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Progress in the chemistry of perhalomethanesulphenyl halides

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ABSTRACT. Results of investigations on perhalomethanesulphenyl halides are systematised and correlated in the review. Methods of obtaining perhalomethanesulphenyl halides are reviewed and their nucleophilic, electrophilic and radical substitution, addition, oxidation and reduction reactions are discussed.

The bibliography contains 232 references.

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I. Introduction

The chemistry of perhalomethanesulphenyl halides began with the synthesis of trichloromethanesulphenyl chloride by Rathke.[1,2] However this region of hetero-organic chemistry had its most rapid development at the beginning of the sixties of the present century after the discovery by Kittleson[3] of the fungicidal properties of *N*-trichloromethanesulphenyl phthalimide and *N*-trichloromethanesulphenyl 1,2,5,6-tetrahydrophthalimide, which have been widely used as standard fungicidal preparations under the commercial names Ftalan and Captan. Trichloromethanesulphenyl chloride is at present the most widely studied perhalomethanesulphenyl halide. Convenient preparative methods (both laboratory and industrial) have been developed for obtaining it, its properties have been studied in detail and areas have been found for its application in practice. The structure of the trichloromethanesulphenyl chloride molecule has been investigated in the gas phase by electron diffraction,[4] from which it was established that the chlorine atom Cl(1) on the sulphur atom and one of the chlorine atoms of the trichloromethanesulphenyl group Cl(4) are in *trans*-disposition. The latter chlorine atom and the sulphur atom are drawn together somewhat because of the deviation of the C–S bond from the three-fold axis of the trichloromethyl residue as a result of which the SCCl(4) bond angle is 102° 5′. Such a peculiarity in the structure of the trichloromethanesulphenyl chloride molecule sets a stamp on its chemical properties. Thus the nonequivalence of one of the chlorine atoms in the trichloromethyl group [as a result of the deviation of the SCCl(4) angle from 109°] is displayed in the increased reactivity of Cl(1) and Cl(4) in free radical processes. The deformation of the SCCl(4) angle also facilitates intramolecular nucleophilic attack of Cl(1) on the carbon atom and makes the generation of dichlorocarbene possible. The other perhalomethanesulphenyl halides known at present have been investigated less and require further study. The interest displayed in the chemistry of perhalomethanesulphenyl halides by many investigators is explained primarily by the synthetic value of these compounds The high lability of the sulphur–halogen bond, its tendency towards heterolytic and homolytic fission, and also two reaction centres (sulphur and carbon) impart the properties of valuable synthons to the perhalomethanesulphenyl halides. On the other hand certain representatives of this class of compound, trichloromethanesulphenyl chloride and dichlorofluoromethanesulphenyl chloride in particular, are widely used in the manufacture of biologically active preparations which are of interest.

Several reviews[3,5–11] partially cover the chemistry of perhalomethylsulphenyl halides up to 1970, however, regretably there are no exhaustive studies. In our view the proferred review may compensate for this omission to some extent. The literature is covered up to 1990.

II. Methods of synthesis of perhalomethanesulphenyl halides

1. Perchloromethanesulphenyl halides

a) Trichloromethanesulphenyl chloride

Trichloromethanesulphenyl chloride was obtained for the first time in 1870 by the chlorination of carbon disulphide with chlorine in the presence of iodine as catalyst.[1,2] For a long time this reaction was the subject of investigation by many scientists with the aim of optimising the process of obtaining trichloromethanesulphenyl chloride both in the laboratory and in industry. This is linked primarily with the fact that in the chlorination of carbon disulphide with chlorine other products are formed in addition to trichloromethanesulphenyl chloride, particularly sulphur mono- and dichlorides and carbon tetrachloride. The probability of forming any particular product is due to a series of factors, mainly by the ratio of reactants, the chlorination conditions and the nature of the solvent. Depending on the ratio of reactants sulphur mono- and dichlorides are formed in addition to trichloromethanesulphenyl chloride in the chlorination of carbon disulphide, as illustrated by the following reactions.

$$2CS_2+5Cl_2\longrightarrow 2CCl_3SCl+S_2Cl_2,$$

$$CS_2+3Cl_2\rightarrow CCl_3SCl+SCl_2.$$

Sulphur mono- and dichloride are formed in the reaction of chlorine with carbon disulphide, the dichloride practically always predominating.[3] The formation of trichloromethanesulphenyl chloride by the reaction of chlorine with carbon disulphide at a ratio

of 2:5 occurs by the following conversions in the opinion of certain authors.[12]

$$2CS_2+2Cl_2\longrightarrow 2ClC(S)SCl,$$
$$2ClC(S)SCl+Cl_2\longrightarrow 2Cl_2C{=}S+S_2Cl_2,$$
$$2Cl_2C{=}S+2Cl_2\longrightarrow 2CCl_3SCl.$$

Although such a mechanism for the chlorination of carbon disulphide is confirmed to a certain extent by the formation of trichloromethanesulphenyl chloride in the reaction of thiophosgene with chlorine,[12,13] it has nevertheless been questioned.[14] These authors[14] considered that the addition of chlorine occurs at the two C=S bonds of carbon disulphide simultaneously with the formation of dichloromethanedisulphenyl chloride, the further chlorination of which leads to the formation of trichloromethanesulphenyl chloride.

$$2CS_2+4Cl_2\longrightarrow 2\left[\begin{array}{c}Cl\\|\\ClS{-}C{-}SCl\\|\\Cl\end{array}\right]\xrightarrow[-S_2Cl_2]{Cl_2}2CCl_3SCl.$$

A change in the ratio of the initial reactants in the direction of increasing the quantity of chlorine leads to a reduction in the yield of trichloromethanesulphenyl chloride and the formation of carbon tetrachloride which arises from the following reaction.[3,15]

$$2CCl_3SCl_2+Cl_2\longrightarrow 2CCl_4+S_2Cl_2.$$

The conversion of trichloromethanesulphenyl chloride into carbon tetrachloride is assisted by sunlight,[3] and also by the presence in the reaction mixture of such metals as iron, tin and copper.[3,5] It is recommended to carry out the chlorination of carbon disulphide with chlorine in the temperature range from 15 to 30 °C.[5] Carrying out this process at higher temperatures assists the formation of carbon tetrachloride, while a reduction in the temperature of the process slows down the rate of chlorination of carbon disulphide. Water,[5] carbon disulphide,[16] organic solvents such as heptane, carbon tetrachloride, etc.[17] are used as reaction medium. In view of the relatively high stability of trichloromethanesulphenyl chloride towards hydrolysis the chlorination of carbon disulphide in an aqueous emulsion is more preferred since the sulphur mono- and disulphides formed in the process are partially decomposed by water to water-soluble products which assists their separation from trichloromethanesulphenyl chloride. Purification of trichloromethanesulphenyl chloride from byproducts is a relatively complex operation. The low-boiling sulphur dichloride and carbon tetrachloride are separated from trichloromethanesulphenyl chloride, which has bp 147 °C, by simple distillation but it is practically impossible to separate sulphur monochloride (bp 136 °C) by simple distillation. Several methods have been developed for purifying trichloromethanesulphenyl chloride from sulphur monochloride. The most widespread are methods comprising steam distillation of trichloromethanesulphenyl chloride[18] and washing trichloromethanesulphenyl chloride with water,[5] or with aqueous solutions of reducing[19] or oxidising[3] agents which convert sulphur monochloride into compounds readily soluble in water. After chlorination the reaction mixture is treated with a fresh portion of carbon disulphide with the aim of converting sulphur mono- and dichlorides to trichloromethanesulphenyl chloride.[3]

$$2S_2Cl_2+CS_2\longrightarrow CCl_3SCl+5S,$$
$$2SCl_2+CS_2\longrightarrow CCl_3SCl+2S.$$

After chlorination, treatment of the reaction mixture with sulphur dioxide has been proposed.[3] This converts sulphur monochloride into thionyl chloride which is readily separable from trichloromethanesulphenyl chloride by simple distillation.

$$S_2Cl_2+SO_2\longrightarrow SOCl_2+S+SO_2.$$

It was reported[3] that the chlorination of carbon disulphide with chlorine in hydrochloric acid leads to the formation of practically pure trichloromethanesulphenyl chloride since sulphur mono- and dichlorides are readily hydrolysed in hydrochloric acid.

$$CS_2+5Cl_2+4H_2O\xrightarrow{HCl}CCl_3SCl+H_2SO_4+6HCl.$$

Other means of obtaining trichloromethanesulphenyl chloride are based on the reaction of chlorine with methane-, chloromethane- or dichloromethanesulphenyl chloride,[3] with dimethyl disulphide,[3] with methyl trichloromethyl sulphide,[3] methyl thiocyanate,[5] dimethyl sulphide,[20] chloromethyltrichloromethyl sulphide,[20] and carbon selenosulphide.[21] However these methods are not widely used due to the low availability of the starting materials, the low yields of trichloromethanesulphenyl chloride and the complexity of isolating it.

b) Trichloromethanesulphenyl bromide

Trichloromethanesulphenyl bromide is formed in quantitative yield by the reaction of trichloromethanesulphenyl chloride with 48% hydrobromic acid at 23–25 °C.[22–24]

$$CCl_3SCl+HBr\longrightarrow CCl_3SBr+HCl.$$

c) Trichloromethanesulphenyl fluoride

The unstable trichloromethanesulphenyl fluoride is formed on heating trichloromethanesulphenyl chloride with activated potassium fluoride and is converted under the reaction conditions into dichlorofluoromethanesulphenyl chloride.[25,26]

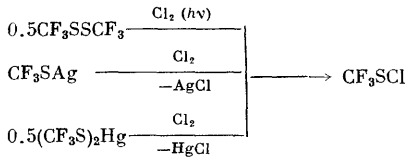
Of the perbromomethanesulphenyl halides only tribromomethanesulphenyl bromide is known and is formed on reaction of dibromochloromethanesulphenyl bromide with 48% hydrobromic acid[22] and by the reaction of bromine with carbon disulphide[8] and carbon selenosulphide.[21]

The formation of the unstable triiodomethanesulphenyl iodide on reaction of carbon disulphide with iodine has been presumed in the literature.[27]

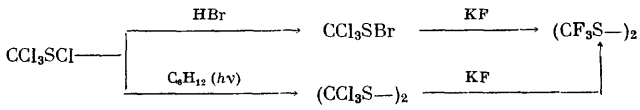
2. Perfluoromethanesulphenyl halides

a) Trifluoromethanesulphenyl chloride

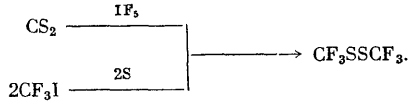
Trifluoromethanesulphenyl chloride is formed in relatively good yield by the reaction of chlorine with hexafluorodimethyldisulphide[8,27] and also with silver[28] and mercury[8,29] trifluoromethylmercaptides.



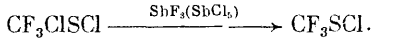
Replacement of the chlorine atoms by fluorine in trichloromethanesulphenyl chloride by the action on it of sodium fluoride,[30] potassium fluoride[31] or hydrogen fluoride[32] also leads to the formation of trifluoromethanesulphenyl chloride, but in low yield, since fission of the C–S bond occurs with the formation of various products in addition to the chlorine–fluorine exchange. Because of this it is more rational to convert trichloromethanesulphenyl chloride into hexafluorodimethyldisulphide as follows.[23]



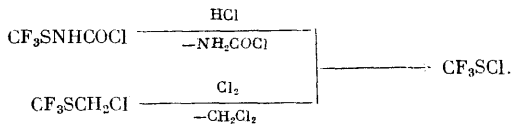
Hexafluorodimethyl disulphide may also be obtained by the fluorination of carbon disulphide or by the reaction of trifluoroiodomethane with sulphur.



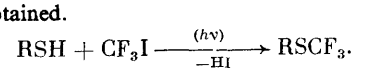
Replacement of chlorine by fluorine in chlorodifluoromethanesulphenyl chloride may be effected with antimony trifluoride.[34]



Fission of the S–N bond of trifluoromethanesulphenamides[35] and also of the S–C bond of trifluoromethyl sulphides[36] by reaction with hydrogen chloride and chlorine also leads to the formation of trifluoromethanesulphenyl chloride.

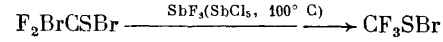


In the latter case the ease of fission of the S–C bond is explained by the structure of the initial sulphide. Consequently there is great interest in the radical perfluorination of thiols[37–39] as a result of which trifluoromethylsulphides themselves of various structure may be obtained.



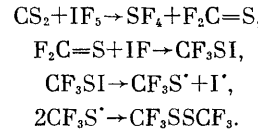
b) Trifluoromethanesulphenyl bromide

Trifluoromethanesulphenyl bromide is obtained in 40% yield by the reaction of bromodifluoromethanesulphenyl bromide with antimony trifluoride in the presence of antimony pentachloride.[34]



c) Trifluoromethanesulphenyl iodide

The unstable trifluoromethanesulphenyl iodide, which readily converts into hexafluorodimethyl disulphide, is formed as an intermediate in the fluorination of carbon disulphide with iodine pentafluoride between 60 and 200 °C.[27]



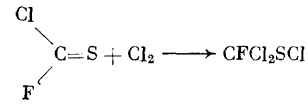
d) Trifluoromethanesulphenyl fluoride

Trifluoromethanesulphenyl fluoride is formed in low yield on exhaustive fluorination of trichloromethanesulphenyl chloride with activated potassium fluoride.[26]

3. Mixed perhalomethanesulphenyl halides

a) Dichlorofluoromethanesulphenyl chloride

Several methods have been developed for obtaining dichlorofluoromethanesulphenyl chloride, however they do not provide a high yield. One of these methods comprises replacement of one of the chlorine atoms in trichloromethanesulphenyl chloride by reaction with potassium fluoride[25,26,31,40] or hydrogen fluoride.[56] Another method is based on the addition of chlorine to the C=S bond of thiocarbonyl chlorofluoride.[24]



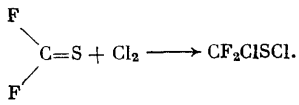
More promising from a preparative standpoint is the replacement of one of the chlorine atoms by fluorine in *N*-(diethyl)-trichloromethanesulphenamide with subsequent fission of the S–N bond in the resulting *N*-(diethyl)dichlorofluoromethanesulphenamide by reaction with hydrogen chloride.[41] A maximum yield (37%) of dichlorofluoromethanesulphenyl chloride was observed at a reactant ratio of 1 : 1, a temperature for fluorination of 55 °C and duration 105 min.



b) Chlorodifluoromethanesulphenyl chloride

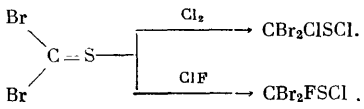
Chlorodifluoromethanesulphenyl chloride is formed in 22% yield on replacing two chlorine atoms by fluorine in *N*-(diethyl)chlorodifluoromethanesulphenamide with subsequent fission of the S–N bond in the resulting *N*-(diethyl)chlorodifluoromethanesulphenamide by reaction with hydrogen chloride.[41] This compound may also be

obtained by the partial fluorination of trichloromethanesulphenyl chloride with potassium fluoride[24] and by the addition of chlorine to the C=S bond of thiocarbonyl difluoride.[8]



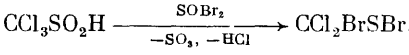
c) Dibromochloromethane- and dibromofluoromethanesulphenyl chlorides

The addition of chlorine or chlorine fluoride to the C=S bond of thiocarbonyl dibromide leads to the formation of dibromochloromethanesulphenyl chloride or dibromofluoromethanesulphenyl chloride in yields of 34 and 18% respectively.[42]



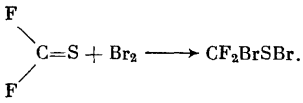
d) Bromodichloromethanesulphenyl bromide

Bromodichloromethanesulphenyl bromide is formed by the reaction of trichloromethanesulphenyl chloride with 48% hydrobromic acid.[3] The formation of this compound has also been mentioned in the reaction of trichloromethanesulphinic acid with thionyl bromide.[43]



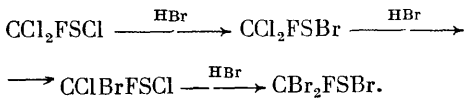
e) Bromodifluoromethanesulphenyl bromide

The addition of bromine to the C=S bond of thiocarbonyl difluoride leads to the formation of bromodifluoromethanesulphenyl bromide in relatively good yield.[44]

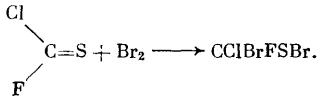


f) Dichlorofluoromethane, dibromofluoromethane- and bromochlorofluoromethanesulphenyl bromides

It has been shown that dichlorofluoromethanesulphenyl chloride is converted by step-wise bromine–chlorine exchange into dichlorofluoromethanesulphenyl bromide, bromochlorofluoromethanesulphenyl bromide and dibromofluoromethanesulphenyl bromide.[24]



Bromochlorofluoromethanesulphenyl bromide is also formed by the addition of bromine to the C=S bond of thiocarbonyl chlorofluoride.[24,44]



III. Reactions of perhalomethanesulphenyl halides

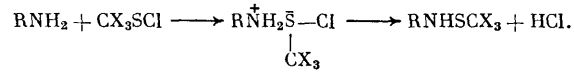
1. Nucleophilic substitution reactions

Perhalomethanesulphenyl halides react vigorously with amines, alcohols, thiols and other nucleophiles with the formation of various perhalomethylthio derivatives. Some of these reactions are fairly unusual compared with the analogous reactions of alkanesulphenyl halides containing no halogen in the alkyl group. In the majority of cases these reactions proceed by an S_N2 mechanism with the formation of a transition state in which the entering and leaving groups are at apices of a trigonal bipyramid.[45]



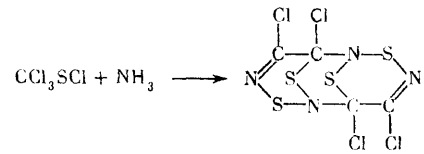
X = Hal.

The possibility of some reactions occurring by an addition–elimination mechanism is not excluded.[45]

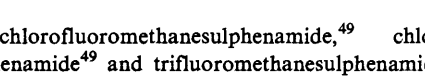


a) Interaction with *N*-nucleophiles

Interaction with ammonia. The vigorous reaction of trichloromethanesulphenyl chloride with ammonia was remarked upon even by Rathke,[1] however the structure of the resulting product was not determined. Significantly more recently the reaction of trichloromethanesulphenyl chloride with ammonia was studied in a heterogeneous medium of benzene and water.[46] The product formed in this reaction was assigned the structure of 3,6-dichloro-1,4-dithia-2,5-diazine, but proved to be more complex.[47] The reaction of trichloromethanesulphenyl chloride with 25% aqueous ammonia solution in a two-phase benzene–water system leads to the formation of 2,3,7,8-tetrachloro-5,10,11,12-tetrathio-1,4,6,9-tetraazatricylo[5,3,11^{2,6}]dodeca-3,8-diene.



Trichloromethanesulphenamide has been proposed[47] as an intermediate in this reaction and was obtained more recently by the reaction of trichloromethanesulphenyl chloride with liquid ammonia in pentane at –70 °C.[48] This unstable compound, which decomposes at room temperature, is preserved at –80 °C without decomposition for 7 days.



Dichlorofluoromethanesulphenamide,[49] chlorodifluoromethanesulphenamide[49] and trifluoromethanesulphenamide,[50] formed by the reaction of the corresponding sulphenyl chlorides with liquid ammonia at –60 °C in trichlorofluoromethane, proved to be more stable. Further reaction of perhalomethanesulphenamides with one

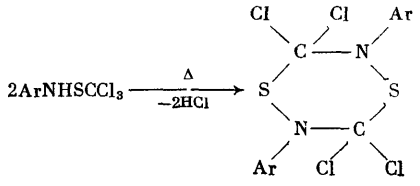
or two moles of perhalomethanesulphenyl chloride leads to the formation of bis-(perhalomethanesulphen)amides and tris-(perhalomethanesulphen)amides.[49,51–53]

$$RSNH_2 + RSCl \xrightarrow[-HCl]{} (RS)_2NH \xrightarrow[-HCl]{RSCl} (RS)_3N,$$
$$R=CCl_2F,\ CClF_2,\ CF_3.$$

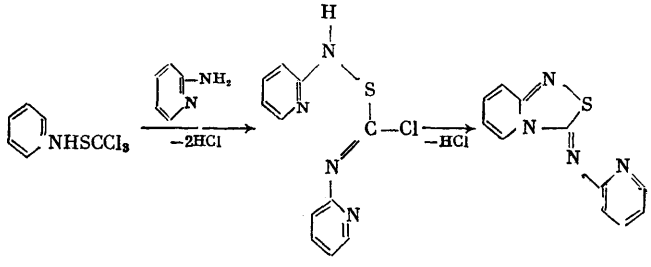
Interaction with amines. The reaction of perhalomethanesulphenyl halides with primary and secondary amines leads to the formation of *N*-substituted amides of perhalomethanesulphenic acids. *N*-Substituted amides have been described for trichloromethanesulphenic,[3,5] trifluoromethanesulphenic,[3,54] dichlorofluoromethanesulphenic,[3,10,55] chlorofluoromethanesulphenic[3,41] and bromochlorofluoromethanesulphenic[3] acids. The formation of *N*-disubstituted trichloromethanesulphenamides has been established in the reaction of trichloromethanesulphenyl chloride with aminals.[56] The instability of *N*-substituted trichloromethanesulphenamides formed by the reaction of trichloromethanesulphenyl chloride with primary amines has been recorded.[10] For example *N*-alkyltrichloromethanesulphenamides are converted into *N*-trialkylguanidines in the presence of alkylamines.

$$AlkNHSCCl_3 + 4AlkNH_2 \xrightarrow[-2AlkNH_2\cdot HCl]{} AlkN{=}C(NHAlk)_2$$

N-Aryltrichloromethanesulphenamides are converted on heating in the presence of alkali into 2,5-diaryl-3,3,6,6-tetrachloro-1,4-dithia-2,5-diazines.[10]



2-(*N*-Trichloromethanesulphenamino)pyridine, formed by the reaction of trichloromethanesulphenyl chloride and 2-aminopyridine, is converted by an excess of the latter into (2-pyridylamino)-3H-1,2,4-thiadiazolo[4,3-α]pyridine.[10,57]



The reaction of perhalomethanesulphenyl halides with tertiary amines proceeds in a more complex manner. For example, the reaction of trichloromethanesulphenyl chloride with triethylamine in benzene at 20 °C leads to the formation of 1,1-bis(trichloromethanesulphenyl)-2-(*N*,*N*-diethylamino)ethylene.[58]

$$2CCl_3SCl + CH_3CH_2N(CH_2CH_3)_2 \xrightarrow{-HCl} (CCl_3S)_2C{=}CHN(CH_2CH_3)_2.$$

Interaction with hydrazine derivatives. The reaction of perhalomethanesulphenyl halides with hydrazine derivatives has been studied mainly for trichloromethanesulphenyl chloride. Reactions have been described for trichloromethanesulphenyl chloride with alkylhydrazines,[59–61] arylhydrazines[61] and alkane(arene)sulphohydrazides.[61] Nucleophilic attack at the sulphur atom is, as a rule, effected by the NH_2 group. However, participation of the NH group in such attack has also been recorded. For example the reaction of trichloromethanesulphenyl chloride with benzenesulphonohydrazide in dimethoxyethane leads to the formation of two products, viz. *N*-benzenesulphono-*N'*-trichloromethanesulphenohydrazide and *N*-benzenesulpho-*N*-trichloromethanesulphenohydrazide.[61]

$$PhSO_2NH{-}NH_2 + CCl_3SCl \rightarrow \begin{cases} PhSO_2NH{-}NHSCCl_3 \\ PhSO_2N(SCCl_3){-}NH_2 \end{cases}$$

The trichloromethanesulphenylation of diacylhydrazines has been carried out in aqueous alkaline medium.[61] Replacement of two hydrogen atoms by trichloromethanesulphenyl groups occurs in this way:

$$RCONH{-}NHCOR + 2CCl_3SCl \xrightarrow[-2NaCl]{NaOH} RCON(CCl_3S){-}N(SCCl_3)COR,$$

R = H, Me, Et, Ph.

Interaction with amides and amidines of carboxylic acids. Replacement of a hydrogen atom on the nitrogen atom of a carboxylic acid amide takes place with significantly more difficulty than in the case of amines. The structure of the starting material, the nature of the solvent and the sulphenylation conditions play an appreciable role. The presence of strongly electron-accepting groups in the acyl fragment hinder the sulphenylation process, but the presence in the acyl fragment of other reactive functional groups frequently leads to sulphenylation of the acyl fragment and not the amide group, as has been mentioned.[3,62] Strongly basic polar solvents such as dioxan, dimethoxyethane, dimethylformamide, etc. are used as reaction medium. An excess of the amide or an organic base (pyridine, triethylamine, etc.) is used as acceptor of hydrogen halide. The trichloromethanesulphenylation of certain carboxylic acid *N*-monosubstituted amides is effected via the sodium salt.[3] It was shown[63] that the reaction of trichloromethanesulphenyl chloride with amides of aliphatic carboxylic acids in dimethoxyethane or dioxan at room temperature leads to the formation of *N*-alkanoyltrichloromethanesulphenamides in 5–22% yield.

$$2RCON(R')H + CCl_3SCl \rightarrow RCON(R')SCCl_3 + RCON(R')H\cdot HCl.$$

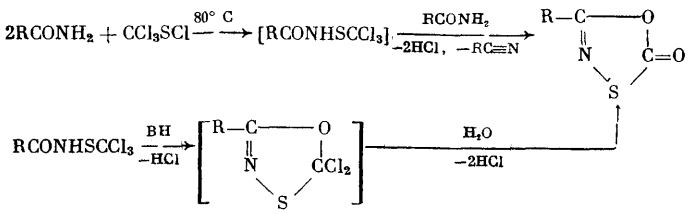
R = R' = H; R = Me, R' = H; R = Et, R' = H; R = n-Pr, R' = H; R = PhCH=CH$_2$, R' = H; R = H, R' = Et; R = H, R' = n-Pr; R = R' = Me; R = Me, R' = n-Pr; R = Me, R' = n-Bu.

Trichloromethanesulphenyl chloride reacts under analogous conditions with urea and its homologues with the formation of the corresponding *N*-trichloromethanesulphenyl derivatives.[63]

$$2RNHCNHR' + CCl_3SCl \longrightarrow RNHCNSCCl_3 + RNHCNH\cdot HCl,$$

$R = R' = H$; $R = Me$, $R = H$, $R = R' = Me$.

Amides of aromatic carboxylic acids do not react under these conditions but heating the reaction mixture leads to 5-aryl-1,3,4-oxathiazol-2-ones,[64] the formation of which was also observed on reacting *N*-aroyltrichloromethanesulphenamides with bases (NaOH, triethylamine, pyridine, etc.).[65–68]



R = Ph; 3-MeC_6H_4; 4-MeC_6H_4; 4-PhC_6H_4; 2-ClC_6H_4; 3-ClC_6H_4; 4-ClC_6H_4; 2,4-$(Cl)_2C_6H_3$; 3,4-$(Cl)_2C_6H_3$; 2-$NO_2C_6H_4$; 3-$NO_2C_6H_4$; 3,4,5-$(MeO)_3C_6H_2$.

It was established[69–71] that the reaction of trichloromethanesulphenyl chloride with amides of aliphatic and aromatic carboxylic acids in dimethylformamide in the presence of pyridine at –10 °C to 0 °C leads to the formation of *N*-acyltrichloromethanesulphenamides in 39–86% yield.

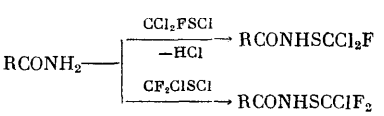
$$RCONH_2 + CCl_3SCl \xrightarrow{-10 \text{ to } 0\ ^\circ C,\ C_5H_5N} RCONHSCCl_3,$$

R = Me; n-Pr; n-Bu; iso-Bu; Ph; 3-MeC_6H_4; 4-MeC_6H_4; 3.5$(Me)_2C_6H_3$; 3-$MeOC_6H_4$; 4-$MeOC_6H_4$.

Trichoromethanesulphenyl chloride reacts under analogous conditions with urethane with the formation of *N,N*-bis-(trichloromethanesulphenyl)urethane[72] which is evidently explained by the fact that the rate of trichloromethanesulphenylation of urethane is less than the rate of trichloromethanesulphenylation of the *N*-trichloromethanesulphenylurethane formed as an intermediate.

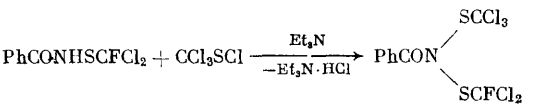
$$EtOCONH_2 + 2CCl_3SCl \xrightarrow{-10 \text{ to } 0\ ^\circ C,\ C_5H_5N} EtOCON(SCCl_3)_2.$$

Dichlorofluoromethanesulphenyl chloride is more reactive than trichloromethanesulphenyl chloride in relation to carboxylic acid amides.[3] For example according to the patent literature[73] the reaction of dichlorofluoromethanesulphenyl chloride with carboxylic acids on heating in dioxan leads to the smooth formation of the corresponding *N*-acyldichlorofluoromethanesulphenamides in relatively good yield. Dichlorofluoromethanesulphenyl and chlorodifluoro-methanesulphenyl chloride also react readily with carboxylic acid amides in dimethylformamide in the presence of pyridine at –5° C to –3 °C.[72,74,75]

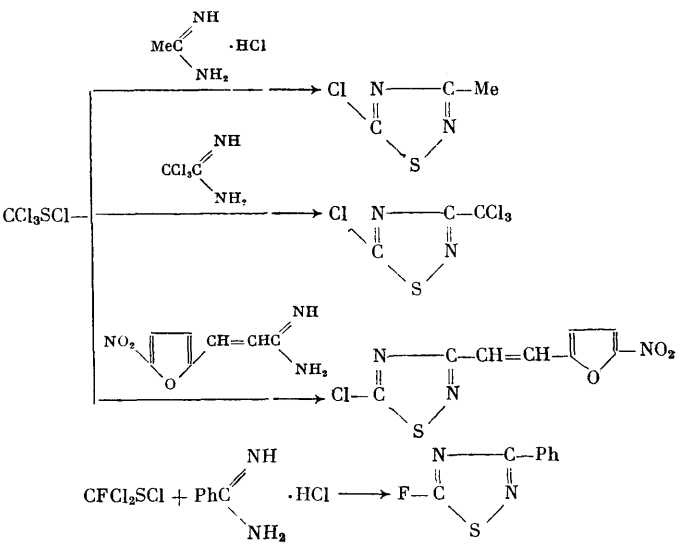


R = Me, Ph, 4-MeC_6H_3.

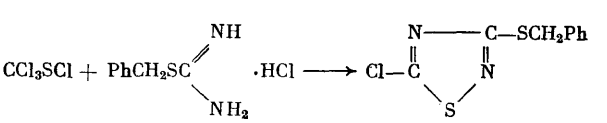
N-Benzoyldichlorofluoromethanesulphenamide reacts with trichloromethanesulphenyl chloride in the presence of triethylamine with the formation of *N*-(dichlorofluoromethylthio)-*N*-(trichloromethylthio)benzamide.[10]



Amidines of carboxylic acids possess a higher reactivity towards perhalomethanesulphenyl halides than do carboxylic acid amides. As a rule both reaction centres (sulphur and carbon) of the perhalomethanesulphenyl halide participate in nucleophilic substitution reactions as a result of which 1,2,4-thiadiazole derivatives are formed.[10,77,78]



S-Alkylisothiouronium salts react like amidines with the formation of 1,2,4-thiadiazole derivatives.

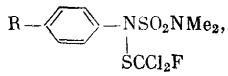


Interaction with sulphonamides. *N*-Substituted amides of alkane- and arenesulphonic acids containing alkyl,[3,80,81] aryl,[3,82] acyl[83] and arenesulphonyl[84,85] groups as substituents react relatively easily with trichloromethanesulphenyl chloride with the formation of *N,N*-disubstituted amides of trichloromethanesulphenic acid. Sulphenylation is carried out in nonaqueous organic solvent (benzene, toluene, chlorobenzene, diethyl ether, etc.) in the presence of organic bases. Occasionally in place of sulphonamides their sodium, lithium or silver salts are used.

$$RSO_2N(X)R' + CCl_3SCl \xrightarrow[-XCl]{} CCl_3SNSO_2R,\ \ R'$$

R=Alk, Ar; R'=Alk, Ar, RCO, $ArSO_2$, X=H, Na, Li, Ag.

N-Substituted alkane- and arenesulphonamides and also *N,N,N'*-trisubstituted sulphonamides react in a similar manner with dichlorofluoromethanesulphenyl chloride, bromochlorofluoromethanesulphenyl chloride and dibromofluoromethanesulphenyl bromide.[3,86] *N,N*-Dimethyl-*N'*-phenyl-*N'*-dichlorofluoromethylthiosulphonamide and *N,N*-dimethyl-*N'*-*p*-tolyl-*N'*-dichlorofluoromethylthiosulphonamide are the most studied of the *N*-perhalomethylthiosulphonamides formed and are widely used as fungicides under the commercial names "Euparen" and "Euparen-M".[118]



R=H, Me.

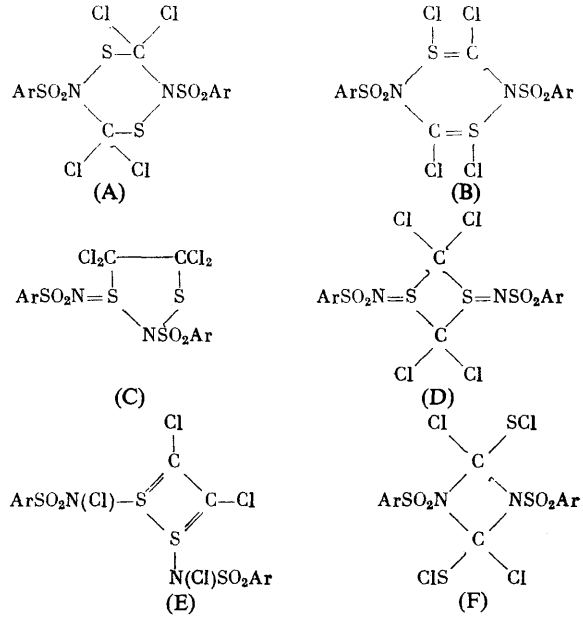
The composition and structure of the products of the reaction of unsubstituted arenesulphonamides with trichloromethanesulphenyl chloride depend on the reaction conditions. It was recorded[87] that the main products of the reaction of arensulphonamides with trichloromethane-sulphenyl chloride in boiling tetrachloroethylene were diaryl disulphides, ammonium chloride and sulphur *N,N*-bis-(arenesulphonyl)diimine. The reaction of arenesulphonamides with trichloromethanesulphenyl chloride in anhydrous benzene in the presence of triethylamine leads to the formation of *N*-arenesulphonyltrichloromethanesulphenamides in 40–60% yield.[88]

$$ArSO_2NH_2 + CCl_3SCl \xrightarrow[-Et_3N\cdot HCl]{20-30^\circ C,\ Et_3N} ArSO_2NHSCCl_3.$$

Arenesulphonamides react similarly with trichloromethanesulphenyl chloride in dimethylformamide in the presence of pyridine at –10 to 0 °C.[67,89] The reaction of arenesulphonamide sodium salts with trichloromethanesulphenyl chloride in carbon tetrachloride at –17 to –10 °C leads to *N,N*-bis(trichloromethanesulphenyl)arenesulphonamides the formation of which was also observed on reaction of *N*-arenesulphonyltrichloromethanesulphenamides with trichloromethanesulphenyl chloride in benzene in the presence of triethylamine.[88]

$$2ArSO_2NHNa + 2CCl_3SCl \xrightarrow[-ArSO_2NH_2,\ -2NaCl]{} ArSO_2N(SCCl_3)_2$$
$$ArSO_2NHSCCl_3 + CCl_3SCl \xrightarrow[-Et_3N\cdot HCl]{Et_3N} \uparrow$$

The reaction of arenesulphonamides with trichloromethanesulphenyl chloride in aqueous alkaline medium leads to the formation of cyclic compounds which were assigned the structure of 2,4-dichloro-2,4-bis(chlorothio)-1,3-bis(arenesulphonyl)-1,3-diazetidines [structure (F)] after analysis of several alternative structures (A–F).[88,90]



These compounds are also formed on reaction of arenesulphonamide sodium salts with trichloromethanesulphenyl chloride in carbon tetrachloride at –1 to +3 °C and also on reaction of *N*-arenesulphonyltrichloromethanesulphenamides with triethylamine.[90]

$$4ArSO_2NH_2 + CCl_3SCl + 4NaOH \xrightarrow[-2ArSO_2NH_2,\ -4NaCl,\ -4H_2O]{-1 \text{ to } 0\ ^\circ C} (E)$$
$$4ArSO_2NHNa + 2CCl_3SCl \xrightarrow[-2ArSO_2NH_2,\ -2NaCl]{-1 \text{ to } 3\ ^\circ C} \uparrow$$
$$2ArSO_2NHSCCl_3 + 2Et_3N \xrightarrow[-2Et_3N\cdot HCl]{} \uparrow$$

Interaction with nitrogen-containing heterocyclic compounds. The reaction of perhalomethanesulphenyl halides with heterocyclic compounds containing an N–H bond leads to the formation of *N*-perhalomethylthio derivatives of the heterocyclic compounds which possess biological activity as a rule. These investigations were particularly widely developed after the discovery in 1951 of the fungicidal properties of *N*-trichloromethylthiophthalimide and *N*-trichloromethylthio-1,2,5,6-tetrahydrophthalimide. As a rule the sulphenylation of heterocyclic compounds is carried out in anhydrous organic solvent in the presence of an organic base (pyridine, triethylamine, etc.). In the case of strongly basic heterocycles an excess of the heterocyclic compound is used as an acceptor of hydrogen halide. Heterocyclic compounds possessing an acidic character are sulphenylated as the sodium salts in aqueous, aqueous-alcoholic or alcoholic solution. *N*-Trichloromethylthio derivatives of the following are known: maleimide,[72] succinimide and its homologues,[91] hexahydrophthalimide and its homologues,[92] pyromellitimide,[93] 2,2-disubstituted malonimide,[94] homologues of

glutarimide,[3] aziridine,[3] caprolactam,[72] pyrrolidine,[95] indole,[3] isatin and its homologues,[96] piperidine,[95] pyrazole and its homologues,[13] imidazole,[3] hydantoin and its homologues,[99,100] uracil,[101] piperazine,[95] benzotriazole and its homologues,[3] benzo-1,2,3-triazin-4-one,[102] oxazolidine-2,4-dione and its homologues,[103] benzoxazolone and its homologues,[3] morpholine,[104] thiazolidine-2,4-dione and its homologues,[103] benzothiazolone,[3] benzoisothiazolone and its homologues,[105] benzoisothiazolone 1,1-dioxide and its homologues,[3] 5-methylthio-1,3,4-thiadiazol-2-one,[3] 5-phenylthio-1,3,4-thiadiazol-2-one,[3] 5-phenyl-1,3,4-thiadiazole-2-thione,[3] phenothiazine[3] and homologues of tetrahydro-1,3-thiazine.[106] The *N*-dichlorofluoromethylthio derivatives of the following have been described:[3,24] phthalimide and 1,2,5,6-tetrahydrophthalimide, hexahydrophthalimide, succinimide, pyrrolidine, homologues of isatin, imidazolin-2-one, benzotriazole, benzoxazolone, 3-methylbenzimidazolone, 1,3,4-oxadiazol-2-one, thiazolidine-2,4-dione, benzothiazolone and benzoisothiazolone 1,1-dioxide and also the *N*-trifluoromethylthio, *N*-dibromofluoromethylthio, *N*-bromodichloromethylthio and *N*-bromochlorofluoromethylthio derivatives of phthalimide and 1,2,5,6-tetrahydrophthalimide. It was shown[107] that the reaction of trichloromethanesulphenyl chloride with hexamethylenetetramine may lead to various products depending on the solvent used. For example 1,3-bis(trichloromethanesulphenyl)hexahydro-1,3,5-triazine is formed in alcohol and 3,7-bistrichloromethanesulphenyl-1,3,5,7-tetraazabicyclo[3,3,1]nonane in dimethoxyethane.

Interaction with other *N*-nucleophiles. The reaction of trichloromethanesulphenyl chloride with an *N*-(trimethylsilyl)-bis(arenesulphonyl)imide[85] or with sulphur *N,N'*-bis(trimethylsilyl)diimine[108] is accompanied by replacement of the trimethylsilyl group on the nitrogen atom by trichloromethanesulphenyl.

$$CCl_3SCl \xrightarrow[-Me_3SiCl]{Me_3SiN(SO_2Ar)_2} CCl_3SN(SO_2Ar)_2$$

$$CCl_3SCl \xrightarrow[-Me_3SiCl]{(Me_3SiN=)_2S} CCl_3SN{=}S{=}NSiMe_3$$

b) Reactions with *O*-nucleophiles

Hydrolysis. Trichloromethanesulphenyl chloride is relatively stable towards hydrolysis and may be steam distilled without decomposition. Partial hydrolysis occurs in concentrated sulphuric acid in the presence of a calculated quantity of water with the formation of a chlorocarbonylsulphenyl chloride.[7,8]

$$CCl_3SCl + H_2O \xrightarrow[-2HCl]{(H_2SO_4)} ClC(O)SCl.$$

It was established[109] that the intermediate in this reaction is dichloromethylene sulphoxide, which readily rearranges in concentrated sulphuric acid into chlorocarbonylsulphenyl chloride.

$$Cl_2C{=}S{=}O \xrightarrow{(H_2SO_4)} ClC(O)SCl.$$

Hydrolysis of trichloromethanesulphenyl chloride in the presence of alkali may, depending on the quantity of the latter, lead to the *S*-trichloromethyl ester of dichloromethanethiosulphonic acid[110] or to the sodium salt of dichloromethanethiosulphonic acid.[111] The formation of the *S*-trichloromethyl ester of dichloromethanethiosulphonic acid occurs as follows.

$$2CCl_2SCl + 3NaOH \xrightarrow[-H_2O]{} Cl_2CHSO_2SCCl_3 + 3NaCl.$$

It was proposed[110] that initially hydrolysis of trichloromethanesulphenyl chloride occurs with the participation of the sulphur atom.

$$2CCl_3SCl + 2NaOH \rightarrow 2CCl_3SOH + 2NaCl.$$

Disproportionation of the unstable trichloromethanesulphenic acid then occurs giving trichloromethanesulphinic acid and trichloromethanethiol.

$$2CCl_3CSOH \rightarrow CCl_3SO_2H + CCl_3SH.$$

In its turn the trichloromethanesulphinic acid is converted into dichloromethylene sulphoxide by elimination of hydrogen chloride and subsequent addition of trichloromethanethiol giving the *S*-trichloromethyl ester of dichloromethanethiosulphonic acid.

$$CCl_3SO_2H \xrightarrow[-HCl]{} Cl_2C{=}SO_2 \xrightarrow{CCl_3SH} Cl_2CHSO_2SCCl_3.$$

An excess of alkali obviously leads to saponification of the *S*-trichloromethyl ester of dichloromethanethiosulphonic acid one of the products of which is the sodium salt of dichloromethanesulphonic acid as has been observed.[111] Controlled hydrolysis of trifluoromethanesulphenyl chloride by alkali leads to the formation of the *S*-trifluoromethyl ester of trifluoromethanethiosulphonic acid and hexafluorodimethyl disulphide.[112]

$$4CF_3SCl + 2H_2O \xrightarrow[-4HCl]{} CF_3SO_2SCF_3 + CF_3SSCF_3.$$

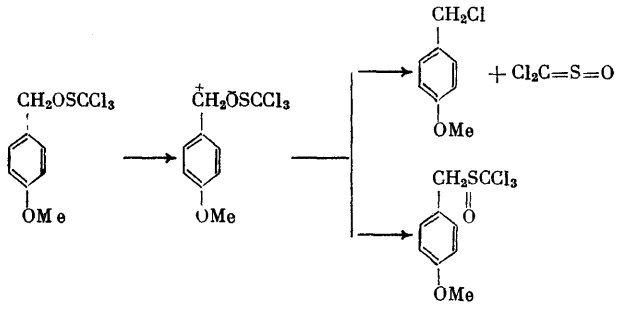
Interaction with alcohols and phenols. The reaction of perhalomethanesulphenyl halides with alcohols and phenols leads to the formation of alkyl and aryl esters of perhalomethanesulphenic acids. The esters of trichloromethanesulphenic,[3,112–116] dichlorofluoromethanesulphenic[3] and trifluoromethanesulphenic[3] acids have been described. Sulphenylation of alcohols is carried out in an excess of alcohol or in another organic solvent in the presence of pyridine or triethylamine. Sulphenylation of phenols or naphthols is better carried out as the sodium salts which prevents the competing electrophilic substitution of hydrogen atoms of the benzene ring.[117,118] Reaction of alkoxides instead of alcohols with trichloromethanesulphenyl chloride, especially an excess of the former, leads to the formation of alkyl orthocarbonates.[119] On reaction of trichloromethanesulphenyl chloride with allyl alcohol the resulting allyl ester of trichloromethanesulphenic acid is converted into allyl trichloromethyl sulphoxide as a result of a [2,3] sigmatropic rearrangement.[120–123]

$$CCl_3SCl + HOCH_2CH{=}CH_2 \xrightarrow[-HCl]{C_5H_5N} \left[CCl_3S \begin{array}{c} CH_2 \\ \diagdown\diagup \\ O \end{array} CH{=}CH_2 \right] \longrightarrow CCl_3S(O)CH_2{-}CH{=}CH_2$$

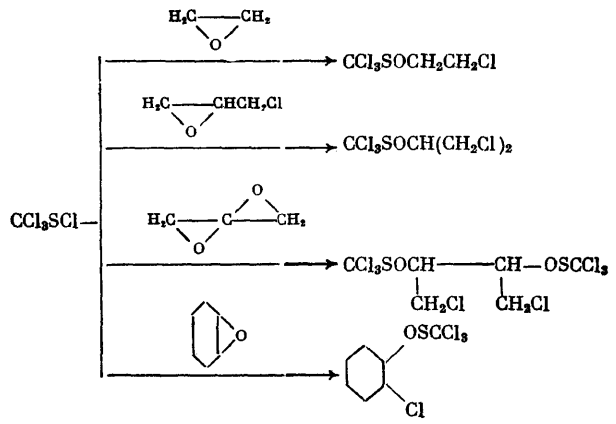
At higher temperatures rearrangement of trichloromethanesulphenic acid allyl ester proceeds without the 1,3-allyl shift with the formation of allyl chloride and dichloromethylene sulphoxide.

$$[CCl_3SOCH_2CH{=}CH_2] \rightarrow CH_2{=}CH{-}CH_2Cl + Cl_2C{=}S{=}O.$$

The propargyl ester of trichloromethanesulphenic acid undergoes an analogous rearrangement.[63] It was noted[123] that trichloromethanesulphenic acid benzyl ester is relatively stable but anisyl esters are rearranged into the sulphoxide and hexane even at 20 °C. Reaction of trichloromethanesulphenyl chloride with anisyl alcohol gives *p*-anisyl chloride and dichloromethylene sulphoxide but trichloromethyl *p*-anisyl sulphoxide is not an intermediate in the process.[123] It was proposed[124] that both rearrangements of anisyl esters proceed according to an ionisation–recombination mechanism by separate schemes.



On reacting trichloromethanesulphenyl chloride with 1,2-epoxides a *trans*-scission of the ring takes place with the formation of β-chloroalkyl sulphenates.[11,125]



Interaction with salts of organic and mineral acids. The reaction of trichloromethanesulphenyl chloride with silver[3,11] and sodium[125,126] salts of carboxylic acids leads to the formation of mixed anhydrides of trichloromethanesulphenic acid and the carboxylic acid.

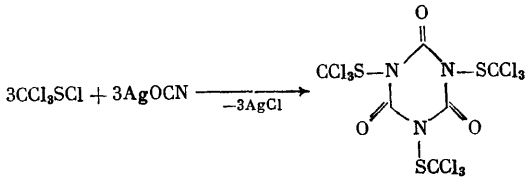
$$RCOOM + CCl_3SCl \rightarrow RCOOSCCl_3,$$

R = Me, Ph, CF_3, *p*-$MeCONHC_6H_4$; M = Ag, Na.

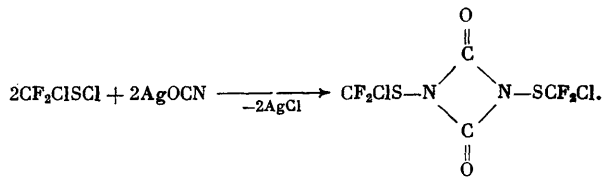
Trifluoromethanesulphenyl chloride reacts ambiguously with silver salts of carboxylic acids. Reaction of it with the silver salt of trifluoroacetic acid leads to the mixed anhydride of trifluoroacetic and trifluoromethanesulphenic acids but a mixture of various products is formed on reaction with the silver salts of chlorodifluoroacetic and pentafluorobenzoic acids.[11,127] Reaction of trichloromethanesulphenyl chloride with silver nitrate leads to the formation of trichloromethanesulphenyl nitrate.[128]

$$CCl_3SCl + AgNO_3 \xrightarrow[-AgCl]{} CCl_3SONO_2.$$

Silver isocyanate reacts with perhalomethanesulphenyl halides with a shift of the reaction centre, i.e. with nitrogen and not oxygen participating in the nucleophilic attack. The character of the reaction products is therefore determined by the form of the perhalomethanesulphenyl halide. For example the product of the reaction of trichloromethanesulphenyl chloride and silver isocyanate is 2,4,6-trioxo-1,3,5-tris(trichloromethanesulphenyl)-1,3,5-triazine which is formed by trimerisation of the unstable trichloromethanesulphenyl isocyanate.[129]



Chlorodifluoromethanesulphenyl chloride reacts with silver isocyanate with the formation of 1,3-bis(chlorodifluoromethanesulphenyl)-2,4-dioxo-1,3-diazetidine.[130,131]



The reaction of trifluoromethanesulphenyl chloride with silver isocyanate leads to the relatively stable trifluoromethanesulphenyl isocyanate.[130,131]

$$CF_3SCl + AgOCN \xrightarrow[-AgCl]{} CF_3SNCO.$$

Interaction with other *O*-nucleophiles. It has been shown[132] that the reaction of trichloromethanesulphenyl chloride with *N,N*-diacylhydroxylamines leads to the formation of *N,N*-diacyl-*O*-(trichloromethylthio)hydroxylamines.

$$CCl_3SCl + HON(COR)_2 \xrightarrow[-HCl]{} CCl_3SON(COR)_2.$$

c) Reactions with *S*-nucleophiles

Interactions with inorganic sulphur-containing reagents. Perhalomethanesulphenyl halides react with elementary sulphur in the presence of triethyl phosphate with the formation of perhalomethanethiosulphenyl halides.[8]

$$RSCl + S \xrightarrow{140-150\,^{\circ}C} RSSCl,$$

R = CCl_3, CCl_2Br, CCl_2F.

The interaction of trifluoromethanesulphenyl chloride with hydrogen sulphide leads to the formation of hexafluorodimethyl trisulphide.[133,134]

$$2CF_3SCl + H_2S \xrightarrow[-2HCl]{} CF_3SSSCF_3.$$

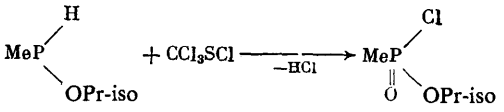
In contrast to silver isocyanate silver isothiocyanate reacts with perhalomethanesulphenyl halides with the participation of the sulphur and not the nitrogen atom.[11,135]

$$RSCl + AgSCN \xrightarrow[-AgCl]{} RSSCN,$$
$$R=CCl_3,\ CF_3.$$

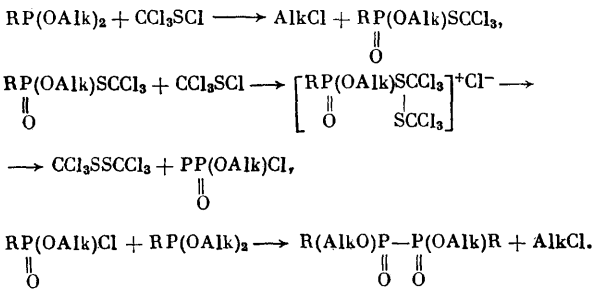
Silver isoselenocyanate reacts with perhalomethanesulphenyl halides in a similar manner.[11] The reaction of trichloromethanesulphenyl chloride with sodium trithiocarbonate leads to the formation of bis(trichloromethyl) trithiocarbonate which is converted into thiophosgene on heating.[136,137]

$$Na_2CS_3 + CCl_3SCl \xrightarrow[-2NaCl]{} CCl_3SC(S)SCCl_3 \xrightarrow{130-190^\circ C} 3ClCCl.$$
$$\qquad\qquad\qquad

The main products of the reaction of isopropyl methylphosphinite with trichloromethanesulphenyl chloride are isopropyl methylphosphonic chloride and thiophosgene.[163]



The reaction of trichloromethanesulphenyl chloride with dialkyl esters of alkylphosphonous acids proceeds in a more complex manner with the formation of a mixture of various products.[164] As was proposed,[164] in the first stage of this reaction the dialkyl esters of alkylphosphonous acids react with trichloromethanesulphenyl chloride by a type of Arbuzov rearrangement with the formation of alkyl halide and an *O*-alkyl *S*-trichloromethyl thiophosphonate which then reacts with the excess of trichloromethanesulphenyl chloride with the formation of the other reaction products.



This process was investigated in a more detailed manner using as example the reaction of trichloromethanesulphenyl chloride with the diethyl and diisopropyl esters of methylphosphonous acid.[163] The authors came to the conclusion that the route of this reaction depends on the reactant ratio, the order of mixing them and the structure of the initial ester. For example, on adding diisopropyl methylphosphonite to trichloromethanesulphenyl chloride at a ratio of 1:1 at −50 °C a mixture of products is formed from which the acid chloride of isopropyl methylphosphonous acid, hexachlorodimethyl disulphide and isopropyl chloride were isolated.

$$CCl_3SCl + MeP(OPr\text{-}iso)_2 \rightarrow MeP(O)(Cl)OPr\text{-}iso +$$

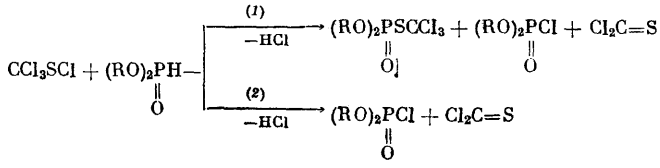
$$+ (CCl_3S-)_2 + iso\text{-}PrCl.$$

On adding one mole trichloromethanesulphenyl chloride to four moles of the diethyl ester of methylphosphonous acid the product formed in 80% yield is that of replacement of all four chlorine atoms.

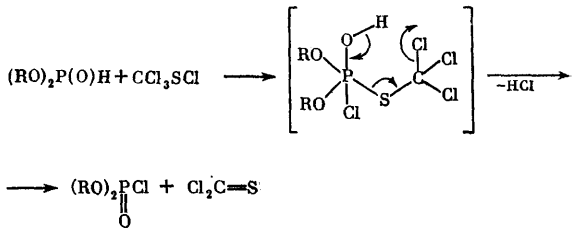
$$4MeP(OEt)_2 + CCl_3SCl \rightarrow$$
$$\rightarrow MeP(O)(OEt)SC[P(O)(Me)OEt]_3 + 4EtCl.$$

In a monograph[165] it was shown that in the case of the diisopropyl ester of methylphosphonous acid no reaction took place due to steric hindrance.

Interaction with dialkyl and trialkyl phosphites. Trichloromethanesulphenyl chloride reacts with dialkyl phosphites according to two alternative routes.[166,167]



The formation of the products of the second route is due to the initially formed phosphorane decomposing according to a six-centre mechanism.[166]



In another study[168] the formation of products by the second route is explained by decomposition of the intermediate salt formed by attack of the dialkyl phosphite at a chlorine atom of trichloromethanesulphenyl chloride.

$$(RO)_2P(O)H + CCl_3SCl \longrightarrow [(RO)_2P(OH)Cl]^+(SCCl_3)^- \longrightarrow$$

$$\longrightarrow (RO)_2\overset{\overset{O}{\|}}{P}Cl + Cl_2CS + HCl.$$

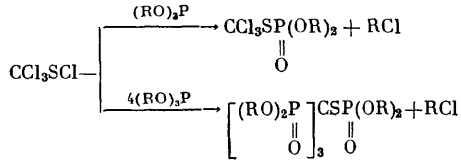
It was shown[169] that reaction of other perhalomethanesulphenyl halides with dialkyl phosphites forms *O,O'*-dialkyl *S*-trihalomethyl thiophosphates mixed with products formed by other routes and with the starting materials which it was impossible to separate by distillation due to the thermal instability of the main products. However reaction of the same sulphenyl chlorides with bis(trimethylsilyl) phosphite or diisopropyl phosphite in anhydrous benzene or toluene at room temperature and a reactant ratio of 2:1 leads to the corresponding *S*-trihalomethyl thiophosphate in quantitative yield.

$$(RO)_2P(O)H + CCl_{3-n}F_nSCl \rightarrow (RO)_2P(O)SCCl_{3-n}F_n,$$

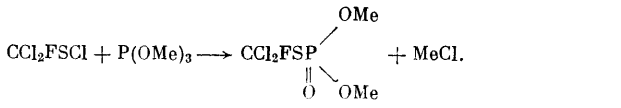
$R = (Me)_3Si$, iso-Pr.

The results of this study formed a basis for the authors[165] to propose that the formation of products of the second reaction route for trichloromethanesulphenyl chloride with dialkyl phosphites may occur during subsequent treatments and not during the reaction. Perhalomethanesulphenyl halides react ambiguously with trialkyl phosphites. For example it was recorded[170–174] that the reaction of trichloromethanesulphenyl chloride with trialkyl phosphites leads to

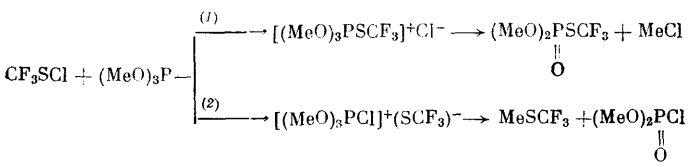
various products, depending on the ratio of reactants, including compounds with three phosphoryl groups.



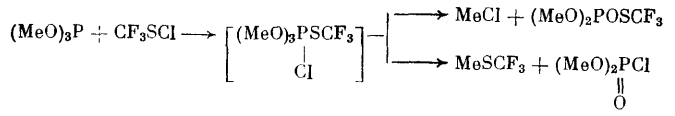
However in more recent work[175] the possibility of forming compounds with three phosphoryl groups on one carbon atom is doubtful based on PMR spectroscopic data. Dichlorofluoromethanesulphenyl chloride reacts with trimethyl phosphite by an Arbuzov rearrangement with the formation of *O,O'*-dimethyl *S*-dichlorofluoromethyl thiophosphate and methyl chloride.[176]



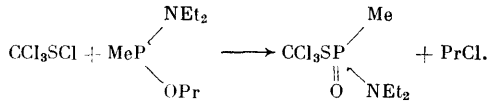
The reaction of trichloromethanesulphenyl chloride with trimethyl phosphite[177] leads to a mixture of four compounds which are formed in pairs as a result of nucleophilic attack of phosphite either at the sulphur atom or at a chlorine atom effecting the two alternative mechanisms (*1*) and (*2*).



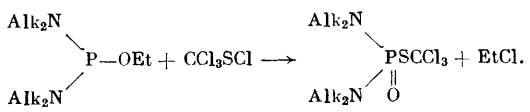
The possibility of forming a compound of five-coordinate phosphorus as an intermediate, which then eliminates methyl chloride or methyl trifluoromethyl sulphide, is not excluded.[177]



Interaction with amidoesters of alkylphosphonous acids, alkoxydiaminophosphines and diamino(hydroxy)phosphines. Trichloromethanesulphenyl chloride reacts with the propyl ester of (diethylamino)methylphosphonous acid according to an Arbuzov rearrangement mechanism.[164]

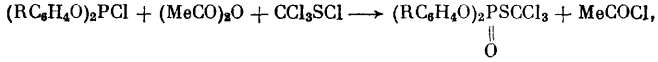


Trichloromethanesulphenyl chloride reacts with alkoxydiaminophosphines in a similar manner.[3]



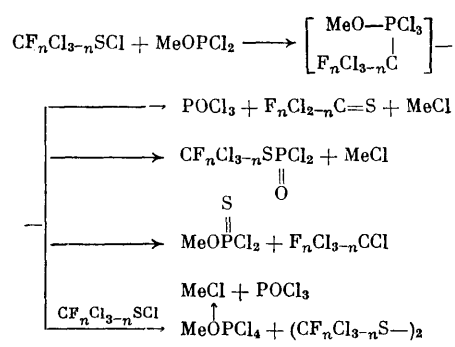
Perhalomethanesulphenyl halides react with tetraalkyldiamino(hydroxy)phosphines with the formation of *S*-trihalomethyl tetraalkyldiaminothiophosphates.[176]

Interaction with chlorodialkoxyphosphines and chlorodi(alkylthio)phosphines. *O,O'*-Diaryl *S*-trichloromethyl thiophosphates, which possess pesticidal properties and are additives for lubricating oils, are formed by the sequential addition of acetic anhydride and trichloromethanesulphenyl chloride to chlorodiaryloxyphosphines.[178]

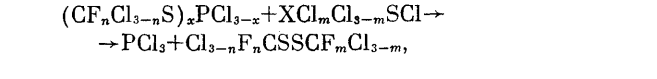


R=H, Me, Cl.

The main products of the reaction of perhalomethanesulphenyl halides $CF_nCl_{3-n}SCl$ (n = 0 to 3) with alkoxydichlorophosphines at −30 to 20 °C are *S*-trihalomethyl thiophosphoryl dichlorides formed in 50% yield.[162] In addition to these compounds *O*-alkyl thiophosphoryl dichlorides, phosphorus oxychloride, alkyl chlorides, bis(trihalomethyl) disulphides, halomethanes (CF_nCl_{4-n}) and thiocarbonyl dihalides ($F_nCl_{2-n}C{=}S$, n = 0 to 2) are formed, the quantity of which varies depending on the ratio of chlorine and fluorine atoms in the sulphenyl chloride molecule. For example it was recorded that on going sequentially from trifluoromethane- to trichloromethanesulphenyl chloride an increase occurred in the yield of *O*-alkylthiophosphoryl dichloride and a decrease in the yield of the corresponding disulphide. It was shown[162] by NMR spectroscopy (^{31}P, ^{19}F) for the reaction of trichloromethanesulphenyl chloride with methoxydichloro-phosphine that an unstable phosphorane was formed as an intermediate, the further conversions of which readily explain the formation of all the reaction products.

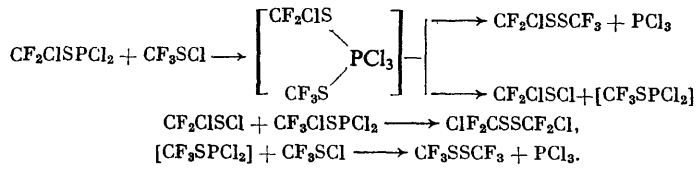


On reacting perhalomethanesulphenyl chlorides with (trihalomethylthio)chlorophosphines at 22−70 °C fission of all the P−S bonds occurs with the formation of unsymmetrical disulphides and phosphorus trichloride.[162]



n, m = 0 to 3; x = 1 to 3.

The formation has also been recorded of a small quantity of symmetrical disulphide and a second sulphenyl chloride which is explained by the formation of a phosphorane intermediate with two perhalomethanethio groups.



$$CF_2ClSCl + CF_3ClSPCl_2 \longrightarrow ClF_2CSSCF_2Cl,$$
$$[CF_3SPCl_2] + CF_3SCl \longrightarrow CF_3SSCF_3 + PCl_3.$$

e) Reactions with *C*-nucleophiles

Interaction with organometallic compounds. Perhalomethanesulphenyl halides react energetically with organomagnesium compounds by a nucleophilic mechanism of substitution of the halogen atom at sulphur by the hydrocarbon radical.

$$CX_3SCl + RMgX \rightarrow CX_3SR + MgXCl,$$
$$X = Hal.$$

As a rule a small quantity (up to 15%) of alkyl halide is formed which hinders isolation of the resulting sulphide. Reactions described include trichloromethanesulphenyl choride with ethylmagnesium bromide[179] and also trichloromethanesulphenyl chloride with alkynylmagnesium halides[180] and arylmagnesium halides.[181] Organomercury compounds react with trifluoromethanesulphenyl chloride in a similar manner to organomagnesium compounds.[182] Simultaneously with substitution of the chlorine atom at sulphur by the hydrocarbon radical, replacement of the mercury halide fragment by chlorine and also demercuration occur.

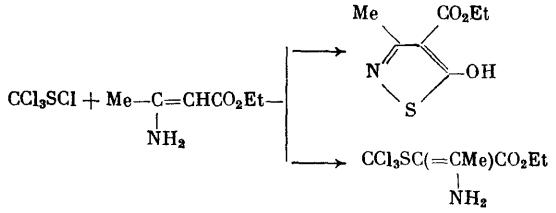
$$p\text{-}RC_6H_4HgCl + CF_3SCl \rightarrow p\text{-}RC_6H_4SCF_3 + p\text{-}RC_6H_4Cl + PhR,$$
$$R = MeO,\ Me,\ H,\ Cl,\ NO_2.$$

Electron-accepting groups R aid the formation of trifluoromethylthio derivatives and electron-donating groups aid the formation of halogen derivatives.

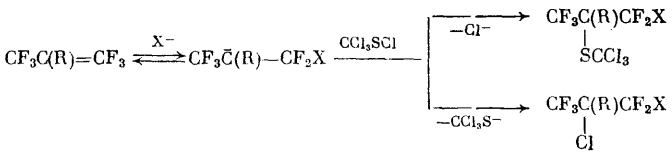
Interaction with CH-acids and their anions. Perhalomethanesulphenyl halides react relatively easily with compounds containing active methyl, methylene or methine groups with the formation of the corresponding sulphides. For example trichloromethanesulphenyl chloride reacts with nitromethane in an aqueous alkaline medium in the cold with the formation of trichloromethyl nitromethyl sulphide.[182]

$$CCl_3SCl + CH_3NO_2 \xrightarrow[-NaCl]{0^\circ C,\ NaOH} CCl_3SCH_2NO_2.$$

Depending on the conditions the amino group[183] or the methine group[184] of β-aminocrotonic acid ethyl ester may participate in nucleophilic attack on the sulphur atom of trichloromethanesulphenyl chloride.



It has been shown[185] that trifluoromethanesulphenylation of CH-acids $RCXCH_2R'$ (X = O, NH; R = Ph, Me; R' = $CONH_2$, CN, $C(S)NHC_6H_4Br$-4) at 0–20 °C in anhydrous chloroform occurs selectively at the α-carbon atom. The reaction of perhalomethanesulphenyl halides with *C*-anions generated by various means occurs by two alternative routes, viz. with the formation of products either of *C*-sulphenylation or of *C*-chlorination. For example the reaction of trichloromethanesulphenyl chloride with carbanions generated by adding fluoride or chloride anions to the multiple bond of fluoroolefins leads to the formation of products of *C*-sulphenylation and *C*-chlorination.



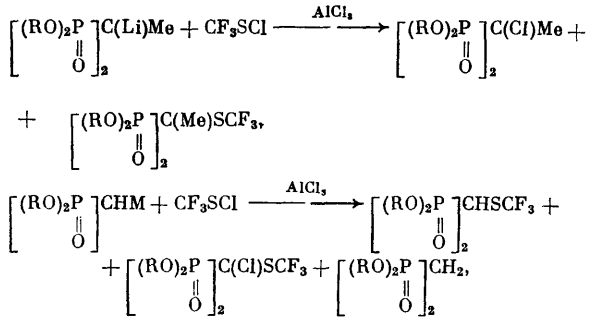
The reaction of perhalomethanesulphenyl chlorides with anions of tetraalkyl methylenephosphonates has been investigated.[187] The anions were generated by the action of butyllithium, sodium hydride or metallic sodium on tetraalkyl methylenephosphonates. It was established that products of sulphenylation and of chlorination were formed both in the presence of $AlCl_3$ and in its absence. In the case of dichlorofluoro- and chlorodifluoromethanesulphenyl chloride sulphenylation products were obtained in which the trihalosulphenyl groups were enriched with fluorine compared with the initial sulphenyl chlorides.

$$[(RO_2)P(O)]_2CHM + CCl_{3-n}F_nSCl \xrightarrow{AlCl_3} \longrightarrow [(RO)_2P(O)]_2CHSCCl_{3-n}F_n + [(RO)_2P(O)]_2CHCl + + [(RO)_2P(O)]_2CHSCCl_{2-n}F_{n+1} + [(RO)_2P(O)]_2CHSCF_3,$$
$$R = \text{iso-Pr};\ M = Li,\ Na$$

The formation of products enriched with fluorine in the trihalomethanesulphenyl group occurs, as discussed,[187] by replacement of chlorine atoms by fluorine in the initial sulphenyl chloride and not in the products of sulphenylation. Fluoride anion acts as a fluorinating agent and arises on decomposition of the trihalomethylthio anion which is a byproduct of the chlorination of tetraalkyl methylenephosphonate anion.

$$[(RO)_2P(O)]_2CHM + CCl_{3-n}F_nSCl \rightarrow \rightarrow [(RO)_2P(O)]_2CHCl + CCl_{3-n}F_nS^-,$$
$$CCl_{3-n}F_nS^- \rightarrow Cl_{3-n}F_{n-1}C{=}S + F^-$$
$$CCl_{3-n}F_nSCl + F^- \rightarrow CCl_{2-n}F_{n+1}SCl + Cl^-$$

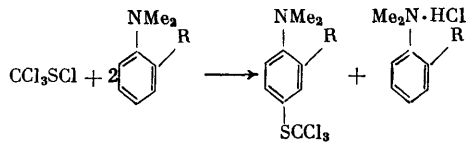
The proportion of chlorination products increases in the sequence $CF_3SCl < CF_2ClSCl \ll CFCl_2SCl$ which is caused[165,187] by the increase in steric hindrance to nucleophilic attack on the sulphur atom by the carbanion. In addition, in the reaction of the lithium derivative of tetraisopropyl ethylidenediphosphonate with trifluoromethanesulphenyl chloride in the presence of aluminium chloride products of chlorination and sulphenylation are formed in a 2:1 ratio while in the case of the tetraisopropyl methylenediphosphonate anion under the same conditions the ratio of (trifluoromethylthio)methylene- and (trifluoromethylthio)chloromethylenediphosphonates was 4.6:1.



R = iso-Pr; M = Li, Na.

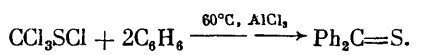
2. Electrophilic substitution reactions

Perhalomethanesulphenyl chlorides react with aromatic compounds by an S_E2 electrophilic substitution mechanism with the formation of trihalomethyl aryl sulphides. The reaction occurs relatively easily with derivatives of benzene and naphthalene containing electron-donating substituents [$N(CH_3)_2$, OH, OCH_3, etc.] but other aromatic compounds react with perhalomethanesulphenyl halides under forcing conditions in the presence of catalysts. For example, trichloromethanesulphenyl chloride reacts relatively easily with dimethylaniline[188] and its derivatives[189] with the formation of the corresponding trichloromethyl aryl sulphides.

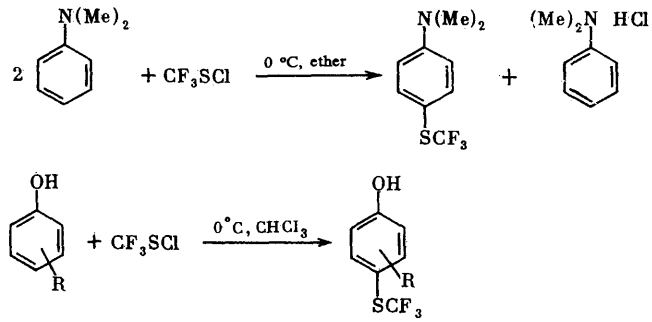


R = H, Me; MeO, MeCOO, $PhCH_2O$.

Trichloromethanesulphenyl chloride reacts anomalously with benzene in the presence of $AlCl_3$ with the formation of diphenyl thioketone.[190]

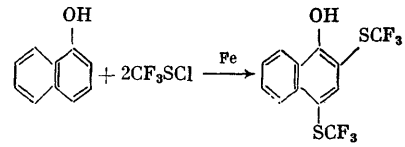


The mechanism of this reaction was not investigated[190] however it is not excluded that thiophosgene is an intermediate in this reaction and as is known,[45] reacts with benzene in the presence of $AlCl_3$ with the formation of diphenyl thioketone. Trifluoromethanesulphenyl chloride reacts with dimethylaniline,[117] and also with phenol and its homologues[118,191] even at 0 °C. The trifluoromethylthio group is directed to the positions *ortho* or *para* to the substituent.

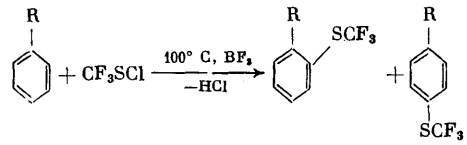


R = H, 2-Me, 3-Me, 2-OH.

Trifluoromethanesulphenyl chloride reacts with α-naphthol in the presence of iron with the formation of 2,4-bis(trifluoromethylthio)-naphthol.[118]



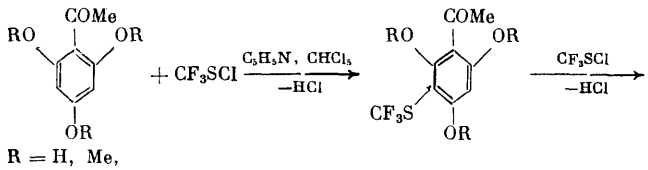
Trifluoromethanesulphenyl chloride reacts with benzene and toluene at 100 °C in an autoclave in the presence of BF_3 with the formation of trifluoromethyl phenyl sulphide and a mixture of 2- and 4-tolyl trifluoromethyl sulphides.



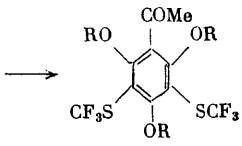
R = H, Me.

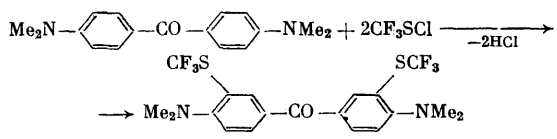
Trifluoromethanesulphonic acid is a more efficient catalyst for the trifluoromethanesulphenylation of benzene, its use enables reduction of the reaction temperature to 20 °C.[192] Introduction of a second trifluoromethylthio group into the benzene nucleus is difficult even in the presence of trifluoromethanesulphonic acid. Trifluoromethanesulphenyl chloride reacts with chlorobenzene under forcing conditions with the formation fo the two isomeric *p*-chloro- and *o*-chlorophenyl trifluoromethyl sulphides.[192] However if there are electron-donating groups (OH, OMe, NMe_2) present in the molecule in addition to electron-accepting groups [MeCO, PhCO, MeOCO, C(O)H], then depending on the conditions one, and in the presence

of iron powder, two or even three trifluoromethylthio groups may be introduced.[191,193]

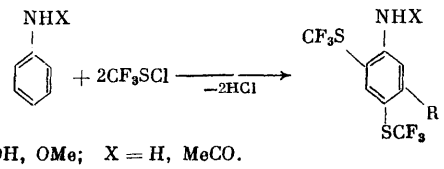


R = H, Me.



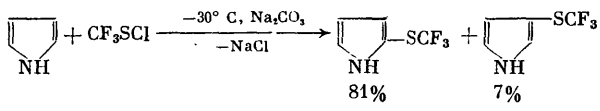


Derivatives of aniline and acetanilide containing the electron-donating groups OH or OMe in the *meta* position also react readily with trifluoromethanesulphenyl chloride with the formation of bis(trifluoromethylthio) derivatives.[194]

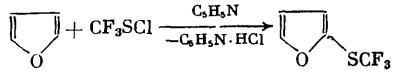


R = OH, OMe; X = H, MeCO.

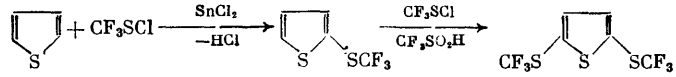
A set of rules has been established[193,195–198] for the electrophilic substitution of hydrogen atoms by the trifluoromethylthio group in heterocycles. For example pyrrole reacts even at –30 °C with trifluoromethanesulphenyl chloride with the formation of 2-trifluoromethylthiopyrrole and a small quantity of 3-trifluoromethylthiopyrrole.[193]



Under the same conditions trifluoromethanesulphenyl chloride reacts with indole with the formation of 3-trifluoromethylthioindole.[193] In the presence of trifluoromethanesulphonic acid two, three or even four hydrogen atoms in the pyrrole ring may be replaced by trifluoromethylthio groups.[195,196] Trifluoromethanesulphenyl chloride reacts with furan in the presence of pyridine with the formation of 2-trifluoromethylthiofuran.[197]



With thiopen, depending on the catalyst used, trifluoromethanesulphenyl chloride forms 2-trifluoromethylthiothiophen or 2,5-bis-(trifluoromethylthio)thiophen.[193,197,198]



3. Radical substitution reactions

Perhalomethanesulphenyl halides react with alkanes and cycloalkanes by a mechanism of radical substitution of hydrogen atom by halogen. For example, trichloromethanesulphenyl chloride reacts in the presence of catalysts of radical processes or under UV irradiation with cyclohexane,[199] n-hexane,[199] n-heptane and other saturated hydrocarbons[200–204] with the formation of the corresponding halogen derivatives and hexachlorodimethyl disulphide.

$$RH + 2CCl_3SCl \xrightarrow{h\nu} RCl + CCl_3SSCCl_3 + HCl.$$

A mechanism has been proposed[199] for the radical chlorination of hydrocarbons with trichloromethanesulphenyl chloride which includes the generation of a trichloromethylthio radical which acts as a chain propagating agent.

$$CCl_3SCl \rightarrow \dot{C}l + \dot{S}CCl_3,$$
$$RH + \dot{C}l \rightarrow R^{\cdot} + HCl,$$
$$R^{\cdot} + CCl_3SCl \rightarrow RCl + \dot{S}CCl_3,$$
$$RH + \dot{S}CCl_3 \rightarrow R^{\cdot} + CCl_3SH,$$
$$CCl_3SH + CCl_3SCl \rightarrow CCl_3SSCCl_3 + HCl.$$

Chain termination may occur by the following processes:

$$R^{\cdot} + R^{\cdot} \rightarrow R{-}R,$$
$$Cl^{\cdot} + Cl^{\cdot} \rightarrow Cl{-}Cl,$$
$$R^{\cdot} + Cl^{\cdot} \rightarrow R{-}Cl,$$
$$R^{\cdot} + \dot{\bar{S}}CCl_3 \rightarrow RSCCl_3,$$
$$CCl_3S^{\cdot} + CCl_3S^{\cdot} \rightarrow CCl_3SSCCl_3.$$

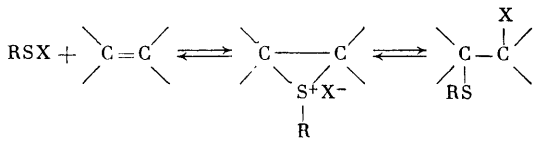
The composition of the mixture of products formed on chlorination of n-heptane with chlorine and trichloromethanesulphenyl chloride has been studied by gas chromatography.[201] It was noted that trichloromethanesulphenyl chloride possesses a higher selectivity than chlorine. Trifluoromethanesulphenyl chloride reacts with saturated hydrocarbons in the same manner as trichloromethanesulphenyl chloride.[199,203,205]

4. Addition reactions

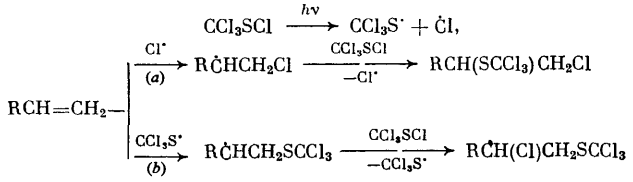
a) Addition to multiple bonds $\diagdown C{=}C \diagup$ and $-C{\equiv}C-$

In contrast to alkanesulphenyl halides the perhalomethanesulphenyl halides react with olefins with difficulty with the formation of β-halogenated sulphides containing a trihalomethyl group. For example, trichloromethanesulphenyl chloride reacts with cyclohexene only on extended heating at 120 °C.[206] Trichloromethanesulphenyl

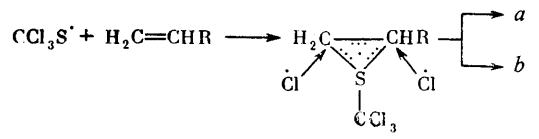
chloride reacts in an even worse manner with allyl chloride and adds to propylene only at 100–110 °C and a pressure of 100 atm. Trichloromethanesulphenyl chloride adds to bicylo[2.2.1]heptene at 100 °C by an ionic mechanism with the formation of *trans*-2-*endo*-chloro-3-*exo*-trichloromethylthiobicyclo[2.2.1]heptane.[207] Addition of trichloromethanesulphenyl chloride to 2,3-dihydrofuran proceeds only in the presence of concentrated hydrochloric acid.[208] Trifluoromethanesulphenyl chloride also adds to vinyl chloride under forcing conditions.[209,210] It was considered[45] that addition of sulphenyl halides to alkenes proceeds by an Ad_E2 mechanism including formation of an episulphonium ion as an intermediate the thermal stability of which, and consequently the thermodynamic advantage, is caused by the character of the R group on the sulphur atom.



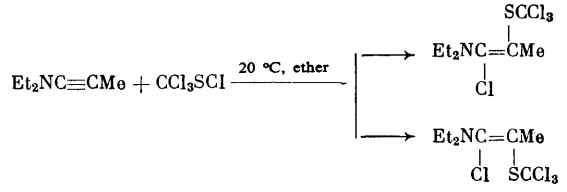
Strongly electron-accepting groups, which trichloro- and trifluoromethyl groups are, reduce the stability and therefore the thermodynamic advantage of the episulphonium ion, which hinders its formation, and consequently the addition reaction. The free radical addition of trichloromethanesulphenyl chloride to cyclohexene, n-hexene, allyl chloride, styrene[211] and aryl vinyl ether[212] proceed readily in the presence of UV light. Depending on the olefin, addition occurs according to two alternative routes with the participation of chlorine radical or of trichloromethylthio radical.



The addition of trichloromethanesulphenyl chloride to styrene, n-hexene and allyl chloride proceeds according to scheme (a)[211] while addition of trichloromethanesulphenyl chloride to aryl vinyl ether, in the opinion of the authors,[212] proceeds by scheme (b). The possibility of forming a non-classical adduct-radical, leading to loss of regioselectivity, is not excluded.[45]

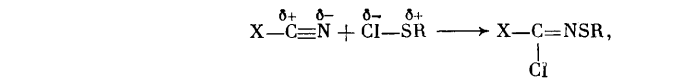


Addition of trichloromethanesulphenyl chloride to the triple bond of ynamines proceeds with the formation of *cis* and *trans* isomers.[213]

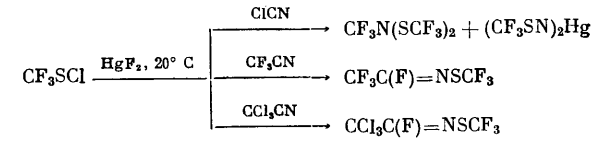


b) Addition to $-C\equiv N$ and $-N\equiv C$ bonds

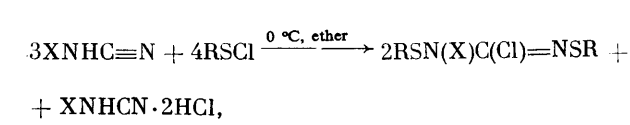
Perhalomethanesulphenyl halides add relatively readily to the polar $-C\equiv N$ bond. As a rule the chlorine atom adds to the electron-deficient carbon atom while the trihalomethylthio group adds to nitrogen with the formation of a S–N sulphenamide bond. Trichloromethanesulphenyl chloride reacts according to this scheme with 2,4-dimethylphenyl cyanate[9] and *N*-benzoylcyanimide,[214] dichlorofluoromethanesulphenyl chloride reacts with cyanogen chloride,[9] trifluoromethanesulphenyl chloride with tetracyanoethylene[215] and cyanogen chloride.[216]



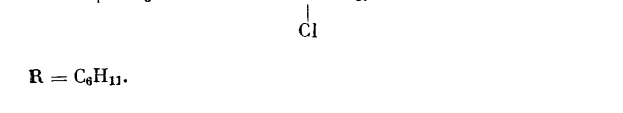
Trichloromethanesulphenyl chloride readily adds to the $C\equiv N$ bond of cyanogen chloride and the nitriles of trichloroacetic and trifluoroacetic acids in the presence of mercury difluoride.[217] Replacement of chlorine by fluorine occurs together with the addition.



Addition of perhalomethanesulphenyl chlorides to the $C\equiv N$ bond of cyanamide and its *N*-alkyl derivatives is accompanied by sulphenylation of the amide group.[218,219]

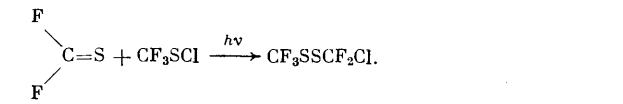


In the case of the reaction of trichloromethanesulphenyl chloride with isonitriles the chlorine atom and the trichloromethylthio group are added to the carbon atom of the isonitrile group.[9]



c) Addition to the C=S bond

Photochemical addition of trifluoromethanesulphenyl chloride to the C=S bond of thiocarbonyl difluoride leads to the formation of trifluoromethyl chlorodifluoromethyl sulphide.[220,221]

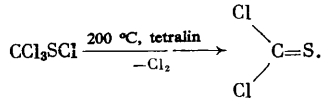


5. Oxidation reactions

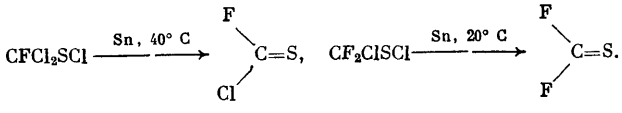
The oxidation of trichloromethanesulphenyl chloride with various oxidising agents is used as a preparative method for obtaining trichloromethanesulphonyl chloride. Oxidising agents include chlorine in aqueous medium,[222,223] chlorine in acetic acid,[224] nitric acid[225] and hydrogen peroxide.[226] These same oxidising agents may be used for converting trifluoromethanesulphenyl chloride into trifluoromethanesulphonyl chloride.[227] *m*-Chloroperbenzoic acid is used for converting trichloromethanesulphenamides into trichloromethanesulphonamides[228] and trichloromethanesulphenates into trichloromethanesulphinates.[229] On heating with nitric acid trifluoro-methyl aryl sulphides are oxidised to trifluoromethyl aryl sulphoxides.[230]

6. Reduction reactions

On reaction with various reducing agents perhalomethanesulphenyl halides are readily reduced to the corresponding thiocarbonyl dihalides. For example heating trichloromethanesulphenyl chloride with tetralin leads to the formation of thiophosgene.[231]



Sulphur dioxide, hydrogen sulphide[232] and tin[44] are also used as reducing agents. In the presence of tin dichlorofluoromethanesulphenyl chloride and chlorodifluoromethanesulphenyl chloride are readily reduced to thiocarbonyl chlorofluoride and thiocarbonyl difluoride respectively.[44]



An attempt has been made in the present review to systematise the available literature data on the methods of synthesis and reactivity of perhalomethanesulphenyl halides in view of the considerable synthetic possibilities which this class of heteroorganic compounds conceals.

References

1. B Rathke *Chem. Ber.*, 1870, **3** 858
2. B Rathke *Liebigs Ann. Chem.*, 1873, **167** 195
3. C Hennart *Bull. Soc. Chem. Fr.*, 1967, (11) 4398
4. N V Alekseev, F K Velichko *Zh. Strukt. Khim.*, 1967, **8**(1) 8
5. C Sosnovsky *Chem. Rev.*, 1958, **58** 509
6. A Senning *Chem. Rev.*, 1965, **65** 385
7. G Zumach, E Kuhle *Angew. Chem.*, 1970, **82**(2) 63
8. E Kuhle *Synthesis*, 1970, (11) 561
9. E Kuhle *Synthesis*, 1971, (11) 563
10. E Kuhle *Synthesis*, 1971, (12) 617
11. A Haas, W Hinsch *Chem. Ztg.*, 1972, **96**(2) 75
12. P Klason *Chem. Ber.*, 1887, **20** 2376
13. FRG P. 1219455; *Chem. Abs.*, 1966, **65** 506
14. G M Dyson *Orth. Synth. Coll.*, 1948, **1** 506
15. V Meyer *Chem. Ber.*, 1894, **27** 3160
16. Weygand-Hilgetag *Experimental Methods in Organic Chemistry* (Translated into Russian), Khimiya, Moscow, 1968, 944
17. M Nodasy, L Harmathy, G Kiraly *Nehezvegyiparikut Inter. Kozl.*, 1970, **3**(3–4) 167
18. G M Dyson *Org. Synth. Coll.*, 1946, **I** 506
19. I P Trunov, E M Sokolov *Khim. Promst. (Moscow)*, 1961, 694
20. F Boberg, G Winter, J Moos *Liebigs Ann. Chem.*, 1958, **613**(1–3) 1
21. H Y A Briscoe, J B Perl, P L Robinson *J. Chem. Soc.*, 1929, 1048
22. US P. 2821554; *Chem. Abs.*, 1958, **52** 10145
23. E A Dear, E E Gilbert *Synthesis*, 1972, (6) 310
24. E Kuhle, E Klauke, F Grewe *Angew. Chem.*, 1964, **76** 807
25. C T Rateliffe, J M Shreeve *J. Am. Chem. Soc.*, 1968, **90** 5403
26. F Seel, W Gombler, R Budenz *Angew. Chem.*, 1967, **79** 686
27. R N Haszeldine, J M Kidd *J. Chem. Soc.*, 1953, 3219
28. H J Emeleus, D E McDuffie *J. Chem. Soc.*, 1961, 2597
29. E H Man, D D Coffman, E Muetterties *J. Am. Chem. Soc.*, 1959, **81** 3575
30. C V Tullock, D D Coffman *J. Org. Chem.*, 1960, **25** 2016
31. F Seel, W Gombler *Angew. Chem.*, 1969, **81** 789
32. FRG P. 1232956; *Chem. Abs.*, 1967, **66** 65093
33. R D Howells, J D McCown *Chem. Rev.*, 1977, **77**(1) 69
34. N N Yarovenko, A S Vasil'eva *Zh. Obshch. Khim.*, 1959, **29** 3787
35. A Haas *Chem. Ber.*, 1965, **98** 1709
36. F Boberg, G Winter, G R Schultze *Liebigs Ann. Chem.*, 1959, **621** 8
37. V N Boiko, G M Shchupak, L M Yagupol'skii *Zh. Org. Khim.*, 1977, **13**(5) 1057
38. V N Boiko, G M Shchupak, L M Yagupol'skii *Zh. Org. Khim.*, 1980, **16**(5) 955
39. N V Kondratenko, A A Kolomeitsev, V I Popov *Zh. Obshch. Khim.*, 1983, **53**(11) 2500
40. F Seel, D Golitz *Z. Anorg. Allg. Chem.*, 1964, **327** 28
41. N N Yarovenko, S P Motornyi, A S Vasil'eva, T P Greshzon *Zh. Obshch. Khim.*, 1959, **29** 2163
42. G Diderrich, A Haas *Chem. Ber.*, 1976, **109**(10) 3432
43. A Senning, S Kaaf, C Jakons, P Kelly *Acta Chem. Scand.*, 1968, **22** 3256
44. N N Yarovenko, A S Vasil'eva *Zh. Obshch. Khim.*, 1959, **29**(11) 3792
45. D H R Barton, W D Ollis *Comprehensive Organic Chemistry* (Translated into Russian), Khimiya, Moscow, Vol. 5, p. 440
46. A Senning *Angew. Chem.*, 1963, **76**(10) 450
47. A Senning, P Kelly *Acta. Chem. Scand.*, 1966, **20**(8) 2261
48. A Haas, R Lorenz *Chem. Ber.*, 1972, **105**(10) 3161
49. A Haas, R Lorenz *Chem. Ber.*, 1972, **105**(1) 273
50. H J Emeleus, S N Nabi *J. Chem. Soc.*, 1960, 1103
51. A Haas, M E Peach, P Schott *Angew. Chem.*, 1965, **77** 458
52. A Haas, P Schott *Chem. Ber.*, 1968, **104** 3407
53. H E Borowski, A Haas *Chem. Ber.*, 1982, **115**(2) 523
54. I L Knunyants, I N Rozhkova *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1970, **10** 2264
55. E Kuhle, H Hagemann *Synthesis*, 1982, (11) 949
56. H Bohme, E Kulow *Chem. Ztg.*, 1978, **102**(2) 64
57. K T Potts, R Armbruster *J. Org. Chem.*, 1971, **36**(13) 1846
58. A Senning, P Kelly *Acta Chem. Scand.*, 1972, **26**(7) 2877
59. R J W Gremlyn *J. Chem. Soc.*, 1963, 1329

60. R J W Gremlyn *J. Chem. Soc.*, 1965, 1132
61. A Senning *Acta Chem. Scand.*, 1970, **24**(1) 221
62. K K Bozena, L Max *J. Fluorine Chem.*, 1987, **35**(2) 317
63. A Senning *Acta Chem. Scand.*, 1967, **21**(6) 1657
64. A Senning, P Kelly *Acta Chem. Scand.*, 1967, **21**(7) 1871
65. I V Koval', A I Tarasenko, M M Kremlev *Voprosy Khimii i Khim. Tekhnologii* (Edited by M A Loshkarev) (Problems in Chemistry and Chemical Engineering), Vishcha Shk., Kharkov, 1981, Vol. 65, p. 51
66. I V Koval', T G Oleinik, A I Tarasenko, M M Kremlev *Zh. Org. Khim.*, 1985, **21** 2578
67. I V Koval', A I Tarasenko, I S Panchenko, N R Molchanova *Zh. Org. Khim.*, 1986, **22** 1712
68. I V Koval' *Usp. Khim.*, 1990, **59**(4) 681 [English translation in *Russ. Chem. Rev.*, 1990(4)]
69. M M Kremlev, A I Tarasenko, I V Koval' in *Voprosy Khimii i Khim. Tekhnologii* (Edited by M A Loshkarev) (Problems in Chemistry and Chemical Engineering), Vishcha Shk., Kharkov, 1973, Vol. 30, p. 40
70. M M Kremlev, I V Koval', N P Bezverkhii, A I Tarasenko, Authors Certificate No. 443028 SSSR; *Byull. Izobret.*, 1974, (34)
71. M M Kremlev, A I Tarasenko, I V Koval', V V Ryabenko *Zh. Org. Khim.*, 1974, **10** 2320
72. I V Koval', A I Tarasenko, M M Kremlev, N R Molchanova *Zh. Org. Khim.*, 1981, **17** 533
73. Netherlands P. 6 402 676; *Chem. Abs.*, 1965, **62** 9071
74. I V Koval', A I Tarasenko, M M Kremlev *II Vsesoyuz. Konferentsiya 'Sovremennoe Sostoyanie i Perspektivy Razvitiya Teoreticheskikh Osnov Proizbodstva Khlororganicheskikh Produktov.' Tez. Dokl.* (IInd All-Union Conference on the 'Present State and Future Developments in the Theoretical Basis of the Manufacture of Organochlorine Products.' Abstracts of Reports), Baku, 1978, Vol. 2, p. 18
75. I V Koval', A I Tarasenko, M M Kremlev *III Vsesoyuz. Konferentsiya po Khimii Ftororganicheskikh Soedinenii. Tez. Dokl.* (IIIrd All-Union Conference on the Chemistry of Organofluorine Compounds. Abstracts of Reports), Odessa, 1978, p. 117
76. J Goerdeler, H Groschopp, U Sommerbat *Chem. Ber.*, 1957, **90** 182
77. H Schroeder, R Ratz, W Schnabel, et al. *J. Org. Chem.*, 1962, **27** 2589
78. I Saikawa, A Takai *Jakugaku Zasshi*, 1965, **85** 918
79. J Goerdeler, G Sperling *Chem. Ber.*, 1957, **90** 892
80. H W Roesky, W Schaper, S Tutkunkardes *Z. Naturforsch.*, 1972, **276**(2) 620
81. M Raban, E H Carlson, S K Lauderback, et al. *J. Am. Chem. Soc.*, 1972, **94**(8) 2738
82. A D Biba, M M Kremlev, N E Kul'chitskaya, G V Protopopova *Ukr. Khim. Zh. (Russ. Ed.)*, 1970, **36**(11) 1145
83. R Brans, R J Gremlyn *J. Chem. Soc., C*, 1970, 225
84. M Z Peretyazhko, P S Pel'kis *Zh. Org. Khim.*, 1967, **3** 2183
85. A Blaschette, M Naveke *Chem. Ztg.*, 1988, **112**(12) 351
86. E Kuhle, E Klauke, F Grewe *Angew. Chem.*, 1964, **76** 807
87. A Senning, P Kelly *J. Chem. Soc., Chem. Commun.*, 1967, (16) 844
88. M M Kremlev, A D Biba, N A Kirsanova, et al. *Ukr. Khim. Zh. (Russ. Ed.)*, 1971, **37** 1026
89. M M Kremlev, S S Gontar' *Zh. Org. Khim.*, 1976, **12** 2001
90. A D Biba, Candidate's Dissertation in Chemical Sciences, Dzerzhinskii Chemical Engineering Institute, Dnepropetrovsk, 1970, 203 pp.
91. F Fischer, O Eacha *J. Prakt. Chem.*, 1961, **12** 172
92. M Raban, F B Jones, G W J Kenney *Tetrahedron Lett.*, 1968, **49** 5055
93. C Hennart *Bull. Soc. Chim. Fr.*, 1967, 1899
94. E Testa, L Fontanella *Liebigs Ann. Chem.*, 1962, **660** 118
95. G Sosnovsky *J. Chem. Soc.*, 1956, 3139
96. C Hennart *Bull. Soc. Chim. Fr.*, 1967, 2968
97. G P Lampson, H O Sincher *J. Org. Chem.*, 1956, **21** 684
98. R J W Gremlyn *J. Chem. Soc.*, 1964, 6240
99. C Hennart *Bull. Soc. Chim. Fr.*, 1967, (11) 4286
100. I I Chizhevskaya, R V Skupskaya, A N Kharitonovich *Zh. Org. Khim.*, 1968, **4** 1497
101. A Haas, W Hinsch *Chem. Ber.*, 1971, **104**(6) 1856
102. C Hennart *Bull. Soc. Chim. Fr.*, 1967, (12) 4691
103. W J Groxall, C P Lo, E Y Shropshire *J. Am. Chem. Soc.*, 1953, **75** 5419
104. A R Kittleson *Science*, 1952, **115** 84
105. R Ponci, A Baruffini, P Borgna *Farmaco. Ed. Sci.*, 1966, **21**(3) 249
106. W Hannefeld, H J Staude *Arch. Pharm. (Weinheim, Ger.)*, 1987, **320**(1) 74
107. A Senning, P Kelly *Acta Chem. Scand.*, 1972, **26**(4) 1663
108. H W Roesky, W Schaper, W Gross-Bowing, M Diete *Z. Anorg. Allg. Chem.*, 1975, **416**(3) 306
109. J Silhanek, M Zbirovsky *J. Chem. Soc., Chem. Commun.*, 1969, (15) 878
110. E Dykman *J. Chem. Soc., Chem. Commun.*, 1974, (21) 1400
111. J Silhanek, M Zbirovsky *Int. J. Sulfur. Chem.*, 1973, **8**(3) 423
112. R N Haszeldine, J M Kidd *J. Chem. Soc.*, 1955, 3871
113. J Horak *Collect. Czech. Chem. Commun.*, 1966, **31**(8) 3189
114. J Horak *Collect. Czech. Chem. Commun.*, 1967, **32**(2) 868
115. J Horak *Collect. Czech. Chem. Commun.*, 1967, **32**(6) 2134
116. S Braverman, D Reisman *Tetrahedron*, 1974, **30**(21) 3891
117. S Andreades, J F Harris, W A Sheppard *J. Org. Chem.*, 1964, **29**(4) 898
118. L M Yagupol'skii *Aromaticheskie i Geterotsiklicheskie Soedineniya c Ftorsoderzhashchimi Zamestitelyami* (Aromatic and Heterocyclic Compounds with Fluorine-Containing Substituents), Nauk. Dumka, Kiev, 1988, p. 319
119. N B Islam, H Kwart, S Khan *J. Chem. Eng. Data*, 1985, **30**(4) 509
120. S Braverman, Y Stabinsky *J. Chem. Soc., Chem. Commun.*, 1967, 270
121. S Braverman, Y Stabinsky *Isr. J. Chem.*, 1967, **5** 71
122. S Braverman *Int. J. Sulphur Chem., C*, 1971, **6** 149
123. S Braverman, B Sredni *Isr. J. Chem.*, 1970, 830
124. S Braverman, B Sredni *Tetrahedron*, 1974, **30** 2379
125. R E Putman, W H Sharmy *J. Am. Chem. Soc.*, 1957, **79** 6526
126. J H Unlenbroek, M J Koopmans *Recl. Trav. Chim. Pays-Bas*, 1957, **7** 666
127. A Haas, D Y Oh *Chem. Ber.*, 1969, **102**(1) 77
128. S N Nabi, S Ahmad, S Ahmad, Jr. *J. Chem. Soc.*, 1963, 2636
129. A Haas, D Y Oh *Chem. Ber.*, 1965, **98** 3353
130. A Haas *Chem. Ber.*, 1965, **98** 111
131. A Haas, D Y Oh *Chem. Ber.*, 1967, **100** 480
132. Brit. P. 779 114; *Chem. Abs.*, 1958, **52** 1246
133. M Zbirovsky, V Ettel *Chem. Listy*, 1958, **52** 95

134. M Zbirovsky, V Ettel *Collect. Czech. Chem. Commun.*, 1959, **24** 273
135. A Senning *Acta. Chem. Scand.*, 1963, **17**(1) 272
136. F Fischer, R Gottfried *Z. Chem.*, 1964, **4**(5) 189
137. F Fischer, R Gottfried *J. Prakt. Chem.*, 1965, **30**(5–6) 232
138. K S Truchlik, V Tichy *Chem. Zvesti*, 1957, **11** 24
139. US P. 2 835 626; *Chem. Abs.*, 1958, **52** 20213
140. US P. 2 839 446; *Chem. Abs.*, 1958, **52** 17296
141. US P. 2 868 687; *Chem. Abs.*, 1959, **53** 13495
142. US P. 2 911 335; *Chem. Abs.*, 1960, **54** 3839
143. US P. 2 922 790; *Chem. Abs.*, 1960, **54** 8857
144. US P. 2 907 763; *Chem. Abs.*, 1960, **54** 2381
145. East German P. 19932; *Chem. Abs.*, 1962, **56** 3416
146. FRG P. 1103324; *Chem. Abs.*, 1962, **56** 5888
147. US P. 3004886; *Chem. Abs.*, 1962, **56** 8749
148. F Runge, A Jumar, F Kohler *J. Prakt. Chem.*, 1963, **21** 39
149. R M De Marinis, W M Bryan *J. Org. Chem.*, 1977, **42**(11) 2024
150. F Fischer, R Gottfried *Z. Chem.*, 1966, **6** 146
151. J F Harris, Jr. *J. Am. Chem. Soc.*, 1960, **82** 155
152. I B Douglass, W J Eves *J. Org. Chem.*, 1964, **29** 419
153. G Stajer, D Korbonits, A E Szabo, et al. *Acta Chim. Acad. Sci. Hung.*, 1977, **93**(1) 67
154. V B Kopylova, M M Khasanova, R Kh Freidlina *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, **10** 2321
155. V B Kopylova, M M Khasanova, R Kh Freidlina *Uzb. Khim. Zh.*, 1968, **2** 29
156. G Yu Epshtein, I A Usov, C Z Ivin *Zh. Obshch. Khim.*, 1964, **34** 2347
157. G Yu Epshtein, I A Usov, S Z Ivin *Zh. Obshch. Khim.*, 1964, **34** 2350
158. B G Boldyrev, S A Gorelov, A T Dvorko *Zh. Obshch. Khim.*, 1961, **31** 2402
159. B G Boldyrev, O M Semotyuk *Zh. Org. Khim.*, 1966, **2** 286
160. J Pintye, G Stajer, E Vinkler *Acta Chim. Acad. Sci. Hung.*, 1977, **95** 307
161. A Haas, D Winkler *Z. Znorg. Allg. Chem.*, 1980, **468**(9) 68
162. US P. 2 836 534; *Chem. Abs.*, 1958, **52** 20056
163. B M Gladshtein, B P Zakharov, M M Sosina, A A Spitsyn *Zh. Obshch. Khim.*, 1970, **40** 1245
164. N S Rylyakova, Yu A Kondrat'ev, S Z Ivin *Zh. Obshch. Khim.*, 1967, **37** 1245
165. Yu G Gololobov, N I Gusar' *Sul'fenilkhloridy* (Sulphenyl Chlorides), Nauka, Moscow, 1989, p. 177
166. M Zbirovsky, V Ettel *Chem. Listy*, 1956, **50**(8) 1265
167. M Zbirovsky, V Ettel *Collect. Czech. Chem. Commun.*, 1956, **21**(6) 1607
168. P A Chopard *Chimia*, 1966, **20**(12) 420
169. G M Blackburn, T W Maciej *J. Chem. Soc., Perkin Trans. 1*, 1985, (7) 1419
170. US P. 2 811 563; *Chem. Abs.*, 1958, **52** 4922
171. US P. 2 811 543; *Ref. Zh. Khim.*, 1959, 28732
172. US P. 2 818 364; *Ref. Zh. Khim.*, 1959, 58295
173. US P. 2 857 415; *Ref. Zh. Khim.*, 1960, 27938
174. US P. 2 861 092; *Chem. Abs.*, 1960, **54** 1297
175. H Gross, B Costisella *J. Prakt. Chem.*, 1972, **314** 87
176. Belg. P. 632757; *Chem. Abs.*, 1964, **31** 9402
177. Y O El Nigumi, H J Emeleus *J. Inorg. Nucl. Chem.*, 1970, **32**(10) 3113
178. Authors Certificate No. 627 137 SSSR; *Byull. Izobret.*, 1978, (37)
179. G Sanna *Gazz. Chim. Ital.*, 1942, **72** 305
180. US P. 3 062 893; *Chem. Abs.*, 1963, **58** 7869
181. W A Sheppard *J. Org. Chem.*, 1964, **29**(4) 895
182. V I Popov, N V Kondratenko, A. Haas *Ukr. Khim. Zh. (Russ. Ed.)*, 1983, **43** 861
183. J A Waite, K R H Wooldridge *Tetrahedron Lett.*, 1972, (4) 327
184. R Howe *J. Org. Chem.*, 1977, **42**(20) 3230
185. W Zankowska-Jasinska *J. Fluor. Chem.*, 1988, **38**(1) 85
186. Yu V Zeifmann, L T Lantseva, I L Knunyants *Vsesoyuz. Konferentsiya po Khimii Ftororganicheskikh Soedinenii. Tez. Dokl.* (All-Union Conference on the Chemistry of Organofluorine Compounds. Abstracts of Reports), Odessa, 1978, p. 107
187. G M Blackburn, T Macojej *J. Chem. Soc., Perkin Trans. 1*, 1985, (9) 1935
188. C S Argyle, G M Dyson *J. Chem. Soc.*, 1937, 1629
189. A Senning *Acta Chem. Scand.*, 1963, **17**(9) 2570
190. D Vorlander, E Mittag *Chem. Ber.*, 1919, **52** 413
191. Belg. P. 624 397; *Chem. Abs.*, 1963, **59** 305
192. A Haas, V Hellwig *J. Fluorine Chem.*, 1975, **6** 521
193. A Haas, U Niemann *Chem. Ber.*, 1977, **110**(1) 67
194. T S Croft *Phosphorus Sulfur*, 1976, **6** 521
195. S Dorn, P Eggenberg, M R C Gerstenberger, et al. *Helv. Chim. Acta*, 1979, **62**(5) 1442
196. M R C Gerstenberger, A Haas, F Liebig *J. Fluorine Chem.*, 1982, **19**(3–6) 461
197. M R C Gerstenberg, A Haas *J. Fluorine Chem.*, 1983, **23**(6) 525
198. A Haas, V Hellwig *Chem. Ber.*, 1976, **109**(7a) 2475
199. V Prey, E Gurschik, H Berbalk *Monatsh. Chem.*, 1960, **91**(3) 556
200. R E A Dear, E E Gilbert *Synthesis*, 1972, (6) 310
201. B Fell, Li-Hoan Kung *Angew. Chem.*, 1963, **75**(3) 165
202. US P. 2 983 751; *Chem. Abs.*, 1961, **55** 17581
203. H Kloosterziel *Recl. Trav. Chim. Pays-Bas*, 1963, **82** 497
204. H Kloosterziel *Recl. Trav. Chem. Pays-Bas*, 1963, **82** 509
205. J R Harris, Jr. *J. Org. Chem.*, 1966, **31** 931
206. K A Petrov, A A Neimasheva *Zh. Obshch. Khim.*, 1959, **29** 3401
207. J Madsen, S O Lawesson *Arkiv. Kemi*, 1968, **25**(5) 389
208. A Senning, S Lawesson *Acta Chem. Scand.*, 1961, **15**(105) 1203
209. M J Baldwin, R K Brown *Can. J. Chem.*, 1968, **46** 1093
210. A M Aleksandrov, L M Yagupol'skii *Zh. Org. Khim.*, 1970, **6** 249
211. V Prey, E Gurschik, H Berbalk *Monatsh. Chem.*, 1960, **91**(5) 794
212. E F Kolmakov, A V Kalabina, Yu K Maksyutin, L N Spiridonov *Zh. Org. Khim.*, 1966, **2** 2048
213. A Sennig *Acta Chem. Scand.*, 1968, **22**(4) 1370
214. Brit. P. 1 167 127; *Chem. Abs.*, 1970, **72** 31480
215. W D Hartzler *J. Org. Chem.*, 1964, **29**(5) 1194
216. A Haas, W Hinsch *Chem. Ztg., 1972*, **96**(2) 75
217. M Geisel, R Mews *Chem. Ber.*, 1987, **120**(10) 1675
218. A Haas, V Plas *Chem. Ber.*, 1972, **105** 2047
219. A Haas, V Plag *Chem. Ber.*, 1973, **106** 3391
220. A Haas, W Klug *Chem. Ber.*, 1968, **101** 2617
221. A Haas, H Reinke, J Sommerhoff *Angew. Chem.*, 1970, **82** 484
222. I B Duglass, V G Simpson, A K Sawler *J. Org. Chem.*, 1942, **14** 272
223. E Dykman, P Bracha *Isr. J. Chem.*, 1969, **7**(4) 589
224. N Kharasch, T C Bauice *J. Am. Chem. Soc.*, 1951, **73** 3340

225. H Brintzinger, M Langneck *Chem. Ber.*, 1953, **86** 557
226. G Sosnovsky *J. Org. Chem.*, 1961, **26**(9) 3506
227. R N Haszeldine, J M Kidd *J. Chem. Soc.*, 1955, 2901
228. R S Glass, R J Swedo *Synthesis*, 1977, (11) 798
229. S Braverman, Y Duar *Tetrahedron Lett.*, 1976, (5) 343
230. L M Yagupol'skii, M S Marenets, N V Kondratenko *Zh. Obshch. Khim.*, 1965, **35**(2) 377
231. FRG P. 853 162; *Chem. Abs.*, 1953, 9314
232. J Horak, M Zbirovsky *Collect. Czech., Chem. Commun.*, 1964, **29**(9) 2194