# II.—*Preparation of 1-Halogeno-2-nitronaphthalenes and 2-Nitronaphthalene.*

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2-NITRO-1-NAPHTHYLAMINE is readily obtained from 2-nitro-1-naphthol, which is itself best prepared by the oxidation of 2-nitroso-1-naphthol (Hodgson and Kilner, J., 1924, **125**, 807). For the preparation of large quantities of 4-nitro-1-naphthylamine Morgan and Micklethwait's modification (J., 1905, **87**, 928) of Lellmann and Remy's method is serviceable.

Hydrolysis of aceto-1-nitro-β-naphthalide proceeds better with acid than with alcoholic potassium hydroxide (Liebermann and Jacobson, *Annalen*, 1882, **211**, 44), which produces a substantial quantity of 1-nitro-2-naphthol.

By very slow decomposition in the cold in presence of cuprous chloride and concentrated hydrochloric acid, diazotised 2-nitro-1-naphthylamine gives a good yield of 1-*chloro*-2-*nitronaphthalene*. Under similar conditions, only poor yields of the corresponding *bromo*- and *iodo*-compounds are obtained, which may be due to the preferential formation of naphthalene-1-diazo-2-oxide (compare Friedländer, *Ber*, 1895, **28**, 1951; Morgan and Evens, J., 1919, **115**, 1126). Vesely's electrolytic method (*Ber*., 1905, **38**, 136) proved unsuitable for the preparation of 1-chloro-2-nitronaphthalene.

These substances all have an extremely irritating action on the skin.

## EXPERIMENTAL.

2-*Nitro*-1-*naphthylamine*.—A finely powdered mixture of 2-nitro-1-naphthol (5 g.) and ammonium carbonate (3 g.) is made into a paste with concentrated ammonia (10 c.c.) and water (6 c.c.), and heated in a sealed tube at 120—130° for 6 hours. The product when cold is pulverised, and boiled with 200 c.c. of water, aqueous ammonia being occasionally added. The solution, containing the ammonium salt of unchanged 2-nitro-1-naphthol (0·31 g.), is filtered and the solid is dried and extracted with boiling alcohol (150 c.c.).

The extract on evaporation leaves 2-nitro-1-naphthylamine (3·8 g.), which melts at 141°, and at 144° after recrystallisation from alcohol (Lellmann and Remy, *Ber.*, 1886, **19**, 797; 1887, **20**, 872, give m. p. 144°). The substance insoluble in alcohol (about 0·52 g.) does not melt at a high temperature and is probably 2 : 2′-dinitrodinaphthylamine (Found: N, 12·0. $C_{20}H_{13}O_4N_3$ requires N, 11·7%). An experiment made in an autoclave produced 16 g. of 2-nitro-1-naphthylamine and 1·3 g. of insoluble material from 20 g. of 2-nitro-1-naphthol, 1·8 g. of which were recovered.

4-*Nitro*-1-*naphthylamine.*—Experiments similar to the above carried out with 4-nitro-1-naphthol indicated an optimum reaction temperature between 140° and 160°. The quantities of 4-nitro-1-naphthylamine, material insoluble in alcohol, and recovered 4-nitro-1-naphthol, respectively, were : (at 120—130°) 0·5 g., ——, and 6·8 g. from 8 g.; (at 140°) 2·82 g., 0·24 g., and 1·73 g. from 5 g.; (at 160—165°) 2·94 g., 1·43 g., and 0·2 g. from 5 g. of 4-nitro-1-naphthol. The nitronaphthylamine obtained at 140° melted at 182°, and at 191° after crystallising once from alcohol.

1-*Nitro*-2-*naphthylamine.*—A mixture of β-naphthylamine * (1 part), 50% acetic acid (5 parts), and acetic anhydride (1 part) is boiled under reflux for 1 hour; on cooling, aceto-β-naphthalide separates in flaky crystals. This product (200 g.) is added in four equal portions to cold glacial acetic acid (250 c.c.), into which, after each of the first three additions, 70% nitric acid (15 c.c.) is run during 1 hour, the temperature being kept at 8—10°. This procedure obviates the stiffening of the reaction mixture which renders Liebermann and Jacobson's process (*loc. cit.*) almost unworkable. After the last addition of aceto-β-naphthalide, 25 c.c. of nitric acid are added to the mixture, which is then kept for 2 days. The orange-yellow aceto-1-nitro-β-naphthalide that has separated is filtered off and washed with ether (yield 170 g.).

Hydrolysis is effected by boiling a solution of the product (125 g.) in alcohol (500 c.c.) with concentrated hydrochloric acid (125 c.c.) for 4 hours; the treatment is repeated if necessary. The mixture is then poured into 4 litres of cold water and the crude 1-nitro-2-naphthylamine filtered off, dried, and recrystallised from twice its weight of hot alcohol; m. p. 122° (Atterberg gives m. p. 124—125°, and Meldola, 126—127°) (Found : N, 15·0. Calc., 14·9%).

1-*Chloro*-2-*nitronaphthalene.*—Five grams of sieved 2-nitro-1-naphthylamine are warmed with 30 c.c. of a mixture of 98% sulphuric acid (3 vols.) and water (1 vol.) (*i.e.*, $H_2SO_4,H_2O$). The solution thus obtained is cooled to 0°, stirred, and solid sodium

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* Pinnow's directions (*Ber.*, 1900, **33**, 417) for acetylating α-naphthylamine give an unsatisfactory result in the case of β-naphthylamine.

nitrite (3—4 g.) gradually added, the temperature being kept below 5°. The diazo-solution is added carefully to a cooled solution of cuprous chloride (5 g.) in concentrated hydrochloric acid (40 c.c.). After 12 hours, the solid is filtered off, dried, and extracted with hot alcohol (50 c.c.). The extract is poured into 1% aqueous sodium hydroxide (100 c.c.), which dissolves any 2-nitro-1-naphthol present. The precipitate is filtered off, washed, and distilled with superheated steam. The solid (2·5 g.) in the distillate, after two crystallisations from alcohol, forms long, pale yellow needles, m. p. 76° (Found: N, 7·1; Cl, 16·7. $C_{10}H_6O_2NCl$ requires N, 6·7; Cl, 17·1%). 1-Chloro-2-nitronaphthalene does not depress the melting point of 2-nitro-1-naphthol.

1-*Bromo*-2-*nitronaphthalene*.—The above procedure was repeated, except that the Sandmeyer reaction was carried out in a cooled mixture of crystallised copper sulphate (5·4 g.), copper bronze (1·4 g.), sodium bromide (15 g.), and water (40 g.). The solid obtained (0·95 g.) crystallised from alcohol in stout, bright yellow needles, m. p. 97° (Found: N, 5·8; Br, 31·5. $C_{10}H_6O_2NBr$ requires N, 5·55; Br, 31·7%).

1-*Iodo*-2-*nitronaphthalene*.—The Sandmeyer reagent in this case was potassium iodide (6 g.) in water (50 c.c.). The solid product was treated with sodium bisulphite solution to remove iodine, and crystallised from alcohol in pale yellow plates, m. p. 111° (yield 1·9 g.) (Found: I, 42·7. $C_{10}H_6O_2NI$ requires I, 42·4%).

2-*Chloro*-1-*nitronaphthalene*.—1-Nitro-2-naphthylamine (5 g.) was diazotised according to Friedländer and Littner (*Ber.*, 1915, **48**, 330), and from the resulting solution 1 g. of 2-chloro-1-nitronaphthalene was obtained.

2-*Nitronaphthalene*.—A mixture of 2-nitro-1-naphthylamine (4·2 g.), alcohol (12 c.c.), and concentrated sulphuric acid (3 c.c.) was cooled to 0°, 3·4 c.c. of aqueous sodium nitrite (50 g. in 100 c.c. of solution) were added during 30 minutes, and the whole was kept in the cold for 4 hours. It was then gradually heated to the boiling point during 5 hours, boiled for 2 hours, poured into cold water (300 c.c.), 20% aqueous sodium hydroxide (20 c.c.) was added, and the mixture was steam-distilled. The pure 2-nitronaphthalene in the distillate solidified in yellow crystals (1·24 g.) with a cinnamon-like odour, m. p. 79° (Found: N, 8·2. Calc., N, 8·1%).

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