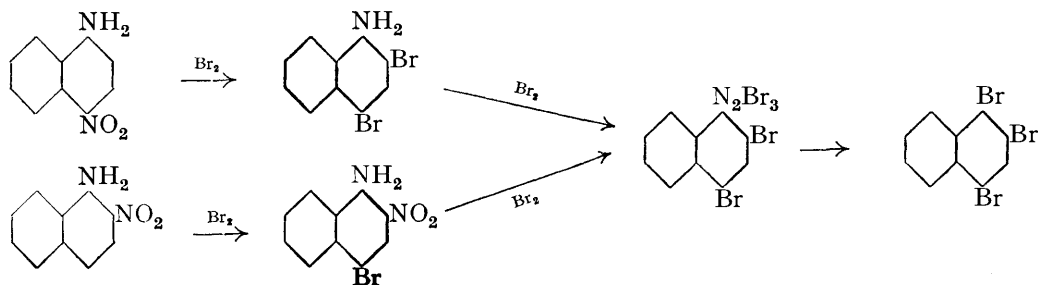


377. *The Action of Bromine on 2- and 4-Nitro-1-naphthylamines.*

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THE work herein described arose from attempts to brominate 4-nitro-1-naphthylamine in chloroform or acetic acid suspension by addition of bromine. In chloroform suspension, the product was 2:4-dibromo-1-naphthalenediazo-perbromide; this lost nitrogen and bromine to furnish 1:2:4-tribromonaphthalene (Meldola, J., 1883, **43**, 4). In acetic acid suspension the principal product was 2-bromo-4-nitro-1-naphthylamine (obtained by Hodgson and Elliot, J., 1934, 1706, by the action of bromine on 4-nitro-1-naphthylamine in nitrobenzene solution), but a small proportion of the diazo-perbromide also was produced.



In both chloroform and acetic acid suspensions 2-bromo-4-nitro-1-naphthylamine with an excess of bromine yielded 2 : 4-dibromo-1-naphthalenediazo-perbromide.

2-Nitro-1-naphthylamine in chloroform or acetic acid suspension reacted cleanly with bromine, with evolution of hydrogen bromide, to furnish 4-bromo-2-nitro-1-naphthylamine. Further bromination produced 2 : 4-dibromo-1-naphthalenediazo-perbromide.

In the benzene series there is apparently no record of the formation of diazo-perbromides by this type of reaction; with bromine, *o*- and *p*-nitroanilines yield bromo-derivatives.

EXPERIMENTAL.

Bromination of 4-Nitro-1-naphthylamine.—(a) To a suspension of the finely powdered nitroamine (2 g.) in chloroform (15 c.c.), bromine (1.5 c.c.; 2.5 mols.) in chloroform (5 c.c.) was added drop by drop; the amine dissolved with evolution of heat. The green mixture thereafter precipitated was collected and repeatedly washed with hot chloroform. The residual orange needles of 2 : 4-dibromo-1-naphthalenediazo-perbromide had a sharp decomposition point between 128° and 136°, depending upon the rate of heating. No hydrogen bromide was liberated throughout the reaction and the chloroform mother-liquor showed no acid reaction [Found : Br, 69.9; Br (labile), 28.1; N, 5.2; N (by heating to decomposition), 5.0. Calc. for C₁₀H₅N₂Br₃ : Br, 72.3; Br (labile), 28.8; N, 5.1%]. The discrepancies in the bromine values are very likely due to the presence of unchanged 4-nitro-1-naphthylamine, in view of the fact that suspensions were worked with.

Both this compound and authentic diazo-perbromide gave 1 : 2 : 4-tribromonaphthalene, m. p. and mixed m. p. 112—113° (Meldola, *loc. cit.*, gives m. p. 113—114°) (Found : Br, 64.5; N, nil. Calc. for C₁₀H₅Br₃ : Br, 65.7%), when heated to the decomposition point or when treated with pyridine; in both cases the residue was crystallised from alcohol or acetic acid. Both substances dissolved slowly in boiling acetic acid or acetic anhydride with liberation of bromine and, on cooling, tribromonaphthalene crystallised.

2 : 4-Dibromo-1-naphthalenediazo-perbromide and 1 : 2 : 4-tribromonaphthalene were prepared by a modification of Meldola's method (*loc. cit.*). 2 : 4-Dibromo-1-naphthylamine (preceding paper) was diazotised in acetic acid with a mixture of sodium nitrite and concentrated sulphuric acid (cf. Hodgson and Walker, J., 1933, 1620). Ice was added and the cold filtered solution was treated with a solution of bromine in hydrobromic acid until a filtered sample gave no further precipitate with bromine solution. The yellow amorphous diazo-perbromide was purified by heating under reflux with chloroform.

(b) To a stirred suspension of 4-nitro-1-naphthylamine (10 g.) in acetic acid (50 c.c.), bromine (3.4 c.c.) in acetic acid (30 c.c.) was gradually added; the pasty mixture was stirred on the water-bath for 30 minutes, hydrogen bromide being evolved. The 2-bromo-4-nitro-1-naphthylamine, mostly in the form of its hydrobromide, was collected and triturated with dilute aqueous ammonia. After crystallisation from alcoholic pyridine it formed orange-red needles (7 g.), m. p. 249° (decomp.) (Found : N, 10.2. Calc. for C₁₀H₇O₂N₂Br : N, 10.5%). Hodgson and Elliott (*loc. cit.*) record m. p. 250°. A small quantity of 2 : 4-dibromo-1-naphthalenediazo-perbromide was deposited from the acetic acid mother-liquor after 12 hours.

2-Bromo-4-nitroaceto-1-naphthalide, obtained by acetylation of the amine with acetic anhydride and a drop of concentrated sulphuric acid, formed yellow needles, m. p. 235—236°, from acetic acid (Found : N, 8.9. C₁₂H₉O₃N₂Br requires N, 9.1%).

The Action of Bromine on 2-Bromo-4-nitro-1-naphthylamine.—To a suspension (1 g.) in chloroform or acetic acid was added an excess of bromine in chloroform. The amine dissolved, forming a green solution, from which a green solid was precipitated. This was washed with hot chloroform, and the orange diazo-perbromide obtained.

Bromination of 2-Nitro-1-naphthylamine.—With 1 mol. of bromine, this substance in either acetic acid or chloroform suspension gave 4-bromo-2-nitro-1-naphthylamine (orange needles, m. p. 199°, from acetic acid) with copious evolution of hydrogen bromide. The acetyl derivative had m. p. 229° (Morgan and Godden, J., 1910, 97, 1709, record m. p.'s 200° and 229° respectively).

With excess of bromine, 4-bromo-2-nitro-1-naphthylamine gave 2 : 4-dibromo-1-naphthalenediazo-perbromide, which was decomposed with boiling acetic acid to give 1 : 2 : 4-tribromonaphthalene, m. p. and mixed m. p. 113°.

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