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 α-nitronaphthalene, α-naphthylamine, and α-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-α-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-α-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-α-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-α-naphthoxide was obtained; this crystallised in orange-red needles from water, and on acidification gave *2-chloro-4-nitro-α-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-α-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. $C_{10}H_6O_2NCl$ 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 *mercuri-iodide*, 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*-α-*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*-α-*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*-α-*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-α-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-α-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-α-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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