Chlorinations with Carbon Tetrachloride under Conditions of Phase Transfer Catalysis

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Anions of ketones, sulfones and esters were α-chlorinated by carbon tetrachloride under conditions of phase transfer catalysis (PTC). Alcohols were unreactive. The observed products show that secondary reactions took place in many cases. The chlorination of the sulfone cis-2,5-diphenyltetra-hydrothiophene-1,1-dioxide (1) occurred with inversion to give trans-2,5-dichloro-2,5-diphenyl-tetrahydrothiophene-1,1-dioxide (2). The structures of cis-1 and trans-2 were determined by X-ray diffraction. The reaction conditions are also applicable to brominations using bromotrichloromethane.

A few years ago Meyers et al.[1] published some interesting reactions of carbon tetrachloride with alcohols, ketones and sulfones under basic conditions. The reactions involve chlorination by carbon tetrachloride of the initially formed α-carbanion followed in many cases by various secondary reactions caused by the base. The use of powdered potassium hydroxide as base and t-butyl alcohol – water as solvents appeared quite critical. It was subsequently shown[2] that similar reactions occurred when carbon tetrachloride was replaced by other perhalomethanes.

In the present paper we report that this type of reaction takes place under conditions of phase transfer catalysis (PTC) using aqueous sodium hydroxide as base and benzyltriethylammonium chloride (TEBA) as catalyst. We also used cetyltriethylammonium chloride and tetrabutylammonium chloride as catalysts without any significant improvement. An excess of carbon tetrachloride was used and in most cases dichloromethane was added as a solvent. The reactions were carried out at ambient temperature during 2–48 h depending on the reactivity of the substrate. Makosza and co-

workers had previously reported the chlorination of phenylacetonitrile[4] and phenylacetylene[5] under such conditions.

The compounds used for this study were either commercially available or prepared by conventional methods. The sulfone 2,5-diphenyltetrahydrothiophene-1,1-dioxide (1), required for reaction 5 (Table 1), was prepared[6] from meso 1,4-dichloro-1,4-diphenylbutane and sodium sulfide in dimethyl formamide followed by peracetic acid oxidation of the initially formed tetrahydrothiophene derivative. Recrystallization of the crude product gave 1, m.p. 176 °C, and the cis-configuration of the phenyl groups was established by X-ray diffraction (vide infra). The sulfone 1, m.p. 165–167 °C, described in the literature[6] was most probably a mixture of stereoisomers; the pure isomers have not previously been reported although they were alluded to by the same authors.[6]

By comparing our results, recorded in Table 1, with those reported by Meyers et al.[1,2] some distinct differences in reactivity of the two base systems become apparent. Under our conditions no reaction was observed with alcohols while benzhydrol, for example, gave a quantitative yield of benzophenone, using the potassium hydroxide method. On the other hand, pinakolone gave comparable yields of pinacolic acid by either method. The reactions with sulfones were of particular interest because of the possibility of subsequent Ramberg-Bäcklund reaction[7] with formation of olefins. Meyers has recorded several examples of such reactions, but under our conditions diisopropyl sulfone was quite unreactive. No reaction took place with cyclohexyl phenyl sulfone, but all the α-hydrogens of methyl tolyl sulfone were replaced by chlorine (reaction 10); the same product was obtained from bromomethyl

Table 1. Reactions with carbon tetrahalide under PTC conditions.

Reaction No.	Substrate	Product	Yield %
CCl_4			
1	Me_3COMe	Me_3CCO_2H	96
2	Ph_2CHOH	No reaction	
3	$PhCH_2CO_2Bu^t$	$PhCCl_2CO_2Bu^t(7)$	75[a]
4	$(i\text{-}Prop)_2SO_2$	No reaction	
5	$(cyclohexyl)PhSO_2$	No reaction	
6	$PhSO_2CH_2Ph$	$PhSO_2CCl_2Ph$	80
7	$(PhCH_2)_2SO_2$	(E)-Stilbene	100
8	*cis-1*	*trans-2*	96
9	$PhCH_2SO_2CHMe_2$	*3, 4*	99
10	$TolSO_2Me$	$TolSO_2CCl_3$	62
11	$TolSO_2CH_2Br$	$TolSO_2CCl_3$	95
$CBrCl_3$			
12	$PhSO_2CH_2Ph$	$PhSO_2CBrClPh$ (8)[b] $PhSO_2CBr_2Ph$ (9)	

[a] In the absence of CH_2Cl_2; the yield is based on recovered starting material (10 %). [b] *8* and *9* are formed in a ratio of 1:1.5. The yield is 87 % based on *9*.

tolyl sulfone (reaction 11). Aryl alkyl sulfones are readily α-chlorinated by Meyers method, but subsequent hydrolysis of the α-chlorosulfones to the corresponding sulfonic acids occurred as well.[1,2] Both benzylic hydrogens of benzyl phenyl sulfone were replaced by chlorine. Dibenzyl sulfone afforded E-stilbene quantitatively apparently by a Ramberg-Bäcklund reaction on the initially formed chloride. Another example of olefin formation was observed in reaction 9, Table 1; benzyl isopropyl sulfone gave as the main product the vinyl chloride *3*, accompanied by a small amount of the *gem*-dichlorocyclopropane derivative *4*. On the other hand, the benzylic sulfone *cis-1* gave an almost quantitative yield of (E)-2,5-dichloro-2,5-diphenyl-tetrahydrothiophene-1,1-dioxide (*2*), the configuration being established by X-ray diffraction (*vide infra*); 1,2-diphenylcyclobutene, the anticipated product of a Ramberg-Bäcklund reaction was not detected.

The reaction of ethyl phenylacetate yielded a mixture of α,α-dichlorophenylacetic acid (*5*) and α-chlorophenylacetic acid (*6*) in a ratio of 6:1 as major products together with some of the corresponding esters. Extensive hydrolysis took also place with t-butyl phenylacetate under the general conditions; a 45 % yield of the acid *5* was isolated besides 21 % of t-butyl α,α-dichlorophenylacetate (*7*). In the absence of dichloromethane, however, a 75 % yield of the ester *7* was obtained.

The difference in reactivity of reactions carried out under conditions of PTC and that of Meyers can find an explanation in the different basicities of the two systems. It seems quite evident that the system powdered potassium hydroxide in *t*-butyl alcohol-water must be considerably more basic than the active base under the present PTC conditions. Previous results indicate that $C-H$ acids weaker than $pK_a \sim 22$ will not form carbanions under the latter conditions,[8] but this cannot hold true for sulfones at least. The pK_a values of the α-hydrogens of sulfones increase in the order dibenzyl, benzyl phenyl, alkyl phenyl, dialkyl within the range of $\sim 22-32$ units. Our results show that sulfones with pK_a values lower than that of methyl tolyl sulfone, $pK_a \sim 27$, will form carbanions under PTC conditions. Alkyl phenyl sulfones seem to represent the borderline as methyl groups react sluggishly while secondary α-hydrogens are unreactive (reactions 4 and 5). It should be kept in mind that our results refer to reactions in dichloromethane as cosolvent; without this solvent methyl tolyl sulfone was quite unreactive. On the other hand, in the case of reaction 6 (Table 1) the dichloride is formed almost quantitatively also in the absence of dichloro-

methane. Dichloromethane is more polar than carbon tetrachloride, but it may be important that it is also a much better solvent for substituted ammonium salts.[9] The α-halosulfones are stronger acids than the parent compounds and it has been shown[10] that they form carbanions under phase transfer conditions; hence, the formation of trichloromethyl phenyl sulfone in reaction 11 (Table 1) is quite expected, although the substitution of bromine with chlorine is in this case an additional feature.

Ramberg-Bäcklund elimination can compete favourably with α-halogenation as demonstrated by the results of reaction 7 and 9 (Table 1); however, from the cyclic sulfone 1 no olefin was obtained. For the 1,3-elimination leading to an episulfone all evidence points to a mechanism which requires a W type conformation for the halogenated sulfone.[11] This can easily be achieved for the α-chlorosulfones initially formed in reactions 7 and 9, and for the reaction of 1 as well, provided the chlorination occurs with retention of configuration. This was expected since α-sulfonyl carbanions are formed and reprotonated with a high degree of retention[12] and furthermore, Meyers et al.[1] had obtained essentially (Z)-2,3-diphenyl-2-butene from the reaction of meso-bis(methylbenzyl)sulfone under their conditions. However, in a separate experiment it was shown that the sulfone cis-1 is actually converted under PTC conditions into an equilibrium mixture consisting essentially of trans-1, m.p. 155 °C. We therefore conclude that inversion of 1 occurs prior to chlorination, leading to a configuration of the monochloride which is unfavourable for 1,3-elimination; hence, a second chlorination takes place to give the observed product 2.

The vinyl chloride 3 isolated as the major product from the reaction of benzyl isopropyl sulfone could have been formed in two ways. Elimination with extrusion of sulfur dioxide from either the α,α-dichloride 10 or the α,α'-dichloride 11 would lead to the observed product; however, considering the results of Table 1 it seems most likely that 10 is the precursor of 3; the inductive effect of the two chlorine atoms increases the acidity of the isopropyl hydrogen sufficiently for carbanion formation. The gem-dimethyl substitution precludes the formation of the alkenesulfonic acid from the intermediate chloro episulfone.[13] The trichloromethyl anion formed in the chlorination step is a source of dichlorocarbene which subsequently adds to the double bond of 3 with formation of the cyclopropane
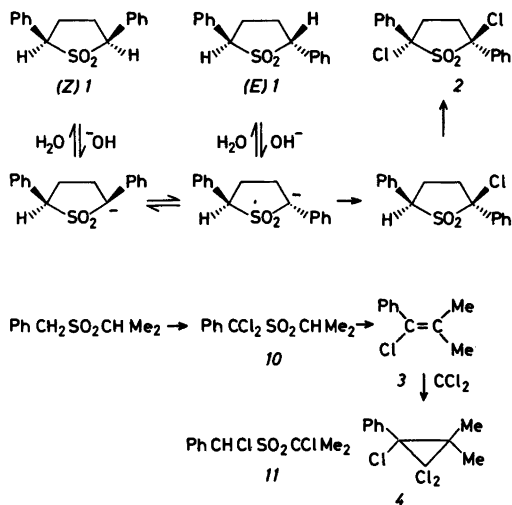
derivative 4.[1] An authentic sample of the latter was actually prepared in this way.

Esters had not previously been chlorinated under PTC conditions; however, Arnold and Kulenovic[14] obtained high yields of α-monochlorides from esters treated with the system lithium diidopropylamide − carbon tetrachloride. The accelerating effect by dichloromethane on the rate of saponification lacks precedence, and we cannot offer any explanation without further work; the result adds to the notion that no general mechanism exists for the saponification of esters under PTC conditions.

The structures of compounds 1 and 2 were determined by X-ray diffraction; ORTEP plots are presented in Figs. 1 and 2 and selected structural data are listed in Table 2.

Bond lengths and valence angles in compound 1 have the expected values. The configuration is cis, the phenyl rings being situated on the same side of the five-membered ring. The tetrahydrothiophene ring has the envelope form with C2 situated 0.75 Å out of the plane through the other four atoms of the ring, the torsion angle C3−C4−C5−S1 being 3.1°.
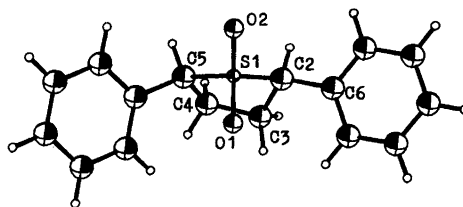

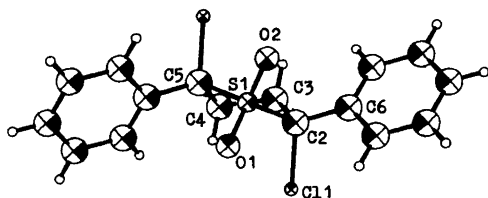Fig. 1. ORTEP plot of cis-2,5-diphenyltetrahydrothiophene-1,1-dioxide (1).

Fig. 2. ORTEP plot of *trans*-2,5-dichloro-2,5-di-phenyltetrahydrothiophene-1,1-dioxide (2) seen along the two-fold symmetry axis.

The conformation about the C2 – C6 bond seems to be determined mainly by contacts between hydrogen atoms on the fivemembered ring and the *ortho* phenyl hydrogen atoms (H – H separations in the range 2.16 – 2.29 Å).

The crystal symmetry requires the chloro-compound 2 to have two-fold symmetry about an axis passing through S1 and halfway between C3 and C4. The conformation of the five-membered ring is thus of the half-chair type; the configuration is

trans with the phenyl groups on each side of the tetrahydrothiophene ring in equatorial positions and the chlorine atoms in axial positions. With one exception the bond lengths and angles are normal and in good agreement with those of compound *1*. The S1 – C2 bond, however, is very long, 1.886(1) Å, which is at least 0.07 Å longer than the normal value. The explanation may be the eclipsed conformation about the S1 – C2 bond (*cf.* Table 2), leading to a non-bonded distance of only 2.96 Å between O1 and Cl1. Other short intermolecular non-bonded separations are those between a C3 hydrogen and the nearest *ortho* phenyl hydrogen atom of 2.02 Å and between Cl1 and the other *ortho* phenyl hydrogen atom of 2.96 Å.

EXPERIMENTAL

NMR spectra were recorded on Varian EM 360A and Jeol JNM FX 60 Fourier transform spectrometers. The mass spectra were obtained on an AEI/EC MS 902 instrument. Elemental analyses were performed by I. Beetz, West Germany.

Table 2. Structural data.

	1	*2*		*1*	*2*
Bond lengths (Å)			Bond angles (°)		
S1 – O	1.441(2)	1.438(1)	O – S1 – O	117.2(1)	118.8(1)
S1 – C2	1.789(3)	1.886(1)	C2 – S1 – C5	94.5(1)	96.1(1)
S1 – C5	1.805(3)		S – C2 – C3	100.7(2)	101.7(1)
C2 – C3	1.525(4)	1.528(2)	C2 – C3 – C4	107.7(3)	107.2(1)
C3 – C4	1.525(4)	1.531(2)	C3 – C4 – C5	111.3(2)	
C4 – C5	1.537(4)		C4 – C5 – S1	104.2(2)	
C2 – Cl1		1.798(1)	S2 – C2 – C6	111.3(2)	111.0(1)
C2 – C6	1.513(3)	1.513(2)	C6 – C2 – C3	119.5(3)	117.8(1)
C—C			S1 – C2 – Cl1		106.7(1)
phenyl ring)	1.375(5)	1.392(2)	C6 – C2 – Cl1		110.1(1)
			C3 – C2 – Cl1		108.8(1)
Torsion angles (°)			Short non-bonded distances (Å)		
C5 – S1 – C2 – C3	– 42.1(2)	14.7(1)	O1 – C6	{ 2.73 / 2.72	
S1 – C2 – C3 – C4	45.2(3)	– 41.0(1)			
C2 – C3 – C4 – C5	– 28.0(3)	56.8(2)	O2 – C6	{ 3.10 / 2.99	2.96
C3 – C4 – C5 – S1	– 3.1(3)	– 41.0(1)			
C4 – C5 – S1 – C2	26.9(2)	14.7(1)	O1 – Cl1		2.96
O1 – S1 – C2 – C6	{ – 57.3(2) / 43.8(2)	– 106.4(1)			
O2 – S1 – C2 – C6	{ 74.5(2) / – 87.6(2)	26.1(1)			
O1 – S1 – C2 – Cl1		13.6(1)			
O2 – S1 – C2 – Cl1		146.1(1)			

Materials. The benzyl or phenyl sulfones were prepared by conventional methods from the respective thiolates and alkyl or benzyl bromides in methanol, followed by oxidation of the sulfides with peracetic acid. Diisopropyl sulfone and diisobutyl sulfone were commercially available from K&K Laboratories, USA.

2,5-Diphenyltetrahydrothiophene-1,1-dioxide (1). cis-1. From a stereoisomeric mixture of 1,4-diphenyl-1,4-butanediol the *meso* isomer, m.p. 102−104 °C, was obtained.[15] It was converted into meso-1,4-dichloro-1,4-diphenylbutane with hydrogen chloride in glacial acetic acid. This yielded with anhydrous sodium sulfide in DMF 2,5-diphenyltetrahydrothiophene; oxidation with peracetic acid afforded the dioxide *cis-1*, m.p. 176 °C.[6] The configuration was established by X-ray diffraction (*vide infra*).

trans-1. A mixture of 0.5 g (Z) *1*, 10 ml CH_2Cl_2, 10 ml NaOH (50 % aqueous) and 0.01 g TEBA was stirred at room temperature for 3 days. Isolation in the usual way gave 0.5 g of crystals which by TLC (silica gel/CH_2Cl_2) showed two components. Separation by preparative TLC gave 0.33 g *trans-1*, m.p. 154−155 °C (from ethanol). The NMR spectra were identical with those of *cis-1*, but the IR spectra were different. A 1:1 mixture with *cis-1* melted at 165−170 °C.

General procedure for reaction of CH-acids with CCl_4 under PTC conditions. About 10 mmol substrate and 0.2 g benzyltriethylammonium chloride (TEBA) were dissolved in 20 ml CCl_4 and 10 ml CH_2Cl_2. To this solution was added 15 ml 50 % aqueous NaOH. When not stated otherwise, the reaction mixture was vigorously stirred at ambient temperature. The products were worked up by addition of water (50−100 ml) and extraction with several portions of CH_2Cl_2. Acidic products were subsequently extracted in the same manner after acidification of the aqueous phase. The extracts were dried ($MgSO_4$) and the solvents were evaporated.

Reaction of 3,3-dimethyl-2-butanone. After 2 h reaction time acidification of the aqueous phase gave 2,2-dimethylpropanoic acid, b.p. 160−165 °C in 96 % yield. Spectroscopic data were identical with those of an authentic sample.

Reaction of dibenzyl sulfone. After 24 h reaction time *E*-stilbene was obtained in quantitative yield, m.p. 122−123 °C. The spectroscopic data were identical with those of an authentic sample.

Reaction of benzyl phenyl sulfone. After 24 h reaction time an 80 % yield of α,α-dichlorobenzyl phenyl sulfone, m.p. 150−151 °C (lit.[16] 151−152 °C), was obtained.

Reaction of cis-2,5-diphenyltetrahydrothiophene-1,1-dioxide *(1).* After 24 h the product was isolated and purified by column chromatography (silica gel/$CHCl_3$). *trans-2,5-dichloro-2,5-diphenyltetrahydrothiophene-1,1-dioxide (2),* m.p. 190 °C, was

obtained in 96 % yield. Anal. $C_{16}H_{14}Cl_2O_2S$: C, H; ^{1}H NMR ($CDCl_3$): δ 3.25 (4H,q); 7.50 (10H, Ph,m); IR (KBr): 1165, 1335 cm^{-1} (sulfone); MS: *m/e*: 278(2.9 %), 276(4.3 %), 140(32.3 %), 138(100 %).

Reaction of benzyl isopropyl sulfone. Heating with reflux for 2 h yielded a mixture of two components which were separated by preparative GLC (15 % QF-1 on Chromosorb W, 190 °C).

The major component (97 % yield), 1-chloro-1-phenyl-2-methylpropene (*3*): ^{1}H NMR ($CDCl_3$): δ 1.65(3H,s), 1.95(3H,s), 7.25(5H,s); IR (liq.film): 710, 770, 1450, 1500, 1580, 1600, 2830, 2860 cm^{-1}; MS: *m/e*: 168(18.6 %), 166(57.5 %), 132(10.9 %), 131(100 %), 116(26.4 %), 115(56.0 %), 91(48.0 %), 77(11.4 %).

The minor component (2 % yield), 1,1,2-trichloro-2-phenyl-3,3-dimethylcyclopropane (*4*): ^{1}H NMR ($CDCl_3$): δ 1.40(3H,s), 1.70(3H,s), 7.40(5H,m); IR (liq.film): 710, 760, 860, 1040, 1100, 1380, 1400, 1460, 1470, 2940, 2960 cm^{-1}; MS: *m/e*: 215(11.3 %), 213(19.2 %), 179(32.8 %), 178(17.9 %), 177(100 %), 162(34.5 %), 143(29.8 %), 142(86.9 %), 141(79.2 %), 139(11.9 %), 77(37.8 %).

An authentic sample of *4* was obtained from *3* and $CHCl_3$ under PTC conditions.[3]

Reaction of p-tolyl methyl sulfone. 24 h yielded 62 % of p-tolyl trichloromethyl sulfone, m.p. 135−138 °C (lit.[17] 140−140.5 °C); ^{1}H NMR ($CDCl_3$): δ 2.50(3H,s), 7.75(4H,q); IR (KBr): 1600, 1350, 1305, 1300, 1190, 1160, 1080, 830, 820 cm^{-1}; MS: *m/e*: 155(66.3 %), 91(100 %).

Reaction of bromomethyl p-tolyl sulfone. After 6 h a 95 % yield of p-tolyl trichloromethyl sulfone, m.p. 133−135 °C, was obtained.

Reaction of t-butyl phenylacetate. After 48 h the reaction mixture was extracted with CH_2Cl_2 to give 21 % of *t*-butyl α,α-dichlorophenylacetate (*7*), b.p. 130−132 °C (10 mm Hg); ^{1}H NMR (CCl_4): δ 1.45(9H,s), 7.2−7.4(3H,m), 7.45−7.7(2H,m); IR (liq.): 1750 cm^{-1}.

Acidification and extraction of the aqueous phase gave 45 % of α,α-dichloro-phenylacetic acid (*5*), m.p. 50−52 °C (lit.[18] 50−55 °C); ^{1}H NMR (CCl_4): 7.2−7.7(3H,m), 7.9−8.2(2H,dd), 11.50(1H,s).

The same reaction without CH_2Cl_2 gave after the usual work-up procedure a 68 % yield of 7 besides 10 % of starting material.

Reaction of ethyl phenylacetate. A mixture of 1.64 g (10 mmol) of ethyl phenylacetate, 20 ml CCl_4, 10 ml NaOH (50 % aq.) and 0.2 g TEBA was stirred at room temperature for 20 h. Extraction with ether gave 0.5 g of a liquid which was shown by ^{1}H NMR to consist of a mixture of mainly unreacted ester and presumably some ethyl α,α-dichlorophenylacetate. Acidification and extraction of the aqueous phase gave 1.34 g (68 %) of a liquid which consisted of α,α-dichlorophenylacetic acid (*5*), and α-chlorophenylacetic acid in a ratio of 6:1. In the ^{1}H NMR

spectrum the latter exhibited resonances as for *5* and in addition a singlet at δ 5.42.

Reaction of benzyl phenyl sulfone with $CBrCl_3$. A mixture of 1.50 g (6.5 mmol) of sulfone, 20 ml $CBrCl_3$, 10 ml CH_2Cl_2, 10 ml NaOH (50 % aq.) and 0.1 g TEBA was stirred at toom temperature for 12 h. Isolation in the usual way gave 2.2 g of a crystalline product which appeared homogeneous on TLC. However, the mass spectrum showed that it was a mixture of α,α-dibromobenzyl phenyl sulfone *9* and α-bromo-α-chlorobenzyl phenyl sulfone *8* by the peaks at m/e 247, 249, 251 ($PhCBr_2$) and 203, 205, 207 (PhCBrCl), respectively. ^{1}H NMR ($CDCl_3$): δ 7.1−7.9 (ar.H,m); ^{13}C NMR ($CDCl_3$): δ 78.68(s), 89.40(s), 127−134(m).

Based on the intensities of the resonances at δ 78.68 and 89.40, compounds *8* and *9* were present in a ratio of 1:1.5.

X-Ray crystal structure determinations of cis-*2,5-diphenyltetrahydrothiophene-1,1-dioxide, (1), and* trans-*2,5-dichloro-2,5-diphenyltetrahydrothiophene-1,1-dioxide, (2). X-Ray data.* Data for unit cell determination and intensity data were collected using a SYNTEX PĪ four-circle diffractometer, MoKα radiation ($\lambda = 0.71069$ Å). The temperature at the crystal site was kept at 18 °C for *1* and −150 °C for *2*, specimen dimensions $0.2 \times 0.4 \times 0.4$ mm. The $\theta/2\theta$ scan technique was employed with scan speeds 4° min^{-1} (*1*) and 3° min^{-1} (*2*), scan range 2.2°. For *1* 1865 independent reflections with sin $\theta/\lambda \leq 0.54$ Å^{-1} were measured; of these 1505 were larger than 2.5 (*I*) and were used for the structure analysis. In the case of *2* 1545 reflections out of the 1711, measured within sin $\theta/\lambda = 0.65$, were retained for the analysis.

Crystal data. 1. $C_{16}H_{16}O_2S$, m.p. 176 °C, monoclinic; $a = 6.069(1)$ Å; $b = 9.653(1)$ Å; $c = 24.163(2)$ Å; $\beta = 97.22(1)°$; $V = 1404.3$ Å; ($t = 18$ °C); $M = 272.36$; $Z = 4$; $D_x = 1.288$ g cm^{-3}; $F(000) = 576$. Space group $P2_1/c$ (No. 14).

2. $C_{16}H_{14}Cl_2O_2S$, m.p. 190 °C, orthorhombic; $a = 8.686(1)$ Å; $b = 10.040(1)$ Å; $c = 16.931(2)$ Å; $V = 1476.5$; ($t = -150$ °C); $M = 341.25$; $Z = 4$; $D_x = 1.535$ gcm^{-1}; $F(000) = 704$. Space group $Pbcn$ (No. 60).

Structure determination. The structures were determined by direct methods.[19] Full-matrix least-squares refinement of positional and anisotropic thermal parameters of the heavy atoms (calculated hydrogen parameters were not refined for *1*; for *2* they were refined with isotropic thermal parameters) converged to the following figures of merit: (*1*) $R = 0.040$; $R_w = 0.049$; $S = 2.19$; overdetermination ratio 8.8. (2) $R = 0.024$; $R_w = 0.030$; $S = 1.88$; overdetermination ratio 12.5. A description of the computer programs employed is given in Ref. 20. Atomic form factors used were those of Doyle and Turner[21] for Cl, S, O and C, and of Stewart, Davidson and

Simpson[22] for H. Listings of parameters and structure factors are available from the authors.

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