120. *The Tetrazotisation of Aryl Diamines with Special Reference to* o-*Phenylenediamine.*

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SCHOUTISSEN (*J. Amer. Chem. Soc.*, 1933, **55**, 4531) has described a method of diazotisation (or tetrazotisation) in which a solution of the amine (or diamine) in concentrated sulphuric acid is mixed with nitrosylsulphuric acid (sodium nitrite dissolved in concentrated sulphuric acid) and diazotisation is effected by subsequent dilution with phosphoric acid. He thus succeeded in tetrazotising *p*-phenylenediamine and obtained from it a 70% yield of *p*-dichlorobenzene by the Sandmeyer process, but he practically failed in the case of *o*-phenylenediamine.

Prior to the publication of Schoutissen's paper, we had applied our method for the diazotisation of nitroamines (J., 1933, 1620) to aryldiamines and found it to be uniformly successful; in particular, *o*-phenylenediamine was tetrazotised without aziminobenzene formation and *o*-dichlorobenzene was obtained from it in 70% yield. Since nitrous acid is present always in excess, the occurrence of secondary reactions is reduced to a minimum or prevented altogether.

Solutions of *m*-tolylenediamine (24·4 g.) and of *o*-, *m*-, and *p*-phenylenediamine (21·6 g.), each in glacial acetic acid (150 c.c.), were added gradually, below 30°, to well-stirred solutions of nitrosylsulphuric acid (prepared by dissolution of sodium nitrite, 32 g., in concentrated sulphuric acid, 320 c.c., at 70°). Test portions poured into excess of water gave no indication of the formation of Bismarck brown from the *m*-diamines or of aziminobenzene from *o*-phenylenediamine. The tetrazo-solutions were poured gradually into solutions of cuprous chloride (40 g.) in concentrated hydrochloric acid (300 c.c.) below 40°, and when the evolution of nitrogen ceased, the mixtures were diluted each with an equal volume of water and steam-distilled. The volatile oils were washed with aqueous caustic alkali and with water, dried, and distilled. The diamines in the order mentioned above gave 24·2 g. of 2 : 4-dichlorotoluene (Found : Cl, 44·0. Calc. : Cl, 44·1%), 20·6 g. of *o*-dichlorobenzene (Found : Cl, 48·1. Calc. : Cl, 48·3%), 20·7 g. of *m*-dichlorobenzene (Found : Cl, 48·2%), and 20·5 g. (crystallised from alcohol) of *p*-dichlorobenzene, m. p. 53° (Found : Cl, 48·1%).

The authors thank Imperial Chemical Industries Ltd. (Dyestuffs Group) for various gifts.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, February* 15*th*, 1935.]