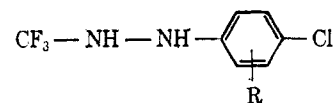
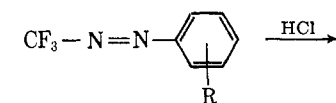
Hexafluoroazomethane can be used as a source of

trifluoromethyl radicals. Photolysis with ultraviolet light or pyrolysis gives perfluoro-2-azapropene, tetrakis(trifluoromethyl)hydrazine, and hexakis(trifluoromethyl)tetrazane (71, 139). Pyrolysis in the presence of tetrafluorohydrazine gives rise to N,N-difluoro-trifluoromethylamine (398). When pyrolyzed in the presence of carbon monoxide at 465°, it is converted to hexafluoroethane. With bromine, bromotrifluoromethane is formed and with sulfur bis(trifluoromethyl)polysulfides are obtained. With iron pentacarbonyl, hexafluoroazomethane is defluorinated to tetrafluoroformazine (71). Hexafluoroazomethane will act as a dienophile in Diels-Alder reactions with dienes or azines (71, 140). While extremely stable towards oxidizing agents, hexafluoroazomethane can be reduced to the corresponding hydrazo compound with hydrogen iodide, hydrogen sulfide, or phosphine in ether or methanol. N,N'-Bis(trifluoromethyl)hydrazine can be reoxidized to the azo compound with potassium permanganate in acetic acid. The azo compound is obtained in the yellow *cis* form which is easily isomerized to the *trans* form by light or by alkali. With ether, acetone, and triethyl phosphite, N,N'-bis(trifluoromethyl)hydrazine forms stable complexes. With aniline,  $(C_6H_5NH)_2C=N-N=C(NHC_6H_5)_2$  is formed and with thiophenol,  $(C_6H_5S)_2C=N-N=C(SC_6H_5)_2$ . Aluminum chloride converts N,N'-bis(trifluoromethyl)hydrazine to the dimer of tetrafluoroformazine (140).

Hexafluoroazomethane adds to its double bond secondary amines, thiols, and sulfinic acids. The addition products react either with excess reagent or split off hydrogen fluoride.



Grignard reagents add to the double bond of hexafluoroazomethane and, after hydrolysis, the corresponding hydrazinecarboxylic acid fluoride is obtained. This



can be converted to the corresponding amides and esters and, by hydrolysis and decarboxylation, to the parent hydrazine (140).

With diazomethane, hexafluoroazomethane forms two products, namely, 1,2-bis(trifluoromethyl)di-aziridine and 1,2-bis(trifluoromethyl)- $\Delta^3$ -tetrazoline (140).

Trifluoromethylazoarenes are converted to the corresponding *p*-chloroarylhydrazines when treated with hot hydrochloric acid while anhydrous hydrogen fluoride initiates a dimerization to a benzidine derivative (140).

#### b. Physical Properties

As most fluorine compounds, N-trifluoromethylamines and related compounds have a high volatility. Many of the lower molecular compounds are gaseous at room temperature.

The atomic distances in perfluorotrimethylamine have been determined by means of electron diffraction measurements (232). Nuclear magnetic resonance spectra of tertiary N-trifluoromethylamines (269, 270), N-trifluoromethylamides (401), N-trifluoromethyl-N-fluoramines (40, 202) [data given in a previous paper (306) were later withdrawn as incorrect (202)], N-trifluoromethylcarbamic acid derivatives (270), perfluoroazomethines (40, 270, 401), bis(trifluoromethyl)nitrosamine (404), and bis(trifluoromethyl)nitramine (167) have been recorded and interpreted.

The  $^{19}\text{F}$  chemical shift of  $-36$  p.p.m. for trifluoromethyl groups bound to nitrogen reported by Muller, Lauterbur, and Svatos (270) was claimed to be erroneous by Bishop, Hynes, and Bigelow who found a value of  $-18$  p.p.m. (40).

The infrared spectra of N-trifluoromethylamines (17, 156), perfluoroazomethines (156), bis(trifluoromethyl)nitrosamine, and bis(trifluoromethyl)nitramine (404) have been recorded and discussed. The absorptions fall within the expected ranges.

The ultraviolet absorption maximum of hexafluoroazomethane was found at  $405\ \mu$  for the *cis* and at  $355\ \mu$  for the *trans* isomer by one group of authors (140) and, without mention of isomerism, at  $365\ \mu$  by another group (203). Other aliphatic N-trifluoromethylazo compounds were found to absorb between  $372$  and  $377\ \mu$  (203).

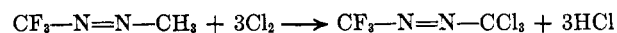
#### 2. N-Trichloromethylamines and Derivatives

Trichloromethylamine has been claimed by Ascher to be formed in 10% yield in the Hofmann degradation of trichloroacetamide with hypobromite (hypochlorite gave rise to complete decomposition). The claimed trichloromethylamine was strongly acidic and formed a monosilver salt with aqueous silver nitrate (5). Hine and Rosscup could only isolate bromotrichloromethane from the same reaction and implicitly challenged Ascher's claim (186).

The chlorination of N,N-diethylthiocarbamoyl chloride yields a white, explosive solid believed to be diethyltrichloromethylamine (393). Similarly, from the chlorination of tetramethylthiuram disulfide a reactive white solid is obtained which reacts with either water or methanol to give N,N-dimethylcarbamoyl chloride (323).

When trichloronitrosomethane is heated to  $120^\circ$  in an inert atmosphere, perchloro-2-azapropene is obtained (295). It is unreactive towards water, dissolves in organic solvents, and is stable to prolonged storage. It does not react with hydrogen sulfide nor with sodium or copper sulfide and yields with excess aniline in anhydrous ether  $(\text{C}_6\text{H}_5\text{NH})_2\text{CCl}-\text{N}=\text{C}(\text{NHC}_6\text{H}_5)_2$  and  $(\text{C}_6\text{H}_5\text{NH})_3\text{C}-\text{N}=\text{C}(\text{NHC}_6\text{H}_5)_2$  (287). With excess hydrogen fluoride, bis(trifluoromethyl)amine is formed (394).

Under ultraviolet irradiation at  $300^\circ$ , N-trifluoromethylazomethane is chlorinated in the methyl group. 1,1,1-Trichloro-4,4,4-trifluoro-2,3-diazabutene-2 is formed in unspecified yield (139).



#### B. TRIHALONITROSOMETHANES AND DERIVATIVES

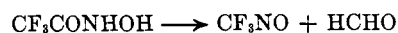
Lacking  $\alpha$ -hydrogen atoms, these compounds are "true" nitroso compounds. They do not, however, show the common dimerization phenomenon, no colorless dimers being formed at low temperatures.

##### 1. Trifluoronitrosomethane and Derivatives

Trifluoronitrosomethane, a deep blue gas, was first encountered by Ruff and Giese in the fluorination of silver cyanide contaminated with the oxide and the nitrate (196). Practical preparations include the treatment of trifluoroiodomethane with nitric oxide (196, 207, 248), thermal breakdown of the mixed anhydride formed from silver trifluoroacetate (13, 196, 357) or trifluoroacetic anhydride (285) and nitrosyl chloride



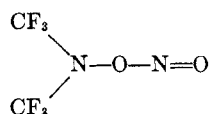
and the thermal degradation of trifluoroacetohydroxamic acid (224)



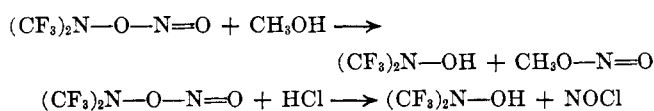
It is also formed in low yield when tris(trifluoromethyl)arsine is treated with nitrosyl chloride or nitric oxide (196).

Trifluoronitrosomethane has been intensively studied with regard to its ultraviolet and infrared spectra both in the gas phase and in solution (196, 245, 248). In the liquid state it is diamagnetic (196) and unassociated as judged by the Trouton constant (208). According to the spectroscopic evidence, trifluoronitrosomethane exhibits extremely weak, if any, hydrogen bonding in aqueous solutions and is not protonated in concentrated sulfuric acid (245).

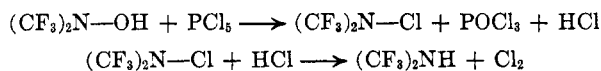
Irradiation of trifluoronitrosomethane with ultraviolet light (177, 246) or treatment with nitric oxide (19, 388) converts it partially to a pale orange gaseous dimer of the structure



After a preliminary erroneous structural assignment on spectroscopic grounds as N,O-bis(trifluoromethyl)-N-nitrosohydroxylamine (208), the dimer has been thoroughly investigated by means of ultraviolet, infrared, and n.m.r. spectroscopy (177, 246) as well as with regard to its chemistry (178, 246). It could be concluded from the spectroscopic evidence that all the fluorine atoms are equivalent, which implies that there is no rotational isomerism at room temperature. N,N-Bis(trifluoromethyl)-O-nitrosohydroxylamine decomposes, especially in the light, yielding mainly nitrogen, nitrous oxide, nitrogen dioxide, carbon dioxide, and silicon tetrafluoride from attack on the glass, trifluoronitrosomethane, perfluoro-2-azapropene, and N,N-bis(trifluoromethyl)nitramine (246). Methanol or hydrogen chloride converts the dimer to N,N-bis(trifluoromethyl)hydroxylamine.



N,N-Bis(trifluoromethyl)hydroxylamine is stable to 20% aqueous hydrochloric acid, while fluoride and nitrite ions are formed in alkaline solution. With phosphorus pentachloride, bis(trifluoromethyl)amine is formed, presumably *via* the N-chloramine (178).



Pyrolysis of trifluoronitrosomethane at 100–150° yields trifluoronitromethane and perfluoro-2-azapropene.

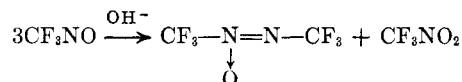


At 250–300°, also N,N,O-tris(trifluoromethyl)hydroxylamine is formed (389).

The flash photolysis of trifluoronitrosomethane has been shown to yield nitric oxide, but no detectable amounts of the species CF expected from the decomposition of trifluoromethyl radicals into CF and F<sub>2</sub>, presumably because the trifluoromethyl radicals are so reactive that the decomposition cannot compete with their reaction with the starting material (199).

The dark decomposition of trifluoronitrosomethane as well as its decomposition by red light have been investigated and the products examined spectroscopically. The decomposition pattern appears to be complex and details still remain obscure (247).

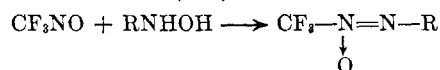
In contact with active charcoal, trifluoronitrosomethane is converted to colorless hexafluoroazoxymethane (196, 207) which is also obtained from the disproportionation of trifluoronitrosomethane in alkaline solution or by its reduction with hypophosphite (388).



Trifluoronitrosomethane is oxidized at higher temperatures to the nitro compound by 30% hydrogen peroxide (196, 207), hypochlorite (388), manganese oxides, lead dioxide, or chromic anhydride (171).

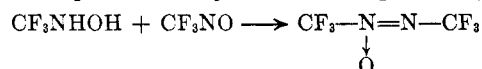
With triethyl phosphite at –70°, trifluoronitrosomethane forms a 1:1 complex which decomposes with excess trifluoronitrosomethane to yield hexafluoroazoxymethane and triethyl phosphate. A similar complex with trimethylamine gives hexafluoroazoxymethane, dimethylamine, and formaldehyde (388).

Phosphinimines convert trifluoronitrosomethane to trifluoromethylazo compounds (389). With N-substituted hydroxylamines the corresponding azoxy compounds are formed (388).

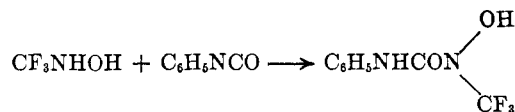


In ethereal solution, trifluoronitrosomethane reacts with hydrogen iodide to form N-trifluoromethylhydroxylamine and iodine, while the reaction with ethanethiol gives the same hydroxylamine and diethyl disulfide (388).

N-Trifluoromethylhydroxylamine gives azoxy compounds with perfluoroalkyl nitroso compounds (388).

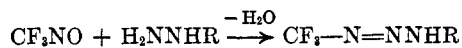


With diazomethane, N-trifluoromethyl-N,O-dimethylhydroxylamine is formed (388, 389). With phenyl isocyanate an addition reaction takes place (388).

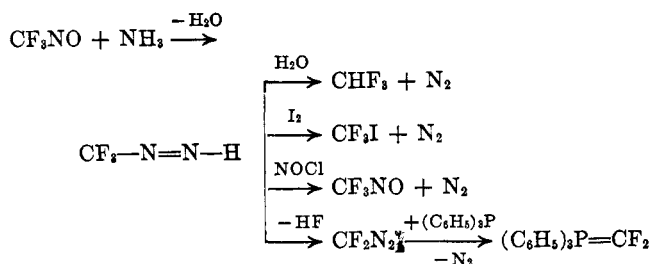


At 100°, trifluoronitrosomethane reacts with nitric oxide to yield unstable N-trifluoromethyl-N,O-bisnitrosohydroxylamine, which is an intermediate in the formation of the dimer (*vide supra*). By the action of base the O-nitroso group can be removed and N-trifluoromethyl-N-nitrosohydroxylamine is obtained. The latter forms complex metal salts of the cupferron type. The salts are easily oxidized to trifluoronitromethane and can be acylated to O-acyl derivatives of N-trifluoromethylhydroxylamine with simultaneous loss of the N- and O-nitroso groups. Methanol removes both nitroso groups of N-trifluoromethyl-N,O-bisnitrosohydroxylamine and converts it to N-trifluoromethylhydroxylamine (389).

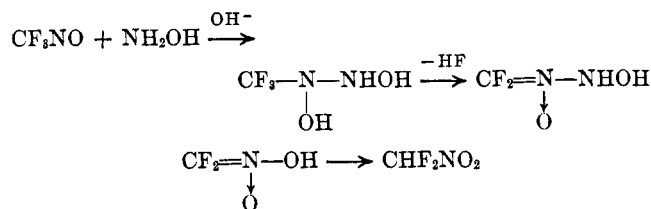
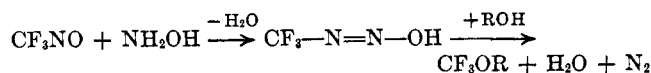
When trifluoronitrosomethane reacts with primary amines, hydrazine, hydrazine derivatives, or O-substituted hydroxylamines, water is eliminated and a nitrogen-nitrogen double bond formed (238).



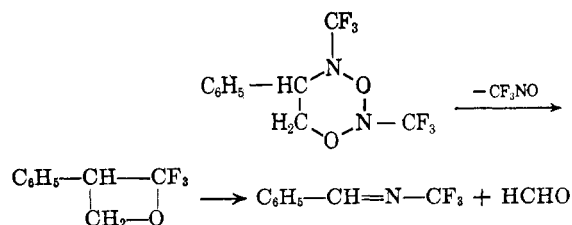
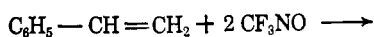
At  $-70^\circ$  in ether solution, trifluoronitrosomethane is converted by ammonia to unstable N-trifluoromethylidene, characterized by its reactions (238).



In alcoholic solutions hydroxylamine converts trifluoronitrosomethane to the corresponding O-trifluoromethyl ethers, while difluoronitromethane is formed in alkaline solution (238).



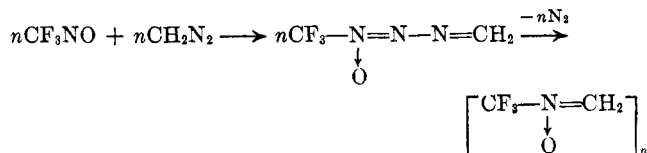
Trifluoronitrosomethane may be added to double bonds to form either four-membered rings or polymeric material (19, 196, 237). With simple perhalogenated olefins, oxazetidines are formed together with 1:1 polymers with a molecular weight of up to 1,500,000. Oxazetidine formation is favored at  $100^\circ$ , while polymerization prevails at low temperatures. Both products could be pyrolyzed to perhalo-2-azapropene and carbonyl dihalide. It could be shown that the orientation in the oxazetidine is opposite to that in the polymer (19). Halogen-free olefins behave in the same fashion. Styrene, however, forms both a 1:1 and a 1:2 adduct. The latter loses trifluoronitrosomethane on heating and gives the oxazetidine, which in turn can be pyrolyzed to the azomethine and formaldehyde.



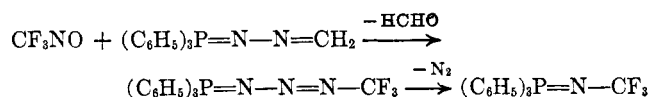
Diphenylketene undergoes a facile addition to yield the corresponding oxazetidinone which on pyrolysis gives trifluoromethyl isocyanate together with traces of trifluoronitrosomethane. Trifluoronitrosomethane also adds to carbon-carbon triple bonds.

The addition of trifluoronitrosomethane to diethyl azodicarboxylate at  $100\text{--}150^\circ$  under pressure gives rise to the carbon-free oxatriazetidine ring system.

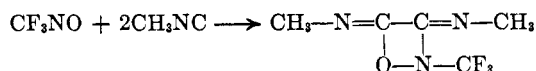
In ethereal solution at  $-70^\circ$ , diazomethane converts trifluoronitrosomethane to a polymeric nitrene with loss of molecular nitrogen.



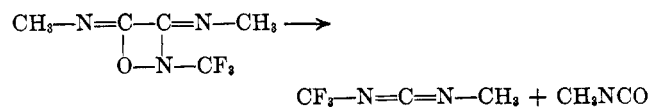
With phosphazines, phosphinimines are formed, *i.e.*



Trifluoronitrosomethane reacts with two molecules of methyl isocyanide to yield a diiminoxazetidine.

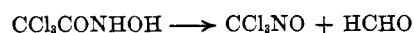


At  $350\text{--}400^\circ$  the oxazetidine is pyrolyzed to methyl isocyanate and N-methyl-N'-trifluoromethylcarbodiimide (237).



## 2. Trichloronitrosomethane

Trichloronitrosomethane was first encountered by Loew, but wrongly assigned the structure  $\text{CCl}_3\text{SO}_2\text{NO}_2$ . Prandtl, *et al.*, explored its chemistry and found that it can be prepared conveniently by adding an aqueous solution of sodium trichloromethanesulfinate, potassium nitrate, and sodium nitrite to 20% aqueous sulfuric acid at  $70^\circ$  (294, 295). Trichloronitrosomethane can also be prepared by heating trichloroacetohydroxamic acid at  $90\text{--}95^\circ$  and 20–30 mm. pressure (224).

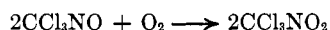
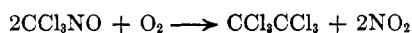


Electrochemical reduction of trichloronitromethane in alcoholic sulfuric acid also yields trichloronitrosomethane. The yield, which is dependent upon the sulfuric acid concentration, the temperature, the current density, and the electrode materials, can reach up to 70% (56). When carbon tetrachloride, bromotrichloromethane, or trichloronitromethane are irradiated with an electron beam of 3 Mev. and treated with nitric oxide, approximately 50% trichloronitrosomethane is ob-

tained (based on 10% conversion of the substrate) (82).

Trichloronitrosomethane has an intense blue color and decomposes completely within 2-3 months when kept in a closed vial at room temperature. It also decomposes at its boiling point at atmospheric pressure (294, 295). Its infrared spectrum has been investigated and found to contain only one peak at  $1616\text{ cm.}^{-1}$  due to N-O valence vibration, and thus trichloronitrosomethane must be monomeric at room temperature (356).

Flash photolysis of trichloronitrosomethane was found to produce trichloromethyl radicals and nitric oxide (199). Pyrolysis of trichloronitrosomethane yields mainly perchloro-2-azapropene, trichloronitromethane, and minor amounts of nitrosyl chloride, nitric oxide, and hexachloroethane. With oxygen two parallel reactions are observed.



Chromic acid oxidation yields trichloronitromethane only. Reduction of trichloronitrosomethane with iron and acetic acid leads to methylamine. Reduction with either stannous chloride, sulfurous acid, or hydrogen sulfide produces dichloroformoxime,  $\text{CCl}_2=\text{NOH}$ . When treated with aqueous sodium hydroxide, trichloronitrosomethane is converted to dichloronitromethane. Excess aniline converts trichloronitrosomethane to phenyliminobenzeneazochloromethane,  $\text{C}_6\text{H}_5-\text{N}=\text{CCl}-\text{N}=\text{N}-\text{C}_6\text{H}_5$  (294, 295). Unlike other nitroso compounds trichloronitrosomethane does not react with nitric oxide (278).

### 3. Tribromonitrosomethane

Tribromonitrosomethane has been obtained by treatment of mercuric fulminate with aqueous potassium hypobromite (110) and from the bromination of sodium fulminate in glacial acetic acid (32). There is no account of its chemical properties.

## C. TRIHALONITROMETHANES

### 1. Trifluoronitromethane (*Fluoropicrin*)<sup>1</sup>

All practical preparations of trifluoronitromethane are based upon the oxidation of trifluoronitrosomethane. Lead dioxide, manganese oxides, chromic oxide, hydrogen peroxide, and oxygen have been employed as oxidants, usually at a temperature of  $100^\circ$  (171, 196). Low yields of trifluoronitromethane have been obtained in the fluorination of bromodifluoronitromethane with chlorine difluoride (196) and in the nitration of trifluoroacetic anhydride with nitric acid (49).

The ultraviolet (11, 196, 245) and infrared (196, 249) spectra of trifluoronitromethane have been recorded and interpreted. Electron diffraction measurements have been employed to calculate the atomic distances

and bond angles in trifluoronitromethane. It was concluded that trifluoromethane exists both in the staggered and in the eclipsed configuration and that the unusually large carbon-nitrogen distance of  $1.56 \pm 0.02\text{ \AA}$ . must be related to the thermal instability of trifluoronitromethane (216).

Pyrolysis of trifluoronitromethane at  $500^\circ$  gave only highly volatile products. No polymerization was observed (171).

### 2. Trichloronitromethane (*Chloropicrin*)

The chemistry of trichloronitromethane has been reviewed (205, 300).

Trichloronitromethane has been investigated by means of ultraviolet (11, 171, 172, 249, 341), infrared (60, 171, 172, 249 (see also 250 for corrections), 250, 341), and Raman (300) spectroscopy. Electron diffraction measurements have been employed to calculate the atomic distances and bond angles in trichloronitromethane (20). Trichloronitromethane has been used as an example in the calculation of latent heat and vapor pressure data by means of a universal equation based upon boiling points (360). The difference between calculated and observed dipole moment has been used to assess mesomeric effects (350). Spectroscopic analysis of the O-O transition at different temperatures showed a phase transition at  $70^\circ$  (58).

Trichloronitromethane forms addition compounds with thiourea (309) and with hydrogen sulfide (as a hydrate) (353).

With Grignard reagents luminescence is observed. Oxidation reactions could be excluded as a cause (96). With methylmagnesium iodide a gas is evolved. Hence trichloronitromethane interferes with the Zerewitinoff determination (138).

Trichloronitromethane reacts with N,N-dichlorobenzene-sulfonamide in the presence of aluminum chloride to yield cyanuric chloride, benzenesulfonyl chloride, and chlorine (228). When aromatic nitro compounds are treated with trichloronitromethane, the aromatic nitro group is replaced by chlorine (293). Trichloronitromethane does not add to the carbon-carbon double bond (23). Trichloronitromethane sensitizes the reaction between hydrogen and oxygen (6) and between hydrogen and chlorine (7). The kinetics of the sensitized reactions have been studied (8).

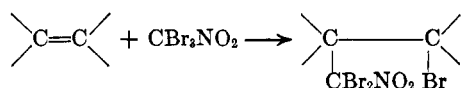
The determination of trichloronitromethane in air (often in the presence of phosgene and nitrosyl chloride, formed in its decomposition) is of great practical interest (80, 268). Typical methods are the conversion of trichloronitromethane to nitrous acid by means of concentrated sulfuric acid (212) or sodium peroxide (131), nitrosation of a suitable aromatic compound, and colorimetry as well as the colorimetric determination of glutaconic aldehyde formed from trichloronitromethane and pyridine (136).

### 3. Tribromonitromethane (Bromopicrin)

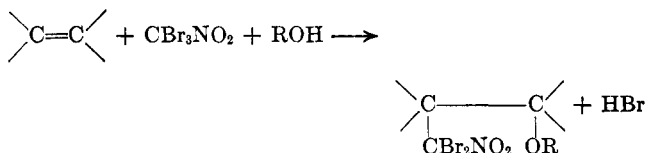
Tribromonitromethane is best made by treatment of picric acid with aqueous hypobromite (197, 318, 372). Small amounts of bromodinitromethane and dibromodinitromethane are encountered as by-products, thought to be formed from tribromonitromethane and calcium nitrite (318). Tribromonitromethane is also obtained in the hydrolysis of compounds containing nitro groups and bromine (29) and by decarboxylation of "hexabromotrinitrovaleric" acid (371). A general analytical procedure for aromatic compounds consists of exhaustive nitration, treatment with hypobromite, and reduction of the tribromonitromethane formed to methylamine (31).

The ultraviolet (171, 172, 341), infrared (171, 172, 249–252), and Raman (251, 252) spectra of tribromonitromethane have been recorded and interpreted. Its molecular refraction has been calculated (10). Electron diffraction measurements were used to calculate the atomic distances and bond angles in tribromonitromethane. It was found that the molecule only exists in the staggered form. The unusually long carbon–nitrogen distance of  $1.59 \pm 0.02 \text{ \AA}$ . was related to the thermal instability of tribromonitromethane (216). The retention of  $^{82}\text{Br}$  recoil atoms has been investigated in neutral-irradiated tribromonitromethane (276, 277).

In the presence of benzoyl peroxide, tribromonitromethane adds to the olefinic double bond (23).



If the addition is carried out in the presence of alcohols or acids, ethers and acyloxy compounds are obtained, respectively (315).

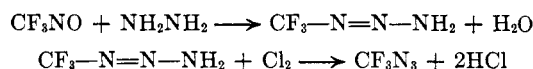


The ease of degradation of tribromonitromethane with colloidal silver, silver ions, and hydroxyl ions has been investigated (286). Potassium cyanide (317), potassium hydroxide, and potassium iodide in aqueous solution and potassium ethoxide in alcoholic solution (197) convert tribromonitromethane in low yield to the dipotassium salt of 1,1,2,2-tetranitroethane. In liquid ammonia, tribromonitromethane is reduced to dibromonitromethane (320). When tribromonitromethane is heated with aqueous potassium hydroxide, nitrogen, carbon monoxide, carbonate, bromide, bromate, nitrite, and nitrate are formed. Treatment with concentrated sulfuric acid at 130–135° yields carbonyl bromide and nitrosyl bromide (258). When tribromonitromethane

is treated with organomagnesium compounds, luminescence is observed. This is not caused by an oxidation reaction (96). With methylmagnesium iodide a gas is evolved. Hence tribromonitromethane interferes with the Zerewitinoff determination (138).

#### D. MISCELLANEOUS N-TRIHALOMETHYL COMPOUNDS

Condensation of trifluoronitrosomethane with hydrazine at  $-70^\circ$  yields unstable 1-(trifluoromethyl)-triazene. This can be converted to trifluoromethyl azide by treatment with chlorine (238). With triphenylphosphine, trifluoromethyl azide forms the corresponding phosphinimine with loss of molecular nitrogen (237).



Treatment of cyanogen bromide with sulfur tetrafluoride affords N-(trifluoromethyl)iminosulfur difluoride,  $\text{CF}_3\text{—N=SF}_2$ . This compound can also be made from sodium thiocyanate, sodium fluoride, and chlorine at 235°, and, in low yields, from sulfur tetrafluoride and metal cyanides, cyanates, or thiocyanates, or cyanuric acid (343).

Its  $^{13}\text{C}$ – $^{19}\text{F}$  n.m.r. spectrum has been recorded and interpreted (269).

### III. O-TRIHALOMETHYL COMPOUNDS

#### A. O-TRIHALOMETHYL ESTERS

##### 1. O-Trifluoromethyl Esters

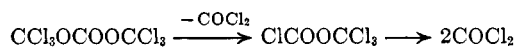
Only two such esters are known, namely bis(trifluoromethyl) sulfate and trifluoromethyl fluorosulfonate. The former is obtained by electrofluorination of dimethyl sulfate in liquid hydrogen fluoride (346, 347), while the latter is formed when methyl chlorosulfonate is treated in the same way (345). Typical by-products are hexafluorodimethyl ether, pentafluorodimethyl ether, and trifluoromethyl fluoromethyl ether (345–347).

Bis(trifluoromethyl) sulfate reacts with iodine either under pressure at 260° or under ultraviolet irradiation to give trifluoroiodomethane and sulfur dioxide (348).

##### 2. O-Trichloromethyl Esters

Trichloromethyl dimethyl phosphate has been obtained by chlorination of trimethyl phosphate irradiated with ultraviolet light (280).

Trichloromethyl chloroformate (diphosgene) and bis(trichloromethyl) carbonate (triphosgene) are characterized by the ease with which they are converted to phosgene.



In many reactions they yield the same products as does phosgene.



Trichloromethyl chloroformate is made by chlorination of methyl formate or chloroformate (24, 184, 190). More recent work with trichloromethyl chloroformate has been summarized (24).

The infrared (155) and Raman (210, 226) spectra of trichloromethyl chloroformate have been recorded and interpreted, so eliminating the possibility of cyclic structures, as had earlier been proposed for this compound.

Trichloromethyl chloroformate is decomposed to phosgene on heating (184). With potassium carbonate complete breakdown to potassium chloride and carbon dioxide occurs (184). Under mild conditions trichloromethyl chloroformate reacts with alcohols and phenols to give trichloromethyl alkyl or aryl carbonates, respectively (150, 183, 185, 255, 273-275). Heating with methanol, however, yields methyl chloroformate and phosgene (183). With amines, symmetrically substituted ureas are formed (185, 261). In some cases (such as diphenylamine and *p*-nitroaniline) the intermediate unstable urethan can be isolated (261). Aluminum chloride catalyzes the decomposition to phosgene, which in turn can be utilized *in situ* (185).

Trichloromethyl ethyl carbonate has been investigated by means of infrared (155) and n.m.r. (152) spectroscopy.

Trichloromethyl methyl carbonate is cleaved at its boiling point at atmospheric pressure to methyl chloroformate and phosgene (183). With aqueous sodium phenoxide diphenyl carbonate is formed. Treatment with ammonia in chloroform solution yields urea and methyl carbamate. Reaction with ethylmagnesium bromide leads to triethyl carbinol (257, 273). Aluminum chloride catalyzes the decomposition of trichloromethyl alkyl carbonates to alkyl chloride, carbon dioxide, and phosgene (256). Interaction of sodium acetate and trichloromethyl alkyl carbonates leads to acetic anhydride, alkyl acetate, sodium chloride, and carbon dioxide (259).

Bis(trichloromethyl) carbonate (triphosgene) is made by chlorination of dimethyl carbonate (76, 183, 190, 219, 244). The intermediate trichloromethyl methyl, chloromethyl, and dichloromethyl carbonates have also been isolated and characterized (219).

The infrared spectrum of bis(trichloromethyl) carbonate has been recorded and interpreted (155).

With alcohols, bis(trichloromethyl) carbonate forms alkyl chloroformates (273). With diols polymers are formed (22).

Trichloromethyl trichloroacetate has been made by light-induced chlorination of methyl trichloroacetate (4) as well as by means of the Kolbe reaction starting with sodium trichloroacetate (101). Hydrolysis of trichloromethyl trichloroacetate leads to trichloroacetic acid, phosgene, and hydrogen chloride. With alcohols, alkyl trichloroacetate, alkyl chloroformate,

dialkyl carbonate, and hydrogen chloride are obtained. With amines ureas are formed (101).

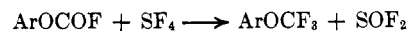
Dimethyl oxalate has been chlorinated to bis(trichloromethyl) oxalate (65). This can be pyrolyzed at 350-400° to phosgene and carbon dioxide. Hydrolysis yields oxalic acid, carbon dioxide, and hydrogen chloride. Dry ammonia converts bis(trichloromethyl) oxalate to urea and ammonium chloride, while treatment with alcohols leads to dialkyl oxalate and alkyl chloroformate (65).

Dimethyl malonate has been photochlorinated to yield bis(trichloromethyl) malonate. Treatment of this compound with polyamines leads to polymers (104).

## B. O-TRICHALOMETHYL ETHERS

### 1. *O*-Trifluoromethyl Ethers

Four general routes have been used to make *O*-trifluoromethyl ethers: the fluorination of methyl ethers (169, 196, 338), the metathetical exchange of chlorine in *O*-trichloromethyl ethers with either antimony trifluoride (with or without added antimony pentachloride) (48, 373, 376, 384, 385, 392) or hydrogen fluoride (without a catalyst) (122), and the fluorination of aryl fluoroformates with sulfur tetrafluoride (332).



A special case is the photolysis of hexafluoroacetone. The trifluoromethyl radicals generated react with the starting material to yield nonafluoro-*t*-butyl trifluoromethyl ether (144).

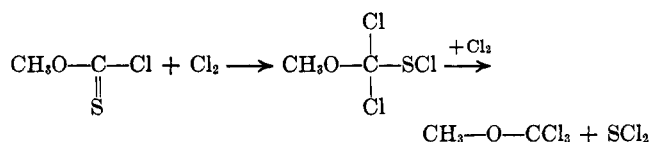
The microwave spectrum of hexafluorodimethyl ether has been recorded and interpreted (370). Much work has been carried out in order to characterize the trifluoromethoxy group as a substituent in aromatic compounds. A number of *O*-trifluoromethyl ethers have been studied by means of infrared (229) and n.m.r. (97, 98, 269, 375) spectroscopy as well as with regard to their dielectric constants, molar polarization, and dipole moments (84, 334). From the latter it was deduced that the coplanarity of the trifluoromethoxy group with an aromatic nucleus is considerably reduced as compared with the corresponding methyl aryl ethers. The Hammett constants of trifluoromethoxybenzoic acids, -anilinium ions, and -phenols have been determined (332, 334, 387). In electrophilic aromatic substitution the trifluoromethoxy group is *ortho-para* directing and strongly deactivating. To express this, the trifluoromethoxy group has been called a "super-halogen" (334).

The nitration of trifluoromethyl phenyl ether with mixed acid has been studied in detail. According to the conditions the *p*-nitro and/or the 2,4-dinitro derivative are obtained in good yields, but attempts to make a trinitro derivative failed (385). The trifluoromethoxy group is extremely stable towards most reagents and survives both nitration, reduction, and hydrolysis. Thus, a number of complicated compounds containing

this group, especially cyanine dyes, have been made in multistep syntheses from simple trifluoromethyl aryl ethers (41, 123, 153, 374, 384, 385).

## 2. O-Trichloromethyl Ethers

The chlorination of dimethyl ether yields the simplest compounds of this type. In this way trichloromethyl methyl, trichloromethyl chloromethyl, pentachlorodimethyl, and hexachlorodimethyl ether have been obtained (82, 298, 301, 304). The chlorination of methyl aryl ethers is carried out at approximately 200° and with phosphorus pentachloride as a catalyst. By this method a large number of trichloromethyl aryl ethers have been prepared (1, 14, 15, 373, 376, 384, 385). Another general procedure which can be carried out at low temperature and which eliminates most side reactions is the chlorination of compounds containing the RO-CS-X grouping (X = halogen or sulfur), such as alkyl or aryl chlorothionformates or xanthogen disulfides (87, 88, 392).



The intermediate alkoxy- or aryloxydichloromethanesulfenyl chloride can be isolated. O-Trichloromethyl ethers are much more stable towards solvolysis than the corresponding chloromethyl or dichloromethyl ethers (186). An important reaction of the O-trichloromethyl ethers is the conversion to O-trifluoromethyl ethers (see section III,B,1). Trichloromethyl methyl ether gives methyl chloroformate with water, methyl phenyl carbonate with sodium phenoxide, benzoyl chloride and methyl chloroformate with benzoic acid, dimethyl carbonate with methanol, diethyl carbonate and methyl chloride with ethanol, and S,S-dimethyl dithiocarbonate with methanethiol, while no reaction is observed with hydrogen sulfide (88). With aniline, N,N'-diphenylurea is obtained (87). Hexachlorodimethyl ether is partially decomposed at its boiling point at atmospheric pressure to carbon tetrachloride and phosgene (82).

## C. MISCELLANEOUS O-TRIFLUOROMETHYL COMPOUNDS

The chemistry of "trifluoromethyl hypofluorite,"  $\text{CF}_3\text{OF}$  (this name is objectionable), has been reviewed recently (189). It can be converted to compounds like  $\text{CF}_3\text{OOCF}_3$ ,  $\text{CF}_3\text{OSF}_5$ ,  $\text{CF}_3\text{OOSO}_2\text{F}$ , and  $\text{CF}_3\text{OR}$ .

Bis(trifluoromethyl) peroxide is produced in the electrolysis of sodium trifluoroacetate (355).

The reaction between bis(trifluoromethyl) peroxide and bis(pentafluorosulfur) peroxide catalyzed by ultraviolet irradiation yields trifluoromethyl pentafluoro-sulfur peroxide (262). Its n.m.r. spectrum has been recorded and interpreted (263).

## IV. S-TRIFLUOROMETHYL COMPOUNDS

Several reviews on S-trifluoromethyl compounds are available (73, 105, 230).

### A. TRIHALOMETHANETHIOLS

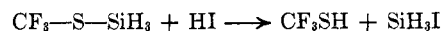
#### 1. Trifluoromethanethiol and Derivatives

Parts of the chemistry of trifluoromethanethiol have been briefly reviewed (105, 230, 351).

Trifluoromethanethiol is made by treating bis(trifluoromethylthio)mercury with hydrogen chloride (173).

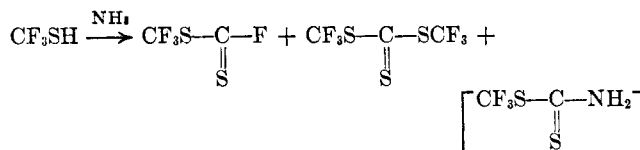


It is also formed by cleavage of trifluoromethyl thio-silane with hydrogen iodide (89).



Its infrared (85, 89, 173), ultraviolet (173), and n.m.r. (89) spectra have been recorded and interpreted. Its entropy and other thermodynamic data have been calculated (86).

Trifluoromethanethiol is slowly decomposed by water and much more rapidly by aqueous sodium hydroxide to fluoride, carbonate, and sulfide. Its photochemical decomposition yields hydrogen, sulfur, trifluoromethane, bis(trifluoromethyl) sulfide, and bis(trifluoromethyl) disulfide (173). Its X-ray- or ultraviolet-catalyzed addition to terminal olefins leads to the corresponding trifluoromethyl sulfides, while no reaction was observed with a nonterminal olefin (81, 166, 351). For the orientation of the adducts which is roughly that predicted for a radical reaction, see a recent review (351). With anhydrous ammonia, trifluoromethanethiol gives trifluoromethyl fluorodithioformate, bis(trifluoromethyl) trithiocarbonate, and an unidentified solid, possibly trifluoromethyl dithiocarbamate.

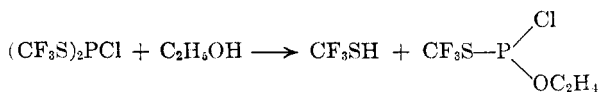


The infrared and ultraviolet spectra of the former two compounds have been recorded and interpreted. Hydrolysis of trifluoromethyl fluorodithioformate yields hydrogen fluoride, hydrogen sulfide, carbon dioxide, and carbonyl sulfide. Its photochlorination gives rise to chlorotrifluoromethane. Bis(trifluoromethyl) trithiocarbonate can also be synthesized from bis(trifluoromethylthio)mercury and thiophosgene or trifluoromethyl fluorodithioformate. Its hydrolysis leads, among other products, to carbonyl sulfide (176).

Bis(trifluoromethylthio)mercury is made by the ultraviolet-catalyzed reaction of hexafluorodimethyl disulfide with mercury (173) or from carbon disulfide and mercuric fluoride (239). Its chemistry has been reviewed (105, 196, 230).

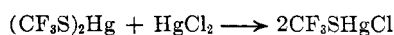
Its infrared (109), Raman (90), and n.m.r. (167) spectra have been recorded and interpreted. Adducts of bis(trifluoromethylthio)mercury with tetramethylammonium halides and with potassium cyanide have been investigated by means of Raman spectroscopy (90). Infrared and Raman studies of solutions of bis(trifluoromethylthio)mercury and mercuric acetate, trifluoroacetate, and nitrate, respectively, in organic solvents indicate the formation of the corresponding  $\text{CF}_3\text{-SHgX}$  compounds in equilibrium with the reactants. With the corresponding silver salts as well as with silver perchlorate reversible complex formation takes place (91).

In acetone solution interaction of bis(trifluoromethylthio)mercury with potassium iodide produces trifluoromethanethiolate anions which rapidly decompose to thiocarbonyl fluoride and fluoride anions (209). Silylation with silyl iodide yields trifluoromethyl silyl sulfide (89). Aqueous potassium iodide degrades bis(trifluoromethylthio)mercury to carbonyl sulfide (109). With polyiodoalkanes, bis(trifluoromethylthio)mercury reacts to yield the corresponding poly(trifluoromethylthio)alkanes (164). Bis(trifluoromethylthio)mercury reacts with phosphorus trichloride to give, according to the ratio of the reactants and the experimental conditions, trifluoromethanethiol, trifluoromethylthiomercurey chloride, trifluoromethylthiodichlorophosphine, bis(trifluoromethylthio)chlorophosphine, and tris(trifluoromethylthio)phosphine. Completely analogous results are obtained with arsenic trichloride. Hydrolysis of trifluoromethylthiodichlorophosphine and bis(trifluoromethylthio)chlorophosphine yields trifluoromethanethiol. Bis(trifluoromethylthio)chlorophosphine is completely degraded by ammonia, while ethanolysis gives trifluoromethanethiol and trifluoromethylthioethoxychlorophosphine.



Chlorinolysis of trifluoromethylthiodichlorophosphine yields trifluoromethanesulfonyl chloride and brominolysis yields trifluoromethanesulfonyl bromide together with hexafluorodimethyl disulfide. With bis(trifluoromethyl)iodophosphine, bis(trifluoromethylthio)mercury forms bis(trifluoromethyl)trifluoromethylthiophosphine. The arsenic analog reacts accordingly (109).

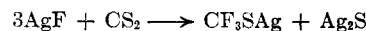
Trifluoromethylthiomercurey chloride is formed from bis(trifluoromethylthio)mercury and mercuric chloride.



Its infrared spectrum has been recorded and interpreted. With silver nitrate or acetate it forms trifluoromethylthiomercurey nitrate and acetate, respectively (109).

Other trifluoromethanethiolates, such as the silver and the copper compound, can be made from bis(trifluoromethylthio)mercury (105, 107, 173). Trifluoro-

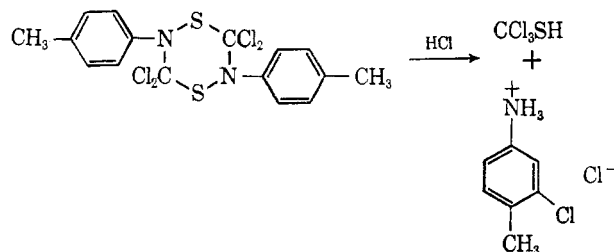
methylthiosilver is best prepared from silver monofluoride and carbon disulfide at  $140^\circ$ .



Its infrared spectrum has been recorded and interpreted. With pyridine and dimethylamine, respectively, it forms 2:1 adducts. With chlorine, trifluoromethanesulfonyl chloride and/or hexafluorodimethyl disulfide are obtained, while reaction with bromine or iodine only gives the disulfide. Methylation with methyl iodide yields trifluoromethyl methyl sulfide (107).

## 2. Trichloromethanethiol

Treatment of an ethereal solution of 3,3,6,6-tetrachloro-2,5-di(*p*-tolyl)tetrahydro-1,4,2,5-dithiadiazine with hydrogen chloride has been claimed to yield 3-chloro-4-methylaniline hydrochloride and trichloromethanethiol.



The "trichloromethanethiol" was described as an orange oil of repulsive odor, b.p.  $125^\circ$  (15 mm.). Oxidation with air oxygen gave a yellow solid (m.p.  $96^\circ$ ) believed to be hexachlorodimethyl disulfide. Pyrolysis led to sulfur dichloride and an unidentified yellow solid. With sodium metal, hydrogen was evolved. Alcoholic mercuric chloride gave a white precipitate and fuming nitric acid converted the "trichloromethanethiol" to trichloronitromethane (74).

Obviously, this substance cannot have the structure claimed. True trichloromethanethiol could certainly not be distilled at  $125^\circ$  without decomposition into thiophosgene and hydrogen chloride. Authentic hexachlorodimethyl disulfide is a colorless liquid. The nuclear chlorination of the *p*-tolyl residue under the conditions stated is hard to understand and, besides, no balance of hydrogen and chlorine atoms can be written for the postulated reaction. A reinvestigation of this reaction is badly needed.

## B. S-TRIHALOMETHYL SULFIDES AND POLYSULFIDES

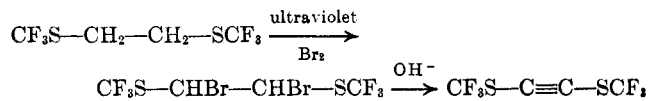
### 1. S-Trifluoromethyl Sulfides and Polysulfides

S-Trifluoromethyl sulfides cannot be prepared by fluorination of S-methyl sulfides as fluorine oxidizes divalent sulfur to the hexavalent state. Thus, many S-trifluoromethyl sulfides have been made from the corresponding S-trichloromethyl sulfides by halogen

exchange, usually with antimony trifluoride containing some antimony pentachloride or with hydrogen fluoride (16, 45, 61, 148, 149, 204, 279, 314, 363, 376-378, 380, 382, 383, 386, 392). Other methods are the addition of trifluoromethanethiol (see section IV,A,1) or trifluoromethanesulfonyl chloride (see section IV,E,1) to multiple bonds and the reaction of trifluoromethanesulfonyl chloride with Grignard reagents, metal acetylides, and phenols (see section IV,E,1). Ultraviolet irradiation of hexafluorodimethyl disulfide results in the elimination of sulfur and formation of hexafluorodimethyl sulfide (52). S-Trifluoromethyl sulfides are also obtained from bis(trifluoromethylthio)mercury and polyiodoalkanes (see section IV,A,1). S-Trifluoromethyl sulfides related to biologically important compounds have been made. Thus, the analog of chloramphenicol in which the nitro group is replaced by a trifluoromethylthio group has been prepared (386). The key intermediate is *p*-(trifluoromethylthio)benzaldehyde made from *p*-(methylthio)benzaldehyde (61). Another example is DL-S-(trifluoromethyl)homocysteine. Here the key intermediate is  $\beta$ -(trifluoromethylthio)propionaldehyde made by addition of trifluoromethanethiol to acrolein (81). 1-(Trifluoromethylthio)-1-(arylthio)methanes have been prepared from trifluoromethyl chloromethyl sulfide and arenethiols (379).

The atomic distances in hexafluorodimethyl sulfide have been calculated from electron diffraction data (50). Infrared (229) and n.m.r. (97, 98, 163, 375) spectra of S-trifluoromethyl sulfides have been recorded and interpreted. The Hammett constants of (trifluoromethylthio)benzoic acids, -anilinium ions, and -phenols have been determined (332, 334, 387). In electrophilic aromatic substitution the trifluoromethylthio group is *ortho-para* directing. Evidence for d-orbital resonance has been obtained (334).

The trifluoromethylthio group is inert towards most reaction conditions so that S-trifluoromethyl sulfides may be subjected to nuclear substitution, reduction, hydrolysis, and other reactions, the trifluoromethylthio group remaining unchanged. In this way trifluoromethylthiosulfonamides (41), -cyanine dyes (378, 381), and -heterocycles (279, 380) have been prepared. Nitration of trifluoromethyl phenyl sulfide with mixed acid at 0-15° has been shown to yield 34% *o*- and 57% *p*-nitro derivative (382). At 70-80°, however, mixed acid converts trifluoromethyl aryl sulfides to the corresponding nitrosulfoxides (321). S-trifluoromethyl sulfides can also be oxidized to the corresponding sulfones. A typical oxidant is chromic oxide in acetic acid (78, 148, 149, 196, 204, 279, 321, 376, 377, 380, 382, 383, 386). 1,2-Bis(trifluoromethylthio)ethane has been photobrominated to 1,2-dibromo-1,2-bis(trifluoromethylthio)ethane which could be converted with potassium hydroxide to 1,2-bis(trifluoromethylthio)acetylene (165).



Trifluoromethyl ethyl disulfide has been made from trifluoromethanesulfonyl chloride and ethanethiol (108). Its infrared spectrum has been recorded and discussed (272). Hexafluorodimethyl disulfide is formed from sulfur and trifluoroiodomethane (52), carbon disulfide and mercuric fluoride (196, 239), iodine pentafluoride (173, 196) or sulfur tetrafluoride containing arsenic trifluoride or boron trifluoride (159), bis(trifluoromethyl) trithiocarbonate and silver difluoride (333), as well as from trifluoromethanethiol and trifluoromethanesulfonyl chloride (230). Hexafluorodimethyl disulfide is produced together with carbon disulfide in the reaction between thiophosgene and sodium fluoride in tetramethylene sulfone. In the same solvent, treatment of trichloromethanesulfonyl chloride with sodium fluoride yields trifluoromethanesulfonyl chloride and hexafluorodimethyl disulfide (365).

Hexafluorodimethyl disulfide has been investigated by means of infrared (53, 272), ultraviolet (53), and n.m.r. (167) spectroscopy. Its atomic distances have been calculated from electron diffraction data (50).

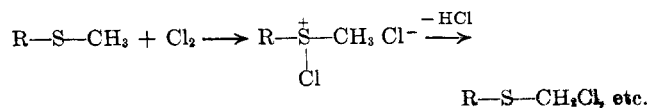
It is a rather unreactive compound. Under forced conditions it yields fluoride in alkaline or acid hydrolysis, chlorotrifluoromethane with chlorine, and trifluoromethylsulfur pentafluoride with cobaltic fluoride. No reaction is observed with hydrogen or iodine (52).

Hexafluorodimethyl trisulfide is made from trifluoromethanesulfonyl chloride and hydrogen sulfide (230). It is also a minor product in the reaction between carbon disulfide and iodine pentafluoride (173, 196). Its atomic distances have been calculated from electron diffraction data (50).

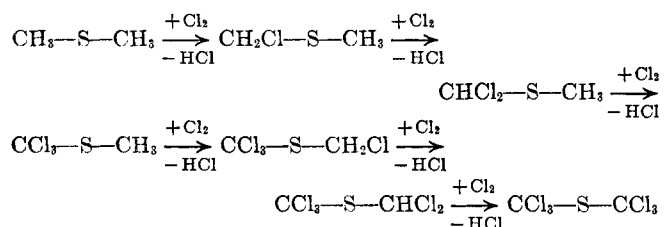
Hexafluorodimethyl tetrasulfide has been mentioned in a review without reference to any original work (105).

## 2. S-Trichloromethyl Sulfides and Polysulfides

The simplest and most often used method for the preparation of S-trichloromethyl sulfides is the chlorination of the corresponding S-methyl sulfides with chlorine, occasionally with sulfuryl chloride, thionyl chloride, or phosphorus pentachloride (14, 16, 26, 43, 45, 46, 61, 99, 130, 148, 149, 204, 279, 291, 292, 303, 314, 328, 329, 363, 376-378, 380, 382, 383, 386, 392, 409-413). The reaction proceeds smoothly well below 100° and the use of irradiation or catalysts sometimes mentioned is unnecessary. The mechanism is a polar one and involves the repeated formation of sulfide dichlorides, elimination of hydrogen chloride, and rearrangement (46, 411).

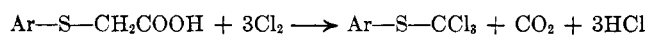


With aromatic sulfides, nuclear chlorination may become a competing reaction. Also, steric hindrance can interfere with the complete chlorination of the S-methyl group as can the presence of substituents which react with either chlorine or chlorinated methylthio groups. Thus, *o*-nitrothioanisole can only be chlorinated to chloromethyl 2-nitrophenyl sulfide while *o*-bromo- and *o*-chlorothioanisole as well as ethyl *o*-(methylthio)benzoate give mixtures of compounds not fully chlorinated in the methyl group (314, 328, 329). An example for the interference of a reactive group is the chlorination of *o*-(methylthio)benzoic acid which yields 2,2-dichloro-1,3-benzothioxan-4-one (328). The chlorination of dimethyl sulfide has been investigated especially thoroughly (26, 43, 46, 130, 363; for a review see 43). It proceeds stepwise, essentially first in one methyl group and then in the other. All possible substitution products have been isolated and characterized.

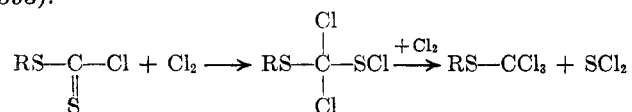


Chlorinolysis is a competing reaction and leads to by-products such as sulfenyl chlorides and disulfides.

Aryl carboxymethyl sulfides can be chlorinated to the corresponding trichloromethyl aryl sulfides (133).



S-Trichloromethyl sulfides can also be made under very mild conditions by chlorination of compounds of the general formula RS-CS-X (X = Cl or S) (392, 393).

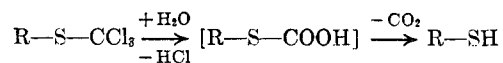


A great number of S-trichloromethyl sulfides may be prepared from trichloromethanesulfenyl chloride (see section IV,E,2). Thus, trichloromethanesulfenyl chloride will substitute aromatic amines in the *para* position (326, 349), add to multiple bonds (92, 330, 349, 351), and give trichloromethyl  $\alpha$ -chloroalkyl sulfides with diazoalkanes (290).

The reported formation of trichloromethyl phenyl sulfide from trichloromethanesulfenyl chloride and phenylmagnesium bromide (313) has been disproved (46, 93, 327).

Trichloromethyl chloromethyl sulfide was isolated in low yield when dimethyl sulfoxide was chlorinated with sulfur chloride (303).

S-Trichloromethyl sulfides are comparatively stable compounds which can be hydrolyzed to the corresponding thiols (46, 409).



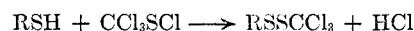
The same initial steps occur when trichloromethyl chloromethyl sulfide is chlorinated in concentrated hydrochloric acid. The final product is then chloromethanesulfonyl chloride (26).

A characteristic reaction which has often been used for structure determinations of S-trichloromethyl sulfides is the formation of the corresponding thiol and N,N',N''-triphenylguanidine upon treatment with aniline (349, 409–413).

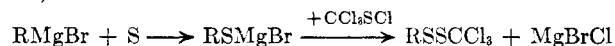
An important reaction of S-trichloromethyl sulfides is the metathetical halogen exchange which yields S-trifluoromethyl sulfides (see section IV,B,1) as well as S-tribromomethyl sulfides (see section IV,B,3). The latter exchange is reversible (44). S-Trichloromethyl sulfides can be oxidized to the corresponding sulfoxides (see section IV,C,2) and sulfones (see section IV,D,2). Trichloromethyl phenyl sulfide has been shown to react with aromatic Grignard reagents to give the corresponding phenyl sulfides. Thus, with phenylmagnesium bromide, diphenyl sulfide is obtained (327).

All known S-trichloromethyl polysulfides have been made from trichloromethanesulfenyl chloride (*cf.* section IV,E,2).

Thus, thiols react smoothly with trichloromethanesulfenyl chloride to give S-trichloromethyl disulfides (194, 242, 243, 307, 312, 349).

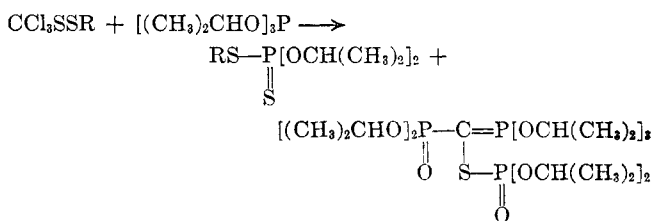


Also, the magnesium thiolate halide can be employed (215).



The ultraviolet spectra of some trichloromethyl alkyl disulfides have been recorded and found to be uncharacteristic (27).

Trichloromethyl alkyl disulfides have been treated with triisopropyl phosphite. The complex products are formulated below (38).



Hexachlorodimethyl disulfide has been encountered in the pyrolysis of trichloromethanesulfenyl chloride and in the reaction of trichloromethanesulfenyl chloride with sulfur (349). It is also formed from trichloromethanesulfenyl chloride and silver or iron powder (128, 349). Trichloromethanesulfenyl chloride reacts with hydrocarbons and other hydrogen donors as a chlorinating agent with the formation of hexachlorodimethyl disulfide (54, 221, 222, 296, 326).



Also with organic peroxides the disulfide is formed. Thus, from cyclohexanone peroxide and trichloromethanesulfonyl chloride, hexachlorodimethyl disulfide and methyl  $\omega$ -chlorocaproate are obtained (54).

The molar refraction of hexachlorodimethyl disulfide has been calculated. Its Raman spectrum has been recorded and interpreted (128).

Hexachlorodimethyl disulfide is unaffected by cold or hot concentrated aqueous sodium hydroxide (128).

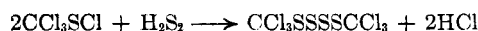
Hexachlorodimethyl trisulfide has been encountered in the pyrolysis of trichloromethanesulfonyl chloride and in the reaction of trichloromethanesulfonyl chloride with sulfur (349). It is most advantageously prepared from trichloromethanesulfonyl chloride and hydrogen sulfide (128, 405, 407). The yield can be raised by employing an ammonium tungstate catalyst (405).

The molar refraction of hexachlorodimethyl trisulfide has been determined. Its Raman spectrum has been recorded and interpreted (128). An X-ray crystal structure analysis has been carried out (28).

Hexachlorodimethyl trisulfide reacts with metal thiolates, such as sodium ethanethiolate, sodium benzenethiolate, potassium ethyl xanthogenate, and sodium *N,N*-dimethyldithiocarbamate according to the following scheme (407).



Hexachlorodimethyl tetrasulfide has been prepared from disulfane and trichloromethanesulfonyl chloride (128).



Its molar refraction has been determined. The Raman spectrum has been recorded and interpreted (128).

### 3. *S*-Tribromomethyl Sulfoxides

Tribromomethyl methyl sulfide, tribromomethyl chloromethyl sulfide, and tribromomethyl bromomethyl sulfide have been prepared from the corresponding chloro compounds by means of halogen exchange with hydrogen bromide. However, hexachlorodimethyl sulfide was indifferent towards hydrogen bromide (44).

The infrared spectra of these *S*-tribromomethyl sulfides have been recorded and interpreted (44).

*S*-Tribromomethyl sulfides exchange halogen on treatment with hydrogen chloride and may be reconverted to the corresponding chloro compounds (44) [cf. the reaction of trichloromethanesulfonyl chloride with hydrobromic acid (sections IV,E,2 and 3)].

#### C. S-TRIHALOMETHYL SULFOXIDES AND SULFINIMINES

##### 1. *S*-Trifluoromethyl Sulfoxides

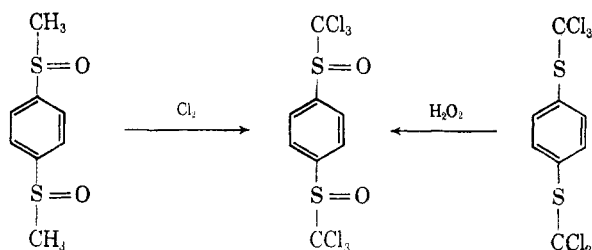
Trifluoromethyl aryl sulfides can be oxidized with nitric acid to the corresponding sulfoxides (314).

The oxidation reaction can also be carried out with simultaneous nuclear nitration.

Trifluoromethyl aryl sulfoxides can be nitrated in the *ortho* and *para* position. Trifluoromethyl aryl sulfones may be obtained on oxidation of the corresponding sulfoxides with strong oxidants, such as chromic oxide in acetic anhydride (321).

##### 2. *S*-Trichloromethyl Sulfoxides and Sulfinimines

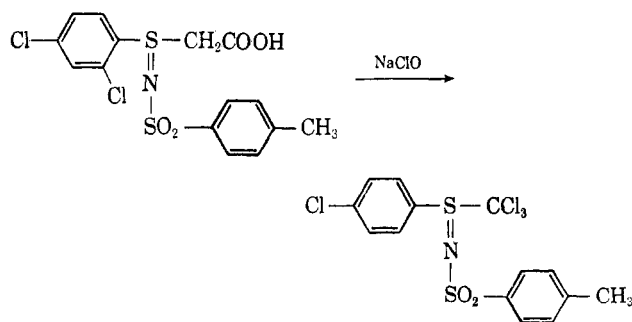
1,4-Bis(trichloromethylsulfinyl)benzene has been prepared both by chlorination of 1,4-bis(methylsulfinyl)benzene with chlorine and by oxidation of 1,4-bis(trichloromethylthio)benzene with hydrogen peroxide.



It does not react with aniline, but gives dimethyl sulfide upon reduction with zinc and acetic acid (409).

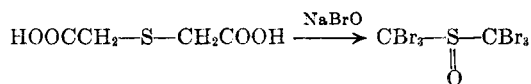
Small amounts of trichloromethyl ethyl sulfoxide and trichloromethyl phenyl sulfoxide have been claimed to be formed in the reaction between trichloromethanesulfonyl chloride (see section IV,G,2) and ethylmagnesium bromide and phenylmagnesium bromide, respectively (313). Since the same paper contains a number of highly questionable statements, caution should be exercised in the acceptance of the above claims.

Treatment of the *N*-*p*-toluenesulfonylsulfinimine derived from (2,4-dichlorophenylthio)acetic acid with aqueous hypochlorite yields the corresponding *S*-trichloromethylsulfinimine (125).



##### 3. *S*-Tribromomethyl Sulfoxides

Hexabromodimethyl sulfoxide is formed by the action of sodium hypobromite in alkaline solution on bis(carboxymethyl) sulfide.



Heated above its melting point, it decomposes to form some hexabromodimethyl sulfone (see section IV,D,3). By sodium iodide in acetone, hexabromodimethyl sulfoxide is debrominated to pentabromodimethyl sulfoxide (125).

#### D. S-TRIHALOMETHYL SULFONES

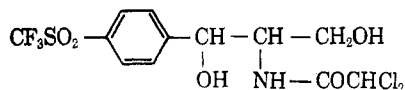
##### 1. *S*-Trifluoromethyl Sulfoxides

The most general method for the preparation of *S*-trifluoromethyl sulfones is the oxidation of the corresponding *S*-trifluoromethyl sulfides (78, 148, 149, 196, 204, 279, 314, 363, 376, 377, 380, 382, 383, 386) (see section IV,B,1) or sulfoxides (321) (see section IV,C,1). Trifluoromethyl 2,6-dichloro-4-nitrophenyl sulfide could not be oxidized to the sulfone, obviously for steric reasons (314). From the reaction between trifluoromethanesulfonyl fluoride and methylmagnesium iodide both trifluoromethyl methyl sulfone and bis(trifluoromethylsulfonyl)methane have been isolated (55, 147).

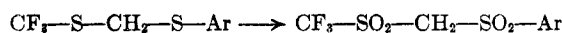
The infrared (147, 229, 379) and n.m.r. (97, 98, 375) spectra of a number of *S*-trifluoromethyl sulfones have been recorded and interpreted. The Hammett constants of trifluoromethylsulfonylbenzoic acids, -anilinium ions, and -phenols have been determined from  $pK_a$  values (332, 334, 387). In electrophilic aromatic substitution the trifluoromethylsulfonyl group is *meta* directing and strongly deactivating. In fact, it is the most powerful uncharged electron-withdrawing substituent known.

The trifluoromethylsulfonyl group is extremely stable and survives nitration, oxidation, reduction, and hydrolysis. Thus, multistep syntheses of cyanine dyes (379, 384), diphenylamine dyes (331), phenothiazines (77, 78, 279), quinoxaline derivatives (380), and thiazole derivatives (380) have been carried out in which the trifluoromethylsulfonyl group remains intact. The absorption spectra of a number of cyanine dyes containing the trifluoromethylsulfonyl group have been recorded (379, 384).

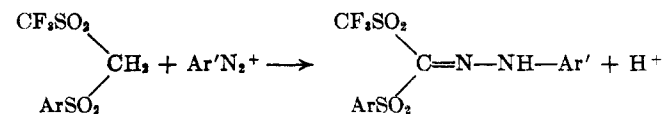
The chloramphenicol analog in which a trifluoromethylsulfonyl group has replaced the nitro group has been prepared (149, 386). 1-(Trifluoromethyl-



sulfonyl)-1-(arylsulfonyl)methanes have been prepared by oxidation of the corresponding disulfides.



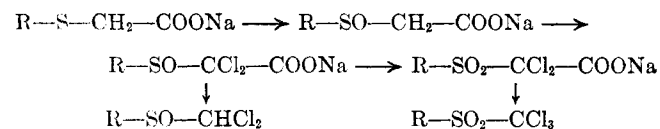
The methylene group of the  $\alpha$ -disulfone couples with diazonium salts.



The infrared spectra of such coupling products have been recorded and interpreted (379).

##### 2. *S*-Trichloromethyl Sulfoxides

*S*-Trichloromethyl sulfones may be made either by oxidation of *S*-trichloromethyl sulfides (46, 99, 291, 303, 363) or by the action of aqueous sodium hypochlorite upon (alkylthio)- or (aryltio)acetic acids (51, 124, 125, 206). In some instances, monoperphthalic acid in ether has been used as an oxidant for *S*-trichloromethyl sulfides (46, 303) though chromic oxide (363) or potassium permanganate (99) in acetic acid or acetic anhydride are equally satisfactory. The reaction between (alkylthio)- or (aryltio)acetic acids and hypochlorite has been shown to proceed through the following steps (125).



In some cases *S*-dichloromethyl sulfoxides appear as by-products.

Sanna and Stefano (313) reported the formation of *S*-trichloromethyl sulfones in the reaction between trichloromethanesulfonyl chloride and Grignard reagents (see also section IV,G,2). Since the physical properties of their products do not check with those of two independent authentic preparations (46, 125), the value of this work is highly doubtful.

Hexachlorodimethyl sulfone liberates iodine from an acetone solution of potassium iodide and is dechlorinated to pentachlorodimethyl sulfone. Dilute aqueous sodium hydroxide rapidly hydrolyzes hexachlorodimethyl sulfone (125). Trichloromethyl chloromethyl sulfone is indifferent toward chlorination in concentrated hydrochloric acid (26).

Trichloromethyl aryl sulfones, however, are indifferent toward potassium iodide in acetone. They are only slowly hydrolyzed by boiling dilute aqueous sodium hydroxide to give the corresponding sulfonate ion and chloride ion (125).

##### 3. *S*-Tribromomethyl Sulfoxides

All known *S*-tribromomethyl sulfones stem from the treatment of organic compounds with aqueous hypobromite. Suitable starting materials are (alkylthio)- and (aryltio)acetic acids (124, 125), arylsulfonylacetic acids (79), benzenesulfonylacetamide (361), and albumin (143). The latter yields hexabromodimethyl sulfone (143). The treatment of benzenesulfonylacetamide with aqueous hypobromite, which gives tribromomethyl phenyl sulfone as the main product, also produces some dibromomethyl phenyl sulfone which in turn can be converted to tribromomethyl phenyl sulfone by means of aqueous hypobromite (361).

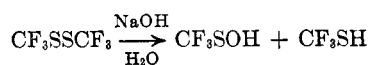


Hexabromodimethyl sulfone liberates iodine from potassium iodide solutions and is debrominated to bis-(dibromomethyl) sulfone (125, 143).

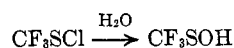
#### E. TRIHALOMETHANESULFENIC ACIDS AND DERIVATIVES

##### 1. Trifluoromethanesulfenic Acid and Derivatives

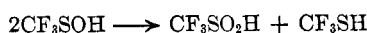
Trifluoromethanesulfenic acid is an unstable hypothetical compound thought to be formed in the hydrolysis of hexafluorodimethyl disulfide (52)



and trifluoromethanesulfonyl chloride (175).



It is assumed to disproportionate rapidly to trifluoromethanesulfenic acid and trifluoromethanethiol (175).



Its most important derivative is trifluoromethanesulfonyl chloride which has been briefly reviewed (105, 196, 230). A suitable method for the large-scale preparation of trifluoromethanesulfonyl chloride is the reaction between trichloromethanesulfonyl chloride and sodium fluoride in tetramethylene sulfone. Considerable quantities of hexafluorodimethyl disulfide are also formed (365). Other preparations include the treatment of bis(trifluoromethylthio)mercury (173), trifluoromethylthiosilver (107), or hexafluorodimethyl disulfide (173) with chlorine. Trifluoromethanesulfonyl chloride is also formed when chlorodifluoromethanesulfonyl chloride is fluorinated with an antimony trifluoride-antimony pentachloride reagent (394).

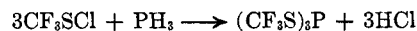
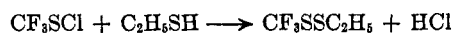
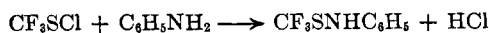
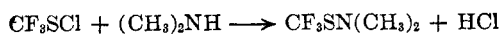
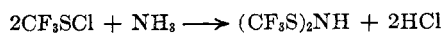
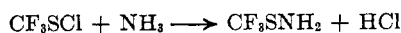
The ultraviolet (173) and infrared (173, 272) spectra of trifluoromethanesulfonyl chloride have been recorded.

The hydrolysis of trifluoromethanesulfonyl chloride (*vide supra*) leads to the final products trifluoromethanesulfenic acid (see section IV,F,1) and hexafluorodimethyl disulfide. When only a total of 0.5 mole of water is added in small portions, trifluoromethyl trifluoromethanethiolsulfonate is formed (175).



The infrared spectrum of trifluoromethyl trifluoromethanethiolsulfonate has been recorded and discussed (175, 305). Its alkaline hydrolysis leads to trifluoromethane and hexafluorodimethyl disulfide (175).

The reactions of trifluoromethanesulfonyl chloride with ammonia, amines, thiols, and phosphine can be summarized in the following equations (108).



Arsine only reduces trifluoromethanesulfonyl chloride to trifluoromethanethiol. All products listed have been characterized by means of ultraviolet and infrared spectroscopy (108, 272).

Trifluoromethanesulfenamide is inert towards water and anhydrous ammonia. Aqueous alkali degrades it completely, while aqueous hydrochloric acid converts it to hexafluorodimethyl disulfide. With dry hydrogen chloride, trifluoromethanesulfonyl chloride is formed. Tris(trifluoromethylthio)phosphine is inert towards dry hydrogen chloride. Aqueous alkali degrades it completely without formation of gaseous products. With chlorine, trifluoromethanesulfonyl chloride is formed. Bis(trifluoromethylthio)phosphine reacts with aqueous alkali in the same way as tris(trifluoromethylthio)phosphine (108).

Oxidation of trifluoromethanesulfonyl chloride with either aqueous chlorine or hydrogen peroxide leads to trifluoromethanesulfonyl chloride (175) (see section IV,G,1).

Trifluoromethanesulfonyl chloride reacts with bis(trifluoromethylthio)mercury to give trifluoromethylthio-mercury chloride and hexafluorodimethyl disulfide (173). For its reactions with substituted thiols, see section IV,B,1.

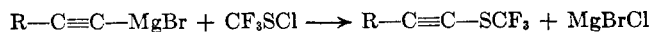
A number of trifluoromethanesulfenic acid esters have been made by treating alcohols with trifluoromethanesulfonyl chloride in the presence of pyridine. The esters have been characterized by means of n.m.r. spectra (3).

N-Trifluoromethylthio compounds are obtained from imides or sulfonamides and trifluoromethanesulfonyl chloride (117).

The addition of trifluoromethanesulfonyl chloride to carbon-carbon double bonds has recently been reviewed (351). This radical reaction has a number of complicating features and leads to products with one or two trifluoromethylthio groups (163, 164). These S-trifluoromethyl sulfides have been characterized by means of n.m.r. spectroscopy (163) (see also section IV,B,1).

Suitably substituted phenols may be substituted in the *para* position with trifluoromethanesulfonyl chloride (anhydrous ferric chloride as a catalyst) to give the corresponding trifluoromethyl aryl sulfides (119).

Trifluoromethanesulfonyl chloride reacts with metal acetylides forming S-trifluoromethyl sulfides containing a triple bond (165).

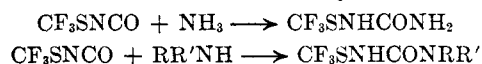


Trifluoromethanesulfonyl bromide has been prepared by fluorination of bromodifluoromethanesulfonyl bromide with an antimony trifluoride-antimony pentachloride reagent (394).



With silver cyanide, trifluoromethanesulfonyl chloride gives trifluoromethyl thiocyanate. By analogy, reaction with silver thiocyanate, selenocyanate, and cyanate leads to trifluoromethanesulfonyl thiocyanate, selenocyanate, and isocyanate, respectively. In the latter case N,N-bis(trifluoromethylthio)carbonyl isocyanate is a by-product. Trifluoromethyl thiocyanate is degraded by aqueous alkali to fluoride, sulfide, polysulfide, carbonate, and cyanate, no cyanide or thiocyanate being formed. Trifluoromethanesulfonyl thiocyanate decomposes upon standing at room temperature producing polythiocyanogen and hexafluorodimethyl disulfide. It is also rapidly hydrolyzed by aqueous alkali. When trifluoromethanesulfonyl selenocyanate is heated at 500° in a sealed tube, selenium, carbon dioxide, carbonyl sulfide, and silicon tetrafluoride (attack on the glass) are produced.

Trifluoromethanesulfonyl isocyanate trimerizes upon heating at 100°. With water it forms N,N'-bis(trifluoromethylthio)urea and carbon dioxide. Its reactions with ammonia and amines may be summarized as



N,N-Bis(trifluoromethylthio)carbonyl isocyanate reacts with water to give N,N-bis(trifluoromethylthio)urea and carbon dioxide (106).



All compounds mentioned above have been characterized by means of infrared and n.m.r. spectroscopy (106, 167).

## 2. Trichloromethanesulfenic Acid and Derivatives

Trichloromethanesulfenic acid is a hypothetical, unstable compound which in several instances has been postulated as the primary product of the hydrolysis of trichloromethanesulfonyl chloride (*vide infra*).

The most important derivative of trichloromethanesulfenic acid and key intermediate for virtually all other derivatives is trichloromethanesulfonyl chloride. Its chemistry has recently been reviewed (92, 349), so that only newer developments will be related here.

Trichloromethanesulfonyl chloride labeled with <sup>36</sup>Cl has been made from dimethyl sulfide and labeled sulfonyl chloride (319).

Recent physicochemical investigations concerning trichloromethanesulfonyl chloride include infrared (217), Raman (129, 157), and <sup>35</sup>Cl quadrupole n.m.r. (191) studies.

Trichloromethanesulfonyl chloride has been shown to form 1:1, 1:2, and 1:3 complexes with *s*-trithiane (33).

Trichloromethanesulfonyl chloride reacts with silver nitrate in glacial acetic acid to give trichloromethanesulfonyl nitrate which is only stable in solution. Unexpectedly, trichloromethanesulfonyl nitrate upon treatment with potassium iodide liberates only 0.25 mole of

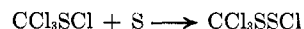
iodine. In tetrachloromethane, the reaction of trichloromethanesulfonyl chloride with potassium iodide has been postulated to proceed *via* trichloromethanesulfonyl iodide, which in turn gives hexachlorodimethyl disulfide and iodine. Secondary reactions then give rise to the thiophosgene actually observed. With antimony pentachloride, the crystalline complexes  $\text{CCl}_3\text{SCl}\cdot\text{SbCl}_5$  and  $2\text{CCl}_3\text{SCl}\cdot\text{SbCl}_5$  can be prepared. Upon gentle warming, these give antimony trichloride, disulfur dichloride, and tetrachloromethane (271).

With mercuric fluoride, trichloromethanesulfonyl chloride reacts to give dichlorofluoromethanesulfonyl chloride (220, 335). This compound was earlier erroneously assumed to be trichloromethanesulfonyl fluoride (225).

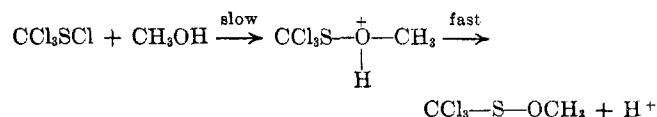
Sodium fluoride in tetramethylene sulfone converts trichloromethanesulfonyl chloride to trifluoromethanesulfonyl chloride and hexafluorodimethyl disulfide (365). Trichloromethanesulfonyl thiocyanate is formed from trichloromethanesulfonyl chloride and potassium thiocyanate in benzene (325). In an aqueous-organic two-phase system inorganic reducing agents such as hydrogen sulfide, potassium hydrogen sulfite, sulfur dioxide, and potassium iodide convert trichloromethanesulfonyl chloride to thiophosgene (408).

When stirred at room temperature with excess concentrated aqueous hydrobromic acid, trichloromethanesulfonyl chloride is converted to trichloromethanesulfonyl bromide. This in turn, upon treatment with more concentrated hydrobromic acid, stepwise exchanges all the remaining chlorine atoms with bromine (284).

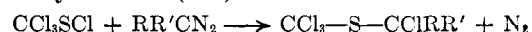
Chlorotrichloromethyl disulfane is obtained from trichloromethanesulfonyl chloride, sulfur, and trialkyl or triaryl phosphate, though in low yield and with many by-products (66).



A kinetic study of the solvolysis of trichloromethanesulfonyl chloride in excess methanol-ether and methanol-water has been made. Under these conditions, the formation of methyl trichloromethanesulfonate is a bimolecular, first-order reaction, unaffected by the addition of either hydrogen chloride or calcium chloride. The following reaction scheme has been suggested (192).



Trichloromethanesulfonyl chloride has been shown to react with diazoalkanes to yield trichloromethyl  $\alpha$ -chloroalkyl sulfides (290).



A recent investigation has further elucidated the reaction between tertiary aromatic amines and trichloromethanesulfonyl chloride. Nuclear substitution





*t*-butoxide. The carbene cannot be generated by pyrolysis of sodium trichloromethanesulfinate (316).

## G. TRIHALOMETHANESULFONIC ACIDS AND DERIVATIVES

### 1. Trifluoromethanesulfonic Acid and Derivatives

Trifluoromethanesulfonic acid was first obtained by oxidation of bis(trifluoromethylthio)mercury with aqueous hydrogen peroxide (174). It is more readily prepared by hydrolysis of trifluoromethanesulfonyl fluoride or chloride (55, 63).

The infrared spectra of the acid and its derivatives have been recorded and discussed (146, 147, 174, 175, 305).

Trifluoromethanesulfonic acid is claimed to be the strongest monobasic acid known. Its conductance in acetic acid has been measured and its Hammett function derived (145; *cf.* 174).

Trifluoromethanesulfonic acid has been suggested for the titration of weak bases in acetic acid. It gives much the same results as perchloric acid (231).

Trifluoromethanesulfonic acid is extremely stable to heat, water, alcohol, and concentrated nitric acid (146, 147, 174). Pyrolysis requires 650° and yields sulfur fluoride, carbonyl fluoride, carbon dioxide, trifluoromethane, and hydrogen fluoride (147).

Trifluoromethanesulfonic acid fumes in air and forms a crystalline, distillable monohydrate (63, 147).

A number of metal (146, 174) and amine (147) salts of trifluoromethanesulfonic acid have been prepared, as well as the *S*-benzylisothiuronium salt (63, 147).

With phosphorus pentoxide, trifluoromethanesulfonic acid forms the anhydride (55, 63, 147). The anhydride is comparatively slowly hydrolyzed by water or dilute alkali (147). It forms esters with alcohols (147) and amides with ammonia or amines (55, 63, 146, 147).

The reaction of trifluoromethanesulfonic acid with ethanol and with ethylene much resembles that of sulfuric acid, a reversible system containing trifluoromethanesulfonic acid, ethanol, ethyl trifluoromethanesulfonate, diethyl ether, and ethylene being formed (147).

Esters of trifluoromethanesulfonic acid are also formed from its metal salts and alkyl halides (55, 146). The esters are strong C-, N-, and O-alkylating agents. Thus, refluxing ethyl trifluoromethanesulfonate with benzene yields ethylbenzene, diethylbenzenes, and trifluoromethanesulfonic acid (147).

The oxidizing power of mixtures of trifluoromethanesulfonic acid and hydrogen peroxide is extremely poor as compared to trifluoroperacetic acid. Thus, the formation of a true peracid in this mixture is doubtful (147).

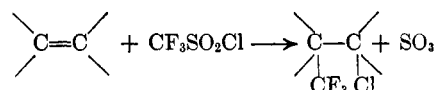
Trifluoromethanesulfonyl fluoride has been made by electrofluorination of methanesulfonyl fluoride or chloride in liquid hydrogen fluoride (55, 63, 146). Tri-

fluoromethanesulfonyl chloride is obtained by electrofluorination of methanesulfonyl chloride in liquid hydrogen fluoride (146), oxidation of trifluoromethanesulfonyl chloride with aqueous hydrogen peroxide or chlorine, oxidation of hexafluorodimethyl disulfide with aqueous chlorine (175), and by treatment of trifluoromethanesulfonic acid with phosphorus pentachloride (55).

For reactions of trifluoromethanesulfonyl chloride leading to derivatives of trifluoromethanesulfonic acid, see section IV, F, 1.

Trifluoromethanesulfonyl fluoride (146) and trifluoromethanesulfonyl chloride (175) are essentially stable toward water at room temperature, while at elevated temperatures hydrolysis to trifluoromethanesulfonic acid occurs. Alkaline hydrolysis of trifluoromethanesulfonyl fluoride yields the corresponding metal trifluoromethanesulfonates (63, 146). Trifluoromethanesulfonyl fluoride and trifluoromethanesulfonyl chloride are *N*-acylating agents (55, 59, 146).

Trifluoromethanesulfonyl fluoride has been converted to the chloride *via* the hydrazide, which in turn was treated with chlorine in concentrated aqueous hydrochloric acid. Trifluoromethanesulfonyl chloride adds to olefins with evolution of sulfur dioxide, a trifluoromethyl group and a chlorine atom being attached to the olefinic carbon atoms (59).



### 2. Trichloromethanesulfonic Acid and Derivatives

Trichloromethanesulfonic acid is obtained by alkaline hydrolysis of trichloromethanesulfonyl chloride (158, 227, 254). It is obtained as a hydrate,  $\text{CCl}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$  (227) or  $\text{CCl}_3\text{SO}_3\text{H} \cdot 1.5\text{H}_2\text{O}$  (158).

Trichloromethanesulfonic acid is a strong acid, its acidity lying between that of perchloric acid and *p*-toluenesulfonic acid. The acidity was determined from the catalytic effect upon the decomposition of diazoacetic ester in acetic or propionic acid (158).

At its boiling point trichloromethanesulfonic acid is partially decomposed to phosgene, sulfur dioxide, and hydrogen chloride. It is unaffected by strong oxidants, such as concentrated nitric acid, aqua regia, or chromic acid (227). A number of metal trichloromethanesulfonates have been prepared (68, 158, 227, 254, 299). At 300° the potassium salt is smoothly pyrolyzed to phosgene, sulfur dioxide, and potassium chloride (227). The influence of magnesium trichloromethanesulfonate upon the solubility of organic liquids in water has been determined (95).

Treatment of trichloromethanesulfonic acid with zinc yields dichloromethanesulfonic acid. In acid aqueous solution, either zinc or electrolytic reduction gives chloromethanesulfonic acid. Complete reduction of trichloromethanesulfonic acid to methane-

sulfonic acid is achieved either with potassium amalgam or by electrolytic reduction in neutral aqueous solution (227). Reduction with potassium sulfite yields dichloromethanesulfonic acid and methanedisulfonic acid (299).

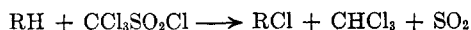
Isoamyl trichloromethanesulfonate has been prepared from trichloromethanesulfonyl chloride and isoamyl alcohol. Alkaline hydrolysis of the ester yields the acid, while treatment with phosphorus pentachloride gives trichloromethanesulfonyl chloride, isoamyl chloride, and phosphoroyl chloride (68).

The most important derivative of trichloromethanesulfonic acid is trichloromethanesulfonyl chloride. Its chemistry has been reviewed (92). In general, it behaves rather as an oxidant than as an acylating agent.

Trichloromethanesulfonyl chloride is prepared by oxidation of trichloromethanesulfinyl chloride (92). It is also formed from trichloromethanesulfinic acid and chlorine (227).

For reactions of trichloromethanesulfonyl chloride leading to derivatives of trichloromethanesulfinic acid, see section IV,F,2.

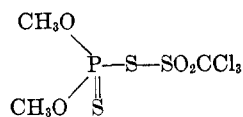
Trichloromethanesulfonyl chloride is a useful chlorinating agent (200).



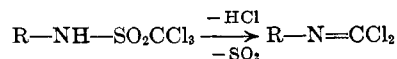
The reaction of trichloromethanesulfonyl chloride with Grignard reagents has been reported to yield the corresponding trichloromethyl sulfones and sulfoxides (313). This claim is highly questionable, since the physical properties of the products do not check with those of authentic preparations.

Trichloromethanesulfonyl bromide is formed from trichloromethanesulfinic acid and bromine (227, 234). When heated with alcohol at 100°, it is cleaved to bromotrichloromethane and sulfur dioxide (234).

O,O-Dimethyldithiophosphoric acid reacts with trichloromethanesulfonyl chloride to give the mixed anhydride (344).



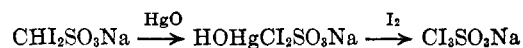
While trichloromethanesulfonamides are not available *via* trichloromethanesulfonyl chloride, they may be obtained by oxidation of trichloromethanesulfenamides with potassium permanganate or hydrogen peroxide. Alkaline hydrolysis of primary trichloromethanesulfonamides yields N-dichloromethylenamines (126).



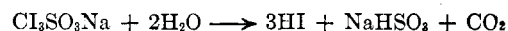
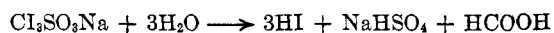
### 3. Triiodomethanesulfonic Acid

Early work with sodium triiodomethanesulfonate has been summarized (30).

It is most advantageously prepared as the dihydrate from sodium diiodomethanesulfonate *via* the hydroxymercuri derivative.



Sodium triiodomethanesulfonate is stable toward water at 100°, but decomposes in the presence of oxygen or light. Two light-induced reactions are thought to proceed in aqueous solution.



In the presence of oxygen, iodine is liberated in aqueous solutions of triiodomethanesulfonate (30).

### H. MISCELLANEOUS S-TRIHALOMETHYL COMPOUNDS

Several S-trifluoromethyl derivatives of sulfur tetrafluoride and of sulfur hexafluoride have been obtained by fluorination of divalent sulfur compounds. Their chemistry has been reviewed (105, 196, 230, 358).

Thus, trifluoromethylsulfur trifluoride, trifluoromethylsulfur pentafluoride, and bis(trifluoromethyl)sulfur tetrafluoride have been isolated among the fluorination products of methanethiol (105), dimethyl sulfide (105, 337), and carbon disulfide (105). Electrofluorination of (methylthio)acetyl chloride in liquid hydrogen fluoride gave, among other products,  $CF_3SF_5$ ,  $CF_3SF_4CF_3$ ,  $CF_3SF_4C_2F_5$ ,  $CF_3SF_4CF_2COF$ , and  $CF_3SF_4CF_3$ , all characterized by means of n.m.r. spectroscopy (397).

The infrared spectrum of trifluoromethylsulfur pentafluoride has been recorded and interpreted (100).

At 500°, trifluoromethylsulfur pentafluoride and bis(trifluoromethyl)sulfur tetrafluoride act as sources of fluorine and trifluoromethyl radicals which may be added to perfluoroolefins (402).

### V. BIOLOGICAL ACTIVITY OF N-, O-, AND S-TRIHALOMETHYL COMPOUNDS

The most powerful physiological agents mentioned in this review are trichloronitromethane ("chloropicrin"), trichloromethyl chloroformate ("diphosgene"), bis(trichloromethyl) carbonate ("triphosgene"), and N-trichloromethylthio-1,2,5,6-tetrahydrophthalimide ("Captan"). For the extensive literature concerning their physiological properties, appropriate reviews (205, 300; 24; 24; 349) should be consulted.

The adduct  $CCl_3NO_2 \cdot 3.7NH_2CSNH_2$  has been claimed as a fumigant (309). The toxicity of trichloronitromethane and of trichloromethyl chloroformate has been shown to be caused by reaction with thiol groups in proteins. Trichloronitromethane is much more active than mustard gas in reducing the thiol contents of proteins and in inhibiting succinic dehydrogenase activity (187). Sulfonylthioureas containing trifluoromethoxy groups are claimed to be active against dia-

betes (123). Trifluoromethyl aryl sulfides and trifluoromethyl aryl sulfoxides have been found to be pesticidal (314). 1-D,L-threo-(p-Trifluoromethylsulfonylphenyl)-2-(dichloroacetamido)-1,3-propanediol has been shown to be of therapeutic value against *Diplococcus pneumoniae* and *Mycobacterium tuberculosis* var. *bovis* (149). A number of trifluoromethyl aryl sulfones have been claimed to be pesticidal (78, 148) and bactericidal (78). A series of trichloromethyl aryl sulfides exhibited insecticidal and fungicidal activity (99, 291, 292, 349). Hexachlorodimethyl trisulfide is claimed to be a pesticide and bactericide, especially suitable for impregnating organic matter (72). A number of trichloromethyl aryl sulfones (99, 291) were found to have some pesticidal activity, although less than the corresponding sulfides. Hexachlorodimethyl sulfone has been patented as a bactericide and fungicide (51). Some tribromomethyl aryl sulfones are fungicidal (79). Virtually all derivatives of trichloromethanesulfonyl chloride have been prepared as potential pesticides (349). Several 1-(trichloromethylthio)pyrazoles have been shown to be potent insecticides, miticides, fungicides, and bactericides (67). Earlier biological studies of the fungitoxicity of N-trichloromethylthio-1,2,5,6-tetrahydrophthalimide have been summarized (302). It has been shown that the reaction of N-trichloromethylthio-1,2,5,6-tetrahydrophthalimide with protein thiol groups is not the basis of the fungitoxic action, but rather competing with it (302). A number of N-trichloromethylthioimides and N-trichloromethylthiosulfonamides exhibit cancerolytic properties (134). The fungistatic properties of a series of aryl trichloromethanesulfenates has been extensively investigated (127). Benzoic acid trichloromethanesulfenic acid anhydride,  $C_6H_5COOSCl_3$ , inhibits hydrogenase activity as well as nitrogen fixation by *Clostridium pasteurianum*. Both effects are canceled by the addition of sodium molybdate (69). A number of S-trichloromethyl thiophosphoric diamide esters were found to be active against two-spotted mites (253). An extensive study of the fungicidal activity of S-trichloromethyl thiol-sulfonates is available (211). Chlorotrichloromethyl disulfane,  $CCl_3SSCl$ , has been shown to possess good fungicidal activity against *Uromyces phaseoli typica* (66). Sodium triiodomethanesulfonate, originally prepared for use as an X-ray contrast medium, was found to be toxic to mice at a level of 0.4 mg./g. body weight and thus unsuitable (30).

#### VI. USES OF N-, O-, AND S-TRICHALOMETHYL COMPOUNDS

Though specific uses have been claimed for most of these compounds, data on actual performance are comparatively rare.

Again, trichloronitromethane ("chloropicrin"), trichloromethyl chloroformate ("diphosgene"), bis(tri-

chloromethyl)carbonate ("triphosgene"), and N-trichloromethylthio-1,2,5,6-tetrahydrophthalimide ("Captan") have the most extensive records of practical applications, and the appropriate reviews (205, 300; 24; 24; 349) should be consulted.

Most perfluoroalkylamines, by virtue of their chemical inertness and thermal stability, have been suggested for use as hydraulic fluids, lubricants, and solvents. Trichloronitromethane may be used as a cathode in dry batteries (141). The polymerization of perfluoroolefins is catalyzed by hexafluorodimethyl disulfide (57) as well as by bis(trifluoromethylthio)mercury (57, 102). A solution of polytetrafluoroethylene in 2,2,2-trifluoroethyl trifluoromethanesulfenate has been used to make filter paper water-repellent (3). Hexachlorodimethyl sulfone is a bactericide and fungicide especially used in soap (51). Esters of trichloromethanesulfenic acid have been used as photosensitizers in the photopolymerization of acrylonitrile (39). Treatment of polyethylene with trichloromethanesulfonyl chloride leads to a rubber-like substance (83). Trichloromethanesulfonic acid has been used as a catalyst for the esterification of cellulose (70) as well as in the cumene hydroperoxide process for the manufacture of phenol and acetone (188).

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