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An examination of the chlorination of phenylmethyl, diphenylmethyl, and triphenylmethyl methylsulfonyl sulfides (1, 2, and 3) in aqueous acetic acid has provided indirect evidence for Pummerer rearrangement during the chlorination of an  $\alpha$ -methylsulfonyl sulfinyl chloride. The results are discussed from both mechanistic and synthetic standpoints.

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L'étude de la chloration des sulfures du phénylméthyle, du diphénylméthyle et du triphénylméthyle méthylsulfonyle (1, 2 et 3) dans une solution aqueuse d'acide acétique fournit une preuve indirecte du réarrangement de Pummerer durant la chloration d'un chlorure de  $\alpha$ -méthylsulfonyle sulfinyle. Les résultats sont discutés des points de vue du mécanisme et de la synthèse. [Traduit par le journal]

In recent years, a widespread interest in the chlorination of organosulfur compounds has become apparent. Research has been primarily directed at the chlorination of sulfides (1-6) and sulfoxides (7-19). Our own work (20, 21) has demonstrated that  $\alpha$ -chlorodialkyl sulfides give rise to sulfonyl chlorides via sulfinyl chlorides upon chlorination in dilute aqueous acetic acid. We have proposed (21) that the sulfinyl chloride is hydrolyzed to the sulfinic acid which then reacts with chlorine to furnish the corresponding sulfonyl chloride.

The present report is the result of a desire to examine the behavior of chloro- and oxochlorosulfonium chloride salts in systems which may undergo either Pummerer rearrangement or dissociation to form carbonium ions and/or intimate ion pairs as well as sulfenyl or sulfinyl chlorides. Dissociation of this sort is not available to simple dialkyl chloro- and oxochlorosulfonium chloride salts.

The particular substrates chosen for examination (1, 2, and 3) offer two potentially useful features for such a study.

1 2 3 4 5  $CH_3 \cdot SO_2 \cdot CH_2 \cdot S \cdot C \times YZ$ 1 X = Y = H; Z = Ph 2 X = H; Y = Z = Ph 3 X = Y = Z = Ph Pummerer rearrangement of intermediate chlorosulfonium chloride salts is directed to C-3 by the  $\alpha$ -sulfonyl group (22) thus preventing chlorination on C-5, so that the polyphenylmethyl groups retain their ability to form carbonium ions (or intimate ion pairs) as the reaction proceeds. Secondly the regular increase of the number of phenyl groups on C-5 in the series  $1 \rightarrow 3$  increased the propensity for cleavage at progressively earlier stages during the reaction in the event that some Pummerer rearrangement preceded cleavage in the reaction of the phenylmethyl sulfide (1).

The sulfone-sulfides (1, 2, and 3) were prepared by refluxing the appropriate thiol anion with chloromethyl methyl sulfone in absolute ethanol (*vide* Scheme 1). Although this reaction

$$RSH + ClCH_2 \cdot SO_2 \cdot CH_3 \xrightarrow{EtOH} R \cdot S \cdot CH_2 \cdot SO_2 \cdot CH_3$$
$$SCHEME 1$$

is precedented (22, 23), reports that  $\alpha$ -halosulfones are inert to nucleophilic substitution can be found in the literature (24–27). Since these reports are based on the failure of non-sulfur containing nucleophiles to displace the  $\alpha$ halogen atoms of  $\alpha$ -halosulfones, we decided to examine two sulfur-containing nucleophiles in this reaction. Both sodium bisulfide and thiourea failed to react with chloromethyl methyl sulfone in refluxing ethanol. It therefore appears that the electronic nature of the nucleophilic sulfur

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atom is quite restricted if substitution reactions are to succeed on  $\alpha$ -halosulfones.

Chlorination of the sulfone-sulfide (1) in aqueous acetic acid furnished the dichlorosulfone-sulfonyl chloride (4) in good yield. Two approaches were undertaken in order to establish the structure of 4. Synthetic support was obtained by the unambiguous preparation of the dichlorosulfone-sulfenyl chloride (7) through the known compounds 1, 5, and 6 (28), followed by oxidation of 7 to 4 as shown in Scheme 2. Degradative support for the structure of 4 was obtained by its hydrolysis to give the dichlorosulfone (8) and an equivalent of sulfuric acid. This hydrolysis reaction appears to be new and is the subject of further studies, already underway, in our laboratories.

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Once the structure of 4 had been established, we directed some effort towards elucidating the pathway by which it was formed from 1. The reaction  $1 \rightarrow 4$  was complete after chlorination for 0.75 h. The product contained approximately 5% of the sulfone-sulfenyl chloride (7) and 95% of the sulfone-sulfenyl chloride (4). When the sulfone-sulfenyl chloride (7) was chlorinated under the same conditions, the reaction was only 70% completed after 14.5 h. Clearly, then, short chlorinations leave almost all intervening sulfone-sulfenyl chloride (7) unreacted and therefore a direct determination of 7 in crude reaction mixtures is a good measure of the amount of starting material giving rise to it.

Therefore only 5% of 1 gives rise to 7 in the reaction  $1 \rightarrow 4$  and 4 does not form via the intermediacy of 7. From our previous studies (20, 21) it is clear that 4 must arise from the

corresponding dichlorosulfone-sulfinyl chloride (9). It is now evident that 9 does not arise from the dichlorosulfone-sulfenyl chloride (7).

Chlorination of the dichlorosulfone-sulfide (6) in aqueous acetic acid furnished a mixture of the dichlorosulfone-sulfonyl chloride (4) and the dichlorosulfone-sulfenyl chloride (7) in the ratio 2:3 respectively. Since little dichlorosulfonesulfonyl chloride (4) could have formed from 7 in such a short time, then 4 must have arisen from 9 and  $10^2$  as depicted in Scheme 3. The relatively large amount of the dichlorosulfonesulfenyl chloride (7) formed from the chlorination of 6 in aqueous acetic acid essentially precludes 6 from consideration as a principal intermediate in the conversion of  $1 \rightarrow 4$ .

The presence of the dichlorosulfone-sulfenyl chloride (7) in the crude product obtained from the chlorination of 6 was established in part by its detection on t.l.c. After development and drying, the plate was sprayed with ammonium hexanitratocerate(IV) solution, a new spray reagent developed in these laboratories (31). This oxidizing spray is sensitive to the nature of the substituents on sulfur and visualizes the spots more slowly as the substituents on sulfur become more electron withdrawing. When a mixture is examined on t.l.c. using an authentic sample of a component for comparison, one can compare both the  $R_{\rm F}$  and the appearance time of the component in question and the authentic sample. Thus the crude product from the chlorination of 6 contained a compound

<sup>2</sup>The intermediacy of the  $\beta$ -disulfone can be ruled out on the basis of results published elsewhere (30).

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which was identical to 7 with respect to  $R_{\rm F}$  and appearance time.

Two possibilities now remain for the pathway  $1 \rightarrow 4$ . Either the benzylic sulfone-sulfide (1) cleaves directly after chlorosulfonium chloride formation or Pummerer rearrangement occurs leading ultimately to 4.

If the longer pathway implicated by Pummerer rearrangement is occurring, then reaction times should be substantially shortened if the structure of the sulfone-sulfide (1) were modified in such a way as to facilitate direct cleavage of the chlorosulfonium chloride salt initially formed.

# $CH_3 \cdot SO_2 \cdot CH_2 \cdot SO \cdot CH_2 \cdot Ph$ 11

We have undertaken two approaches to facilitating immediate cleavage and suppressing Pummerer rearrangement. In our first approach, the sulfone-sulfoxide (11) was prepared. When 11 reacts with chlorine an oxochlorosulfonium chloride salt is formed. The sulfur atom in this case is more electron deficient than the sulfur atom in a chlorosulfonium chloride salt and should constitute a better leaving group, thereby facilitating direct cleavage without Pummerer rearrangement. Such an analysis is consistent with our previous results (20) in which we found that  $\alpha$ -polychlorosulfoxides cleave to furnish sulfinyl chlorides upon treatment with molecular chlorine, whereas *a*-polychlorosulfides either react via a Pummerer rearrangement to furnish more highly chlorinated sulfides or do not react at all with molecular chlorine. Chlorination of 11 furnished 4 in the same yield with the same chlorination time as observed for 1.

In our second approach, the diphenylsulfonesulfide (2) and the triphenyl sulfone-sulfide (3) were prepared. The chlorosulfonium chloride salts of 2 and 3 would be expected to dissociate in an  $S_N$ l type process more readily than the corresponding salt of 1 on the grounds that the resultant carbonium ion should be more stable as the number of phenyl rings on the central atom of the carbonium ion is increased. Again the chlorination times<sup>3</sup> and yields were essentially identical with those observed for 1. These results suggest that there is no Pummerer rearrangement occurring prior to cleavage.

If, in any of these cases, cleavage is occurring prior to Pummerer rearrangement, then either or both of the intervening sulfenyl or sulfinyl chlorides must be undergoing Pummerer rearrangement in order for the dichlorosulfonesulfonyl chloride (4) to be the observed product. Such a process is abnormal for sulfenyl or sulfinyl chlorides both of which are normally oxidized, under these conditions, to the corresponding sulfonyl chlorides. To examine the possibility that benzylic sulfides undergo direct cleavage upon chlorination under these reaction

<sup>&</sup>lt;sup>3</sup>Exhaustive chlorinations were terminated when the reactions were no longer exothermic.



conditions, we decided to chlorinate a benzylic sulfide that would give rise to a sulfenyl and/or sulfinyl chloride which would be oxidized to the corresponding sulfonyl chloride without complicating Pummerer rearrangement. The experiment was carried out on benzyl methyl sulfide. The product obtained was an approximately equimolar mixture of methanesulfonyl chloride and benzyl chloride.<sup>4</sup>

Clearly the cleavage has occurred before any Pummerer rearrangement has occurred (see Scheme 4). Furthermore, it now appears likely that all three sulfone-sulfides 1, 2, and 3 have undergone direct cleavage upon chlorination in aqueous acetic acid.

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Since the dichlorosulfone-sulfonyl chloride 4 must arise from the dichlorosulfone-sulfinyl chloride 9 and it seems very likely that chlorination of 1 leads to direct cleavage, then the precursor of 9 must be the monochlorosulfonesulfinyl chloride 12 as shown in Scheme 5. As previously mentioned the dichlorosulfonesulfenyl chloride (7) has been excluded as an intermediate.

A direct examination of the behavior of  $\alpha$ sulfonyl-sulfenyl and  $\alpha$ -sulfonyl-sulfinyl chlorides cannot be undertaken until synthetic methods become available for their preparation.

Implicit in the results presented in this article is the fact that sulfonyl compounds with an  $\alpha$ -sulfur atom are unsuitable for the preparation of simple  $\alpha$ -sulfonyl-sulfonyl chlorides (*e.g.* methylsulfonylmethanesulfonyl chloride) because of the propensity of the intermediate species to undergo Pummerer rearrangements. The method of Opitz (32) by which sulfenes are dimerized and subsequently treated with HCl to provide  $\alpha$ -sulfonyl-sulfonyl chlorides remains the only available method for their preparation.

## Experimental

General

The i.r. spectra were recorded on a Perkin-Elmer 237 B grating spectrophotometer. The n.m.r. spectra were obtained on a Varian T-60 instrument using TMS as the internal standard. The mass spectra were recorded on a Dupont-CEC model 21-104 mass spectrometer. The samples were directly introduced using an all glass probe and the spectra run at 30 eV with a source temperature of 150 °C. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. The t.l.c. was carried out on  $5 \times 20$  cm analytical plates (0.75 mm thickness) spread with silica gel HF-254 (A.G. Merck). Spots were detected by spraying with ammonium hexanitratocerate(IV) spray (31) or by 250 nm u.v. light.

#### Chlorinations

Chlorine flow rates were standardized by the use of a rotameter. The rotameter was calibrated by bubbling chlorine into an aqueous solution of potassium iodide for a fixed period of time. The flow rate was calculated from the weight of chlorine trapped and the bubbling time using the ideal gas law.

## Preparation of $PhCH_2 \cdot S \cdot CH_2 \cdot SO_2 \cdot CH_3$ (1)

The preparation and properties of this compound have been described elsewhere (28).

# Preparation of $Ph_2CH \cdot S \cdot CH_2 \cdot SO_2 \cdot CH_3$ (2)

Sodium metal (1.894 g) was dissolved in absolute ethanol (100 ml). Diphenylmethanethiol (33) (15.504 g) was added to the solution, followed by chloromethyl methyl sulfone (28) (8.028 g). The resultant reaction mixture was refluxed for 1 h. The reaction mixture was poured into ice-water (100 ml) and the resultant mixture extracted with chloroform (four 100 ml aliquots). The chloroform layers were combined, dried (MgSO<sub>4</sub>), filtered, and rotary evaporated. The residue was recrystallized from benzene, furnishing 2 (14.890 g, 81.5%). The product had m.p. 118-120 °C and was homogeneous on t.l.c.  $(R_F, 0.29)$  when developed with chloroform. The i.r. bands were present (CHCl<sub>3</sub>), 1325 and 1145 cm<sup>-1</sup>. The n.m.r. spectrum (CDCl<sub>3</sub>) showed signals at  $\tau$  2.70 (10H, m), 4.20 (1H, s), 6.40 (2H, s), and 7.03 (3H, s). The mass spectrum exhibited ions at m/e 215 (23%), 167 (100%), 105 (22%), 79 (9%), and 77 (14%).

Anal. Calcd. for C<sub>15</sub>H<sub>16</sub>S<sub>2</sub>O<sub>4</sub>: C, 61.61; H, 5.52. Found: C, 61.23; H, 5.72.

### Preparation of $Ph_3C \cdot S \cdot CH_2 \cdot SO_2 \cdot CH_3$ (3)

Sodiumi metal (0.759 g) was dissolved in absolute ethanol (100 ml). Triphenylmethanethiol (9.518 g) was added to the solution, followed by chloromethyl methyl sulfone (4.030 g). The resultant reaction mixture was refluxed for 1 h. The reaction mixture was poured into ice-water (100 ml) and the resultant mixture extracted with chloroform (four 100 ml aliquots). The combined chloroform layers were dried (MgSO<sub>4</sub>), filtered, and rotary evaporated. The dark brown resinous residue (12 g) was dissolved in chloroform (250 ml), boiled with norite (1 g), filtered, and the process repeated. The chloroform was evaporated furnishing a light brown resinous

<sup>&</sup>lt;sup>4</sup>An immediate consequence of this result is the synthetic utility of benzylic sulfides as precursors for the preparation of sulfonyl chlorides. Further work on this method is already underway in our laboratories.

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# **SCHEME 5**

sample (10 g). This material was chromatographed on silica gel (720 g) with chloroform eluent (100 ml aliquots). Fractions 15–27 furnished the triphenylsulfone-sulfide (3) (5.3 g, 43.5%). After recrystallization from benzene, the product had m.p. 131.5–133.5 °C and was homogeneous on t.l.c. ( $R_{\rm F}$ , 0.41) when developed with chloroform. The i.r. bands were present (CHCl<sub>3</sub>), 1312 and 1130 cm<sup>-1</sup>. The n.m.r. spectrum displayed signals at  $\tau$  2.80 (15H, m), 6.37 (2H, s), and 7.54 (3H, s). The mass spectrum showed ions at *m/e* 243 (100%), 166 (37%), and 79 (3%).

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Anal. Calcd. for  $C_{21}H_{20}S_2O_2$ : C, 68.45; H, 5.55. Found: C, 68.09; H, 5.32.

## Preparation of $PhCH_2$ · S·CHCl·SO<sub>2</sub>·CH<sub>3</sub> (5)

The sulfone-sulfide (1) (0.263 g) was added to methylene chloride (5 ml) and the solution brought to gentle reflux. A solution of sulfuryl chloride (0.165 g) in methylene chloride (5 ml) was added dropwise over 8 min. The reaction mixture was refluxed for 1 h. The methylene chloride was rotary evaporated and the residue spotted on two preparative t.l.c. plates. The plates were developed with chloroform and the lower band ( $R_{\rm F}$ , 0.55) was scraped.

The silica gel was covered with chloroform (60 ml) and the mixture stirred for 1 h. The mixture was filtered and the chloroform rotary evaporated affording a colorless oil (0.149 g). The product had  $R_{\rm F}$  0.41 when developed with chloroform. The i.r. bands were present (CHCl<sub>3</sub>), 1330 and 1135 cm<sup>-1</sup>. The n.m.r. showed signals at  $\tau$  2.66 (5H, s), 4.56 (1H, s), 5.76 (2H, q, J = 13 Hz) and 6.93 (3H, s). The mass spectrum exhibited ions at m/e 250 (1.5%), 171 (21%), 91 (100%), and 65 (12%).

Anal. Calcd. for  $C_{9}H_{11}ClS_{2}O_{2}$ : C, 43.11; H, 4.42. Found: C, 43.31; H, 4.28.

## Preparation of $PhCH_2 \cdot S \cdot CCl_2 \cdot SO_2 \cdot CH_3$ (6)

The preparation and properties of this compound have been described elsewhere (28).

### Preparation of $Cl \cdot S \cdot CCl_2 \cdot SO_2 \cdot CH_3$ (7)

The dichlorosulfone-sulfide (6) (4.941 g) was dissolved in methylene chloride (25 ml) and chlorine (232 ml/min) was bubbled through the reaction mixture for 1 h.

The methylene chloride was rotary evaporated furnishing a residue containing a 1:1 mixture of the dichlorosulfenyl chloride (7) and benzyl chloride. The benzyl chloride was distilled off and established as identical to authentic material by n.m.r., i.r., b.p., and t.l.c. The residue was distilled furnishing the sulfenyl chloride (7) (3.420 g), b.p. 128-130 °C/1.5 mm (86.1%). The sulfenyl chloride solidified and was recrystallized from carbon tetrachloride which furnished pale yellow needles. The recrystallized sulfenyl chloride had m.p. 55-57 °C and was homogeneous on t.l.c.  $(R_F, 0.51)$  when developed with chloroform. The i.r. bands were present (CHCl<sub>3</sub>), 1350 and 1155 cm<sup>-1</sup>. The n.m.r. spectrum displayed signals at  $\tau$  6.66 (s). The mass spectrum showed ions at m/e 193 (2.7%), 149 (100%), 79 (73%), 63 (21%), and 36 (30%).

Anal. Calcd. for  $C_2H_3Cl_3S_2O_2$ : C, 10.47; H, 1.32. Found: C, 10.62; H, 1.05.

### Preparation of $PhCH_2 \cdot SO \cdot CH_2 \cdot SO_2 \cdot CH_3$ (11)

The preparation and properties of this compound have been described elsewhere (28).

#### Chlorination of 1

The sulfone-sulfide (1) (5.003 g) was dissolved in glacial acetic acid (25 ml) and distilled water (5 ml) was added. Cl<sub>2</sub> (232 ml/min) was bubbled into the reaction mixture for 45 min. During the chlorination the temperature was maintained at 25-30 °C with an ice-water bath. The acetic acid was distilled off affording a residue containing benzyl chloride (1.293 g, 44%), benzyl acetate (0.845 g, 24%), and the dichlorosulfone-sulfonyl chloride (4) (5.659 g, 93.5%). The residue was carefully fractionated providing samples of benzyl chloride and benzyl acetate which were established as identical to authentic samples by n.m.r., i.r., b.p., and t.l.c. The dichlorosulfone-sulfonyl chloride (4) was distilled (b.p. 110-115 °C/1 mm). The distilled material was recrystallized from CCl<sub>4</sub> (5×) after which it had m.p. 72-74 °C. The i.r. bands were present (CHCl<sub>3</sub>), 1390, 1355, 1180, and 1155 cm<sup>-1</sup>. The n.m.r. spectrum displayed a signal at  $\tau$  6.50 (s). The mass spectrum has been discussed previously (34).

Anal. Calcd. for  $C_2H_3Cl_3S_2O_4$ : C, 9.19; H, 1.16. Found: C, 9.25; H, 1.16.

#### Chlorination of 6

The dichlorosulfone-sulfide (6) (31.75 g) was dissolved in glacial acetic acid (150 ml) and distilled water (18 ml) was added. Cl<sub>2</sub> (448 ml/min) was bubbled through the reaction mixture for 30 min, during which the temperature was maintained at 25-30 °C. Distilled water (150 ml) was added and the resultant solution extracted with chloroform (six 100 ml aliquots). The combined chloroform layers were washed with aqueous sodium hydroxide (5%) until the aqueous layer remained basic. The chloroform was washed with distilled water (100 ml), dried (MgSO<sub>4</sub>), filtered, and the chloroform rotary evaporated furnishing a residue containing benzyl chloride (4.322 g, 30.6%), benzyl acetate (2.871 g, 17%), the dichloro-sulfone-sulfenyl chloride (7) (9.296 g, 36.4%), and the dichlorosulfone-sulfonyl chloride (4) (6.778 g, 23.8%). The benzyl chloride and benzyl acetate were distilled off and a sample of each shown to be identical to authentic material by i.r., n.m.r., b.p., and t.l.c.

The addition of a small portion of the dichlorosulfonesulfenyl chloride (7) to a sample of the distillation residue showed the signal at 6.7  $\tau$  to have the same chemical shift as the methyl group of 7. The distillation residue showed a compound present which was identical to 7 on t.l.c. by both  $R_{\rm F}$  and appearance time ((NH<sub>4</sub>)<sub>2</sub>-Ce(NO<sub>3</sub>)<sub>6</sub> spray).

A portion of the distillation residue (8.004 g) was dissolved in glacial acetic acid (50 ml) and distilled water (6.6 ml) was added. Cl<sub>2</sub> (448 ml/min) was passed through the solution for 3 h. Water (100 ml) was added and the resultant solution extracted with chloroform (three 100 ml aliquots). The combined chloroform layers were washed with 2.5% NaOH (100 ml aliquots) until the aqueous layer was basic. The chloroform was washed with distilled water, dried (MgSO<sub>4</sub>), filtered, and rotary evaporated furnishing impure 4 (6.981 g). The sample was dissolved in carbon tetrachloride, cooled, and seeded. Crystals identical to 4 (as obtained from 1) by n.m.r., i.r., m.s., and m.p. were obtained.

#### Chlorination of 7

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The sulfone-sulfenyl chloride (7) (4.990 g) was dissolved in glacial acetic acid (25 ml) and distilled water (3.3 ml) was added. Cl<sub>2</sub> (232 ml/min) was bubbled through the reaction mixture for 14.5 h. The acetic acid was distilled off at reduced pressure affording a residue of the sulfonesulfonyl chloride (4) (3.996 g, 70%) and unreacted sulfone-sulfenyl chloride (7) (1.019 g, 20%). A portion of the residue was crystallized, with seeding, from carbon tetrachloride. The first crop was shown to be identical to 4 (as obtained from 1) by n.m.r., i.r., m.p., and mixture m.p.

#### Hydrolysis of 4

The sulfone-sulfonyl chloride (4) (1.431 g) was added to distilled water (10 ml). The mixture was refluxed for 1 h. Shortly after reflux began the solution became homogeneous. Upon completion of the reflux, the solution was extracted with chloroform (five 15 ml aliquots) and *the aqueous phase* set aside. The combined chloroform layers were dried (MgSO<sub>4</sub>), filtered, and the chloroform rotary evaporated yielding the dichlorosulfone (8) (0.700 g, 79%). The sulfone was recrystallized from 95% ethanol and established as identical to authentic material (29) by m.s., i.r., m.p., mixture m.p., and n.m.r.

The aqueous phase was diluted with distilled water to a volume of 200 ml. A standard gravimetric sulfate determination (35) furnished  $BaSO_4$  (0.892 g, 70%). The  $BaSO_4$  isolated was identical to authentic material by i.r. (KBr).

## Chlorination of 11

The sulfone-sulfoxide (11) (5.001 g) was dissolved in glacial acetic acid (25 ml) and distilled water (3.3 ml) was added. Cl<sub>2</sub> (232 ml/min) was bubbled through the reaction mixture for 45 min. The acetic acid was distilled off at reduced pressure giving a residue of crude dichloro-sulfone-sulfonyl chloride (4) (5.259 g, 93.5%). A portion of the sample was crystallized from carbon tetrachloride furnishing 4 which was identical to previous samples by n.m.r., i.r., m.p., and mixture m.p.

#### Chlorination of 2

The diphenylsulfone-sulfide (2) (6.006 g) was added to a solution of glacial acetic acid (25 ml) and distilled water (3.3 ml). Chlorine (232 ml/min) was bubbled through the reaction mixture for 45 min. The acetic acid was distilled off furnishing a residue containing diphenylchloromethane (2.989 g, 72%) and the dichlorosulfone-sulfonyl chloride (4) (4.4896 g, 84%). The crude mixture was stored in a freezer. After some time crystals of diphenylchloromethane appeared and were rapidly filtered. They were identical to authentic material by n.m.r., i.r., and b.p. The filtered solution was added to carbon tetrachloride (5 ml), stored in a freezer, and seeded with 4. The crystals were filtered and shown to be identical to 4 by n.m.r., i.r., m.p., and mixture m.p.

#### Chlorination of 3

The triphenylsulfone-sulfide (3) (10.7544 g) was added to a solution of glacial acetic acid (50 ml) and distilled water (6.6 ml). Cl<sub>2</sub> (232 ml/min) was bubbled into the reaction mixture for 45 min. During the chlorination a solid formed in the reaction mixture. At the end of the reaction the solid was filtered off and shown to be triphenylchloromethane (3.967 g). The acetic acid was distilled off affording a residue containing triphenylchloromethane (1.502 g, total 67%) and the dichlorosulfone-sulfonyl chloride (4) (5.497 g, 72%). The triphenylchloromethane was identical to authentic material by n.m.r., i.r., and t.l.c. The dichlorosulfone-sulfonyl chloride (4) was recrystallized from carbon tetrachloride ( $4 \times$ ) and shown to be identical to previously isolated 4 by n.m.r., i.r., m.p., and mixture m.p.

### Chlorination of Benzyl Methyl Sulfide

Benzyl methyl sulfide (7.706 g) was added to a solution of glacial acetic acid (25 ml) and distilled water (3.3 ml). Chlorine (232 ml/min) was bubbled into the reaction mixture for 30 min. Distilled water (35 ml) was added and the solution extracted with chloroform (three 50 ml aliquots). The combined chloroform layers were washed with  $2\frac{1}{27}$  w/v NaOH (two 50 ml aliquots), distilled water (75 ml), dried (MgSO<sub>4</sub>), filtered, and the chloroform distilled off. The residue contained benzylsulfonyl chloride (0.368 g, 3.5%), benzyl chloride (5.958 g, 84%), and methanesulfonyl chloride (4.774 g, 75%).

After standing overnight, crystals formed, which were filtered off and shown to be identical to authentic benzylsulfonyl chloride by n.m.r., i.r., m.p., and t.l.c. Some of

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the filtered residue (2.194 g) was chromatographed on silica gel (120 g) using carbon tetrachloride eluant. Elution with carbon tetrachloride (1.5 l) furnished benzyl chloride which was identical to authentic material by i.r., n.m.r., and b.p. Further elution with chloroform (500 ml) furnished methanesulfonyl chloride which was identical to authentic material by n.m.r., i.r., and b.p.

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- 1. D. L. TULEEN and V. C. MARCUM. J. Org. Chem. 32, 204 (1967).
- 2. D. L. TULEEN, J. Org. Chem. 32, 4006 (1967).
- 3. G. E. WILSON, JR. and M. G. HUANG. J. Org. Chem. 35, 3002 (1970).
- 4. G. E. WILSON, JR. and R. ALBERT. J. Org. Chem. 38, 2160 (1973).
- 5. H. KWART, R. W. BODY, and D. M. HOFFMAN. Chem. Commun. 765 (1967).
- H. KWART and P. S. STRILKO. Chem. Commun. 767 (1967).
- G. TSUCHIHASHI and S. IRIUCHIJIMA. Bull. Chem. Soc. Jpn. 43, 2271 (1970).
- R. N. LOEPPKY and D. C. K. CHANG. Tetrahedron Lett. 5415 (1968).
- 9. M. CINQUINI, S. COLONNA, and F. MONTANARI. Chem. Commun. 607 (1969).
- 10. G. TSUCHIHASHI and S. IRIUCHIJIMA. Tetrahedron Lett. 5259 (1969).
- 11. M. CINQUINI and S. COLONNA. J. Chem. Soc. Perkin Trans. 1, 1883 (1972).
- 12. M. CINQUINI, S. COLONNA, R. FORNASIER, and F. MONTANARI. J. Chem. Soc. Perkin Trans. 1, 1886 (1972).
- 13. M. CINQUINI, S. COLONNA, and D. LANDINI, J. Chem. Soc. Perkin Trans. 2, 297 (1972).
- P. CALZAVARA, M. CINQUINI, S. COLONNA, R. FORNASIER, and F. MONTANARI. J. Am. Chem. Soc. 95, 7431 (1973).

- 15. J. KLEIN and H. STOLLAR. J. Am. Chem. Soc. 95, 7437 (1973).
- 16. G. TSUCHIHASHI and K. OGURA. Bull. Chem. Soc. Jpn. 44, 1726 (1971).
- 17. K. C. TIN and T. DURST. Tetrahedron Lett. 4643 (1970).
- 18. T. DURST, K. C. TIN, and M. J. MARCIL. Can. J. Chem. 51, 1704 (1973).
- 19. M. CINQUINI, R. ANNUNZIATA, and S. COLONNA. J. Chem. Soc. Perkin Trans. 1, 2057 (1972).
- 20. J. S. GROSSERT, W. R. HARDSTAFF, and R. F. LANGLER. Chem. Commun. 50 (1973).
- 21. J. S. GROSSERT and R. F. LANGLER. Chem. Commun. 49 (1973).
- W. G. PHILLIPS and K. W. RATTS. J. Org. Chem. 36, 3145 (1971).
- 23. P. ROBSON, P. SPEAKMAN, and D. STEWART. J. Chem. Soc. C, 2180 (1968).
- 24. F. G. BORDWELL and W. T. BRANNEN. J. Am. Chem. Soc. 86, 4645 (1964).
- 25. L. A. PAQUETTE. J. Am. Chem. Soc. 86, 4085 (1964).
- F. G. BORDWELL and B. JARVIS. J. Org. Chem. 33, 1182 (1968).
- 27. M. CINQUINI, D. LANDINI, and A. MAIA. Chem. Commun. 734 (1972).
- 28. W. R. HARDSTAFF, and R. F. LANGLER. Org. Mass Spectrom. 10, 215 (1975).
- 29. W. E. TRUCE, G. H. BIRUM, and E. T. MCBEE, J. Am. Chem. Soc. 74, 3594 (1952).
- 30. S. W. LEE and G. DOUGHERTY. J. Org. Chem. 5, 81 (1940).
- 31. J. S. GROSSERT and R. F. LANGLER. J. Chromatogr. 97, 83 (1974).
- 32. G. OPITZ. Angew. Chem. Int. Ed. Eng. 6, 107 (1967).
- 33. M. KLENK, C. SUTER, and S. ARCHER. J. Am. Chem. Soc. **70**, 3846 (1948).
- 34. W. R. HARDSTAFF, R. F. LANGLER and M. J. NEWMAN. Org. Mass Spectrom. 9, 1156 (1974).
- 35. D. A. Skoog and D. WEST. Fundamentals of analytical chemistry. Holt, Rinehart and Winston, New York. 1963. p. 203.

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