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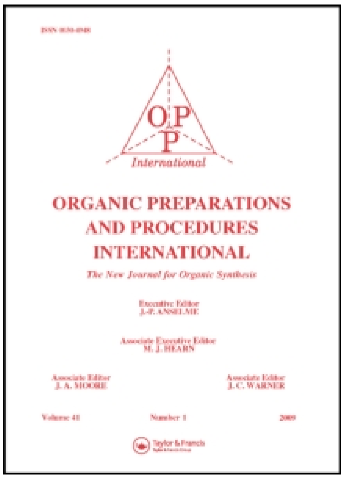

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# REACTIONS OF THIOCARBONYL COMPOUNDS WITH CHLORINE AND WITH SULFUR DICHLORIDES. A REVIEW

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ORGANIC PREPARATIONS AND PROCEDURES INT. 17(4-5), 275-315 (1985)

# REACTIONS OF THIOCARBONYL COMPOUNDS WITH CHLORINE AND WITH SULFUR DICHLORIDES. A REVIEW

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# REACTIONS OF THIOCARBONYL COMPOUNDS WITH CHLORINE AND WITH SULFUR DICHLORIDES. A REVIEW

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## I. INTRODUCTION AND SCOPE

Although this review does not attempt an exhaustive coverage of the relevant literature we do wish to point out a number of salient features of the title reactions. Some papers already cited in previous reviews covering topics overlapping with the present review [1-5] are referred to below in order to illustrate the variety of possible products. The emphasis will be on the reactions of thioketones, thiocarboxylic acid esters, and thiocarbonic acid esters since the latest results have appeared within these classes of compounds. Compounds in which the C=S function is a part of a cumulene system, *e.g.* isothiocyanates R-N=C=S and sulfines RR'C=S=O, and selenocarbonyl compounds also react with halogens,[6] but are not included in the discussion. Reports on reactions of thiocarbonyl compounds with halogens other than chlorine are scarce in the literature and a few will be mentioned only incidentally.

A brief general outline is given in Section II. TABLES 1 and 2 and SCHEMES 1-4, rather than stating actual mechanisms, are meant to serve as a phenomenological description by rationalization and classification of the specific results from the literature summarized under appropriate headings in Sections III and IV according to classes of substrates. Finally, references concerning addition of sulfenyl chlorides to thiocarbonyl compounds are given without comments at the end of Section II.

## II. GENERAL CONSIDERATIONS

The influence of the reaction conditions (chlorinating agent, purity of the starting material, solvent, temperature, and isolation procedure) on the product distribution has been extensively studied by Barany *et al.*[7-12] Chlorine itself under anhydrous conditions is by far the most widely used chlorinating agent, but sulfuryl chloride in an appropriate solvent has proved to be the reagent of choice in many cases when mild conditions are required. Phosphorus pentachloride,[13-15] oxalyl dichloride,[16] thionyl chloride,[17] and phosgene [16,18] have been used for chlorination and simultaneous desulfurization. Aqueous chlorine[19] and sulfur dichloride [20-22] have also been employed.

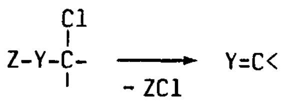
Although a thiocarbonyl group in general is attacked when exposed to chlorine and the isolated product in many cases is the α-chloro sulfenyl chloride 8, the expected addition product, a number of other products may result instead as depicted in SCHEMES 1-3 and exemplified in TABLES 1-2. Prior to a reaction with the C=S function weak bonds elsewhere in the molecule 1 may be cleaved and the thiocarbonyl group retained as in product 4. Charge-transfer complexes 2 and ionic adducts 5, 12, 22/23/24/25, and 27 may be intermediates in the formation of covalent products or are even isolable in some cases.

The lability of the α-chlorine is an important factor in the stability of 8 and for its further transformations.[23] Substituents X and Y which are mesomerically electron-donating tend to stabilize a positive charge on the central carbon atom of 8. This may facilitate cleavage of the C-Cl bond and eventually reversal to the starting compound 1 or hydrolysis of 8, 5 or 2 during work-up to give the carbonyl compounds 3.

Of importance for synthesis is the hydrolysis of certain α-chloro sulfenyl chlorides 8 to give sulfines, XYC=S=O,[6] *e.g.* Eq. 9 below. Oxidation of thioureas and trithiocarbonates with various oxidizing agents gives dithiocarbenium salts 12 (SCHEME 2).[114] In the case of thioureas, oxidative coupling has been observed in reactions with chlorine, bromine, and iodine.[116,117]

Products with a low solubility in organic solvents formed by halogenation of trithiocarbonates and described as complexes (see references in Section 3.13, *e.g.* chlorination of 1,3-dithiolane-2-thione)[86] might be salts of the type 12. Such salts are formed when 1,3-dithiolane-2-thione is oxidized with nitrosonium tetrafluoroborate.[114]

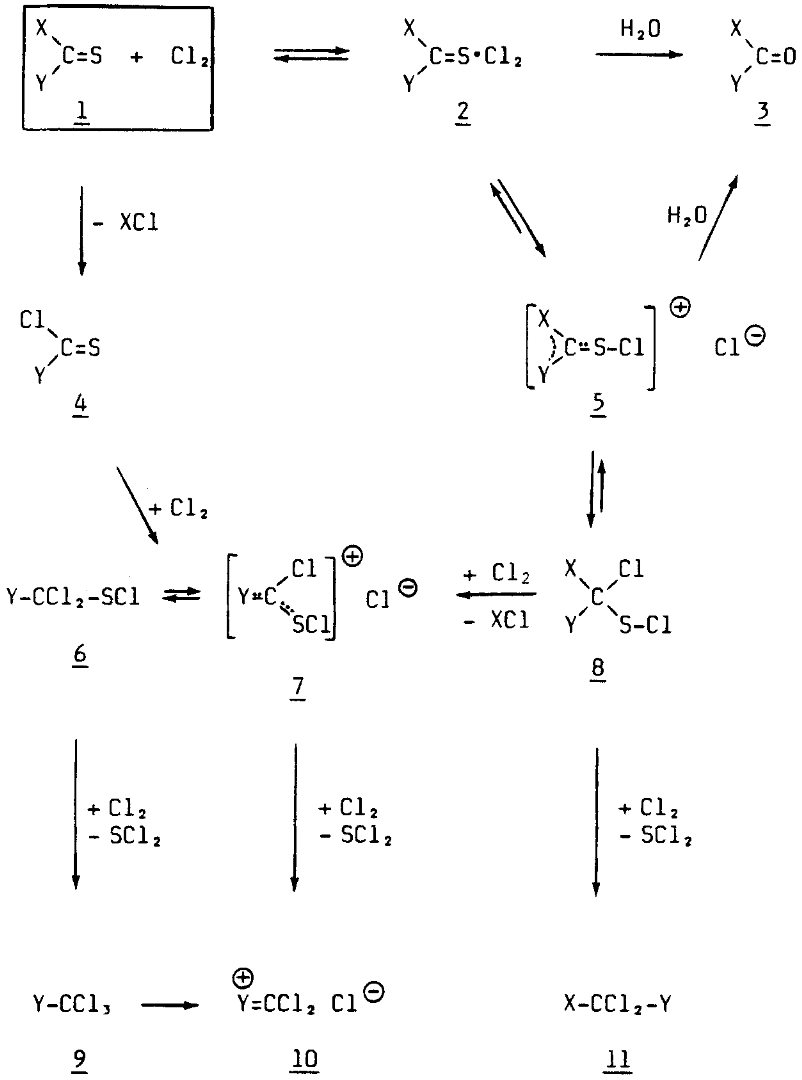
In the SCHEMES the substituents X and Y can be any of the following groups: hydrogen, alkyl, aryl, amino, alkoxy, aryloxy, alkylthio, alkyldithio, arylthio and halogen, though not all reactions shown are possible for a given pair (X,Y). By means of TABLE 1 actual examples from the text can be found. The nature of Z and Y in the elimination reactions is explained in TABLE 2.



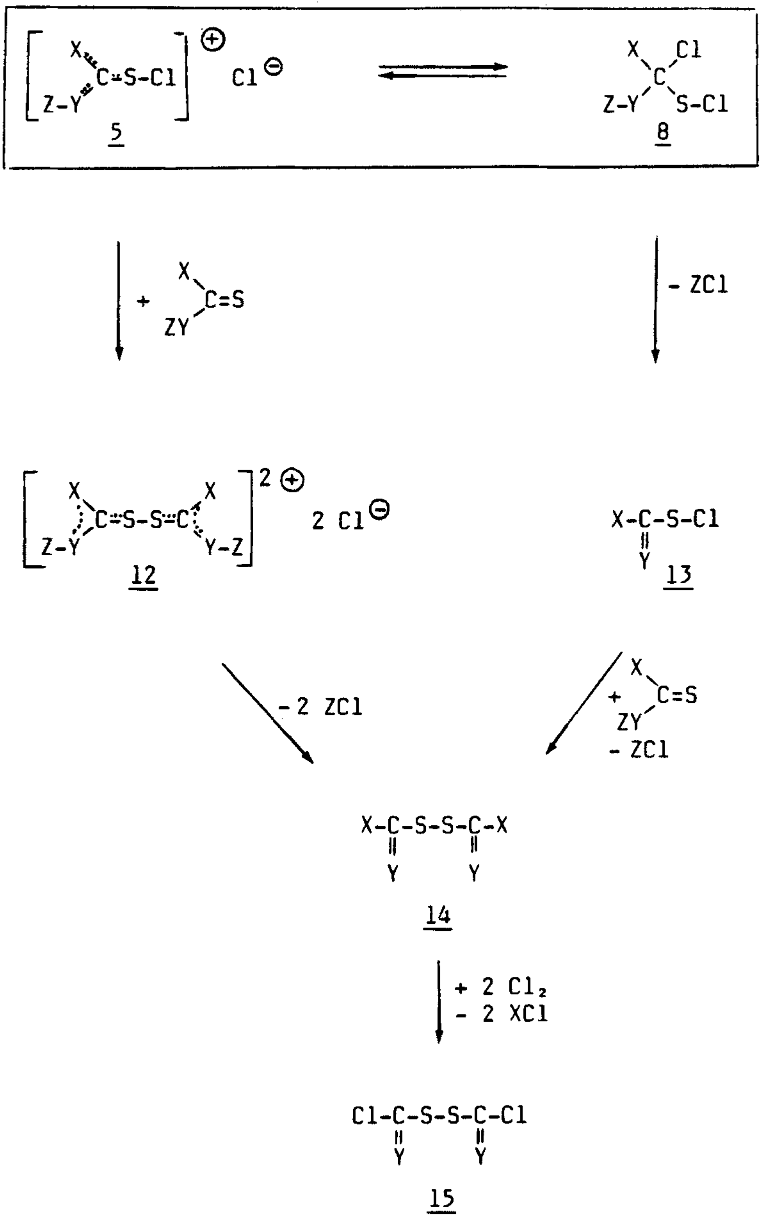
$$\mathrm{Z{-}Y{-}\overset{Cl}{\underset{|}{\overset{|}{C}}}{-}} \xrightarrow[-\mathrm{ZCl}]{} \mathrm{Y{=}C{<}}$$

If one of the substituents at the central carbon is an alkoxy, an alkylthio, a primary or a secondary amino group, or a carbon bearing a hydrogen the adducts 8, 12, 26, and 27 may eliminate hydrogen chloride or alkyl chloride to give more stable products such as carbonyl, thiocarbonyl, or imino compounds, or alkenes (13, 14, 18-20, 28, 30). Similar eliminations may occur for 6 and 16. Examples are given in TABLE 2.

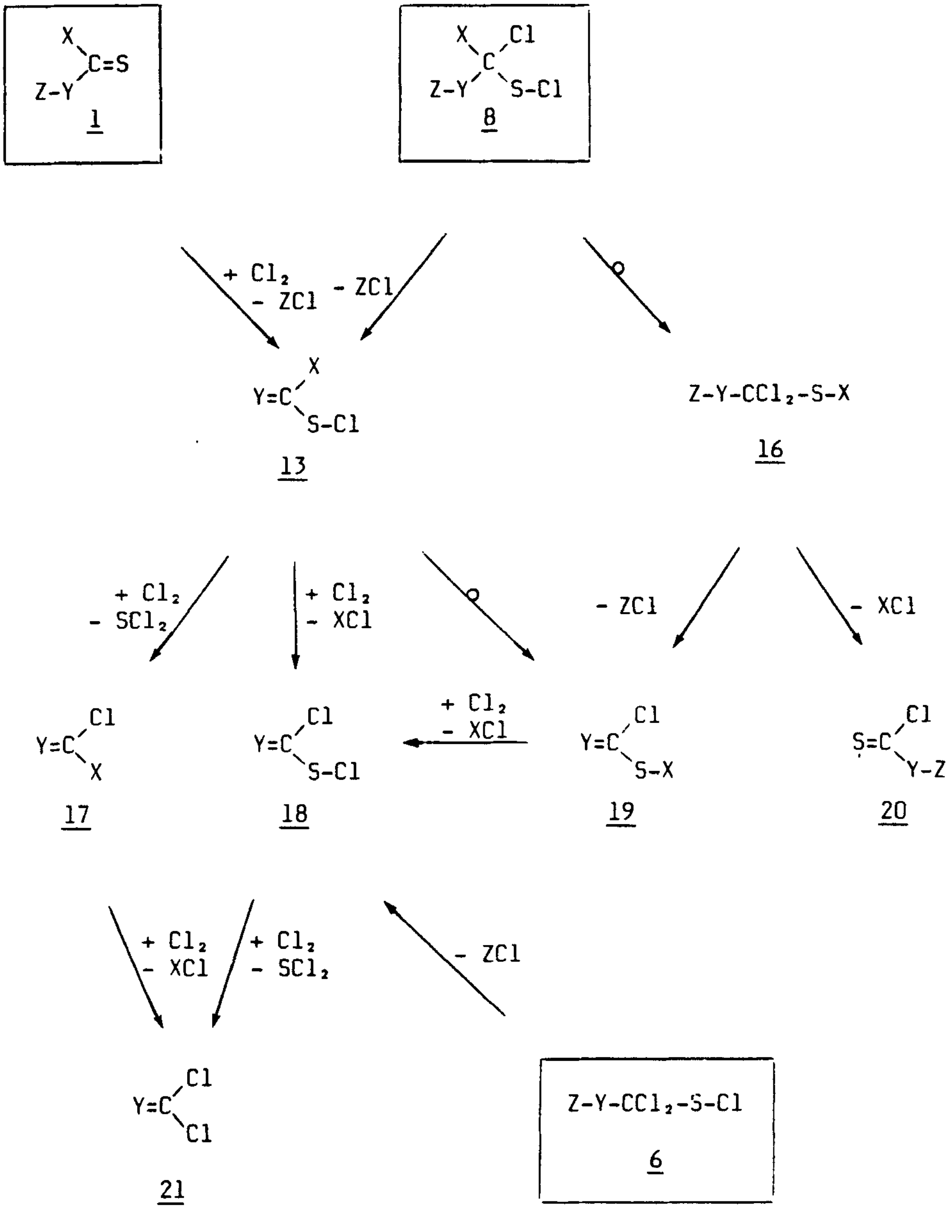
SCHEME 1. Reactions of thiocarbonyl compounds 1 with chlorine



SCHEME 2. Oxidative couplings



SCHEME 3. Further transformations of 1, 8, and 6



SCHEME 4. Reactions of thiocarbonyl compounds with sulfur dichlorides

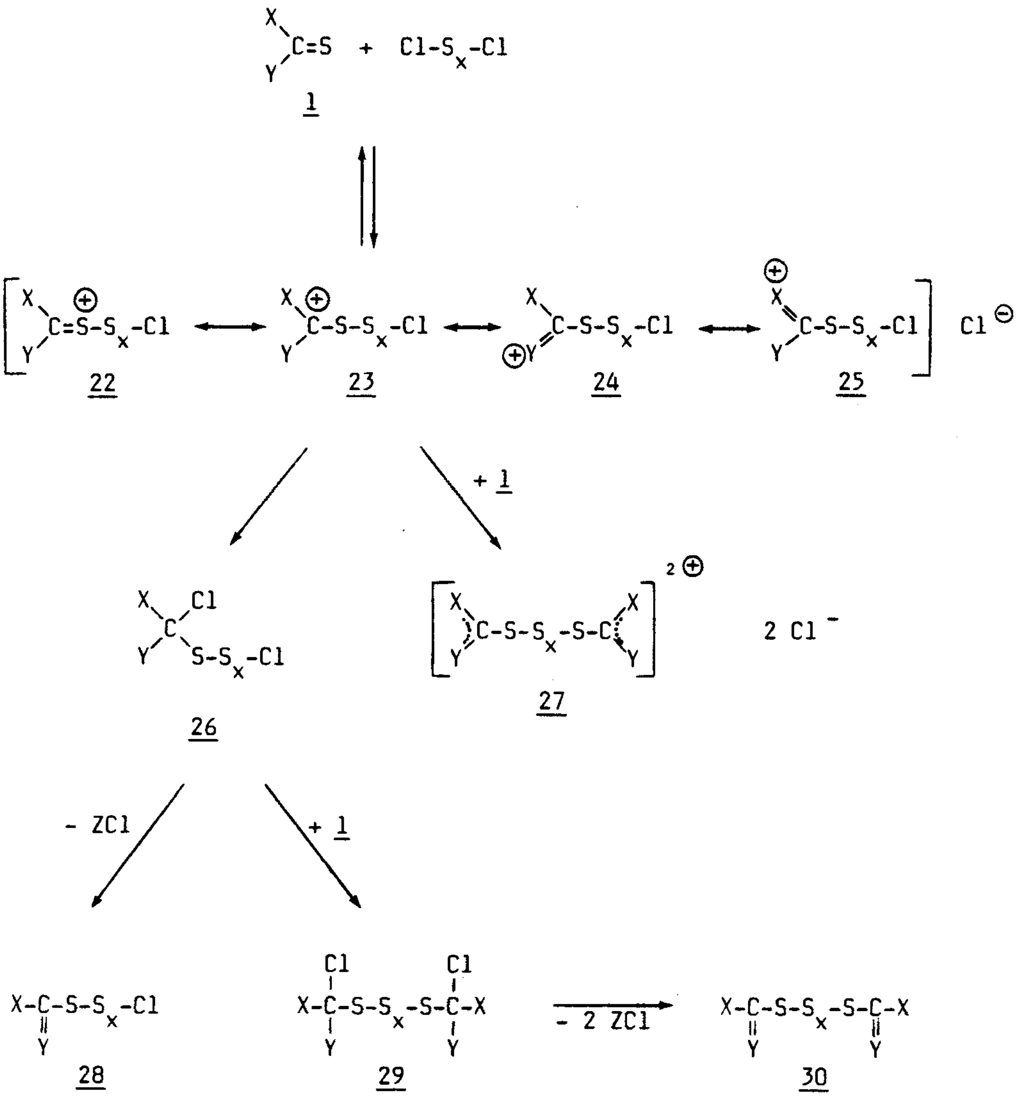
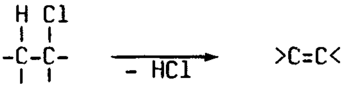
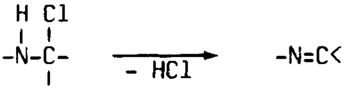
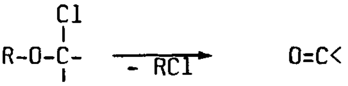
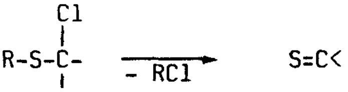


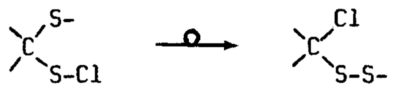
TABLE 1. Products from Reactions of Thiocarbonyl Compounds with Chlorine and with Sulfur Dichlorides

| Type of product (or intermediate) | Examples |
|---|---|
| 2/5 | 58; complexes of halogens: Section III.4, III.13 and ref. 120 |
| 3 | 61; may form when water is not excluded.[23,62,70] |
| 4 | 33, 34, 82, 99, 116 |
| 6 | 53, 88 |
| 8 | 36, 38-41, 51, 90, 101, 107, 109, 112. See also TABLES 4 and 5 |
| 9 | 56, 89, 108, 110 |
| 10 | 35, 78, 83 |
| 11 | 37, 48, 54, 59, 113 |
| 12 | 60 |
| 13 | 43, 63-65, 85, 95, 119 |
| 14 | 71, 80, 86, 94 |
| 15 | 81 |
| 16 | 91, 102, 103 |
| 17 | 44, 46, 49, 55, 62, 69, 70 |
| 18 | 73, 97 |
| 19 | 92 |
| 20 | 104 |
| 21 | 74 |
| 22/23/24/25 | 120, 121, 123/124 |
| 26 | 139, 141, 145, 146, 118 |
| 27 | 130 |
| 28 | 143 |
| 29 | 127, 142, 147, 148 |
| 30 | 131, 137, 138, 144 |
| other | 42, 45, 47, 63, 64, 66, 67, 76, 93, 117, 125, 126, 133-135 |

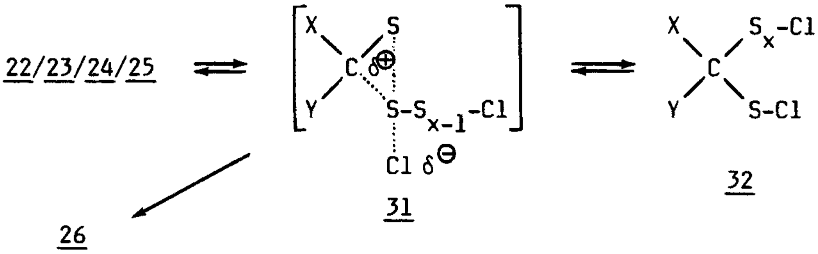
TABLE 2. Elimination Reactions of Adducts between Thiocarbonyl Compounds and Chlorine or Sulfur Dichloride

| Elimination reaction | Examples of products |
|---|---|
|  $\mathrm{-\overset{\displaystyle H}{\underset{\vert}{\overset{\vert}{C}}}-\overset{\displaystyle Cl}{\underset{\vert}{\overset{\vert}{C}}}-} \xrightarrow[-\ \mathrm{HCl}]{} \mathrm{>C{=}C<}$ | unidentified,[21] 119 |
|  $\mathrm{-\overset{\displaystyle H}{\overset{\vert}{N}}-\overset{\displaystyle Cl}{\underset{\vert}{\overset{\vert}{C}}}-} \xrightarrow[-\ \mathrm{HCl}]{} \mathrm{-N{=}C<}$ | 70, 71, 73, 74, 80, 81, 121, TABLE 3 |
|  $\mathrm{R-O-\overset{\displaystyle Cl}{\underset{\vert}{\overset{\vert}{C}}}-} \xrightarrow[-\ \mathrm{RCl}]{} \mathrm{O{=}C<}$ | 49, 69, 85, 86, 131, 133-135, 137, 138, 143, 144 |
|  $\mathrm{R-S-\overset{\displaystyle Cl}{\underset{\vert}{\overset{\vert}{C}}}-} \xrightarrow[-\ \mathrm{RCl}]{} \mathrm{S{=}C<}$ | 55, 104 (R = $CH_3S$) |

Rearrangements 8 → 16 and 13 → 19 (SCHEME 3, examples in TABLE 1) have been observed in several cases and seem to apply in general to sulfenyl chlorides with α-alkylthio or α-alkyldithio groups. The tendency of 8 to rearrange depends strongly on the substituents at the central carbon, compounds with alkoxy groups being the most reactive. The rearranged product 16 may be formed directly by chlorination of 1,[7,9,10,12] whereas in cases of more stable 8 a catalyst, preferentially $HgCl_2$,[24] heating,[25] or a highly polar solvent [26] is required.



Sulfur dichloride, $SCl_2$, is an unstable liquid in equilibrium with chlorine and disulfur dichloride: $2\ SCl_2 \rightleftharpoons Cl_2 + S_2Cl_2$. This disproportionation can be suppressed by addition of $PCl_5$ or trialkyl phosphites.[27] In any case it is important to use freshly distilled $SCl_2$ and as far as possible to avoid high temperatures and light. Reference 9 should be consulted for $S_3Cl_2$ and $S_4Cl_2$. The reactions of thiocarbonyl compounds with sulfur dichlorides, $S_xCl_2$, as shown in SCHEME 4 parallel those shown in SCHEMES 1-3 and account satisfactorily for the observed products. In analogy with the reactions of sulfenyl chlorides with alkenes,[28] a cyclic cationoid adduct such as 31 could be invoked; in principle it could rearrange to either 26 or 32. However, no well-documented example exists of a reverse addition



reaction of $S_xCl_2$ to a thiocarbonyl group, *i.e.* formation of a product such as 32 has not been observed (see Section IV.3, Eq. 45). Species 31 is analogous to the proposed intermediate[7] in the above-mentioned rearrangement 8 → 16, and accordingly 32, if formed, would be expected to rearrange to 26.

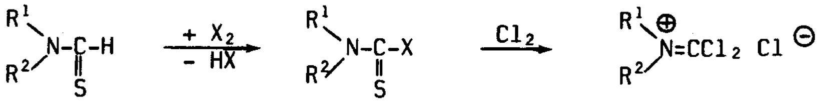
Reactions of thiocarbonyl compounds with sulfenyl chlorides RSCl, are well documented [7-10,12,25,26,29-51] and closely related to the reactions with sulfur dichlorides, but fall beyond the scope of this review. A few examples are given below (Eqs. 33, 53 and 55).

## III. CHLORINATION OF THIOCARBONYL COMPOUNDS

### 1. Thioformamides

When N,N-disubstituted thioformamides are chlorinated or brominated, hydrogen is replaced to yield thiocarbamoyl halides[1] or iminium salts

(X = Cl).[52] N-Mono- and N,N-disubstituted thioformamides have been successfully chlorinated with $SCl_2$/pyridine, see Section IV.1, but chlorination with $SO_2Cl_2$ failed to give well-defined products.[21]



35

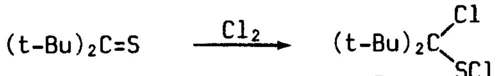
(1)

X = Cl 33

X = Br 34

## 2. Thioketones

Thioketones are decolorized instantaneously when treated with chlorine, but isolation of 1:1 adducts as well as attempted preparations of derivatives of such adducts have so far been unsuccessful, except for the perfluoro thioketones shown below. Loose thione-chlorine adducts which easily revert to the starting thione have been reported for thiobenzophenone,[2] 4,4'-dimethoxythiobenzophenone,[23] and thiocamphor.[23] The $^{13}C$ NMR spectrum of what is believed to be the α-chloro sulfenyl chloride 36 has been recorded.[53] Dichlorodiphenylmethane was the only isolated product from a reported exothermic chlorination of thiobenzophenone.[54] Isolable α-halo sul-



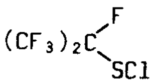
36

(2)

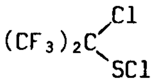
$$Ph_2C{=}S \xrightarrow{Cl_2} Ph\text{-}CCl_2\text{-}Ph \qquad (3)$$

37

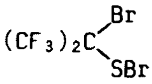
fenyl halides 38-40 can be prepared from hexafluorothioacetone and ClF,[25] $Cl_2$,[55] and $Br_2$,[55] respectively. Compound 41 has been prepared in the same way.[56]



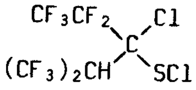
38



39



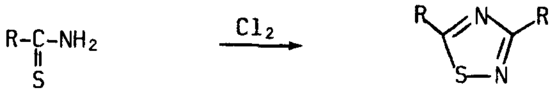
40



41

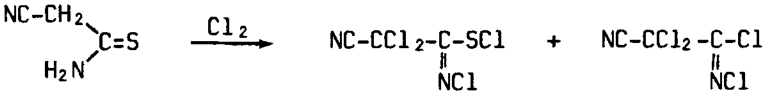
### 3. Thiocarboxylic Acid Amides

Chlorine, $SO_2Cl_2$, and $SCl_2$ are just a few of a large number of oxidizing agents which have been used in syntheses of 3,5-disubstituted 1,2,4-thiadiazoles from thioamides.[20] Contrary to expectations, cyanothioacetamide yields the two products 43 and 44, but no thiadiazole, upon chlorination in $CCl_4$.[57] At low temperature the formation of N,2,2-trichlorocyanoacetimidosulfenyl chloride 43 is favored; at room temperature 44 is the main product.[57] Under the same conditions $R(C{=}S)NH_2$ (R = methyl and R = 3-



42

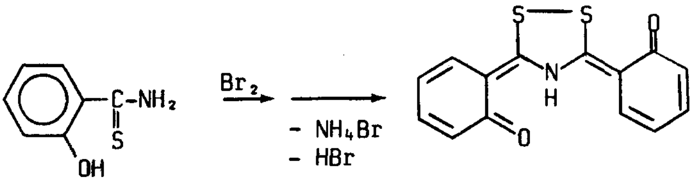
(4)



43 44

(5)

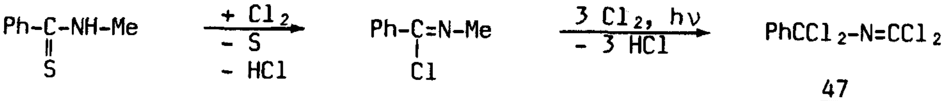
pyridyl) react according to Eq. 4.[57] Oxidation of 2-hydroxythiobenzamide with bromine followed by hydrolysis gives 1,2,4-dithiazolidinyl-3,5-bis(o-benzoquinonemethide).[73]



45

(6)

Exhaustive chlorination of N-methylthiobenzamide produces N-(phenyldichloromethyl)-dichloromethaneimine.[58]

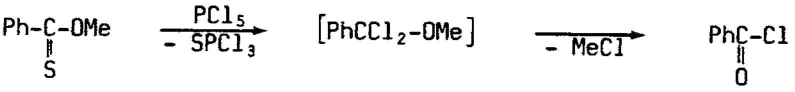


$$\text{Ph-}\underset{\underset{\displaystyle S}{\|}}{C}\text{-NH-Me} \xrightarrow[\substack{-\ S \\ -\ HCl}]{+\ Cl_2} \text{Ph-}\underset{\underset{\displaystyle Cl}{|}}{C}\text{=N-Me} \xrightarrow[-\ 3\ HCl]{3\ Cl_2,\ h\nu} PhCCl_2\text{-N=}CCl_2 \qquad (7)$$

46 47

## 4. Thiocarboxylates

O-Methyl propanethioate forms with chlorine a thermally unstable 1:1 adduct which is probably not covalently bonded.[59] O-Methyl thiobenzoate gives benzoyl chloride with PCl₅.[14]

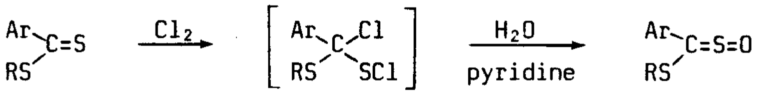


$$\text{Ph-}\underset{\underset{\displaystyle S}{\|}}{C}\text{-OMe} \xrightarrow[-\ SPCl_3]{PCl_5} [PhCCl_2\text{-OMe}] \xrightarrow[-\ MeCl]{} \text{Ph}\underset{\underset{\displaystyle O}{\|}}{C}\text{-Cl} \qquad (8)$$

48 49

### 5. Dithiocarboxylates

In the chlorination/hydrolysis procedure for the preparation of sulfines 52, α-chloro sulfenyl chlorides 51 are likely intermediates, but were not isolated.[23] The sulfine synthesis described in Eq. 9 applies only to 50

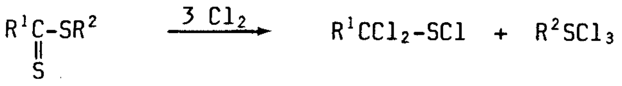


50 51 52

(9)

with *ortho*-disubstituted Ar, *e.g.* Ar = mesityl. Thus phenyl 2,5-dimethyl-4-methoxydithiobenzoate, mesityl 3,5-dimethyl-4-methoxydithiobenzoate, and ethyl dithioacetate yielded only starting material and the corresponding thioloester.[23]

Exhaustive chlorination of dithiocarboxylic acid esters leads to α,α-dichloro sulfenyl chlorides 53, which in turn ($R^1$ = aryl) can be dechlorinated with triphenylphosphine to give thioacid chlorides, or hydrolyzed to give chlorosulfines.[23]



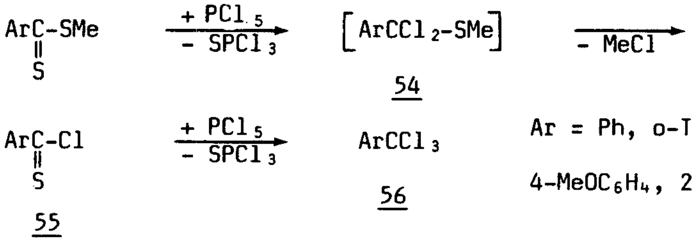
$$R^1\underset{\underset{S}{\|}}{C}\text{-}SR^2 \xrightarrow{3\ Cl_2} R^1CCl_2\text{-}SCl + R^2SCl_3 \qquad (10)$$

53

$R^1$ = Me, Et; $R^2$ = Me: Ref. 59, 118

$R^1$ = Aryl; $R^2$ = Et: Ref. 23

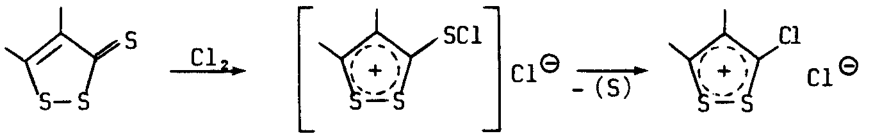
(Trichloromethyl)-arenes 56 are formed by chlorination/desulfurization of methyl dithiobenzoates with phosphorus pentachloride.[14]



(11)

Ar = Ph, o-Tol, m-Tol, p-Tol, 4-MeOC$_6$H$_4$, 2-Me-5-i-Pr-C$_6$H$_3$

Trithiones [121] (1,2-dithiole-3-thiones) 57 are precursors for 3-chloro-1,2-dithiolium salts 59. The transformation 57 → 59 has been effected by chlorination with oxalyl dichloride, phosgene, chlorine,[16] and sulfur dichloride.[22] The proposed intermediate 58 was not isolated.[16]



(12)

57 58 59

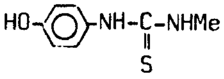
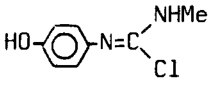
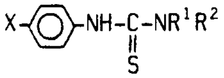
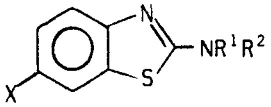
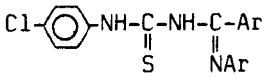
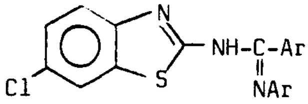
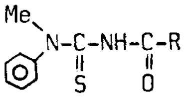
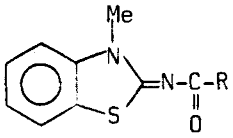
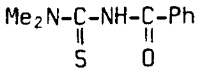
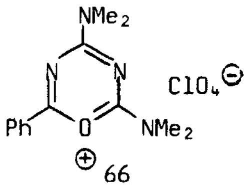
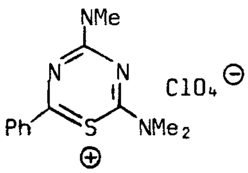
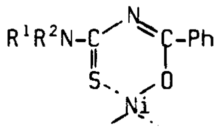
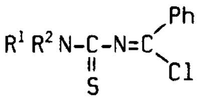
## 6. Thiocarboxylic Acid Halides

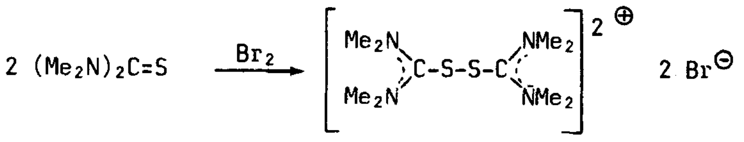
The formation of (trichloromethyl)-arene 56 *via* thiobenzoyl chloride 55 as assumed in Eq. 11 is supported by an independent experiment proving that (trichloromethyl)-benzene is formed when thiobenzoyl chloride is treated with PCl$_5$.[14]

## 7. Thioureas

Halogenation of thiourea,[116] N,N,N',N'-tetramethylthiourea,[60,61] and 1,3-dimethylimidazoline-2-thione[115] produces thiouronium salts by oxidative coupling.[120] Similarly, dithiobiuret [(H$_2$N)C(=S)]$_2$NH cyclizes upon oxidation with *e.g.* iodine to give the hydriodide of 3,5-diimino-1,2-dithiazolidine.[117] Oxidation with ICl and titration of the liberated iodine

TABLE 3. Halogenation Products of Substituted Thioureas

| Substrate | Reagent | Product | Refs |
|---|---|---|---|
|  | $Cl_2C=O$ | <br>62 | 18 |
|  | $Br_2$ | <br>63 | 63 |
|  | $Cl_2$ | <br>64 | 64 |
|  | $SOCl_2$ | <br>65 | 17 |
| <br>$Me_2N-\underset{\underset{S}{\|}}{C}-NH-\underset{\underset{O}{\|}}{C}-Ph$ | $PCl_5$<br>or $SOCl_2$ | <br>66 | 15 |
| | $POCl_3$ | <br>67 | 65 |
|  | $SOCl_2$ | <br>68 | 66,67 |



(13)

60

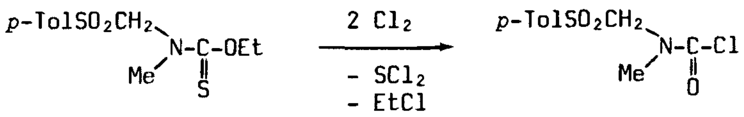
constitutes an analytical method for thioureas.[62]

$$(RHN)_2C{=}S + 8\ ICl + 5\ H_2O \longrightarrow \underset{\underline{61}}{(RNH)_2C{=}O} + 4\ I_2 + H_2SO_4 + 8\ HCl \qquad (14)$$

Halogenation products of some N,N'-substituted thioureas are shown in TABLE 3. Dehydrohalogenation, desulfurization, and chlorination of N-(4-hydroxyphenyl)-N'-methylthiourea occur in reaction with phosgene to give a substituted carbamimidic chloride 62.[18] An intramolecular cyclization may follow halogenation of N-arylthioureas leading to the formation of 2-aminobenzothiazoles 63 and 64 [63,64] or 2-iminobenzothiazoles 65 in case the ring nitrogen is substituted.[17] Depending on the reagent, N-aroyl-N',N'-dialkylthioureas may yield 2-aryl-4,6-diamino-1,3,5-oxadiazinium salts 66 or 1,3,5-thiadiazinium salts 67 by cyclocondensation. Complexation of N-aroyl-N',N'-dialkylthioureas with nickel(II) protects the thiocarbonyl group from chlorination, and by treatment of the complex with thionyl chloride N-thiocarbamoylbenzimidoyl chlorides 68 are obtained.[66,67]

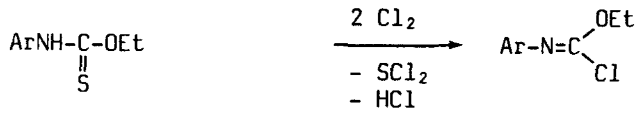
## 8. Thiocarbamates

O-Alkyl N,N-disubstituted thiocarbamates react with dry chlorine in methylene chloride to give the corresponding carbamoyl chlorides 69 in good yields.[68] Under the same conditions O-alkyl N-monosubstituted thiocarbamates eliminate hydrogen chloride and sulfur dichloride to yield chloroimidoformates 70.[68]



69

(15)

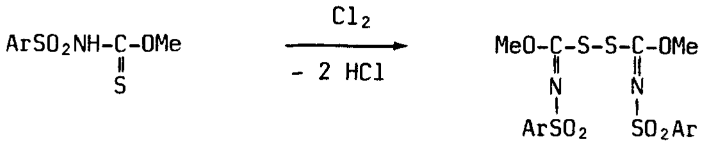


70

(16)

Ar = Ph, 4-$(O_2N)C_6H_4$

An oxidative coupling occurs upon chlorination of O-methyl N-arenesulfonylthiocarbamates.[69] Conversion of thionocarbamates to carbamates and cyclic carbonates has been observed in the chlorination of carbohydrate derivatives under conditions where moisture was not excluded.[70]



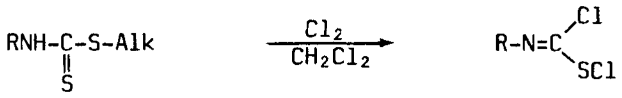
71

(17)

## 9. Dithiocarbamates and Related Compounds

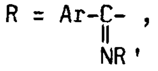
Unstable iminochloromethanesulfenyl chlorides 73 are obtained by chlorination of N-monosubstituted dithiocarbamates.[64,68] Reaction of 73

(R = Ar(C=NR')) with 4-chloroaniline gives hydrochlorides of the amidines. 64.[64] Chlorination of 72 in refluxing toluene gives iminodichloromethanes



72 73 (18)

R = $p$-TolSO$_2$CHR', Alk = Et: Ref. 68

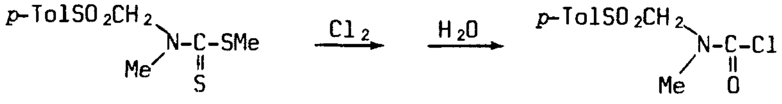


R = $\mathrm{Ar{-}\underset{\underset{NR'}{\|}}{C}{-}}$ , Ar = $C_6H_5$, 4-ClC$_6$H$_4$, Alk = Bu: Ref. 64

74.[68] N-Acyldithiocarbamates 72 (R = Ar(C=O)- and R = EtO(C=O)-) react similarly.[19,71]

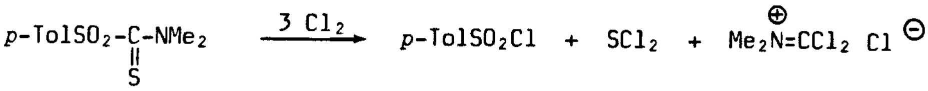
$$\underline{72} \xrightarrow{Cl_2} \underset{\underline{74}}{R\text{-}N\text{=}CCl_2} \qquad (19)$$

The chlorination product of the N,N-disubstituted dithiocarbamate 75 hydrolyzed during work-up to give the carbamoyl chloride 76.[68]



75 76 (20)

C-Sulfonylthioformamide 77 is cleaved by chlorine in boiling tetrachloromethane to give tosyl chloride, sulfur dichloride, and N,N-dimethyldichloromethyliminium chloride 78.[72] However, the precursor for 77 is the corresponding thiocarbamoyl chloride,[72] which also gives 78 upon chlorination (see Section III.10).

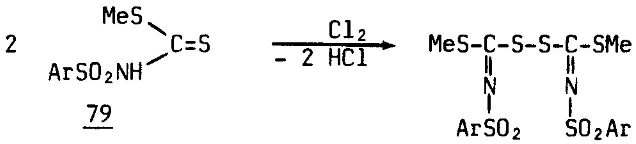


$$p\text{-TolSO}_2\text{-}\underset{\underset{S}{\|}}{C}\text{-NMe}_2 \xrightarrow{3\ Cl_2} p\text{-TolSO}_2Cl + SCl_2 + Me_2\overset{\oplus}{N}{=}CCl_2\ Cl^{\ominus}$$

77 78

(21)

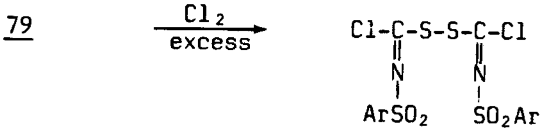
Like the monothio analogs in Eq. 17, N-arenesulfonyldithiocarbamates are oxidized by 1/2 equivalent of chlorine.[69] Exhaustive chlorination gives



79 80

(22)

the bis(N-arenesulfonyliminochloromethyl) disulfanes 81.[69]

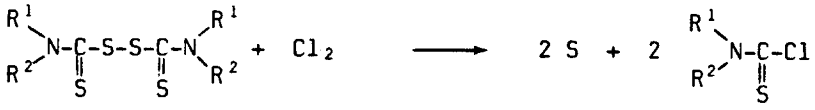


$$79 \xrightarrow[\text{excess}]{Cl_2} Cl\text{-}\underset{\underset{\underset{ArSO_2}{|}}{N}}{\overset{}{\underset{\|}{C}}}\text{-S-S-}\underset{\underset{\underset{SO_2Ar}{|}}{N}}{\underset{\|}{C}}\text{-Cl}$$

81

(23)

Reaction of thiuram disulfides with chlorine constitutes a useful synthesis of thiocarbamoyl chlorides in good yields. The chlorination may con-



82

(24)

$R^1$, $R^2$ = Et, Ph;  $-(CH_2)_5-$ ; [74]

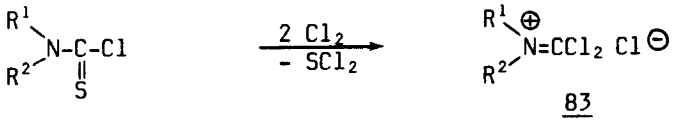
$R^1 = R^2$ = Me, Et, *i*-Pr, Bu, *i*-Bu; [74-77]

veniently be carried out with sulfuryl chloride instead of chlorine.[78]

N,N,N',N'-Tetramethylthiuram monosulfide is desulfurized and chlorinated by phosgene to give N,N-dimethyldichloromethyliminium chloride 78, and since carbonyl sulfide is the only by-product, 78 is obtained very pure, particularly free of chlorine.[79]

## 10. Thiocarbamoyl Chlorides

Sulfur is extruded as $SCl_2$ and iminium salts 83 are formed when thiocarbamoyl chlorides are chlorinated. An alternate synthesis of 83 ($R^1$ = $R^2$ = Me) is given at the end of Section III.9.



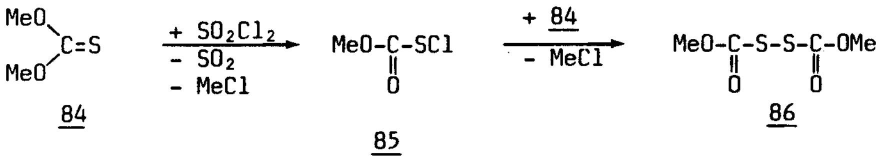
(25)

$R^1 = R^2 =$ Me, Et; [13,80]

$R^1 =$ Me, $R^2 =$ Aryl;[81]

## 11. Thiocarbonates

Treatment of O,O'-dimethyl thiocarbonate with 1/2 equivalent of sulfuryl chloride at 0°C leads to the rapid formation of bis(methoxycarbonyl) disulfane 86.[7] The intermediacy of 85 was established by trapping with N-methylaniline.[7] Oxidation of a thiocarbonate with chlorine without rigorous exclusion of moisture to give a carbonate has been reported.[70]

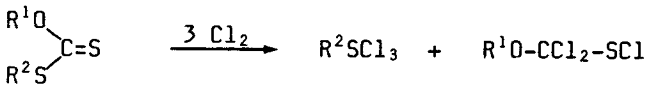


(26)

## 12. Dithiocarbonates and Related Compounds

Thorough investigations in the field of thiocarbonic acid derivatives have recently been reported in a series of papers comparing new methods with earlier literature methods.[7-11] Only the results directly related to chlorination reactions are summarized in this section.

Alkoxydichloromethanesulfenyl chlorides 88 are available by anhydrous chlorination of O,S-dialkyl dithiocarbonates.[9] Further chlorination gives a trichloromethyl ether.[82] With aqueous chlorine alkyl chloroformates and



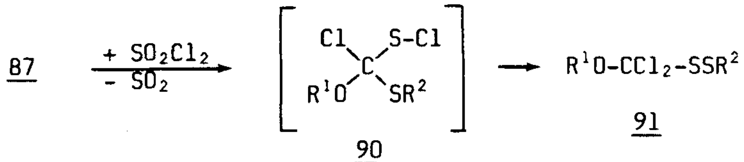
87 88 (27)

$R^1 = R^2 = $ Me, Et

$R^1 = $ Me, $R^2 = $ Pr, *i*-Pr

$$\underset{88}{} \xrightarrow[-\ SCl_2]{+\ Cl_2} \underset{89}{R^1\text{-}O\text{-}CCl_3} \qquad (28)$$

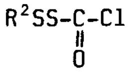
alkanesulfonyl chlorides are obtained.[19] Chlorination of the mixed thioanhydride $ROC(=S)SC(=O)CH_3$ gives 141 *via* 140 and $SCl_2$,[108] cf. Section IV.6. An unstable product isolated from a carefully controlled chlorination of an S-methyl dithiocarbonate derived from a sugar has been assigned an α-chloro sulfenyl chloride structure.[70] However, using sulfuryl chloride as the chlorinating agent Barany *et al.*[7,10] have demonstrated that for O-alkyl S-



90 91 (29)

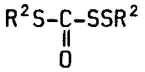
methyl dithiocarbonates a rapid rearrangement of the initially formed adduct takes place.

Chlorination of 87 ($R^1$ = *sec*- or *tert*-alkyl, $R^2$ = Me) gives varying amounts of the products 92, 93, and 94.[10] The formation of these products



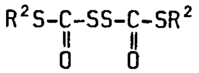
$R^2SS\text{-}\underset{\underset{O}{\|}}{C}\text{-}Cl$

92



$R^2S\text{-}\underset{\underset{O}{\|}}{C}\text{-}SSR^2$

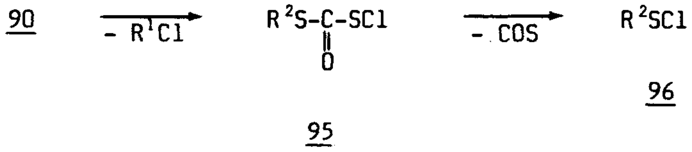
93



$R^2S\text{-}\underset{\underset{O}{\|}}{C}\text{-}SS\text{-}\underset{\underset{O}{\|}}{C}\text{-}SR^2$

94

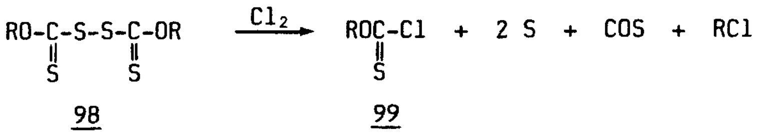
can be explained by the intermediacy of the sulfenyl chlorides 95 and 96 formed in turn by elimination of alkyl chloride from the primary product 90 ($R^2$ = Me) followed by loss of carbonyl sulfide.[10] Spontaneous elimina-



$$\underline{90} \xrightarrow[-\ R^1Cl]{} \underset{\underline{95}}{R^2S\text{-}\underset{\underset{O}{\|}}{C}\text{-}SCl} \xrightarrow[-\ COS]{} \underset{\underline{96}}{R^2SCl} \qquad (30$$

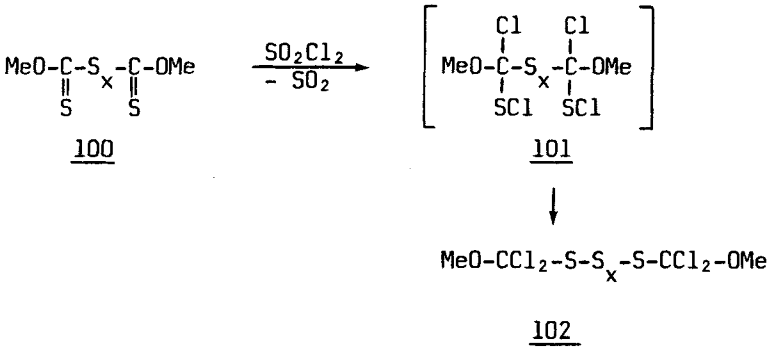
tion of *sec*-alkyl chloride from the rearranged product 91 leads to the (alkyldithio)carbonyl chloride 92 which upon further chlorination gives chlorocarbonylsulfenyl chloride, Cl-(C=O)-SCl (97). This method provided the final steps in the preparation of $^{18}O$-enriched 97.[11]

The preparation of O-alkyl chlorothioformate 99 from bis(alkoxythiocarbonyl)disulfane by the method of Sasse [83,113] involving chlorination and distillation proceeds, according to Barany *et al*.[8] with the stoichio-



$$\underset{\underline{98}}{RO\text{-}\underset{\underset{S}{\|}}{C}\text{-}S\text{-}S\text{-}\underset{\underset{S}{\|}}{C}\text{-}OR} \xrightarrow{Cl_2} \underset{\underline{99}}{RO\underset{\underset{S}{\|}}{C}\text{-}Cl} + 2\ S + COS + RCl \qquad (31)$$

metry shown in Eq. 31. Alkoxydichloromethanesulfenyl chloride 88,[59,84] or alkyl trichloromethyl ether 89,[85] can be prepared directly from 98 by treatment with the appropriate amount of chlorine. Chlorination of 100 ( x = 1, 2) with $SO_2Cl_2$ in refluxing petroleum ether yields rearranged products 102 quantatively.[7,9]

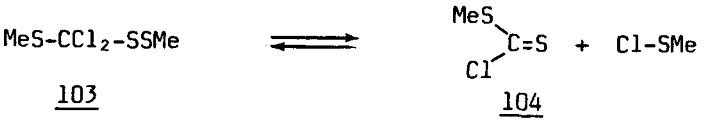


$$\underset{\underline{100}}{MeO-\underset{\underset{S}{\|}}{C}-S_x-\underset{\underset{S}{\|}}{C}-OMe} \xrightarrow[-\ SO_2]{SO_2Cl_2} \left[\underset{\underline{101}}{MeO-\overset{Cl}{\underset{SCl}{C}}-S_x-\overset{Cl}{\underset{SCl}{C}}-OMe}\right] \longrightarrow \underset{\underline{102}}{MeO-CCl_2-S-S_x-S-CCl_2-OMe} \qquad (32)$$

## 13. Trithiocarbonates and Related Compounds

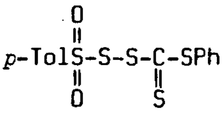
Isolation of unidentified "addition products", complete degradation to trivial products and complex formation are some characteristics of early reports concerning reactions of trithiocarbonic acid esters with halogens.[86-89]

Successful halogenations giving α-halo sulfenyl halides are listed in TABLE 4. Bis(methylthio)chloromethanesulfenyl chloride is the product isolated when the reaction between dimethyl trithiocarbonate and $SO_2Cl_2$ is performed in pentane at - 15°C, whereas in chloroform at 25°C the isomeric (methylthio)dichloromethyl methyl disulfane 103 is formed in equilibrium with methanesulfenyl chloride and methyl chlorodithioformate.[12]



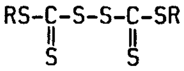
$$\underset{\underline{103}}{MeS-CCl_2-SSMe} \rightleftharpoons \underset{\underline{104}}{(MeS)(Cl)C{=}S} + Cl-SMe \qquad (33)$$

(Phenylthio)thiocarbonyl *p*-toluenesulfonyl disulfane 105 is cleaved when treated with an equimolar amount of $SO_2Cl_2$ in $CCl_4$ to give phenyl chlorodithioformate and bis(*p*-toluenesulfonyl)trisulfane as the main products.[90] Chlorodithioformates are formed by chlorination of 106.[91]



$p\text{-TolS}(=O)_2\text{-S-S-C}(=S)\text{-SPh}$

105



$RS\text{-C}(=S)\text{-S-S-C}(=S)\text{-SR}$

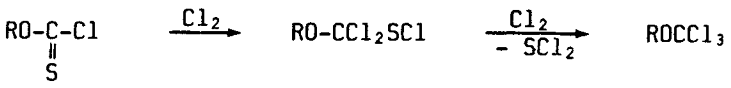
106

Treatment of the cyclic trithiocarbonate 4,4-dichloro-1,3-dithietane-2-thione with sulfuryl chloride yields a 1:1 adduct 2/5 (X + Y = $S\text{-}CCl_2\text{-}S$); infrared and $^{13}C$ NMR spectral data rule out a covalent structure.[122]

2 (X + Y = $SCCl_2S$) 5

## 14. Halothioformates and Halodithioformates

Chlorination of O-alkyl and O-aryl chlorothioformates yields alkoxy- and aryloxydichloromethanesulfenyl chlorides, and, by further chlorinations,[85,96] trichloromethyl ethers.



$$RO\text{-}C(=S)\text{-}Cl \xrightarrow{Cl_2} RO\text{-}CCl_2SCl \xrightarrow[-\,SCl_2]{Cl_2} ROCCl_3 \qquad (34)$$

99 107 108

R = Alkyl;[59,84,85] 99 formed as intermediate: see Section III.12.

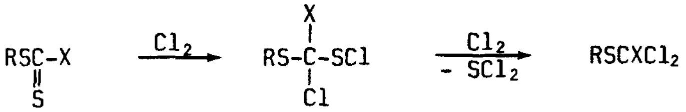
R = $C_6H_5$;[96] $C_6Cl_5$.[97]

TABLE 4. Halogenation of Trithiocarbonate Type Compounds

| $Q^1$ | $Q^2$ | X | Y | Yield (%) | Refs |
|---|---|---|---|---|---|
| PhS | $PhSO_2$ | Cl | | 80 | 92 |
| PhS | *p*-$TolSO_2$ | Cl | | 88 | 92 |
| $CF_3S$ | | F | Cl | 32 | 29, 24 |
| $CF_3S$ | | Cl | | 90 | 93, 94 |
| $CF_3S$ | | Br | | 60 | 94 |
| $CF_3Se$ | | Cl | | c) | 95 |
| $CH_3S$ | | Cl a) | | 53(90 b)) | 12 |
| NCS- | | Cl | | 73 | 112 |
| $CCl_3SS$ | | Cl | | 91 | 31, 26 |
| $CCl_3CCl_2SS$ | | Cl | | 97 | 26 |
| $CFCl_2CCl_2SS$ | | Cl | | 100 b) | 26 |

a) Chlorination with $SO_2Cl_2$ b) Crude yield c) Yield not reported.

Phenyl dichlorofluoromethyl ether is formed by chlorination of O-phenyl fluorothioformate.[80] Similar reactions apply to halodithioformates. 1:1



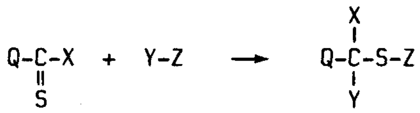
$$RS\underset{\underset{S}{\|}}{C}\text{-}X \xrightarrow{Cl_2} RS\text{-}\overset{\overset{X}{|}}{\underset{\underset{Cl}{|}}{C}}\text{-}SCl \xrightarrow[-\ SCl_2]{Cl_2} RSCXCl_2 \qquad (35)$$

109

110

Adducts of the type 109 are listed in TABLE 5. Trihalomethyl sulfides 110 (R, X = $ClCH_2CH_2$, Cl; $ClCH_2CH_2$, Cl; $C_6H_5$, F)[80] have been prepared according to Eq. 35 without isolation of the intermediates 109.

TABLE 5. Dihalomethanesulfenyl Chlorides from Halogenation of Halodithioformates and -selenothionoformates



$$Q-\underset{\underset{S}{\|}}{C}-X + Y-Z \longrightarrow Q-\overset{\overset{X}{|}}{\underset{\underset{Y}{|}}{C}}-S-Z$$

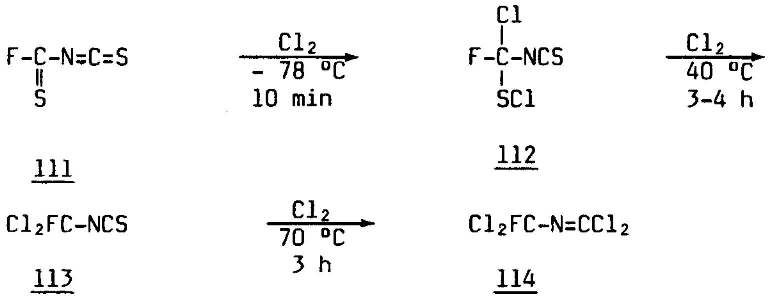
| Q | X | Y | Z | Yield (%) | Refs |
|---|---|---|---|---|---|
| $CH_3S$ | Cl | Cl | Cl[a] | 73 | 12 |
| $CF_3S$ | F | F | Cl | 30 | 24, 25 |
| $CF_3S$ | F | Cl | Cl | b) | 93 |
| $CF_3S$ | Cl | Cl | Cl | 93 | 29 |
| $CF_3S$ | Br | Cl | Cl | c) | 25 |
| $CF_3S$ | Br | F | Cl | 34 | 25 |
| $CF_3Se$ | F | Cl | Cl | b) | 95 |
| $CF_3Se$ | Cl | Cl | Cl | 51 | 98 |
| $CCl_3S$ | Cl | Cl | Cl | 60 | 99 |
| $CCl_3SCCl_2S$ | Cl | Cl | Cl | 60 | 100 |
| $2\text{-}C_{10}H_7S$ | Cl | Cl | Cl | 53[d] | 97 |
| $4\text{-}(O_2N)C_6H_4S$ | Cl | Cl | Cl | 83 | 97 |
| $2,4,5\text{-}Cl_3C_6H_2S$ | Cl | Cl | Cl | 71 | 97 |
| $C_6F_5S$ | Cl | Cl | Cl | 88 | 97 |
| $C_6Cl_5S$ | Cl | Cl | Cl | 93 | 97 |

a) Chlorination with $SO_2Cl_2$ b) Yield not reported c) Rearranged within 12 hrs to give 90% yield of $CF_3SSCCl_2Br$ d) Decomposes at room temperature

## 15. Thiocarbonyl Dihalides and Pseudohalides

In general thiocarbonyl dihalides react with halogens (FCl, $Cl_2$, $Br_2$) and a large number of trihalomethanesulfenyl halides have been prepared (see ref. 3, pp. 645-646).

The difference in reactivity of the two thiocarbonyl groups in thiocarbonyl fluoride isothiocyanate 111 is demonstrated in the reaction with chlorine.[30] The 1:1 adduct between ClF and 111 is a sulfenyl chloride $F_2(NCS)C\text{-}SCl$.[25] In the same way selenocarbonyl difluoride adds chlorine and bromine to give the corresponding selenenyl halides.[95,98]

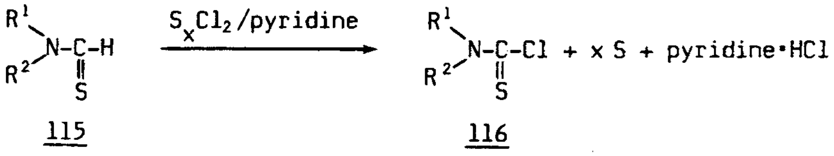


(36)

## IV. REACTIONS OF THIOCARBONYL COMPOUNDS WITH SULFUR DICHLORIDES

### 1. Thioformamides[21]

A 1:1 complex of sulfur dichloride and pyridine acts as a chlorinating agent in reactions with N,N-disubstituted thioformamides and a series of thiocarbamoyl chlorides have been prepared in this way in moderate to good yields. Disulfur dichloride/pyridine reacts similarly.

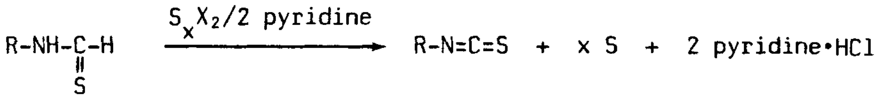


(37)

$R^1$ = Me, $R^2$ = Ph

$R^1 = R^2$ = Me, Pr, *i*-Pr, $-(CH_2)_4-$, $-(CH_2)_5-$, $-(CH_2)_2O(CH_2)_2-$

Thiocarbamoyl bromides could not be isolated from the reaction of 115 with $S_2Br_2$/pyridine but the crude product yielded O-ethyl thiocarbamate on ethanolysis. N-Monosubstituted thioformamides produce moderate yields of isocyanates by oxidation with sulfur dihalides/pyridine:



$$\text{R-NH-}\underset{\underset{\text{S}}{\|}}{\text{C}}\text{-H} \xrightarrow{S_xX_2/2\ \text{pyridine}} \text{R-N=C=S} + x\,\text{S} + 2\ \text{pyridine}\cdot\text{HCl} \qquad (38)$$

117

R = $C_6H_5$, c-$C_6H_{11}$ , $C_4H_9$

x = 1 or 2

X = Cl or Br

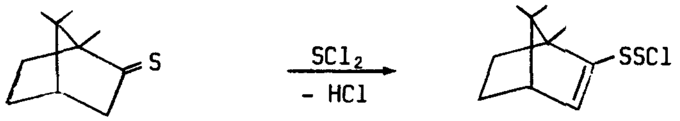
2. Thioketones[53,101]

Aromatic and sterically hindered aliphatic thioketones afford α-chloro thiosulfenyl chlorides (chloro disulfanes, 118) by reaction with sulfur dichloride in dry carbon disulfide under nitrogen at room temperature.

(39)

118

Thiobenzophenone, xanthione, 4,4'-dimethoxythiobenzophenone, 2,2,4,4-tetramethyl-3-pentanethione, adamantanethione, and thiofenchone react according to Eq. 39. The thiocamphor adduct under the same conditions eliminates hydrogen chloride to give the α,β-unsaturated chloro disulfane 119.



119

(40)

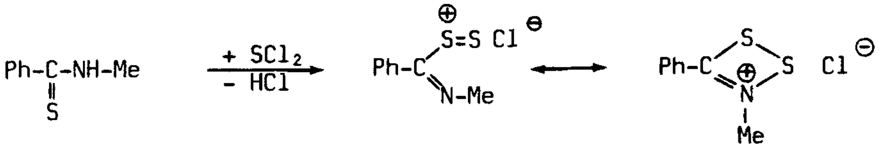
A thermally unstable compound with the proposed salt-like structure 120 precipitates when the addition is carried out in ether at - 78 °C.

$$Ph_2C{=}S \ + \ SCl_2 \longrightarrow Ph_2C{=}\overset{\oplus}{S}{-}S{-}Cl \ \ Cl^{\ominus} \qquad (41)$$

120

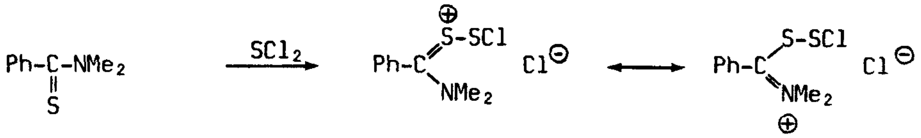
## 3. Thiocarboxylic Acid Derivatives

The oxidizing action of $SCl_2$ upon N-unsubstituted thiocarboxylic amides to give 1,2,4-thiadiazoles[20] 42 was mentioned in Section III.3. N-Methyl- and N,N-dimethylthiobenzamide react with sulfur dichloride to give unstable crystalline compounds.[102,103] Of the possible isomers in question, the products were ascribed the salt-like structures 121/122 and 123/124, respectively.



121 122

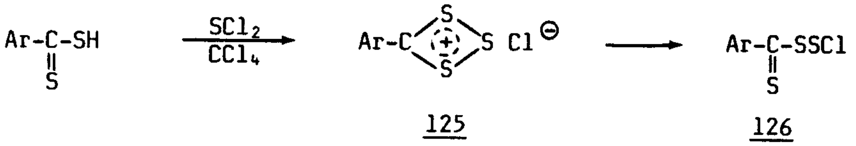
(42)



123 124

(43)

A four-membered ring tropylium analog, the trithiethanylium cation 125, has been suggested as the most reasonable structure of the unstable yellow salts obtained from the reaction of sulfur dichloride with dithiobenzoic acids.[51] Upon standing the salts decompose to red oils tentatively

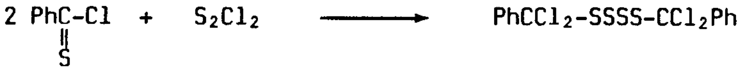


(44)

Ar = $C_6H_5$, $4\text{-}CH_3C_6H_4$, $1\text{-}C_{10}H_7$

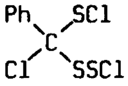
assumed to be thioaroyl chloro disulfane 126 mixed with aroyl chloro disulfane and polysulfanes.[51]

Chlorination of trithiones to dithiolium salts has been effected with $SCl_2$ (see Section III.5). By analogy with related reactions mentioned in this review, the 2:1 adduct from the reaction of thiobenzoyl chloride with disulfur dichloride[104,105] probably should be ascribed the tetrasulfane structure 127 rather than the isomeric structure 129 which for no obvious reason was assumed earlier[104,105] to be the more likely one. A 1:1 adduct 128 was proposed as an intermediate in the formation of the 2:1 adduct.[105]

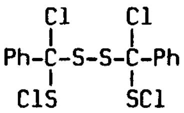


$$2\ \underset{\substack{\| \\ S}}{PhC}\text{-}Cl + S_2Cl_2 \longrightarrow PhCCl_2\text{-}SSSS\text{-}CCl_2Ph \qquad (45)$$

127



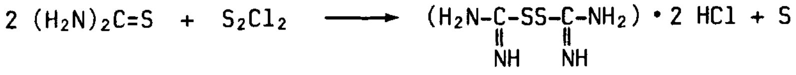
128



129

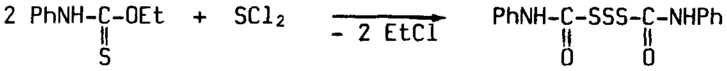
## 4. Thioureas and Thiocarbamates

An early report describes the reaction of thiourea with disulfur dichloride in boiling ethanol. Based on elemental analysis, the product was identified as a thiouronium salt 130.[106] Elimination of ethyl chloride accompanies the 1:2 addition of sulfur dichloride to O-ethyl (N-phenyl)thiocarbamate.[107] The reaction of $SCl_2$ with the unsaturated thiocarbamic esters 132 yields 2-thiazolidinones and/or 3-dithiazinones depending on the N-substituent.[107]



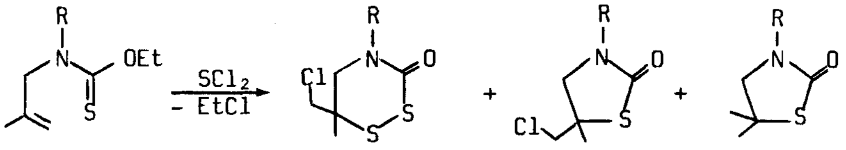
$$2\ (H_2N)_2C{=}S + S_2Cl_2 \longrightarrow (H_2N\text{-}\underset{\underset{NH}{\|}}{C}\text{-}SS\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH_2)\cdot 2\ HCl + S \qquad (46)$$

130



$$2\ PhNH\text{-}\underset{\underset{S}{\|}}{C}\text{-}OEt + SCl_2 \xrightarrow[-\ 2\ EtCl]{} PhNH\text{-}\underset{\underset{O}{\|}}{C}\text{-}SSS\text{-}\underset{\underset{O}{\|}}{C}\text{-}NHPh \qquad (47)$$

131

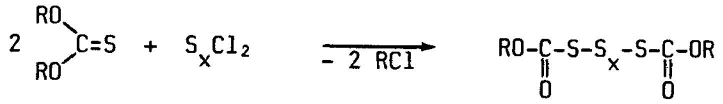


(48)

132 133 134 135

## 5. Thiocarbonic Acid Derivatives

Recently bis(alkoxycarbonyl) oligosulfanes 137 (which are also accessible by other methods) have been prepared by treatment of oligosulfur dichlorides with 2 equivalents of O,O'-dialkyl thiocarbonates.[9] Addition

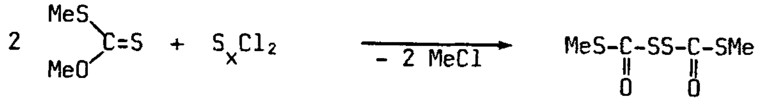


136 137 (49)

R = Me, Et

x = 1, 2, 3, 4

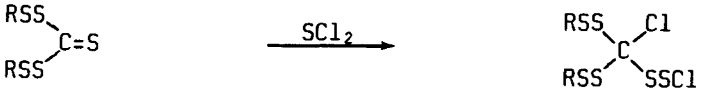
of 136 (R = Me) to an excess of $S_xCl_2$ (x = 1, 2) also gave 2:1 addition/elimination products 137, *i.e.* the 1:1 derivatives RO-(C=O)-S-$S_x$Cl could not be prepared.[9] In the same way bis (methylthio)carbonyl oligosulfanes have been prepared.[10]



x = 1, 2, 3, 4

138 (50)

Bis(perhaloalkyl)pentathiobis(peroxy)carbonates react with sulfur dichloride to yield chloro disulfanes.[26,31]



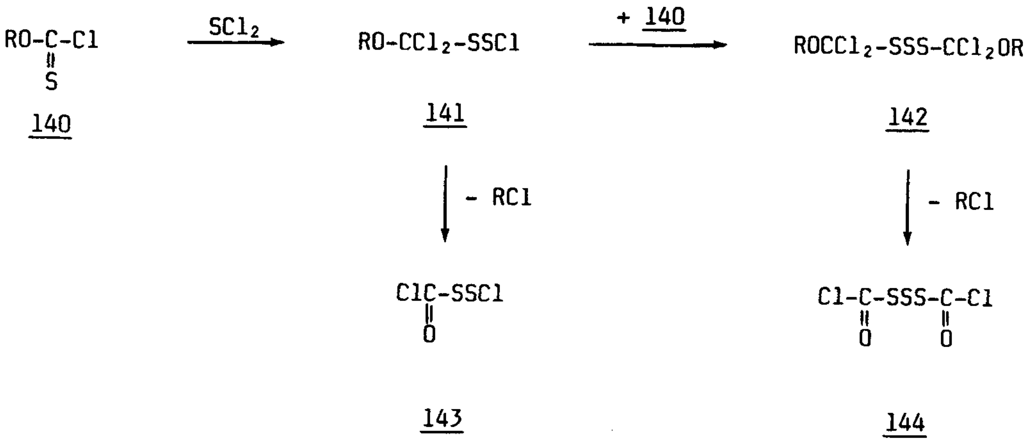
R = $CCl_3$, $CCl_3CCl_2$

139 (51)

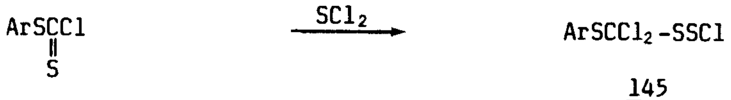
6. Halothioformates and Halodithioformates

O-Methyl and O-ethyl chlorothioformate form stable 1:1 [108,9] and 2:1 adducts[9] with sulfur dichloride; elimination of alkyl chloride to the corresponding carbonyl compounds 143 and 144 is catalyzed by $FeCl_3$ (Scheme 5).[9]

SCHEME 5



O-Pentachlorophenyl thioformate failed to react with $SCl_2$, even when refluxed overnight with iodine as a catalyst.[97] Pentafluorophenyl and pentachlorophenyl chlorodithioformate give (arylthio)dichloromethyl chloro disulfanes when treated with sulfur dichloride.[97]



$$\mathrm{ArSC(=S)Cl} \xrightarrow{SCl_2} \mathrm{ArSCCl_2\text{-}SSCl} \qquad (52)$$

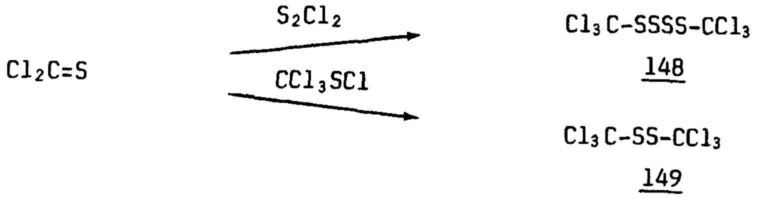
145

7. Thiocarbonyl Dihalides

Last century, Rathke noted the formation of bis(trichloromethyl) trisulfane 147 by the action of sulfur dichloride on thiophosgene.[109] The

$$\mathrm{Cl_2C{=}S} \xrightarrow{SCl_2} \underset{146}{\mathrm{Cl_3C\text{-}S\text{-}SCl}} \xrightarrow{Cl_2C=S} \underset{147}{\mathrm{Cl_3C\text{-}SSS\text{-}CCl_3}} \qquad (53)$$

first step in Eq. 53 is a convenient route to chloro(trichloromethyl)-disulfane.[110,119] The second step in Eq. 53 has also been accomplished as a separate reaction.[119] Treatment of disulfur dichloride with excess thiophosgene in acetonitrile gives bis(trichloromethyl)tetrasulfane, and in a related reaction the disulfane 149 has been prepared from thiophosgene and trichloromethanesulfenyl chloride in acetonitrile.[111]



(54)

(55)

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