acid in 20 mL of methylene chloride. To the reaction mixture, which was allowed to warm to 20 °C over a period of 40 min, was then added 0.5 g of dimethyl sulfide followed (after 5 min) by a solution of 0.3 g (2.4 mmol) of *p*-anisidine in 10 mL of methylene chloride. The mixture was stirred at room temperature for 12 h, filtered, and the filtrate was concentrated and passed over basic alumina (elution with chloroform) to give 0.136 g (32%) of **6d** as a brown solid: mp 108–109 °C; NMR δ 3.94 (s, 3 H, OCH_3), 7.05 (d, 2 H), 7.35 (t, 1 H), 8.18 (d, 2 H), 8.96 (d, 2 H).

Anal. Calcd for $C_{11}H_{10}N_4O$: C, 61.67; H, 4.71; N, 26.15. Found: C, 61.46; H, 4.78; N, 26.00.

2-[(*p*-Methoxyphenyl)azo]pyrazine (6e) was prepared in 64% yield as an orange solid from *S,S*-dimethyl-*N*-(2-pyrazinyl)sulfilimine as described above for **6d**: mp 116–117 °C; NMR δ 3.83 (s, 3 H, OCH_3), 6.90 (d, 2 H), 7.91 (d, 2 H), 8.47 (s, 2 H), 8.88 (s, 1 H).

Anal. Calcd for $C_{11}H_{10}N_4O$: C, 61.67; H, 4.71; N, 26.15. Found: C, 61.87; H, 4.38; N, 26.44.

2-Nitropyridine (7a). Method A. Ozone carried by oxygen was bubbled through a solution of 1.0 g of 2-nitrosopyridine in 200 mL of methylene chloride maintained at 0 °C until the green color disappeared (~2 h). The solution was then purged with nitrogen and evaporated to dryness under reduced pressure to give 1.14 g (100%) of crude 2-nitropyridine, mp 68–69 °C. Recrystallization from ethanol raised the melting point to 71 °C (lit.[13] mp 71 °C).

Method B. To a solution of 540 mg (5 mmol) of 2-nitrosopyridine in 50 mL of benzene was added a freshly prepared solution of 580 mg (1.7 mmol) of tetra-*n*-butylammonium hydrogen sulfate in 20 mL (10 mmol) of commercial bleach (5.25% NaOCl) adjusted to pH 10 with dilute sulfuric acid. The two-phase system was stirred vigorously for 12 min, by which time it had become colorless. The layers were separated, the aqueous phase was extracted several times with benzene, and the combined benzene extracts were washed with water, dried (Na_2SO_4), and evaporated to give 560 mg (90%) of pale yellow crystals of 2-nitropyridine, mp 70–71 °C, identical with the material prepared above by method A.

1-Nitroisoquinoline (7c). Ozone was bubbled through a solution of 1-nitrosoisoquinoline, prepared in situ from *N*-(1-isoquinolinyl)-*S,S*-dimethylsulfilimine as described above for the preparation of **3c**, and the reaction mixture was worked up in the same manner as described for **7a** to give 1-nitroisoquinoline: 36% yield; mp 65–66 °C (lit.[14] mp 65–66 °C).

2-Nitropyrimidine (7d). Ozone was bubbled through a solution of 2-nitrosopyrimidine, prepared in situ from *S,S*-dimethyl-*N*-(2-pyrimidinyl)sulfilimine as described above for the preparation of **6d**, and the reaction mixture was worked up in the same manner as described for **7a** to give 2-nitropyrimidine (33%; mp 57–58 °C) after purification by preparative TLC (silica gel 60 F-254, with chloroform as the developing solvent): NMR δ 7.83 (t, 1 H), 9.08 (d, 2 H).

Anal. Calcd for $C_4H_3N_3O_2$: C, 38.41; H, 2.42; N, 33.59. Found: C, 38.37; H, 2.51; N, 33.75.

2-Nitropyrazine (7e). This compound was prepared in 70% yield by ozone oxidation of 2-nitrosopyrazine, prepared in situ from *S,S*-dimethyl-*N*-(2-pyrazinyl)sulfilimine as described above under **3e**: mp 58–59 °C; NMR δ 8.81 (dd, 1 H), 9.16 (dd, 1 H), 9.67 (d, 1 H).

Anal. Calcd for $C_4H_3N_3O_2$: C, 38.41; H, 2.42; N, 33.59. Found: C, 38.48; H, 2.42; N, 33.59.

Registry No. a, 42860-85-5; **1b**, 79917-35-4; **1c**, 79917-36-5; **1d**, 54214-58-3; **1e**, 62135-46-0; **2a**, 79917-37-6; **2b**, 79917-38-7; **2c**, 79933-06-5; **2d**, 79917-39-8; **2e**, 79917-40-1; **3a**, 79917-41-2; **3b**, 79917-42-3; **3c**, 79917-43-4; **3e**, 79917-44-5; **4a**, 79917-45-6; **4b**, 79917-46-7; **5a**, 14458-12-9; **5b**, 79917-47-8; **5e**, 79917-48-9; **6a**, 79917-49-0; **6b**, 79917-50-3; **6c**, 79917-51-4; **6d**, 79917-52-5; **6e**, 79917-53-6; **7a**, 15009-91-3; **7c**, 19658-76-5; **7d**, 79917-54-7; **7e**, 79917-55-8; 2,3-dimethyl-1,3-butadiene, 513-81-5; 1,3-diphenylisobenzofuran, 5471-63-6; *p*-chloroaniline, 106-47-8; *p*-anisidine, 104-94-9.

(13) Kirpal, A.; Bohm, W. *Chem. Ber.* **1931**, *64*, 767.

(14) Hayashi, E.; Akahori, Y.; Yamamoto, Y. *Yakugaku Zasshi* **1967**, *87*, 1342–1345.

Synthesis of α-Chlorothiosulfenyl Chlorides. A New Class of Reactive Organosulfur Compounds

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The reaction of various aromatic and suitably substituted aliphatic thiones with sulfur dichloride in dry carbon disulfide affords the corresponding α-chlorothiosulfenyl chlorides ($R_2C(Cl)SSCl$), the first simple compounds of this type. Reaction of the α-chlorothiosulfenyl chlorides with triphenylphosphine regenerates the thiones, accompanied by the corresponding ketones. Possible mechanisms for these transformations are presented.

Several reports have appeared on the reactions of sulfur dichloride with thiocarbonyl compounds such as dithio acids,[1] thio amides,[2] thiocarbamate esters,[3] and 1,2-dithiole-3-thiones,[4] but the reaction of simple thiones with this reagent has not been previously reported. Our current interest in thiosulfines[5-7] led us to investigate this reaction as a possible source of these novel compounds from thiones such as **1** (Scheme I).

Results and Discussion

Addition of sulfur dichloride to thiobenzophenone **1a** in diethyl ether at −78 °C yielded a white precipitate. When this solid was filtered off and allowed to warm to room temperature, it quickly reverted to the starting thione **1a**. By analogy with the reaction of 4-methoxy-*N,N*-di-

(1) Campaigne, E.; Pragnell, M.; Haaf, F. *J. Heterocycl. Chem.* **1968**, *5*, 141.

(2) (a) El'tsov, A. V.; Lopatin, V. E.; Mikhel'son, M. G. *Zh. Org. Khim.* **1970**, *6*, 394. (b) El'tsov, A. V.; Lopatin, V. E. *Ibid.* **1971**, *7*, 1319. (c) Hasserodt, U. *Chem. Ber.* **1968**, *101*, 13.

(3) (a) Mühlstädt, M.; Widera, R. *J. Prakt. Chem.* **1978**, *320*, 123. (b) For reactions of thiocarbamates with sulfenyl chlorides see: Harris, J. F. *J. Am. Chem. Soc.* **1960**, *82*, 155.

(4) Klingsberg, E. *J. Org. Chem.* **1972**, *37*, 3226.

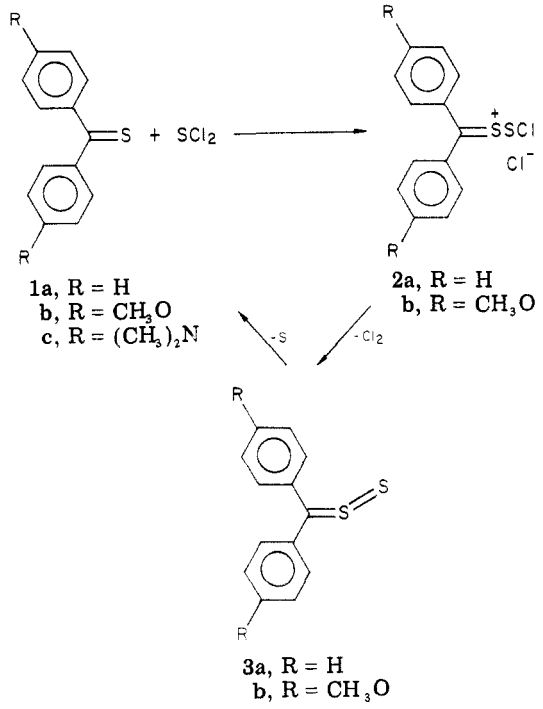
(5) Kutney, G. W.; Still, I. W. J. *Can. J. Chem.* **1980**, *58*, 1233.

(6) Kuipers, J. A. M.; Lammerink, B. H. M.; Still, I. W. J.; Zwanenburg, B. *Synthesis* **1981**, 295.

(7) Still, I. W. J.; Kutney, G. W., *J. Org. Chem.* **1981**, *46*, 4911.

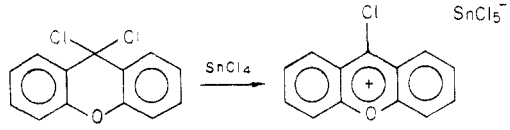
0022-3263/82/1947-0555$01.25/0

Scheme I



methylthiobenzamide with sulfur dichloride,[2b] we believe this white solid to have structure **2a**. Upon warming, this salt may lose chlorine, yielding an intermediate thiosulfine **3a** which would be expected to eliminate sulfur, yielding thiobenzophenone (**1a**).

Due to the relatively unstable nature of thiobenzophenone, xanthione **4** was instead reacted with sulfur dichloride under the same reaction conditions (see Scheme II). No solid precipitated from this reaction, and upon workup only xanthone **6** (88%) could be isolated. The reaction with xanthione was repeated at 25 °C in dry carbon disulfide in the presence of stannic chloride. An orange precipitate formed (100%). Infrared and NMR spectral data indicated that the orange solid was the salt **5b** (X = $SnCl_5$). Support for this assignment was found from the reaction of 9,9-dichloroxanthene (**7**) with stannic chloride to yield **8** (eq 1). The ^1H NMR spectra of the salts **5b** and **8** were very similar (see Experimental Section).

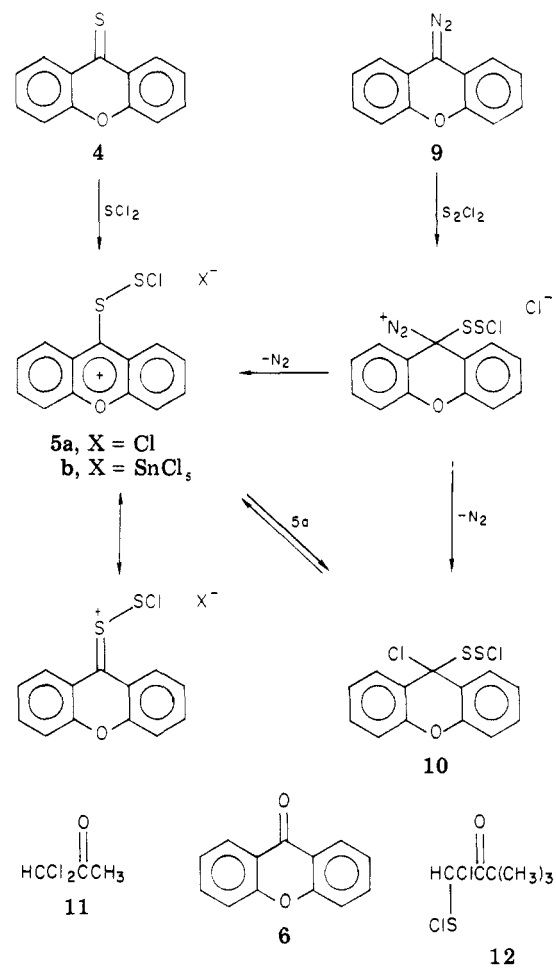


7 8 (1)

As already observed for **2a**, the pentachlorostannate salt **5b** decomposed on standing in air, or slowly in solution, to give the starting thione.

Reaction of xanthione **4** with sulfur dichloride in dry carbon disulfide in the absence of stannic chloride, on the other hand, yielded a pale yellow solution. ^1H NMR and IR data confirmed the absence of thione. The ^1H NMR spectrum indicated the presence of only one compound, with a characteristic doublet of doublets centred at δ 7.85 (J = 8, 2 Hz) for the pair of peri hydrogens, closely resembling the ^1H NMR spectrum of 9,9-dichloroxanthene (see Experimental Section) and other xanthene derivatives. The most likely structure for this material is the covalently bonded α-chlorothiosulfenyl chloride **10** (Scheme II), possibly in equilibrium in solution with the ionic form **5a**. This assignment is further substantiated by the reaction of 9-diazoxanthene[8] (**9**) with disulfur dichloride which

Scheme II



yields the same product (Scheme II).

^{13}C NMR data support the assigned structure **10** (Table I). As expected, the ^{13}C NMR spectrum of 9,9-dichloroxanthene (**7**) is very similar to that of 9-chloro-9-(chlorodithio)xanthene (**10**), except for the shifts of the C-9 atoms. The upfield shift of 5.8 ppm observed for C-9 in compound **10** compared to C-9 in the *gem*-dichloride **7** is in accord with comparable data reported for structurally related α-chlorosulfenyl chlorides and *gem*-dichloro compounds. For example, the chemical shift of C-1 in 1,1-dichloro-2-propanone (**11**) occurs at δ 70.2,[9] while 1-chloro-1-(chlorothio)-3,3-dimethyl-2-butanone (**12**) reveals the C-1 signal at δ 65.5.[10] The ^{13}C NMR chemical shifts of xanthione **4** and xanthone **6** are also listed in Table I for comparison. Our attempts to synthesize 9-chloro-9-(chlorothio)xanthene (**14**) from xanthene (**13**, or its anion) and thionyl chloride, or by the addition of chlorine to xanthione, were uniformly unsuccessful (Scheme III).

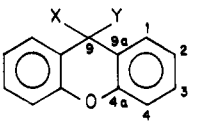
Addition of sulfur dichloride in carbon disulfide at 25 °C to thiobenzophenone (**1a**) and 4,4'-dimethoxythiobenzophenone (**1b**) produced similar results. Addition of sulfur dichloride to 4,4'-bis(dimethylamino)thiobenzophenone (**1c**), on the other hand, did not appear to produce the corresponding α-chlorothiosulfenyl chloride. Instead, a solid precipitated from the solution which we have tentatively identified as the double salt **15**.[11]

(8) For the reaction of diazomethane with S_2Cl_2 see: Petrov, K. A.; Sokol'skii, G. A.; Neimysheva, A. A. *Zh. Obshch. Khim.* **1957**, *27*, 780. Cf.: *Chem. Abstr.* **1957**, *51*, 16334*d*.

(9) Yalpani, M.; Modarai, B.; Khoshdel, E. *Org. Magn. Reson.* **1979**, *12*, 254.

(10) Adiwidjaja, G.; Günther, H.; Voss, J. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 563.

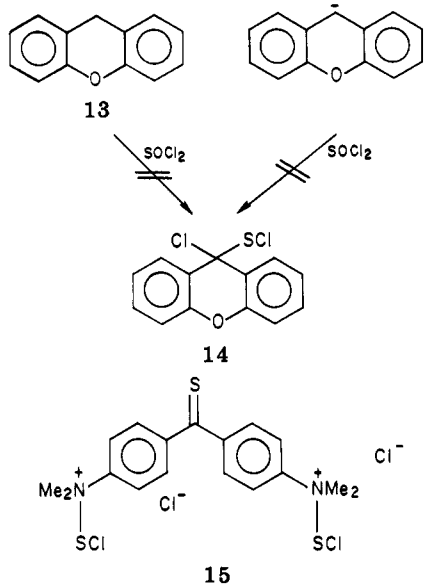
Table I. ^{13}C NMR Chemical Shifts of Xanthene and Its Derivatives[a]



compd	substituent X	substituent Y	shift, δ C-1	C-2	C-3	C-4	C-4a	C-9a	C-9
7	Cl	Cl	129.6	123.8	130.9	116.4	147.2	123.6	80.8
10	Cl	SSCl	130.4	123.7	130.8	116.2	149.9	123.3	75.0
13[b]	H	H	128.8	122.9	127.5	116.4	152.0	120.5	27.9
4	=S		129.5	124.4	134.5	118.0	150.1	128.7	204.4
6	=O		126.3	123.5	134.4	117.7	155.7	121.5	176.6

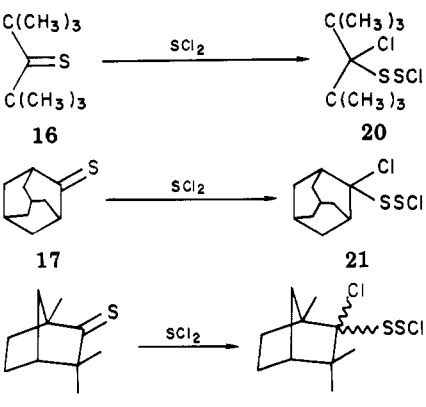
[a] In $CDCl_3$. [b] Isbrandt, L. R.; Jensen, R. K.; Petrakis, L. *J. Magn. Reson.* 1973, *12*, 143.

Scheme III



13 14 15

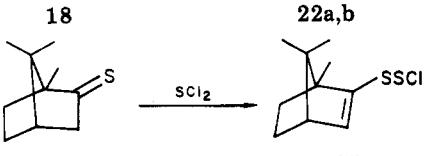
We turned next to the reactions of nonaromatic thiones such as 2,2,4,4-tetramethyl-3-pentanethione (**16**, di-*tert*-butyl thioketone), adamantanethione (**17**), and thiofenchone (**18**), with sulfur dichloride in dry carbon disulfide. The di-*tert*-butyl thioketone did not react instantaneously, but after 5–10 min the characteristic magenta color of this thione had disappeared. Monitoring of the reaction with sulfur dichloride by ^{13}C NMR confirmed the disappearance of the thione carbon signal at δ 277.7 and the appearance of a new band at δ 102.0, which we believe to be characteristic of the >C(Cl)SSCl carbon, the remaining signals at δ 45.7 and δ 30.5 being in the expected range for the quaternary and methyl signals, respectively, of the *tert*-butyl groups. When the sample was allowed to stand overnight in solution ($CDCl_3$) at 25 °C, a new downfield signal at δ 105.2 appeared, which we feel is attributable to the *gem*-dichloride 3,3-dichloro-2,2,4,4-tetramethylpentane (**23b**), the other (*tert*-butyl)



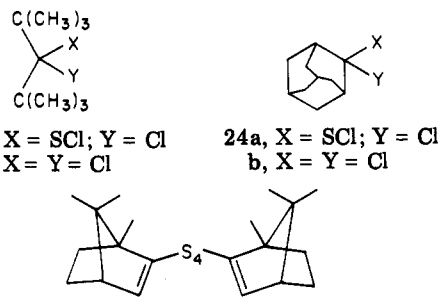
16 20 (2)

17 21 (3)

18 22a,b (4)



19 25 (5)



23a, X = SCl; Y = Cl
b, X = Y = Cl

24a, X = SCl; Y = Cl
b, X = Y = Cl

26

signals remaining virtually constant. The presence of another potential product, the α-chlorosulfenyl chloride **23a**, in this reaction was ruled out by a separate control experiment involving the reaction of the thione **16** with chlorine, according to the procedure of Zwanenburg et al.[12] The product from this reaction indeed showed a distinct signal at δ 101.1 for the central carbon atom, indicative of the formation of **23a**. The remaining signals for the *tert*-butyl groups appeared at δ 47.3 and 30.7, again slightly different from those assigned to the α-chlorothiosulfenyl chloride **20**.

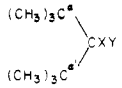
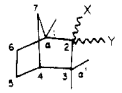
These data and analogous ^{13}C NMR results for the adamantanethione (**17**) and thiofenchone (**18**) reactions with sulfur dichloride are summarized in Table II and effectively confirm the presence of the expected products **21** and **22**, respectively. In the case of thiofenchone, the addition of sulfur dichloride not unexpectedly produces a mixture of diastereomers (**22a,b**).

The chemical shifts of the α (and α′) carbons are also included for comparison. Generally speaking, replacement of an sp^2 thiocarbonyl center with an sp^3 carbon bearing Cl in combination with another Cl, or an SCl or SSCl substituent, appears to produce a consistent upfield shift at the α-carbons of between 5 and 8 ppm, with little dif-

(11) It was observed that when 1 equiv of sulfur dichloride was used some solid precipitated from solution while the rest remained unreacted. With excess sulfur dichloride, no thione remained in solution.

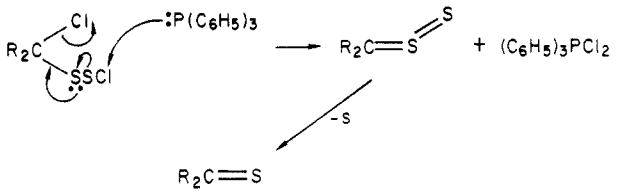
(12) Veenstra, G. E.; Bronold, N. M.; Smits, J. F. M.; Tangerman, A.; Zwanenburg, B. *Recl. Trav. Chim. Pays-Bas* 1977, *96*, 139.

Table II. ^{13}C NMR Chemical Shifts for Aliphatic/Alicyclic Analogues of 10 and Related Compounds[a]

system	compd	substituent X	substituent Y	shift, δ C(X,Y)	shift, δ C-α	shift, δ C-α′
	16	=S		277.7	53.5	
	20	SSCl	Cl	102.0	45.7	
	23a	SCl[b]	Cl[b]	101.1	47.3	
	23b	Cl	Cl	105.2	46.4	
		=S		279.6	66.0	57.4
	18	SSCl	Cl	100.4,	57.7,	49.3,
	22a,b			100.15[c]	57.0[c]	49.0[c]
	17	=S		270.0	57.4	
	21	SSCl	Cl	93.1[d,e]	39.7[d,e]	
	24a	SCl[b]	Cl[b]	92.7[d]	38.4[d]	
	24b	Cl[f]	Cl[f]	100.7	45.0	

[a] In $CDCl_3$ at 32 °C unless otherwise stated. [b] Prepared according to the method of Zwanenburg et al.[12] [c] Mixture of diastereomers. [d] These values did not change significantly when recorded at −25 °C. [e] After 2 days in solution at 25 °C, some conversion to the α-chlorosulfenyl chloride (X = SCl, Y = Cl) had occurred. [f] 2,2-Dichloroadamantane was prepared by the procedure used by M. A. McKervey, D. Grant, and H. Hamill, *Tetrahedron Lett.* 1970, 1975.

Scheme IV

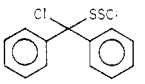
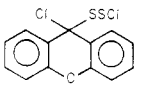
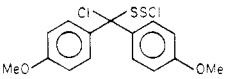
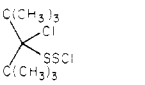
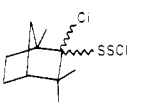
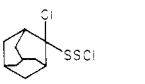


ferentiation in this respect between the last three types of compound. The adamantane analogues **21** and **24a** do not fit this general pattern but we have no convincing explanation at present for this observation.

In contrast to the above results, thiocamphor **19** did not yield the corresponding α-chlorothiosulfenyl chloride on reaction with sulfur dichloride. ^1H NMR and IR spectra of the product indicated the presence of a double bond, and elimination of HCl was detected during the reaction. This product is most likely the unsaturated thiosulfenyl chloride **25** (eq 5), since a vinylic proton was present in the ^1H NMR spectrum. Attempted isolation of this material, however, led to a complex mixture of products. Compound **25** readily reacted with potassium iodide (characteristic of sulfenyl chlorides), but the expected tetrasulfide **26** could not be isolated. The loss of HCl in the initial reaction is similar to the reported reaction of *N*-methylthiobenzamide with sulfur dichloride.[2b] The result obtained with thiocamphor indirectly substantiates the formation of α-chlorothiosulfenyl chlorides in these reactions, as this is the only example studied where β elimination of HCl is possible.

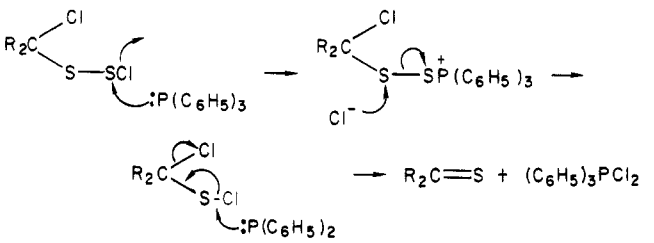
Several thiosulfenyl chlorides have previously been reported[13] but they have never previously been obtained from thiones and no examples of simple α-chlorothiosulfenyl chlorides are known.[14] As noted above, however, α-chlorosulfenyl chlorides are known and several recent reports have dealt with the formation (or the intermediacy) of these compounds.[9,10,15-20]

Table III. Reactions of α-Chlorothiosulfenyl Chlorides with Triphenylphosphine

compd	% yield >C=S	>C=O	⩾P=O	⩾P=S
	0[a]	100	16	11
	24	56	18	51
	50	48	35	30
	70	5	29	17
	30	20	25	17
	48	47	29	17

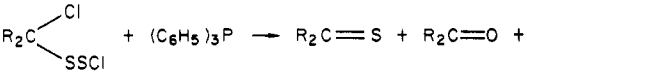
[a] Thiobenzophenone formed (intense blue color) but decomposed to ketone upon attempted purification.

Scheme V



Oka[15] has reported that the reaction of triphenylphosphine with α-chlorosulfenyl chlorides yields the corresponding thiones. In a similar manner, reaction of α-chlorothiosulfenyl chlorides would be expected to yield the corresponding thiosulfines which might then lose sulfur to form the corresponding thiones (Scheme IV).

We have thus examined the reaction of triphenylphosphine with 9-chloro-9-(chlorodithio)xanthene (**10**). This reaction yielded xanthione **4** (24%) and triphenylphosphine oxide (18%, presumably formed from the hydrolysis of $(C_6H_5)_3PCl_2$ on workup), as expected. More surprisingly, xanthone **6** (56%) and triphenylphosphine sulfide (51%) were also isolated from this reaction (eq 6). Similar results were obtained with the other α-chlorothiosulfenyl chlorides, and these results are summarized in Table III.



$$(C_6H_5)_3PS + (C_6H_5)_3PO \quad (6)$$

Triphenylphosphine sulfide may originate by the competing reaction of triphenylphosphine with the interme-

(13) Kharasch, N.; Ariyan, Z. S. *Intra-Sci. Chem. Rep.* **1969**, *1*, 337.
(14) (a) A patent has appeared which claims the synthesis of several polychlorothiosulfenyl chlorides: California Research Institute, French Patent 1 323 322, 1963; cf. *Chem. Abstr.* **1964**, *60*, 1597. (b) See also Gielow, P., Hass, A. *Chem.-Ztg.* **1971**, *95*, 1010.
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diate thiosulfine, and the ketone 6 could then be accounted for by rapid hydrolysis of unreacted α-chlorothiosulfenyl chloride during workup. An alternative explanation may involve prior removal of one of the sulfur atoms from the thiosulfenyl chloride by direct attack of triphenylphosphine, yielding the corresponding α-chlorosulfenyl chloride. If the latter reaction is occurring, the thiones may then be formed via the α-chlorosulfenyl chlorides[15] (Scheme V). The ketone would again in this case result from the decomposition of unreacted α-chlorothiosulfenyl chloride or unreacted α-chlorosulfenyl chloride with water during the workup. Attack of triphenylphosphine at the alternative (electrophilic) sulfur atom (Scheme V) also cannot be ruled out as a possible pathway to the α-chlorosulfenyl chloride. The α-chlorothiosulfenyl chlorides are, in fact, highly unusual in having no fewer than five *adjacent* electrophilic sites (including the C atom). Further work on the reactivity and potential synthetic utility of these compounds is continuing.

Experimental Section

The IR spectra were recorded on a Perkin-Elmer 257 grating spectrophotometer, UV spectra on a Unicam SP-8000 instrument, and ^{1}H NMR spectra on a Varian EM-360 spectrometer. Natural-abundance, proton-decoupled, ^{13}C NMR spectra were obtained on a Varian XL-100-15 spectrometer at 25.6 MHz in the pulsed Fourier transform mode. The temperature of the probe was 32 ● 3 °C. Spectral widths of 8000 Hz were routinely used, with acquisition times of 0.5 s and pulse widths of 8 μs. Mass spectra were routinely recorded with a Bell and Howell 21-490 instrument.

Elemental analyses were performed by the Scandinavian Microanalytical Laboratory. All melting points are uncorrected. The sulfur dichloride, disulfur dichloride, and thione **1b** used in this study were obtained from the Aldrich Chemical Co. Inc.

Reaction of Thiobenzophenone[21] (1a) with SCl_2 at −78 °C. Freshly distilled sulfur dichloride (1.99 g, 19.51 mmol) in diethyl ether (25 mL) was dropped over a period of 15 min into thiobenzophenone (3.86 g, 19.50 mmol) in diethyl ether (100 mL) cooled in a dry ice–acetone bath. The blue color of the solution faded, and a white precipitate formed. During attempted filtration of the white solid the characteristic blue color of the thione returned.

Reaction of Xanthione[21] (4) with SCl_2. (a) In Diethyl Ether. Sulfur dichloride (0.26 g, 2.5 mmol) in diethyl ether (10 mL) was slowly added to xanthione (0.53 g, 2.5 mmol) in diethyl ether (50 mL) cooled in a dry ice–acetone bath under nitrogen. The color of the thione quickly disappeared. After the mixture was stirred for 2.5 h at −78 °C, the solvent was removed under vacuum. Purification by TLC (silica gel, CH_2Cl_2) yielded sulfur, traces of thione, and xanthone **6**, 0.43 g (88%).

(b) In Carbon Disulfide in the Presence of $SnCl_4$. Sulfur dichloride (0.20 g, 2.0 mmol) in dry CS_2 (10 mL) was slowly dropped into **4** (0.42 g, 2.0 mmol) and stannic chloride (0.52 g, 2.0 mmol) in dry CS_2 (35 mL) in a glovebox under nitrogen. An orange salt (**5b**) precipitated from solution: 1.15 g (100%); dec 170 °C; (the salt when left exposed to the air or in solution (e.g., in nitromethane-d_3) slowly reverted to the thione); ^{1}H NMR (CD_3NO_2) δ 7.5–9.1 (m, 8 H); ^{13}C NMR (CD_3NO_2) δ 117.8, 120.6, 121.2, 121.3, 127.5, 128.5, 129.1, 129.7, 130.2, 131.9, 142.5, 143.3, 147.1, 154.8, 159.6, 169.9, 179.6 (partial decomposition of the sample had occurred); IR (Nujol) 1617, 1605, 1577, 1544, 1512, 1292, 1250, 1214, 1178, 1150, 1028, 980, 950, 873, 788, 760, 730, 643 cm^{-1}; mass spectrum, *m/e* 269–256 ($SnCl_4$), 233–219, 212 (thione, 100%), 198, 168, 162–151, 139, 131, 128, 124, 122–113, 106, 69. Anal. Calcd for $C_{13}H_8Cl_6OS_2Sn$: C, 27.12; H, 1.40; Cl, 36.95; S, 11.14. Found: C, 27.49; H, 2.14; Cl, 35.13; S, 9.87.

(c) In CS_2. Sulfur dichloride (0.11 g, 1.1 mmol) in dry CS_2 (2 mL) was added to **4** (0.21 g, 1.0 mmol) in dry CS_2 (5 mL) under nitrogen. The characteristic green color of the thione faded to pale yellow almost instantly, and the unstable product (**5a** or **10**) was isolated on evaporation as a yellow-brown solid: ^{1}H NMR ($CDCl_3$) δ 7.0–7.5 (m, 6 H), 7.85 (dd, 2 H, *J* = 8, 2 Hz); ^{13}C NMR ($CDCl_3$) δ 75.0, 116.2, 123.3, 123.7, 130.4, 130.8, 149.9; IR (CS_2) 1335, 1255, 1230, 1190, 1160, 1110, 1045, 915, 895, 865 cm^{-1}. Anal. Calcd for $C_{13}H_8Cl_2OS_2$: C, 49.53; H, 2.56; S, 20.34. Found: C, 50.06; H, 2.57; S, 21.52.

Reaction of 9-Diazoxanthene[22] with Disulfur Dichloride. Xanthone hydrazone[23] (0.42 g, 2 mmol) was dissolved in dry ether (10 mL) and shaken for 30 min with magnesium sulfate (0.40 g) and silver oxide (0.43 g, 2.2 mmol).[24] The resultant green solution was filtered free of silver, and the solvent was evaporated in the cold. The green crystalline solid obtained was dissolved in CS_2 (4 mL) and added slowly to disulfur dichloride (0.27 g, 2 mmol) in CS_2 (1 mL) at 0 °C with stirring. The green solution immediately turned orange, with evolution of nitrogen, and the ^{1}H NMR spectrum was recorded immediately. Although the reaction was not as clean as that described in part c, the spectra of the major product from this reaction and that derived from the thione with SCl_2 were clearly identical: ^{1}H NMR (CS_2) δ 7.2–7.7 (m, 6 H), 8.15 (dd, 2 H, *J* = 8, 2 Hz).

Reaction of 9,9-Dichloroxanthene with Stannic Chloride. 9,9-Dichloroxanthene[25,26] (0.05 g, 0.2 mmol) was dissolved in nitromethane-d_3 (0.5 mL). Stannic chloride (2 drops) was added to this colorless solution, which immediately turned bright orange. The ^{1}H NMR spectrum of this mixture was recorded at once: ^{1}H NMR (CD_3NO_2) δ 7.6–8.9 (m, 8 H).

Reactions of Other Thiones (1, 16–19) with Sulfur Dichloride. The general procedure followed that used in the reaction of xanthione with sulfur dichloride in CS_2.

Thiobenzophenone[21] (1a): ^{1}H NMR (CS_2) δ 7.18–8.0 (m); IR (CS_2) 1340, 1280, 1220, 1180, 1155, 1115, 1070, 1035, 1005, 940, 920, 850 cm^{-1}.

4,4′-Dimethoxythiobenzophenone (1b): ^{1}H NMR (CS_2) δ 3.90 (s, 6 H), 6.92 (m, 4 H), 7.57 (m, 4 H); IR (CS_2) 1315, 1265, 1185, 1125, 1040, 925, 895 cm^{-1}.

4,4′-Bis(dimethylamino)thiobenzophenone[21] (1c). A precipitate formed during the addition. ^{1}H NMR and IR indicated the solution contained only thione.

2,2,4,4-Tetramethyl-3-pentanethione[27] (16): ^{1}H NMR (CS_2) δ 1.40 (s, 18 H); IR (CS_2) 1376, 1200, 1040, 920, 855 cm^{-1}.

Adamantanethione[28] (17): ^{1}H NMR (CS_2) δ 1.88 (m, 8 H), 2.47 (m, 6 H); IR (CS_2) 1350, 1335, 1305, 1270, 1215, 1093, 1030, 955, 895 cm^{-1}.

Thiofenchone[29] (18): ^{1}H NMR (CS_2) δ 1.32 (s, 3 H), 1.40 (s, 3 H), 1.48 (s, 3 H), 1.68–2.30 (m, 7 H); IR (CS_2) 1310, 1285, 1260, 1245, 1215, 1195, 1105, 1005, 965, 905 cm^{-1}.

Reaction of Thiocamphor[21] (19) with SCl_2. Formation of 2-(Chlorodithio)-1,7,7-trimethyl-2-norbornene (25). During the addition of SCl_2, bubbling occurred, and HCl was detected in the evolved gas: ^{1}H NMR (CS_2) δ 0.80–2.50 (m, 14 H), 6.40 (d, 1 H, *J* = 6 Hz); IR (CS_2) 1605 (C=C), 1215, 1110, 1040, 1025 cm^{-1}.

Attempted Conversion of 25 to the Tetrasulfide 26. After the addition of SCl_2, potassium iodide (0.42 g, 2.5 mmol) was added. The color of iodine was immediately produced. The solution was washed with aqueous sodium thiosulfate and water and the organic layer dried ($MgSO_4$). Evaporation yielded a brown oil. TLC (silica gel, pentane) yielded four major compounds: (a) yellow oil, 0.08 g, decomposed on standing; (b) yellow oil, 0.15 g, decomposed on standing; (c) thione **19**, 0.09 g (21%); (d) an unidentified yellow oil, 0.05 g.

Reaction of Xanthene with Thionyl Chloride. Xanthene (**13**; 0.91 g, 5.0 mmol), pyridine (3 drops), and thionyl chloride (7.65 g, 64.8 mmol) were refluxed for 45 min. No reaction occurred.

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(26) 9,9-Dichloroxanthene has ^{1}H NMR ($CDCl_3$) signals at δ 6.95–7.50 (m, 6 H), 8.00 (dd, 2 H, *J* = 8, 2 Hz).

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Attempted Reaction of 9-Lithioxanthene with Thionyl Chloride. Thionyl chloride (7.65 g, 64.8 mmol) was added to a three-necked flask, cooled in a dry-ice acetone bath under nitrogen. Xanthene (0.91 g, 5.0 mmol) in dry diethyl ether (20 mL) was added to a dropping funnel attached to the above three-necked flask. *n*-Butyllithium (0.48 g, 7.5 mmol) was added to the ether solution and the reaction left for 15 min. The resulting deep red solution was then dropped into the thionyl chloride over a period of 20 min. The reaction was stirred for a further 20 min at −78 °C and for 2 h at 25 °C. Filtration yielded a solid which quickly decomposed in air and upon addition of water, fizzed, and gave the odor of xanthene. Evaporation of the slightly yellow ether solution yielded a deep purple solid. Extraction with water slowly eliminated the color, and a gas was evolved. TLC analysis indicated a complex mixture including xanthene.

Reaction of α-Chlorothiosulfenyl Chlorides with Triphenylphosphine. General Procedure. Sulfur dichloride (0.11 g, 1.1 mmol) in dry CS_2 (2 mL) was added to the corresponding thione (1.0 mmol) in dry CS_2 (5 mL) under N_2. After the mixture was stirred for 20 min, triphenylphosphine (0.27 g, 1.1 mmol) was added, and the reaction was stirred for a further 30 min. Addition of water, extraction, drying of the organic layer (Na_2SO_4), and evaporation yielded a mixture of four spots by TLC. Thick-layer chromatography (SiO_2, CH_2Cl_2) yielded thione (least polar), triphenylphosphine sulfide, ketone, and triphenylphosphine oxide (most polar). The results are summarized in Table III.

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Registry No. **1a**, 1450-31-3; **1b**, 958-80-5; **1c**, 1226-46-6; **2a**, 79991-60-9; **3b**, 79991-61-0; **4**, 492-21-7; **5a**, 79991-62-1; **5b**, 79992-45-3; **6**, 90-47-1; **7**, 20735-05-1; **8**, 79992-47-5; **9**, 51933-61-0; **10**, 80010-06-6; **13**, 92-83-1; **15**, 79991-63-2; **16**, 54396-69-9; **17**, 23695-65-0; **18**, 875-06-9; **19**, 7519-74-6; **20**, 79991-64-3; **21**, 79991-65-4; **22a**, 79991-66-5; **22b**, 79991-67-6; **23a**, 79991-68-7; **23b**, 79991-69-8; **24a**, 79991-70-1; **24b**, 7419-57-0; **25**, 79991-71-2; 9-lithioxanthene, 40102-97-4; 1,1′-[(chloro)(chlorodithio)methylene]bisbenzene, 79991-72-3; 1,1′-[(chloro)(chlorodithio)methylene]bis[4-methoxybenzene], 79991-73-4; benzophenone, 119-61-9; bis(4-methoxyphenyl)-methanone, 90-96-0; 2,2,4,4-tetramethyl-3-pentanone, 815-24-7; fenchone, 1195-79-5; adamantanone, 700-58-3; triphenylphosphine oxide, 791-28-6; triphenylphosphine sulfide, 3878-45-3.

Notes

Convenient Method for the Conversion of Thiols and Disulfides to the Corresponding Chlorides

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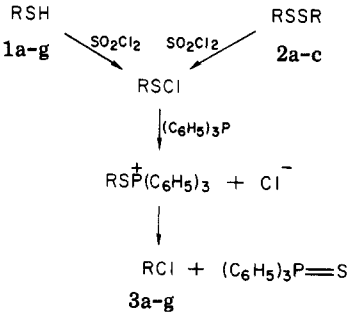
Many versatile procedures exist in the literature for the conversion of alcohols to alkyl chlorides. It is surprising, therefore, that few attempts have been made to develop reagents for the formally analogous conversion of thiols to alkyl chlorides. The reverse of this procedure, on the other hand, i.e., the conversion of alkyl halides to thiols, is, of course, a well-documented synthetic manipulation.[1]

Two of the early procedures which have been reported[2,3] for the conversion of thiols to alkyl chlorides are clearly limited to special cases, while another approach, using the reaction of sulfenyl chlorides with trialkyl phosphites,[4] although more general, leads to alkyl chlorides only as side products, resulting from Arbuzov reaction of chloride ion on the initially formed phosphonium salt. More recently, Weiss and Snyder[5] used the system triphenylphosphine–carbon tetrachloride for the conversion of alcohols and, in two instances only, thiols to chlorides at 50–55 °C. Clive and Denyer[6] also successfully converted a number of *primary* aliphatic thiols to the corresponding chlorides using a two-step procedure involving initial reaction of the thiol with (chlorocarbonyl)sulfenyl chloride, followed by triphenylphosphine. In the one case where a secondary thiol was used, these authors obtained an alkene as the major product under their reaction conditions.

Scheme I



As part of our recent study of the behavior of sulfenyl chlorides and thiosulfenyl chlorides[7] we have found a new procedure for the rapid conversion of aliphatic thiols (primary, secondary, tertiary, *and* benzylic) to the corresponding chlorides under very mild conditions (Table I). The method involves chlorination of the thiol at low temperatures with sulfuryl chloride (chlorine may also be used), followed by reaction of the intermediate sulfenyl chloride (not isolated) with triphenylphosphine[8] to give the chloride. The reaction gives somewhat higher yields with disulfides (Table I). In the latter case, we believe that our procedure again requires the intermediacy of the sulfenyl chloride, although the cleavage of disulfides to thiols directly, by using tri-*n*-butylphosphine[9] or triphenylphosphine and water,[10] has been reported and also

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