

**373. The 3-Halogeno-1-nitro-, -1-amino-, and -1-hydroxy-naphthalenes.**

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THE preparation of the 3-chloro-, 3-bromo-, and 3-iodo-derivatives of  $\alpha$ -nitronaphthalene,  $\alpha$ -naphthylamine, and  $\alpha$ -naphthol has been rendered possible by the availability of 4-nitro-1-naphthylamine (Hodgson and Walker, J., 1933, 1205) and by the new method for the diazotisation of nitro-amines (*ibid.*, p. 1620). Most of the reactions described proceed normally and give the anticipated products in excellent yields. During the acid hydrolysis of 2-chloro-4-nitroaceto- $\alpha$ -naphthalide, about 5% of the chlorine was removed, thereby showing the labile character of its attachment under these conditions. Direct chlorination of 4-nitro-1-naphthylamine resulted in a very poor yield of the 2-chloro-derivative, whereas chlorination of the acetylated amine afforded a 95% yield.

Since all the products could be obtained from the *mercuriacetate* of 4-nitro-1-naphthylamine, it follows that the mercuriacetate group is in position 2 and that the reactions described are homonuclear.

*Preparation of 3-Chloro-1-nitronaphthalene.*—4-Nitroaceto- $\alpha$ -naphthalide (10 g.), dissolved in glacial acetic acid (50 c.c.), was treated at 100° with chlorine. The crystals that separated after 10 minutes were removed and chlorine was again passed into the filtrate, producing a second crop (total yield, 11 g.; 95%). The 2-chloro-4-nitroaceto- $\alpha$ -naphthalide, recrystallised from glacial acetic acid, formed fine cream needles, m. p. 231° (Found: Cl, 13.2.  $C_{12}H_9O_3N_2Cl$  requires Cl, 13.4%). When it was boiled with 20% aqueous sodium hydroxide, a flocculent orange precipitate of sodium 2-chloro-4-nitro- $\alpha$ -naphthoxide was obtained; this crystallised in orange-red needles from water, and on acidification gave 2-chloro-4-nitro- $\alpha$ -naphthol, which crystallised from 90% formic acid in pale yellow micro-plates, m. p. 231° (Found: Cl, 15.7.  $C_{10}H_6O_3NCl$  requires Cl, 15.9%).

2-Chloro-4-nitroaceto- $\alpha$ -naphthalide (25 g.) was boiled under reflux for 10 hours with 50% sulphuric acid (200 c.c.) and ethyl alcohol (200 c.c.); complete solution never occurred. The deep yellow plates of 2-chloro-4-nitro-1-naphthylamine were filtered off after cooling (20 g., m. p. 240°) and recrystallised from alcohol and from nitrobenzene, being obtained as bright yellow needles, m. p. 249° (Found: Cl, 15.8.  $C_{10}H_7O_2N_2Cl$  requires Cl, 15.9%). The mother-liquor from the hydrolysis, on dilution with water, afforded 1 g. of 4-nitro-1-naphthylamine.

A solution of 2-chloro-4-nitro-1-naphthylamine (5 g.) in hot glacial acetic acid (75 c.c.) was chilled to give a fine crystalline suspension and added gradually to a well-stirred solution of

sodium nitrite (15 g.) in concentrated sulphuric acid (60 c.c.) below 20°. The mixture was poured into ethyl alcohol (200 c.c.) and heated on the water-bath for 2½ hours, ethyl acetate, acetaldehyde, and the excess of alcohol distilling away. On cooling, a mixture of 3-chloro-1-nitronaphthalene and sodium sulphate separated, which was washed with water; the residue (16.8 g., m. p. 94°) crystallised from 90% formic acid or nitrobenzene in fine greenish-brown needles, m. p. 105° (Found: Cl, 16.9.  $C_{10}H_7O_2NCl$  requires Cl, 17.1%).

*Preparation of 3-Bromo- and 3-Iodo-1-nitronaphthalenes.*—4-Nitro-1-naphthylamine (50 g. in 300 c.c. of dry nitrobenzene) was treated gradually at room temperature with bromine (10 c.c. in 50 c.c. of nitrobenzene). The hydrobromide of 2-bromo-4-nitro-1-naphthylamine separated as a white solid, which was washed with and crystallised from dry nitrobenzene; no m. p. (Found: HBr, 23.3.  $C_{10}H_7O_2N_2Br$ , HBr requires HBr, 23.3%). On trituration with water, 2-bromo-4-nitro-1-naphthylamine was liberated (25 g.); this crystallised from glacial acetic acid or 90% formic acid in deep yellow needles, m. p. 250° (Found: Br, 29.8.  $C_{10}H_7O_2N_2Br$  requires Br, 30.0%).

4-Nitro-1-naphthylamine (10 g.), dissolved in boiling glacial acetic acid (180 c.c.), was treated gradually with a hot solution of mercuric acetate (17 g.) in glacial acetic acid (30 c.c.), and the mixture subsequently heated on the water-bath for 45 minutes. The copious heavy precipitate of the mercuriacetate, which was filtered off after cooling, was washed with glacial acetic acid; it crystallised from this solvent in orange-yellow needles, which do not melt (Found: Hg, 44.5.  $C_{12}H_{10}O_4N_2Hg$  requires Hg, 44.9%). Treatment of separate portions with hydrochloric, hydrobromic, and hydriodic acid, and with sodium hydroxide gave respectively: the mercurichloride, which crystallised from glacial acetic acid in fine orange-red needles, m. p. 244° (decomp.) (Found: Hg, 47.1.  $C_{10}H_7O_2N_2ClHg$  requires Hg, 47.4%); the mercuribromide, yellowish-red needles from glacial acetic acid, m. p. 249° (decomp.) (Found: Hg, 42.5.  $C_{10}H_7O_2N_2BrHg$  requires Hg, 42.9%); the mercuriiodide, deep red, prismatic needles from glacial acetic acid, m. p. 259° (decomp.) (Found: Hg, 38.6.  $C_{10}H_7O_2N_2IHg$  requires Hg, 39.0%); and the mercurihydroxide, which crystallised from glacial acetic acid in very deep red prisms, that do not melt (Found: Hg, 49.2.  $C_{10}H_8O_3N_2Hg$  requires Hg, 49.6%).

When an aqueous suspension of the mercuriacetate above (5 g.) was shaken with a solution of bromine (0.6 c.c.) in aqueous potassium bromide, 2-bromo-4-nitro-1-naphthylamine was formed. Similarly, treatment with chlorine gave 2-chloro-4-nitro-1-naphthylamine.

3-Bromo-1-nitronaphthalene, formed when 2-bromo-4-nitro-1-naphthylamine was submitted to the deamination procedure employed for the chloro-analogue, crystallised from 90% formic acid in grey-white needles, m. p. 101° (Found: Br, 31.6. Calc. for  $C_{10}H_6O_2NBr$ : Br, 31.7%). Veselý and Chudozilov (*Chem. Listy*, 1925, 19, 260) give m. p. 97–98°.

2-Iodo-4-nitro-1-naphthylamine was obtained by treating the mercuriacetate above (5 g.) with a solution of iodine (2.84 g.) in aqueous potassium iodide and heating the mixture on the water-bath for 30 minutes; the solid was then filtered off, washed with concentrated aqueous potassium iodide and with water, and crystallised from nitrobenzene, forming deep canary-yellow plates, m. p. 234° (Found: I, 40.2. Calc. for  $C_{10}H_7O_2N_2I$ : I, 40.4%). 3-Iodo-1-nitronaphthalene, obtained from the preceding amine by deamination, crystallised from 90% formic acid in fine greenish-yellow needles, m. p. 108° (Found: I, 42.2. Calc. for  $C_{10}H_6O_2NI$ : I, 42.5%). Cumming and Howie (J., 1931, 3176) also give m. p. 234° and 108° for these two compounds.

*Preparation of 3-Chloro-, 3-Bromo-, and 3-Iodo-1-naphthylamine.*—A mixture of 3-chloro-1-nitrobenzene (5 g.), tin (6 g.), and concentrated hydrochloric acid (18 c.c.; *d* 1.16) was heated on the water-bath until the tin had disappeared. The solution, filtered hot, deposited, on cooling, the hydrochloride of 3-chloro-1-naphthylamine in buff-brown crystals, m. p. 219° (Found: Cl, 33.0.  $C_{10}H_8NCl$ , HCl requires Cl, 33.2%). This salt on basification gave 3-chloro-1-naphthylamine which crystallised from alcohol in small colourless needles, m. p. 62° (Found: Cl, 19.9.  $C_{10}H_8NCl$  requires Cl, 20.0%). 3-Chloroaceto- $\alpha$ -naphthalide crystallised from glacial acetic acid in colourless needles, m. p. 197° (Found: Cl, 16.0.  $C_{12}H_{10}ONCl$  requires Cl, 16.2%), and 3-chlorobenzo- $\alpha$ -naphthalide from 90% formic acid in almost colourless prisms, m. p. 162° (Found: Cl, 12.5.  $C_{17}H_{12}ONCl$  requires Cl, 12.6%). 1:3-Dichloronaphthalene, obtained from the base by the Sandmeyer reaction, crystallised from alcohol in colourless needles, m. p. 61.5° (Found: Cl, 35.9. Calc.: Cl, 36.0%).

3-Bromo-1-naphthylamine, obtained by the same procedure as the chloro-analogue, crystallised from alcohol in colourless needles, m. p. 70° (Found: Br, 35.8.  $C_{10}H_8NBr$  requires Br, 36.0%). The hydrochloride formed colourless micro-plates (from hydrochloric acid), m. p. 247° (Found: HCl, 14.0.  $C_{10}H_8NBr$ , HCl requires HCl, 14.1%); 3-bromoaceto- $\alpha$ -naphthalide, colourless needles (from glacial acetic acid), m. p. 174° (Found: Br, 30.2.  $C_{12}H_{10}ONBr$  requires Br, 30.3%);

and 3-bromobenzo- $\alpha$ -naphthalide, colourless needles (from 90% formic acid), m. p. 166° (Found : Br, 24.4.  $C_{17}H_{12}ONBr$  requires Br, 24.5%).

A mixture of 3-iodo-1-nitronaphthalene (2 g.), stannous chloride crystals (16 g.), concentrated hydrochloric acid (20 c.c.), and alcohol (5 c.c.) was heated, at first cautiously, and then for 30 minutes on the water-bath with further addition of acid (10 c.c.). On cooling, the *hydrochloride* of 3-iodo-1-naphthylamine separated in needles, m. p. 238° (Found : HCl, 12.0.  $C_{10}H_8NI, HCl$  requires HCl, 11.9%). This product on basification gave 3-iodo-1-naphthylamine, which crystallised from alcohol in colourless needles, m. p. 84° (Found : I, 46.9.  $C_{10}H_8NI$  requires I, 47.2%). 3-Iodoaceto- $\alpha$ -naphthalide crystallised from glacial acetic acid in colourless prisms, m. p. 207° (Found : I, 40.5.  $C_{12}H_{10}ONI$  requires I, 40.8%), and 3-iodobenzo- $\alpha$ -naphthalide from 90% formic acid in colourless needles, m. p. 174° (Found : I, 33.9.  $C_{17}H_{12}ONI$  requires I, 34.0%).

*Preparation of 3-Chloro-, 3-Bromo-, and 3-Iodo-1-naphthol.*—A solution of 3-chloro-1-naphthylamine (2 g.) in glacial acetic acid (25 c.c.) was diazotised by addition to a solution of sodium nitrite (1 g.) in concentrated sulphuric acid (5 c.c.). After destruction of the excess of nitrous acid by means of urea, the diazo-solution was subjected to the standard decomposition-steam distillation process (Hodgson, E.P., 200,714). From the aqueous steam-distillate, 3-chloro-1-naphthol separated in brownish needles, and the dissolved portion was recovered by benzene extraction; recrystallisation from benzene, alcohol, or 80% aqueous acetic acid gave cream-coloured feathery needles, m. p. 143° (Franzen and Stäuble, *J. pr. Chem.*, 1921, **103**, 352, give m. p. 134—135°) (Found : Cl, 19.8. Calc. for  $C_{10}H_7OCl$  : Cl, 19.9%), soluble in aqueous caustic alkalis and thence combining with diazonium salts. Addition of bromine water to the above solution gave 3-chloro-2 : 4-dibromo-1-naphthol, which crystallised from 90% formic acid in almost colourless (yellowish) prisms, m. p. 112° (Found : Cl + Br, 57.8.  $C_{10}H_5OClBr_2$  requires Cl + Br, 58.1%).

3-Bromo-1-naphthol, similarly obtained, crystallised from benzene, alcohol, or 80% acetic acid in cream-coloured needles, m. p. 61° (Found : Br, 35.8.  $C_{10}H_7OBr$  requires Br, 35.9%), and on treatment with bromine water gave 2 : 3 : 4-tribromo-1-naphthol, which crystallised from 90% formic acid in yellowish needles, m. p. 133° (Found : Br, 62.9.  $C_{10}H_5OBr_3$  requires Br, 63.0%).

3-Iodo-1-naphthol, also similarly obtained, crystallised from alcohol in pale yellow needles, m. p. 119° (Found : I, 46.8.  $C_{10}H_7OI$  requires I, 47.0%), and when treated with bromine water gave 2 : 4-dibromo-3-iodo-1-naphthol, which crystallised from 90% formic acid in yellowish needles, m. p. 191° (Found : Br + I, 66.8.  $C_{10}H_5OBr_2I$  requires Br + I, 67.1%).

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