289. *Some Reactions of* 8-*Nitro*-1-*naphthylamine and its Derivatives.*

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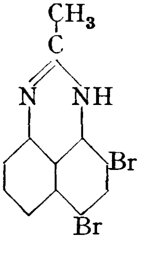
The work now described had for its object the study of the influence of the 8-nitro-group on the reactivity of the nucleus containing the amino-group.

For nitration, 8-nitroaceto-1-naphthalide required nitric acid of *d* 1·5, whereas aceto-1-naphthalide was readily nitrated by acid of *d* 1·4 (Hodgson and Walker, J., 1933, 1209). Further, the nitro-group in the 8-position inhibited nitration in the 2-position, since only 4 : 8-*dinitroaceto*-1-*naphthalide* could be isolated, whereas aceto-1-naphthalide gave a mixture containing considerable amounts of both the 2- and the 4-mononitro-derivative.

Monobromination of 8-nitroaceto-1-naphthalide at 120° in glacial acetic acid in the presence of sodium acetate gave 4-*bromo*-8-*nitroaceto*-1-*naphthalide*, whose constitution was established by hydrolysis and deamination to form 5-bromo-1-nitronaphthalene. Further bromination gave the 2 : 4-*dibromo*-compound, whose constitution was established by hydrolysis to the *base*, conversion of this into 1-*chloro*-2 : 4-*dibromo*-8-*nitronaphthalene*, and, finally, reduction to the amine with subsequent deamination to give 1-*chloro*-2 : 4-*dibromonaphthalene*, identical with a specimen prepared from authentic 2 : 4-dibromo-1-naphthylamine. The retarding influence of the 8-nitro-group was therefore very pronounced, since aceto-1-naphthalide readily reacted with bromine at room temperature to form first the 4-monobromo- and then the 2 : 4-dibromo-derivative (Rother, *Ber.*, 1871, **4**, 850; Meldola, *Ber.*, 1878, **11**, 1906).

Reduction of 2 : 4-dibromo-8-nitroaceto-1-naphthalide with acid stannous chloride in glacial acetic acid solution did not give the anticipated 2 : 4-dibromo-8-aminoaceto-1-naphthalide, since condensation occurred with formation of 7 : 9-*dibromo*-2-*methylperimidine* (inset), which, like methylperimidine itself (Sachs, *Ber.*, 1906, **39**, 3027), was green.



Direct dibromination of 8-nitro-1-naphthylamine gave 2 : 4-dibromo-8-nitro-1-naphthylamine, but attempts at monobromination always resulted in mixtures. This amine readily formed a diacetyl derivative which easily underwent alkaline hydrolysis to give 2 : 4-dibromo-8-nitroaceto-1-naphthalide; this was soluble in aqueous sodium hydroxide, indicating the facile ionisation of the hydrogen atom in the acetamido-group caused by the combined electron-attracting effect of the kationoid nitro-group and bromine atoms.

Experimental.

Nitration of 8-*Nitroaceto*-1-*naphthalide*.—(a) *By nitric acid only.* 8-Nitroaceto-1-naphthalide (10 g.) was added gradually to nitric acid (35 c.c., *d* 1·5) cooled in ice-water, the temperature being kept below 20°. After 5 minutes' stirring, the solution was poured into water (300 c.c.), the precipitate of 4 : 8-*dinitroaceto*-1-*naphthalide* (11·7 g., m. p. 223°) filtered off, washed with water, and dissolved in hot glacial acetic acid, from which it separated on cooling in colourless plates (m. p. 231°) (Found : N, 15·5. $C_{12}H_9O_5N_3$ requires N, 15·3%).

(b) *In glacial acetic acid solution.* The naphthalide (23 g., 0·1 mol.) was added to a solution of nitric acid (4·9 c.c., *d* 1·5) in glacial acetic acid (100 c.c.) at 20°. After 30 minutes' stirring the mixture was heated gradually to 80° and kept at this temperature for 30 minutes; on cooling, the 4 : 8-dinitro-compound (7·7 g., m. p. 227°) crystallised; a further 12·8 g. of cruder material was obtained by diluting the mother-liquor. The product was recrystallised from glacial acetic acid; m. p., and mixed m. p. with product from (a), 231° (Found : N, 15·5%).

4 : 8-*Dinitro*-1-*naphthylamine.*—The above acetyl compound (3·5 g.) was heated under reflux with a mixture of concentrated sulphuric acid (15 c.c.) and water (15 c.c.) until dissolution occurred; on cooling and dilution with water, the base (2·1 g.) was precipitated; it crystallised from glacial acetic acid in orange-brown or light crimson needles, m. p. 193° (uncorr.), the colour varying with the concentration and rate of cooling of the solution (Found : N, 18·2. Calc. for $C_{10}H_7O_4N_3$: N, 18·0%). The m. p. was not raised by further recrystallisation, and no decomposition occurred on melting, the resolidified material melting again at the same temperature (contrast Ullmann and Consanno, *Ber.*, 1902, **35**, 2802, who give m. p. 197°, decomp.); it was very sparingly soluble in boiling ligroin, but rather more soluble in boiling alcohol. The *benzoyl* derivative was obtained from the amine in small yield by the Schotten–Baumann reaction, and was precipitated from its solution in aqueous sodium hydroxide by a current of carbon dioxide; it crystallised from aqueous alcohol in small, yellow, glistening leaflets, m. p. 224° (after softening) (Found : N, 12·7. $C_{17}H_{11}O_5N_3$ requires N, 12·5%). 4 : 8-Dinitro-1-naphthylamine was readily converted by the Sandmeyer reaction into 1-chloro-4 : 8-dinitronaphthalene (identified by m. p. and mixed m. p.) (Found : Cl, 13·9. Calc. : Cl, 14·0%). 4 : 8-*Dinitro*-1-*naphthaleneazo*-β-*naphthol* formed red micro-crystals from glacial acetic acid (Found : N, 14·7. $C_{20}H_{12}O_5N_4$ requires N, 14·4%), which were turned green by alkalis, the red colour being restored by acids.

Monobromination of 8-*Nitroaceto*-1-*naphthalide.*—The naphthalide (23 g., 0·1 mol.) and anhydrous sodium acetate (9 g.) were dissolved in boiling glacial acetic acid (100 c.c.), bromine (5·4 c.c., 5% excess) in glacial acetic acid (50 c.c.) then added, and the mixture boiled under reflux until all the bromine had disappeared (*ca.* 45 minutes). The solution on cooling deposited 4-*bromo*-8-*nitroaceto*-1-*naphthalide* (24 g.), which, crystallised first from glacial acetic acid and then from ligroin (b. p. 120°), formed colourless plates, m. p. 202° (Found: Br, 25·8. $C_{12}H_9O_3N_2Br$ requires Br, 25·9%). The base was obtained by boiling the acetyl compound (24 g.) with a mixture of ethyl alcohol (130 c.c.), concentrated sulphuric acid (50 c.c.), and water (90 c.c.) for 3 hours under reflux. The sulphate, which crystallised from the cooled solution, was filtered off, and basified by trituration with aqueous sodium carbonate; 4-*bromo*-8-*nitro*-1-*naphthylamine* crystallised from ligroin (b. p. 90—100°) as long, slender, deep red needles, m. p. 116° (Found : Br, 30·2. $C_{10}H_7O_2N_2Br$ requires Br, 30·0%), readily soluble in glacial acetic acid, alcohol, and nitrobenzene. The *hydrochloride*, m. p. 185° (after partial dissociation) (Found: Cl + Br, 37·8. $C_{10}H_7O_2N_2Br,HCl$ requires Cl + Br, 38·0%), and *hydrobromide*, m. p. 209° (partial dissociation) (Found : Br, 46·1. $C_{10}H_7O_2N_2Br,HBr$ requires Br, 46·0%), both crystallised from alcohol in colourless needles and were partially hydrolysed by washing with water or exposure to the atmosphere. 4-*Bromo*-8-*nitrobenzo*-1-*naphthalide* crystallised from glacial acetic acid in colourless needles, m. p. 218° (Found : Br, 21·4. $C_{17}H_{11}O_3N_2Br$ requires Br, 21·6%).

1-*Chloro*-4-*bromo*-8-*nitronaphthalene*, prepared from 4-bromo-8-nitro-1-naphthylamine by the Sandmeyer reaction, crystallised from ligroin in pale yellow needles, m. p. 107·5° (Found : Cl + Br, 40·1. $C_{10}H_5O_2NClBr$ requires Cl + Br, 40·3%). The 1 : 4-dibromo-compound, obtained in analogous fashion, crystallised from ligroin in pale yellow needles, m. p. 116° (Jolin, *Bull. Soc. chim.*, 1877, **28**, 515, gives m. p. 116·5°) (Found : Br, 48·3. Calc. : Br, 48·4%). 4-*Bromo*-1-*iodo*-8-*nitronaphthalene* crystallised from ligroin or alcohol in pale yellow needles, m. p. 115·5° (Found : Br + I, 54·6. $C_{10}H_5O_2NBrI$ requires Br + I, 54·8%).

Dibromination of 8-*Nitroaceto*-1-*naphthalide.*—A mixture of the naphthalide (5·8 g.), anhydrous sodium acetate (4 g.), and glacial acetic acid (25 c.c.) was boiled under reflux while bromine (2·7 c.c.) in glacial acetic acid (30 c.c.) was added gradually. The heating was continued until all the bromine had reacted; addition of water to the cooled solution precipitated the 2 : 4-*dibromo*-compound as a pale yellow powder (m. p. *ca.* 190°) which crystallised from glacial acetic acid in almost colourless needles, m. p. 198° (Found : Br, 40·9. $C_{12}H_8O_3N_2Br_2$ requires Br, 41·2%).

Direct Bromination of 8-*Nitro*-1-*naphthylamine.*—A mixture of the base (18·8 g., 0·1 mol.)

and glacial acetic acid (150 c.c.) was liquefied by addition of nitrobenzene (*ca.* 30 c.c.), cooled to 0°, and stirred while a solution of bromine (10·3 c.c.) in glacial acetic acid (50 c.c.) was added gradually. The almost colourless hydrobromide of the 2 : 4-dibromo-compound which separated (and was superficially dissociated by moisture) was filtered off and triturated with aqueous sodium carbonate; 2 : 4-*dibromo*-8-*nitro*-1-*naphthylamine* crystallised from its light red solution in glacial acetic acid as bright crimson, elongated plates (27 g.), m. p. 150° (Found : Br, 45·8. $C_{10}H_6O_2N_2Br_2$ requires Br, 46·2%); it was less soluble in boiling ligroin, in which it formed a yellow solution, than in glacial acetic acid, and was only sparingly soluble in boiling alcohol. The *hydrobromide* had no m. p. and charred gradually on heating (Found : Br, 56·0. $C_{10}H_6O_2N_2Br_2,HBr$ requires Br, 56·2%). Dibromination also readily took place in carbon tetrachloride, chloroform, or nitrobenzene solution; but monobromination could not be effected (see p. 1338).

2 : 4-*Dibromo*-8-*nitrodiaceto*-1-*naphthalide* was prepared by boiling the base with excess of acetic anhydride and 2 or 3 drops of concentrated sulphuric acid for 5 minutes. The product precipitated by water from the cooled solution crystallised from glacial acetic acid in long, slender, colourless needles, m. p. 190° (Found : Br, 37·1. $C_{14}H_{10}O_4N_2Br_2$ requires Br, 37·2%). This diacetyl compound in boiling alcohol was boiled with 20% aqueous sodium hydroxide for 5 minutes after the initially colourless solution had become deep yellow, and addition of dilute hydrochloric acid to the cooled and diluted solution until the yellow colour was discharged then precipitated the monoacetyl compound; crystallised from alcohol or glacial acetic acid, this had m. p. 198°, undepressed when mixed with the dibromination product of 8-nitroaceto-1-naphthalide (Found : Br, 40·8%). 2 : 4-*Dibromo*-8-*nitrobenzo*-1-*naphthalide* crystallised from glacial acetic acid in colourless needles, m. p. 228° (Found : Br, 35·4. $C_{17}H_{10}O_3N_2Br_2$ requires Br, 35·6%).

1-*Chloro*-2 : 4-*dibromo*-8-*nitronaphthalene*.—A solution of 2 : 4-dibromo-8-nitro-1-naphthylamine (5 g.) in boiling glacial acetic acid (20 c.c.) was cooled rapidly to 0° and diazotised by gradual addition to a solution of sodium nitrite (1·5 g., 50% excess) in concentrated sulphuric acid (20 c.c.) at 0—20° (see Hodgson and Walker, J., 1933, 1620). After 10 minutes' stirring, the diazo-solution was added to a cold (15°) solution of cuprous chloride (4 g.) in concentrated hydrochloric acid (30 c.c.), and the precipitate of 1-*chloro*-2 : 4-*dibromo*-8-*nitronaphthalene* (4·8 g.) was filtered off, washed with dilute aqueous ammonia to remove copper compounds, and crystallised from glacial acetic acid (charcoal), giving slender, light yellow needles, m. p. 146° (Found : Cl + Br, 53·8. $C_{10}H_4O_2NClBr_2$ requires Cl + Br, 53·5%), readily soluble in boiling glacial acetic acid, less soluble in boiling ligroin, and very sparingly soluble in boiling alcohol.

1 : 2 : 4-*Tribromo*-8-*nitronaphthalene*.—The diazo-solution, prepared as above from the amine (5 g.), was added to a cold solution of cuprous bromide (6 g.) in concentrated hydrobromic acid (25 c.c.). The precipitate of the 1 : 2 : 4-*tribromo*-compound crystallised from glacial acetic acid (charcoal) in light yellow, flocculent needles, m. p. 133° (Found : Br, 58·4. $C_{10}H_4O_2NBr_3$ requires Br, 58·5%), having similar solubilities to those of the 1-chloro-analogue.

The diazo-solution, prepared as above from the amine, was added to a solution of potassium iodide (2 g. per 3 g. amine) in ice-water. The precipitated 2 : 4-*dibromo*-1-*iodo*-8-*nitronaphthalene* crystallised from glacial acetic acid (charcoal) in light brownish-yellow needles, m. p. 171° (Found : Br + I, 62·6. $C_{10}H_4O_2NBr_2I$ requires Br + I, 62·8%), very sparingly soluble in boiling alcohol.

Some Halogeno-1-*naphthylamines*.—8-*Chloro*-5 : 7-*dibromo*-1-*naphthylamine*. A solution of 1-chloro-2 : 4-dibromo-8-nitronaphthalene (3·5 g.) in alcohol (30 c.c.), to which concentrated hydrochloric acid (2 drops) had been added, was boiled under reflux while iron powder (1·8 g.) was introduced gradually (cf. West, J., 1925, **127**, 494); the mixture was then refluxed for 1 hour, and the liquid rendered just alkaline by means of aqueous sodium carbonate. After 5 minutes' boiling, the liquid was filtered, and the residue extracted again with boiling alcohol (15 c.c.). The combined filtrates were diluted with water until crystallisation commenced, 8-*chloro*-5 : 7-*dibromo*-1-*naphthylamine* separating in colourless needles, m. p. 159° (Found : Cl + Br, 58·2. $C_{10}H_6NClBr_2$ requires Cl + Br, 58·3%); the *picrate* crystallised from alcohol in yellow needles, m. p. 160° (Found : Cl + Br, 34·3. $C_{16}H_9O_7N_4ClBr_2$ requires Cl + Br, 34·7%). The *acetyl* derivative crystallised from aqueous acetic acid or alcohol in colourless prisms, m. p. 227° (Found : Cl + Br, 51·8. $C_{12}H_8ONClBr_2$ requires Cl + Br, 51·8%), and the *benzoyl* derivative crystallised from glacial acetic acid in colourless needles, m. p. 237° (Found : Cl + Br, 44·4. $C_{17}H_{10}ONClBr_2$ requires Cl + Br, 44·4%).

5 : 7 : 8-*Tribromo*-1-*naphthylamine*. The corresponding nitro-compound was reduced by the above method, and the 5 : 7 : 8-*tribromo*-compound crystallised from aqueous alcohol in

colourless needles or elongated plates, m. p. 155° (Found : Br, 62·9. $C_{10}H_6NBr_3$ requires Br, 63·0%); the *picrate* crystallised from alcohol in small yellow needles, m. p. 157—158° (Found : Br, 39·0. $C_{16}H_9O_7N_4Br_3$ requires Br, 39·4%), the *acetyl* derivative (m. p. 232°) from aqueous acetic acid (Found : Br, 57·1. $C_{12}H_8ONBr_3$ requires Br, 56·8%), and the *benzoyl* derivative (m. p. 225°) from glacial acetic acid (Found : Br, 49·4. $C_{17}H_{10}ONBr_3$ requires Br, 49·6%), the last two forming colourless needles.

1-*Chloro*-2 : 4-*dibromonaphthalene*, prepared from 8-chloro-5 : 7-dibromo-1-naphthylamine by elimination of the amino-group by the usual procedure, crystallised from aqueous alcohol in long, slender, colourless needles, m. p. and mixed m. p., with a specimen prepared by the Sandmeyer reaction on the known 2 : 4-dibromo-1-naphthylamine, 100° (Found : Cl + Br, 60·9. $C_{10}H_5ClBr_2$ requires Cl + Br, 61·0%).

2 : 4-*Dibromo*-1 : 8-*naphthylenediamine* was obtained by the reduction (West's method, *loc. cit.*) of 2 : 4-dibromo-8-nitro-1-naphthylamine; it crystallised from 30% aqueous alcohol in colourless elongated plates (turning pink in air), m. p. 110—112° (darkening) (Found : Br, 50·3. $C_{10}H_8N_2Br_2$ requires Br, 50·6%).

Reduction of 2 : 4-*Dibromo*-8-*nitroaceto*-1-*naphthalide*.—(a) A solution of the nitro-compound (2 g.) in glacial acetic acid (25 c.c.) was heated on the water-bath with stannous chloride (7 g.) and concentrated hydrochloric acid (15 c.c.); a heavy precipitate of pale greenish-yellow prisms of the tin double salt of 7 : 9-dibromo-2-methylperimidine separated, which was practically insoluble in boiling dilute hydrochloric or acetic acid. Basification with sodium carbonate gave 7 : 9-*dibromo*-2-*methylperimidine*, which separated from its deep green solution in hot aqueous alcohol (charcoal) in light green micro-needles, m. p. 176—177° (to a deep green liquid) (Found : Br, 46·8. $C_{12}H_8N_2Br_2$ requires Br, 47·0%), sparingly soluble in ligroin (b. p. 100—120°) but readily soluble in acetic acid.

(b) West's method (*loc. cit.*) afforded the same product, m. p. and mixed m. p. 176—177° (Found : Br, 46·7%).

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