THE CHEMISTRY OF TRICHLOROMETHANESULFENYL CHLORIDE

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I. INTRODUCTION

A. HISTORICAL

Trichloromethanesulfenyl chloride was discovered by Rathke (64) around 1870. He is credited with the assignment of the correct structure of this compound, a method for its preparation which is still used commercially, and a number of excellent studies dealing with its chemistry. Since Rathke, a number of other chemists have studied this remarkable compound. It is surprising, however, how strongly Rathke's influence is still felt in the later work.

Trichloromethanesulfenyl chloride received little industrial attention until recently, when Kittleson (42) discovered the tetrahydrophthalimide derivative. This derivative, commercially known as Captan, possesses outstanding fungicidal properties and is at present used in agriculture. Trichloromethanesulfenyl chloride itself is manufactured by several companies in the United States and Europe.

B. SCOPE AND LIMITATIONS OF PRESENT REVIEW

Since the discovery of trichloromethanesulfenyl chloride much has been published concerning this compound, particularly in recent years. In spite of this extensive literature the chemistry of trichloromethanesulfenyl chloride has not been reviewed previously. The present article is an attempt to present a comprehensive and critical review of the existing knowledge of the subject.

This discussion is limited to the chemistry of trichloromethanesulfenyl chloride and to compounds derived from it. Trichloromethanesulfenyl chloride derivatives prepared by methods in which no use was made of trichloromethanesulfenyl chloride are not discussed in detail. Brief reference to some of these derivatives is made in connection with their biological properties. The literature has been surveyed through 1955; however, several more recent publications have been included.

C. NOMENCLATURE

Trichloromethanesulfenyl chloride was originally called perchloromethyl mercaptan by Rathke, and most of the workers in this field have continued to use this name. However, the compound bears no similarity to mercaptans in either its chemical or its physical properties, and it appears that the name trichloromethanesulfenyl chloride (adopted by *Chemical Abstracts*) is more suitable.

In this review the nomenclature of *Chemical Abstracts* is employed whenever possible. In some cases, to avoid possible confusion, the nomenclature used by the different authors in their publications is retained unchanged.

II. FORMATION, PREPARATION, AND PURIFICATION

The formation of trichloromethanesulfenyl chloride has been observed during the chlorination of dimethyl sulfide (25), methyl thiocyanide (35), and carbon sulfidoselenide (12). From the preparative standpoint none of these reactions are of importance, and all methods in present use are based on Rathke's original reaction (64) in which carbon disulfide is treated with chlorine in the presence of a catalytic quantity of iodine at a temperature below 30°C.:

$$2CS_2 + 5Cl_2 \xrightarrow{I_2} 2CSCl_4 + S_2Cl_2$$

Other by-products of this reaction are sulfur monochloride, sulfur dichloride, some carbon tetrachloride, and traces of thiophosgene. The reaction was studied in some detail by Klason (51), who concluded that several steps are involved:

(1) $CS_2 + Cl_2 \rightarrow CSCl \cdot SCl$
(2) $2CSCl \cdot SCl + Cl_2 \rightarrow 2CSCl_2 + S_2Cl_2$
(3) $CSCl_2 + Cl_2 \rightarrow CSCl_4$
(4) $2CSCl_4 + Cl_2 \rightarrow 2CCl_4 + S_2Cl_2$

Conditions favoring the formation of carbon tetrachloride are the presence of certain metals, sunlight, overchlorination, and reaction temperatures above 30°C. Also, chlorination temperatures below 15°C. result in diminished yields of trichloromethanesulfenyl chloride; e.g., at −15°C. to −10°C. only an 11 per cent yield and at 0°C. to −5°C. only a 55 per cent yield is obtained (71).

In the original method of Rathke the reaction mixture was washed with water to hydrolyze the sulfur chlorides:

$$2SCl_2 + 2H_2O \rightarrow 2S + 4HCl + SO_2$$

Trichloromethanesulfenyl chloride (which resists hydrolysis) was then distilled. While later workers in this field used essentially the same chlorination procedure, their methods of working up the reaction mixture and their purification procedures varied. Johnson and Hemingway (36) followed the method of Rathke, while others (4, 26) washed the reaction mixture with cold or hot water and then steam distilled the product or, alternately, steam distilled the reaction mixture directly (23, 24). In another method (33) the reaction mixture was allowed to stand for 48 hr. before being worked up. The lower-boiling materials (to 100°C.) were distilled off and the reaction mixture, consisting mainly of sulfur monochloride and trichloromethanesulfenyl chloride, was steam distilled. Also, chlorination under slight pressure followed by fractional distillation has been reported (68).

In all these methods the yields vary between 50 and 70 per cent. Recently improvements in yields (80 to 90 per cent) have been claimed as the result of different methods of purification. In one method (15) the chlorinated reaction mixture is heated with carbon disulfide and iodine to convert sulfur chlorides (S_2Cl_2 and SCl_2) into trichloromethanesulfenyl chloride and sulfur. A continuous process based on this procedure has been described (57). In other methods the impurities are removed by treating the reaction mixture with one of the following reagents: sulfur dioxide, neutral or acid sulfites at −10°C. (37), sulfur trioxide (39), aqueous hydrochloric acid and chlorine (63), or hypochlorites and chlorates (38).

Of the methods discussed those involving steam distillation of the crude reaction mixture are the most cumbersome and hazardous. As a laboratory procedure the following method was found most satisfactory (71). Carbon disulfide is chlorinated in the presence of 0.1 per cent iodine at 20–25°C. until about 2.5 moles of chlorine are absorbed per mole of carbon disulfide. The reaction mixture is distilled through a short column to remove most of the sulfur chlorides until a

TABLE 1

Physical constants of trichloromethanesulfenyl chloride

Boiling point, °C	146.5–149 (12, 20, 51, 64)
Density:	
d_4^{20}	1.6996 (12); 1.6947 (21)
d_4^{0}	1.7278 (21); 1.722 (5, 20, 51)
Surface tension at 20°C., γ	35.02 dynes/cm. (12)
Mol parachor, $M\gamma^{1/4}/D$	266.1; calculated for CCl_3SCl, 268.5 (12)
Refractive index, n_D^{20}	1.5395 (21)

head temperature of 140°C. is reached. The remaining oil may now be washed safely with cold and then hot water until no more sulfur is deposited. Distillation of the remaining mixture gives a product of about 90 per cent or higher purity, which is satisfactory for most preparative work.

III. Physical Properties

Trichloromethanesulfenyl chloride is a heavy oil which is volatile with steam. At atmospheric pressure it can be distilled with only slight decomposition.

The structure of trichloromethanesulfenyl chloride seems to be established beyond doubt as a result of studies of the Raman and infrared spectra of this and related compounds (22, 40, 41). The spectra are closely related to those of carbon tetrachloride and sulfur monochloride. Physical data of trichloromethanesulfenyl chloride are summarized in table 1.

In 1893 Nasini and Carrara (14, 55) investigated the atomic refraction of sulfur in thiophosgene and in trichloromethanesulfenyl chloride. In this connection values were reported for the density and refractive index of trichloromethanesulfenyl chloride which differ from those given in table 1.

IV. Chemical Properties

A. HYDROLYSIS

Although trichloromethanesulfenyl chloride is fairly stable toward aqueous alkalies and acids at room temperature, at elevated temperatures considerable hydrolysis occurs with formation of carbon dioxide, hydrochloric acid, and sulfur (30, 64).

$$CSCl_4 + 2H_2O \xrightarrow{160°C.} CO_2 + 4HCl + S$$

When aqueous ammonia is used, the decomposition of trichloromethanesulfenyl chloride is extensive even at room temperature, and a brown powder of unknown composition is formed. Also, ammonium thiocyanate is believed to be formed in small amounts during this reaction (64).

B. THERMAL DECOMPOSITION AND REACTION WITH SULFUR

Even during the distillation of trichloromethanesulfenyl chloride at atmospheric pressure some decomposition occurs; it becomes more severe at higher temperatures. The reaction products are carbon disulfide, carbon tetrachloride, thiophosgene, sulfur chloride, hexachlorodimethyl disulfide (I), and hexachlorodimethyl trisulfide (II).

$$\underset{\text{I}}{Cl_3CS_2CCl_3} \qquad \underset{\text{II}}{Cl_3CS_3CCl_3}$$

The same products are obtained from the interaction of trichloromethanesulfenyl chloride with sulfur at 150–170°C. (51). The reaction mechanism of the thermal decomposition is complex. However, it seems probable that the primary step is the formation of carbon tetrachloride and sulfur:

$$(1)\quad CCl_4S \rightleftharpoons CCl_4 + S$$

$$(2)\quad 2Cl_3CSCl + 2S \xrightarrow{150\text{–}160°C.} Cl_3CS_2CCl_3 + S_2Cl_2$$

$$(3)\quad Cl_3CS_2CCl_3 + S \xrightarrow{170°C.} Cl_3CS_3CCl_3$$

Hexachlorodimethyl disulfide is an oil (b.p. 130–135°C./10 mm.); the trisulfide is a solid (b.p. 190°C./10 mm.; m.p. 57°C.). Hexachlorodimethyl trisulfide when heated at atmospheric pressure decomposes into carbon disulfide, carbon tetrachloride, thiophosgene, trichloromethanesulfenyl chloride, and sulfur monochloride. When the reaction between sulfur and trichloromethanesulfenyl chloride is carried out at 220°C. instead of at 150–170°C., the products are almost exclusively carbon disulfide and sulfur chloride (51).

C. DECOMPOSITION IN THE PRESENCE OF IRON AND OTHER METALS

The mixture consisting of carbon disulfide, trichloromethanesulfenyl chloride, and sulfur monochloride, which is usually obtained from the chlorination of carbon disulfide in the presence of iodine, decomposes in the presence of iron to give carbon tetrachloride, sulfur, and sulfur monochloride. Pure trichloromethanesulfenyl chloride reacts similarly in the presence of iron (20, 26).

While carbon disulfide in the presence of iodine is chlorinated to trichloromethanesulfenyl chloride, the chlorination proceeds further to give carbon tetrachloride when iron is also present. The action of iodine, therefore, is nullified by the presence of iron. Tin has a similar effect on trichloromethanesulfenyl chloride, whereas "copper bronze" has only a slight adverse effect on the activity of iodine. Lead appears to be without effect on this reaction. When trichloromethanesulfenyl chloride is allowed to stand in the presence of iron for several months, sulfur monochloride and hexachlorodimethyl disulfide, as well as carbon tetrachloride, are formed (20).

$$4Cl_3CSCl \xrightarrow{Fe} S_2Cl_2 + 2CCl_4 + S_2C_2Cl_6$$

The first step of this reaction is probably the decomposition of trichloromethanesulfenyl chloride to carbon tetrachloride and sulfur. When a mixture of trichloromethanesulfenyl chloride, carbon disulfide, and iron powder is heated on a water bath and the low-boiling products are distilled off, hexachlorodimethyl trisulfide is obtained.

From the existing literature (20) it is not clear whether the iron has a function in this reaction. This reaction has been formulated (20) as an attack of trichloromethanesulfenyl chloride on carbon disulfide similar to that of sulfur monochloride on carbon disulfide.

$$4CCl_3SCl + CS_2 \rightarrow 2Cl_3CS_3CCl_3 + CCl_4$$

$$2S_2Cl_2 + CS_2 \rightarrow 3S_2 + CCl_4$$

The formation of trisulfide could also be explained by the decomposition of trichloromethanesulfenyl chloride into carbon tetrachloride and sulfur, which, according to Klason (51), gives hexachlorodimethyl disulfide and sulfur monochloride.

There is some doubt about the decomposition of the trisulfide in the presence of iron at 100°C. (20). The products are essentially the same as those from the thermal reaction of the trisulfide in the absence of iron (51).

$$2C_2Cl_6S_3 \rightarrow 3CCl_4 + CS_2 + 4S$$

$$C_2Cl_6S_3 + S \rightarrow CCl_4 + CS_2 + S_2Cl_2$$

The exothermic reaction of trichloromethanesulfenyl chloride with silver powder leads to the formation of small quantities of thiophosgene (64).

$$CCl_4S + 2Ag = CCl_2S + 2AgCl$$

It is probable (51) that hexachlorodimethyl disulfide is a primary product which decomposes to form thiophosgene and trichloromethanesulfenyl chloride.

$$CCl_3S_2CCl_3 \rightarrow Cl_3CSCl + CSCl_2$$

D. REACTION WITH INORGANIC COMPOUNDS

Trichloromethanesulfenyl chloride can act as an oxidizing agent; thus it oxidizes sodium arsenite to sodium arsenate.

$$CCl_4S + Na_3AsO_3 + 8NaOH \rightarrow Na_3AsO_4 + Na_2SO_3 + Na_2S + 4NaCl + 4H_2O$$

When trichloromethanesulfenyl chloride is heated with sodium stannite in the presence of a large excess of alkali, the first product is a precipitate of stannous sulfide which is slowly converted into soluble sodium thiostannate (30).

Potassium iodide is oxidized by trichloromethanesulfenyl chloride to form iodine (60).

When trichloromethanesulfenyl chloride is refluxed with zinc fluoride, halogen exchange does not occur; instead, carbon tetrachloride is formed (33).

Trichloromethanesulfenyl chloride reacts with potassium sulfite and to a lesser extent with sodium and ammonium sulfites to form the corresponding salts of mercaptomethanetrisulfonates. Isolation of the intermediate thiophosgene demonstrates that the sulfonates are not formed directly from trichloromethanesulfenyl chloride. Thiophosgene, in turn, reacts with the sulfites to form mercaptomethanetrisulfonates (1, 5, 16).

$$(1)\quad CSCl_4 + M_2SO_3 + H_2O \rightarrow CSCl_2 + M_2SO_4 + 2HCl$$

$$(2)\quad 2HCl + 2M_2SO_3 \rightarrow 2MHSO_3 + 2MCl$$

$$(3)\quad 2MHSO_3 + CSCl_2 \rightarrow CS(SO_3M)_2 + 2HCl$$

$$(4)\quad CS(SO_3M)_2 + MHSO_3 \rightarrow C(SH)(SO_3M)_3$$

M = K, Na, or NH_4.

E. CHLORINATION

In the absence of a catalyst, trichloromethanesulfenyl chloride absorbs chlorine at room temperature, but when the reaction mixture is heated, most of the absorbed chlorine is liberated. However, when traces of iodine are present, the reaction takes a different course. Carbon tetrachloride and sulfur monochloride are then formed (51).

$$2CCl_3SCl + 2Cl_2 \xrightarrow{I_2} 2CCl_4 + 2S_2Cl_2$$

A similar effect is shown also by other catalysts, such as tin or iron (26). This result shows that the presence of an excess of chlorine in the preparation of trichloromethanesulfenyl chloride will reduce the yield.

F. OXIDATION

Trichloromethanesulfenyl chloride is oxidized by nitric acid (64) to trichloromethanesulfonyl chloride, Cl_3CSO_2Cl, a white solid which sublimes readily and melts at 135–140°C. If the reaction is carried out in a mixture of acetic and nitric acids, the yield is about 50 per cent (68).

Trichloromethanesulfonyl chloride can be made also by the action of moist chlorine on carbon disulfide (52, 67) or by refluxing a chloroform solution of trichloromethanesulfenyl chloride with calcium hypochlorite (74). In another method (71) 30 per cent hydrogen peroxide is added to a solution of trichloromethanesulfenyl chloride in glacial acetic acid until a white sublimate appears in the reflux condenser. The reaction mixture is then diluted with water and the product collected. The yield and the quality of the product are good, and this method is most suitable for laboratory purposes.

G. REDUCTION: PREPARATION OF THIOPHOSGENE

The reduction can be accomplished with a number of reagents. Stannous chloride or tin and hydrochloric acid appear to be the best agents for this purpose. The yields of thiophosgene vary from 55 to 60 per cent. For optimum yields the reagents must be combined at a certain rate; the success of the operation depends to a large extent on the skill of the operator. When the reaction is conducted as a large-scale continuous process, yields of only about 35 per cent can be expected (24).

When the reduction is carried out with iron and acetic acid at 35–40°C., yields of from 44 to 50 per cent are obtained (27); furthermore, 38 per cent of the trichloromethanesulfenyl chloride is recovered. With hydrogen sulfide as the reducing agent yields as high as 51 per cent are obtained. Copper or copper bronze reacts slowly with trichloromethanesulfenyl chloride. In the presence of water a crystalline mass precipitates which, when heated, dissolves with formation of thiophosgene (20, 27), as is the case in the reaction of trichloromethanesulfenyl chloride with silver dust (51, 64). It is probable that hexachlorodimethyl disulfide is formed in the primary step and then decomposes to thiophosgene.

Zinc dust is unsatisfactory for the preparation of thiophosgene. Under a variety of conditions only low yields of thiophosgene are obtained (27), and under certain conditions the reduction product is methane (33).

Recently a new approach to the preparation of thiophosgene has been reported (58). When trichloromethanesulfenyl chloride is treated with an aromatic hydrocarbon, such as benzene, toluene, xylene, etc., in the presence of Friedel–Crafts catalysts at 140–150°C., thiophosgene is obtained in high yield (82 per cent). It is of interest that in 1919 Vorlaender and Mittag (80) reported the formation of thiobenzophenone under these conditions.

H. REACTION WITH GRIGNARD REAGENTS

Trichloromethanesulfenyl chloride reacts with ethylmagnesium bromide to form trichloromethyl ethyl sulfide (b.p. 85°C./10 mm.). Phenylmagnesium bromide under similar conditions gives trichloromethyl phenyl sulfide. In both cases hexachlorodimethyl disulfide is found as a by-product (67).

$$\mathrm{Cl_3CSCl + RMgBr \rightarrow CCl_3SR + MgBrCl}$$

$\mathrm{R = C_2H_5, C_6H_5}$.

In this connection the reaction of trichloromethanesulfonyl chloride and Grignard reagents (67) is of interest. Ethylmagnesium bromide and trichloromethanesulfonyl chloride give trichloromethyl ethyl sulfone (b.p. 130°C. in vacuum, pressure not specified) and small quantities of trichloromethyl ethyl sulfoxide. With phenylmagnesium bromide, trichloromethyl phenyl sulfone (m.p. 121°C.), biphenyl, and trichloromethyl phenyl sulfoxide (m.p. 118°C.) are formed.

$$\mathrm{CCl_3SO_2Cl + C_6H_5MgBr \rightarrow CCl_3SO_2C_6H_5 + MgBrCl}$$

$$\mathrm{CCl_3SO_2C_6H_5 + 2C_6H_5MgBr \rightarrow CCl_3SOC_6H_5 + (C_6H_5)_2 + MgBr_2\cdot MgO}$$

I. REACTION WITH UNSATURATED COMPOUNDS

Trichloromethanesulfenyl chloride adds to the double bonds of octene, diisobutylene, vinylcyclohexene, allyl ether, and allyl acetate. The reaction requires 18 to 66 hr. at temperatures near 100°C. (49). In table 2 results of such additions are summarized. From the available data it is not clear whether free-radical initiators have any effect on the nature of the products. Further work is required.

J. REACTION WITH ALCOHOLS: FORMATION OF *S*-ALKOXYTRICHLOROMETHYLTHIOLS AND ESTERS OF ORTHOCARBONIC ACID

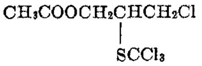
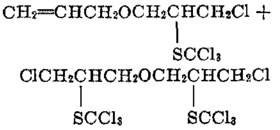
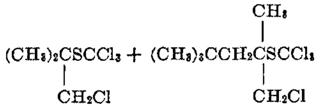
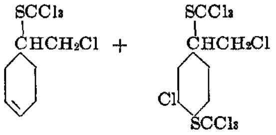
Alcohols condense with trichloromethanesulfenyl chloride in the presence of bases to form *S*-alkoxytrichloromethylthiols.

$$\mathrm{ROH + ClSCCl_3 \rightarrow ROSCCl_3 + HCl}$$

Derivatives of simple alcohols, such as methyl and ethyl alcohol, can be conveniently prepared by using sodium or magnesium alkoxides (18, 72). Alcoholic potassium hydroxide solutions of the lower alcohols can also be successfully employed. When an excess of alcohol is undesirable or the above reagents cause degradations of the desired products, pyridine may be used to good advantage (72). In every case it is advisable to avoid a large excess of condensing agent and to run the reaction at a low temperature, preferably near 0°C.

TABLE 2

Reactions of trichloromethanesulfenyl chloride with unsaturated compounds

Unsaturated Compound	Product	Boiling Point	Reference
		°C.	
1-Octene	$C_6H_{13}CH(SCCl_3)CH_2Cl + C_6H_{13}CH(Cl)CH_2(SCCl_3)$	119–121/2 mm.	(49)
Allyl acetate	 $CH_3COOCH_2\underset{SCCl_3}{CH}CH_2Cl$	110–117/3 mm.	(49)
Allyl ether	 $CH_2{=}CHCH_2OCH_2\underset{SCCl_3}{CH}CH_2Cl +$ $ClCH_2\underset{SCCl_3}{CH}CH_2OCH_2\underset{SCCl_3}{CH}CH_2Cl$	109–115/2 mm.	(49)
Diisobutylene	 $(CH_3)_2\underset{CH_2Cl}{C}SCCl_3 + (CH_3)_3CCH_2\overset{CH_3}{\underset{CH_2Cl}{C}}SCCl_3$	88–98/2 mm.	(49)
Vinylcyclohexene			(49)

The products are oils with a characteristic odor; compounds of low molecular weight have a rather unpleasant odor, while higher members have agreeable or even pleasant odors. Most of the products are rather unstable, are hydrolyzed readily, and decompose on standing. However, they can be distilled at reduced pressure without decomposition.

When the reaction between an alcohol and trichloromethanesulfenyl chloride is carried out at room temperature in the presence of an excess of alkoxide, further reaction between *S*-alkoxytrichloromethylthiol and the alkoxide takes place, and esters of orthocarbonic acid are obtained.

$$ROSCCl_3 + 3NaOR \rightarrow ROSC(OR)_3 \rightarrow (RO)_4C + 3NaCl + S$$

By this method the yields of ortho ester are higher than those usually obtained by other methods, e.g., the chloropicrin method (18, 75). The results of these reactions are summarized in tables 3 and 4.

K. REACTION WITH PHENOLS

Like the alkoxides, sodium phenoxides react with trichloromethanesulfenyl chloride to give *S*-aryloxytrichloromethylthiols (table 5).

$$C_6H_5ONa + ClSCCl_3 \rightarrow C_6H_5OSCCl_3 + NaCl$$

These are unstable solids or oils which are hydrolyzed slowly by hot water and rapidly by aqueous alkali. They can be distilled only at reduced pressure. Treatment with dry hydrogen chloride regenerates the phenols and trichloromethanesulfenyl chloride. Reduction with zinc dust in acetic acid gives methyl mercaptan (17). Reaction with sodium ethoxide gives *S*-ethoxytrichloromethylthiol (18).

TABLE 3

Products of the reaction of trichloromethanesulfenyl chloride with alcohols

CCl_3SR

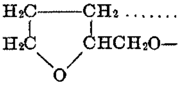
R	Product	Boiling Point	Reference
		°C.	
CH_3O—	*S*-Methoxytrichloromethylthiol	63/30 mm.	(72)
C_2H_5O—	*S*-Ethoxytrichloromethylthiol	160/760 mm. (d.)	(18)
$CH_3CH_2CH_2O$—	*S*-*n*-Propoxytrichloromethylthiol	36–38/1 mm.	(72)
$(CH_3)_2CHO$—	*S*-Isopropoxytrichloromethylthiol	67–68/12 mm.	(72)
$CH_3CH_2CH_2CH_2O$—	*S*-*n*-Butoxytrichloromethylthiol	90–92/11 mm.	(72)
$(CH_3)_2CHCH_2O$—	*S*-Isobutoxytrichloromethylthiol	63–64/5 mm.	(72)
$CH_2{=}CHCH_2O$—	*S*-Allyloxytrichloromethylthiol	106–108/9 mm.	(72)
$CH_2{=}CH(CH_2)_3O$—	*S*-Pent-4-enyloxytrichloromethylthiol	72/1 mm.	(72)
	*S*-Tetrahydrofurfuryloxytrichloromethylthiol	116/2 mm.	(72)

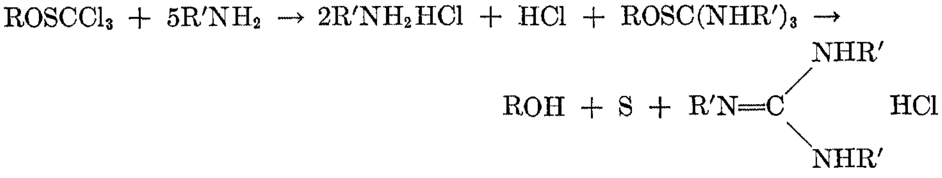
TABLE 4

Alkyl orthocarbonates, $(RO)_4C$

R	Product	Yield	Boiling Point	Reference
		per cent	*°C.*	
CH_3—	Methyl orthocarbonate	71	114/760 mm.	(75)
C_2H_5—	Ethyl orthocarbonate	78	158/760 mm.	(18)
C_3H_7—	Propyl orthocarbonate	70	224/760 mm.	(75)
C_4H_9—	Butyl orthocarbonate	60	273/760 mm.	(75)

$$C_6H_5OSCCl_3 + C_2H_5ONa \rightarrow C_2H_5OSCCl_3 + C_6H_5ONa$$

Treatment with an excess of an aromatic amine (such as aniline or *p*-toluidine) at elevated temperatures gives a fair yield of a guanidine hydrochloride.



$$ROSCCl_3 + 5R'NH_2 \rightarrow 2R'NH_2HCl + HCl + ROSC(NHR')_3 \rightarrow ROH + S + R'N{=}C\begin{matrix} NHR' \\ \\ NHR' \end{matrix}\quad HCl$$

This reaction provides a simple and useful method for the preparation of substituted guanidines (17). Examples are given in table 19.

L. REACTION WITH MERCAPTANS AND THIOPHENOLS

Trichloromethanesulfenyl chloride reacts with mercaptans and thiophenols with elimination of hydrogen chloride to give asymmetric disulfides.

$$Cl_3CSCl + HSR \rightarrow Cl_3CSSR + HCl$$

R = alkyl or aryl.

When this reaction is carried out in the presence of an alkoxide, different results are obtained. With mercaptans trichloromethanesulfenyl chloride gives symmetric disulfides.

TABLE 5

Products of the reaction of trichloromethanesulfenyl chloride with phenols

Cl_3CSR

R	Product	Formula	Boiling Point or Melting Point	Reference
			°C.	
C_6H_5O—	*S*-Phenoxytrichloromethylthiol	$C_6H_5OSCCl_3$	100–103/2.5 mm. 196/760 mm. (d.)	(71) (17)
2-ClC_6H_4O—	*S*-2-Chlorophenoxytrichloromethylthiol	2-$ClC_6H_4OSCCl_3$	96–98/0.5 mm. 180/756 mm. (d.)	(71) (17)
4-ClC_6H_4O—	*S*-4-Chlorophenoxytrichloromethylthiol	4-$ClC_6H_4OSCCl_3$	48 (m.p.)	(71)
2,4-$Cl_2C_6H_3O$—	*S*-2,4-Dichlorophenoxytrichloromethylthiol	2,4-$Cl_2C_6H_3OSCCl_3$	54 (m.p.)	(71)
2-CH_3-4-ClC_6H_3O—	*S*-2-Methyl-4-chlorophenoxytrichloromethylthiol	2-CH_3-4-$ClC_6H_3OSCCl_3$	66 (m.p.)	(71)
$C_6H_5C_6H_4O$—	*S*-Diphenyl-2-oxytrichloromethylthiol	$C_6H_5C_6H_4OSCCl_3$	58 (m.p.)	(17)
4-$CH_3C_6H_4O$—	*S*-4-Methylphenoxytrichloromethylthiol	2-$CH_3C_6H_4OSCCl_3$	183/755 mm. (d.)	(17)

$$2Cl_3CSCl + 2NaSR \rightarrow Cl_3CSSCCl_3 + RSSR + 2NaCl$$

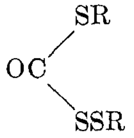
$$Cl_3CSSCCl_3 + 6NaSR \rightarrow (RS)_3CSSC(SR)_3 + 6NaCl$$

With thiophenols hexaarylthiodimethyl trisulfides are obtained (7).

$$Cl_3CSCl \xrightarrow{NaSR} RSSR + (RS)_3CSSSC(SR)_3 + NaCl$$

The results of these reactions are given in tables 6, 7, 8, and 9. Although oxygen might have a decisive effect on the course of the reaction, there is no indication in the literature of efforts to insure an inert atmosphere. The mechanism of this reaction seems to be complex.

It is of interest that oxidation of the trisulfides by hydrogen peroxide leads to esters of trithiopercarbonic acids (III) (7).



$$OC(SR)(SSR)$$

III

M. REACTION WITH SULFINATES

Trichloromethanesulfenyl chloride reacts with sodium sulfinates with elimination of sodium chloride to form trichloromethyl thiolsulfonates (8, 54, 62).

$$RSO_2Na + ClSCCl_3 \rightarrow RSO_2SCCl_3 + NaCl$$

Examples of this reaction are given in table 10. These sulfonates are cleaved by alkali into sodium sulfinates, sulfur, sodium carbonate, and sodium chloride (8).

$$C_6H_5SO_2SCCl_3 + 6NaOH \rightarrow C_6H_5SO_2Na + S + Na_2CO_3 + 3NaCl + 3H_2O$$

TABLE 6

Products of the reaction of trichloromethanesulfenyl chloride with mercaptans

$RSSCCl_3$

R	Product	Yield	Boiling Point	n_D	d_4^{25}	Reference
		per cent	°C.			
CH_3—	Methyl trichloromethyl disulfide	90	77–78/13 mm.	1.575 (15°C.)	1.526	(6)
C_2H_5—	Ethyl trichloromethyl disulfide	94	91–92/14 mm.	1.561 (15°C.)	1.439	(6)
C_3H_7—	*n*-Propyl trichloromethyl disulfide	90	104/12 mm.	1.548 (15°C.)	1.374	(6)
$(CH_3)_2CH$—	Isopropyl trichloromethyl disulfide	94	106.5–117/30 mm.	1.546 (18°C.)	1.360	(6)
$(CH_3)_3C$—	*tert*-Butyl trichloromethyl disulfide	91	107–108/12 mm.	1.540 (25°C.)	1.317	(6)
C_4H_9—	*n*-Butyl trichloromethyl disulfide	87	118–119/10.5 mm.	1.538 (25°C.)	1.321	(6)
C_3H_5—	Allyl trichloromethyl disulfide	80.5	100–101/10.5 mm.	1.570 (15°C.)	1.414	(6)
$(C_2H_5)_2\underset{CH_3}{\underset{\vert}{C}}$—	3-Methylpentyl trichloromethyl disulfide	90	118–120/4 mm.	1.541 (25°C.)	1.278	(6)
C_6H_{11}—	Cyclohexyl trichloromethyl disulfide	90.5	156–158/14 mm.	1.563 (25°C.)	1.400	(6)
$C_6H_5CH_2$—	Benzyl trichloromethyl disulfide	88	155–158/5 mm.	1.613 (25°C.)	1.411	(6)

TABLE 7

Products of the reaction of trichloromethanesulfenyl chloride with thiophenols

$RSSCCl_3$

R	Product	Yield	Boiling Point or Melting Point	n_D	d_4	Reference
		per cent	°C.			
C_6H_5—	Phenyl trichloromethyl disulfide	84	123–126/4 mm.	1.623 (25°C.)	1.447 (25°C.)	(6)
p-$CH_3C_6H_4$—	*p*-Tolyl trichloromethyl disulfide	90	141–144/3 mm.	1.617 (25°C.)	1.400 (25°C.)	(6)
o-$CH_3C_6H_4$—	*o*-Tolyl trichloromethyl disulfide	45.5	150.5–151.5/4 mm.	1.618 (15°C.)	1.403 (20°C.)	(6)
m-$CH_3C_6H_4$—	*m*-Tolyl trichloromethyl disulfide	82	139.5–140/2.5 mm.	1.618 (15°C.)	1.405 (20°C.)	(6)
p-$(CH_3)_3CC_6H_4$—	*p*-*tert*-Butylphenyl trichloromethyl disulfide	91	151–153/2 mm.	1.591 (15°C.)	1.286 (20°C.)	(6)
p-ClC_6H_4—	*p*-Chlorophenyl trichloromethyl disulfide	82	154–155/2 mm. 56–56.6 (m.p.)			(6)
o-ClC_6H_4—	*o*-Chlorophenyl trichloromethyl disulfide	81	170.5–172/6 mm.	1.635 (20°C.)		(6)
o-$NO_2C_6H_4$—	*o*-Nitrophenyl trichloromethyl disulfide + *o*,*o*′-dinitrodiphenyl disulfide	62 24.5	70.5 (m.p.)			(6)
m-$NO_2C_6H_4$—	*m*-Nitrophenyl trichloromethyl disulfide	51	132–133/2 mm.	1.607 (15°C.)	1.292 (20°C.)	(6)
p-$NO_2C_6H_4$—	*p*-Nitrophenyl trichloromethyl disulfide (+ *p*,*p*′-dinitrodiphenyl disulfide)	52	66–67 (m.p.)			

When sodium sulfinate and an excess of sodium thiophenoxide are employed, hexaphenylthiodimethyl trisulfide and diphenyl disulfide are obtained (8).

$$C_6H_5SO_2SCCl_3 \xrightarrow{NaSC_6H_5}$$

$$C_6H_5SO_2Na + (C_6H_5S)_3CSSSC(SC_6H_5)_3 + C_6H_5SSC_6H_5$$

TABLE 8

Products of the reaction of trichloromethanesulfenyl chloride with sodium mercaptides

$(RS)_3CSSC(SR)_3 + RSSR$

R	Product	Yield	Boiling Point or Melting Point	n_D	Reference
		per cent	°C.		
C_2H_5—	Hexaethylthiodimethyl disulfide	13	100/0.001 mm.	1.594 (25°C.)	(7)
	Diethyl disulfide	73	58–60/12 mm.		
C_3H_7—	Hexa-*n*-propylthiodimethyl disulfide	12	100/0.0005 mm.	1.552 (22°C.)	(7)
	Di-*n*-propyl disulfide	77			
$(CH_3)_3C$—	Hexa-*tert*-butylthiodimethyl disulfide	18–31	59.5–60 (m.p.)		
	Di-*tert*-butyl disulfide	68	73–75/10 mm.	1.4921 (20°C)	(7)
C_4H_9—	Hexa-*n*-butylthiodimethyl disulfide	13.5			
	Di-*n*-butyl disulfide	68			

TABLE 9

Products of the reaction of trichloromethanesulfenyl chloride with sodium thiophenoxides

$(RS)_3CSSSC(SR)_3 + RSSR$

R	Product	Yield	Melting Point	Reference
		per cent	°C.	
C_6H_5—	Hexaphenylthiodimethyl trisulfide	66.5 (at −12°C.) 18 (at 78°C.)	98–99	(7)
	Diphenyl disulfide		60–61	(7)
p-$CH_3C_6H_4$—	Hexa-*p*-tolythiodimethyl trisulfide	61	118–119	(7)
m-$CH_3C_6H_4$—	Hexa-*m*-tolythiodimethyl trisulfide	37	82–82.5	(7)
p-$(CH_3)_3CC_6H_4$—	Hexa-*p*-*tert*-butylphenylthiodimethyl trisulfide	25.5	113.5–114	(7)
	Bis(*p*-*tert*-butylphenyl) disulfide		88.5–89	
$(CH_3)_3C_6H_2$—	Hexamesitylthiodimethyl trisulfide	47	170–170.5	(7)
	Dimesityl disulfide		125	
p-ClC_6H_4—	Hexa-*p*-chlorophenylthiodimethyl trisulfide	62	140–141	(7)
	Bis(*p*-chlorophenyl) disulfide			
o-ClC_6H_4—	Hexa-*o*-chlorophenylthiodimethyl trisulfide	25	75.5–76	(7)
	Bis(*o*-chlorophenyl) disulfide	18	89–90	(7)

N. *N*-TRICHLOROMETHYLTHIO DERIVATIVES OF IMIDES

In the search for new, effective fungicides a series of trichloromethanesulfenyl chloride derivatives containing the $=NSCCl_3$ group have been prepared during the last decade. The general method of preparation consists in treatment of trichloromethanesulfenyl chloride with an imide in the presence of sodium hydroxide at temperatures between 0° and 35°C.

$$=NH + ClSCCl_3 + NaOH \rightarrow =NSCCl_3 + NaCl + H_2O$$

Occasionally trichloromethanesulfenyl chloride is condensed with the alkali salt of the imide by refluxing the mixture in a solvent such as benzene. In most cases the yields are high and the products are stable solids. These derivatives are listed in tables 11, 12, 13, 14, 15, and 16. One such compound, *N*-trichloromethylthiotetrahydrophthalimide (Captan), shows particularly outstanding

TABLE 10

Products of the reaction of trichloromethanesulfenyl chloride with sulfinates

RSO_2SCCl_3

R	Product	Yield	Boiling Point	Melting Point	References
		per cent	°C.	°C.	
C_6H_5—	Trichloromethyl benzenethiolsulfonate	51.5–58.5	148–150 /2 mm.		(8, 54, 62)
p-$CH_3C_6H_4$—	Trichloromethyl *p*-toluenethiolsulfonate	46.5–57		65.5–68.5	(8, 54, 62)
$(CH_3)_3C_6H_2$—	Trichloromethyl mesitylenethiolsulfonate	46.5		86.5	(8)
$CH_3CONHC_6H_4$—	Trichloromethyl *p*-acetamidobenzenethiolsulfonate	70		150–155 (d.)	(62)
4-ClC_6H_4—	Trichloromethyl *p*-chlorobenzenethiolsulfonate	80		56–57.5	(54)
3,4-$Cl_2C_6H_3$—	Trichloromethyl 3,4-dichlorobenzenethiolsulfonate	47		53–54.5	(54)
3-$NO_2C_6H_4$—	Trichloromethyl 3-nitrobenzenethiolsulfonate	79		65.5–66	(54)
4-$NO_2C_6H_4$—	Trichloromethyl 4-nitrobenzenethiolsulfonate	37		92–93	(54)
2-Cl-5-$NO_2C_6H_3$—	Trichloromethyl 2-chloro-5-nitrobenzenethiolsulfonate	88		118–119	(54)
4-Cl-3-$NO_2C_6H_3$—	Trichloromethyl 4-chloro-3-nitrobenzenethiolsulfonate	63		67–68	(54)
4-$CH_3OC_6H_4$—	Trichloromethyl 4-methoxybenzenethiolsulfonate	92		52.5–54	(54)
2-$C_{10}H_7$—	Trichloromethyl naphthalenethiolsulfonate	47	Oil		(54)
3-Cl_3CSSO_2-4-$CH_3OC_6H_3$—	Trichloromethyl 4-methoxybenzene-1,3-thiolsulfonate	33.6		124.5–127	(54)

TABLE 11

Products of the reaction of trichloromethanesulfenyl chloride with dicarboxylic acid imides

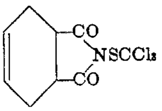
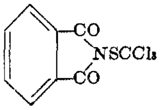
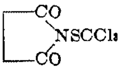
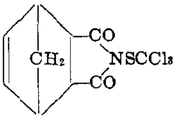
Imide	Product	Formula	Melting Point	Reference
			°C.	
cis-Δ^4-Tetrahydrophthalimide	*N*-Trichloromethylthio-*cis*-Δ^4-tetrahydrophthalimide		172–173	(42)
Phthalimide	*N*-Trichloromethylthiophthalimide		176–177	(42)
Succinimide	*N*-Trichloromethylthiosuccinimide		140–141	(42)
3,6-Endomethylene-Δ^4-tetrahydrophthalimide	*N*-Trichloromethylthioendomethylenetetrahydrophthalimide		152–153	(42)

TABLE 12

Products of the reaction of trichloromethanesulfenyl chloride with amides and imides of various acids

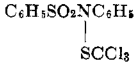
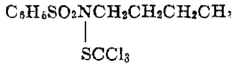
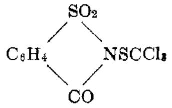
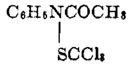
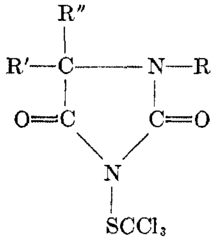
Imide	Product	Formula	Melting Point	Reference
			°*C.*	
N-Phenylbenzenesulfonamide	*N*-Trichloromethylthio-*N*-phenylbenzenesulfonamide	 $C_6H_5SO_2N(SCCl_3)C_6H_5$	112–113	(50)
N-Butylbenzenesulfonamide	*N*-Trichloromethylthio-*N*-butylbenzenesulfonamide	 $C_6H_5SO_2N(SCCl_3)CH_2CH_2CH_2CH_3$		(32)
o-Benzoic sulfimide (saccharin)	*N*-Trichloromethylthiobenzoic sulfimide		143–144	(50)
Acetanilide	*N*-Trichloromethylthioacetanilide	 $C_6H_5N(SCCl_3)COCH_3$	95–96	(50)
Diacetamide	*N*-Trichloromethylthiodiacetamide	$(CH_3CO)_2NSCCl_3$	Oil	(50)

TABLE 13

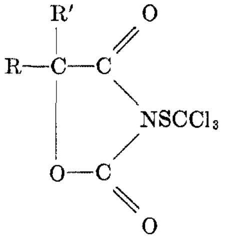
Products of the reaction of trichloromethanesulfenyl chloride with mono- and disubstituted hydantoins: 3-trichloromethylthiohydantoins



R	R′	R″	Formula	Melting Point	Reference
				°*C.*	
H—	CH_3—	$(CH_3)_3C$—	$C_9H_{13}Cl_3N_2O_2S$	213	(53)
H—	CH_3—	3-Methylbuten-2-yl-	$C_{10}H_{13}Cl_3N_2O_2S$	158–159	(53)
H—	CH_3—	Carbethoxymethyl-	$C_9H_{11}Cl_3N_2O_4S$	173	(53)
H—	CH_3—	Carboxymethyl-	$C_7H_7Cl_3N_2O_4S$	189–190	(53)
H—	CH_3	Carboxyethyl-	$C_8H_9Cl_3N_2O_4S$	153	(53)
H—	$(CH_3)_3C$—	Carboxymethyl-	$C_{10}H_{13}Cl_3N_2O_4S$	234	(53)
H—	C_6H_{11}—	Carbethoxymethyl-	$C_{13}H_{19}Cl_3N_2O_4S$	124–125	(53)
H—	C_2H_5—	$(CH_3)_2CH$—	$C_9H_{13}Cl_3N_2O_2S$	182	(53)
H—	2,6-Dimethylhepten-6-yl-	H—	$C_{13}H_{19}Cl_3N_2O_2S$	99–100	(53)
H—	C_6H_6—	C_6H_5—	$C_{16}H_{11}Cl_3N_2O_2S$	176	(53)
Acetyl	C_6H_5—	C_6H_5—	$C_{18}H_{13}Cl_3N_2O_3S$	145–147	(53)
Butyryl	C_6H_5—	C_6H_6—	$C_{20}H_{17}Cl_3N_2O_3S$	114	(53)
Acetyl	CH_3—	Carbethoxymethyl-	$C_{11}H_{13}Cl_3N_2O_5S$	63–66	(53)
H—	CH_3—	CH_3—	$C_6H_7Cl_3N_2O_2S$	169–171	(45)
NO_2—	CH_3—	CH_3—	$C_6H_6Cl_3N_3O_4S$	125–126	(45)
Acetyl	CH_3—	CH_3—	$C_8H_9Cl_3N_2O_3S$	94–97	(45)
H—	CH_3—	$(CH_3)_2CHCH_2$—	$C_9H_{13}Cl_3N_2O_2S$	133–134	(45)

TABLE 14

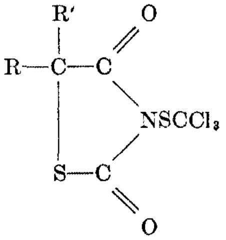
Products of the reaction of trichloromethanesulfenyl chloride with substituted oxazolidine-2,4-diones: 3-trichloromethanesulfenyloxazolidine-2,4-diones



R	R′	Formula	Melting Point	References
			°C.	
CH_3—	CH_3—	$C_6H_6Cl_3NO_3S$	88-89; 91-93	(19, 45)
CH_3—	C_2H_5—	$C_7H_8Cl_3NO_3S$	83-84; 86-88	(19, 45)
—$CH_2CH_2CH_2CH_2CH_2$—		$C_9H_{16}Cl_3NO_3S$	111-112	(45)
CH_3—	$(CH_3)_2CHCH_2$—	$C_9H_{12}Cl_3NO_3S$	89-90	(45)
Cyclopropyl	CH_3—	$C_8H_8Cl_3NO_3S$	108-109	(45)
CH_3—	C_6H_5—	$C_{11}H_8Cl_3NO_3S$		(48)
Isoöctyl	H—	$C_{12}H_{18}Cl_3NO_3S$		(48)
H—	H—	$C_4H_2Cl_3NO_3S$	119-120	(19)
CH_3—	H—	$C_5H_4Cl_3NO_3S$	Oil	(19)

TABLE 15

Products of the reaction of trichloromethanesulfenyl chloride with substituted thiazolidine-2,4-diones: 3-trichloromethanesulfenylthiazolidine-2,4-diones



R	R′	Formula	Melting Point	Reference
			°C.	
H—	H—	$C_4H_2Cl_3NO_2S_2$	117-118	(19)
CH_3—	H—	$C_5H_4Cl_3NO_2S_2$	Oil	(19)
CH_3—	CH_3—	$C_6H_6Cl_3NO_2S_2$	70-71	(19)

fungicidal activity, and its preparation (42, 43, 47, 48), properties (13, 34), and analysis (44) have been the subject of detailed investigations.

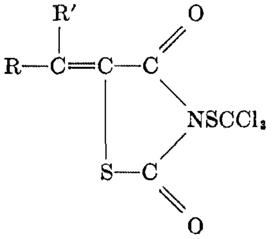
O. REACTION WITH PRIMARY AMINES AND SECONDARY DIALKYL- AND ARALKYLAMINES

1. Preparation of substituted guanidines

Primary aliphatic (and aromatic) and secondary aralkyl- and dialkylamines react with trichloromethanesulfenyl chloride in the presence of bases, such as

TABLE 16

Products of the reaction of trichloromethanesulfenyl chloride with 5-alkylidene- and 5-aralkylidenethiazolidine-2,4-diones: 3-trichloromethanesulfenylthiazolidine-2,4-diones



R	R′	Formula	Melting Point	Reference
			°C.	
$(CH_3)_2CH—$	H—	$C_8H_8Cl_3NO_2S_2$	54–56	(19)
$C_8H_{17}—$	H—	$C_{13}H_{18}Cl_3NO_2S_2$	52–53.5	(19)
$OCH{=}CHCH{=}C—$	H—	$C_9H_4Cl_3NO_3S_2$	149–150	(19)
$C_6H_5—$	H—	$C_{11}H_6Cl_3NO_2S_2$	159–161	(19)
$2\text{-}ClC_6H_4—$	H—	$C_{11}H_5Cl_4NO_2S_2$	141–143	(19)
$4\text{-}ClC_6H_4—$	H—	$C_{11}H_5Cl_4NO_2S_2$	170–172	(19)
$3\text{-}NO_2C_6H_4—$	H—	$C_{11}H_5Cl_3N_2O_4S_2$	148–150	(19)
$4\text{-}CH_3OC_6H_4—$	H—	$C_{12}H_8Cl_3NO_3S_2$	189–190	(19)
$3,4\text{-}(OCH_2O)C_6H_3—$	H—	$C_{12}H_6Cl_3NO_4S_2$	178–179	(19)
$C_6H_5CH{=}CH—$	H—	$C_{13}H_8Cl_3NO_2S_2$	173–174	(19)
$CH_3—$	$CH_3—$	$C_7H_6Cl_3NO_2S_2$	114–115	(19)
$—CH_2CH_2CH_2CH_2CH_2—$		$C_{10}H_{10}Cl_3NO_2S_2$	169–171	(19)

TABLE 17

Products of the reaction of trichloromethanesulfenyl chloride with primary alkyl- and arylamines

Cl_3CSNHR and $(Cl_3CSNH)_2R$

R	Product	Boiling Point or Melting Point	References
		°C.	
$C_6H_5—$	*S*-Anilinotrichloromethylthiol	Oil	(16, 64)
p-$CH_3C_6H_4—$	*S*-*p*-Toluidinotrichloromethylthiol	73 (m.p.)	(16, 72)
o-$CH_3C_6H_4—$	*S*-*o*-Toluidinotrichloromethylthiol	Oil	(72)
m-$CH_3C_6H_4—$	*S*-*m*-Toluidinotrichloromethylthiol	Oil	(72)
p-$ClC_6H_4—$	*S*-*p*-Chloroanilinotrichloromethylthiol	Oil	(16)
p-$BrC_6H_4—$	*S*-*p*-Bromoanilinotrichloromethylthiol	57–58 (m.p.)	(71)
p-$CH_3OC_6H_4—$	*S*-*p*-Methoxyanilinotrichloromethylthiol	Oil	(16)
$CH_3(CH_2)_5CH_2—$	*S*-*n*-Heptylaminotrichloromethylthiol	170/760 mm. (d.)	(18)
$CH_2{=}CHCH_2—$	*S*-Allylaminotrichloromethylthiol	170/760 mm. (d.)	(18)
$CH_3(CH_2)_3—$	*S*-*n*-Butylaminotrichloromethylthiol	82–83/3 mm.	(71)
$—CH_2CH_2—$	1,4-Bis(trichloromethylthio)ethylenediamine	42–43 (m.p.)	(72)

sodium hydroxide, sodium carbonate (16), pyridine (72), or an excess of the reacting amines (72), to form *S*-aminotrichloromethylthiols.

$$RNH_2 + ClSCCl_3 \rightarrow RNHSCCl_3 + HCl \quad (R = \text{alkyl or aryl})$$

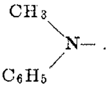
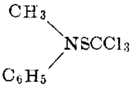
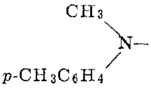
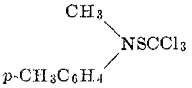
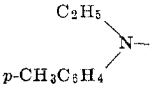
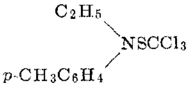
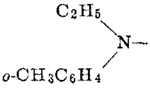
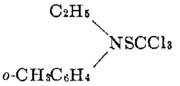
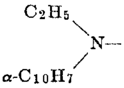
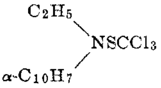
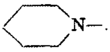
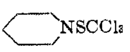
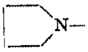
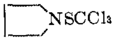
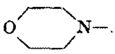
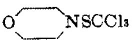
$$RR'NH + ClSCCl_3 \rightarrow RR'SCCl_3 + HCl \quad (R' = \text{alkyl})$$

The products are listed in tables 17 and 18. During this reaction it is essential

TABLE 18

Products of the reaction of trichloromethanesulfenyl chloride with dialkyl- and aralkylamines

Cl_3CSR and $(Cl_3CS)_2R$

R	Formula	Boiling Point	Melting Point	Reference
		°C.	°C.	
$(CH_3)_2N—$	$(CH_3)_2NSCCl_3$	74/13 mm.		(2)
$(C_2H_5)_2N—$	$(C_2H_5)_2NSCCl_3$	96/15 mm.		(2)
$[(CH_3)_2CHCH_2]_2N—$	$[(CH_3)_2CHCH_2]_2NSCCl_3$	127/15 mm.		(2)
 $(CH_3)(C_6H_5)N—$	 $(CH_3)(C_6H_5)NSCCl_3$	Unstable oil		(2)
 $(CH_3)(p\text{-}CH_3C_6H_4)N—$	 $(CH_3)(p\text{-}CH_3C_6H_4)NSCCl_3$	Unstable oil		(2)
 $(C_2H_5)(p\text{-}CH_3C_6H_4)N—$	 $(C_2H_5)(p\text{-}CH_3C_6H_4)NSCCl_3$	Unstable oil		(2)
 $(C_2H_5)(o\text{-}CH_3C_6H_4)N—$	 $(C_2H_5)(o\text{-}CH_3C_6H_4)NSCCl_3$	Unstable oil		(2)
 $(C_2H_5)(\alpha\text{-}C_{10}H_7)N—$	 $(C_2H_5)(\alpha\text{-}C_{10}H_7)NSCCl_3$	Unstable oil		(2)
$(C_6H_5CH_2)_2N—$	$(C_6H_5CH_2)_2NSCCl_3$	Unstable oil		(2)
$(ClCH_2CH_2)_2N—$	$(ClCH_2CH_2)_2NSCCl_3$	Oil		(11)
		108–109/1.5 mm.	29–30	(72)
		68–70/1 mm.		(72)
			86–87	(31)
			164–165	(72)

that the temperature be low, preferably around zero. At higher temperatures, if excess of amine is present, further reaction takes place, and elimination of all chlorine and sulfur occurs. Depending on the amine used, trialkyl- or triarylguanidine hydrochlorides separate from the reaction mixture (17, 18, 64). The

$$RNHSCCl_3 + 4R'NH_2 \rightarrow R'NH_2 \cdot HCl + 2HCl + RNHSC(NHR')_3 \rightarrow$$
$$RNH_2 \cdot HCl + S + R'N{=}C(NHR')_2 \cdot HCl$$

products of this reaction are listed in table 19.

All substituted *S*-aminotrichloromethylthiols are unstable substances. Aralkyl derivatives seem to be less stable than those of primary aliphatic amines. The

TABLE 19

Trialkyl- and triarylguanidines prepared from S-alkoxy- and S-amino derivatives of trichloromethanesulfenyl chloride

Starting Material ($ROSCCl_3$)	+ Amine	Product $RN{=}C{=}(NHR)_2$	Yield	Melting Point	Reference
			per cent	°C.	
S-Phenoxytrichloromethylthiol	+Aniline	Triphenylguanidine	45–60	143	(17)
S-*o*-Chlorophenoxytrichloromethylthiol					
S-Xylyloxytrichloromethylthiol					
S-*p*-Tolyloxytrichloromethylthiol					
S-Diphenylyl-2-oxytrichloromethylthiol					
S-Phenoxytrichloromethylthiol	+*p*-Toluidine	Tri-*p*-tolylguanidine	43	122	(17)
S-*o*-Chlorophenoxytrichloromethylthiol			24		
S-*p*-Tolyloxytrichloromethylthiol			40		
$(RNHSCCl)_3$					
S-Anilinotrichloromethylthiol	+ Aniline	Triphenylguanidine		143	(17)
p-Toluidinotrichloromethylthiol	+ *p*-Toluidine	Tri-*p*-tolylguanidine		122	(17)
		$RN{=}C{=}(NHR)_2 \cdot HCl$			
S-Allylaminotrichloromethylthiol	+ Allylamine	Triallylguanidine hydrochloride		176	(18)
S-Benzylaminotrichloromethylthiol	+ Benzylamine	Tribenzylguanidine hydrochloride		201	(18)
S-Isoamylaminotrichloromethylthiol	+ Isoamylamine	Triisoamylguanidine hydrochloride		206	(18)
$RR'NSCCl_3$		$RN{=}C{=}(NHR)_2$			
S-Dimethylaminotrichloromethylthiol	+ Aniline	Triphenylguanidine	60	143	(2)
S-Diisobutylaminotrichloromethylthiol			46	143	(2)
S-Methylanilinotrichloromethylthiol			35	143	(2)
S-Ethylanilinotrichloromethylthiol			32	143	(2)
S-Methyl-*p*-toluidinotrichloromethylthiol			37	143	(2)
S-Piperidinotrichloromethylthiol			28	143	(2)

hydrolysis of these compounds is illustrated by the behavior of *S*-*p*-toluidinotrichloromethylthiol (16). With boiling water it is hydrolyzed to trichloromethanesulfenyl chloride, *p*-toluidine, hydrogen chloride, and *p*-tolyl isothiocyanates.

$$p\text{-}CH_3C_6H_4NHSCCl_3 \xrightarrow[H_2O]{100°C.} Cl_3CSCl + CH_3C_6H_4NH_2 \cdot HCl + HCl + p\text{-}CH_3C_6H_4N{=}CS$$

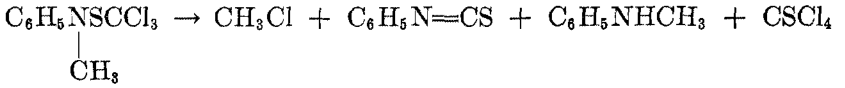
Dry hydrogen chloride in chloroform regenerates the amine and trichloromethanesulfenyl chloride.

$$p\text{-}CH_3C_6H_4NHSCCl_3 \xrightarrow{HCl} p\text{-}CH_3C_6H_4NH_2 \cdot HCl + CSCl_4$$

Treatment with dilute alkali, even in the cold, gives *p*-tolyl isocyanide and *p*-tolyl isothiocyanate.

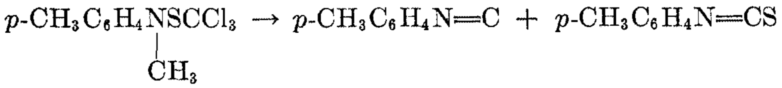
$$p\text{-}CH_3C_6H_4NHSCCl_3 \xrightarrow{OH^-} p\text{-}CH_3C_6H_4N{=}C + p\text{-}CH_3C_6H_4N{=}CS$$

S-Methylanilino- and *S*-methyl-*p*-toluidinotrichloromethylthiols serve as examples of the decomposition of secondary aralkylamine derivatives (2). Thermal decomposition of the *S*-methylanilino compound results in the formation of methyl chloride, trichloromethanesulfenyl chloride, methylaniline, and phenyl isothiocyanate.



$$C_6H_5\underset{\underset{CH_3}{|}}{N}SCCl_3 \rightarrow CH_3Cl + C_6H_5N{=}CS + C_6H_5NHCH_3 + CSCl_4$$

Boiling water and alkali hydrolyze these compounds to aryl isocyanides and isothiocyanates. In the case of *S*-methyl-*p*-toluidinotrichloromethylthiol, *p*-tolyl isocyanide and *p*-tolyl isothiocyanate are formed.

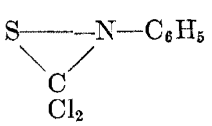


$$p\text{-}CH_3C_6H_4\underset{\underset{CH_3}{|}}{N}SCCl_3 \rightarrow p\text{-}CH_3C_6H_4N{=}C + p\text{-}CH_3C_6H_4N{=}CS$$

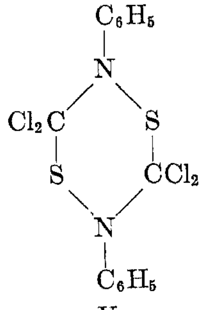
These results suggest that an unusual isomerization or rearrangement occurs during these reactions. At present it is not clear by what mechanism the initial arrangement of atoms in the thiols, $-C-N-S-C\equiv$, is transformed into the atomic arrangement of isocyanides, $-C-N{=}C$, and isothiocyanates, $-C-N{=}C{=}S$. It seems that further investigation of the question would be warranted.

2. Preparation of 3,3,6,6-tetrachloro-2,3,5,6-tetrahydro-2,5-diaryl-1,4-dithia-2,5-diazines

It has been shown that *S*-arylaminotrichloromethylthiols are sensitive to aqueous alkali even in the cold, decomposing into aryl isocyanides and aryl isothiocyanates. When, however, alcoholic potassium hydroxide is added slowly to a cold ethereal solution of the thiol, a white precipitate is formed. This reaction was first investigated by Rathke (65), who finally proposed two alternative structures for the product:

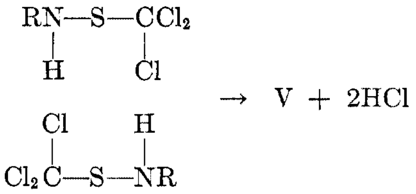


IV



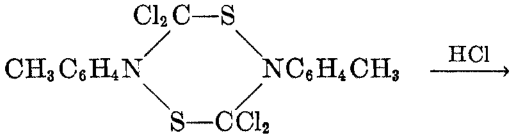
V

Connolly and Dyson (16) confirmed structure V, which suggests an interaction between two molecules of the thiol.



Similar compounds have been prepared from several arylamines, often without isolation of the unstable *S*-aminotrichloromethylthiols. The dithiadiazine derivatives are listed in table 20. Symmetrical trichloroaniline and 3,5-dibromo-*p*-toluidine do not react under similar conditions, while *m*-2-xylidine and 2,4-dichloroaniline derivatives give only the corresponding aryl isothiocyanates (16). Furthermore, aliphatic *S*-alkylaminotrichloromethylthiols do not undergo cyclization (18).

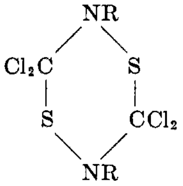
In contrast to the intermediate thiols the heterocyclic substances are stable toward a variety of reagents. For example, the *p*-tolyl derivative is unaffected by water, hydrochloric acid, tin and hydrochloric acid, permanganate, hydrogen peroxide, and weak alkali. Strong alkali converts it to *p*-tolyl isothiocyanate. Dry hydrogen chloride in ether cleaves the compound into 3-chloro-*p*-toluidine hydrochloride and trichloromethyl mercaptan (16).



$$2CCl_3SH + (2CH_3C_6H_4NHCl) \rightarrow 2CH_3C_6H_3ClNH_2$$

TABLE 20

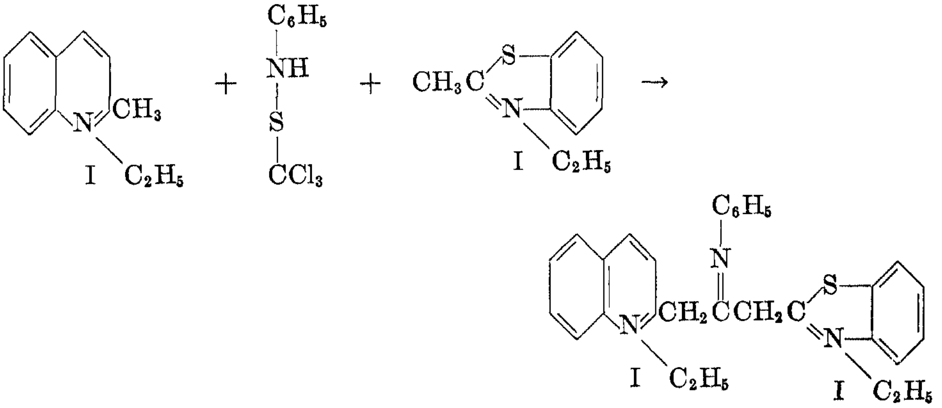
3,3,6,6-Tetrachloro-2,3,5,6-tetrahydro-2,5-diaryl-1,4-dithia-2,5-diazines



R	Product (aryl)	Melting Point	References
		°C.	
C_6H_5—	Phenyl	154	(71)
		145.5 (d.)	(16, 65)
p-$CH_3OC_6H_4$—	*p*-Anisyl	113	(16)
p-ClC_6H_4	*p*-Chlorophenyl	160	(16)
		174	(71)
p-BrC_6H_4	*p*-Bromophenyl	196–198	(71)
p-$CH_3C_6H_4$—	*p*-Tolyl	142.5	(16, 65, 72)
o-$CH_3C_6H_4$—	*o*-Tolyl	111–112	(72)
m-$CH_3C_6H_4$—	*m*-Tolyl	106	(72)

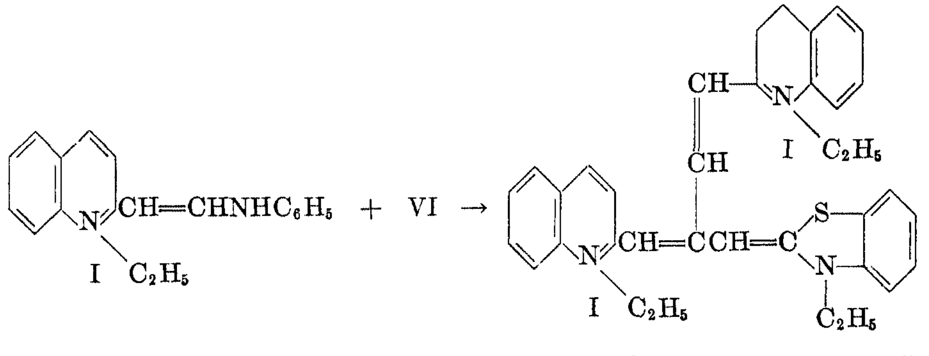
3. Preparation of intermediates for Brooker-type cyanine dyes

The reactivity of *S*-arylaminotrichloromethylthiols can be utilized for the preparation of intermediates in the synthesis of Brooker-type cyanine dyes (73). For instance, when *S*-anilinotrichloromethylthiol is heated with 2-methyloxazole or 2-methylthiazole ethiodide, and quinaldine ethiodide, or with a mixture of the three compounds, all chlorine and sulfur atoms are eliminated, and the carbon atom of the trichloromethylthio group becomes the central carbon atom of the dyestuff molecule.



VI

These intermediates can be treated with a heterocyclic compound such as 2-(anilinovinyl)quinolinium ethiodide to form the desired Brooker dye.



By this method unsymmetrical dyes containing two or three different heterocyclic nuclei can be prepared. In table 21 the intermediates are listed.

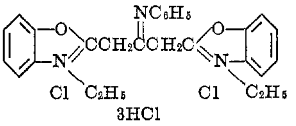
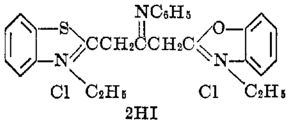
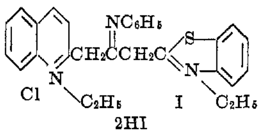
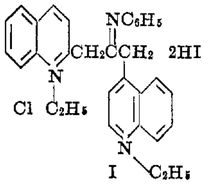
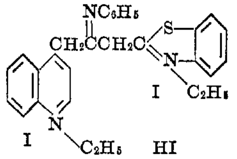
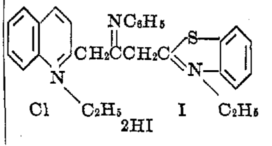
P. REACTION WITH SECONDARY AND TERTIARY ARYLAMINES

1. Reaction with secondary arylamines

It has been shown that the reaction of trichloromethanesulfenyl chloride with secondary aliphatic amines or aralkylamines results in the formation of unstable compounds of the type $RR'NSCCl_3$. The reaction of trichloromethane-

TABLE 21

Intermediates for Brooker-type cyanine dyes

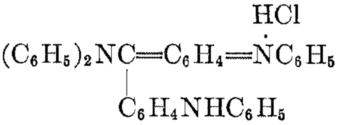
Starting Material	Product	Formula	Melting Point	Reference
			°C.	
$C_6H_5NHSCCl_3$ + 2-methylbenzoxazole ethiodide	1,1′-Diethyl-2,2′-trimethylene-9-anilinoöxacyanine dichloride trihydrochloride		203 (d.)	(73)
$C_6H_5NHSCCl_3$ + 2-methylbenzthiazole ethiodide + 2-methylbenzoxazole ethiodide	1,1′-Diethyl-2,2′-trimethylene-mesoanilinothiaoxacyanine dichloride dihydroiodide		178 (d.)	(73)
$C_6H_5NHSCCl_3$ + quinaldine ethiodide + 2-methybenzothiazole ethiodide	1,1′-Diethyl-mesoanilinotrimethylenequinothiacyanine chloride iodide dihydroiodide		185 (d.)	(73)
$C_6H_5NHSCCl_3$ + lepidine ethiodide + quinaldine ethiodide	1,1′-Diethyl-mesoanilino-4,2′-trimethylenequinocyanine chloride iodide dihydroiodide		151 (d.)	(73)
$C_6H_5NHSCCl_3$ + lepidine ethiodide + 2-methylbenzothiazole ethiodide	1,1′-Diethyl-mesoanilino-(4-quino-2′-thia)trimethylenecyanine diiodide hydroiodide		146 (d.)	(73)
$C_6H_5NHSCCl_3$ + quinaldine ethiodide + 2-methylbenzothiazole ethiodide	1,1′-Diethyl-mesoanilino-2,2′-trimethylenequinothiacyanine chloride iodide dihydroiodide		186 (d.)	(73)

sulfenyl chloride with diarylamines or tertiary arylamines takes an entirely different course and triphenylmethane dyes are the main reaction products. For example, when a mixture of diphenylamine and trichloromethanesulfenyl chloride is warmed, an exothermic reaction occurs. From the reaction mixture N,N',N''-triphenylpararosaniline hydrochloride (VII) can be isolated.

$$(C_6H_5NHC_6H_4)_2{=}C{=}C_6H_4{=}\underset{\displaystyle HCl}{\underset{\bullet}{N}}C_6H_5$$

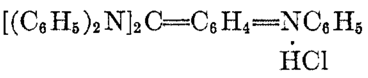
VII

In addition to this dye a deep red microcrystalline powder (VIII or IX) and tetraphenylthiourea (X) can be isolated (2).



$$(C_6H_5)_2N\underset{C_6H_4NHC_6H_5}{C}=C_6H_4=\overset{HCl}{\dot{N}}C_6H_5$$

VIII



$$[(C_6H_5)_2N]_2C=C_6H_4=\underset{HCl}{\dot{N}}C_6H_5$$

IX

$$S=C[N(C_6H_5)_2]_2$$

X

The red compound is a member of the class of triphenylmethane dyes, and all evidence suggests structure VIII; however, formula IX cannot be excluded. Identical mixtures of these compounds are also obtained from the reaction of diphenylamine with thiophosgene (2).

In spite of the efforts of Argyle and Dyson (2) the mechanism of the formation of these products remains somewhat obscure. The problem can be better understood, however, on the basis of the results obtained with tertiary amines.

2. Reaction with tertiary arylamines

Rathke found that the reaction between dimethylaniline and trichloromethanesulfenyl chloride leads to crystal violet, and in 1885 the Bayer Company patented a process for the preparation of hexamethylpararosaniline, trimethyltriphenylpararosaniline, and pentamethylphenylpararosaniline by the reaction of trichloromethanesulfenyl chloride with the corresponding amine. However, Argyle and Dyson (2) must be credited with elucidating the mechanism of this process by isolating the intermediate compounds (XI: $R = CH_3, C_2H_5$).

XI

For instance, from the reaction mixture of dimethylaniline and trichloromethanesulfenyl chloride they were able to isolate both the intermediate *p*-dimethylaminophenyl trichloromethyl sulfide (XII) and crystal violet (XIII).

$$(CH_3)_2NC_6H_4SCCl_3 \qquad [(CH_3)_2NC_6H_4]_2C=C_6H_4=N(CH_3)_2Cl$$

XII XIII

In the presence of condensing agents, such as the chloride of zinc or aluminum, compound XII reacts further with aromatic tertiary amines to form dyes identical with those obtained directly from trichloromethanesulfenyl chloride and the corresponding amine; e.g., with diphenylmethylamine *N*,*N*′,*N*″-triphenyl-*N*,*N*′,*N*″-trimethylpararosaniline is formed.

$$(CH_3)_2NC_6H_4SCCl_3 + 3N(C_6H_5)_2CH_3 \rightarrow (CH_3)_2NC_6H_4SC[C_6H_4N(CH_3)C_6H_5]_3$$

$$+ 3HCl \rightarrow (CH_3)_2NC_6H_4SH + [C_6H_5(CH_3)NC_6H_4]_2C=C_6H_4=NCH_3C_6H_5Cl$$

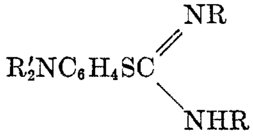
Dimethylaniline, diphenylamine, and triphenylamine yield crystal violet, *N*,*N*′,*N*″-triphenylpararosaniline, and hexaphenylpararosaniline, respectively. This leaves little doubt about the mechanism of the reaction between a tertiary amine and trichloromethanesulfenyl chloride. At the same time it suggests possible intermediate steps in the reaction of secondary arylamines with trichloromethanesulfenyl chloride.

Compound XII is hydrolyzed by water to form carbon dioxide, hydrogen chloride, and *p*-dimethylaminothiophenol (m.p. 32°C.), which is oxidized rapidly to bis(*p*-dimethylaminophenyl) disulfide (m.p. 118°C.) (2).

$$\underset{\text{XII}}{(CH_3)_2NC_6H_4SCCl_3} \rightarrow CO_2 + HCl + (CH_3)_2NC_6H_4SH$$

$$(CH_3)_2NC_6H_4SH \rightarrow [(CH_3)_2NC_6H_4S]_2$$

Reduction of XII with zinc dust and glacial acetic acid gives dimethylaniline and methyl mercaptan (2), nitration gives a dinitro derivative, and bromination gives a monobromo derivative. When hydrogen chloride is passed into a solution of XII in ligroin, the hydrochloride precipitates (2). A homologous diethylamino derivative is also known (2). These compounds are listed in table 22. However, the methyl ethyl, di-*n*-propyl, and di-*n*-butyl analogs could not be prepared in crystalline form. Diethylaniline, *p*-bromodimethylaniline, dimethyl-*p*-toluidine, and tetramethyldiaminodiphenylmethane react rapidly with trichloromethanesulfenyl chloride, undergoing partial demethylation, and thiophosgene is formed. Under similar conditions tribenzylamine gives benzyl chloride and thiophosgene (2). Compound XII reacts with primary arylamines to form *S*-(*p*-dimethylaminophenyl)-*N*,*N'*-diarylisothioureas (XIV). Structure XIV has been established by degradation and alternative synthesis (2). In table 23 various substituted isothioureas are listed.



$$R'_2NC_6H_4SC\begin{matrix} // NR \\ \\ \backslash NHR \end{matrix}$$

XIV

TABLE 22

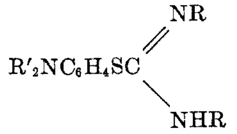
Products of the reaction of trichloromethylsulfenyl chloride with tertiary amines

$RSCCl_3$

R	Product	Formula	Melting Point	Reference
			°C.	
$(CH_3)_2NC_6H_4$—.........	*S*-*p*-Dimethylaminophenyl trichloromethyl sulfide	$C_9H_{10}NCl_3S$	71	(2)
$(CH_3)_2NC_6H_2(NO_2)_2$—...	*S*-*p*-Dimethylaminodinitrophenyl trichloromethyl sulfide	$C_9H_8O_4N_3Cl_3S$	123	(2)
$(CH_3)_2NC_6H_3(Br)$—.....	*S*-*p*-Dimethylaminobromophenyl trichloromethyl sulfide	$C_9H_9NCl_3BrS$	146 (d.)	(2)
$(CH_3)_2NC_6H_4$—......... $\cdot HCl$	*S*-*p*-Dimethylaminophenyl trichloromethyl sulfide hydrochloride		129–130 (d.)	(2)
$(C_2H_5)_2NC_6H_4$—........	*S*-*p*-Diethylaminophenyl trichloromethyl sulfide	$C_{11}H_{14}NCl_3S$	44	(2)

TABLE 23

Products of the reaction of S-p-dialkylaminophenyl trichloromethyl sulfides with primary arylamines: S(p-dialkylaminophenyl)-N,N'-diarylisothioureas

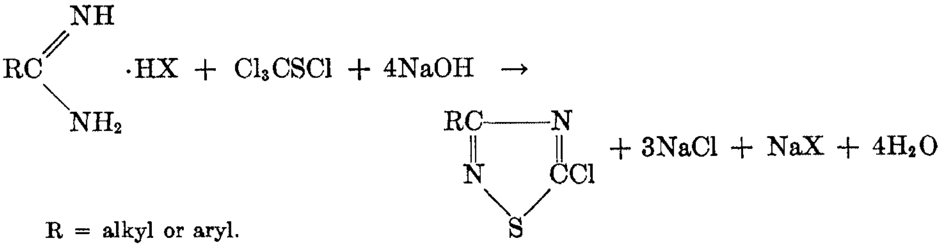


$$R'_2NC_6H_4SC\begin{matrix}\diagup NR\\ \diagdown NHR\end{matrix}$$

R'	R	Formula	Melting Point	Reference
			°C.	
CH_3—	C_6H_5—	$C_{21}H_{21}N_3S$	175	(2)
CH_3—	p-$CH_3C_6H_4$—	$C_{23}H_{25}N_3S$	142	(2)
CH_3	p-ClC_6H_4—	$C_{21}H_{19}N_3Cl_2S$	157	(2)
CH_3—	p-BrC_6H_4—	$C_{21}H_{19}N_3Br_2S$	167	(2)
C_2H_5—	C_6H_5—	$C_{23}H_{25}N_3S$	128	(2)
n-C_3H_7—	C_6H_5—	$C_{25}H_{29}N_3S$	125	(2)

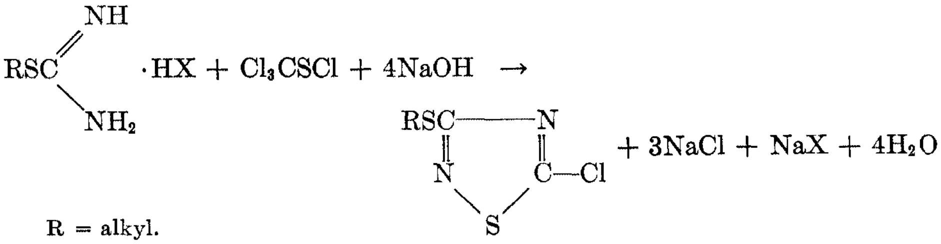
Q. REACTION WITH ALIPHATIC AND AROMATIC AMIDINES AND ALKYLISOTHIOUREAS

When amidines are treated with trichloromethanesulfenyl chloride at 0°C. in the presence of alkali, 5-chloro-3-alkyl- or arylthia-1,2,4-diazoles are formed (28) in yields of 40 to 70 per cent.



R = alkyl or aryl.

The reaction between trichloromethanesulfenyl chloride and alkylisothioureas proceeds in a similar manner with the formation of 3-alkylmercapto-5-chloro-1,2,4-thiadiazoles (29).

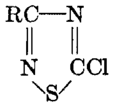


R = alkyl.

Depending on the isourea used, the yields range from 35 to 65 per cent. The chlorine atoms in these thiadiazoles are very reactive and can be exchanged with a variety of groups, such as —SH, —OH, —OR, —$NHCH_3$, etc. The foregoing synthesis is a new approach to otherwise difficultly obtainable materials. Compounds of this class are listed in tables 24 and 25.

TABLE 24

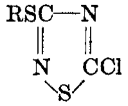
Products of the reaction of trichloromethanesulfenyl chloride with aliphatic or aromatic amidines: 5-chloro-3-alkyl- or aryl-1,2,4-thiadiazoles



R	Formula	d_4	n_D	Boiling Point or Melting Point	Reference
				°C.	
CH_3—.............	$C_3H_3N_2ClS$	1.355 (20°C.)	1.52075 (22.5°C.)	51/21 mm.	(28)
C_2H_5—.............	$C_4H_5N_2ClS$	1.203 (20°C.)	1.5129 (24°C.)	60/17 mm.	(28)
C_6H_5—.............	$C_8H_5N_2ClS$			52 (m.p.) 115/3 mm.	(28)
$C_6H_5CH_2$—.........	$C_9H_7N_2ClS$	1.305 (16°C.)	1.5904 (19°C.)	122–123/3 mm.	(28)

TABLE 25

Products of the reaction of trichloromethanesulfenyl chloride with alkylisothioureas: 3-alkylmercapto-5-chloro-1,2,4-thiadiazoles



R	Formula	d	n_D	Boiling Point or Melting Point	Reference
				°C.	
CH_3—.............	$C_3H_3N_2ClS_2$			98/17 mm. 29–30 (m.p.)	(29)
C_2H_5—.............	$C_4H_5N_2ClS_2$	1.3861 (18°C.)	1.58285 (21°C.)	115/13 mm.	(29)
n-C_3H_7—...........	$C_5H_7N_2ClS_2$	1.3177 (18°C.)	1.56865 (21°C.)	131/18 mm.	(29)
n-C_4H_9—...........	$C_6H_9N_2ClS_2$	1.2650 (18°C.)	1.55805 (21°C.)	140/14 mm.	(29)
tert-C_4H_9—..........	$C_6H_9N_2ClS_2$	1.2560 (18°C.)	1.55635 (21°C.)	118/14 mm.	(29)
Iso-C_5H_{11}—.........	$C_7H_{11}N_2ClS_2$	1.2233 (18°C.)	1.54785 (21°C.)	148/14 mm.	(29)
$C_6H_5CH_2$—.........	$C_9H_7N_2ClS_2$			120/0.2 mm. 49–50 (m.p.)	(29)

V. THE ROLE OF TRICHLOROMETHANESULFENYL CHLORIDE IN ORGANIC TECHNOLOGY

To date trichloromethanesulfenyl chloride has had only limited industrial application. Attempts were made to utilize the compound and its condensation products with phenols and thiophenols as herbicides (3, 10), diesel fuel additives, and extreme-pressure lubricants (9). The early efforts to use trichloromethanesulfenyl chloride in the dyestuff industry have been mentioned. Trichloromethanesulfonyl chloride was also considered for similar purposes (9, 59, 66, 69, 70) and as an intermediate for the synthesis of 1,1,1,3-tetrachloroalkanes (76, 77).

$$RCH{=}CH_2 + Cl_3CSO_2Cl \rightarrow RCHClCH_2CCl_3 + SO_2$$

R = alkyl or aryl.

TABLE 26

Products of the reaction of trichloromethanesulfenyl chloride with unsaturated compounds

Starting Material	Product	Boiling Point	n_D	Reference
		°C.		
Styrene	1,1,1,3-Tetrachloropropylbenzene, $C_6H_5CHClCH_2CCl_3$	85–87/0.2 mm.	1.5557 (20°C.)	(75)
Ethylene	1,1,1,3-Tetrachloropropane	40/10 mm.	1.4825 (20°C.)	(74)
Octene	1,1,1,3-Tetrachlorononane	75–77/0.3 mm.	1.4771 (20°C.)	(74)
Isoprene	1,1,1,5-Tetrachloro-3-methyl-2-pentene	96–98/6 mm.	1.5129 (20°C.)	(74)
Allyl acetate	2,4,4,4-Tetrachlorobutyl acetate	66/0.3 mm.		(74)
Allyl alcohol	2,4,4,4-Tetrachlorobutanol	60–62/0.5 mm.	1.5065 (20°C.)	(74)

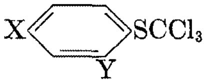
Compounds prepared by this method are given in table 26. Of all the derivatives of trichloromethanesulfenyl chloride, the *N*-(trichloromethylthio)tetrahydrophthalimide, known as Captan, SR-406, or Orthocide (discovered by Kittleson), has attained the greatest importance in industry. Because of its high fungicidal activity, wide spectrum, and excellent stability, it is probably the best fungicide in its class; it finds wide application in agriculture (13, 46).

VI. Physiological and Pharmacological Properties of Trichloromethanesulfenyl Chloride and its Derivatives

The vapors of trichloromethanesulfenyl chloride are toxic. Its toxicity to dogs is about one-third and to mice one-eighth of the toxicity of phosgene. The compound was tried as a war gas in World War I (33), but its use was abandoned, mainly because of its low toxicity and instability. In small quantities the compound has sterilizing, fungicidal, and herbicidal properties. In the form of 1–5 per cent emulsions, or wettable powder preparations, it kills chick weed, dandelions, purslane, and pinto beans and defoliates cotton, tomatoes, and potatoes (3).

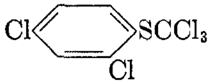
Its oxidation product, trichloromethanesulfonyl chloride, acts as a contact poison on weevils and is toxic to the flour beetle (*Tribolium confusum*) (66). Of the more complex derivatives of trichloromethanesulfenyl chloride, *N*-trichloromethylthioimides, *N*-trichloromethylthiohydantoins, *N*-trichloromethylthioöxazolidinediones, and *N*-trichloromethylthiosulfonamides show fungicidal activity against *Alternaria solani* and *Sclerotinia fructicola* (46). Various alcohol, amine (72), and substituted benzenethiolsulfonate (62) derivatives of trichloromethanesulfenyl chloride are also effective against fungi. Condensation products of phenols and thiophenols with trichloromethanesulfenyl chloride exhibit herbicidal action on corn and bean plants (10). Condensation products of trichloromethanesulfenyl chloride with unsaturated compounds such as octene show activity against the German roach (*Blattella germanica*), the American roach (*Periplanatus americanus*), the milkweed bug (*Oncopeltus fasciatus*), and *Alternaria solani* and *Sclerotinia fructicola* (49). Substituted phenyl trichloromethyl sulfides (XV), which have not been mentioned earlier in the text because their preparation does not involve reactions of trichloromethanesulfenyl chloride, show remarkable fungistatic activity against

Trichophyton gypseum and exhibit contact insecticidal activity against *Drosophila melanogaster* (61). The 2,4-dichlorophenyl trichloromethyl sulfide (XVI) compares favorably with DDT in its activity against *Drosophila melanogaster*.



XV

X = F, Cl, Br, I, CH_3, CH_3O, NO_2



XVI

Y = Cl, Br, SCN, CN

VII. Structure and Biological Activity of Trichloromethanesulfenyl Chloride Derivatives

In considering the class of trichloromethanesulfenyl chloride derivatives it is observed that a great number of substances are active, not only against either fungi or bacteria, but rather against both; in addition, they exhibit herbicidal and insecticidal activity (71). This is an uncommon property. When one compares most other classes of biologically active substances, it will be found more often than not that a given chemical is very specific in its action. Thus, a compound with good fungicidal activity is often devoid of any bactericidal or herbicidal activity or vice versa.

The essential feature for the biological activity of trichloromethanesulfenyl chloride derivatives was first attributed to the presence of the $=NSCCl_3$ group. This conclusion was drawn because a variety of derivatives of trichloromethanesulfenyl chloride having this group were potentially active (46). Later investigations (10, 61, 72) have shown that the presence of nitrogen is not essential and that compounds containing other elements, such as oxygen, sulfur, or carbon, may be as effective as those containing the $=NSCCl_3$ group. Therefore, the bulk of the activity must be attributed to the presence of the $-SCCl_3$ group, which also determines to a great extent the chemical behavior of the molecule. However, this is not the only factor which determines the biological activity of the compound. The physical and the chemical properties of the other part, its geometrical arrangement, and its influence on the reactivity of the $-SCCl_3$ group are also important. Favorable combinations of the physical and chemical factors will result in substances of high activity, while unfavorable combinations will result in substances with little or no activity. The importance of the $-SCCl_3$ group appears to be predominant in a variety of substances, and, as a consequence, nearly all trichloromethanesulfenyl chloride derivatives exhibit marked biological effects regardless of structure. When one of the chlorine atoms of the $-SCCl_3$ group is removed owing to the formation of a heterocyclic compound, the newly formed compound, in spite of the presence of the NSCCl atomic arrangement, is lacking in biological activity. This evidence supports the general belief (71) that the great reactivity of the $-SCCl_3$ radical is responsible for the biological activity of the trichloromethanesulfenyl chloride derivatives.

No attempt has yet been made to investigate the fate of these substances in the living cell. A possible transformation of the amine derivatives may proceed in a manner similar to the transformation of disodium ethylenebis(dithiocarbamate) (XVII).

$$NaSSCNHCH_2CH_2NHCSSNa$$

XVII

This compound, one of the most popular fungicides, has been studied for some years to determine its mode of action. One theory (78, 79) ascribes the action to the formation of the diisothiocyanate, $SCNCH_2CH_2NCS$.

Since the amino derivatives of trichloromethanesulfenyl chloride are often converted to isothiocyanates, it is possible that the biological action of compounds such as *N*,*N'*-bis(trichloromethylthio)ethylenediamine (XVIII) (72) may also be related to that of the thiocarbamates.

$$Cl_3CSNHCH_2CH_2NHSCCl_3$$

XVIII

As anticipated, compound XVIII shows a wide range of activity (71, 72). However, the degree of activity is lower than that of the thiocarbamates. This may be attributed to a different rate of transformation of the two compounds into their active principles in the living cell.

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