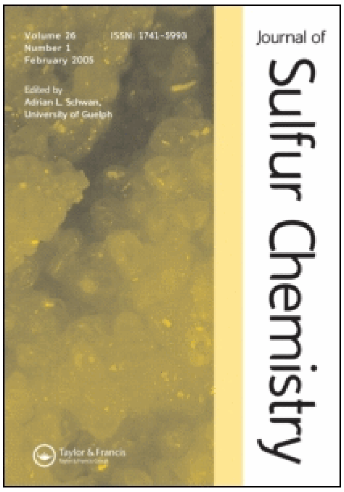

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CARBON CHLORIDE SULFIDES $C_xCl_yS_z$

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This review covers the preparation and reactions of carbon chloride sulfides, based on online CAS and Beilstein searches. One hundred and thirty-five compounds are listed together with 238 literature references. A section on unreported compounds with the composition $C_xCl_yS_z$ is also included.

Keywords: Carbon chloride sulfides; disulfides; oligosulfides; sulfenyl chlorides; sulfides; thiocarbonyl compounds

CONTENTS

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1. INTRODUCTION

As restrictive as the definition of carbon chloride sulfides $C_xCl_yS_z$ may sound to the casual reader it allows for a remarkably rich chemistry and encompasses, together with more exotic specimens, well-known chemical workhorses such as thiophosgene and trichloromethanesulfenyl chloride. One of us has, over almost four decades, gathered considerable experience in this area and we have therefore deemed it appropriate to present the state of the art to a broader audience. The chemistry of carbon chloride sulfides has benefited roughly equally from the efforts of industrial and academic chemists, a healthy state of affairs which adds to the fascination of this area of research.

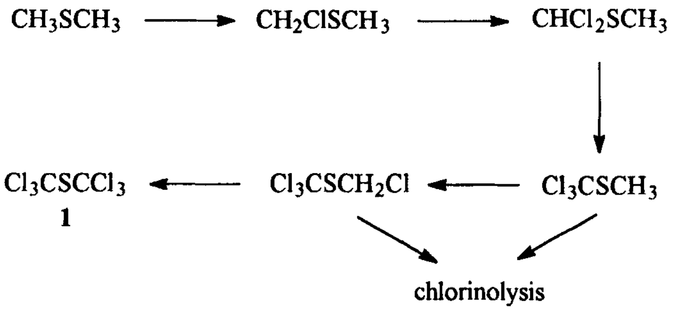
While a considerable number of mixed perhalo compounds (such as a plethora of trifluoromethyl compounds) would fit snugly into the framework depicted here this review has for practical reasons been restricted to the title compounds. Interested readers will be able to access this extended range of compounds via a large number of contemporary reviews on organic fluorine chemistry.

1. SULFIDES

1.1. Aliphatic Sulfides

1.1.1. Alkyl sulfides

Bis(trichloromethyl) sulfide **1** (m.p. 17 °C, b.p. 47 °C/0.2 mm Hg) has mainly been prepared by chlorination of dimethyl sulfide. Truce *et al.* prepared it in very low yield by chlorination of dimethyl sulfide with sulfuryl chloride.[1] By-products were found difficult to remove. Boberg *et al.*[2] prepared **1** by chlorination of dimethyl sulfide or a mixture of unsymmetric di-, tri-, and tetrachlorodimethyl sulfide with chlorine gas at 80 °C to give the product in 60%. The main problem in the synthesis was that the highly chlorinated dimethyl sulfides formed from unsymmetric tetrachlorodimethyl sulfide are subject to competing chlorinolysis.



This chlorinolysis has being attributed to the poorer donor ability of the unbonded electrons on the sulfur atom of the highly chlorinated compounds. No chlorinolysis occurred for **1** until 80 °C.[2,3] Moltzen *et al.* prepared **1** in good yield by the desulfurization of dichloro(trichloromethylthio)methanesulfenyl chloride upon treatment with chlorine for 12 h at room temperature.[4]

Bis(pentachloroethyl) sulfide **2** could be prepared in good yield by chlorination of bis(tetrachloroethyl) sulfide with chlorine gas in carbon tetrachloride in the presence of sulfuric acid.[5]

$$Cl_5C_2\text{-}S\text{-}C_2Cl_5$$

2

1.1.2. Alkenyl sulfides

Unsaturated sulfur-containing compounds have been found effective as fungicides. For example bis(trichloroethenyl) sulfoxide, prepared from bis(trichloroethenyl) sufide, is 100% effective for the control of *Panagerellus* and *Rhabditis*.[6]

Bis(trichloroethenyl) sulfide **3** (b.p. 71-3 °C/0.03 mm Hg) has been synthesized in 83% yield by addition of SCl_2 or trichloromethanesulfenyl chloride to dichloroacetylene in the presence of ferric chloride during 3 h at 30 °C, or by reduction of bis(trichloethenyl) sulfoxide in a mixture of acetic acid and acetic anhydride with 20% $TiCl_3$ in concentrated hydrochloric acid.[7]

Bis(trichloroethenyl) sulfide is oxidized to the corresponding sulfoxide when treated with 30% hydrogen peroxide in acetic acid.

$$CCl_2{=}CCl\text{-}S\text{-}CCl{=}CCl_2$$

3

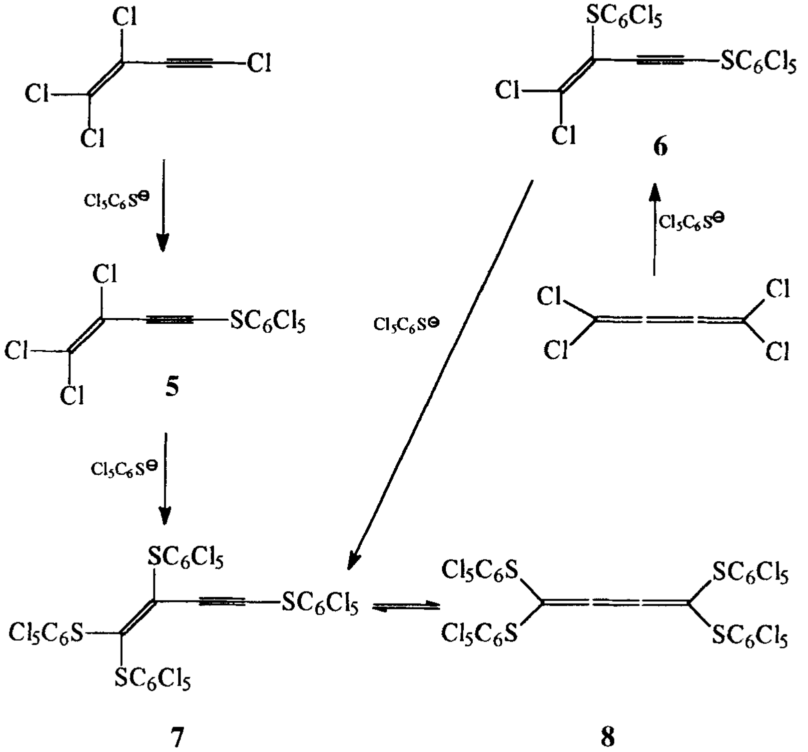
Bis(1,2,3,4,4-pentachloro-1,3-butadienyl) sulfide **4** is formed in nanogram quantities upon high-temperature treatment of fly ash with sulfur.[8] The metal catalyzed destruction of the macromolecules on the surface of the fly ash particles is dependent on the temperature (250–500 °C). The formation of **4** is favored over that of aromatic compounds at high temperatures.

$$CCl_2{=}CCl\text{-}CCl{=}CCl\text{-}S\text{-}CCl{=}CCl\text{-}CCl{=}CCl_2$$

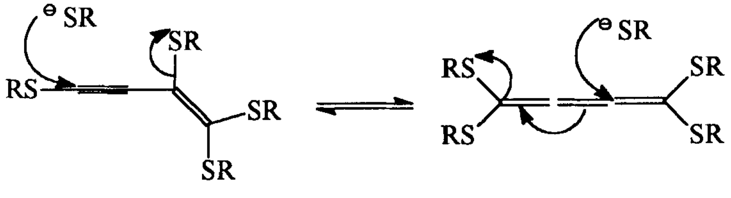
4

1.1.3. Butenynyl sulfides

Four compounds of this group have been reported.[9–12] They have been synthesized by nucleophilic attack of sodium pentachlorobenzenethiolate on perchlorobutenyne and perchlorobutatriene, respectively.



The mechanism of the transformation of **7** to **8** is assumed to be as follows:[12]



1,1,2-Trichloro-4-(pentachlorophenylthio)-1-buten-3-yne **5** (m.p. 100–1 °C) was obtained when perchlorobutenye was stirred with a suspension of sodium pentachlorobenzenethiolate in DMSO for 5 h.[10]

1,1-Dichloro-2,4-bis(pentachlorophenylthio)-1-butenyne **6** (m.p. 181 °C) was similarly obtained in 85% yield.[12]

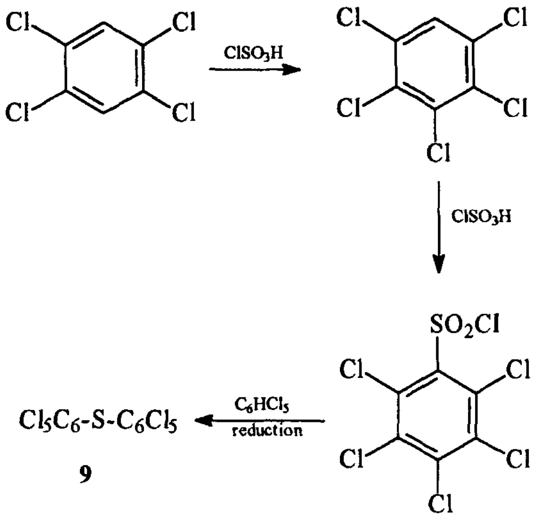
Tetrakis(pentachlorophenylthio)-1-buten-3-yne **7** (m.p. 297°C) has been prepared from perchlorobutenyne in 49% yield,[11] from **5** in 90% yield[12] and from **6** in 68% yield.[12]

1.2. Aromatic Sulfides

Silberrad utilized a mixture of disulfur dichloride and anhydrous aluminum chloride in sulfuryl chloride solution (BMC reagent) to obtain a polychlorinated benzene.[13] Kharasch and Ariyan,[14] Glidewell and Walton,[15] and Adrian *et al.*[16] employed the same reagent to convert diphenyl sulfide to bis(pentachlorophenyl) sulfide **9** (m.p. 265 °C) in about 60% yield.

The pattern of reactivity of BMC with arenes showed that the perchlorination is controlled by a step involving attack on the aromatic nucleus of an electrophile which may be either SCl_3^+ or $ClSO_2^+$.

Compound **9** could also be prepared when 1,2,4,5-tetrachlorobenzene was heated with chlorosulfonic acid.[17] The following equation shows the steps of the reaction.



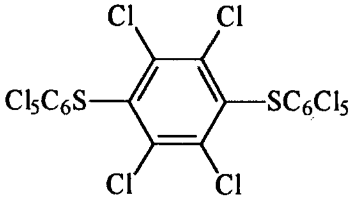
Attempts to oxidize **9** to the corresponding sulfoxide or sulfone with peracetic acid or chromium trioxide in acetic acid were unsuccessful.[18]

Irradiation for 150 h of a solution of **9** in carbon tetrachloride with a low pressure cold cathode mercury arc, housed in a Vycor 7910 tube, yields 42% of octachlorodibenzothiophene.[14]

Bis(pentachlorophenyl) sulfide and related compounds have been used to prepare fire-resistant resins.[19]

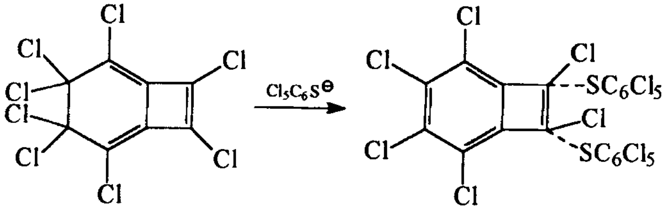
X-Ray spectroscopy has been used to determine the extent of conjugation between the sulfur atom and the aromatic rings of **9**.[20]

2,3,5,6-Tetrachloro-1,4-bis(pentachlorophenylthio)benzene **10** has been prepared by heating of hexachlorobenzene with anhydrous sodium sulfide at 100 °C for 5 h in a nitrogen atmosphere.[21] Water was added to the reaction mixture to give the pure compound.



10

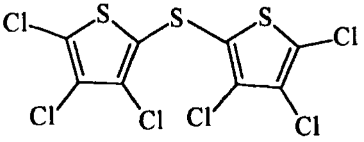
Sodium pentachlorobenzenethiolate as a nucleophile attacks very easily perchlorobicyclo[4.2.0]octa-1,5,7-triene at room temperature to give *cis*-2,3,4,5,7,8-hexachloro-7,8-bis(pentachlorophenylthio)bicyclo[4.2.0]octa-1,3,5-triene **11** (m.p. 297 °C).[22]



11

1.3. Heteroaromatic Sulfides

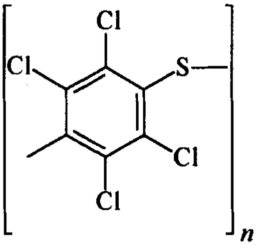
n-Butyllithium in hexane has been added to a solution of terachlorothiophene in ether at 15–20 °C to give 2,2′-thiobis(3,4,5-trichlorothiophene) **12** (m.p. 97–9 °C) in 62% yield.[23]



12

1.4. Polymeric Sulfides

Pure polythio(2,3,5,6-tetrachloro-1,4-phenylene) **13** has been prepared by heating of sodium pentachlorobenezenethiolate at 90–170 °C in pyridine.[24] Semi-conductive materials have been obtained from this compound.



13

2. DISULFIDES

2.1. Aliphatic Disulfides

2.1.1. Alkyl disulfides

2.1.1.1. Alkyl monodisulfides Prey *et al.* prepared bis(trichloromethyl) disulfide **14** (b.p. 131–5 °C/11 mm Hg) in 80% yield by photolysis of trichloromethanesulfenyl chloride in hexane.[25] Kaae and Senning purified the crude disulfide by repeated distillation at 87 °C/0.5 mm Hg, then bubbling through ozone/oxygen for complete decolorization.[26]

Hansen *et al.* prepared **14** in 81% yield when trichloromethanesulfenyl chloride and thiophosgene were allowed to react in acetonitrile.[27] Compound **14** could also be prepared in low yield when trichloromethanesulfenyl chloride was allowed to react with methylphosphonous acid mono- or diesters.[28]

Christensen and Senning reported the presence of bis(trichloromethyl) disulfide as a 0.8% contaminant in commercial trichloromethanesulfenyl chloride, prepared by reaction of carbon disulfide with chlorine gas.[29] The disulfide could be detected by gas chromatographic analysis.

Wilkes detected the presence of bis(trichloromethyl) disulfide in a technical grade of the fungicide captan [*N*-(trichloromethylthio)-4-cyclohexene-1,2-dicarboximide].[30] It was assumed that the disulfide is a product of the thermal decomposition of captan.[31] A study of the genotoxicity of **14** showed that it fails to induce a response in the small intestine nuclear aberration assay in a wide dose range under a variety of experimental conditions.[32]

$Cl_3C\text{-}SS\text{-}CCl_3$

14

It has been reported that bis(trichloromethyl) disulfide is extremely indifferent toward oxidizing agents.[26,33,34] Partial hydrolysis leads to the formation of the corresponding mono- and dicarbonyl compound:[35]

$Cl\text{-}CO\text{-}SS\text{-}CO\text{-}Cl$ $Cl_3C\text{-}SS\text{-}CO\text{-}Cl$

Dear and Gilbert were able to effect a halogen exchange reaction when they treated bis(trichloromethyl) disulfide with potassium fluoride at 160 °C.[36]

Pentachloroethanesulfenamide was dissolved in excess acetone and left at room temperature for 11 d to give bis(pentachloroethyl) disulfide **15** (m.p. 76–80 °C) in 13% yield rather than the expected imine.[37]

$Cl_5C_2\text{-}SS\text{-}C_2Cl_5$

15

2.1.1.2. Alkyl trisdisulfides Hansen and Senning reported that trichloromethanesulfenyl chloride reacts very slowly with bis(trichlo-romethyl) pentathiodipercarbonate even when neat sulfenyl chloride is used as the solvent.[38] If acetonitrile is used as reaction medium the reaction rate is dramatically enhanced.[39] Chlorotris(trichloromethyldithio)methane **16** (m.p. 78–9 °C) is formed in 49% yield. The pentachloroethyl derivative **17** (m.p. 148–9 °C) could be similarly prepared in 56% yield.

$$RSCl + (RSS)_2C{=}S \longrightarrow (RSS)_3CCl$$

16: $R = CCl_3$

17: $R = C_2Cl_5$

2.1.2. *Alkenyl disulfides*

Bis(trichloroethenyl) disulfide **18** has been reported in several patents.[40–45] Pentachloroethanesulfenyl chloride reacts with $M(CO)_n$ (M = Cr, Fe, Ni; n = 6, 5, 4) under mild conditions to give the corresponding disulfide with subsequent partial dehalogenation yielding **18**.[46] Laifa *et al.* found that a 55% yield of **18** is obtained upon reduction of pentachloroethanesulfenyl chloride with aqueous potassium iodide and sulfur dioxide in a diphasic dichloroethane/water system.[47] This occurs probably via bis(pentachloroethyl) disulfide, but other pathways cannot be ruled out.

$$Cl_2C{=}CCl\text{-}SS\text{-}CCl{=}CCl_2$$

18

2.2. Aromatic Disulfides

The preparation of pentachlorophenyl trichloromethyl disulfide **19** is not reported in the references collected in our search. However, it has been claimed as a component of a rubber vulcanization mixture.[48]

$$Cl_5C_6\text{-}SS\text{-}CCl_3$$

19

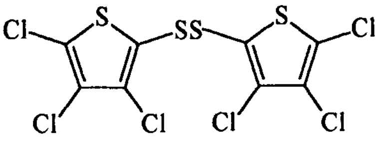
Pentachlorobenzenesulfenyl chloride reacts with water and mineral acid to give a mixture of bis(pentachlorophenyl) disulfide **20** and $Cl_5C_6\,SO_2SC_6Cl_5$.[49] Compound **20** has been used in polyamide preparation by polymerization of dicarboxylic acids with diamines.[50,51] It is also one of the components of a vulcanization mixture.[52]

$$Cl_5C_6\text{-}SS\text{-}C_6Cl_5$$

20

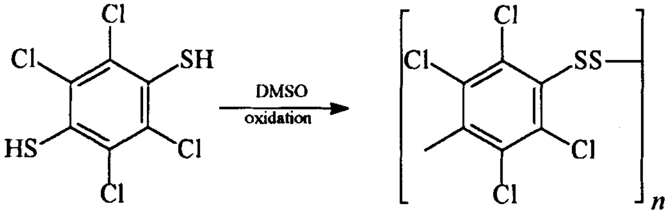
2.3. Heteroaromatic Disulfides

3,4,5-Trichloro-2-thiophenethiol, dissolved in aqueous sodium hydroxide, can be oxidized with iodine to bis(3,4,5-trichloro-2-thienyl) disulfide **21** (m.p. 78–9 °C) in 17% yield.[23,53]



21

The oxidation of aromatic 1,4-dithiols has been the subject of many studies. 1,4-Benzenedithiol has been reported to give polymeric disulfides.[54,55] Raasch reported that tetrafluoro-1,4-benzenedithiol can be oxidized with DMSO to give the corresponding four-unit macrocyclic tetrakisdisulfide.[56] 2,3,5,6-Tetrachloro-1,4-benzenedithiol gave an oxidation product **22** (m.p. 335–7 °C), but the determination of its molecular weight was precluded by its extreme insolubility.



22

3. OLIGOSULFIDES

3.1. Aliphatic Oligosulfides

3.1.1. Alkyl oligosulfides

Trichloromethanethiosulfenyl chloride reacts with thiophosgene in acetonitrile or with hydrogen sulfide at 30 °C in a tube containing charcoal granules to give bis(trichloromethyl) trisulfide **23** (m.p. 54–6 °C) in 28% yield.[27,57]

$Cl_3C\text{-}SSS\text{-}CCl_3$

23

Bis(trichloromethyl) trisulfide was detected by GC/MS in a technical grade of the fungicide captan.[30]

Seventeen oxidation products of **23** are theoretically possible. However, none of them could be obtained. At room temperature **23** fails to react with ozone, nickel peroxide, or peracetic acid, while treatment with peracetic acid at higher temperatures only affords water soluble products. It does not react with chloramine-T in absolute ethanol.[26]

The kinetics[58] and the dynamic behavior of an isothermal continuously stirred tank reactor and of a 2-element series of continuously stirred tank reactors in the course of the reaction of **23** with aniline and methanol[59] have been studied. The reaction is autocatalytic with a chain mechanism. The sulfur-sulfur bonds are probably the transferring part of the chain. The reaction is accelerated by nucleophilic agents (*e.g.* sodium methoxide, hydrogen sulfide, 2-mercaptobenzothiazole, and potassium iodide) even in very low concentrations.

Bis(trichloromethyl) trisulfide **23** is useful as seed disinfectant.[57] It also exhibits fungicidal[57,60–62] and insecticidal[57,60–63] effects.

Bis(trichloromethyl) tetrasulfide **24** (m.p. 38 °C) has been prepared in 92% yield by treatment of a solution of trichloromethanethiosulfenyl chloride in carbon tetrachloride with an aqueous solution of potassium iodide.[64] It could also be prepared in 52% yield when disulfur dichloride and thiophosgene were allowed to react in acetonitrile.[26] Steudel recently prepared **24** in 20% yield by reaction of the dinuclear titanocene oligosulfide $(C_5H_4CH_3)_4Ti_2S_4$ with trichloromethanesulfenyl chloride.[65]

$Cl_3C\text{-}SSSS\text{-}CCl_3$

24

Trichloromethanesulfenyl chloride reacts with titanocene pentasulfide, $(C_5H_5)_2TiS_5$, in carbon disulfide within 12–15 h. After removal of the by-products bis(trichloromethyl) heptasulfide **27** (m.p. 38 °C) can be obtained in 50% yield.[65]

Bis(trichloromethyl) heptasulfide is stable for weeks at 4 °C; however, prolonged heating to 40 °C or above results in a reaction according to the following equation:[65]

$$2\ (CCl_3)_2S_7 \rightleftharpoons (CCl_3)_2S_{(7-x)} + (CCl_3)_2S_{(7+x)}$$

This reaction was followed by reversed-phase HPLC and all members of the series with 4–12 sulfur atoms were observed.[65]

$Cl_3C\text{-}S_n\text{-}CCl_3$

24-32:
$n = 4\text{-}12$

Pentachloroethanethiosulfenyl chloride and thiophosgene, when allowed to react in acetonitrile at 40 °C for 5 h, afford pentachloroethyl trichloromethyl trisulfide **33** (m.p. 51–3 °C)in 71% yield.[27]

$Cl_5C_2\text{-}SSS\text{-}CCl_3$

33

Bis(pentachloroethyl) tetrasulfide **34** (m.p. 158 °C) has been prepared according to the following equation:[37]

$$Cl_5C_2\text{-}SS\text{-}COCH_3 \xrightarrow[-CH_3COCl]{Cl_2} Cl_5C_2SSCl + \underset{\mathbf{34}}{Cl_5C_2\text{-}S_4\text{-}C_2Cl_5}$$

Reaction of pentachloroethanesulfenyl chloride with hydrogen sulfide requires elevated temperature and extended time. Instead of the expected bis(pentachloroethyl) trisulfide only the pentasulfide **35** could be isolated as a yellow oil in 36% yield.[47]

$Cl_5C_2\text{-}S_5\text{-}C_2Cl_5$

35

A suspension of bis(pentachloroethyldithio)chloromethanesulfenyl chloride in acetonitrile was stirred at room temperature for 7 d to give dichloro(pentachloroethyldithio)methyl pentachloroethyl trisulfide **36** (m.p. 45–49 °C).[39]

$Cl_5C_6\text{-}SSS\text{-}CCl_2\text{-}SS\text{-}C_6Cl_5$

36

A mixture of pentachloroethanethiosulfenyl chloride and bis(pentachloroethyl) pentathiodipercarbonate was stirred overnight in acetonitrile at room temperature to give chlorobis(pentachloroethyldithio)methyl pentachloroethyl trisulfide **37** (m.p. 116–8 °C) in 4% yield.[27]

$$(Cl_5C_2SS)_2CCl\text{-}SSS\text{-}C_2Cl_5$$

37

Chloromethylidenetris(trichloroethyl trisulfide) **38** (m.p. 98–9 °C) has been prepared in 13% yield by reaction of trichloromethanethiosulfenyl chloride and barium trithiocarbonate in acetonitrile.[39]

$$(Cl_3CSSS)_3CCl$$

38

3.1.2. Alkenyl oligosulfides

Kohn prepared bis(trichloroethenyl) trisulfide **39** by the reaction of tetrachloroethanesulfenyl chloride with hydrogen sulfide in ether at 20 °C for 64 h.[66]

The reduction of pentachloroethanesulfenyl chloride with aqueous potassium iodide/sodium thiosulfate in dichloroethane/water gives **39** in 45% yield.[47]

Bis(trichloroethenyl) trisulfide has been claimed as a seed disinfectant.[66]

$$Cl_2C{=}CCl\text{-}SSS\text{-}CCl{=}CCl_2$$

39

3.2. Aromatic Oligosulfides

Pentachlorophenyl trichloromethyl trisulfide **40** (m.p. 107–9 °C) has been prepared in 84% yield by reaction of equimolecular amounts of pentachlorothiophenol and trichloromethanethiosulfenyl chloride in an inert solvent.[67]

$$Cl_5C_6\text{-}SSS\text{-}CCl_3$$

40

Pentachorobenzenesulfenyl chloride in methylene chloride reacts rapidly with sodium trithiocarbonate to give bis(pentachlorophenyl) trisulfide **41** (m.p. 193–6 °C).[39]

$Cl_5C_6\text{-}SSS\text{-}C_6Cl_5$

41

Compound **41** has been used in the preparation of a vulcanization mixture.[48,52]

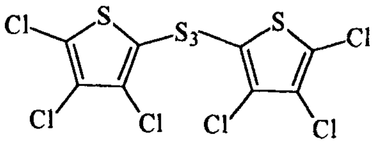
Bis(pentachlorophenyl) tetrasulfide **42** has been described a component of a vulcanization mixture.[52,68] Its preparation is, however, not reported in the references collected in our search.

$Cl_5C_6\text{-}SSSS\text{-}C_6Cl_5$

42

3.3. Heteroaromatic Oligosulfides

3,4,5-Trichloro-2-thiophenesulfenyl chloride reacts with hydrogen sulfide to give bis(3,4,5-trichlorothienyl) trisulfide **43** (m.p. 84–7 °C) in 12% yield.[53]



43

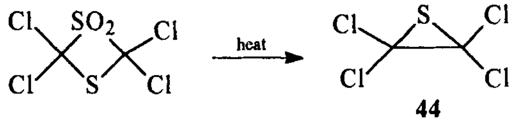
Compound **43** exhibits marginal pesticidal activity.[53]

4. HETEROCYCLIC COMPOUNDS

4.1. Thiiranes

Phenyl(bromodichloromethyl)mercury has been found to react with sulfur, thiophosgene, carbon disulfide, or with alkyl isothiocyanates to give 2,2,3,3-tetrachlorothiirane **44** (b.p. 36–8 °C/0.1 mm Hg) in moderate yields.[68–70]

Schork and Sundermeyer found that 2,2,4,4-tetrachloro-1,3-dithietane 1,1-dioxide can be converted to **44** by heating in a mixture of acetic acid and water.[71]

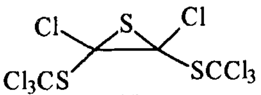


44

Pyrolysis of the neat dioxide at 450 °C *in vacuo* gave **44** in 85% yield.[71] Tetrachlorothiirane is stable at room temperature. Desulfurization can be accomplished by treatment with phosphorus trichloride or with triphenylphosphine in ether. Reaction with diethylamine in benzene at 50 °C gives a yellow-brown nonvolatile product. Anhydrous hydrogen chloride is without effect on tetrachlorothiirane at room temperature. Chlorination at room temperature results in desulfurization, giving hexachloroethane.[68–70]

Compound **44** is useful in the manufacturing of polymers, as vulcanizing agent, insecticide and in flameproofing.[68]

2,3-Bis(trichloromethylthio)-2,3-dichlorothiirane **45** (m.p. 83–5 °C) could be obtained as a minor by-product during the synthesis of trichloromethyl chlorodithioformate by the reaction of carbon monosulfide with trichloromethanesulfenyl chloride.[72]



45

4.2. Dithiiranes

Dichlorodithiirane **125** has been postulated as an elusive intermediate (cf. Section 7.6).

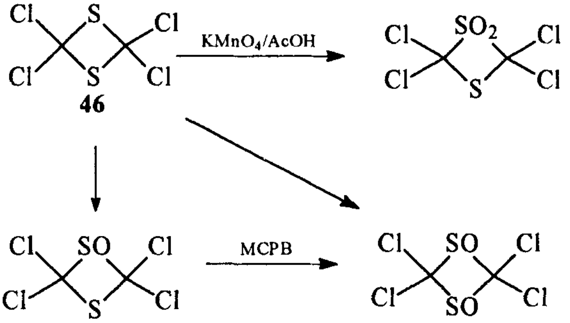
4.3. Dithietanes

Photochemical dimerization of thiophosgene by UV light leads to the formation of 2,2,4,4-tetrachloro-1,3-dithietane **46**. [72–75]

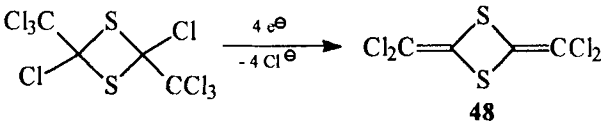
Bose *et al.* studied the crystal structure of **46**.[76] Its UV spectrum was interpreted in terms of D_{2n} symmetry with the aid of computer resolution and CNDO calculations.[77]

Oxidation of **46** with potassium permanganate in glacial acetic acid leads to the formation of the 1,1-dioxide. [73-79] Oxidation with *m*-chloroperbenzoic acid at 0 °C leads to the corresponding monoxide, then to the 1,3-dioxide. A direct oxidation to the 1,3-dioxide is also possible.[73]

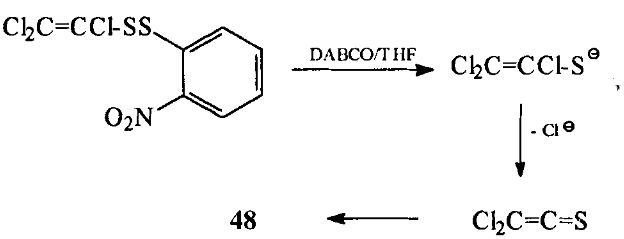
Cathepsine D, obtained from bovine spleen, was inactivated by **46**.[78]



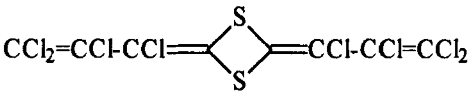
trans-2-4-Bis(trichloromethyl)-2,4-dichloro-1,3-dithietane **47** (m.p. 218 °C) has been prepared by the facile photodimerization of trichlorothioacetyl chloride in concentrated methylene chloride solution in 23% yield.[80] The *trans*-structure was established by X-ray crystallography. Pyrolysis of **47** regenerates the monomer.[80] Compound **47** can be reduced electrochemically in an H-cell at room temperature according to the following equation.[81]



2,4-Bis(dichloromethylene)-1,3-dithietane **48** (m.p. 125-6 °C) could also be obtained from the reaction of 2-nitrophenyl 1,2,3-trichloroethenyl disulfide with 1,4-diazabicyclo[2.2.2]octane (DABCO) in dry THF.[81,82]

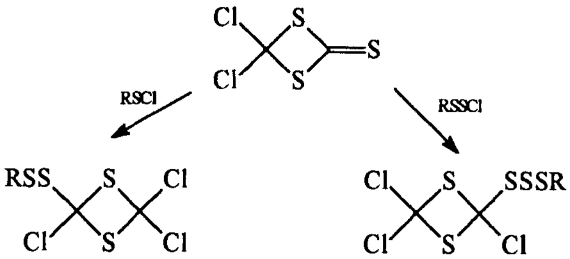


Dichlorothioketene could be generated by flash vacuum pyrolysis of **48**.[83] 2,4-Bis(1,2,3,3-tetrachloro-2-propenylidene)-1,3,-dithietane **49** has been prepared by reaction of 2-nitrophenyl 1,2,3,4,4-pentachlorobuta-1,3,-dienyl disulfide with DABCO in dry THF.[82]



49

Chlorosulfenylation and chlorothiosulfenylation of 4,4-dichloro-1,3-dithietane-2-thione proceeds rapidly in acetonitrile according to the following equation:[84]



50: R = CCl_3

51: R = C_2Cl_5

52: R = CCl_3

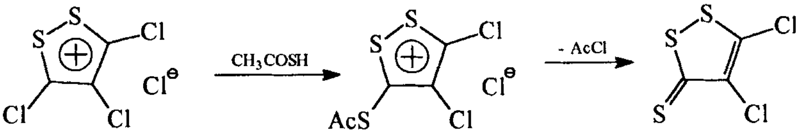
53: R = C_2Cl_5

The high reactivity of this dithietanethione can be explained by reduction of ring strain upon $sp^2 \rightarrow sp^3$ rehybridization of C-2 of the dithietane system.

2,2,4-Trichloro-4-(trichloromethyldithio)-1,3-dithietane **50** (m.p. 59–61 °C), 2-(pentachloroethyldithio)-2,4,4-trichloro-1,3,dithietane **51** (m.p. 125–6 °C), 2,2,4-trichloro-4-(trichloromethyltrithio)-1,3-dithietane **52** (m.p. 112–3 °C), and 2-(pentachloroethyltrithio)-2,4,4-trichloro-1,3-dithietane **53** (m.p. 115–22 °C) have been obtained from 4,4-dichloro-1,3-dithietane-2-thione and the appropriate sulfenyl or thiosulfenyl chlorides, respectively.

4.4. Dithioles

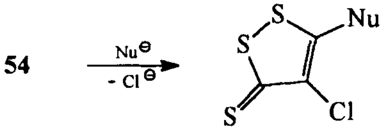
3,4,5-Trichloro-1,2,-dithiolium chloride reacts with a solution of thioacetic acid in dry benzene to give 4,5-dichloro-3-thioxo-3*H*-1,2-dithiole **54** (m.p. 76 °C) in 35% yield.[85]



54

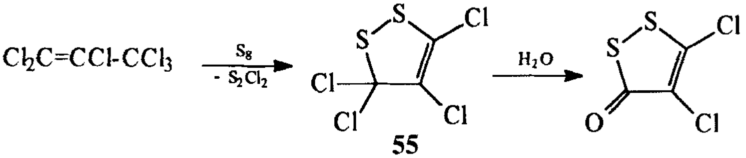
Compound **54** reacts with *N*,*N*-dichlorobenzenesulfonamide and *N*,*N*-dichloro-*N*′,*N*′-dimethylsulfamide to give the corresponding *N*-(4,5-dichloro-3*H*-1,2-dithiol-3-ylidenyl)amides.

It reacts with nucleophilic agents (e.g., sodium benzenesulfinate, morpholine, thiophenol, and aniline) to give the corresponding derivatives.[85]



Hexachloropropene and sulfur has been heated at 180–90 °C for 8 h in the absence of moisture to afford 3,3,4,5-tetrachloro-3*H*-1,2-dithiole **55** (m.p. 215–20 °C) in 30% yield.[86]

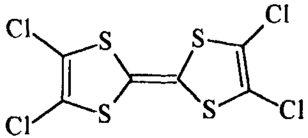
It has also been reported that lowering of the reaction temperature to 160 °C increases the yield to 65%.[87]



55

The dichloromethylene group of **55** could be easily attacked with water or methanol to give 3,4-dichloro-1,2-dithiol-2(2*H*)-one.[86,87]

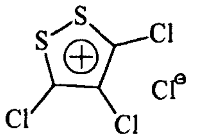
4,5-Dichloro-2-(4,5-dichloro-1,3-dithiol-2-ylidene)-1,3-dithiole **56** (m.p. 221–3 °C) could be prepared when a solution of 2-(1,3-dithiol-2-ylidene)-1,3-dithiol in dry THF was lithiated with phenyllithium, butyllithium, or lithium diisopropylamide, followed by chlorination with hexachloroethane or *p*-toluenesulfonyl chloride.[88–90]



56

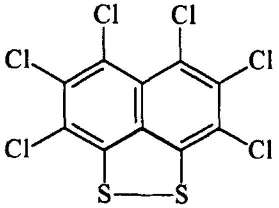
The crystal structure,[90] cyclic voltammetric data,[90] and MNDO calculations[91] of **56** have been reported.

A mixture of hexachloropropene and sulfur was heated at 180–190 °C until disulfur dichloride started to reflux. The reflux continued 90 min to give 3,4,5-trichloro-1,2-dithiolium chloride **57** (m.p. 235 °C) in 65% yield. This compound is easily hydrolyzed with water at room temperature to 4,5-dichloro-1,2-dithiol-2(2*H*)-one.[92]



57

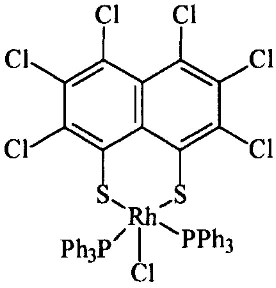
A solution of disodium disulfide (prepared from sodium sulfide and sulfur) was allowed to react with octachloronaphthalene to give hexachloronaphtho[1,8-*cd*]-1,2-dithiole **58** (m.p. 283-5 °C) in 88% yield.[93,94] Its crystal structure has been reported.[95,96]



58

Oxidation of **58** with chromium trioxide in boiling acetic acid gives the 1-oxide. Treatment of **58** with Raney nickel in 2-(diethylamino)ethanol at 160 °C for 60 min leads to the formation of 2,3,4,5,6,7-hexachloronaphthalene.[94]

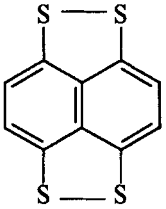
The trinuclear nickel complex [$Ni_3(PPh_3)_3(S_2C_{10}Cl_6)_3$] has been prepared by reaction of equimolecular amounts of [Ni(cycloocta-1,5-diene), PPh_3, and **58**.[97] The latter also reacts with $RhC(PPh_3)_3$ to give the following complex.[98]



Fusion with sulfur at 320 °C converts **58** into a bis-1,2-dithiole derivative.[93]

A mixture of octachloronaphthalene and sulfur was fused to give 3,4,7,8-tetrachloronaphtho[1,3-*cd*:4,5-*c'd'*;]bis[1,2]dithiole **59** (m.p. 347–9 °C) in 73% yield.[93,99]

The electric conductivity and the electronic structure of this compound have been studied.[100]



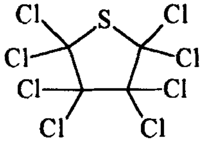
59

Oxidation of **59** with chromic acid in acetic acid gives the corresponding tetraoxide.[99] It gives a complex titanocene compound upon treatment with titanocene chloride in the presence of sodium tetrahydridoborate and tetra-*n*-butylammonium bromide in DMF.[101] Compound **59** reacts with $Pt(PPh_3)_4$ to give a platinum complex with interesting electrochemical properties.[102] It mixes with linear, branched, or crosslinked polymers to produce antistatic and electrically conductive polymers and molding compositions containing charge transfer complexes.[103]

4.5. Thiophenes

4.5.1. Monocyclic thiophenes

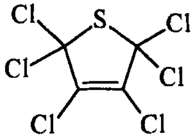
The chlorination of thiophene at 100 °C and under a pressure of 30 atm. with chlorine leads to the formation of octachlorotetrahydrothiophene **60**.[104] Chlorination of tetrachlorothiophene or hexachloro-2,5-dihydrothiophene also leads to **60** in good yields.[105–107]



60

This compound showed good fungicidal activity.[105] It is oxidized to octachlorotetrahydrothiophene 1,1-dioxide when treated with chromium trioxide in acetic acid.[108] It can be hydrolyzed with sulfuric acid to give dichloromaleic anhydride and tetrachlorosuccinic anhydride.[106] Fluorination with anhydrous HF in the presence of $SbCl_5$ gives tetrachlorothiophene and a mixture of polychlorofluorotetrahydrothiophenes.[109]

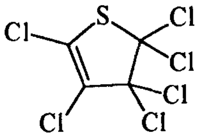
A cold solution of tetrachlorothiophene in carbon tetrachloride was saturated with chlorine gas and then exposed to sunlight for 10 d to give 2,2,3,4,5,5-hexachloro-2,5-dihydrothiophene **61** (m.p. 40 °C) in 85% yield.[107]



61

Chlorination of **61** leads to **60**.[107] The dechlorination of **61** to tetrachlorothiophene can be accomplished by heating with sulfur for 4 h at 200 °C[107,100] or by heating with SCl_2 or copper powder.[107] Hydrolysis with sulfuric acid leads to the formation of tetrachloro-2,5-dioxotetrahydrothiophene.[107,111]

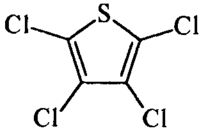
Hexachloro-2,3-dihydrothiophene **62** has been assigned a CAS registry number without reference to any document.



62

Chlorination of thiophene in the presence of ferric chloride gives 2,3,4,5-tetrachlorothiophene **63** (b.p. 61–4 °C/1.2 mm Hg, m.p. 29–30 °C) in 48% yield.[112]

Compound **63** could also be prepared when a solution of 2,5-dichlorothiophene in thionyl chloride reacted with aluminum chloride.[112] It has furthermore been prepared by dechlorination of **60** or **61**.[109,110,113] Sulfur reacts with perchlorobutadiene to give **63**.[92]



63

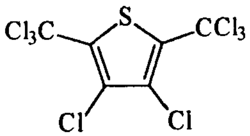
Swindlehurst reported that **63** is a pollutant in the Mediterranean region.[114] It has been described as one of the organic compounds in hazardous waste incinerator flue gas and has been detected by capillary gas chromatography.[115]

It can be chlorinated to **60**[104] and **61**.[107] 2,3,5-Trichlorothiophene can be produced by entrainment Grignard reaction of **63**, followed by hydrolysis.[112]

Silver difluoride reacts with **63** at 0 °C to give 2,2,5,5-tetrafluoro-3,4-dichloro-2,5-dihydropthiophene.[113] Halogen-metal exchange of tetrachlorothiophene with butyllithium at –70 °C gives 3,4,5-trichloro-2-thienyllithium.[116] Electrochemical trimethylsilylation of **63** has been carried out. The reduction potential of **63** has been determined by cyclic voltammetry.[117]

Compound **63** has been used in the synthesis of thienylpyrrole fungicides[118] and thienylpyrrolecarbonitrile insecticides and acaricides.[119]

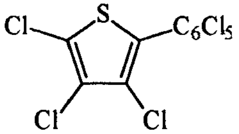
When chlorine was passed through a solution of 2,5-bis(dibromomethyl)-3,4-dibromothiophene in carbon tetrachloride with UV irradiation for 24 h 2,5-bis(trichloromethyl)-3,4-dichlorothiophene **64** (m.p. 83–6 °C) was obtained in low yield.[113]



64

Treatment of **64** with silver difluoride results in the exchange of the side chain chlorine atoms by fluorine to give 2,5-bis(trifluoromethyl)-3,4-dichlorothiophene.[113]

2,3,4-Trichloro-5-(pentachlorophenyl)thiophene **65** has been prepared by coupling of (pentachlorophenyl)copper with 2,3,4-trichloro-5-iodothiophene in a high boiling ether.[120]

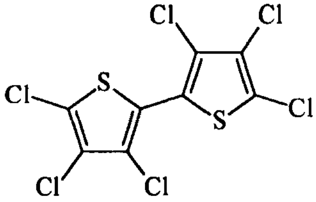


65

Halogen-metal exchange reactions of **65** with *n*-butyllithium give the corresponding mono- and dilithium reagents in good yields, magnesium reacting preferentially in the homocyclic part of the molecule.[121]

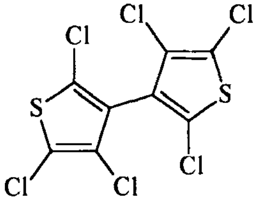
4.5.2. *Dithienyls*

Hexachloro-2,2′-dithienyl **66** (m.p. 187–9 °C) has been prepared by an intermolecular Ullmann reaction. Thus, a suspension of 2,3,4-trichloro-5-iodothiophene and copper bronze in DMF was stirred under reflux during 1 h to give **66** in 75% yield.[122] It could also be prepared by self-condensation of 2,3,4-trichlorothiophene in the presence of $Al(OH)_3$ as a catalyst or from **61** and $Al(OH)_3$.[123]



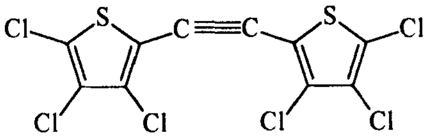
66

2,2′,4,4′-Tetrabromo-3,3′-dithienyl has been treated with chlorine in carbon tetrachloride to give hexachloro-3,3′-dithienyl **67** (m.p. 130–2 °C) in 81% yield.[124]



67

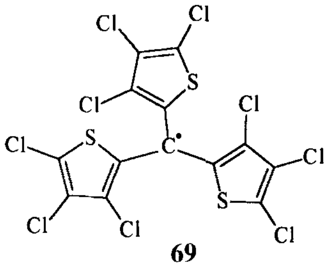
2,2′-(1,2-Ethynediyl)bis(3,4,5-trichlorothiophene) **68** has been prepared from (trichloro-2-thienyl)copper.[125]



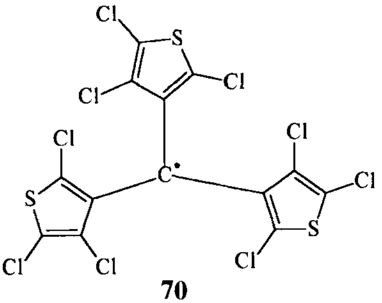
68

4.5.3. Trithienylmethyls

Tris(3,4,5-trichloro-2-thienyl)methyl radical **69** and tris(2,4,5-trichloro-3-thienyl)methyl radical **70** have been formed from the corresponding carbinols by treatment of their solutions in acetonitrile/trifluromethanesulfonic acid with tetrabutylammonium iodide.



69

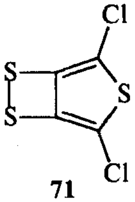


70

These radicals were then studied by ESR spectroscopy. The 2-thienyl radical is unstable, disappearing within tens of minutes at 23 °C. The 3-thienyl radical is stable for many hours.[116]

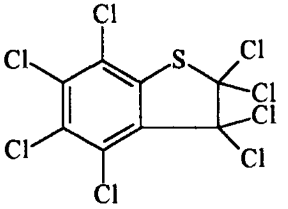
4.5.4. Condensed Thiophenes

2,5-Dichlorothietano[2]thiophene **71** (m.p. 80 °C, dec.) has been prepared by reaction of 3,4-dichloro-2,5-dihydrothiophene with disulfur dichloride in 90% yield.[126]



71

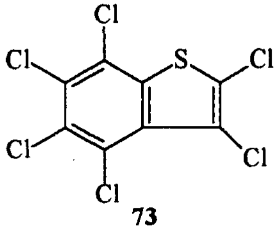
Chlorine reacts with benzothiophene in the presence of iodine to form octachloro-2,3-dihydrobenzothiophene **72** (m.p. 117–8 °C) in 59% yield.[108]



72

Oxidation of **72** with chromium trioxide in acetic acid provides the corresponding 1,1-dioxide.[108] Pyrolysis of **72** at 240 °C or treatment with zinc gives hexachlorobenzothiophene[108] **73** (m.p. 158–9 °C).

Neumann and Bender prepared **73** by reaction of benzothiophene with chlorine at 300 °C in a fixed or fluidized bed reactor in the presence of a halogenating catalyst (active carbon, coke, Al_2O_3, silica gel, or mixtures thereof).[127]



73

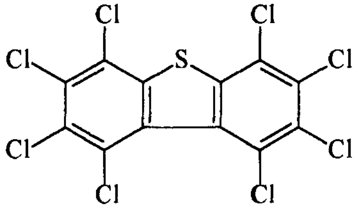
Compound **73** has been identified in waste gas washing water.[128]

Oxidation of **73** with pertrifluoroacetic acid gives the corresponding 1,1-dioxide;[129] oxidation with chromium trioxide in acetic acid gives hexachloro-2,3-dihydrobenzothiophen-2-one.[108] It reacts with one equivalent or excess butyllithium to give the 2-lithio or 2,6-dilithio derivative, respectively. It gives with magnesium a mixture of the 2- and 2,6-Grignard reagents. Its reaction with $LiAlH_4$ results in hydrodechlorination at C-2.

Sodium benzenethiolate replaces randomly the chlorine atom of the five-membered ring, while monosubstitution can be achieved by reaction with sodium isopropoxide in pyridine. Catalytic hydrogenation gives 4,5,6,7-tetrachlorobenzothiophene.[129]

Treatment of dibenzothiophene with chlorine in the presence of iodine in a pressure vessel[108] or in the presence of iron(iii) chloride[130] gives octachlorodibenzothiophene **74** (m.p. 304–7 °C) in 84% yield. Compound **74** could also be prepared in 62% yield when a solution of pentachlorobenzenesulfenyl chloride in carbon tetrachloride was irradiated for 150 h in a low pressure cold cathode mercury arc, housed in a Vycor 7910 tube.[14]

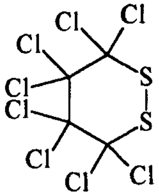
Miltsov *et al.* prepared **74** by reaction of polychlorobiphenyl with $ClSO_3H$ to give the corresponding sulfone which was subsequently reduced by treatment with $LiAlH_4$.[131]



74

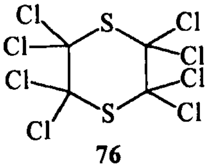
4.6. Dithianes and Dithiins

Octachloro-1,2-dithiane **75** (m.p. 218 °C) has been obtained as a by-product of the reaction of tetrachloroethylene with disulfur dichloride in the presence of anhydrous aluminum chloride.[132]



75

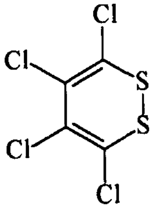
A solution of tetrachloro-1,4-dithiin in carbon tetrachloride was saturated for one week with chlorine in the dark at room temperature to give octachloro-1,4-dithiane **76** (m.p. 174 °C) in 50% yield.[132] Addition of anhydrous aluminum chloride increases the yield to 85%.



76

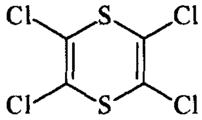
Reduction of **76** with zinc in acetic acid gave the corresponding tetrachlorodithiin.[132]

Tetrachloro-1,2-dithiin **77** (m.p. 138–9 °C) has been prepared in 13% yield by reaction of octachloro-1,2-dithiane with zinc in acetic acid.[132]



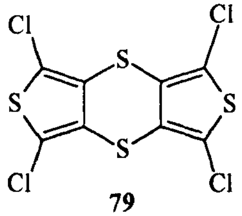
77

Tetrachloro-1,2-dithiin **78** (m.p. 129 °C) was formed as a by-product during the reaction of tetrachloroethylene with disulfur dichloride and anhydrous aluminum chloride in 6% yield.[132]



78

The oxidation of **78** with hydrogen peroxide in acetic acid affords the corresponding monosulfoxide. Chlorination with chlorine leads to the formation of octachloro-1,4-dithiane.[132] The reaction of 2,5-dichloro-3,4-dilithiothiophene with an equivalent amount of disulfur dichloride gave a mixture of products. Tetrachloridithieno[3,4-*b*:3′,4′-*e*][1,4]dithiin **79** (m.p. 283 °C), the major product, was obtained in 35% yield.[126,133]



79

4.7. Trithianes

2,4,6-Tris(dichloromethylene)-1,3,5-trithiane (m.p. 126 °C) has been prepared by dehydrochlorination of 2,4,6-tris(trichloromethyl)-1,3,5-trithiane. Its chlorination yields 2,4,6-trichloro-2,4,6-tris(trichloromethyl)-1,3-5-trithiane (m.p. 175 °C)[233] while its pyrolysis fails to generate the expected dichlorothioketene **113** (cf. Section 7.2).[234]

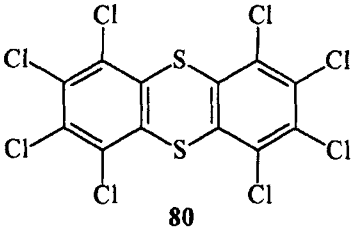
4.8. Tetrathianes

3,3,6,6-Tetrachloro-1,2,5,6-tetrathiane is formed in miscellaneous reactions, most likely by dimerization of the hypothetical chlorothiocarbonylsulfenyl chloride **127**.[235]

4.9. Thianthrenes

Reaction of sulfur with tetrachloro-*o*-phenylenemercury trimer $(HgC_6Cl_4)_3$, the heterocycle $Te_2(C_6Cl_4)_2$ hexachlorobenzene or with pentachloroiodobenzene in the presence of iodine gives octachlorothianthrene **80** (m.p. > 360 °C).[14,134,135]

Compound **80** was isolated after photolysis of pentachlorobenzenesulfenyl chloride in carbon tetrachloride for 24 h as a highly insoluble crystalline product.[14]

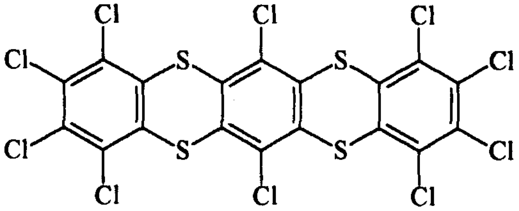


80

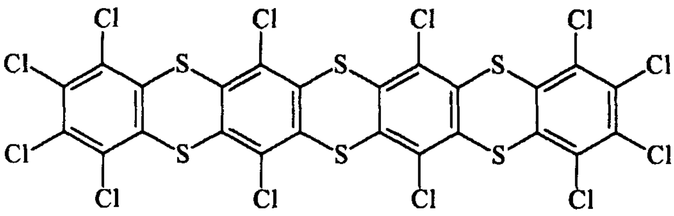
It has been detected as a pollutant formed from the pentachlorothiophenol used in vulcanization. It is assumed to originate by condensation of pentachlorobenzenethiolate.[136]

Octachlorothianthrene is used as a co-catalyst with $SbCl_3$, $FeCl_3$, or PbS in the chlorination of alkylbenzenes.[137]

Decachloro[1,4]benzodithieno[2,3-*b*]thianthrene **81**, and dodecachloro[1,4]dithieno[2,3-*b*:5,6-*b*]dithianthrene **82** can be obtained from hexachlorobenzene and excess sulfur at 300 °C.[135]



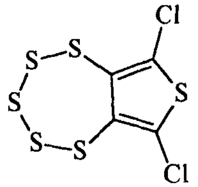
81



82

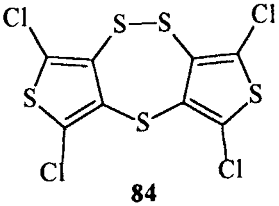
4.10. Seven-membered Rings

3,4-Dilithio-2,5-dichlorothiophene reacts with two equivalents of sulfur to give $(C_4Cl_2S)(SLi)_2$, which can be converted to 6,8-dichlorothieno-[3,4-*f*][1,2,3,4,5]pentathiepin **83** (m.p. 126 °C) by treatment with sulfur dichloride.[126]



83

1,3,6,8-Tetrachlorodithieno[3,4-*c*:3′,4′-*f*][1,2,5]trithiepin **84** has been obtained as one of a range of compounds resulting from the reaction between 2,5-dichloro-3,4-dilithiothiophene and disulfur dichloride. Compound **84** was detected by mass spectroscopy.[126]

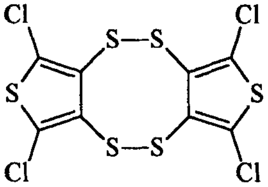


84

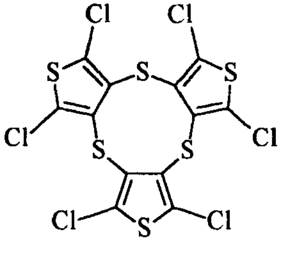
4.11. Macrocycles

1,3,6,8-Tetrachlorodithieno[3,4-*c*:3′,4′-*g*]tetrathiocin **85** (m.p. 171 °C) and 1,3,6,8,10,12-hexachlorotrithieno[3,4-*c*:3′,4′-*f*:3″,4″-*i*]tetrathionin **86** (m.p. 224 °C) could be isolated from a mixture of compounds obtained by reaction of 2,5-dichloro-3,4-dilithiothiophene with sulfur dichloride by fractional crystallization from toluene or by column chromatography on alumina.[128] A polymeric material could be obtained from the above reaction with the structure $[(C_4Cl_2S)_2]_x$. This material could be depolymerized in boiling nitrobenzene to give **85**.[126]

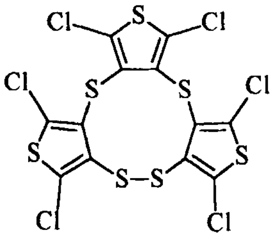
2,3,5,7,9,11-Hexachlorotrithieno[3,4-*b*:3′,4′-*e*:3″,4″-*h*][1,4,7]trithiecin **87** could be obtained from the same mixture and was detected by mass spectroscopy.[126]



85

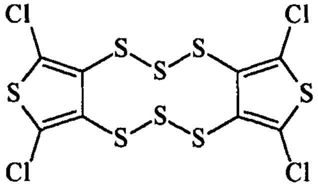


86



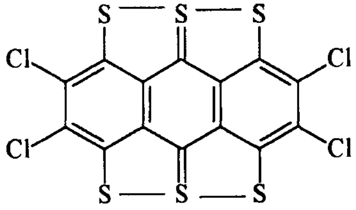
87

1,3,7,9-Tetrachlorodithieno[3,4-*d*:3′,4′-*i*][1,2,3,6,7,8]hexathiecin **88** (m.p. 228 °C) has been prepared by reaction between sulfur dichloride and $(C_4Cl_2S)(SLi)_2$, obtained from 2,5-dichloro-3,4-dilithiothiophene and sulfur.[126]



88

The commercial dyestuff indanthrene olive GG has been obtained by the action of disulfur dichloride on anthracene. It was assumed that this dye has the structure tetrachlorohexacyclopenta[*mno*]pentaleno[2,1,6,5-*fghi*]aceanthrylene **89**.[138]



89

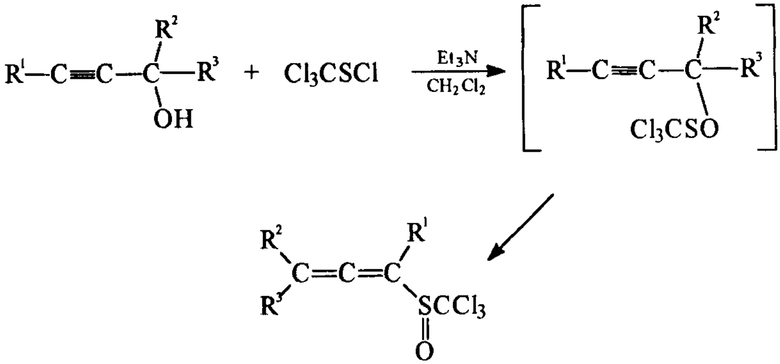
5. SULFENYL CHLORIDES

5.1. Monosulfenyl Chlorides

The commercially available trichloromethanesulfenyl chloride **90** is prepared by chlorination of carbon disulfide in the presence of iodine, or of thiophosgene.[139–147]

Compound **90** reacts with titanocene pentasulfide $(C_5H_5)TiS_5$ to give the heptasulfane $(CCl_3)_2S_7$ and with $(C_5H_4CH_3)_4Ti_2S_4$ to yield the tetrasulfane $(CCl_3)_2S_4$.[59]

Highly dienophilically reactive allenyl trichloromethyl sulfoxides were obtained from the reaction of propargyl alcohol with **90** according to the following equation:[148]



Compound **90** reacts with different *N*-monosubstituted benzophenone hydrazone derivatives to give the corresponding *N*-sulfenyl derivatives with excellent insecticidal activity combined with low mammalian toxicity.[149,150]

It is used to introduce a trichloromethylthio group in different phenylpyrazoles to give compounds having arthropodicidal, nematocidal, protozoacidal, and anthelmintic activities.[152] It reacts with thioacetamide and thiobenzamide in refluxing chloroform to give 3-methyl- and 3-phenyl-1,2,4-dithiazole-5-thione, respectively.[238] Bis(trichloromethyl) pentathiodicarbonate is formed by reaction of **90** with metal trithiocarbonates.[39] Gaseous carbon monosulfide reacts with **90** to give trichloromethyl chlorodithioformate in high yield.[72]

Pentachloroethanesulfenyl chloride **91** has been prepared by the reaction of tetrachloroethylene with sulfur dichloride in the presence of benzoyl or cumene peroxide as catalyst.[153]

Cl_5C_2-SCl
91

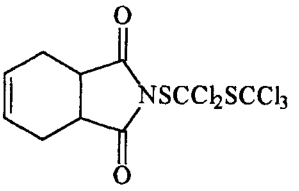
Compound **91** is reduced with $SnCl_2$ and HCl to give the unstable trichlorothioacetyl chloride.[80,154] Laifa *et al.* reduced **91** with SO_2/I^- to yield **18**, with $S_2O_3^{2-}/I^-$ to give **39**, and with H_2S to give **35**.[56] Compound **91** adds to 4,4-dichloro-1,3-dithietane-2-thione in acetonitrile solution.[84]

Reaction of **91** with ammonia and amines gives the corresponding pentachloroethanesulfenamides.[155,156] It reacts with imidazolidinedione derivatives to give the corresponding *N*-pentachloroethylthio derivatives which are active against *Botrytis cinerea* on beans.[157]

Chlorine in carbon tetrachloride has been added to a solution of trichloromethyl chlorodithioformate in the same solvent at 0 °C to give dichloro(trichloromethylthio)methanesulfenyl chloride **92** (m.p. 134–7 °C/ 11 mm Hg) in 60% yield.[72]

Cl_3C-S-CCl_2-SCl
92

Chlorine desulfurizes **92** to give **1** in good yield. Compound **92** reacts with tetrahydrophthalimide anion, thioacetic acid, and carbon monosulfide, respectively, to give the following products:[4]



Cl_3CSCCl_2-SS-$COCH_3$

Cl_3CSCCl_2-S-CS-Cl

Dichloro(trichloromethyldithio)methanesulfenyl chloride **93** has been prepared by treatment of chlorothiocarbonyl trichloromethyl disulfide with SO_2Cl_2 in methylene chloride in 90% yield. Attempts at purification, both by distillation and by chromatography, resulted in decomposition of the compound.[158]

$Cl_3C\text{-}SS\text{-}CCl_2\text{-}SCl$

93

Dichloro(pentachloroethyldithio)methanesulfenyl chloride **94** (b.p. 114–5 °C/0.3 mm Hg) has been prepared by reaction of chlorothiocarbonyl pentachloroethyl disulfide with SO_2Cl_2 in 50% yield.[158]

$Cl_5C_2\text{-}SS\text{-}CCl_2\text{-}SCl$

94

Chlorine and bis(trichloromethyl) pentathiodipercarbonate give chlorobis(trichloromethyldithio)methanesulfenyl chloride **95** (m.p. 41–2 °C) in 90% yield.[38]

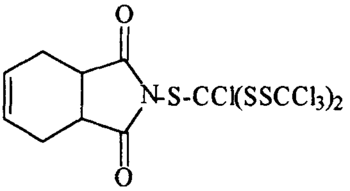
$(Cl_3CSS)_2CCl\text{-}SCl$

95

Compound **95** converts to **36** when allowed to stand in acetonitrile at ambient temperature for some days or in chloroform with $HgCl_2$ as a catalyst.[39] It reacts with *p*-toluenethiosulfonate to give the corresponding dithioperoxysulfonate:[38]

$(Cl_3CSS)_2CCl\text{-}SS\text{-}SO_2\text{-}Ar$

The reaction of **95** with tetrahydrophthalimide anion gives the expected product:



Chlorobis(pentachloroethyldithio)methanesulfenyl chloride **96** (m.p. 85–7 °C) has been prepared in 97% yield by reaction of bis(pentachloroethyl) pentathiodipercarbonate and chlorine.[38,39]

$$(Cl_5C_2SS)_2CCl\text{-}SCl$$

96

Ozonization of trichloroethenesulfenyl chloride **97** in dry chloroform gives the corresponding sulfinyl chloride.[159]

$$Cl_2C{=}CCl\text{-}SCl$$

97

Compound **97** reacts with different 2,6-dialkylphenols to give the corresponding 4-(trichloroethenylthio) derivatives which are useful as insecticides for the control of *Aedes aegypti* and as mosquito larvicides.[160–162] It reacts with different formamide and carboxamide derivatives to give the corresponding *N*-[(trichloroethenyl)thio] derivatives which exhibit pesticidal activity.[163–167]

It reacts with benzoxathiazinone to give the corresponding *N*-[(trichloroethenyl)thio] derivative with activity against *Pythirium ultimum.*[168]

To a solution of hexachloro-1,3-butadiene in abs. ethanol and *tert*-butanethiol was added a solution of sodium hydroxide in abs. ethanol. After 30 min *tert*-butyl pentachloro-1,3-butadienyl sulfide was formed which gave a 6% yield of pentachloro-1,3-butadiene-1-sulfenyl chloride **98** (b.p. 73.6 °C/0.4 mm Hg) when treated with chlorine.[169]

$$Cl_2C{=}CCl\text{-}CCl{=}CCl\text{-}SCl$$

98

Compound **98** reacts with hydrocarbon elastomers such as crepe rubber to form flame-resistant plastic polymers.[169]

Pentachlorobenzenesulfenyl chloride **99** (m.p. 99–100 °C) was prepared in 92% yield by Putnam and Sharkey[170] by passing dry chlorine through a solution of pentachlorobenzenethiol in refluxing carbon tetrachloride containing a few crystals of iodine.

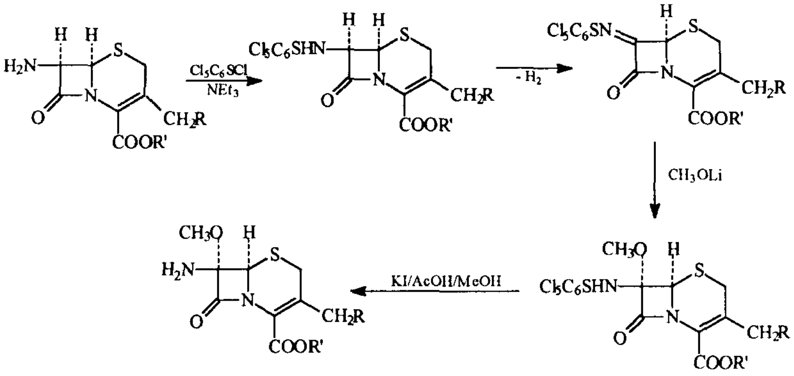
$$Cl_5C_6\text{-}SCl$$

99

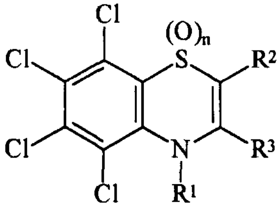
When **99** reacts with water and optional mineral acid it affords a mixture of bis(pentachlorophenyl) disulfide and sulfone derivatives. It can be reduced to pentachlorobenzenethiol.[49] Bis(pentachlorophenyl) pentathiopercarbonate has been synthesized by reaction of **99** with metal trithiocarbonates; the heptathio analog was prepared similarly.[39] Compound **99** reacts with ammonia, aniline, sulfonamides, and ethylendiamine, respectively, to give the corresponding sulfenamides which exhibit fungicidal and bactericidal activity.[171]

2-Oxazolidinone and 2-thiazolidinone derivatives were treated with **99** in chloroform at room temperature to yield the corresponding *N*-(pentachlorophenyl)thio derivatives which were recognized as antiasthmatics, inhibiting both leukocyte migration and lipoxygenase.[172]

Prior to the introduction of a methoxy group in the 7-position of cephalosporins the latter were treated with **99** to protect the amino group at this position according to the following scheme:[173]



Compound **99** condenses with different enamine derivatives which can be oxidized to the corresponding sulfones and then cyclized with butyllithium to give benzothiazine derivatives:[174–176]



Transformation of penicillins into cephalosporins has been performed by ring opening of the thiazoline moiety with **99**, followed by ring closure with ammonia in DMF.[177]

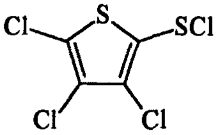
Dichloro(pentachlorophenylthio)methanesulfenyl chloride **100** (m.p. 88–90 °C) has been prepared in 93% yield by the reaction of chlorine with pentachlorophenyl chlorodithioformate.[178]

$$\underset{}{Cl_5C_6\text{-}S\text{-}CS\text{-}Cl} + Cl_2 \longrightarrow \underset{\mathbf{100}}{Cl_5C_6\text{-}S\text{-}CCl_2\text{-}SCl}$$

The reaction of **100** with sodium trithiocarbonate gives pentachlorophenyl chlorodithioformate and a second product assigned the following structure:[39]

$$Cl_5C_6\text{-}S\text{-}CS\text{-}S\text{-}CS\text{-}S\text{-}C_6Cl_5$$

3,4,5-Trichlorothiophenethiol has been treated with chlorine to give 3,4,5-trichloro-2-thiophensulfenyl chloride **101** (b.p. 78 °C/0.1 mm Hg) in 75% yield.[179]



101

Compound **101**, when treated with ammonia, phthalimide anion, morpholine, or thioacetic acid, gives the corresponding *N*-thio derivatives.[179] It reacts with tetrachlorothiophene and butyllithium to give **43**. Treatment of **101** with hydrogen sulfide gives **43**.[23]

5.2. Disulfenyl Dichlorides

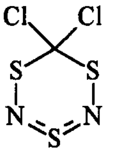
Dichloromethanedisulfenyl dichloride **102** (b.p. 36–7 °C/0.03 mm Hg) has been prepared by the chlorination of (acetyldithio)dichloromethanesulfenyl chloride ($CH_3COSSCCl_2SCl$).[4] It has also been prepared by photochemical chlorination of carbon disulfide.[180,181]

$ClS\text{-}CCl_2\text{-}SCl$

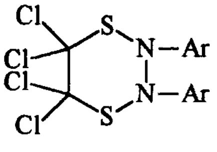
102

Christensen and Senning detected by gas chromatographic analysis the presence of **102** as a contaminant in commercial trichloromethanesulfenyl chloride prepared by iodine catalyzed chlorination of carbon disulfide.[29]

Compound **102** reacts with *N,N′*-bis(trimethylsilyl)sulfur diimide ($Me_3SiN{=}S{=}NSiMe_3$) to give 6,6-dichloro-1,3,5,2,4-trithiadiazine.[180]

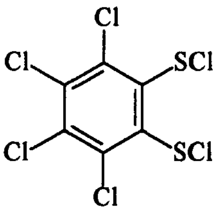


Nielsen and Senning could prepare 1,1,2,2-tetrachloro-1,2-ethanedisulfenyl dichloride **103** in 32% yield when 2,3-bis(4-methylphenyl)-5,5,6,6-tetrachloro-2,3,5,6-tetrahydro-1,4,2,3-dithiadiazine was treated with gaseous hydrogen chloride.[182]



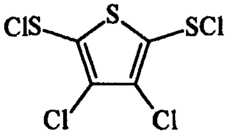
Compound **103** reacts with phenylmethanethiol to furnish the corresponding bisdisulfide.[185]

3,4,5,6-Tetrachloro-1,2-benzenedisulfenyl dichloride **104** is utilized in the preparation of the complex $[Fe(S_2C_6Cl_4)_2]_n$ used in the preparation of 3,4,5,6-tetrachlorobenzene-1,2-dithiol.[183,184]



104

3,4-Dichloro-2,5-thiophenedisulfenyl dichloride **105** could be prepared by chlorination of 3,4-dichlorothiophene-2,5-dithiol in carbon tetrachloride. This compound is very unstable. After removal of excess chlorine with a stream of nitrogen it could be derivatized by treatment with morpholine.[179]



105

6. THIOSULFENYL CHLORIDES

Trichloromethanethiosulfenyl chloride **106** (b.p. 55–65 °C/2.5–3.8 mm Hg) is formed when a mixture of trichloromethanesulfenyl chloride, sulfur, and triethyl phosphate is heated for 7 h at 140–5 °C.[185]

Compound **106** reacts with terminal alkynes and butyllithium to give the corresponding alkynyl disulfides.[186] (5-Chloro-2-thienyl) trichloromethyl trisulfide could be obtained from the reaction between **106** and 5-chlorothiophene-2-thiol.[187] The reaction of **106** with sodium trithiocarbonate gives the corresponding heptathio compound:[39]

$$Cl_3C\text{-}SSCl \; + \; Na_2CS_3 \longrightarrow (Cl_3CSSS)_2C{=}S$$

Thioacetic acid reacts with **106** at ambient temperature to yield acetyl trichloromethyl trisulfide.[188] It reacts with alkoxydithioformate anions ROC(S)5 to give the corresponding alkoxythiocarbonyl trichloromethyl trisulfides $Cl_3CS_3C(S)OR$.[189] Reaction of **106** with carbon monosulfide leads to the formation of chlorothiocarbonyl trichloromethyl disulfide.[158] Compound **106** reacts with thiophosgene to give **23**.[27] It reacts with 4,4-dichloro-1,3-dithietane-2-thione to yield **52**.[84]

Compound **106** is useful for the introduction of the trichloromethyldithio group into different nitrogen-containing heterocycles which have been tested *in vitro* for their fungicidal activity.[190]

The reaction of **91** with thioacetic acid gives the corresponding disulfide which can be chlorinated with chlorine to give pentachloroethanethiosulfenyl chloride **107** (b.p. 77–80 °C/0.35 mm Hg) in 73% yield.[37, 191]

$$\mathbf{91} + CH_3COSH \longrightarrow Cl_5C_2\text{-}SS\text{-}COCH_3 \xrightarrow{Cl_2} \underset{\mathbf{107}}{Cl_5C_2\text{-}SSCl}$$

Compound **107** reacts with thioacetic acid to yield acetyl pentachloroenthyl trisulfide.[188] Its reaction with sodium trithiocarbonate affords the corresponding heptathio compound.[39] It reacts with CS according to the following equation:[158]

$$\mathbf{107} + CS \longrightarrow Cl_5C_2SS\text{-}CS\text{-}Cl$$

It reacts with thiophosgene in acetonitrile to give **34**.[27] With 4,4-dichloro-1,3-dithietane-2-thione **53** is formed.[84]

Bis(trichloromethyl) pentathiodipercarbonate was dissolved in sulfur dichloride at 0 °C and allowed to react overnight at room temperature to give chlorobis(trichloromethyldithio)methanethiosulfenyl chloride **108** as a yellow oil in high yield. This compound decomposes rapidly on silica gel plates.[38]

$$(Cl_3CSS)_2CCl\text{-}SSCl$$

108

The reaction of **108** with *p*-toluensulfinate gives the corresponding dithioperoxysulfonate.[38]

$$(Cl_3CSS)_2CCl\text{-}SS\text{-}SO_2\text{-}Ar$$

Chlorobis(pentachloroethyldithio)methanethiosulfenyl chloride **109** (m.p. 67–70 °C) has been prepared in quantitative yield by reaction of sulfur dichloride with bis(pentachloroethyl) pentadithiopercarbonate.[39]

$$(Cl_5C_2SS)_2CCl\text{-}SSCl$$

109

Dichloro(pentachlorophenylthio)methanethiosulfenyl chloride **110** (m.p. 75–9 °C) has been prepared in 80% yield from pentachlorophenyl chlorodithioformate and sulfur dichloride.[178]

$$Cl_5C_6\text{-}S\text{-}CCl_2\text{-}SSCl$$

110

Cyclohexyl isocyanide is inserted into the S-Cl bond of **110** to give the following product.[178]

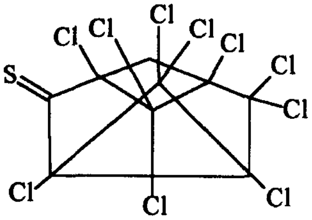
Cl_5C_6-S-CCl_2-SS-CCl=NC_6H_{11}

6,9,12,15,18-Pentachloro-1-(chlorodithio)-1,6,9,12,15,28-hexahydro[5,6]-fullerene-C_{60}-I_n **111** may be represented by the formula $C^f_nCl_5$(SSCl). In this formula, C^f_n is a fullerene having at least one corrannulene ring structure. Compound **111** can be made by prolonged heating of the appropriate fullerene with sulfur dichloride.[192]

7. THIOCARBONYL COMPOUNDS

7.1. Thioketones

The perchlorinated 1,3,4-metheno-2*H*-cyclobuta[*cd*]pentalene-2-thione **112** has been prepared from the corresponding hexachlorocyclopentadiene dimer, probably by sulfhydrolysis.[193]

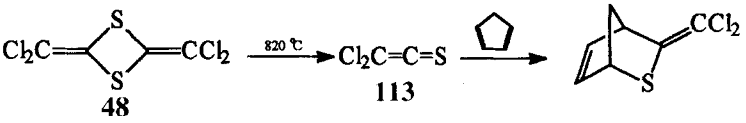


112

It is a fire retarding pigment and can be added to conventional decorative paint. It is insensitive to water.[193]

7.2. Thioketenes

Dichlorothioketene **113** could be generated by flash vacuum pyrolysis of the 1,3-dithietane **48** at 820 °C/10^{-4} mm Hg. For the trapping of the thioketene produced the pyrolysis products were allowed to condense on a matrix of solid 1,3-cyclopentadiene kept at −196 °C.[83]



48

113

Compound **113** could also be obtained by cycloreversion of appropriate 1,3-dithiolane derivatives. However, upon attempted trapping with electrophiles oligomerization prevails.[194,195]

Mutagenic effects have been observed with the thioketene **114** and related compounds. This mutagenicity is dependent on the ability of the compound to react with DNA constituents.[196,197]

$$Cl_2C=CCl-CCl=C=S$$

114

7.3. Thiocarbonyl Chlorides

Several reviews[198–200] have been published describing the synthesis, properties, reactions and applications of thiophosgene **115** (b.p. 80 °C).

The commercially applied method for the synthesis of thiophosgene is the reduction of trichloromethanesulfenyl chloride with hydrogen sulfide at 110–114 °C (96% yield).[201]

$$\underset{\textbf{90}}{Cl_3C\text{-}SCl} \xrightarrow{\text{reduction}} \underset{\textbf{115}}{Cl_2C=S}$$

A number of other reducing agents have been used,[202] e.g. tin in conc. hydrochloric acid.[203] A number of procedures have been developed to optimize the yield of thiophosgene obtained from the thermal decomposition of suitable trichloromethylthio compounds, in particular with sulfuric acid in the presence of a catalyst (disulfur dichloride, sulfur dichloride, alkali metal iodide, and/or iodine).[204–207] Compound **115** could also be prepared by reduction of trichloromethanesulfenyl chloride with sulfur dioxide in the presence of potassium iodide and disulfur dichloride.[208,209] Replacement of disulfur dichloride with hydrogen sulfide increases the yield.[210]

The recent literature reports many reactions of thiophosgene. Thiophosgene can be used to functionalize macrocyclic chelating agents, such as tetraazacyclododecanetetraacetic acid,[211] (hydroxybenzyl)ethylenetriaminediacetic acid,[212] and tetraazaundecane[213] derivatives). The activation proceeds by conversion of an amino group of the chelating agent to an isothiocyanate group by thiophosgene. These modified chelating agents are useful for conjugating different proteins, antigen antibodies, and radionucleotides for diagnosis or therapy.

Thiophosgene reacts with $^{15}NH_4Cl$ and $H_2{}^{17}O$ to give the corresponding isotopically labeled thiourea used in the preparation of isotopically labeled uridine and cytidine.[214]

Thiophosgene has been used to convert amino groups to thioureido group such as in the synthesis of 3-[2-(*S*-methylureidoethyl)] analog of a compound used, respectively, as releaser of nitric oxide and inhibitor of nitric oxide synthetase.[215]

Pentachloroethanesulfenyl chloride reacts with $SnCl_2 \cdot 2H_2O$ and 37% HCl to give trichlorothioacetyl chloride **116**.[80]

$Cl_3C\text{-}CS\text{-}Cl$

116

This compound is stable in the dark in dilute solutions. It photodimerizes in concentrated solutions to **47**, the pyrolysis of which reverses this reaction.[80] Compound **116** reacts with morpholine to give trichlorothioacetomorpholide.[80]

7.4. Chlorothioformic Acid Derivatives

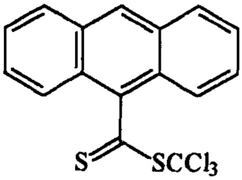
Trichloromethyl chlorodithioformate **117** (b.p. 98–100 °C/14 mm Hg) has been prepared in 75% yield by reaction of trichloromethanesulfenyl chloride with carbon monosulfide.[72] Structure **117** was earlier erroneously assigned to the photodimer of thiophosgene **46** (cf. Section 4.3).

$Cl_3C\text{-}S\text{-}CS\text{-}Cl$

117

A minor by-product was obtained during the preparation of **117**. It was identified as **45**, and its formation attributed to reaction between **117** and carbon monosulfide.[72]

Compound **117** reacts with chlorine to afford Cl_3CSCCl_2SCl and with dibenzylamine to give the corresponding *N*-substituted derivative. Reaction with anthracene does not lead to the expected Diels-Alder adduct, but rather to:[72]



Reaction of sodium hydroxide, pentachlorobenzenethiol, and thiophosgene gives pentachlorophenyl chlorodithioformate **118** (m.p. 114–9 °C) in 91% yield.[170] The same compound could also be prepared by reaction of **100** with sodium trithiocarbonate.[39]

Cl_5C_6-S-CS-Cl
118

Treatment of **118** with chlorine gas at room temperature converts it to **100**. Reaction of **117** with sulfur dichloride leads to the formation of **110**.[170] Treatment of **118** with sodium sulfinate and tetrabutylammonium hydrogen sulfate gives the corresponding *C*-sulfonyldithioformate.[216–218]

Dichloro(trichloromethylthio)methyl chlorodithioformate **119** has been prepared in 49% yield as an orange oil by reaction of **92** with carbon monosulfide.[4]

Cl_3C-S-CCl_2-S-CS-Cl
119

Addition of trichloromethanethiosulfenyl chloride to carbon monosulfide gives trichloromethyl chlorotrithioperformate **120** (b.p. 78–80 °C/ 0.04 mm Hg). The crude product was chromatographed to give 57% **120** as an orange oil.[158]

Cl_3C-SS-CS-Cl
120

Compound **120** reacts with SO_2Cl_2 to give dichloro[(trichloromethyl) dithio]methanesulfenyl chloride **92**.[158]

Passing of carbon monosulfide through a solution of **107** gives pentachloroethyl chlorotrithioperformate **121** (b.p. 108–9 °C/0.03 mm Hg) in 19% yield.[158]

$$Cl_5C_2\text{-}SS\text{-}CS\text{-}Cl$$

121

Compound **121** can be converted to **94** with SO_2Cl_2.[158]

7.5. Thiocarbonic Acid Derivatives

Bis(pentachlorophenyl) trithiocarbonate **122** has been claimed as a masticating agent.[219]

$$Cl_5C_6S\text{-}CS\text{-}SC_6Cl_5$$

122

Bis(trichloromethyl) pentathiodipercarbonate **123** (m.p. 39–40 °C) has been prepared by reaction of trichloromethanesulfenyl chloride with aqueous sodium trithiocarbonate in 70% yield.[38,220]

$$(Cl_3CSS)_2C{=}S$$

123

Oxidation of **123** with *m*-chloroperbenzoic acid gives the corresponding sulfine:[38]

$$(Cl_3CSS)_2C{=}S{=}O$$

The fast reaction of **123** with chlorine gives a quantitative yield of **95**.[38,39] Reaction with sulfur dichloride gives the corresponding chlorothiosulfenyl chloride.[38,39] Compound **123** reacts with trichloromethanesulfenyl chloride in acetonitrile to give **16**.[39] It reacts with a number of aminothiazoles,[221] benzothiazoles, benzimidazoles, and benzoxazoles[222] to give the corresponding isothiocyanato derivatives which are used as anthelmintics.

Interaction of pentachloroethanesulfenyl chloride with barium trithiocarbonate in acetonitrile gives bis(pentachloroethyl) pentathiopercarbonate **124** (m.p. 113–4 °C) in 73% yield.[39]

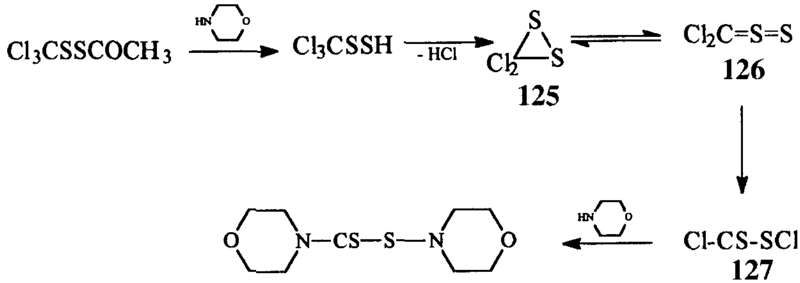
$$(Cl_5C_2SS)_2C{=}S$$

124

Compound **124** reacts with **107** to give a low yield of **37**.[39]

7.6. Miscellaneous Thiocarbonyl Compounds

Chlorothiocarbonylsulfenyl chloride **127** has been postulated to be formed via transient **125** ⇆ **126** according to the following equation:[223,224] A compound formed by heating of thiophosgene with sulfur and earlier believed to possess the structure **127** was later shown to be 3,3,6,6-tetrachloro-1,2,4,5-tetrathiane (cf. Section 4.8).



Intermediate **126** is a thiosulfine, a group of compounds with no known isolable representatives.

Carbonothioyl bis(trichloromethyl) trisulfide **128** could be obtained in 58% yield from the reaction of trichloromethanesulfenyl chloride with barium trithiocarbonate in acetonitrile overnight at room temperature. The product appears unstable with respect to loss of carbon disulfide.[39]

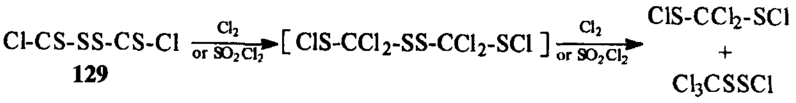
$$(Cl_3CSSS)_2C{=}S$$

128

Compound **128** reacts with trichloromethanethiosulfenyl chloride to give **38**.[39]

The unstable bis(chlorothiocarbonyl) disulfide **129** has been prepared in 50% yield by reaction of carbon monosulfide with disulfur dichloride.[225] It has been trapped with diethylamine in carbon tetrachloride to give tetraethylthiuram disulfide.[225]

Compound **129** can be chlorinated with chlorine or SO_2Cl_2 according to the following equation:[225]

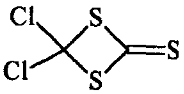


$$\underset{\mathbf{129}}{\text{Cl-CS-SS-CS-Cl}} \xrightarrow[\text{or } SO_2Cl_2]{Cl_2} [\,\text{ClS-CCl}_2\text{-SS-CCl}_2\text{-SCl}\,] \xrightarrow[\text{or } SO_2Cl_2]{Cl_2} \begin{matrix}\text{ClS-CCl}_2\text{-SCl}\\ + \\ \text{Cl}_3\text{CSSCl}\end{matrix}$$

Bis(pentachlorophenyl) pentathiodicarbonate (m.p. 130 °C, dec.) has been prepared by reaction of aqueous sodium trithiocarbonate with **100**. It precipitated as a by-product of the reaction in 17% yield.[39]

$$\mathbf{100} \xrightarrow[CH_2Cl_2/H_2O]{CS_3^{2-}} \mathbf{117} + Cl_5C_6\text{-S-CS-S-CS-S-}C_6Cl_5$$

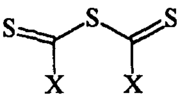
4,4-Dichloro-1,3-dithietane-2-thione **130** (m.p. 57–8 °C) was first obtained in 1888 by Rathke by sulfhydrolysis of tetrachloro-1,3-dithietane (dimeric thiophosgene).[226] Its synthesis and reactions have been reviewed.[227]



130

Compound **130** has been prepared in 85% yield by the reaction of **46** with trithiocarbonic acid.[228,229] It could also be prepared by reaction of dimeric thiophosgene with *tert*-butanethiol in benzene in the presence of aluminum chloride.[230]

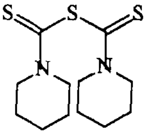
It reacts with $KMnO_4$ to form 4,4-dichloro-1,3-dithietan-2-one.[229,230] With NaX (X = OMe, OEt, OPh, SMe, SEt, SPh) **130** gives:[228,231]

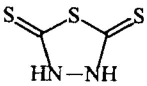


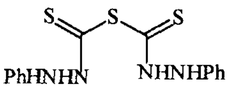
Compound **130** reacts with ammonia to give ammonium isothiocyanate and with primary amines to yield the corresponding isothiocyanates.[231]

$$\mathbf{130} + RNH_2 \longrightarrow RNCS + 2\,HCl$$

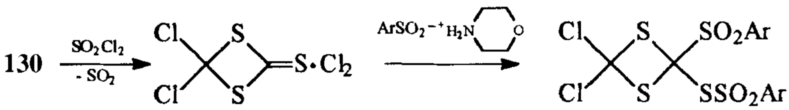
It reacts with piperidine, with hydrazine, and with phenylhydrazine to afford:[231]







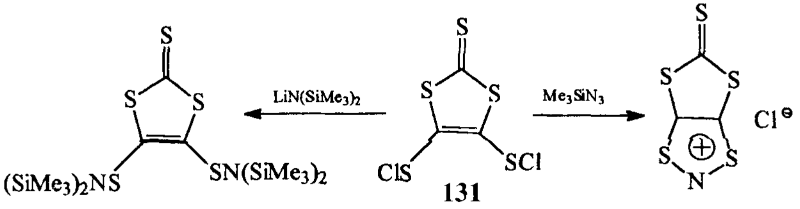
Chlorination of **130** with SO_2Cl_2 leads only to a loose adduct with chlorine which, however, upon treatment with morpholinium *p*-toluenesulfinate reacts according to the following equation:[84]



It reacts also with perhaloalkanesulfenyl and -thiosulfenyl chlorides to give (alkyldithio)- and (alkyltrithio)trichloro-1,3-dithietanes, respectively.[84]

2-Thioxo-1,3-dithiole-4,5-disulfenyl dichloride **131** has been prepared in 89% yield by reaction of a solution of $(Bu_4N]_2[Zn(C_3S_5)_2]$ in methylene chloride with SO_2Cl_2.[232]

Treatment of **131** with two equivalents of $LiN(SiMe_3)_2$ and Me_3SiN_3 gives the following products:[232]



8. UNREPORTED CARBON CHLORIDE SULFIDES

At least three unreported simple thiocarbonyl compounds should be capable of existence: 1,1,1,3,3,3-hexachloro-2-propanethione (probably less prone to dimerization to the corresponding 1,3-dithietane than its known hexafluoro counterpart), bis(pentachlorophenyl) thioketone, dithiooxalyl chloride (in equilibrium with 3,4-dichloro-1,2-dithiete), 1,1,1,4,4,4-hexachlorobutane-2,3-dithione (in equilibrium with 3,4-bis(trichloromethyl)-1,2-dithiete), and 1,2-bis(pentachlorophenyl)ethane-1,2-dithione (in equilibrium with 3,4-bis(pentachlorophenyl)-1,2-dithiete). The preparation of 2,3,4,5-tetrachloro-2,4-cyclopentadiene-1-thione **133** has been attempted in two instances.[236,237] While the transient existence of **133** appears likely no straightforward trapping experiments unequivocally characterizing **133** are on record.

In analogy with the remarkably stable di-*tert*-butylthioketene also the corresponding perchlorocarbyl analogs bis(trichloromethyl)thioketene and bis(pentachlorophenyl)thioketene might well be rewarding goals for synthetic efforts.

More questionable is the stability to be expected of polyfunctional sulfenyl chlorides such as chloromethanetrisulfenyl trichloride, methanetetrasulfenyl tetrachloride, 1,2,2,2-tetrachloroethane-1,1-disulfenyl dichloride, the higher perchloroethaneoligosulfenyl chlorides (beyond the known 1,1,2,2-tetrachloroethane-1,2-disulfenyl dichloride) and the corresponding ethene derivatives (beyond the known 1,2,2-trichloroethenesulfenyl chloride).

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