

**328.** *Nitrous Acid as a Nitrating and Oxidising Agent. Part III. The Nitration of 4-Dimethylaminoaceto-1-naphthalide, of 4-Chlorodimethyl-1-naphthylamine, and of Dimethyl- $\beta$ -naphthylamine.*

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THE work on the reaction of nitrous acid with aromatic dimethylamines (Hodgson and Kershaw, J., 1930, 277; Hodgson and Crook, J., 1932, 1812) has been extended to analogous naphthalene derivatives in order to determine what influence, if any, the second benzenoid ring has on the course of the reaction.

The reaction of nitrous acid with 4-dimethylaminoaceto-1-naphthalide is different from that with 4-dimethylaminoacetanilide, for, instead of formation of the expected 3-nitro-

derivative, oxidation took place with the formation of  $\alpha$ -naphthaquinone. When the last precipitation of this quinone had been removed, the mother-liquor, after being made alkaline with sodium carbonate, afforded complex coloured products which could not be purified: traces of nitroso- and diazo-compounds also were detected. Nitric acid, at equivalent dilution and entirely free from nitrous acid, did not react with 4-dimethylamino-aceto-1-naphthalide.

4-Chlorodimethyl-1-naphthylamine, however, behaved as anticipated, and 4-chloro-2-nitrodimethyl-1-naphthylamine was practically the only product formed, being obtained in excellent yield and purity; its constitution was established by synthesis from dimethylamine and 1:4-dichloro-2-nitronaphthalene.

Although  $\beta$ -naphthol is readily nitrosated in the  $\alpha$ -position to give 1-nitroso-2-naphthol ( $\beta$ -naphthaquinone-1-oxime), the action of nitrous acid on dimethyl- $\beta$ -naphthylamine is much more complex, 1-nitrodimethyl-2-naphthylamine being formed together with a brown resin, which is insoluble in dilute but soluble in concentrated hydrochloric acid, and two yellow substances, m.p. 80—90° and 145—155°, which have defied purification but are more basic than the 1-nitro-product above, since they are soluble, whereas the latter is insoluble, in very dilute hydrochloric acid. None of the products were nitroso-compounds, and it is suggested that nitration may also have occurred in positions other than 1. The 1-nitrodimethyl-2-naphthylamine was synthesised from dimethylamine and 2-chloro-1-nitronaphthalene.

The second benzenoid nucleus would thus appear to have a definite rôle in the nitrous acid reaction in that oxidation appears to be promoted, but in the case of 4-chlorodimethyl-1-naphthylamine this effect is prevented by the stabilising action of the chlorine atom. Such an effect of the chlorine is found in the cases of 3-chloro-2-, -4-, and -6-aminophenols (Hodgson and Kershaw, J., 1928, 2703), which are very stable compared with the unsubstituted aminophenols.

#### EXPERIMENTAL.

4-Dimethylaminoaceto-1-naphthalide.—An intimate mixture of methyl sulphate (190 c.c.) and  $\alpha$ -naphthylamine (143 g.) was heated on the water-bath for 2 hours and then made alkaline with aqueous sodium hydroxide. The separated oil was treated with acetic anhydride (see Gokhlé and Mason, J., 1930, 1757), and the dimethyl- $\alpha$ -naphthylamine removed by steam distillation. The *picrate* crystallised from alcohol in lemon-yellow needles, m. p. 145° (Found: N, 14.3.  $C_{18}H_{16}O_7N_4$  requires N, 14.0%).

Sulphanilic acid (17.3 g.) was diazotised and the suspension, after treatment with urea and sodium acetate, was poured into a solution of dimethyl- $\alpha$ -naphthylamine (16 c.c.) in glacial acetic acid (200 c.c.) at 0°; 4-*p*-sulphobenzeneazodimethyl- $\alpha$ -naphthylamine separated almost immediately in fine steel-blue needles. The mixture was stirred for 15 minutes, concentrated hydrochloric acid (60 c.c.) and stannous chloride crystals (54.0 g.) added, and the whole heated at 70—80° until the red colour had disappeared; sodium hydroxide was added to the cooled solution until it was strongly alkaline, and the liberated base was extracted with ether. (1) Dry hydrogen chloride precipitated 4-aminodimethyl-1-naphthylamine dihydrochloride from the extract as a sticky mass, which rapidly became crystalline (turning brown in air) (Found: HCl, 27.8.  $C_{12}H_{14}N_2 \cdot 2HCl$  requires HCl, 28.2%). (2) When the extract was treated with acetic anhydride, 4-dimethylaminoaceto-1-naphthalide was formed. It crystallised from alcohol in colourless plates, m.p. 195° (Friedländer and Welms, *Ber.*, 1888, 21, 3124, give m. p. 194—195°) (Found: N, 12.4. Calc.: N, 12.3%). The *picrate* crystallised from alcohol in slender lemon-yellow needles, m. p. 201° (decomp. after softening) (Found: N, 15.5.  $C_{20}H_{10}O_8N_5$  requires N, 15.3%).

4-Chlorodimethyl-1-naphthylamine.—A solution of 4-aminodimethyl-1-naphthylamine dihydrochloride (10.4 g.) in water (100 c.c.) containing concentrated hydrochloric acid (15 c.c.) at 90° was rapidly cooled to 0° and diazotised with sodium nitrite (2.8 g.) in water (30 c.c.). After addition of urea the mixture was poured into a solution of cuprous chloride (5 g.) in concentrated hydrochloric acid (50 c.c.) at 25—30°, heated at 50° for a few minutes, cooled, and made alkaline with ammonia; an ethereal extract of the product was shaken with concentrated hydrochloric acid (ca 15 c.c.); 4-chlorodimethyl-1-naphthylamine hydrochloride, which separated, crystallised from dilute hydrochloric acid in colourless compact prisms, m.p. 215° (with evolution of gas) (Found: Cl, 29.3.  $C_{12}H_{12}NCl \cdot HCl$  requires Cl, 29.4%).

The *picrate*, formed from the base in ether and alcoholic picric acid, crystallised from alcohol in very large, elongated prisms, m. p. 146° (to an orange liquid) (Found : Cl, 8.0.  $C_{18}H_{15}O_7N_4Cl$  requires Cl, 8.2%); mixed m. p. with dimethyl- $\alpha$ -naphthylamine picrate (m. p. 145°) *ca.* 120° after softening. 4-Chlorodimethyl-1-naphthylamine was obtained from the hydrochloride by basification with sodium carbonate; it was slowly volatile in steam as a colourless oil.

When  $\beta$ -naphthylamine (50 g.) was added with stirring to methyl sulphate (75 c.c.) at 110°, the temperature rose to 140°. After 5 minutes, the solution was cooled and made alkaline, and the liberated oil treated with acetic anhydride and steam-distilled from a suspension in aqueous sodium carbonate. Pure dimethyl- $\beta$ -naphthylamine passed over as a colourless solid (turning pink), m. p. 46° (Hantzsch, *Ber.*, 1880, 13, 2054, gives m. p. 46°). The *picrate* crystallised from glacial acetic acid in yellow plates, m. p. 200° (decomp.) (Found : N, 14.2.  $C_{18}H_{16}O_7N_4$  requires N, 14.0%), very sparingly soluble in boiling alcohol.

*Action of Nitrous Acid on 4-Dimethylaminoaceto-1-naphthalide.*—The naphthalide (2 g.), dissolved in concentrated hydrochloric acid (5 c.c.) and water (30 c.c.), was diazotised at 0° with sodium nitrite (2 g.) in water (18 c.c.). After 1 hour's stirring, the yellow crystals (1.2 g.) were removed; m. p. 125° after recrystallisation from alcohol. This product was  $\alpha$ -naphthoquinone containing a trace of a nitroso-compound (intense coloration in the Liebermann test). The filtrate coupled slightly with alkaline  $\beta$ -naphthol, indicating the presence of a diazonium compound. A very similar result was obtained when dilute nitric acid (containing a trace of nitrous acid) at equivalent dilution was employed. 4-Dimethylaminoaceto-1-naphthalide was, however, completely unaffected by the latter reagent in the presence of urea, even after several days' standing at room temperature.

*Action of Nitrous Acid on 4-Chlorodimethyl-1-naphthylamine.*—The hydrochloride of this base (2 g.) was dissolved in concentrated hydrochloric acid (35 c.c.) and water (300 c.c.) at 100° and diazotised at 0° with sodium nitrite (2.3 g.) in water (20 c.c.), added quickly with vigorous stirring. After 1 hour's agitation, the light orange precipitate of 4-chloro-2-nitrodimethyl-1-naphthylamine (2 g.; m. p. 54—55°) was removed (it gave no Liebermann test) and steam-distilled; it passed over very slowly as an orange oil, which solidified and then crystallised from light petroleum in large, orange-red, hexagonal prisms, m. p. 58° (Found : Cl, 14.0.  $C_{12}H_{11}O_2N_2Cl$  requires Cl, 14.2%).

*Synthesis of 4-Chloro-2-nitrodimethyl-1-naphthylamine.*—A solution of 2-nitroaceto-1-naphthalide (20 g.) (Hodgson and Walker, *J.*, 1933, 1206) in glacial acetic acid (100 c.c.) was rapidly treated with chlorine at 100° for 30 minutes. 4-Chloro-2-nitroaceto-1-naphthalide, separated after cooling, crystallised from glacial acetic acid in colourless needles, m. p. 219° (Found : Cl, 13.2.  $C_{12}H_9O_3N_2Cl$  requires Cl, 13.4%). On hydrolysis with boiling alcoholic sulphuric acid for 6 hours, 4-chloro-2-nitro-1-naphthylamine was obtained; it crystallised from glacial acetic acid or ethylene dichloride in slender orange needles, m. p. 202° (Found : Cl, 15.8.  $C_{10}H_9O_2N_2Cl$  requires Cl, 15.9%). (The preparation and orientation of the above two products have been supplied by Hodgson and Elliott—unpublished work.)

A solution of 4-chloro-2-nitro-1-naphthylamine (5 g.) in boiling glacial acetic acid (70 c.c.) was cooled to 10° and diazotised by addition to sodium nitrite (2 g.) dissolved in concentrated sulphuric acid (40 c.c.). When this mixture was poured into a cold solution of cuprous chloride (8 g.) in concentrated hydrochloric acid (80 c.c.), a yellow precipitate (4.7 g.) of 1 : 4-dichloro-2-nitronaphthalene separated; this crystallised from glacial acetic acid in bright yellow, slender needles, m. p. 116.5° (Found : Cl, 29.0.  $C_{10}H_5O_2NCl_2$  requires Cl, 29.4%). When the diazo-solution (above) was poured into cold aqueous potassium iodide, 1-chloro-4-iodo-3-nitronaphthalene separated, which crystallised from glacial acetic acid or alcohol in yellow needles, m. p. 107° (Found : Cl + I, 48.5.  $C_{10}H_5O_2NClI$  requires Cl + I, 48.8%).

1 : 4-Dichloro-2-nitronaphthalene (2.5 g.) was heated on the water-bath (under reflux) for 4 hours with dimethylamine (3.5 g.) in alcohol (25 c.c.). Steam-distillation gave the volatile 4-chloro-2-nitrodimethyl-1-naphthylamine (1.7 g.), which, after crystallisation from light petroleum, had m. p. and mixed m. p. with the previously described specimen, 58° (Found : Cl, 14.1%). After 8 hours' heating on the water-bath with 10% aqueous sodium hydroxide, the specimens prepared by both methods gave the same 4-chloro-2-nitro-1-naphthol (Hodgson and Smith, *J.*, 1935, 673), m. p. and mixed m. p. with an authentic specimen, 155° (decomp.), in each case.

4-Chloro-2-nitrodimethyl-1-naphthylamine was obtained by boiling for 8 hours a mixture of 1 : 4-dichloro-2-nitronaphthalene, monomethylamine hydrochloride, sodium acetate, and alcohol; it crystallised from glacial acetic acid in small orange needles, m. p. 175° (Found : Cl, 14.8.  $C_{11}H_9O_2N_2Cl$  requires Cl, 15.0%).

*Action of Nitrous Acid on Dimethyl- $\beta$ -naphthylamine.*—A solution of the amine (6 g.) in con-

centrated hydrochloric acid (40 c.c.) and water (120 c.c.) at 0° was treated gradually with sodium nitrite (4.2 g.) in water (6.0 c.c.). After 1 hour, the yellow-brown resin which had separated was removed, the filtrate diluted with ice-water (1 l.), and the excess of nitrous acid destroyed by urea. The orange precipitate of 1-nitrodimethyl-2-naphthylamine (1.8 g.), which separated during 15 minutes, was removed, washed, dried, and extracted with boiling light petroleum; on cooling, the pure product crystallised in large, crimson, elongated prisms, m. p. 76—77° (Found: N, 13.2.  $C_{15}H_{12}O_2N_2$  requires N, 13.0%), which were readily soluble in concentrated hydrochloric acid and reprecipitated by water.

*Synthesis of 1-Nitrodimethyl-2-naphthylamine.*—2-Chloro-1-nitronaphthalene (2 g.) was heated for 2 hours under reflux with dimethylamine (2 g.) dissolved in alcohol (40 c.c.). The cooled solution, when cautiously diluted with water, deposited 1-nitrodimethyl-2-naphthylamine (1.8 g.), which crystallised from light petroleum in crimson elongated prisms, m. p. and mixed m. p. with the specimen obtained as above, 76—77° (Found: N, 13.2%).

4-Nitrodimethyl-1-naphthylamine was formed when 4-chloro-1-nitronaphthalene (2 g.) was refluxed for 2 hours with dimethylamine (2 g.) and alcohol (40 c.c.); it crystallised from light petroleum in small, light yellow needles, m. p. 64° (Found: N, 13.3. Calc.: N, 13.0%) (Vésély and Vojtech, *Coll. Czech. Chem. Comm.*, 1929, 1, 104, give m. p. 65—66°).

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