102. *The Separation of* 3-*Nitro*-1-*naphthylamine and* 4-*Nitro*-2-*naphthylamine by Maleic Anhydride, and the Monobromination of* 4-*Nitro*-2-*naphthylamine.*

By Herbert H. Hodgson and David E. Hathway.

A mixture of 4-nitro-2-naphthylamine and 3-nitro-1-naphthylamine has been separated by preferential acylation of the former compound by maleic anhydride. A thermal analysis diagram has been constructed to enable both the acetic anhydride and the maleic anhydride separation to be almost quantitatively effected. Two equivalents or more of bromine will only monobrominate 4-nitro-2-naphthylamine to give 1-bromo-4-nitro-2-naphthylamine. Reduction of 1 : 3-dinitronaphthalene by sodium hyposulphite gives 1 : 3-naphthylenediamine.

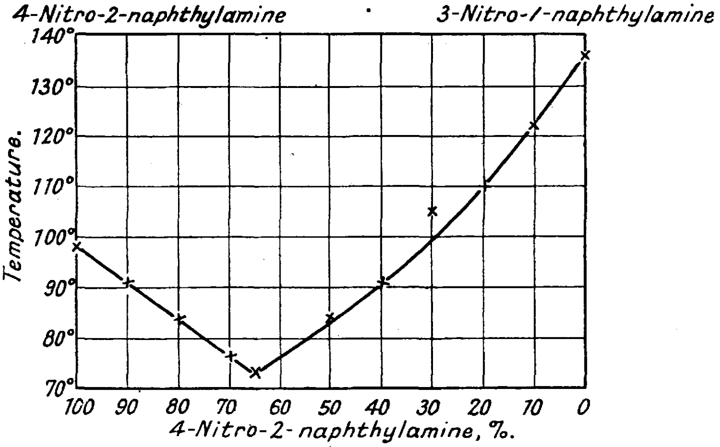
The separation of 4-nitro-2-naphthylamine from 3-nitro-1-naphthylamine, previously effected with acetic anhydride (Hodgson and Birtwell, this vol., p. 75), has now been accomplished with maleic anhydride. A thermal analysis diagram has been constructed to enable the requisite amount of acetic or maleic anhydride to be computed.

The mixed amines obtained by sodium sulphide reduction of 1 : 3-dinitronaphthalene (Hodgson and Birtwell, *loc. cit.*) comprise *ca.* 16% of 4-nitro-2- and 84% of 3-nitro-1-naphthylamine, as deduced from the m. p. 114° of the mixture and subsequent isolation of the separate amines. Reduction in glacial acetic acid by alcoholic stannous chloride (Vesely and Dvorăk, *Bull. Soc. chim.*, 1923, **33**, 319) gave a mixture of amines, m. p. 120°, corresponding to 11% of 4-nitro-2- and 89% of 3-nitro-1-naphthylamine. Reduction of 1 : 3-dinitronaphthalene with sodium hyposulphite (hydros) in amount just sufficient for monoreduction gave equal quantities of 1 : 3-naphthylenediamine and unchanged 1 : 3-dinitronaphthalene; no nitronaphthylamines were detected.

Bromination of 4-nitro-2-naphthylamine differs from that of its isomeride in that more than 2 equivalents of bromine will only effect monobromination to 1-bromo-4-nitro-2-naphthylamine, whereas less than one equivalent of bromine will dibrominate 3-nitro-1-naphthylamine to 2 : 4-dibromo-3-nitro-1-naphthylamine, leaving unchanged initial material (Hodgson and Hathway, this vol., p. 21). The constitution of the 1-bromo-4-nitro-2-naphthylamine was confirmed by its deamination to 1-bromo-4-nitronaphthalene.

EXPERIMENTAL.

Separation of 4-*Nitro*-2- *from* 3-*Nitro*-1-*naphthylamine.*—When hot solutions of maleic anhydride (0·5 g.) and the mixed amines (4 g.) obtained by sodium sulphide reduction of 1 : 3-dinitronaphthalene (Hodgson and Birtwell, *loc. cit.*) in chloroform (5 c.c. and 30 c.c. respectively) were mixed, heat was evolved, and 4-*nitro*-2-*naphthylmaleamic acid* separated on cooling (1·35 g.); it crystallised from ethyl alcohol in pale lemon, parallelepipeds, m. p. 193° (Found : N, 9·7. $C_{14}H_{10}O_5N_2$ requires N, 9·8%). Three successive additions of maleic anhydride (0·2 g.) to the filtrate effected further separations (0·55 g.) of the above compound, contaminated, however, by an increasing content of 3-nitro-1-naphthylmaleamic acid as shown by m. p. sequences of 178°, 171, and 165°. Further addition of maleic anhydride afforded pure 3-*nitro*-1-*naphthylmaleamic acid*, which crystallised from alcohol (charcoal) in sheaves of slender golden-yellow needles, m. p. 170° (Found : N, 9·7%). Mixed m. p.'s with the maleamic acids prepared from the pure nitroamines established identity. Both the above maleamic acids dissolve in aqueous sodium carbonate and are precipitated unchanged from the solutions on acidification.



4-Nitro-2-naphthylamine was isolated from the maleamic acid (1·3 g.) by heating it for 1 hour under reflux with a mixture of sulphuric acid (15 c.c., *d* 1·84), ethyl alcohol (30 c.c.), and water (15 c.c.), precipitation of 4-nitro-2-naphthylamine sulphate by addition of water (150 c.c.), and subsequent basification by cautious addition of 10% aqueous ammonia at 0°; it crystallised from 50% aqueous ethyl alcohol in long, felted, scarlet needles, m. p. 98·5° (Veselý and Dvorăk, *loc. cit.*, give m. p. 95°; Hodgson and Birtwell, *loc. cit.*, give m. p. 97°) (Found : N, 14·9. Calc. : N, 14·9%). It gave an apple-green colour with concentrated sulphuric acid which became scarlet on dilution, whereas 3-nitro-1-naphthylamine gave an intense dirty brown colour with a green fluorescence, also turning scarlet on dilution.

4-*Nitrobenzo*-2-*naphthalide*, prepared by the Schotten–Baumann reaction in acetone, crystallised from ethyl alcohol in golden-yellow plates, m. p. 169° (Found : N, 9·6. $C_{17}H_{12}O_3N_2$ requires N, 9·6%).

Thermal Analysis of Mixtures of 3-*Nitro*-1- *and* 4-*Nitro*-2-*naphthylamine.*—Synthetic mixtures of the pure nitroamines were fused in ignition tubes, the melt allowed to solidify, then finely powdered, and the m. p. taken when the sintered substance just became a clear liquid. The results are plotted in the diagram. The eutectic temperature is 73° and a synthetic mixture having the eutectic composition, *viz.*, 35% of 3-nitro-1-naphthylamine (0·035 g.) and 65% of 4-nitro-2-naphthylamine (0·065 g.), was found to melt at 73°.

The mixed amines (7·4 g.) obtained by reduction of 1 : 3-dinitronaphthalene (11 g.) by sodium sulphide (Hodgson and Birtwell, *loc. cit.*) had m. p. 114°, corresponding to 16% of 4-nitro-2- and 84% of 3-nitro-1-naphthylamine; separation by maleic anhydride resulted in the isolation of pure 4-nitro-2-naphthylamine (0·8 g., *ca.* 70% of the predicted yield) and of 3-nitro-1-naphthylamine (6·5 g., m. p. 129°, of 95% purity).

Monobromination of 4-*Nitro*-2-*naphthylamine.*—When 4-nitro-2-naphthylamine (2 g.), dissolved in dry chloroform (9 c.c.), was treated dropwise at 40—50° with 4·7 c.c. of a solution of bromine (1 c.c.) in dry chloroform (9 c.c.), 1-bromo-4-nitro-2-naphthylamine hydrobromide (3·2 g.) was precipitated. Dilute aqueous ammonia liberated 1-*bromo*-4-*nitro*-2-*naphthylamine* (2·8 g.), which crystallised from alcohol (charcoal) in felted tan-coloured parallelepipeds, m. p. 153° (Found : Br, 29·8. $C_{10}H_7O_2N_2Br$ requires Br, 30·0%). 1-*Bromo*-4-*nitroaceto*-2-*naphthalide* crystallised from glacial acetic acid in buff, almost colourless, rectangular plates, m. p. 177° (Found : Br, 25·7. $C_{12}H_9O_3N_2Br$ requires Br, 25·9%).

1-Bromo-4-nitronaphthalene was formed when a solution of 1-bromo-4-nitro-2-naphthylamine (1·3 g.) in glacial acetic acid (30 c.c.) was stirred below 20° into one of sodium nitrite (0·5 g.) in sulphuric acid (7 c.c., *d* 1·84) and the diazonium mixture, after 15 minutes, stirred into a suspension of cuprous oxide (1 g.) in ethyl alcohol (50 c.c.), the stirring being continued until reaction ceased. The mixture was poured into ice-water (500 c.c.), and 1-bromo-4-nitronaphthalene extracted from the resulting precipitate by boiling alcohol (1 g.), from which it crystallised on cooling : recrystallised (charcoal) from the same solvent, it formed pale yellow micro-needles, m. p. 87° (John, *Bull. Soc. chim.*, 1877, **28**, 515, gives m. p. 85°) (Found : Br, 31·5. Calc. : Br, 31·7%).

Attempted Dibromination of 4-*Nitro*-2-*naphthylamine.*—A solution of the amine (0·3 g.) in dry chloroform (2 c.c.) at 50° was treated with 2 c.c. of the bromine reagent above, and the precipitated hydrobromide removed and basified. Only 1-bromo-4-nitro-2-naphthylamine (0·35 g.) was obtained, which, after recrystallisation from alcohol, had m. p. and mixed m. p. with authentic specimen, 153°. 4-*Nitronaphthalene*-2-*azo*-β-*naphthol* was precipitated when a solution of 4-nitro-2-naphthylamine (0·5 g.) in glacial acetic acid (7 c.c.) was diazotised by addition to sodium nitrite (0·3 g.) in sulphuric acid (5 c.c., *d* 1·84) below 20°; after 30 minutes, the solution was diluted with ice and stirred into one of β-naphthol (0·4 g.) in 20% aqueous sodium hydroxide (55 c.c.) below 25°. After 1 hour, the azo-compound (0·9 g.) was removed and crystallised from glacial acetic acid; it formed deep red, micro-needles, m. p. 240° (Found : N, 12·3.

$C_{20}H_{13}O_3N_3$ requires N, 12·2%), which gave with concentrated sulphuric acid a deep purple colour that turned scarlet on dilution with water.

The authors thank I.C.I. Ltd., Dyestuffs Division, for gifts of chemicals.

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[*Received, February 25th,* 1944.]