221. *The Preparation of Some 2 : 3-Naphthalene Derivatives.*

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1 : 3-Dibromo-2-nitronaphthalene is reduced by tin and hydrochloric acid to 3-bromo-2-naphthylamine (cf. Consden and Kenyon, J., 1935, 1595). The latter compound provides a convenient starting point for many 2 : 3-disubstituted naphthalenes. 3-Nitro-2-naphthylamine has now been obtained pure and does not show chromoisomerism (cf. Hodgson and Turner, J., 1943, 689).

1 : 3-Dibromo-2-nitronaphthalene (Hodgson and Hathway, J., 1944, 21) when reduced in alcoholic solution by tin and hydrochloric acid gave 3-bromo-2-naphthylamine, behaving like 1 : 3-dibromo-2-naphthylamine under similar conditions (Consden and Kenyon, J., 1935, 1595). This result, with its excellent yields through-

out, makes some 2 : 3-naphthalene derivatives readily available. By this means 2-*chloro*-3-*bromo*- and 2-*bromo*-3-*iodo*-*naphthalenes* and also the known 2 : 3-dibromonaphthalene have been obtained.

In addition to the method of Hodgson and Elliott (J., 1936, 1151) for preparing 3-halogeno-2-nitronaphthalenes by means of the nitration in the 2-position of 3-halogeno-aceto-1-naphthalides, 3-halogeno-2-nitronaphthalenes have now been obtained by means of the mercuration of 3-nitro-1-naphthylamine in the 2-position (Hodgson and Hathway, this vol., p. 123) and the nitration of 3-nitroaceto-1-naphthalide in the 2-position (Hodgson and Turner, J., 1943, 689).

An attempt to replace the bromine atom in the 1-position of 1 : 3-dibromo-2-nitronaphthalene with an amino-group, by heating under pressure at 150° with alcoholic ammonia, was unsuccessful.

Repetition of the work of Hodgson and Turner (*loc. cit.*) on the preparation of 3-nitro-2-naphthylamine showed that the chromoisomerism there reported does not exist, the previously described mixture of red and orange-yellow needles being probably due to the presence of unchanged 2 : 3-dinitronaphthalene. As now obtained, 3-nitro-2-naphthylamine crystallises in scarlet needles and has m. p. 140° and not m. p. 86·5° as previously stated.

EXPERIMENTAL.

3-*Nitro*-2-*acetoxymercuri*-*aceto*-1-*naphthalide* was obtained by refluxing a mixture of 3-nitro-1-naphthylamine-2-mercuriacetate (11·2 g.), acetic anhydride (10 c.c.) and ethyl acetate (30 c.c.) for 3 hours. The separated material (pale yellow rods, 11 g.) was recrystallised from acetic acid and had m. p. 250° (decomp.) (Found: Hg, 39·1. $C_{14}H_{12}O_5N_2Hg$ requires Hg, 39·5%).

2-*Bromo*-3-*nitro*-*aceto*-1-*naphthalide*.—The above compound (9·8 g.) was made into a paste with a little alcohol and 20% aqueous potassium bromide (100 c.c.) and the mixture vigorously shaken with a solution of bromine (3·4 g.) in 20% aqueous potassium bromide (15 c.c.) and kept for several days. The solid was removed, washed, dried at 100° and when crystallised from acetic acid was obtained (3·5 g.) in clusters of small colourless prisms, m. p. 240° (Found : Br, 25·5. $C_{12}H_9O_3N_2Br$ requires Br, 25·9%).

2-*Bromo*-3-*nitro*-1-*naphthylamine*.—2-Bromo-3-nitro-aceto-1-naphthalide (3·5 g.) was refluxed for 1 hour with a mixture of sulphuric acid (18 c.c., *d* 1·84), ethanol (36 c.c.) and water (18 c.c.). The yellow precipitate (sulphate), obtained on dilution of the cooled solution with ice (200 g.), was converted into 2-*bromo*-3-*nitro*-1-*naphthylamine* by treatment with ammonia. This was washed with water, dried at 80° (3 g.) and, after crystallisation from ethanol (charcoal) was obtained in felted red needles, m. p. 107° (Found : Br, 29·9. $C_{10}H_7O_2N_2Br$ requires Br, 30·0%).

3-Bromo-2-nitronaphthalene was formed when a solution of 2-bromo-3-nitro-1-naphthylamine (2·7 g.) in acetic acid (20 c.c.) at below 0° was stirred and added dropwise to a mixture of sodium nitrite (1 g.) and sulphuric acid (12 c.c., *d* 1·84). The mixture was kept for 30 minutes to ensure complete diazotisation and the solution of the diazonium sulphate then stirred into a suspension of cuprous oxide (3 g.) in methanol (100 c.c.). After complete reaction the mixture was poured on to ice (400 g.), the precipitate washed with water, dried, extracted with ethanol and the crude 3-bromo-2-nitro-naphthalene (1·8 g.) precipitated from the extract by water. It was purified by dissolution in chloroform, washing the solution with 2% aqueous sodium hydroxide, drying the chloroform layer, and, after evaporation of the chloroform, the residue crystallised from ethanol in brownish needles, m. p. 84°, identical with that of an authentic specimen (Hodgson and Elliott, *loc. cit.*, m. p. 84°).

3-*Bromo*-2-*naphthylamine*.—1 : 3-Dibromo-2-nitronaphthalene (5 g.) was refluxed for 4 hours with tin (7 g.), hydrochloric acid (45 c.c., *d* 1·18), and ethanol (50 c.c.). The hot filtered solution deposited 3-*bromo*-2-*naphthylamine hydrochloride* (3·9 g.) in colourless prismatic needles (Found : HCl, 14·0. $C_{10}H_8NBr,HCl$ requires HCl, 14·1%). This was treated with hot 5% alcoholic potassium hydroxide (40 c.c.) and the base crystallised from ethanol (charcoal). 3-Bromo-2-naphthylamine was obtained in glistening colourless plates, m. p. 170° (Consden and Kenyon, J., 1935, 1595, m. p. 170°) (Found: N, 6·2. Calc. for $C_{10}H_8NBr$: N, 6·3%). 3-*Bromo*-*benzo*-2-*naphthalide*, prepared by the Schotten–Baumann reaction in acetone, crystallised from ethanol (charcoal) in clusters of pale pink sagittate crystals, m. p. 176°, on admixture with 3-bromo-2-naphthylamine (Found : Br, 24·4. $C_{17}H_{12}ONBr$ requires Br, 24·5%).

2 : 3-Dibromonaphthalene was formed when a solution of 3-bromo-2-naphthylamine (1 g.) in glacial acetic acid (10 c.c.) was diazotised as above by nitrosyl sulphuric acid, and the solution of the diazonium sulphate decomposed by addition to a mixture of cuprous bromide (2 g.) in hydrobromic acid (10 c.c., *d* 1·7). After 24 hours, the whole was poured on to ice (100 g.), and the precipitated 2 : 3-dibromonaphthalene (1 g.) washed and crystallised from ethanol (charcoal) in lustrous plates, m. p. 140° (Wynne, P., 1914, 204, m. p. 140°; cf. Kenner, Ritchie, and Wain, J., 1937, 1518) (Found : Br, 55·8. Calc. for $C_{10}H_6Br_2$: Br, 55·9%). 2-*Chloro*-3-*bromonaphthalene* (1·0 g.) was formed when a glacial acetic acid solution of 3-bromo-2-naphthalenediazonium sulphate prepared as above was decomposed by addition of cuprous chloride (2 g.) in hydrochloric acid (10 c.c., *d* 1·18). It crystallised from ethanol in glistening white plates, m. p. 115° (0·2128 G. gave 0·2900 g. AgCl + AgBr. $C_{10}H_6ClBr$ requires 0·2920 g.). 2-*Bromo*-3-*iodonaphthalene* (1 g.) was formed when a glacial acetic solution of 3-bromo-2-naphthalene-diazonium sulphate was stirred into an ice-cold aqueous solution of potassium iodide (20 g.). It crystallised from ethanol in very pale pink plates, m. p. 95° (0·1380 G. gives 0·1730 g. AgBr + AgI. $C_{10}H_6BrI$ requires 0·1750 g.).

3-*Bromonaphthalene*-2-*azo*-*β*-*naphthol* (0·9 g.) was prepared by stirring a glacial acetic acid solution of 3-bromo-2-naphthalene-diazonium sulphate (from 3-bromo-2-naphthylamine, 0·6 g.) into a solution of β-naphthol (0·4 g.) in 20% aqueous sodium hydroxide (85 c.c.) containing crushed ice (20 c.c.). It crystallised from acetic acid in crimson needles having a metallic lustre, m. p. 185°, which gave a claret colour with concentrated sulphuric acid changing to scarlet on dilution (Found : Br, 21·0. $C_{20}H_{13}ON_2Br$ requires Br, 21·2%).

3-Nitro-2-naphthylamine, prepared by the sodium sulphide reduction of 2 : 3-dinitronaphthalene, crystallised from ligroin in clusters of scarlet needles, m. p. 140° (Hodgson and Turner, *loc. cit.*, give m. p. 86·5°) (Found: N, 15·0. Calc. for $C_{10}H_8O_2N_2$: N, 14·9%).

3-*Chloro*-2-*nitronaphthalene*, prepared by the Sandmeyer decomposition of 3-nitro-2-naphthalenediazonium sulphate with acid cuprous chloride, crystallised from ethanol in brownish needles, m. p. 94·5° (Hodgson and Elliott, *loc. cit.*, m. p. 94·5°) (Found : N, 17·0. Calc. for $C_{10}H_2O_2NCl$: N, 16·8%).

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