382. *The Diazotisation of Aromatic Nitro-amines and the Prevention of Diaryl Formation in the Sandmeyer Reaction.*

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The diazotisation of weak bases such as 2- and 4-nitro- and 2 : 4-dinitro-1-naphthylamine is rapid and complete when a solution of the nitro-amine in glacial acetic acid is added to one of sodium nitrite in concentrated sulphuric acid : reversal of the order of addition precipitates the sulphate of the base and greatly retards the rate of diazotisation.

(1) When the diazo-solution thus obtained is added in the cold to a solution of cuprous chloride or bromide in the corresponding concentrated acid, or to a saturated aqueous solution of potassium iodide, decomposition rapidly takes place and the almost pure halogenonitro-compound is precipitated in at least 80% yield : diaryl formation has not been detected. *o*-, *m*-, and *p*-Nitroaniline, 2 : 4-dinitroaniline, 2-, 4-, and 5-nitro-1-naphthylamine, 2 : 4-dinitro-1-naphthylamine, and 1-nitro-2-naphthylamine have thus been converted into the corresponding chloro-, bromo-, and iodo-nitro-compounds. Moreover, 4 : 4′-dichloro-3 : 3′-dinitrodiphenyl has been obtained in 80% yield from 3 : 3′-dinitrobenzidine, whereas Cain, Coulthard, and Micklethwait (J., 1913, **103**, 2074) obtained only 4″ : 4‴-dichlorotetranitrobenzerythrene from this base (then regarded as 3 : 5′-dinitrobenzidine) by the usual process.

If, prior to treatment with the cuprous chloride or bromide solution, the diazo-solution is diluted with water (ice), the Sandmeyer reaction does not proceed satisfactorily, tar being frequently formed, and in the case of 2 : 4-dinitro-1-naphthylamine (Morgan and Evens, J., 1919, **115**, 1126), 4-nitronaphthalene-1-diazo-2-oxide being produced.

(2) If an equal volume of ethyl alcohol is added, with cooling, to the undiluted diazo-solution, and the temperature is then gradually raised to 80°, elimination of the diazo-

group takes place. By this means 50% yields of 2-nitronaphthalene and 1 : 3-dinitronaphthalene (hitherto difficultly accessible; compare Veselý and Dvořák, *Bull. Soc. chim.*, 1923, **33**, 319) have been obtained from 2-nitro- and 2 : 4-dinitro-1-naphthylamine respectively.

Experimental.

General Method of Diazotisation.—A solution of the nitro-amine in hot glacial acetic acid (1 g. per 12 c.c.) is rapidly cooled to room temperature and gradually stirred into a solution of sodium nitrite in concentrated sulphuric acid (1 g. per 7 c.c.). The latter solution is prepared as follows: the finely powdered nitrite is added to the cooled acid with vigorous stirring, the temperature is raised to 70° until the nitrite has dissolved, and the solution is then cooled to room temperature and, if desired, filtered from sodium bisulphate. The diazotisation is conducted below 20° and a 10% excess of sodium nitrite is used (compare the usual descriptions of diazotisations in concentrated sulphuric acid solution, in which 500% excess is often recommended).

4 : 4′-*Dichloro*-3 : 3′-*dinitrodiphenyl.*—3 : 3′-Dinitrobenzidine was prepared by the following improved method of hydrolysing 3 : 3′-dinitrodiacetylbenzidine (compare Hodgson and Gorowara, J., 1926, 1758). 15 G. were heated on the water-bath with a mixture of ethyl alcohol (50 c.c.), concentrated sulphuric acid (80 c.c.), and water (20 c.c.) until a clear solution was obtained (30—60 minutes), and this was poured into water to precipitate the crude diamine (if ethyl alcohol is omitted, an inferior product is obtained). The 3 : 3′-dinitrobenzidine, m. p. 275°, after crystallisation from nitrobenzene, was powdered and stirred (2·74 g.) gradually below 20° into a solution of sodium nitrite (1·5 g.) in concentrated sulphuric acid (15 c.c.) prepared as described above, until complete dissolution had taken place; an equal volume of glacial acetic acid was then added, the temperature being maintained below 30°. This diazo-solution was run gradually into a well-stirred solution of cuprous chloride (4 g.) in concentrated hydrochloric acid (40 c.c.), and, after evolution of nitrogen had ceased, the precipitate of 4 : 4′-dichloro-3 : 3′-dinitrodiphenyl was filtered off (yield, 80%) and crystallised from nitrobenzene, forming colourless needles, m. p. 237° (Found: N, 9·0; Cl, 22·6. Calc.: N, 8·95; Cl, 22·7%).

1-Chloro-2 : 4-dinitronaphthalene, now rendered much more accessible, crystallises from benzene in pale yellow needles, m. p. 147° (Ullmann and Bruck, *Ber.*, 1908, **41**, 3932, give m. p. 146·5°) (Found: Cl, 13·9. Calc.: Cl, 14·0%).

1-*Bromo*-2 : 4-*dinitronaphthalene* separates from glacial acetic acid in almost colourless prisms, m. p. 160° (Found: N, 9·5; Br, 26·7. $C_{10}H_5O_4N_2Br$ requires N, 9·4; Br, 26·9%).

1-*Iodo*-2 : 4-*dinitronaphthalene* crystallises from cellusolve in pale straw-coloured microprisms, m. p. 183° (Found: N, 8·3; I, 36·6. $C_{10}H_5O_4N_2I$ requires N, 8·1; I, 36·9%).

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