CLIII.—*The Disulphonation of* m-*Dichlorobenzene and of* s-*Trichlorobenzene.*

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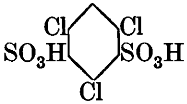
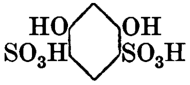
WHEN this investigation was begun it was hoped that the chlorine atoms in (I) and (II) would be very reactive, as they are in (III) (compare Davies and Hickox, J., 1922, **121**, 2640), and would lend themselves to similar condensations. The easy elimination of the sulphonic groups from the condensation products would then give mixed aromatic–aliphatic compounds of some synthetic importance. The chlorine atoms in (I) and (II) are, however, practically non-reactive compared with those in (III), and the contemplated condensations could not be brought about.

(I.)



(II.)

(III.)



(IV.)

The disulphonic acid formed by the direct sulphonation of *m*-dichlorobenzene gives a sulphonyl chloride identical with that already prepared by the action of phosphorus pentachloride on salts of (IV) (Pollak and Wienerberger, *Monatsh.*, 1914, **35**, 1472). Hence the constitution (I) is justified. Nothing was previously known of the disulphonic acid of *s*-trichlorobenzene, which must, however, have the formula indicated (II). Both *m*-dichlorobenzene and *s*-trichlorobenzene are much less readily sulphonated than the corresponding methyl derivatives of benzene, despite the fact that the chlorine atom is considered to have a greater directive power than the methyl group (Holleman, *Chem. Reviews*, 1924—1925, I, 2, 202).

EXPERIMENTAL.

1 : 3-*Dichlorobenzene*-4 : 6-*disulphonic Acid.*—*m*-Dichlorobenzene (30 g.) is dropped with cooling into fuming sulphuric acid (70 c.c.; 45% SO_3), and the mixture heated at 140—150° for 5 hours. The product after cooling and treatment with ice is converted into the

barium salt, and this into the sulphonyl chloride by heating it with phosphorus pentachloride at 130—140° for 6 hours. The sulphonyl chloride crystallises from petroleum (b. p. 100—120°) in large, thick rhombohedra, and also less frequently in long, thin needles, both forms melting at 122—123° (Pollak and Wienerberger, *loc. cit.*, record m. p. 122—123°). The crystals provide an excellent example of triboluminescence, the flashes being sufficiently brilliant to be seen in ordinary electric light (Found: C, 20·7; H, 0·9. Calc.: C, 20·9; H, 0·6%).

1 : 3-*Dichlorobenzene*-4 : 6-*disulphonic acid* forms plates very soluble in water, and can be crystallised from concentrated sulphuric acid. The *amide*, colourless needles, m. p. 276°, is readily soluble in hot and sparingly soluble in cold water. The sodium and the barium salt are very soluble in cold water, but the *potassium* salt is very soluble in hot and only moderately easily soluble in cold water, from which it separates in colourless prisms (Found in the air-dried salt: H_2O, 1·25. $C_6H_2O_6Cl_2S_2K_2,\frac{1}{4}H_2O$ requires H_2O, 1·2. Found in anhydrous salt: K, 20·3. $C_6H_2O_6Cl_2S_2K_2$ requires K, 20·4%). When the potassium salt is boiled for 24 hours with excess of aqueous-alcoholic potassium hydroxide, the quantity of chlorine displaced is less than 0·5% of that calculated for the displacement of one atom of chlorine. Bromine water attacks the salts or the acid extremely slowly, in marked contrast to the action with *m*-xylene-4 : 6-disulphonic acid.

s-*Trichlorobenzenedisulphonic Acid*.—2 : 4 : 6-Trichloroaniline has hitherto been prepared by passing chlorine into a solution of aniline in chloroform (Meyer and Sudborough, *Ber.*, 1894, **27**, 3151; Willgerodt and Wilcke, *Ber.*, 1910, **43**, 2747). This process produces large quantities of mono- and di-chloroanilines, the formation of which is hindered in the following method. Aniline (100 g.) is added drop by drop to a cold solution of chlorine (160 g.) in carbon tetrachloride (1000 g.). During the reaction a good stream of chlorine is passed, and excess of chlorine maintained. It is essential to keep the reaction mixture cold during the experiment, which requires about 5 hours. The product is worked up after the method of Willgerodt and Wilcke (*loc. cit.*); the yield of trichloroaniline is 120 g. (W. and W. obtained 78 g.). The conversion of trichloroaniline into *s*-trichlorobenzene by the method of Jackson and Lamar (*J. Amer. Chem. Soc.*, 1896, **18**, 667) gives an excellent yield. The yield is increased by treating the residue with 70% sulphuric acid, in the usual way, to remove aniline.

s-Trichlorobenzene is recovered unchanged after being heated with concentrated sulphuric acid at 100° for 56 hours, and is only partly sulphonated when heated at this temperature with fuming sulphuric acid (12% SO_3) for 6 hours. But when *s*-trichlorobenzene (9 g.) is heated on the water-bath with fuming sulphuric acid (25 c.c.; 72% SO_3) for 15 hours, complete disulphonation occurs. Disulphonation also takes place with this strength of acid in 5 hours at 115—120°, but the product is not so pure as that obtained at the lower temperature. The dry sodium salt (17 g.) is prepared *via* the calcium or barium sulphonate in the usual way, and when heated for 3 hours with three times its weight of phosphorus pentachloride and a little phosphorus oxychloride, is smoothly converted into the sulphonyl chloride (70% yield of the pure product). s-*Trichlorobenzenedisulphonyl chloride* crystallises from petroleum (b. p. 100—120°) or ethyl acetate in prisms, m. p. 161·5° (Found: Cl, 47·1; S, 16·6. $C_6HO_4Cl_5S_2$ requires Cl, 46·8; S, 16·9%). Owing to the high melting point of the sulphonyl chloride the *amide* cannot be easily obtained by the action of aqueous ammonia in the usual way; it is formed, however, by the addition of concentrated aqueous ammonia to the sulphonyl chloride in benzene. It is readily soluble in boiling and sparingly soluble in cold water, from which it separates in minute, colourless needles, m. p. 248° (Found: N, 8·5. $C_6H_5O_4N_2Cl_3S_2$ requires N, 8·3%).

s-*Trichlorobenzenedisulphonic acid* separates from concentrated sulphuric acid, in which it is moderately easily soluble, in colourless needles very soluble in water. The normal *sodium* salt is extremely soluble in water, and the normal *barium* salt (needles) dissolves in about its own weight of water at the ordinary temperature, but both salts are sparingly soluble in absolute alcohol. The *potassium* salt is slightly soluble in boiling and sparingly soluble in cold water, from which it crystallises in small, compact prisms (Found in air-dried material: H_2O, 0·1%. Found in anhydrous salt: K, 18·6. $C_6HO_6Cl_3S_2K_2$ requires K, 18·7%). Prolonged treatment of the potassium salt with boiling potassium hydroxide solution produces only a trace of potassium chloride, showing that the chlorine atoms are not reactive under the particular conditions investigated.

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