

713. *The Reactions of Phosphorothiolates with Halogens.*

By C. J. M. STIRLING.

Chlorine and bromine react with triethyl and *S*-benzyl diethyl phosphorothiolate in anhydrous conditions to give the sulphenyl halides and phosphorohalidates. In water, alkanesulphonyl halides and alkyl halides are formed together with diethyl hydrogen phosphate. The mechanisms of the reactions are discussed; the aqueous reactions involve initial formation of sulphenyl halides.

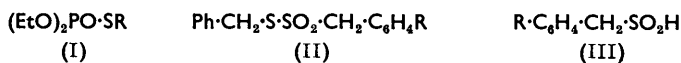
SAVILLE¹ observed formation of ethanesulphonyl bromide in the reaction of bromine water with triethyl phosphorothiolate. In this paper, reactions of chlorine and of bromine with alkyl phosphorothiolates in aqueous and anhydrous conditions are reported.

Triethyl (I; R = Et) and *S*-benzyl diethyl phosphorothiolate (I; R = PhCH₂), in aqueous suspension, react rapidly with chlorine and with bromine, to give diethyl hydrogen phosphate and the appropriate alkanesulphonyl halide with minor amounts of the alkyl halide derived from the *S*-alkyl group (see Tables, p. 3601). When less chlorine than is required for complete reaction was used, the alkanesulphinic acid was isolated; and benzyl toluene- ω -thiolsulphonate (II; R = H) was obtained from the benzyl ester. Similar results have been obtained by Douglass and Johnson² on aqueous chlorination of thiolcarboxylic esters. Dibenzyl disulphide was an intermediate in the chlorination of benzyl thiolbenzoate, in addition to toluene- ω -sulphinic acid (III; R = H) and benzyl toluene- ω -thiolsulphonate. No dibenzyl disulphide, however, has been isolated from reactions with the phosphorus ester.

¹ Saville, *Chem. and Ind.*, 1956, 660.

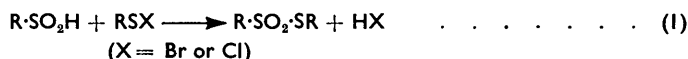
² Douglass and Johnson, *J. Amer. Chem. Soc.*, 1938, **60**, 1486.

The formation of alkyl halides must occur by the displacement of sulphur at some stage. Halogenation of the intermediate, toluene- ω -sulphinic acid, gives mixtures of toluene- ω -sulphonyl halide and benzyl halide, similar to those obtained from the phosphorothiolate. It is probable, therefore, that S-C bond fission occurs in the final stage of



the oxidation. Certain alkanesulphonyl halides, however, have been shown³ to decompose at room temperature with the formation of the corresponding alkyl halide. Toluene- ω -sulphonyl halides have been found to be unstable and 30% of the benzyl halide obtained can be accounted for by their decomposition.

The origin of thiolsulphonate is less clear. Douglass and Johnson⁴ suggested that the formation of benzyl toluene- ω -thiolsulphonate in the aqueous chlorination of benzyl thiocyanate was due to the disproportionation of toluene- ω -sulphinic acid which was also isolated from the reaction. However, toluene- ω -sulphinic acid does not disproportionate under the present experimental conditions: the only decomposition product which could be isolated was benzaldehyde.⁵ Lee and Dougherty⁶ have shown that benzyl toluene- ω -thiolsulphonate is obtained on the aqueous chlorination of dibenzyl disulphide. Evidence presented below, however, suggests that the formation of thiolsulphonate from disulphide (even if it is formed in the reaction with the phosphorus ester) is not a direct reaction but that S-S fission is the primary step. It was considered possible that thiolsulphonate is formed by the reaction of a sulphenyl halide, initially formed in the reaction, with sulphinic acid:



Although silver sulphinates react with sulphenyl halides to give thiolsulphonates⁷ no instance of the reaction with the free acid has been recorded. Toluene- ω -sulphenyl bromide has been found to react rapidly with toluene- ω -sulphinic acid with evolution of hydrogen bromide and formation of benzyl toluene- ω -thiolsulphonate. Proof that the reaction is not a disproportionation of the sulphinic acid has been obtained by the use of *p*-chlorotoluene- ω -sulphinic acid (III; R = Cl), benzyl *p*-chlorotoluene- ω -thiolsulphonate (II; R = Cl) being then isolated from reactions with both toluene- ω -sulphenyl chloride and toluene- ω -sulphenyl bromide. Thiolsulphonates are known⁸ to be formed in the hydrolysis of sulphenyl halides, but no hydrolysis products could be detected in the experiments with the substituted sulphinic acid, despite the presence of water in the reaction mixtures.

The possibility that sulphenyl halides were formed in the aqueous halogenation of phosphorothiolates prompted an examination of the reactions in anhydrous conditions. Douglass and Osborne⁹ have shown that with chlorine, anhydrous thiolcarboxylic and thiolsulphonic esters give acyl and sulphonyl chlorides respectively, together with sulphenyl trichlorides which were considered to arise by further chlorination of sulphenyl chlorides.¹⁰ In the present work, treatment of the phosphorus esters in anhydrous carbon tetrachloride with two atoms of chlorine or bromine per mole of ester gave, except in the triethyl phosphorothiolate-chlorine reaction, the corresponding sulphenyl halides. These have been characterised by the formation of β -halogeno-sulphides¹¹ with ethylene or cyclohexene. Ethanesulphenyl chloride could not be identified in the reaction of chlorine with the

³ Truce and Vriesen, *J. Amer. Chem. Soc.*, 1953, **75**, 5032.

⁴ Douglass and Johnson, *ibid.*, 1939, **61**, 2548.

⁵ Cf. Kurzer and Powell, *J.*, 1952, 3728.

⁶ Lee and Dougherty, *J. Org. Chem.*, 1940, **5**, 81.

⁷ Child and Smiles, *J.*, 1926, 2696.

⁸ Zinke and Eismayer, *Ber.*, 1918, **51**, 751.

⁹ Douglass and Osborne, *J. Amer. Chem. Soc.*, 1953, **75**, 4582.

¹⁰ Douglass, Brower, and Martin, *ibid.*, 1952, **74**, 5770.

¹¹ Cf. Fuson, Price, Bauman, Bullit, Hatchard, and Maynert, *J. Org. Chem.*, 1946, **11**, 469.

triethyl ester, but four atoms of chlorine per mole of ester gave ethanesulphenyl trichloride. The failure to obtain ethanesulphenyl chloride is considered to be due to preferential formation of the trichloride.¹⁰ Toluene- ω -sulphenyl trichloride was similarly obtained from the benzyl ester :

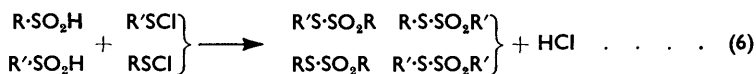
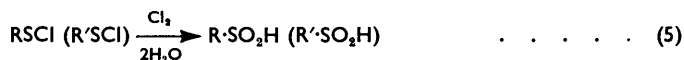


Diethyl phosphorochloridate was isolated from the triethyl phosphorothiolate-chlorine reactions. In the remainder, the phosphorohalidate has been hydrolysed in alkali to give diethyl sodium phosphate. Anhydrous chlorination of benzyl toluene- ω -thiolsulphonate likewise gave a mixture of the sulphenyl and sulphonyl chloride directly, although reaction occurs less readily than with the phosphorus esters.

The high reactivity of aliphatic sulphenyl halides has, however, precluded their isolation from aqueous reactions of halogens with phosphorothiolates. Indirect evidence for their formation in aqueous reactions has been obtained in two ways. First, the partial aqueous chlorination of *S*-benzyl diethyl phosphorothiolate has been carried out in the presence of *p*-chlorotoluene- ω -sulphinic acid: isolation of benzyl *p*-chlorotoluene- ω -thiolsulphonate confirmed the view, not only that thiolsulphonate does not arise by disproportionation but also that it results from the attack on free sulphinic acid of a species in which the sulphur atom is in the +2 oxidation state. Secondly, aqueous chlorination of benzyl ethyl disulphide has been examined. If the oxidation of an unsymmetrical disulphide to a thiolsulphonate does not involve S-S fission, then only two products, both of which contain dissimilar alkyl groups, can result:

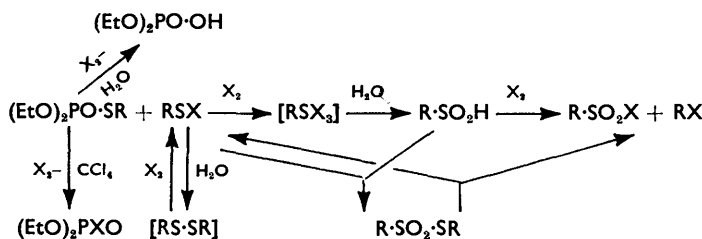


If, however, the initial reaction with chlorine causes S-S fission with the formation of sulphenyl chlorides, formation of thiolsulphonate according to (1) should give four products:



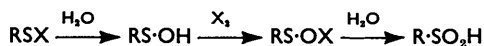
In two of the possible products, the alkyl groups are the same. Isolation of benzyl toluene- ω -thiolsulphonate, therefore, from the aqueous chlorination of benzyl ethyl disulphide, is considered to support this mechanism.

On the basis of the above considerations, the annexed scheme * is proposed for halogen-

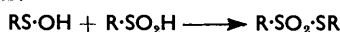


ation of thiol esters not only in respect of this investigation but also of those referred to above. The isolation of dibenzyl disulphide from the aqueous chlorination of benzyl

* The intermediate formation of sulphenyl trihalide in aqueous reactions is speculative. An alternative route is:



Thiolsulphonate may then arise thus:



thiolbenzoate² may be explained by the hydrolysis of the intermediate sulphenyl chloride. It has been confirmed that the anhydrous reaction gives benzoyl chloride and toluene- ω -sulphenyl chloride directly.

EXPERIMENTAL

The light petroleum used had b. p. 40—60°. Extracts were dried over MgSO₄.

*Triethyl Phosphorothiolate.*¹²—Diethyl hydrogen phosphite (55.2 g.) was added to a solution of sodium (9.2 g.) in absolute ethanol (300 ml.). Sulphur (12.8 g.) was added slowly with cooling, followed by ethyl bromide (44 g.). The solution was boiled under reflux for 2 hr., then the precipitated sodium bromide was filtered off. Distillation gave the ester (44 g.), b. p. 78.5—79°/1.3 mm., n_D^{25} 1.4570.

S-Benzyl Diethyl Phosphorothiolate.—The above procedure was used, with benzyl chloride instead of ethyl bromide. The product (79 g.) had b. p. 130°/0.2 mm., n_D^{25} 1.5229 (Found: C, 50.7; H, 6.7. Calc. for C₁₁H₁₇O₃SP: C, 50.8; H, 6.6%). Schrader¹³ gives b. p. 165—170°/2 mm.

Reactions with Excess of Aqueous Chlorine.—(a) *With triethyl phosphorothiolate.* The ester (20 g.) was suspended in water (150 ml.) and chlorine was passed in with cooling and stirring at 0—5° until an excess was present. Excess of chlorine was removed in air and the suspension then extracted with benzene (3 × 50 ml.). The dried extracts were evaporated and distillation of the residue gave ethanesulphonyl chloride (12.2 g.), b. p. 76—79°/22 mm., n_D^{25} 1.4472, which, on treatment with *p*-toluidine, gave ethanesulphonyl-*p*-toluidine, m. p. and mixed m. p. 79—80° (80%). The aqueous extracts were basified with sodium carbonate and were evaporated to dryness. The residue was extracted with boiling absolute ethanol (400 ml.) and evaporation of the extracts gave diethyl sodium phosphate (13.6 g.) which was identified by its infrared spectrum and formation of the *S*-benzylthiuronium salt, m. p. 153—154°, as needles from acetone (Found: C, 44.8; H, 6.9. C₁₂H₂₁O₄N₂SP requires C, 45.0; H, 6.6%).

(b) *With S-Benzyl diethyl phosphorothiolate.* The ester (20 g.) was chlorinated as above, at <30°. Extraction was with chloroform (2 × 100 ml.). The dried extracts were evaporated and addition of light petroleum (100 ml.) to the residue precipitated toluene- ω -sulphonyl chloride (11.1 g.), which, after crystallisation from benzene-light petroleum, had m. p. 93° (Found: C, 43.9; H, 3.9. Calc. for C₇H₇O₂ClS: C, 44.1; H, 3.7%). Evaporation of the mother-liquors gave a further 0.8 g. of sulphonyl chloride, m. p. 86—91°. The residual solution was evaporated and the residue, which had an odour of benzyl chloride, was dissolved in methanol (25 ml.). Diethylamine (6 ml.) was added and the solution was refluxed for 2 hr. Methanol and diethylamine were distilled off and ether (100 ml.) was added. The suspension was extracted with 2*N*-hydrochloric acid (100 ml.), and the extracts were basified with sodium hydroxide and extracted with benzene. The benzene extracts were dried and evaporated. Methanol (25 ml.) and methyl iodide (10 ml.) were added and the solution was refluxed for 2 hr. Solvent was removed and the addition of ether (150 ml.) to the residue gave benzyldiethylmethylammonium iodide, m. p. and mixed m. p. 150.5—152° (from acetone) (0.2 g.). Hazard, Corteggiani, and Renard¹⁴ give m. p. 150°. The aqueous extracts yielded sodium diethyl phosphate (10.8 g.), identified as before.

Reactions with Excess of Aqueous Bromine.—(a) *With triethyl phosphorothiolate.* The ester (12 g.), suspended in water (100 ml.), was treated with an excess of saturated bromine water at 0—5°. Excess of bromine was removed by ethylene, and the solution then extracted with ether (2 × 150 ml.). Drying and distillation of the extracts gave ethanesulphonyl bromide (6.8 g.), b. p. 81—83°/13 mm., n_D^{25} 1.5005. Johnson and Sprague¹⁵ give b. p. 85—86°/18 mm., n_D^{25} 1.5010. The ethereal distillates were washed with aqueous sodium carbonate and dried. A solution of sodium methoxide in methanol (from 3 g. of sodium) was added and the mixture set aside for 2 days. Water (50 ml.) was added. The aqueous layer was acidified with halogen-free nitric acid: addition of aqueous silver nitrate gave a slight precipitate of silver bromide. The original aqueous extracts were evaporated to a small volume and treated with chlorine to remove bromide. Evaporation to dryness and extraction of the residue with ethanol gave sodium diethyl phosphate (5.7 g.).

¹² Cf. Foss, *Acta Chem. Scand.*, 1947, **1**, 8.

¹³ Schrader, U.S.P. 2,597,534.

¹⁴ Hazard, Corteggiani, and Renard, *Compt. rend.*, 1948, **227**, 1180.

¹⁵ Johnson and Sprague, *J. Amer. Chem. Soc.*, 1936, **58**, 1348.

(b) *With S-benzyl diethyl phosphorothiolate.* The ester (10 g.) was treated as in the preceding experiment and after the removal of excess of bromine the solution was extracted with chloroform (100 ml.). The dried extracts were evaporated and treatment of the residue with light petroleum (50 ml.) gave toluene- ω -sulphonyl bromide (3.6 g.), m. p. 78.5° (from light petroleum) (Found: C, 35.6; H, 3.2. Calc. for $C_7H_7O_2BrS$: C, 35.8; H, 3.0%). Holmberg¹⁶ gives m. p. 79—80°. Treatment of the mother-liquors as before with diethylamine and methyl iodide gave crude benzyldiethylmethylammonium iodide (4 g.), m. p. 152° (from acetone) (1.3 g.; and 1.0 g., m. p. 145°). The original aqueous extracts were treated as before, to give sodium diethyl phosphate (2.4 g.).

The results of these experiments are shown in the Tables.

Products (mole/mole) obtained in aqueous chlorinations.

	(EtO) ₂ PO-OH	R-SO ₂ Cl	RCl
(EtO) ₂ PO-SEt	0.77	0.94	—
(EtO) ₂ PO-S-CH ₂ Ph	0.80	0.82	0.02
Ph-CH ₂ -SO ₂ H	—	0.81	0.01

Products (mole/mole) obtained in aqueous brominations.

	(EtO) ₂ PO-OH	R-SO ₂ Br	RBr
(EtO) ₂ PO-SEt	0.54	0.65	trace
(EtO) ₂ PO-S-CH ₂ Ph	0.35	0.40	0.29
Ph-CH ₂ -SO ₂ H	—	0.47	0.31

Partial Aqueous Chlorinations.—(a) *Triethyl phosphorothiolate.* The ester (15 g.) was suspended in water (100 ml.) and chlorine was passed in slowly for 5 min. at 0—5°. The solution was extracted with chloroform (2 × 15 ml.), and the extracts were extracted with ice-cold 10% aqueous sodium carbonate (2 × 10 ml.). The chloroform extracts were suspended in water and chlorine was again passed in for 5 min. The procedure was repeated several times and then the combined alkaline extracts were heated under reflux with benzyl chloride (2 g.) for 2 hr. The mixture was extracted with chloroform, and the dried extracts were evaporated. Ethanol (10 ml.) was added to the residue and, after several days, needles of benzyl ethyl sulphone separated, having m. p. and mixed m. p. 84° (from benzene-light petroleum).

(b) *S-Benzyl diethyl phosphorothiolate.* (i) Chlorine was passed into a suspension of the ester (10 g.) in water (200 ml.) until solid separated. The solid was filtered off and dissolved in benzene. The solution was extracted with 10% aqueous sodium carbonate (2 × 15 ml.), and treatment of the extracts with benzyl chloride as before gave dibenzyl sulphone, m. p. and mixed m. p. 150°.

(ii) The ester (10 g.), partly dissolved and partly suspended in light petroleum (100 ml.), was stirred with water (100 ml.) while chlorine was passed in at 5—10°. After the separation of an appreciable amount of solid, the mixture was filtered and the filtrate was treated with excess of chlorine. The mixture was filtered again and the combined residues were dried and treated with ether (75 ml.). The undissolved portion (0.2 g.) was benzyl toluene- ω -thiol-sulphonate, m. p. and mixed m. p. 107°. Aniline (10 g.) was added to the solution which was kept overnight over saturated aqueous sodium hydrogen carbonate. The ethereal solution was extracted with dilute hydrochloric acid and then with 2N-sodium hydroxide (3 × 50 ml.). Acidification of the alkaline extracts gave toluene- ω -sulphonanilide (3.8 g.), m. p. and mixed m. p. 103°. The ethereal solution was evaporated and the residue, on treatment with ethanol, gave a further amount of benzyl toluene- ω -thiol-sulphonate (0.7 g.), m. p. and mixed m. p. 107°.

Reactions with Sulphinic Acids.—*Toluene- ω -sulphinic acid.* Reduction of toluene- ω -sulphonyl chloride with aqueous sodium sulphite¹⁷ gave the acid, m. p. 59—60.5°, in 45% yield. Holmberg¹⁶ gives m. p. 61—63°.

(a) *Halogenation.* Aqueous chlorination and bromination of toluene- ω -sulphinic acid were carried out in the same way as the halogenations of the phosphorus esters. The results are in the Tables.

(b) *Stability in acid solutions.* Toluene- ω -sulphinic acid (1 g.) was added to a 50 ml. portion of the aqueous extracts of a reaction mixture from the complete chlorination of the benzyl ester. After being stirred for 30 min. at 100°, the suspension was extracted with chloroform

¹⁶ Holmberg, *Arkiv Kemi, Min., Geol.*, 1940, **14**, A, No. 8.

¹⁷ Cf. Smiles and Bere, *Org. Synth.*, Coll. Vol. I, 2nd edn., p. 7.

(2 × 15 ml.). The extracts were washed with saturated aqueous sodium hydrogen carbonate and evaporated. A small amount of dark material remained but no benzyl toluene- ω -thiol-sulphonate could be obtained from it. Acidification of the alkaline washings gave the sulphinic acid (0.6 g.), m. p. and mixed m. p. 59—60°. Similar experiments were carried out with 2*N*-hydrochloric and -hydrobromic acid at 20° for 24 hr. In each case more than 50% of the acid was recovered and no thiolsulphonate was isolated. A trace of benzaldehyde was identified in the neutral residue from the experiment with hydrobromic acid as the semicarbazone, m. p. and mixed m. p. 210—213°. There was no evidence for the formation of alkyl halides in these experiments.

(c) *Reaction with toluene- ω -sulphenyl bromide.* A solution of the sulphenyl bromide in benzene (100 ml.) was prepared from toluene- ω -thiol (1 g.) and *N*-bromosuccinimide (1.7 g.).¹⁸ Toluene- ω -sulphinic acid (1.8 g.) and water (50 ml.) were added to the solution which was vigorously shaken. The colour of the suspension was rapidly discharged and after 1 hr. the layers were separated. The benzene layer was washed with sodium carbonate and evaporated. Addition of ethanol to the residue gave benzyl toluene- ω -thiolsulphonate (1.3 g.), m. p. and mixed m. p. 106°.

p-Chlorotoluene- ω -sulphinic Acid.—*p*-Chlorotoluene- ω -sulphonyl chloride was prepared by chlorination¹⁵ of an aqueous solution of *S*-*p*-chlorobenzylthiuronium hydrochloride and had m. p. 93—94° (from benzene-light petroleum) (Found: Cl, 31.2. Calc. for C₇H₆O₂Cl₂S: Cl, 31.5%). Jackson and White¹⁹ give m. p. 85.5°. Reduction of the sulphonyl chloride with aqueous sodium sulphite gave *p*-chlorotoluene- ω -sulphinic acid as plates, m. p. 104° (from ether) (Found: C, 44.0; H, 3.9; S, 17.0. C₇H₇O₂ClS requires S, 16.8%). A solution of the acid in aqueous sodium carbonate on treatment with *p*-chlorobenzyl chloride at 100° gave di-(4-chlorobenzyl) sulphone, m. p. 246—247° (from acetone). Overberger, Lighthelm, and Swire²⁰ give m. p. 246—247°.

(a) *Reaction with toluene- ω -sulphenyl chloride.* Dibenzyl disulphide (2 g.), in carbon tetrachloride (20 ml.), was added dropwise with stirring to a solution of sulphuryl chloride (1.1 g.) in carbon tetrachloride (30 ml.) at -30°. The mixture was warmed to 20° and *p*-chlorotoluene- ω -sulphinic acid (2 g.) was added. The mixture was thoroughly shaken and water (25 ml.) was added. When the colour of the mixture had almost disappeared, the layers were separated and the organic layer was washed with aqueous sodium carbonate and dried. Solvent was removed and crystallisation of the residue gave benzyl *p*-chlorotoluene- ω -thiolsulphonate as needles, m. p. 118° (from ethanol) (Found: C, 53.3; H, 4.4. C₁₄H₁₃O₂ClS₂ requires C, 53.8; H, 4.2%).

(b) *Reaction with toluene- ω -sulphenyl bromide.* The experiment was carried out as described for toluene- ω -sulphinic acid. Crude benzyl *p*-chlorotoluene- ω -thiolsulphonate (1.2 g.), m. p. 112°, was obtained. Crystallisation from ethanol raised the m. p. to 118°, alone or mixed with the compound obtained in the previous experiment.

(c) *Partial chlorination of S-benzyl diethyl phosphorothiolate in the presence of p-chlorotoluene- ω -sulphinic acid.* Partial chlorination of the benzyl ester was repeated except that *p*-chlorotoluene- ω -sulphinic acid (15 g.) was added. The residue from the evaporation of the chloroform extracts, after the removal of the excess of aniline and the mixture of sulphonanilides, gave, on treatment with ethanol, benzyl *p*-chlorotoluene- ω -thiolsulphonate (0.3 g.), m. p. and mixed m. p. 116°.

Reactions with Anhydrous Chlorine.—(a) *With S-benzyl diethyl phosphorothiolate.* (i) The ester (20 g.), in anhydrous carbon tetrachloride (100 ml.), was shaken at 20° with a solution of chlorine (5.5 g.) in carbon tetrachloride (100 ml.), and set aside for 15 min. Ethylene was passed into the yellow solution for 45 min. during which time the colour faded. After being washed with 10% aqueous sodium hydroxide, the solution was dried and evaporated. A portion (2 g.) of the dark residue (14.2 g.) was heated with 30% hydrogen peroxide in acetic acid, to give benzyl 2-chloroethyl sulphone which crystallised from benzene-light petroleum as plates, m. p. 97° (Found: C, 49.6; H, 5.5. Calc. for C₉H₁₁O₂ClS: C, 49.4; H, 5.1%). Heyna and Riemenschneider²¹ give m. p. 96°. The remainder of the residue was distilled to a purple oil (9.6 g.), b. p. 144—148°/13 mm., n_D^{25} 1.5564, which, on treatment with 20% aqueous

¹⁸ Emde, G.P. 804,572.

¹⁹ Jackson and White, *Amer. Chem. J.*, 1880, **2**, 158.

²⁰ Overberger, Lighthelm, and Swire, *J. Amer. Chem. Soc.*, 1950, **72**, 2856.

²¹ Heyna and Riemenschneider, G.P. 887,505.

chloramine- τ gave *S*-benzyl-*S*-2-chloroethyl-*N*-*p*-toluenesulphonylsulphidimine, m. p. 134° (from ethanol) (Found: N, 4.1. Calc. for $C_{16}H_{18}O_2NClS_2$: N, 3.9%). Dawson²² gives m. p. 133—134°.

(ii) The ester (15 g.) in carbon tetrachloride (60 ml.) at -20° was treated with chlorine (8.2 g., 4 atom-equivs.) in carbon tetrachloride (90 ml.). The solid which separated was rapidly filtered off on a chilled filter and when added to ice-cold 10% aqueous sodium carbonate (25 ml.) reacted with vigorous evolution of carbon dioxide. The solution was heated with benzyl chloride, giving dibenzyl sulphone (0.35 g.), m. p. and mixed m. p. 149.5°.

(b) *With triethyl phosphorothiolate.* Treatment of the ester with 2 atom-equivs. of chlorine and subsequent addition of ethylene or cyclohexene failed to give identifiable products. The ester (10 g.) was treated as in the preceding experiment with 4 atoms of chlorine per mole. The solid which separated, on treatment with sodium carbonate and benzyl chloride as before, gave benzyl ethyl sulphone (1.2 g.), m. p. 75°. Crystallisation from benzene–light petroleum raised the m. p. to 84° (and mixed m. p.). The filtrate was evaporated and distillation of the residue gave a fraction (4.2 g.), b. p. 91—93°/17 mm., n_D^{25} 1.4247, which, on treatment with aniline in benzene solution, gave aniline hydrochloride, m. p. 197°, and diethyl phenylphosphoramidate, m. p. and mixed m. p. 94—95°.

(c) *With benzyl toluene- ω -thiolsulphonate.* The following method for the preparation of the ester was superior to Hinsberg's:²³ toluene- ω -sulphinic acid (18 g.), in carbon tetrachloride (150 ml.), was added to a solution of toluene- ω -sulphenyl chloride [from dibenzyl disulphide (20 g.) and chlorine (6 g.)] in carbon tetrachloride (150 ml.). The solution was agitated under reduced pressure and the ester was precipitated as needles (30 g.) which, after being washed with light petroleum, had m. p. and mixed m. p. 107.5°.

(i) The ester (8 g.), in alcohol-free anhydrous chloroform (50 ml.), was treated with chlorine (2 g.) in carbon tetrachloride (30 ml.). After the passage of ethylene (1 hr.) solvent was removed and light petroleum was added to the residue. The solid which separated was treated with aniline in benzene as above, to give toluene- ω -sulphonanilide (1.2 g.), m. p. and mixed m. p. 98—100°. Starting material (0.5 g.), m. p. and mixed m. p. 106°, was recovered. The light petroleum mother-liquors were evaporated and treatment of the residue with hydrogen peroxide in acetic acid gave benzyl 2-chloroethyl sulphone (0.2 g.), m. p. 89° raised on crystallisation to 94—95° alone or mixed with an authentic specimen.

(ii) The preceding experiment was repeated except that cyclohexene (10 ml.) was used in place of ethylene. Toluene- ω -sulphonanilide (3.3 g.), m. p. and mixed m. p. 99—101°, was obtained and starting-material (3.1 g.) was recovered. The residue from the evaporation of the light petroleum mother-liquors, on treatment with hydrogen peroxide, gave *benzyl 2-chloro-cyclohexyl sulphone* (0.3 g.), m. p. 106°, raised to 108—109° on crystallisation from ethanol (Found: Cl, 12.7; S, 12.0. $C_{13}H_{17}O_2ClS$ requires Cl, 13.0; S, 11.8%).

(d) *With benzyl thiolbenzoate.* The ester (12 g.) was treated with two atomic proportions of chlorine in carbon tetrachloride. After the passage of ethylene (30 min.), the solution was evaporated and distillation of the residue gave benzoyl chloride (5.1 g.), b. p. 81°/13 mm. (benzamide, m. p. and mixed m. p. 127°), and benzyl 2-chloroethyl sulphide (5.7 g.), b. p. 148—153°/13 mm., n_D^{25} 1.5712 (sulphone, m. p. and mixed m. p. 97°; *N*-*p*-toluenesulphonylsulphidimine, m. p. and mixed m. p. 134°).

Reactions with Anhydrous Bromine.—(a) *With triethyl phosphorothiolate.* The ester (15 g.) in carbon tetrachloride (100 ml.) was treated with bromine (12.1 g.) in carbon tetrachloride (80 ml.), and ethylene was passed into the solution for 1 hr. The solution was extracted with 10% aqueous sodium carbonate and, after being washed and dried, solvent was removed. Distillation of the residue gave impure 2-bromoethyl ethyl sulphide (9.8 g.), b. p. 68—71°/15 mm., n_D^{25} 1.5219 (Found: C, 27.7; H, 5.3. Calc. for C_4H_9BrS : C, 28.4; H, 5.3%). Steinkopf, Herold, and Stöhr²⁴ give b. p. 83—86°/29 mm. Treatment of the product with chloramine- τ gave the sulphidimine, m. p. 147—148°, needles from ethanol (Found: N, 4.1. Calc. for $C_{11}H_{16}O_2NBrS_2$: N, 4.1%). Dawson²² gives m. p. 146°.

(b) *With S-benzyl diethyl phosphorothiolate.* The ester (20 g.), in carbon tetrachloride (100 ml.), was treated with a solution of bromine (12.3 g.) in carbon tetrachloride (100 ml.). The

²² Dawson, *J. Amer. Chem. Soc.*, 1947, **69**, 968.

²³ Hinsberg, *Ber.*, 1908, **41**, 2836.

²⁴ Steinkopf, Herold, and Stöhr, *Ber.*, 1920, **53**, 1007.

mixture was treated as in the preceding experiment and a portion (2 g.) of the residue (22 g.), after the removal of solvent, was oxidised with 5% aqueous potassium permanganate to give *benzyl 2-bromoethyl sulphone*, m. p. 134—135° (plates from benzene-light petroleum) undepressed on admixture with the sulphone obtained by the oxidation of *benzyl 2-bromoethyl sulphide*²⁵ with hydrogen peroxide in acetic acid (Found: C, 41.2; H, 4.6. $C_9H_{11}O_2BrS$ requires C, 41.1; H, 4.2%). Distillation of the remainder of the residue gave no *benzyl 2-bromoethyl sulphide*, but a fraction, b. p. 90°/0.2 mm., on treatment with permanganate in acetic acid, gave *dibenzyl sulphone*, m. p. and mixed m. p. 151°. The experiment was repeated and oxidation of the entire residue gave *benzyl 2-bromoethyl sulphone* (8.8 g.), m. p. and mixed m. p. 131—132°.

In each of the above experiments with phosphorus esters and anhydrous halogens, sodium diethyl phosphate was isolated from the alkaline extracts.

Benzyl Ethyl Disulphide.—A mixture of ethanethiol (40 g.) and toluene- ω -thiol (40 g.), in carbon tetrachloride (300 ml.), was cooled to 0° and a slight excess of a 10% solution of bromine in carbon tetrachloride was added with stirring. The solution was washed with aqueous sodium carbonate and dried. Removal of the solvent and fractional distillation of the residue gave *benzyl ethyl disulphide* (17 g.), b. p. 75°/0.1 mm., n_D^{25} 1.5820 (Found: C, 58.6; H, 7.0. $C_9H_{12}S_2$ requires C, 58.7; H 6.6%). During 2 weeks, the product deposited a small amount of *dibenzyl disulphide* and samples used in the experiment below were redistilled just before use.

Partial Aqueous Chlorination of Benzyl Ethyl Disulphide.—Chlorine was passed slowly into a suspension of *benzyl ethyl disulphide* (15 g.), in water (150 ml.), at 0—5° until solid separated. The suspension was extracted with chloroform and the dried extracts were evaporated. The residue was treated as before with aniline to remove sulphonyl halides, and the neutral material crystallised from ethanol, giving needles of *benzyl toluene- ω -thiolsulphonate* (0.7 g.), m. p. and mixed m. p. 107—108°.

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²⁵ Schneider, *Chem. Ber.*, 1951, **84**, 911.