165. *The Bromination of 6-Nitro-1-naphthylamine.*

By Herbert H. Hodgson and Raymond E. Dean.

6-Nitro-1-naphthylamine dibrominates in chloroform solution at −5° to give 2 : 4-dibromo-6-nitro-1-naphthylamine whatever the amount of bromine used. The monobromination previously reported by Hodgson and Turner (*J.*, 1943, 392) using the calculated amount of bromine is found to give a mixture of 2 : 4-dibromo-6-nitro-1-naphthylamine and unchanged 6-nitro-1-naphthylamine.

1-Bromo-7-nitronaphthalene has been prepared recently by the deamination of 1-bromo-7-nitro-2-naphthylamine (see p. 818), and is not identical with the specimen reported by Hodgson and Turner (*J.*, 1943, 392), which was obtained by the deamination of 4-bromo-6-nitro-1-naphthylamine, itself prepared by the apparent monobromination of 6-nitro-1-naphthylamine in chloroform with the calculated amount of bromine. Since it appeared unlikely that monobromination of 7-nitro-2-naphthylamine would occur in any than the 1-position, and therefore that the compound reported by Hodgson and Dean (*loc. cit.*) was 1-bromo-7-nitronaphthalene, the original bromination of 6-nitro-1-naphthylamine has been repeated. Under the conditions previously employed by Hodgson and Turner (*loc. cit.*), it was found that dibromination always occurred with formation of 2 : 4-dibromo-6-nitro-1-naphthylamine, even when only sufficient bromine was used to effect monobromination. This result is in line with the nitration of toluene-*p*-sulphon-1-naphthalide which always gives the dinitro-compound (Hodgson and Walker, *J.*, 1934, 180).

Repeated fractional crystallisation, with microscopic examination, of Hodgson and Turner's original specimen revealed it to be a mixture of unchanged 6-nitro-1-naphthylamine and its 2 : 4-dibromo-derivative, which would account for the analytical data obtained.

Experimental.

Preparation of 2 : 4-*Dibromo*-6-*nitro*-1-*naphthylamine.*—A solution of 6-nitro-1-naphthylamine (2·15 g., in chloroform (55 c.c.) was cooled to −5°, and bromine (1·3 c.c.) in chloroform (12 c.c.) was stirred in dropwise during ten minutes. The mixture was kept for 30 minutes at −5° with occasional stirring to ensure completion of the reaction, and the cream precipitate of 2 : 4-*dibromo*-6-*nitro*-1-*naphthylamine hydrobromide* (Found : Br, 56·0. $C_{10}H_7O_2N_2Br_3$ requires Br, 56·2%) filtered off and washed with chloroform and ether; it tended to hydrolyse in the air. The salt was basified with ammonia, the 2 : 4-dibromo-6-nitro-1-naphthylamine (2·3 g.) filtered off, washed with water, dried at 100°, and recrystallised twice from ethanol; it was obtained in red needles, m. p. 202° (Found : N, 8·5; Br, 46·0. Calc. for $C_{10}H_6O_2N_2Br_2$: N, 8·1; Br, 46·2%). In an attempt to obtain a monobromo-derivative, the above procedure was repeated with less bromine (0·25 c.c.), whereby a mixture of 2 : 4-dibromo-6-nitro-1-naphthylamine and 6-nitro-1-naphthylamine was obtained.

1 : 3-*Dibromo*-7-*nitronaphthalene.*—2 : 4-Dibromo-6-nitro-1-naphthylamine (2·1 g.) was dissolved in boiling glacial acetic acid (35 c.c.) and the solution rapidly chilled to 15° to obtain a fine suspension of the amine, which was then diazotised by addition to a stirred solution of sodium nitrite (1 g.) in sulphuric acid (20 c.c.; *d* 1·84) below 20°. After 30 minutes the solution of the diazonium sulphate was stirred into a hot suspension of cuprous oxide (4 g.) in methanol (70 c.c.), and the mixture was stirred for 1 hour and added to iced water (60 c.c.). Next morning the solid was filtered off, washed in the sequence water (300 c.c.), 2% aqueous sodium carbonate (300 c.c.), and water (300 c.c.), and then extracted with boiling ethanol. The extract was filtered, boiled with animal charcoal, and filtered again; the filtrate was allowed to evaporate. The 1 : 3-*dibromo*-7-*nitronaphthalene* (0·45 g.) crystallised from ethanol in pale yellow rods, m. p. 195° (Found : N, 4·59; Br, 48·0. $C_{10}H_5O_2NBr_2$ requires N, 4·23; Br, 48·3%), which were very sparingly soluble in cold and rather more soluble in hot ethanol.

1 : 2 : 4-*Tribromo*-6-*nitronaphthalene.*—A solution of the above amine (1·0 g.) in boiling hydrobromic acid (1·3 c.c.; *d* 1·7) and water (7·5 c.c.) was chilled to 0° to give a fine suspension of the hydrobromide) which was then diazotised at 0° with a solution of sodium nitrite (1 g.) in the minimum amount of water. After 30 minutes the filtered solution was stirred into one of cuprous bromide (2·0 g.) in hydrobromic acid (5 c.c.; *d* 1·7) at 60°, and, when the reaction had ceased, the mixture was poured into iced water and the yellow precipitate filtered off, washed in the sequence water (300 c.c.), 2% aqueous sodium carbonate (100 c.c.), and water (300 c.c.), dried at 70°, and dissolved in boiling ethanol (charcoal). This solution

was filtered and allowed to evaporate, whereupon the *tribromo*-compound separated in clusters of bright yellow needles (0·6 g.), m. p. 165° (Found : Br, 58·2. $C_{10}H_4O_2NBr_3$ requires Br, 58·5%).

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TECHNICAL COLLEGES OF BRADFORD AND HUDDERSFIELD.

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