XI.—3:5-Dichloro-o-phthalic Acid.

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IN a recent number of the *Berichte* (1909, 42, 3529), Villiger described the preparation of three of the four possible dichloro-o-phthalic acids (Cl:Cl, 3:6, 3:4, 4:5) by the direct chlorination of phthalic anhydride. Villiger points out (*ibid.*, p. 3532) that a fourth isomeride was described by Crossley and Le Sueur in 1902 (*Trans.*, 81, 1533), and regards the acid as 3:5-dichloro-o-phthalic acid, although "its constitution has never been controlled."

The acid described by Crossley and Le Sueur was prepared by the direct oxidation with dilute nitric acid of a substance believed to be 3:5-dichloro-o-xylene. This chloro-derivative (III) was obtained as a by-product in the action of phosphorus pentachloride on

dimethyldihydroresorcin (I) [the main product being 3:5-dichloro-1:1-dimethylcyclohexadiene (II)], and this structure was assigned to it because there did not appear to be any reason to presume that, in the conversion of the hydroaromatic into the aromatic dichloro-derivative, the chlorine atoms would alter their positions. During the reaction, however, a methyl group must have wandered, and this was shown to have migrated to the ortho-position, because on oxidation an acid was obtained which readily gave an anhydride, and also the fluorescein reaction. Villiger is right in saying that, at that time (1902), the constitution of the dichloro-acid had not been controlled either by an analytical or a synthetical method, but this check on the constitution has since been recorded.

In 1904 (*Trans.*, 85, 284) Crossley showed that the dichloro-o-xylene, obtained from dimethyldihydroresorcin, gave, on treatment with a nitrating mixture, a dichlorodinitro-o-xylene melting at 175—176°, and in 1909 (*Trans.*, 95, 205) Crossley and Renouf showed that this same dichlorodinitro-o-xylene could be obtained from 3:5-(or 4:6-)dinitro-o-xylene by reducing the two nitro-groups to amino-groups, replacing the latter by chlorine atoms, and nitrating the dichloro-o-xylene so obtained. This series of reactions obviously proved that the dichloroxylylene obtained from dimethyldihydroresorcin is identical with that prepared by replacing the nitro-groups in 3:5-dinitro-o-xylene by chlorine atoms, and hence it must be

3:5-dichloro-*o*-xylene. The properties of the two specimens of dichloro-*o*-xylene were not, however, carefully compared, nor was the dichloroxylylene, obtained from 3:5-dinitro-*o*-xylene, oxidised to the corresponding phthalic acid, but this has now been completed under similar conditions to those previously described, and the results are given in the following table:

	From dimethyl- dihydroresorcin.	From 3:5-di- nitro- <i>o</i> -xylene.
Dichloroxylylene	Yellow, refractive liquid; slight aromatic odour. B. p. 226°, m. p. 3—4°.	Yellow, refractive liquid; slight aromatic odour. B. p. 226°, m. p. 5—7°.
Dichlorodinitroxylylene	M. p. 175—176°.	M. p. 176°.
Dichlorophthalic acid	M. p. 164° (previous soft- ening) with evolution of gas.	M. p. 164° (previous soft- ening) with evolution of gas.
Dichlorophthalic anhydride	M. p. 89°.	M. p. 89°.
Dichlorophthalanil	M. p. 150—150·5°.	M. p. 150°.

In all cases the above melting points of the two corresponding series of substances were checked by the mixed melting-point method.

This direct synthesis of 3:5-dichloro-*o*-phthalic acid proves beyond doubt the correctness of the conclusions as to the constitution of the acid obtained by Crossley and Le Sueur from dimethyldihydro-resorcin.

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