938. *The Reaction of Sulphinyl Chlorides with Zinc.*

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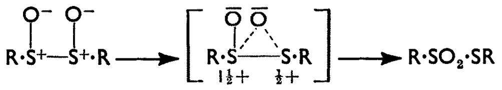
Aryl and alkyl sulphinyl chlorides react readily with zinc, to give good yields of the corresponding thiolsulphonates instead of the expected disulphoxides.

THE controversy over the constitution of the so-called disulphoxides (I) has been resolved in favour of the thiolsulphonate structure (II) (for spectroscopic evidence and literature survey see Cymerman and Willis [1]) and no authenticated example of (I) appears to be known.

(I) $R\cdot SO\cdot SO\cdot R$ $\qquad$ $R\cdot SO_2\cdot S\cdot R$ (II)

Benzenesulphenyl chloride reacts with zinc,[2] and toluenesulphonyl chloride with potassium,[3] to yield diphenyl disulphide and ditolyl disulphone respectively, and it therefore seemed possible that the highly reactive sulphinyl chlorides would undergo a similar coupling reaction to give (I). However benzenesulphinyl chloride reacted smoothly with zinc to give, not diphenyl disulphoxide, but phenyl benzenethiolsulphonate (II; R = Ph) in quantitative yield; and ethanesulphinyl chloride similarly gave ethyl ethanethiolsulphonate (II; R = Et) as the major product.

These results might be explained either by (*a*) the re-arrangement of the initially formed disulphoxide into the more stable thiolsulphonate:



or (*b*) oxygen transfer between sulphinyl radicals with subsequent coupling of the resulting sulphonyl and sulphenyl radicals, although in this case the concomitant formation of disulphide and disulphone would be expected. However di-*p*-chlorophenyl disulphide present during the reaction of zinc with benzenesulphinyl chloride was recovered as a mixed *p*-chlorophenyl phenyl disulphide although no exchange of sulphenyl groups occurred between the disulphide and phenyl benzenethiolsulphonate under the same conditions. The opposing evidence for the formation of free sulphenyl radicals in the reaction can be reconciled by the hypothesis that the transfer of negatively charged oxygen from one sulphinyl radical to a like radical occurs to give ions, or an ion pair, with a unique mode of coupling, the interaction of either of the ionic species with a disulphide resulting in the observed interchange of sulphenyl groups:

$$2R\cdot\dot{S}\rightarrow O \longrightarrow R\cdot\bar{S}O_2 + \overset{+}{\dot{S}}\cdot R \longrightarrow R\cdot SO_2\cdot S\cdot R$$

EXPERIMENTAL

Benzenesulphinic Acid.—Benzenesulphonyl chloride (44 g.), anhydrous sodium sulphite (63 g.), and water (300 ml.) were shaken together for 2 hr., the pH being maintained at 8—9 by periodical addition of 50% sodium hydroxide solution. The resulting solution was acidified

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[1] Cymerman and Willis, *J.*, 1951, 1332.

[2] Lecher and Holschneider, *Ber.*, 1924, **57**, 755.

[3] Pearl, Evans, and Dehn, *J. Amer. Chem. Soc.*, 1938, **60**, 2478.

at 0° with 60% sulphuric acid until precipitation of the sulphinic acid was imminent. Sodium sulphate was filtered off, the filtrate diluted with water (40 ml.), and the acidification completed, to give the sulphinic acid (23 g.) which, after being washed with a little ice-water and dried at 0° *in vacuo* for 1 day over phosphoric oxide was virtually free from sodium sulphate and had m. p. 83—84°.

Benzenesulphinyl Chloride.—Purified thionyl chloride (14 ml.) was added slowly with stirring to freshly prepared benzenesulphinic acid (12 g.) suspended in dry ether (50 ml.) at 0°. Dry benzene (25 ml.) was added and the solvent and excess of thionyl chloride distilled at 10 mm. into a liquid-air trap. This operation was repeated with an equal volume of benzene, leaving the sulphinyl chloride in almost quantitative yield. Distillation of the product in a high vacuum occasionally led to an almost explosive decomposition and was not therefore generally attempted.

Reaction of Benzenesulphinyl Chloride with Zinc.—The chloride was added in dry ether (50 ml.) slowly to a stirred suspension of zinc powder (6 g.) in ether (50 ml.) at room temperature. The mixture became slightly warm and was kept overnight. Isolation of the product in the usual manner gave phenyl benzenethiolsulphonate (10·15 g., 96%), m. p. 33—35° which, after one crystallisation from 10 : 1 light petroleum (b. p. 40—60°)–ethanol, had m. p. and mixed m. p. 37·5—38·5° (Found: C, 57·5; H, 4·0; S, 25·6. Calc. for $C_{12}H_{10}O_2S_2$: C, 57·6; H, 4·0; S, 25·6%). Other specimens of this thiolsulphonate prepared by the following methods: (*a*) oxidation of diphenyl disulphide by peracetic acid and by ozone, (*b*) thermal decomposition of benzenesulphinic acid and (*c*) disproportionation of phenyl benzenethiolsulphinate, also had this m. p. (N.P.L. standard thermometer; uncorr.), unchanged by further crystallisation from light petroleum or aqueous ethanol, as opposed to the values 42—46° quoted in the literature. All specimens were spectrally identical with that described by Cymerman and Willis [1] of m. p. 45°.

*Reaction of Benzenesulphinyl Chloride with Zinc in the Presence of Di-*p*-chlorophenyl Disulphide.*—Benzenesulphinyl chloride (4·8 g.) was treated with zinc (2 g.) as above in the presence of di-*p*-chlorophenyl disulphide (2·0 g.). The disulphide was extracted from the oily product with light petroleum (b. p. 60—80°, 50 ml.) an aliquot part (10 ml.) of which was then run down a column of silica gel (20 g., 100—200 mesh) and the disulphide eluted with carbon tetrachloride (150 ml.). It now had m. p. 45—56° and from its analysis disclosed 18·8 moles % of phenyl groups (Found: C, 52·7; H, 3·1; S, 23·3; Cl, 21·1. Calc. for $C_{12}H_{8\cdot38}S_2Cl_{1\cdot62}$: C, 52·6; H, 3·1; S, 23·3, Cl, 21·0%). No sulphenyl group interchange was observed when equimolar amounts of di-*p*-chlorophenyl disulphide and phenyl benzenethiolsulphonate were (*a*) melted together at 75° for 30 min., (*b*) kept in carbon tetrachloride solution for 24 hr. at 20°, and (*c*) kept in ether in the presence of an equimolar amount of zinc chloride for 24 hr. at 20°. Only slight interchange (6 moles %) occurred when a solution of the two components in benzene was irradiated with light from a mercury-vapour lamp for 3 hr.

Ethanesulphinyl Chloride.—This compound [4] had b. p. 47·5—48·5°/11 mm., n_D^{20} 1·4978 (Found: C, 21·5; H, 4·8; S, 28·7; Cl, 32·2. Calc. for C_2H_5OSCl: C, 21·3; H, 4·5; S, 28·5; Cl, 31·6%).

Ethyl Ethanethiolsulphonate.—Chlorination of diethyl disulphide (37 g.) in acetic acid (160 ml.) containing water (23·5 g.) essentially according to the method of Lee and Dougherty [5] gave ethyl ethanethiolsulphonate (28·5 g.) as the major product together with ethanesulphonyl chloride (16·8 g.). The thiolsulphonate had b. p. 70°/0·02 mm., n_D^{20} 1·4988 (Found: C, 31·4; H, 6·5; S, 41·4. Calc. for $C_4H_{10}O_2S_2$: C, 31·2; H, 6·5; S, 41·6%), with characteristic sulphone absorption bands in the infrared region at 1338 cm.$^{-1}$ (ε 616) and 1139 cm.$^{-1}$ (ε 808).[6]

Reaction of Ethanesulphinyl Chloride with Zinc.—The chloride (12·9 g.) in dry ether (50 ml.) was added slowly to a stirred suspension of zinc powder (12 g.) in ether (50 ml.) at 20°. The yellow oil isolated (7·12 g.) was mainly ethyl ethanethiolsulphonate (88% purity by infrared spectroscopy) and fractionation gave an almost pure sample (4·8 g.; 95% purity), b. p. 70°/0·02 mm., n_D^{20} 1·4998 (Found: C, 31·0; H, 6·5; S, 42·0%). Reaction at 0° gave only a 50% yield of thiosulphonate and the infrared spectrum of the total product indicated the presence of a component with absorption in the sulphoxide region at 1118 cm.$^{-1}$. The shift in frequency from a simple dialkyl sulphoxide (*ca.* 1050 cm.$^{-1}$) would be in keeping with the expected properties of

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[4] Douglass and Poole, *J. Org. Chem.*, 1957, **22**, 536.

[5] Lee and Dougherty, *ibid.*, 1940, **5**, 81.

[6] Evans and Higgins, unpublished work.

a disulphoxide [6] (cf. ethyl ethanethiolsulphinate, 1093 cm.$^{-1}$, and ethanesulphinyl chloride, 1159 cm.$^{-1}$). The substance decomposed on attempted isolation.

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