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The Formal Oxidation Products of Bis(trichloromethyl) Disulfide and Trisulfide: An Experimental Approach

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Attempts were made at the synthesis of the five possible oxidation products of bis(trichloromethyl) disulfide *I* as well as of some of the seventeen formal oxidation products of bis(trichloromethyl) trisulfide *VII*. Only trichloromethyl trichloromethanethiolsulfonate *IV* and 1,3-bis(trichloromethyl)trisulfane 1,1-dioxide *VIII* could be obtained. Their chemical properties were investigated. The mass spectra of *I*, *IV*, *VII*, and *VIII* were recorded and interpreted.

In theory, a symmetrical disulfide such as bis(trichloromethyl) disulfide *I* can be oxidized to five oxygenated compounds:

$CCl_3-SO-S-CCl_3$ (*II*) $\quad CCl_3-SO-SO-CCl_3$ (*III*) $\quad CCl_3-SO_2-S-CCl_3$ (*IV*)

$CCl_3-SO_2-SO-CCl_3$ (*V*) $\quad CCl_3-SO_2-SO_2-CCl_3$ (*VI*)

The syntheses and properties of such compounds have been reviewed after the completion of our present work, and the reader is referred to these reviews.[22,29] One of the purposes of the present investigation was to obtain evidence for the existence or non-existence of *II*—*VI*. On one hand it could be anticipated that some of these hypothetical compounds would be destabilized by the presence of the bulky trichloromethyl groups, on the other hand, the same steric hindrance might prevent reagents to attack the sulfur-oxygen groupings and thus increase the stability of otherwise highly reactive species.

Once these objectives were set, several unique traits of trichloromethylsulfur chemistry had to be borne in mind. It had been previously reported [31,32] that *I* is extremely indifferent towards oxidizing agents and this was confirmed by additional experiments of our own. Thus the direct approach, namely the oxidation of *I*, was out of the question as a path to *II*—*VI*. Another peculiarity to be taken into account was the fact that trichloro-

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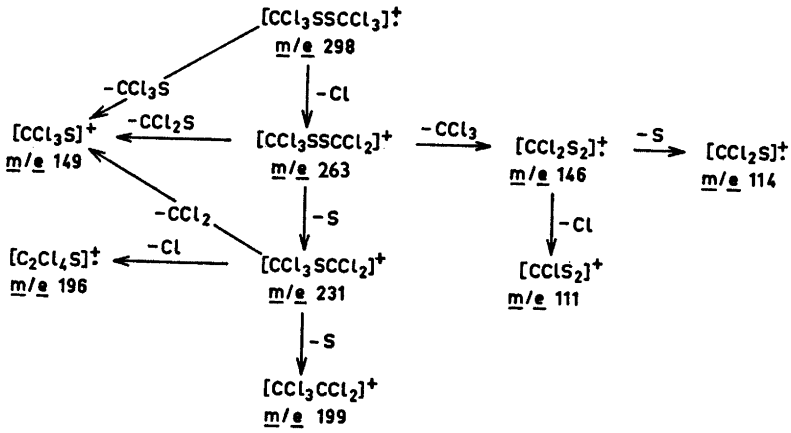


Scheme 1. The main fragmentation of *I* upon electron impact.

methanesulfonyl chloride has distinct oxidizing properties and in many instances will be unable to afford reaction products expected from sulfonyl chlorides in general.[31] A third limiting factor for the contemplated work was the strong feeling gained from several other authors' experience that radical reactions might be unsuitable to introduce the trichloromethanesulfonyl group into a molecule since the trichloromethanesulfonyl radical seems to lose sulfur dioxide extremely rapidly.[27]

Table 1. The mass spectrum of bis(trichloromethyl) disulfide *I*.

m/e	*I* (%)	Assignment
44	16.7	$[CS]^+$
47	11.4	$[CCl]^+$
55	3.8	?
64	8.2	$[S_2]^+$
67	3.1	$[ClS]^+$
76	4.0	$[CS_2]^+$
79	58.3	$[CClS]^+$
82	13.6	$[CCl_2]^+$
111	2.1	$[CClS_2]^+$
114	17.0	$[CCl_2S]^+$
117	100.0	$[CCl_3]^+$
146	4.8	$[CCl_2S_2]^+$
149	17.1	$[CCl_3S]^+$
196	0.9	$[C_2Cl_4S]^+$
199	0.9	$[C_2Cl_5]^+$
231	0.9	$[C_2Cl_5S]^+$
263	14.9	$[C_2Cl_5S_2]^+$
298	4.1	$[C_2Cl_6S_2]^+$

No metastable transitions were observed.

Trichloromethyl trichloromethanethiolsulfinate (II). Since neither trichloromethanethiol nor trichloromethanesulfenic acid nor their anions are known, substitution reactions were out of the question as a route to *II*.[4]

Neither was the recently published report about the formation of aryl arenethiolsulfinates in the hydrolysis of arenesulfenyl chlorides[15] of any help since trichloromethanesulfenyl chloride is extremely resistant to hydrolysis.

Thus the only remaining possibility was the direct oxidation of *I* under controlled conditions. This, however, was rendered impossible by *I*'s extreme indifference towards a wide variety of oxidants. Specific attempts to make *II* by treating *I* with ozone (*cf.* Ref. 5) or peracetic acid (*cf.* Ref. 20) failed.

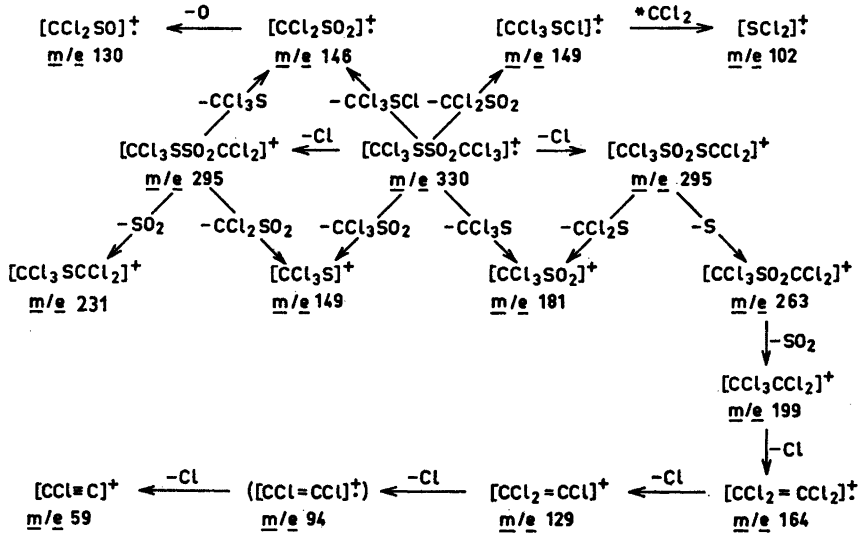
Bis(trichloromethyl) disulfoxide (III). Here again, a direct substitution reaction is ruled out by the instability of trichloromethanesulfenic acid.

It remained to be seen whether *III* could be prepared from trichloromethanesulfinyl chloride by treatment with a metal (*cf.* Ref. 6). This reaction was tried, but no *III* nor any other products related to it could be isolated.

Trichloromethyl trichloromethanethiolsulfonate (IV). We considered this compound to be the most easily accessible of the five and this proved to be correct. A straightforward synthesis from sodium trichloromethanesulfinate and trichloromethanesulfenyl chloride was achieved in 50 % yield according to (1).

$$CCl_3-SO_2^- + CCl_3-S-Cl \longrightarrow IV + Cl^- \qquad (1)$$

Though trichloromethanesulfenyl chloride reacts with a large number of sulfinates to yield the corresponding trichloromethyl thiolsulfonates,[33] trichloromethanesulfinic acid does not seem to have been employed in the



Scheme 2. The main fragmentation of *IV* upon electron impact.

Table 2. The mass spectrum of trichloromethyl trichloromethanethiolsulfonate *IV*.

m/e	*I* (%)	Assignment
44	27.6	$[CS]^+$
47	55.7	$[CCl]^+$
48	29.7	$[SO]^+$
58.5	0.3	$[CCl_3]^{++}$
59	0.4	$[C_2Cl]^+$
60	1.0	$[COS]^+$
63	4.4	$[ClCO]^+$
64	20.2	$[SO_2]^+$ and/or $[S_2]^+$
67	5.5	$[ClS]^+$
70	2.1	$[Cl_2]^+$
76	6.9	$[CS_2]^+$
79	100.0	$[CClS]^+$
80	3.5	?
82	54.8	$[CCl_2]^+$
85	3.3	?
91	0.1	$[C_2ClS]^+$
102	0.4	$[Cl_2S]^+$
114	8.5	$[CCl_2S]^+$
117	60.6	$[CCl_3]^+$
129	<0.1	$[C_2Cl_3]^+$
130	<0.1	$[CCl_2OS]^+$
146	<0.1	$[CCl_2O_2S]^+$ and/or $[CCl_2S_2]^+$
149	0.9	$[CCl_3S]^+$
161	0.1	$[C_2Cl_3S]^+$
164	0.1	$[C_2Cl_4]^+$
181	0.2	$[CCl_3O_2S]^+$
184	0.3	$[CCl_4S]^+$
199	3.5	$[C_2Cl_5]^+$
231	0.2	$[C_2Cl_5S]^+$
263	0.1	$[C_2Cl_5O_2S]^+$
295	0.1	$[C_2Cl_5O_2S_2]^+$
330	0.1	$[C_2Cl_6O_2S_2]^+$

A metastable transition was observed at *m/e ca.* 56–59.

synthesis of thiolsulfonates. In order to show the general usefulness of trichloromethanesulfinic acid for the synthesis of thiolsulfonates we also prepared methyl trichloromethanethiolsulfonate from methanesulfenyl chloride[11] and the free acid.

In order to compare the reactivity of *IV* with that of thiolsulfonates in general, it was treated with bromine, morpholine, and chloramin T, respectively. In all three cases a cleavage of the sulfur-sulfur bond occurs.[5]

$$IV + Br_2 \longrightarrow CCl_3{-}SO_2{-}Br + CCl_3{-}S{-}Br \quad (2)$$

$$IV + 2\ HN(CH_2CH_2)_2O \longrightarrow CCl_3{-}SO_2^-\ \overset{+}{H_2}N(CH_2CH_2)_2O + CCl_3{-}S{-}N(CH_2CH_2)_2O \quad (3)$$

$$IV + 2\ C_7H_7SO_2NNaCl + H_2O \longrightarrow CCl_3{-}S{\diagup\!\!\!\diagdown}\begin{matrix}N{-}SO_2{-}C_7H_7\\ NH{-}SO_2{-}C_7H_7\end{matrix} + CCl_3{-}SO_3H + 2\ NaCl \quad (4)$$

However, methanesulfonyl azide failed to attack the divalent sulfur atom in *IV* and only underwent its normal uncatalyzed pyrolysis (*cf.* Ref. 21).

The neat and quantitative cleavage of *IV* with morpholine according to (3) follows the general behavior of thiolsulfonates [9,16] and is in contrast to the behavior of trichloromethyl thiolsulfonates, $R-SO_2-S-CCl_3$, in general which also give rise to appreciable amounts of thioureas and sulfonamides as a consequence of the "reverse" cleavage due to the electronic influence of the trichloromethyl group.[16] For the reaction of the corresponding trifluoromethyl compounds, see Ref. 7. We must therefore assume that the electron distribution in *IV* closely resembles that found in "ordinary" thiolsulfonates since the influences of the two trichloromethyl groups offset each other. Ammonia cleaves the sulfur-sulfur bond in *IV* as easily as morpholine. However, the only well-defined product is ammonium trichloromethanesulfinate. Specifically, neither trichloromethanesulfenamide nor any products attributable to its transient formation could be isolated.

Also the reaction between *IV* and chloramin T (*cf.* Ref. 25) according to (4) is perfectly "normal" as opposed to the inertness of bis(trichloromethyl) disulfide *I* towards oxidizing agents. The resulting sulfinamidine has acidic properties and can be titrated with base in aqueous solution. It is attacked by oxidizing agents, but we were unable to isolate well-defined oxidation products. Both acid and alkaline hydrolysis of the sulfinamidine lead to *p*-toluenesulfonamide. Sulfinamidines in general are most conveniently prepared from thiols [14] or disulfides [1] and chloramin T.

Trichloromethylsulfinyl trichloromethyl sulfone (V). Trichloromethanesulfinyl chloride failed to yield *V* with either trichloromethanesulfinic acid or its sodium, silver, or tetramethylammonium salt. Nor was the other standard procedure, *i.e.* the dehydration of trichloromethanesulfinic acid, able to yield *V*. Thus, no *V* was obtained after treatment of the sulfinic acid with *N*-sulfinyl-*p*-nitroaniline (*cf.* Ref. 24) or phosphorus pentoxide, respectively.

The reaction between trichloromethanesulfinic acid and dicyclohexylcarbodiimide proceeded according to (5).

$$CCl_3-SO_2H + C_6H_{11}-N=C=N-C_6H_{11} \longrightarrow$$

$$C_6H_{11}-N=\underset{\displaystyle SO_2-CCl_3}{\underset{|}{C}}-NH-C_6H_{11} \quad \text{or} \quad C_6H_{11}-N=\underset{\displaystyle O-SO-CCl_3}{\underset{|}{C}}-NH-C_6H_{11} \qquad (5)$$

A *B*

The adduct is very unreactive (no reaction with trichloromethanesulfinic acid; at room temperature no hydrolysis with 1 N NaOH or concentrated HCl) and we therefore favor structure *A* (of an isothiourea *S,S*-dioxide) although its IR spectrum lacks prominent sulfonyl absorptions between 1300 and 1400 cm^{-1}. It does, however, contain a weak peak at 1320 cm^{-1} and a medium strong peak at 1295 cm^{-1}. The reproducibility of this reaction was very poor and therefore this matter was not pursued further. We have earlier (unpublished work by A.S.) observed a similar addition of benzenesulfinic acid to dicyclohexylcarbodiimide, but had to discontinue the experiments because of poor reproducibility.

It remained to be seen whether *V* could be made by mild oxidation of *IV*. No reaction was observed with ozone, peracetic acid (*cf.* Ref. 19), iodine pentoxide, and nickel peroxide,[26] respectively, while the only well-defined

product isolated after treatment with *t*-butyl hypochlorite at −55° (*cf.* Ref. 3) was trichloromethanesulfonyl chloride.

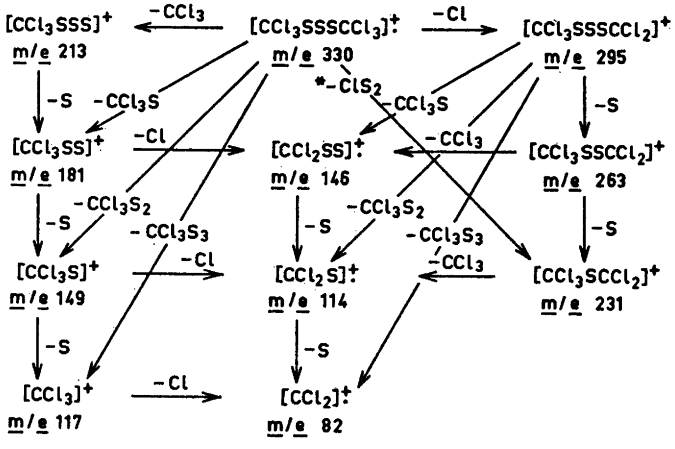
In order to check whether an unsymmetrical sulfinyl sulfone with one trichloromethyl group could be made, the reaction of trichloromethanesulfinyl chloride with *p*-chlorobenzenesulfinate and the reaction of *p*-chlorobenzenesulfinyl chloride with a trichloromethanesulfinate were tried. In the former case, the only well-defined product isolated was a small amount of *p*-chlorobenzenesulfinyl *p*-chlorophenyl sulfone [10] and, in the latter case, only a small amount of *p*-chlorobenzenesulfonic acid anhydride [5,13] was found.

Bis(trichloromethyl) disulfone (VI). Since *IV* had proved resistant to oxidation not involving cleavage of the sulfur-sulfur bond it remained to be seen whether *VI* could be made by oxidation of trichloromethanesulfinic acid (*cf.* Ref. 2), by a reaction of a trichloromethanesulfinate with trichloromethanesulfonyl chloride, or, finally, by reaction of trichloromethanesulfonyl chloride with magnesium. This was not the case. (Earlier attempts gave only hexachloroethane [17]).

Thus, oxidation of trichloromethanesulfinic acid with aqueous permanganate [2] or with Fenton's reagent only led to the formation of hexachloroethane. Treatment of the acid with bromine in carbon tetrachloride yielded only trichloromethanesulfonyl bromide.[27] Likewise, treatment of trichloromethanesulfonyl chloride with either the sodium or the silver sulfinate in dry organic solvents did not lead to any noticeable reaction.

To explore the possibility of formation of unsymmetrical disulfones with one trichloromethyl group we treated an aqueous solution of sodium trichloromethanesulfinate with methanesulfonyl chloride. After 15 h of stirring, no water-insoluble compound was found besides recovered methanesulfonyl chloride.

The formal oxidation products of bis(trichloromethyl) trisulfide (VII). As far as this part of our investigation is concerned, we expected from the outset that few, if any of the seventeen theoretically possible oxidation products of *VII* could be actually synthesized.



Scheme 3. The main fragmentation of *VII* upon electron impact.

Table 3. The mass spectrum of bis(trichloromethyl) trisulfide *VII*.

m/e	*I* (%)	Assignment
44	6.5	$[CS]^+$
47	14.0	$[CCl]^+$
59	3.3	$[C_2Cl]^+$
64	30.3	$[S_2]^+$
67	4.4	$[ClS]^+$
76	12.6	$[CS_2]^+$
79	35.9	$[CClS]^+$
82	2.1	$[CCl_2]^+$
96	2.1	$[S_3]^+$
99	1.4	$[ClS_2]^+$
111	3.2	$[CClS_2]^+$
114	9.6	$[CCl_2S]^+$
117	100.0	$[CCl_3]^+$
146	4.3	$[CCl_2S_2]^+$
149	2.3	$[CCl_3S]^+$
181	3.4	$[CCl_3S_2]^+$
213	0.4	$[CCl_3S_3]^+$
231	3.2	$[C_2Cl_5S]^+$
263	0.1	$[C_2Cl_5S_2]^+$
295	5.5	$[C_2Cl_5S_3]^+$
330	1.7	$[C_2Cl_6S_3]^+$

A metastable transition was observed at m/e = *ca.* 161—165.

While the synthesis of *VII* has been studied rather extensively,[31,34] very little is known about its reactions.[31] Thus, an examination of its behavior towards oxidizing agents was warranted. However, none of the desired products could be obtained. At room temperature, *VII* fails to react with either ozone, nickel peroxide,[26] or peracetic acid while treatment with peracetic acid at higher temperatures only affords water-soluble products. Nor does *VII* react with chloramin T in absolute ethanol.

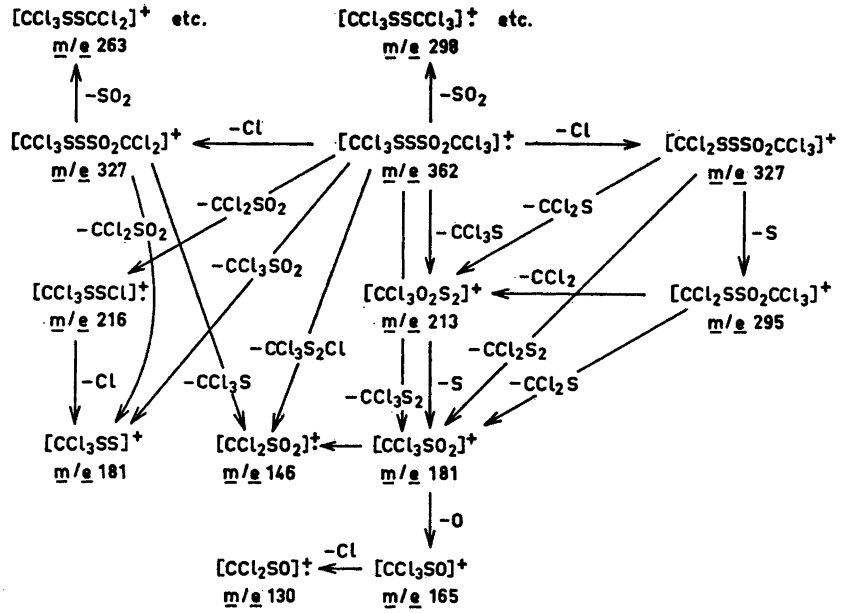
When an ethereal solution of trichloromethanesulfinic acid was allowed to react with trichloromethylchlorodisulfane, $CCl_3—S—S—Cl$,[12] the desired 1,3-bis(trichloromethyl)trisulfane 1,1-dioxide *VIII* was obtained in 50 % yield.

$$CCl_3—SO_2H + CCl_3—S—S—Cl \longrightarrow \underset{VIII}{CCl_3—SO_2—S—S—CCl_3} + HCl \qquad (6)$$

VIII reacts with morpholine according to (7):

$$VIII + 2\ HN(CH_2CH_2)_2O \longrightarrow CCl_3—SO_3^- \overset{+}{H_2}N(CH_2CH_2)_2O + \underset{C}{CCl_3—S—S—N(CH_2CH_2)_2O} \qquad (7)$$

The structure of *C* is also apparent from its direct synthesis from trichloromethylchlorodisulfane and morpholine.



Scheme 4. The main fragmentation of *VIII* upon electron impact.

VIII did, however, contrary to *IV* not react with chloramin T in absolute ethanol. Furthermore, it could not be oxidized to well-defined water-insoluble products.

A possible route to some of the remaining oxygen derivatives of *VII* was the reaction between trichloromethanesulfinic acid and sulfur dichloride, thionyl chloride, and sulfuryl chloride, respectively. As thionyl chloride is known to convert trichloromethanesulfinic acid to the acid chloride, $CCl_3-SO-Cl$, only sulfur dichloride and sulfuryl chloride were tried and found to oxidize the acid to CCl_3-SO_2-Cl.

Likewise, none of the desired products were obtained from the reactions between cobalt(II) sulfoxylate trihydrate [8] and trichloromethanesulfenyl chloride or trichloromethanesulfinyl chloride, respectively.

The mass spectra of I, IV, VII, and VIII. Mass spectrometry is superbly suited for the characterization of perchlorosulfur compounds since IR and especially UV spectra reveal few of the structural details and NMR spectroscopy is inapplicable.

Thus, the mass spectra of bis(trichloromethyl) disulfide *I*, bis(trichloromethyl) trisulfide *VII*, trichloromethyl trichloromethanethiolsulfonate *IV*, and 1,3-bis(trichloromethyl)trisulfane 1,1-dioxide *VIII* were recorded both to check the purity of our materials and to chart some of the fragmentation patterns of perchlorosulfur compounds in general.

In the tables shown we present the mass spectra of the compounds as well as our interpretation in terms of breakdown schemes. Peaks below *m/e* 40 as well as peaks due to ^{34}S and/or ^{37}Cl have been omitted. The inten-

Table 4. The mass spectrum of 1,3-bis(trichloromethyl)trisulfane 1,1-dioxide *VIII*.

m/e	*I* (%)	Assignment
44	23.3	$[CS]^+$ ($[CO_2]^+$)
47	24.7	$[CCl]^+$
48	25.7	$[OS]^+$
58.5	1.0	$[CCl_3]^{++}$
60	1.2	$[COS]^+$
63	3.2	$[CClO]^+$
64	21.0	$[SO_2]^+$ and/or $[S_2]^+$
67	4.6	$[ClS]^+$
70	1.2	$[Cl_2]^+$
76	23.7	$[CS_2]^+$
79	16.7	$[CClS]^+$
81	20.9	?
82	39.4	$[CCl_2]^+$
83	2.8	$[ClOS]^+$
85	3.3	?
111	3.1	$[CClS_2]^+$
114	11.4	$[CCl_2S]^+$
117	100.0	$[CCl_3]^+$
120	1.3	?
130	0.5	$[CCl_2OS]^+$
146	10.8	$[CCl_2O_2S]^+$ and/or $[CCl_2S_2]^+$
149	3.8	$[CCl_3S]^+$
165	0.4	$[CCl_3OS]^+$
181	1.8	$[CCl_3S_2]^+$ and/or $[CCl_3O_2S]^+$
213	0.2	$[CCl_3O_2S_2]^+$ ($[CCl_3S_3]^+$)
216	0.2	$[CCl_4S_2]^+$ and/or $[CCl_4O_2S]^+$
231	very weak	$[C_2Cl_5S]^+$
263	0.8	$[C_2Cl_5S_2]^+$ and/or $[C_2Cl_5O_2S]^+$
295	0.06	$[C_2Cl_5S_3]^+$ and/or $[C_2Cl_5O_2S_2]^+$
298	0.06	$[C_2Cl_6S_2]^+$ and/or $[C_2Cl_6O_2S]^+$
327	0.5	$[C_2Cl_5O_2S_3]^+$
362	very weak	$[C_2Cl_6O_2S_3]^+$

No metastable peaks were observed.

sities of the isotopic peaks checked well with the calculated intensities based upon natural isotope abundance.

Our mass spectrometric data are to a great extent self-explanatory. However, a few remarks might be in order. There are a number of ambiguities, mostly due to the fact that only low-resolution mass spectra were obtained. Thus we were unable to identify the peaks at *m/e* 55 (Table 1), *m/e* 80 (Table 2), *m/e* 81 (Table 4), *m/e* 85 (Tables 2 and 4), and *m/e* 120 (Table 4). In the cases of the oxygen-containing compounds *IV* and *VIII*, a number of peaks can be explained in terms of two isobaric ions due to the equivalence 2 O = S. Moreover, in these two compounds the two trichloromethyl groups are non-equivalent and it is impossible on the basis of our data to decide which of the two trichloromethyl groups, if any, has lost a chlorine atom preferentially in the M—Cl ion. An interesting feature in the spectra of *IV* and *VIII* are the sulfene-like species $[Cl_2C{=}SO_2]^+$ and $[Cl_2C{=}SO]^+$, the former presumably

formed by elimination of $CCl_3—S—Cl$ and $CCl_3—S—S—Cl$, respectively, from the molecular ions.

Only the thiolsulfonic ester has a metastable peak at m/e = *ca.* 56—59.

$$[CCl_3SCl]^+ \longrightarrow [SCl_2]^+ + CCl_2 \quad (m^* = 56.6)$$

This is in agreement with the fact that only the thiolsulfonic ester has a peak for $[CCl_3SCl]^+$.

Likewise only the trisulfide has a metastable peak at m/e = *ca.* 161—166.

$$[CCl_3SSSCCl_3]^+ \longrightarrow [CCl_3SCCl_2]^+ + ClS_2 \quad (m^* = 161.6)$$

EXPERIMENTAL

Melting and boiling points are uncorrected.

The mass spectrum of *I* was recorded with an Atlas CH 4 apparatus (direct inlet system). The mass spectra of *IV*, *VII*, and *VIII* were recorded with a Hitachi Perkin-Elmer RMU-6D apparatus (direct inlet system) with ion source temp. 225° and EM voltage 2000.

Bis(trichloromethyl) disulfide I was prepared according to Prey, Gutschik and Berbalk.[28] Since it was felt that the elaborate purification procedure described in the literature [18] was too tedious for our purposes, the following shortcut was employed: The crude disulfide was vacuum distilled twice at 87°/0.5 mm Hg. The residual faint yellow color was almost completely removed by bubbling through ozone/oxygen followed by another distillation at 48°/0.02 mm Hg, n_D^{25} 1.5880 (lit.[18] b.p. 131.5°/11 mm Hg, n_D^{20} 1.5926). This material was subsequently employed throughout this investigation and was quite pure as judged from mass spectrometry.

Trichloromethanesulfinic acid was prepared according to Loew.[31] Aqueous solutions of the sodium salt were obtained by neutralization with the calculated amount of sodium hydroxide solution. Evaporation of the water *in vacuo* yielded the crystalline salt.[31]

Silver trichloromethanesulfinate was prepared in ether suspension from the acid and silver carbonate. The salt decomposes slowly above 200°. (Found: C 4.38; H 0.14. Calc. for $CAgCl_3O_2S$: C 4.13; H 0.00).

Tetramethylammonium trichloromethanesulfinate was obtained by neutralizing the acid with aqueous tetramethylammonium hydroxide and evaporation to dryness. The salt decomposes slowly above 200°. (Found: C 24.03; H 4.65. Calc. for $C_5H_{12}Cl_3NO_2S$: C 23.42; H 4.72).

Trichloromethanesulfinyl chloride was made according to Schöllkopf and Hilbert [30] from trichloromethanesulfinic acid and thionyl chloride in ether, b.p. 34—38°/1 mm Hg (lit.[30] b.p. 36—38°/1 mm Hg).

Methyl trichloromethanethiolsulfonate. A mixture of 14.0 g (0.076 mole) trichloromethanesulfinic acid and 6.25 g (0.076 mole) methanesulfenyl chloride [11] in 10 ml dry ether was stirred for 2 h. After evaporation of the ether a practically quantitative yield of the brownish liquid crude product was obtained. Methyl trichloromethanethiolsulfonate can be vacuum distilled with partial decomposition at 47°/0.07 mm Hg. After recrystallization from petroleum ether it melts at 42—44°. (Found: C 10.69; H 1.41; Cl 45.68; S 27.77. Calc. for $C_2H_3Cl_3O_2S_2$: C 10.45; H 1.31; Cl 46.36; S 27.94).

Trichloromethyl trichloromethanethiolsulfonate IV. With vigorous stirring, a solution of 125 g (0.61 mole) sodium trichloromethanesulfinate in 150 ml water was treated with excess trichloromethanesulfenyl chloride at 40° for 3 h (*cf.* Ref. 33). The aqueous layer was discarded, the organic layer distilled *in vacuo* to remove excess trichloromethanesulfenyl chloride, and a residue of 115 g (0.35 mole, 57 %) raw *IV*, m.p. 34—38°, was obtained. Two subsequent molecular distillations at 50—60°/0.1 mm Hg raised the melting point to 39—41° and 43—44°, respectively. (Found: C 7.39; H 0.00; Cl 63.75; O 9.85; S 19.39. Calc. for $C_2Cl_6O_2S_2$: C 7.22; H 0.00; Cl 63.91; O 9.61; S 19.26). IR spectrum in carbon disulfide (in cm^{-1} ($\pm$ 4 cm^{-1}), s = strong, m = medium, and w = weak): 1380s and 1163s (sulfonyl group), 825s, 808s, 777w, 727m, and 561s.

Degradation of trichloromethyl trichloromethanethiolsulfonate IV with bromine. Equimolar amounts of *IV* and bromine were mixed and kept for 50 h. Distillation afforded

trichloromethanesulfenyl bromide,[31] b.p. 66°/10 mm Hg, the residue consisting of trichloromethanesulfonyl bromide, m.p. (after sublimation *in vacuo*) 134–136° (lit.[27] m.p. 138°).

Degradation of trichloromethyl trichloromethanethiolsulfonate IV with morpholine. Trichloromethyl trichloromethanethiolsulfonate (11 g, 0.033 mole) was dissolved in dry ether. Morpholine (6.0 g, 0.069 mole) was dissolved in dry ether and added dropwise, with stirring. After stirring for another 20 min, the precipitated morpholinium trichloromethanesulfinate was filtered off. Yield 8.6 g (96 %), m.p. 100–105° (decomp.). (Found: C 23.32; H 3.99. Calc. for $C_5H_{10}Cl_3NO_3S$: C 23.12; H 3.71). Evaporation of the filtrate yielded 7.4 g (94 %) *N*-(trichloromethanesulfenyl)morpholine, m.p. 52–56° (after sublimation *in vacuo*). The literature[23] gives m.p. 86–87°, but an authentic sample prepared from morpholine and trichloromethanesulfenyl chloride had identical m.p., mixed m.p., IR, and NMR spectra. Ammonia bubbled through 3.71 g (0.0111 mole) trichloromethyl trichloromethanethiolsulfonate in ether at −60°C gave 2.65 g white precipitate. IR indicated the presence of NH_4^+ and $CCl_3SO_2^-$. The precipitate consisted according to the analytical data of 2.23 g (0.0111 mole) $NH_4SO_2CCl_3$ and 0.46 g (0.0086 mole) NH_4Cl. After evaporation of the ether a fatty, unidentified mass remained.

N,N′-*Bis(*p*-toluenesulfonyl)trichloromethanesulfinamidine.* Chloramin T trihydrate (22.52 g, 0.08 mole) and 13.32 g (0.04 mole) trichloromethyl trichloromethanethiolsulfonate were dissolved in 400 ml abs. ethanol and stirred for 3 h (*cf.* Ref. 25). The precipitated sodium chloride was filtered off, most of the ethanol stripped off, and the residue collected on a filter and washed with water and ether. 10 g (50 %) *N,N′*-bis(*p*-toluenesulfonyl)trichloromethanesulfinamidine was obtained, m.p. 168–169° (decomp.). (Found: C 36.91; H 3.11; Cl 20.63; N 5.61; S 18.81. Calc. for $C_{15}H_{15}Cl_3N_2O_4S_3$: C 36.89; H 3.10; Cl 21.47; N 5.73; S 19.47. Equiv. wt. (found by potentiometric titration with 0.1 N NaOH): 520. Calc. 490).

S-*Trichloromethyl*-N,N′-*bis(cyclohexyl)isothiourea* S,S-*dioxide.* 8.10 g (0.0393 mole) dicyclohexylcarbodiimide was added to 7.1 g (0.039 mole) trichloromethanesulfinic acid in 60 ml dry ether and stirred for 1 h. 0.70 g (0.0031 mole) precipitated *N,N′*-dicyclohexylurea was filtered off, most of the ether evaporated and the solution cooled. A colorless solid was filtered off. Recrystallization from acetonitrile gave 5.0 g (0.0128 mole, 33 %) of the compound, m.p. 110–112°. (Found: C 42.68; H 5.73; Cl 26.69; N 7.09; S 8.47. Calc. for $C_{14}H_{23}Cl_3N_2O_2S$: C 43.14; H 5.95; Cl 27.29; N 7.18; S 8.23).

Trichloromethylchlorodisulfane.[12] 170 g (0.91 mole) trichloromethanesulfenyl chloride, 40 g (1.25 mole) sulfur and 8 g triphenyl phosphate were mixed and kept at 140–150° for 7 h. Vacuum distillation yielded besides unidentified fractions 60.7 g (0.28 mole, 30 %) trichloromethylchlorodisulfane, b.p. 35–45.5/0.4 mm Hg, n_D^{20} 1.5915–1.6028 and 29.7 g (0.089 mole, 10 %) bis(trichloromethyl) trisulfide, b.p. 110–135°/0.4 mm Hg, m.p. 52–58°. Distillation of the disulfane afforded a fraction with b.p. 35°/0.4 mm Hg and n_D^{20} 1.6028. (Found: C 5.50; H 0.00; Cl 64.72; S 29.93; Calc. for CCl_4S_2: C 5.51; H 0.00; Cl 65.06; S 29.42).

*Trichloromethyl(*N*-morpholino)disulfane C.* To a solution of 8.7 g (0.01 mole) morpholine in ether was added dropwise 10.9 g (0.05 mole) trichloromethylchlorodisulfane under stirring. After filtration of the morpholinium chloride the ether was distilled off to leave 9.25 g (0.36 mole, 69 %) raw *C*, m.p. 85.5–88°. After two subsequent recrystallizations from light petrol: m.p. 89–91.5°. (Found: S 23.78. Calc.: S 23.88).

Bis(trichloromethyl) trisulfide VII was prepared according to Zbirovský and Ettel.[34] After sublimation at 40–50°/0.06 mm Hg, the compound was colorless, m.p. 51–54° (lit.[34] m.p. 57.5°).

1,3-Bis(trichloromethyl)trisulfane 1,1-dioxide VIII. To 4.36 g (0.02 mole) trichloromethyl chlorodisulfane in dry ether was added dropwise 3.67 g (0.02 mole) trichloromethanesulfinic acid in ether, the mixture stirred for 1 h, the ether evaporated and the residue recrystallized from ether to leave 4.0 g (0.0011 mole, 55 %) *VIII*, m.p. 111–113°. Sublimation at 80–90°/0.06 mm Hg raised the m.p. to 115–117°. (Found: C 6.86; Cl 57.99; S 25.71. Calc. for $C_2Cl_6O_2S_3$: C 6.58; Cl 58.29; S 26.36). IR spectrum (in cm^{-1} (± 4 cm^{-1}), s: strong and m = medium): 1372s and 1153s (sulfonyl group), 814s, 793s, 767s, 738m, and 561m.

Degradation of VIII with morpholine. 3.65 g (0.01 mole) *VIII* was dissolved in dry ether. Morpholine (1.8 g, 0.021 mole) was dissolved in ether and added dropwise with stirring. After 20 min the precipitated morpholinium trichloromethanesulfinate was

filtered off (2.65 g, 98 %). Evaporation of the ether yielded 2.49 g (92 %) of trichloromethyl(*N*-morpholino)disulfane identical with the sample described above.

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