148. *The Preparation of Some Halogenonaphthylamines, Dihalogenonaphthalenes, 2-Bromo-1-naphthol, and Related Derivatives.*

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The facile reduction of halogenonitronaphthalenes by means of iron in neutral environment and in presence of ferrous ammonium (or ferrous) sulphate has facilitated the preparation of halogenonaphthylamines in excellent yield. Many derivatives of these amines are also described, together with 2-bromo-1-naphthol.

The ready diazotisation of nitronaphthylamines by Hodgson and Walker's procedure (J., 1933, 1620), and the prevention of diazo-oxide formation by working with the minimum of water present in the subsequent Sandmeyer reaction, has enabled a number of halogenonitro-compounds to be obtained which were formerly inaccessible, and Hodgson and Marsden's reduction method (this vol., p. 398) has brought about their conversion into the respective amines in almost quantitative yield. By these simplified processes the risk of side reactions has been reduced to a minimum. In particular, we now report the preparation of the 2-halogeno-1- and 4-halogeno-2-naphthylamines, from which several new 1 : 2- and 1 : 3-dihalogenonaphthalenes have been made, together with 2-bromo-1-naphthol and many relevant derivatives.

It is noteworthy that the m. p.'s of the 4-halogeno-2-naphthylamines show a gradual rise in the sequence Cl < Br < I but are all considerably lower than the m. p. of 2-naphthylamine; on the other hand, the m. p.'s of the isomeric 3-halogeno-1-naphthylamines exhibit a gradual rise in the sequence Cl < Br < I, being above the m. p. of 1-naphthylamine. These sequences indicate, respectively, retardation and facilitation by the halogen in 4-position of the resonance of 2-naphthylamine into the 1 : 2- and the 2 : 6-ionic resonance structures (cf. Pauling, " Nature of the Chemical Bond," Cornell Univ. Press, 1940, p. 152).

Experimental.

General Method for Reduction of 2-Halogeno-1-nitronaphthalenes.—The halogenonitro-compound (5 g.) was boiled under reflux with iron (pin dust, 10 g.) and water (100 c.c.) containing ferrous ammonium (or ferrous) sulphate (1 g.) for 1½ hours, and the mixture then steam-distilled or extracted with a solvent. 2-Chloro-1-naphthylamine (4 g.) was thus obtained in colourless needles (from alcohol), m. p. 60° (Cleve, *Ber.*, 1887, **20**, 450, and Charrier and Ferreri, *Gazzetta*, 1911, **41**, II, 726, give m. p. 56°) (Found : N, 8·0. Calc. : N, 7·9%), volatile in steam (3 g. per l.). 2-Chloroaceto-1-naphthalide crystallised from glacial acetic acid in glistening, white, rectangular plates, m. p. 192° (Charrier and Ferreri, *loc. cit.*, give m. p. 191°) (Found : N, 6·5. Calc. : N, 6·4%). *2-Chlorobenzo-1-naphthalide*, prepared by the Schotten–Baumann reaction in acetone, crystallised from alcohol (charcoal) in glistening, rectangular plates, m. p. 158° (Found : N, 5·2. $C_{17}H_{12}ONCl$ requires N, 5·0%).

2-Bromo-1-naphthylamine (yield, 4·1 g.) crystallised from aqueous alcohol in glistening needles, m. p. 65° (Found : N, 6·4. $C_{10}H_8NBr$ requires N, 6·3%), volatile in steam (2 g. per l.). Its *benzoyl* derivative, prepared as above, crystallised from aqueous alcohol in rosettes of colourless needles, m. p. 179° (Found : N, 4·3. $C_{17}H_{12}ONBr$ requires N, 4·3%), and its *acetyl* derivative crystallised from glacial acetic acid in colourless plates, m. p. 198° (Found : N, 5·4. $C_{12}H_{10}ONBr$ requires N, 5·3%).

2-Iodo-1-naphthylamine crystallised from aqueous alcohol in very pale straw-coloured needles, m. p. 85° (Found : N, 5·3. $C_{10}H_8NI$ requires N, 5·2%), which darkened on keeping; volatility in steam, 0·8 g. per l. The *hydrochloride* was obtained in colourless needles by passing dry hydrogen chloride into a benzene solution of the amine (Found : HCl, 11·6. $C_{10}H_8NI,HCl$ requires HCl, 11·5%). The acetyl derivative, prepared (m. p. *ca.* 230°) by addition of acetyl chloride to a benzene solution of the amine, decomposed with separation of iodine on attempted recrystallisation. The *benzoyl* derivative, prepared by the Schotten–Baumann reaction in acetone, crystallised from alcohol (charcoal) in colourless micro-needles, m. p. 212° (Found : N, 4·0. $C_{17}H_{12}ONI$ requires N, 3·8%).

Some Derivatives of 3-Nitro-1-naphthylamine.—*3-Nitro-1-phthalimidonaphthalene* was prepared by refluxing for 2 hours a solution of the amine (1·5 g.) and phthalic anhydride (1·3 g.) in tetralin (7 c.c.), the water formed being allowed to escape. On cooling, the phthalimide crystallised out overnight; it was dried at the pump as far as possible, and coloured impurity removed by xylene extraction (Soxhlet); it then crystallised from tetralin in rhombic plates, m. p. above 300° (Found : N, 8·8. $C_{18}H_{10}O_4N_2$ requires N, 8·8%). *3-Nitro-1-succinimidonaphthalene* was similarly prepared (yield, 1·1 g.) from the amine (1·9 g.) and succinic anhydride (1 g.); it crystallised from tetralin in rhombic plates, m. p. above 300° (Found : N, 10·4. $C_{14}H_{10}O_4N_2$ requires N, 10·4%).

3-Nitro-NN-bistoluene-p-sulphonyl-1-naphthylamine was obtained when the amine (1·5 g.) and toluene-*p*-sulphonyl chloride (4·0 g.) were ground together, and the mixture heated on the water-bath for 2 hours with water (30 c.c.) and acetone (7 c.c.), with addition of sodium carbonate when necessary to keep it alkaline. The crude naphthalide was separated and extracted with 4% aqueous sodium hydroxide (200 c.c.) at 100° for 30 minutes to remove any monosulphonyl compound. The insoluble disulphonyl compound (2·5 g.) crystallised from acetone in pale buff, rectangular plates which sintered at 249°, m. p. 257° (Found : N, 5·8. $C_{24}H_{20}O_6N_2S_2$ requires N, 5·6%).

3-Nitro-NN-diacetyl-1-naphthylamine was obtained when the monoacetyl compound (0·5 g.) was refluxed for 4 hours with a mixture of acetyl chloride (7 c.c.) and acetic anhydride (7 c.c.); the filtered solution was concentrated and deposited a greyish-white, crystalline powder; fractional crystallisation from glacial acetic acid afforded first the unchanged acetyl compound, and then the diacetyl compound in white, glistening needles, m. p. 145° (Found : N, 10·4. $C_{14}H_{12}O_4N_2$ requires N, 10·3%). Acetic anhydride alone did not effect the further acetylation. *3-Nitro-NN-dibenzoyl-1-naphthylamine* was formed when the monobenzoyl compound (1·5 g.) and benzoyl chloride (10 c.c. containing 1 c.c. of acetic anhydride) were heated together in a sealed tube for 6 hours at 200°; the product was triturated with aqueous sodium carbonate, then crystallised once from glacial acetic and twice from ethyl alcohol, the dibenzoyl derivative being obtained in yellow plates, m. p. 205° (Found : N, 7·4. $C_{24}H_{16}O_4N_2$ requires N, 7·1%).

3-Nitronaphthaleneazo-β-naphthol was made by the addition below 15° of 3-nitronaphthalene-1-diazonium sulphate (prepared from the amine by Hodgson and Walker's procedure, *loc. cit.*) to alkaline β-naphthol; it crystallised from glacial acetic acid in maroon, micro-needles, m. p. 215° (Found : N, 12·0. $C_{20}H_{13}O_3N_3$ requires N, 12·2%), that gave a deep purple colour with concentrated sulphuric acid, changing to scarlet on dilution.

4-Halogeno-2-nitronaphthalenes and -2-naphthylamines.—The nitro-compounds were obtained more conveniently from 3-nitro-1-naphthylamine than by Hodgson and Elliott's procedure (J., 1935, 1851), and were converted by the above

iron reduction method into the corresponding naphthylamines, 6 g. of nitro-compound yielding *ca.* 3·5 g. of amine. 4-Chloro-2-nitronaphthalene crystallised from alcohol in felted, lemon needles, m. p. 129° (Hodgson and Elliott, *loc. cit.*, give m. p. 127°). *4-Chlorobenzo-2-naphthalide*, prepared by the Schotten–Baumann reaction in acetone, crystallised from alcohol in colourless plates, m. p. 135° (Found : N, 5·3. $C_{17}H_{12}ONCl$ requires N, 5·0%), and the *bromo*-analogue similarly formed buff micro-plates, m. p. 142° (Found : N, 4·3. $C_{17}H_{12}ONBr$ requires N, 4·3%).

Some Dihalogenonaphthalenes, and 2-Bromo-1-naphthol.—*2-Bromo-1-iodonaphthalene.* 2-Bromo-1-naphthylamine (2·2 g.) was suspended as the finely divided sulphate in sulphuric acid (3 c.c., *d* 1·84) and water (15 c.c.) and stirred below 10° with aqueous sodium nitrite (0·7 g.). Excess of nitrous acid was removed by urea, and the solution was then stirred into saturated aqueous potassium iodide (5 g.) below 15°. After being stirred for 4 hours, the mixture was kept overnight and then poured on ice, the precipitate washed with sodium thiosulphate, extracted with ether, the extract washed successively with 5% aqueous sodium hydroxide and thiosulphate, the ether removed from the extract, and the residue crystallised twice from ethyl alcohol, *2-bromo-1-iodonaphthalene* being obtained in very pale flesh-coloured plates, m. p. 65° (0·0486 G. gave 0·0630 g. of AgBr + AgI. $C_{10}H_6BrI$ requires 0·0617 g.).

2-Bromo-1-naphthol. 2-Bromo-1-naphthylamine sulphate (3·3 g.) was diazotised as above, excess of nitrous acid removed, and the filtered solution added dropwise to boiling 50% aqueous sulphuric acid through which steam was passing (cf. Hodgson, B.P. 200,714); the colourless needles of *2-bromo-1-naphthol* (0·5 g.) which separated from the steam-distillate on cooling (ice) were removed and then crystallised from light petroleum, forming rosettes of colourless needles, m. p. 45° (Found : Br, 35·6. $C_{10}H_7OBr$ requires Br, 35·9%). *4-Benzeneazo-2-bromo-1-naphthol* crystallised from acetone in red micro-needles, m. p. 150° (Found : Br, 24·1. $C_{16}H_{11}ON_2Br$ requires Br, 24·5%), which gave a fine purple colour with concentrated sulphuric acid, turning scarlet on dilution.

1-Chloro-3-bromonaphthalene. 4-Chloro-2-naphthylamine (1·5 g.) was diazotised as for 2-nitro-1-naphthylamine (Hodgson and Walker, *loc. cit.*), and the solution stirred into one of cuprous bromide (2·5 g.) in hydrobromic acid (5 c.c., *d* 1·7); the mixture was poured on ice, the yellowish-brown precipitate of *1-chloro-3-bromonaphthalene* removed, washed, dried, dissolved in benzene, the solution filtered, extracted with 5% aqueous sodium hydroxide, and the benzene layer removed, washed, and dried; on evaporation of the benzene at room temperature, 1-chloro-3-bromonaphthalene crystallised out; it recrystallised from methyl alcohol containing a little acetone in long, colourless needles, m. p. 60° (0·0864 G. gave 0·1176 g. of AgCl + AgBr. $C_{10}H_6ClBr$ requires 0·1186 g.).

1-Chloro-3-iodonaphthalene was formed when the diazonium solution, prepared as above, was stirred into a saturated solution of potassium iodide (5 g.), and was purified as for the preceding compound except for an additional extraction of the benzene solution with aqueous sodium thiosulphate; it crystallised from methyl alcohol containing acetone in rosettes of large, colourless, sabre-shaped crystals, m. p. 58° (0·0706 G. gave 0·0910 g. of AgCl + AgI. $C_{10}H_6ClI$ requires 0·0924 g.).

3-Chloro-1-bromonaphthalene was prepared from 4-bromo-2-naphthylamine (1·1 g.) by the usual Sandmeyer reaction and purified like its isomeride (above); it crystallised from methyl alcohol containing acetone in fine, colourless needles, m. p. 56° (0·0800 G. gave 0·1090 g. of AgCl + AgBr. $C_{10}H_6ClBr$ requires 0·1100 g.).

1-Bromo-3-iodonaphthalene was prepared like the 2-bromo-1-iodo-isomeride from 4-bromo-2-naphthylamine; it crystallised from ether in long, pink needles, which recrystallised from methyl alcohol containing acetone and ligroin in rosettes of colourless, sagittate crystals, m. p. 65° (0·1224 G. gave 0·1530 g. of AgBr + AgI. $C_{10}H_6BrI$ requires 0·1555 g.).

1 : 3-Di-iodonaphthalene was prepared from 4-iodo-2-naphthylamine as above, and purified by dissolution in benzene with subsequent extraction of the solution by 5% aqueous sodium hydroxide and sodium thiosulphate, after which the extracted benzene was dried and allowed to evaporate slowly at room temperature; the di-iodo-compound was deposited and, after two crystallisations from acetone containing methyl alcohol, it separated from acetone in almost colourless micro-needles, m. p. 76° (Found : I, 66·6. $C_{10}H_6I_2$ requires I, 66·8%).

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

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, May 1st*, 1944.]