Chlorotrithioperformates – a New Class of Compounds. Preparation and Some Applications**

Ejner K. Moltzen, Birgit Jensen and Alexander Senning*

Department of Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

Moltzen, Ejner K., Jensen, Birgit and Senning, Alexander, 1986. Chlorotrithioperformates – a New Class of Compounds. Preparation and Some Applications. – Acta Chem. Scand. B 40: 609–618.

The α additions of thiosulfenyl chlorides to carbon monosulfide (CS) constitute a general route to compounds containing the so far inaccessible functional group ClC(S)SS. Four examples are presented, $CH_3C(O)-$, $ClC(O)-$, Cl_3C-, and $Cl_5C_2-SSC(S)Cl$, all of which were prepared in good yields. The versatility of this new class of compounds as synthetic precursors is demonstrated by chlorination of the thiocarbonyl groups to the corresponding new α,α-dichloroalkanesulfenyl chlorides. The preparation of several derivatives of these sulfenyl chlorides is described. Considering the variety of thiosulfenyl chlorides available, a large group of new compounds has become accessible via this synthetic pathway.

Prompted by the successful α additions of sulfenyl chlorides to carbon monosulfide (CS) previously reported by us,[1,2] we extended our investigations on CS chemistry to include the corresponding reactions with thiosulfenyl chlorides, *1*. The α addition of *1* to CS according to (1) is a route to the so far inaccessible disulfides *2*. Hitherto, only one compound containing the functional group ClC(S)SS has been described in the literature, namely the unstable bis(chlorothiocarbonyl) disulfide,[1] *7*, which was prepared by double insertion of CS into the S–Cl bonds of disulfur dichloride. In principle, several routes to *2* can be proposed, but there are major obstacles to most of them: unavailability of starting materials, such as chlorodithioformic acid and chlorothiocarbonylsulfenyl chloride; the great risk of secondary reactions as in the condensation of hydrogen disulfides, RSSH,[3] with thiophosgene; and in the thionations of acyl chlorides. None of these are mentioned in the literature. The acid-catalyzed sulfhydrolysis of trichloromethyl disulfides, $RSSCCl_3$, analogous to the corresponding hydrolysis,[4] is not a feasible route to *2*, since neither *2* nor H_2S can survive the necessary reaction conditions. Evidently, there are no obvious alternatives to (1) for the preparation of *2*.

As with sulfenyl chlorides, CS was indeed very reactive towards thiosulfenyl chlorides and several disulfides of the structure *2* were obtained in good yields. Furthermore, *2* turned out to be versatile precursors for a series of new compounds.

Results and discussion

Four thiosulfenyl chlorides were treated with CS and the corresponding α addition products *3–6* were obtained according to (1). Carbon monosulfide showed a remarkable reactivity in these reactions. Usually, polymeric CS is formed as a

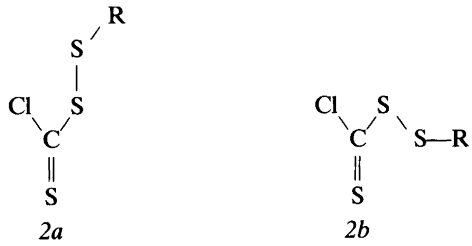
$$\underset{1}{RSSCl} + CS \longrightarrow \underset{2}{RSSC(=S)Cl} \qquad (1)$$

3, R = CH_3CO
4, R = ClCO
5, R = Cl_3C
6, R = Cl_5C_2

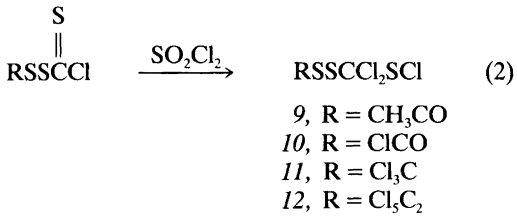
*To whom correspondence should be addressed.
**Carbon Monosulfide Chemistry in Solution, Part 5. For Part 4, see Ref. 20.

major by-product in reactions with CS,[1,5] but in this case, all the CS was consumed and only at the end of the reactions could formation of $(CS)_n$ be observed. Thus, these reactions can be performed as a kind of "titration" with CS. All four products were isolated in good yield and characterized, but the stability of *3–6* varied considerably (see Experimental below). The disulfide *4* was the most stable. This was quite surprising considering the unstable nature of the perthio analog *7*.[1] The preparation of *4* completed the series *4*, *7*, and *8*,[4] compounds of considerable interest as amino protecting groups.[6] In contrast to *7* and *8*, *4* contains both a chlorocarbonyl and a chlorothiocarbonyl group and the different reactivities of these two groups make available applications in syntheses which are not possible with *7* and *8*.

The infrared spectra of *3–6* showed an interesting feature. Thiocarbonyl groups usually have one strong absorption in the region 1000–1300 cm^{-1}, but the compounds *3–6* all displayed a splitting of this absorption (see Experimental below). This splitting must be due to the existence of two rotamers, *2a* and *2b*, in neat *2*. A similar behavior of certain thiocarbonyl compounds has previously been described in the literature.[7]

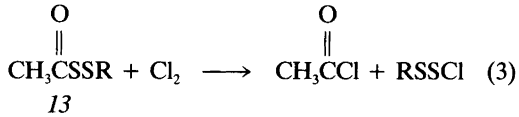


Chlorinations of thiocarbonyl groups are well established reactions[8] and the compounds *3–6* were chlorinated to yield the corresponding new sulfenyl chlorides according to (2). These chlorinations had to be performed carefully under mild conditions in order to avoid overchlorination. The disulfide bond is especially susceptible



(2)

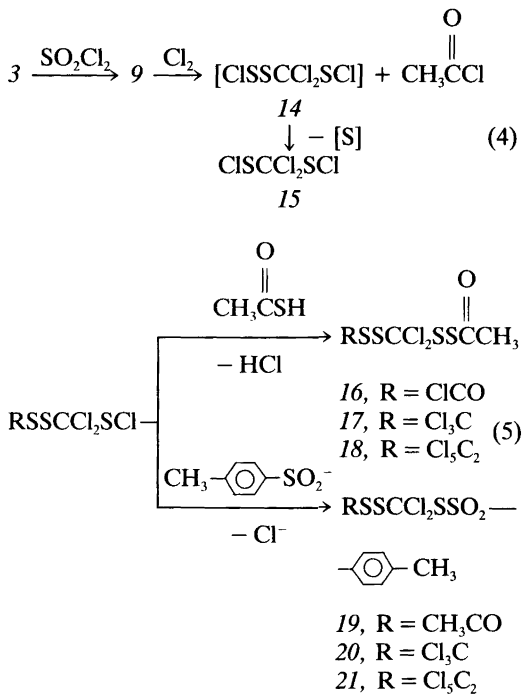
to attack by chlorine giving sulfenyl chlorides;[9] furthermore, the initially formed sulfenyl chloride group can be chlorolytically desulfurized to give the corresponding trichloromethyl group.[10,11] In order to avoid these side reactions, sulfuryl chloride was chosen as the clorinating agent as recommended by Barany and Mott.[12–14] The chlorinations of *4*, *5* and *6* were straightforward. However, while *10* and *12* were obtained in good yields by distillation, *11* was considerably less stable. Attempts to purify *11* both by distillation and chromatography resulted in decomposition with thiophosgene as the major decomposition product. In the chlorination of the acetyl substituted disulfide *3*, another problem had to be considered. It is well known that acetyl disulfides, *13*, can be cleaved unsymmetrically by chlorine according to (3)[15,16] and, obviously, *3* can undergo the same reaction.



(3)

Since thiocarbonyl groups are more susceptible to chlorination than S–S and C–S bonds,[8] the reaction sequence (4) is likely to take place. By very careful treatment of *3* with sulfuryl chloride, *9* was obtained in moderate yield. However, formation of the bis(sulfenyl chloride) *15* in low yield could not be avoided. Treatment of *9* with chlorine at −10 °C gave dichloromethanebis(sulfenyl chloride) *15* together with elemental sulfur. All attempts to isolate the intermediate *14* failed; obviously *14* is unstable and loses sulfur. Another explanation for the absence of *14* is cleavage of the S–S bond in *9* instead of the Ac–S bond, but this possibility can be ruled out since acetylsulfenyl chloride[15] was not present in the reaction mixture.

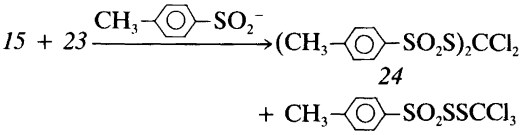
Besides characterization by spectroscopy and elemental analyses, several so far unknown derivatives of *9–12* were prepared by derivatization both with thioacetic acid and *p*-toluenesulfinate according to (5).



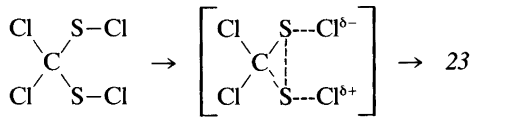
(4)

(5)

(6)



(7)



The bis(sulfenyl chloride) *15* is of considerable interest as precursor for a series of compounds and it has been described once in the literature.[17] It was prepared by saturation of carbon disulfide with chlorine at −5 °C followed by irradiation of the mixture with UV for several hours. But since this procedure gives a mixture of *15* and trichloromethanesulfenyl chloride, it is not an optimal route. Another approach to *15* is chlorination of *7* according to (6), but all attempts to chlorinate *7* with chlorine or sulfuryl chloride in various solvents and at various temperatures resulted in a mixture of *15* and trichloromethanethiosulfenyl chloride *23* as shown both by spectroscopy and by derivatization with *p*-toluenesulfinate, which yielded a mixture of *24* and *25*.[18] The new derivative *24* was also obtained in good yield by treating pure *15* (from reaction (4)) with *p*-toluenesulfinate.

A possible pathway to *23* is the unsymmetrical cleavage of the disulfide group in the intermediate *22*, but a more likely route is rearrangement of *15* according to (7), perhaps catalyzed by a species which is present in (6), but not in (4). These types of rearrangements of both sulfenyl chlorides and thiosulfenyl chlorides having alkylthio groups in the α position are well precedented.[8] The occurrence of this mixture of *15* and *23* is very inconvenient; separation by distillation is impossible due to the very close boiling points. Evidently, the treatment of *3* with two equivalents of chlorine is thus far the cleanest and most practical route to pure *15*.

Conclusion

The preparation of compounds containing the functional group ClC(S)SS by treatment of thiosulfenyl chlorides with CS is a method which has no competition. Furthermore, considering the variety of thiosulfenyl chlorides available,[13,15,16,21–59] a large group of new compounds has become accessible via this synthetic pathway.

Experimental

^{1}H NMR spectra were recorded at 60 MHz on a Varian EM-360 spectrometer. ^{13}C NMR spectra were recorded at 25.2 MHz on a Varian XL-100 spectrometer. TMS was used as an internal standard and chemical shifts are expressed in δ values. $CDCl_3$ was used as solvent. IR spectra were

recorded on a Nicolet 5 MX Fourier transform spectrometer. Mass spectra were recorded on a Micromass 7070 E spectrometer operating at 70 eV using direct inlet. Elemental analyses were carried out by Løvens Kemiske Fabrik, DK-2750 Ballerup, Denmark.

General procedure for the CS experiments. Since only partial descriptions of the procedure for the CS experiments have been published previously[2,19,20] a complete description is given here. Carbon monosulfide gas was produced in a conventional vacuum line (Fig. 1) by dissociation of CS_2 by a high voltage AC discharge. The internal diameter of the discharge tube was 15 mm and the distance between the electrodes 450 mm. The power supply was a conventional neon transformer operating at 12 kV and, maximally, 20 mA. The whole system was first evacuated to a pressure of 0.02–0.05 mmHg for 1–2 h. After filling the system with nitrogen, a toluene solution of the thiosulfenyl chloride was placed in the reaction flask with a stirring bar and the solution cooled to −78 °C with stirring. The 3-way valves, I, were opened in the direction J−I−I−G and the system evacuated to 0.02–0.05 mmHg. When the stirred solution had stopped degassing, the cold traps, H and J, were cooled with liquid nitrogen and the high voltage turned on. The needle valve, E, was opened to allow a stream of 15–20 ml/h of CS_2 vapor to pass through the discharge tube. The CS_2 container, D, was placed in cold water to maintain a constant evaporation temperature. During the reaction, the mixture turned red and the glass walls above the solution

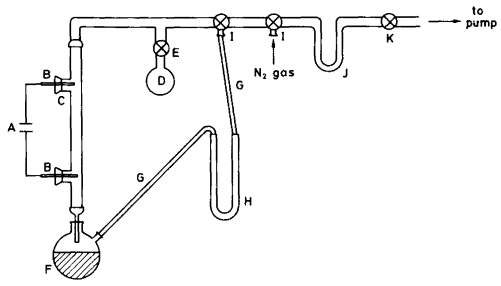


Fig. 1. A: power supply. B: brass electrodes. C: discharge tube. D: CS_2 container. E: needle valve. F: reaction flask. G: rubber vacuum tubes. H: metal cold trap. I: 3-way valves. J: glass cold trap. K: vacuum gauge.

slowly turned brown due to formation of polymeric CS. By the end of the reaction, the mixture and the glass walls rapidly turned black and small explosions in the metal cold trap due to the violent polymerization of condensed monomeric CS were heard. These explosions are the reason for using a metal cold trap – glass would probably break. When the reaction was finished, the discharge was turned off and the needle valve, E, closed. The system was filled with nitrogen and the reaction mixture allowed to warm up to room temperature. This was followed by the usual work-up procedures. A rather thick layer of polymeric CS and sulfur had built up on the inner walls of the glass equipment. This layer was readily removed by careful treatment with fuming nitric acid.

By applying this method, the yield of CS based on the amount of CS_2 consumed is ~70 %, but it is recommended that at least 4 equivalents of CS_2 relative to the substrate be used. Besides CS, the gas mixture leaving the discharge tube contains CS_2, together with small amounts of elementary sulfur and carbon subsulfide. If the substrate reacts with these compounds, a metal cold trap can be placed between the discharge tube and the reaction flask as previously described.[20]

Acetyl chlorothiocarbonyl disulfide 3. Filtration of the black reaction mixture gave a dark red solution. Removal of the solvent *in vacuo* gave a dark red oil which could be purified on a chromatographic column (silica gel, eluent 1:9 mixture of ether/petroleum ether) yielding 9.9 g (50 %) of an orange oil which was identified as *3*. Attempts to distil crude or purified *3* at 0.05 mmHg resulted in decomposition.

Chlorocarbonyl chlorothiocarbonyl disulfide 4. Filtration of the reaction mixture and removal of the solvent *in vacuo* gave a dark red oil which was purified by distillation (b.p. 55–56 °C/0.04 mmHg) yielding 6.8 g (53 %) of a red oil identified as *4*.

Chlorothiocarbonyl trichloromethyl disulfide 5. Filtration of the reaction mixture and removal of the solvent *in vacuo* gave a dark red oil which was purified on a chromatographic column (silica gel, eluent petroleum ether) yielding 8.9 g (57 %) of an orange oil identified as *5*. Purified *5* could be

Table 1. Reactions with thiosulfenyl chlorides

Starting material/g (mmol)	Amount toluene/ml	CS_2 consumed/ml (mmol)
$CH_3C(=O)SSCl$[15] 15 (106)	40	25 (410)
$ClC(=O)SSCl$[21] 10 (62)	70	30 (500)
Cl_3CSSCl[22] 13 (60)	70	40 (660)
Cl_5C_2SSCl[16] 30 (100)	75	25 (410)

distilled, but with considerable loss (b.p. 78–80 °C/0.04 mmHg).

Chlorothiocarbonyl pentachloroethyl disulfide 6. Filtration of the reaction mixture and removal of the solvent gave an orange oil which was distilled yielding 6.5 g (19 %) of an orange oil (b.p. 108–9 °C/0.03 mmHg) identified as *6*.

Acetyldithio-dichloromethanesulfenyl chloride 9. To a solution of 4.1 g (22 mmol) of *3* in 50 ml of CH_2Cl_2, a solution of 2.9 g (22 mmol) of freshly distilled SO_2Cl_2 in 30 ml of CH_2Cl_2 was added dropwise at 0 °C with stirring. After 3 h at 0 °C, the solvent was removed *in vacuo* and the remaining red oil was distilled yielding two fractions: 1) 0.6 g (12 %) of a yellow oil (b.p. 36–37 °C/0.03 mmHg) identified as *15;* 2) 2.0 g (35 %) of a yellow oil (b.p. 79–80 °C/0.03 mmHg) identified as *9*.

(Chlorocarbonyldithio)-dichloromethanesulfenyl chloride 10. A solution of 2.0 g (15 mmol) of freshly distilled SO_2Cl_2 in 25 ml of CH_2Cl_2 was added dropwise to a solution of 3.0 g (15 mmol) of *4* in 25 ml of CH_2Cl_2 at room temperature. After stirring for 4 h, the solvent was removed *in vacuo* and the remaining yellow oil was distilled yielding 3.5 g (85 %) of a yellow oil (b.p. 88–90 °C/0.05 mmHg) identified as *10*.

Dichloro-(trichloromethyldithio)methanesulfenyl chloride 11. To a solution of 7.5 g (30 mmol) of *5* in 80 ml of CH_2Cl_2 a solution of 4.1 g (30 mmol) of freshly distilled SO_2Cl_2 in 30 ml of CH_2Cl_2 was added during 1 h with stirring at 0 °C. After stirring for 12 h at room temperature, the solvent was removed *in vacuo* yielding 8.6 g (90 %, crude) of a yellow oil identified as *11*. Attempts at purification both by distillation at 0.04 mmHg and by chromatography resulted in decomposition.

Dichloro-(pentachloroethyldithio)methanesulfenyl chloride 12. To a solution of 45 g (130 mmol) of *6* in 100 ml of CCl_4, a solution of 17.4 g (130 mmol) of freshly distilled SO_2Cl_2 in 50 ml of CCl_4 was added during 1 h with stirring at 0 °C. After 2 h of stirring at room temperature, the solvent was removed *in vacuo* and the remaining yellow oil was distilled yielding 15.5 g (50 %, corrected for recovered *6*) of a yellow oil (b.p. 144–5 °C/0.3 mmHg) identified as *12*.

(Acetyldithio)-(chlorocarbonyldithio)-dichloromethane 16. A solution of 0.8 g (11 mmol) of thioacetic acid in 5 ml of ether was added dropwise to a solution of 2.9 g (11 mmol) of *10* in 80 ml of ether at room temperature. After stirring for 1/2 h at room temperature, the solvent was removed *in vacuo* and the remaining yellow oil distilled yielding 1.1 g (32 %) of a yellow oil (b.p. 125–35 °C/0.2 mmHg) identified as *16*.

(Acetyldithio)-dichloro-(trichloromethyldithio)-methane 17. To a solution of 3.3 g (10 mmol) of *11* in 25 ml of CH_2Cl_2, a solution of 0.8 g (10 mmol) of thioacetic acid in 25 ml of CH_2Cl_2 was added dropwise at 5 °C with stirring. After stirring for 12 h at room temperature, the solvent was removed *in vacuo*. The remaining yellow oil was purified on a chromatographic column (silica gel, eluent 1:19 mixture of ether/petroleum ether) yielding 1.8 g (49 %) of a slightly yellow oil identified as *17*.

Dichloro-(trichloromethyldithio)methyl S-p-*toluenethiosulfonate* 20. To a solution of 3.3 g (10 mmol) of *11* in 25 ml of CH_2Cl_2, a solution of 2.5 g (10 mmol) of morpholinium *p*-toluenesulfinate[60] in 25 ml of CH_2Cl_2 was added during 1/2 h. After stirring for 12 h at room temperature, the reaction mixture became colorless and a colorless precipitate of morpholinium chloride formed. Filtration and removal of the solvent *in vacuo* gave a viscous oil which was purified on a chromatographic column (silica gel, eluent 1:3 mixture of ether/petroleum ether) yielding 3.1 g

Table 2. Spectral and analytical data of the obtained compounds

No.	IR (cm^{-1})	^1H NMR ($CDCl_3$, TMS), δ	^{13}C NMR ($CDCl_3$, TMS), δ	MS	Elemental analyses[a]
					C H Cl S
3	(NaCl) 1720 (C=O), 1120/1110 (C=S), 750 (C–Cl)	2.51 (s,3H)	29.00, 186.83, 193.62	76 (CS_2^+), 43 (Ac^+)	$C_3H_3ClOS_3$ Calc.: 19.30 1.62 18.99 51.52 Found: 19.80 1.99 20.41 49.63
4	(NaCl) 1780 (C=O), 1120/1090 (C=S), 800/750 (C–Cl)		160.89, 190.44	206 (M^+), 143 (M^+–ClCO), 111 (M^+–ClCOS), 76 (CS_2^+)	$C_2Cl_2OS_3$ Calc.: 11.60 0.00 34.23 46.44 Found: 11.50 0.08 35.44 45.15
5	(NaCl) 1130/ 1090 (C=S), 790/ 760/740 (C–Cl)		98.86, 193.94	260 (M^+), 225 (M^+–Cl), 149 (Cl_3CS^+), 117 (Cl_3C^+)	$C_2Cl_4S_3$ Calc.: 9.17 0.00 54.12 36.17 Found: 8.84 0.05 54.21 35.88
6	(NaCl) 1120/ 1090 (C=S), 780/ 770/740 (C–Cl)		103.52, 105.47, 195.81	342 (M^+), 307 (M^+–Cl), 298 (M^+–CS), 263 (M^+–CSCl), 231 (M^+–CS_2Cl), 199 ($C_2Cl_5^+$)	$C_3Cl_6S_3$ Calc.: 10.45 0.00 61.67 27.88 Found: 10.42 0.04 61.85 26.97
9	(NaCl) 1750 (C=O), 1100 (CO–S), 795/ 765/720 (C–Cl)	2.51 (s,3H)	28.83, 100.58, 189.69	256 (M^+), 181 ($CCl_3S_2^+$), 146 ($CCl_2S_2^+$)	$C_3H_3Cl_3OS_3$ Calc.: 13.99 1.17 41.29 37.34 Found: 13.27 1.15 43.91 36.26
10	(NaCl) 1795 (C=O), 800/730 (C–Cl)		99.12, 162.95	241 (M^+–Cl), 206 (M^+–Cl_2), 181 (M^+–COCl)	$C_2Cl_4OS_3$ Calc.: 8.64 0.00 51.01 34.60 Found: 8.77 0.05 51.02 34.37
11	(NaCl) 790/770/740 (C–Cl)		98.27, 99.70	295 (M^+–Cl), 260 (M^+–Cl_2), 225 (M^+–Cl_3), 181 ($Cl_3CS_2^+$), 149 (Cl_3CS^+), 117 (Cl_3C^+)	
12	(NaCl) 785/ 745 (C–Cl)		98.93, 103.10, 105.14	412 (M^+), 377 (M^+–Cl), 345 (M^+–SCl), 298 (M^+–Cl_2CS), 263 (M^+–Cl_3CS), 199 ($C_2Cl_5^+$), 164 ($C_2Cl_4^+$)	$C_3Cl_8S_3$ Calc.: 8.67 0.00 68.20 23.13 Found: 9.02 0.06 66.67 22.34
15	(NaCl) 825/780/725 (C–Cl)		99.79	216 (M^+), 181 (M^+–Cl), 146 (M^+–Cl_2), 114 (M^+–SCl_2)	
16	(NaCl 1790/ 1750 (C=O), 1105 (CO–S), 795 (C–Cl)	2.52 (s,3H)	28.98, 99.59, 163.38, 189.65	316 (M^+), 281 (M^+–Cl), 253 (M^+–COCl), 239 (M^+–AcS), 221 (M^+–ClCOS), 209 (M^+–AcS_2), 189 (M^+–$ClCOS_2$)	$C_4H_3Cl_3O_2S_4$ Calc.: 15.12 0.95 33.54 40.37 Found: 14.88 0.92 33.93 40.60

(Continued)

Table 2 (continued)

No.	IR (cm^{-1})	^1H NMR ($CDCl_3$, TMS), δ	^{13}C NMR ($CDCl_3$, TMS), δ	MS	Elemental analyses[a]
					C H Cl S
17	(NaCl) 1750 (C=O), 1100 (CO–S), 790/765/735 (C–Cl)	2.53 (s,3H)	28.65, 98.15, 98.30, 189.39	370 (M^+), 335 (M^+–Cl), 292 (M^+–AcCl), 189 ($M^+-Cl_3CS_2$), 117 (Cl_3C^+)	$C_4H_3Cl_5OS_4$ Calc.: 12.89 0.81 47.58 34.43 Found: 13.22 0.85 46.35 35.03
18	(KBr) 1740 (C=O), 1110 (CO–S), 780/740 (C–Cl)	2.56 (s,3H)	28.77, 99.33, 103.02, 105.17, 189.64	452 (M^+), 417 (M^+–Cl), 345 (M^+-AcS_2), 199 ($C_2Cl_5^+$) 189 ($M^+-C_2Cl_5S_2$)	$C_5H_3Cl_7OS_4$ Calc.: 13.18 0.66 54.48 28.15 Found: 13.25 0.68 54.15 27.87
19	(NaCl) 1750 (C=O), 1340/1250 (SO_2), 740 (C–Cl)	2.23 (s,3H), 2.51 (s,3H), 7.11–7.33 (m,2H), 7.59–7.87 (m,2H)	21.88, 28.98, 94.87, 128.35, 128.73, 130.09, 140.77, 146.37, 189.91	268 (M^+-AcS_2), 189 ($M^+-CH_3C_6H_4SO_2S$), 155 ($CH_3C_6H_4SO_2^+$)	$C_{10}H_{10}Cl_2O_3S_4$ Calc.: 31.83 2.67 18.79 33.99 Found: 31.50 2.74 19.75 32.78
20	(NaCl) 1340/1150(SO_2), 795/765/735 (C–Cl)	2.44 (s,3H), 7.17–7.44 (m,2H), 7.70–7.91 (m,2H)	21.39, 93.25, 97.96, 128.16, 129.65, 140.16, 146.02	Only low-molecular fragments	$C_9H_7Cl_5O_2S_4$ Calc.: 23.88 1.56 39.16 28.33 Found: 24.78 1.72 37.24 27.90
21	(KBr) 1340/1150 (SO_2), 785/750 (C–Cl)	2.42 (s,3H), 7.13–7.38 (m,2H), 7.67–7.88 (m,2H))	21.47, 94.14, 102.71, 104.92, 128.22, 129.70, 140.29, 146.07	377 ($M^+-CH_3C_6H_4SO_2$), 345 ($M^+-CH_3C_6H_4SO_2S$), 269 ($Cl_5C_2S_2^+$), 155 ($CH_3C_6H_4SO_2^+$)	$C_{10}H_7Cl_7O_2S_4$ Calc.: 22.43 1.32 46.34 23.94 Found: 22.58 1.37 46.10 22.92
24	(KBr) 1340/1160 (SO_2), 765 (C–Cl)	2.44 (s,6H), 7.10–7.31 (m,4H), 7.57–7.83 (m,4H)	21.88, 89.72, 128.72, 130.08, 140.72, 146.62	155 ($CH_3C_6H_4SO_2^+$), 114 (CCl_2S^+)	$C_{15}H_{14}Cl_2O_4S_4$ Calc.: 39.39 3.08 28.04 15.50 Found: 39.90 3.27 27.84 14.80
25	(KBr) 1340/1160 (SO_2), 790/760 (C–Cl)	2.42 (s,3H), 7.11–7.38 (m,2H), 7.52–7.81 (m,2H)	21.70, 98.36, 128.20, 129.99, 140.08, 146.18	301 (M^+–Cl), 155 ($CH_3C_6H_4SO_2^+$)	$C_8H_7Cl_3O_2S_3$ Calc.: 28.45 2.08 31.50 28.48 Found: 29.17 2.22 30.76 27.97

[a]Deviations from the calculated values are due to either instability or inseparable impurities.

(69 %) of a viscous colorless oil (still containing small amounts of impurities) identified as *20*.

(Acetyldithio)-dichloro-(pentachloroethyldithio)-methane 18. To a solution of 5.0 g (12 mmol) of *12* in 50 ml of ether, a solution of 1.4 g (18 mmol) of thioacetic acid in 20 ml of ether was added at room temperature. After stirring for 12 h at room temperature, the solvent was removed *in vacuo* leaving a yellow oil. Crystallization from petroleum ether yielded 1.7 g (30 %) of colorless crystals (m.p. 43–45 °C) identified as *18*.

Dichloro-(pentachloroethyldithio)methyl S-p-*toluenethiosulfonate* 21. To a solution of 5.0 g (12 mmol) of *12* in 50 ml of benzene, a solution of 2.9 g (12 mmol) of morpholinium *p*-toluenesulfinate[60] in 25 ml of water was added. After stirring for 1 h at 40–50 °C, the reaction mixture was washed with 3×50 ml of water and the organic phase dried over Na_2SO_4. Removal of the solvent *in vacuo* gave a yellow oil. Crystallization from petroleum ether yielded 2.2 g (34 %) of colorless crystals (m.p. 79–81 °C) identified as *21*.

Dichloromethane bis(sulfenyl chloride) 15. 1) From *9*/Cl_2: To a solution of 1.9 g (7.4 mmol) of *9* in 15 ml of CCl_4, a solution of 0.5 g (7.4 mmol) of chlorine in 15 ml of CCl_4 was added during 1 h with stirring at −10 °C. After stirring for 2 h at −10 °C, a yellow precipitate of sulfur formed. Filtration through charcoal and removal of the solvent *in vacuo* gave a yellow oil which was distilled to yield 0.9 g (56 %) of a yellow oil (b.p. 36–37 °C/0.03 mmHg) identified as *15*. 2) From *7*/Cl_2: To a solution of 42 g of crude *7*[1] in 100 ml of CCl_4, a solution of 26 g (37 mmol) of chlorine in 100 ml of CCl_4 was added dropwise with stirring at 0 °C. After stirring for 2 h at 0 °C, the solvent was removed *in vacuo* and the remaining yellow oil distilled to yield 9.2 g of a yellow oil (b.p. 90–100 °C/12 mmHg) which consisted of a mixture of *15* and *23* as evidenced by both ^{13}C NMR ($CDCl_3$, TMS): δ 99.78 (*15*), 100.16 (*23*) and derivatization with *p*-toluenesulfinate: to a solution of 2.4 g of the mixture of *15/23* in 25 ml of CH_2Cl_2, a solution of 6.0 g (25 mmol) of morpholinium *p*-toluenesulfinate[60] in 25 ml of CH_2Cl_2 was added at 0 °C with stirring. After stirring for 2 h at 0 °C, a colorless precipitate of morpholinium chloride formed. The reaction mixture was washed with 3×40 ml of water and the organic phase dried over $CaSO_4$. Removal of the solvent *in vacuo* gave a slightly yellow oil which was separated on a chromatographic column (silica gel, eluent 1:1 mixture of ether/petroleum ether). Two fractions were obtained: 1) a colorless solid which was recrystallized from ether to yield 1.9 g of colorless crystals (m.p. 106–8 °C) identified as *24;* 2) a colorless solid which was recrystalllized from petroleum ether to yield 1.5 g of colorless crystals (m.p. 48–50 °C; lit.[18] 50.5–51.5 °C) identified as *25*.

(Acetyldithio)-dichloromethyl S-p-*toluenethiosulfonate* 19. A solution of 1.0 g (3.9 mmol) of *9* in 10 ml of CH_2Cl_2 and a solution of 1.1 g (4.7 mmol) of morpholinium *p*-toluenesulfinate[60] in 5 ml of CH_2Cl_2 were mixed. After stirring for 1/2 h at room temperature, a colorless precipitate of morpholinium chloride formed. The reaction mixture was washed with 3×50 ml of water and the organic phase dried over $CaCl_2$. Removal of the solvent under vacuum gave a yellow oil which was purified by TLC (silica gel, eluent 1:3 mixture of ether/petroleum ether) yielding 0.72 g (49 %) of a slightly contaminated viscous colorless oil identified as *19*.

*Dichloromethylene bis(*S-p-*toluenethiosulfonate)* 24. A solution of 0.5 g (2.3 mmol) of *15* and 1.1 g (4.6 mmol) of morpholinium *p*-toluenesulfinate[60] in 20 ml of CH_2Cl_2 was stirred for 2 h at room temperature. The colorless precipitate of morpholinium chloride was washed with 3×50 ml of water and the organic phase dried over $CaCl_2$. Removal of the solvent *in vacuo* gave a yellow oil which was purified by TLC (silica gel, eluent 1:3 mixture of ether/petroleum ether) to give a colorless solid. Recrystallization from ether yielded 0.4 g (38 %) of colorless crystals (m.p. 108–10 °C) identified as *24*.

Acknowledgment. We thank NATO for a travel-study grant.

References

1. Klabunde, K. J., Kramer, M. P., Senning, A. and Moltzen, E. K., *J. Am. Chem. Soc. 106* (1984) 263.
2. Moltzen, E. K., Senning, A., Kramer, M. P. and Klabunde, K. J. *J. Org. Chem. 49* (1984) 3854.

3. For a review of RSSH see: Houben-Weyl. *Methoden der Organischen Chemie,* Vol. E 11, p. 129 ff. Georg Thieme Verlag, Stuttgart 1985.
4. Kobayashi, N., Osawa, A. and Fujisawa, T. *Chem. Lett.* (1973) 1315.
5. Krebs, A., Güntner, A., Senning, A., Moltzen, E. K., Klabunde, K. J. and Kramer, M. P. *Angew. Chem. Int. Ed. Engl. 23* (1984) 729.
6. Barany, G., Schroll, A. L., Mott, A. W. and Halsrud, D. A. *J. Org. Chem. 48* (1983) 4750.
7. Scheithauer, S. and Mayer, R. *Thio- and Dithiocarboxylic Acids and their Derivatives.* In: Senning, A. Ed. *Topics in Sulfur Chemistry,* Vol. 4, p. 192 ff. and references therein. Georg Thieme Verlag, Stuttgart 1979.
8. Hansen, H. C. and Senning, A. *Org. Prep. Proced. Int. 17* (1985) 275.
9. Kühle, E. *The Chemistry of the Sulfenic Acids,* p. 5 ff. Georg Thieme Verlag, Stuttgart 1973.
10. Kühle, E. *Synthesis* (1971) 563.
11. Yarovenko, N. N. and Vasileva, A. S. *Zh. Obshch. Khim. 28* (1958) 2502; *Chem. Abstr. 53* (1959) 3116.
12. Barany, G. *Tetrahedron Lett. 24* (1983) 5683.
13. Barany, G. and Mott, A. W. *J. Org. Chem. 49* (1984) 1043.
14. Mott, A. W. and Barany, G. *J. Chem. Soc., Perkin Trans. 1* (1984) 2615.
15. Böhme, H. and Clement, M. *Liebigs Ann. Chem. 576* (1952) 61.
16. Senning, A., Chevallier, M.-A. and Jensen, B. *Sulfur Lett. 3* (1985) 177.
17. Pitt, H. M. and Bender, H. *US Pat.* 3, 331, 872 (1964); *Chem. Abstr. 67* (1967) 63784.
18. Uhlenbroek, H. J. and Koopmans, M. J. *Recl. Trav. Chim. Pays-Bas 76* (1957) 657.
19. Klabunde, K. J., White, C. W. and Efner, H. F. *Inorg. Chem. 13* (1974) 1778.
20. Moltzen, E. K., Senning, A., Kramer, M. P. and Klabunde, K. J. *J. Org. Chem. Submitted for publication.*
21. Böhme, H., Brinkmann, M. and Steudel, H. P. *Liebigs Ann. Chem.* (1981) 1244.
22. Kohn, G. K., Clay, R. B. and Moore, J. E. *Br. Pat.* 962,021 (1962); *Chem. Abstr. 61* (1964) 6921.
23. Böhme, H. and Ham, G. v. *Liebigs Ann. Chem. 617* (1958) 62.
24. Evers, W. J. and Hall, J. *Fr. Pat.* 2,007,063 (1970); *Chem. Abstr. 74* (1971) 41912.
25. Louthan, R. P. and Kruse, C. W. *US Pat.* 2,886,593 (1959); *Chem. Abstr. 53* (1959) 18066.
26. Fehér, F. and Kruse, W. *Chem. Ber. 91* (1958) 2528.
27. Bennett, G. and Brunten, G. *J. Chem. Soc., Chem. Commun.* (1979) 62.
28. Müller, E. and Schmidt, E. W. *Chem. Ber. 97* (1964) 2622.
29. Harpp, D. N. and Ash, D. K. *Int. J. Sulfur Chem., Part A 1* (1971) 211.
30. Hageman, H. A. *US Pat.* 3,832,378 (1974); *Chem. Abstr. 81* (1974) 135485.
31. Harris, M. and Feisst, J. *Helv. Chim. Acta 49* (1966) 2344.
32. Vasil'eva, T. P., Lin'kova, M. G., Kil'disheva, O. W. and Knunyants, I. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* (1974) 643; *Chem. Abstr. 81* (1974) 3049.
33. Lecher, H. and Simon, K. *Chem. Ber. 54* (1921) 2249.
34. Fujisawa, T. and Tsuchihashi, G. *Bull. Chem. Soc. Jpn* (1970) 3615.
35. Almasi, L. and Hautz, A. *Chem. Ber. 99* (1966) 3288.
36. Ariyan, Z. S. and Wiles, L. A. *J. Chem. Soc.* (1961) 4510; *J. Chem. Soc.* (1962) 1725.
37. Airan, J. W. and Shah, S. V. *J. Ind. Chem. Soc. 22* (1945) 359.
38. Livingston, J. M. and Peach, M. E. *J. Fluorine Chem. 9* (1977) 85.
39. Gombler, W. *Z. Anorg. Allg. Chem. 416* (1975) 235.
40. Bur-Bur, F., Haas, A. and Klug, W. *Chem. Ber. 108* (1975) 1365.
41. Zack, R. N. and Shreeve, J. M. *Inorg. Nucl. Chem. Lett. 10* (1974) 619.
42. Gielow, P. and Haas, A. *Z. Anorg. Allg. Chem. 394* (1972) 53.
43. Epshtein, G. Y., Usov, I. A. and Ivin, S. Z. *Zh. Obshch. Khim. 34* (1964) 1951; *Chem. Abstr. 61* (1964) 8178.
44. Knunyants, I. L. and Fokin, A. V. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (1955) 627; *Chem. Abstr. 50* (1956) 7069.
45. Shkurak, S. N., Kolomiets, A. F. and Fokin, A. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* (1982) 959; *Chem. Abstr. 97* (1982) 38451.
46. Bekker, R. A., Popkova, V. Y. and Knunyants, I. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* (1983) 1689; *Chem. Abstr. 100* (1984) 5786.
47. Shkurak, S. N., Kolomiets, A. F. and Fokin, A. V. *Zh. Org. Khim. 18* (1982) 1549; *Chem. Abstr. 97* (1982) 162310.
48. Still, I. W., Kutney, G. W. and McLean, D. *J. Org. Chem. 47* (1982) 555.
49. Appel, R., Janssen, H., Siray, M. and Knoch, F. *Chem. Ber. 118* (1984) 1632.
50. Fehér, F. and Becker, W. *Z. Naturforsch. 20b* (1965) 1126.
51. Balin, A. I. and Veretenova, T. N. *USSR Pat.* 670, 566 (1979); *Chem. Abstr. 91* (1979) 177900.
52. Fehér, F., Glinka, K. and Malcharek, F. *Angew. Chem. 83* (1971) 439.
53. Lingmann, H. and Linke, K.-H. *Chem. Ber. 104* (1971) 3723.

54. Böhme, H. and Steudel, H. P. *Liebigs Ann. Chem. 730* (1969) 121.
55. D'Silva, T. D. J. *US Pat.* 4,091,016 (1978); *Chem. Abstr. 89* (1978) 129291.
56. D'Silva, T. D. J. *US Pat.* 4,066,689 (1978); *Chem. Abstr. 88* (1978) 104715.
57. D'Silva, T. D. J. *US Pat.* 4,058,549 (1977): *Chem. Abstr. 88* (1978) 50329.
58. D'Silva, T. D. J. *Ger. Offen.* 2,530,278 (1976); *Chem. Abstr. 84* (1976) 135347.
59. Fehér, F. and Grodan, D. *Z. Naturforsch. 26b* (1971) 614.
60. Brauer, G. M. and Burns, F. R. *J. Polymer Sci. 19* (1956) 311.

Received December 12, 1985.