241. *The Preparation of Certain 2 : 3-Naphthalene Derivatives.*

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2 : 3-NAPHTHALENE derivatives are still generally inaccessible, and the present paper records an investigation for the facile production of the 2 : 3-halogenonitronaphthalenes from which a large number of 2 : 3-substituted naphthalenes might be obtained.

In a previous investigation (Hodgson and Elliott, J., 1935, 1850) 2-halogeno-*NN'*-diacetyl-1 : 4-naphthylenediamines had been prepared in over 90% yields, and it was expected that subsequent nitration would occur in the 3-position; actually, however, the halogen was displaced by the nitro-group whether the reagent was diacetyl orthonitric acid or nitric acid. The ease of replacement was in the order I > Cl > Br, and prolonged reaction gave 2 : 3-*dinitro*-NN'-*diacetyl*-1 : 4-*naphthylenediamine* in each case; that nitration was entirely homonuclear was established by the oxidation of each product to phthalic acid and never to a derivative of it. Further evidence was obtained by acid hydrolysis of the 2-nitro-*NN'*-diacetyl-1 : 4-naphthylenediamine to 2-*nitro*-1 : 4-*naphthylenediamine*, which, by the usual diazotisation–deamination procedure, gave 2-nitro-1-naphthylamine, thereby showing that only the 4-amino-group had reacted under the conditions employed; 2-nitro-1 : 4-naphthylenediamine therefore reacts with nitrous acid in the same way as its phenyl analogue.

2-Nitro-*NN'*-diacetyl-1 : 4-naphthylenediamine is readily soluble in hot aqueous caustic alkalis and is precipitated unchanged by acids, although it is slowly decomposed by prolonged boiling of the solution. In contrast, 2 : 3-dinitro-*NN'*-diacetyl-1 : 4-naphthylenediamine is readily converted by hot alkalis into 2 : 3-*dinitro*-1 : 4-*dihydroxynaphthalene*, whereas boiling alcoholic sulphuric acid hydrolyses both products to 2-nitro- and 2 : 3-dinitro-1 : 4-naphthylenediamine respectively.

The above 2-nitro- and 2 : 3-dinitro-*NN'*-diacetyl-1 : 4-naphthylenediamines were easily reduced by the standard alcoholic stannous chloride–hydrochloric acid procedure (Hodgson and Elliott, *loc. cit.*) to give *tin* double salts, but subsequent attempts at hydrolysis were attended by complications and no free amine has yet been isolated, although by boiling the solution of the hydrolysed product from the initial 2-nitro-compound with acetic anhydride, 1 : 2 : 4-triacetamidonaphthalene has been obtained (m. p. above 400°) (Found : N, 14·2. Calc.: N, 14·05%).

Nitration of the isomeric 4-halogeno-*NN'*-diacetyl-1 : 2-naphthylenediamines occurred in the 3-position with the chloro- and bromo-compounds, but in the 4-position, with replacement of iodine by the nitro-group, in the iodo-analogue.

An important experimental result for the success of this investigation was the almost exclusive nitration of the 3-halogeno-aceto-1-naphthalides in the 2-position by both diacetyl orthonitric acid and concentrated nitric acid (*d* 1·42). This reaction was to be anticipated on theoretical grounds, and is also in harmony with the coupling of diazonium salts at the 2- and 7-positions in H-acid, and not at the 4- and 5-carbon atoms which are deactivated by the 3- and the 6-sulphonic acid group respectively.

The absence of 4-nitro-products was established by dissolution of the mononitrated halogeno-compounds in hot alcohol, addition of caustic soda to retain in solution any naphthols which had been formed by secondary decompositions (none detected), reprecipitation of the nitro-products by dilution with water, removal of any free amine from the latter by treatment of the precipitate with excess of nitrous acid, and final hydrolysis to a 3-halogeno-2-nitro-1-naphthylamine, which was deaminated to give a 3-halogeno-2-nitronaphthalene different from the isomeric 1 : 2-, 2 : 1-, 1 : 3-, and 3 : 1-halogenonitronaphthalenes. The original 3-halogeno-2-nitroaceto-1-naphthalides and the re-acetylated 3-halogeno-2-nitro-1-naphthylamines differed from the isomeric 2-halogeno-4-nitroaceto-1-naphthalides. If the nitration temperatures of the 3-halogenoaceto-1-naphthalides rise above 30°, halogen is eliminated and 2 : 3-*dinitroaceto*-1-*naphthalide* obtained. During the alcoholic deamination of the 3-halogeno-2-nitro-1-naphthylamines to form the 3-halogeno-2-nitronaphthalenes, the temperature of diazotisation must be kept below 20°, otherwise complex azo-products are formed reminiscent of the deep purple powder obtained by the attempted diazotisation of 2-chloro-1 : 4-naphthylenediamine (Hodgson and Elliott, *loc. cit.*).

3-*Iodo*-2-*nitroacet*-1-*naphthalide* exhibits certain differences from its chloro- and bromo-analogues in that it melts considerably higher, and is hydrolysed by alcoholic sulphuric acid with much greater difficulty, requiring 10½ hours under conditions which hydrolyse the bromo- and the chloro-compound in 1½ and 5—6 hours, respectively.

EXPERIMENTAL.

Nitration of 2-*Iodo*-NN′-*diacetyl*-1 : 4-*naphthylenediamine.*—The finely powdered substance (10 g.) was added rapidly with vigorous stirring to a mixture of nitric acid (70·4 c.c.; *d* 1·42) and water (100 c.c.); the temperature rose to 40° and complete dissolution (yellow-brown) ensued. After about 2 minutes, a copious separation of very pale yellow feathery crystals of 2-nitro-*NN*′-diacetyl-1 : 4-naphthylenediamine occurred, and the mixture was then poured into cold water (1 l.), the precipitate filtered off, washed with cold water, dried (crude m. p. 293°), and recrystallised from alcohol or, preferably, glacial acetic acid; m. p. and mixed m. p. with authentic specimen, 309° (lit. 295°) (Found: N, 14·7. Calc.: N, 14·6%). The displaced iodine was found in the filtrate as iodic acid. From the three analogues of the 2-halogeno-*NN*′-diacetyl-1 : 4-naphthylenediamine, chlorine was displaced initially by 44·4% nitric acid, bromine by 49%, and iodine by 42% acid.

2-*Nitro*-1 : 4-*naphthylenediamine.*—The above diacetyl compound (8 g.) was refluxed with a mixture of 50% aqueous sulphuric acid (60 c.c.) and alcohol (80 c.c.) until complete dissolution had occurred (about 1 hour); the solution was allowed to cool, the brown deposit filtered off (crude m. p. 213°), redissolved in glacial acetic acid (3 g. per 10 c.c.), 1 c.c. of concentrated hydrochloric acid added, and the monohydrochloride, which then crystallised out, basified by trituration with water. The 2-*nitro*-1 : 4-*naphthylenediamine* thus obtained crystallised from glacial acetic acid in deep yellow needles, m. p. 241° (Found: N, 20·9. $C_{10}H_9O_2N_3$ requires N, 20·7%).

2 : 3-*Dinitro*-NN′-*diacetyl*-1 : 4-*naphthylenediamine.*—(*a*) Any of the 2-halogeno-*NN*′-diacetyl-1 : 4-naphthylenediamines (5 g.) was added to externally ice-cooled and vigorously stirred diacetyl orthonitric acid (30 c.c.); dissolution occurred (deep-brown) during a somewhat violent reaction, and the temperature was then raised to 60°, the mixture kept for 24 hours at room temperature, and the resulting precipitate of 2 : 3-*dinitro*-NN′-*diacetyl*-1 : 4-*naphthylenediamine* recrystallised from nitrobenzene, separating in deep yellow micro-crystals, m. p. above 360° (Found: N, 17·1. $C_{14}H_{12}O_6N_4$ requires N, 16·9%).

(*b*) The above 2-nitro-compound (10 g.) was added with stirring to nitric acid (60 c.c.; *d* 1·42), the mixture gradually heated to and kept at 50° (above which there was a brisk evolution of nitrous fumes and considerable oxidation, see below) for 10 minutes, then stirred into 500 c.c. of ice-water. The precipitated 2 : 3-dinitro-compound was filtered off and treated as above.

Reduction of 2-*Nitro- and of* 2 : 3-*Dinitro*-NN′-*diacetyl*-1 : 4-*naphthylenediamine.*—By the standard procedure (Hodgson and Elliott, *loc. cit.*) these compounds gave the *stannichlorides* of 2-amino- [Found: Cl, 24·9. $(C_{14}H_{16}O_2N_3)_2SnCl_6$ requires Cl, 25·1%], and 2 : 3-diamino-*NN*′-diacetyl-1 : 4-naphthylenediamine [Found: Cl, 35·0. $(C_{14}H_{18}O_2N_4)SnCl_6$ requires Cl, 35·2%], which formed respectively silvery and colourless needles.

2 : 3-*Dinitro*-1 : 4-*dihydroxynaphthalene.*—2 : 3-Dinitro-*NN*′-diacetyl-1 : 4-naphthylenediamine (5 g.) was boiled for 30 minutes with 20% aqueous sodium hydroxide (100 c.c.); complete dissolution occurred with evolution of ammonia, and, after careful acidification with hydrochloric acid, a brown gelatinous precipitate of 2 : 3-*dinitro*-1 : 4-*dihydroxynaphthalene* was obtained, which crystallised from alcohol in yellow needles, m. p. 357° (Found: N, 11·3. $C_{10}H_6O_6N_2$ requires N, 11·2%). Treatment of this product (0·3 g.) with 20% aqueous sodium hydroxide (100 c.c.) and methyl sulphate (10 c.c.) at 60° for 30 minutes gave deep red nodules of 2 : 3-*dinitro*-1 : 4-*dimethoxynaphthalene*, which crystallised from nitrobenzene in red micro-crystals, m. p. 190° (Found: N, 10·2. $C_{12}H_{10}O_6N_2$ requires N, 10·1%).

2 : 3-*Dinitro*-1 : 4-*naphthylenediamine.*—The diacetyl compound above (5 g.) was refluxed for 90 minutes with 70% sulphuric acid (100 c.c.) and alcohol (35 c.c.); dissolution occurred, and, on pouring into water, deep brown crude 2 : 3-*dinitro*-1 : 4-*naphthylenediamine* was formed, which separated from glacial acetic acid in brown crystals, m. p. 207° (Found: N, 22·8. $C_{10}H_8O_4N_4$ requires N, 22·6%).

Nitration of 4-*Chloro*-NN′-*diacetyl*-1 : 2-*naphthylenediamine.*—The finely powdered substance (3 g.) was added to nitric acid (30 c.c.; *d* 1·42), immediate dissolution occurring, with gradual rise of temperature to 40° during 30 minutes; after a further hour, the *4-chloro-3-nitro-*NN′-*diacetyl-*1 : *2-naphthylenediamine* separated in colourless micro-crystals, m. p. 208° (Found : Cl, 10·9. $C_{14}H_{12}O_4N_3Cl$ requires Cl, 11·0%), which on oxidation with alkaline permanganate gave phthalic acid. Obtained in like manner, the *4-bromo-*analogue also forms colourless micro-crystals, m. p. 195° (Found : Br, 21·7. $C_{14}H_{12}O_4N_3Br$ requires Br, 21·9%).

Nitration of 4-*Iodo-*NN′-*diacetyl-*1 : *2-naphthylenediamine.*—A temperature of 60—70° was required for dissolution of the product (2 g.) in nitric acid (50 c.c.; *d* 1·42), and no reaction occurred below 90—95°. After 5 minutes at this temperature, the mixture was poured into water, and the *4-nitro-*NN′-*diacetyl-*1 : *2-naphthylenediamine* filtered off; it separated from alcohol in deep yellow crystals, m. p. 124° (Found : N, 14·7. $C_{14}H_{13}O_4N_3$ requires N, 14·6%).

The 3-*Halogeno-*2-*nitroaceto-*1-*naphthalides.*

Nitration of 3-*Chloroaceto-*1-*naphthalide.*—(a) *By diacetyl orthonitric acid.* The finely powdered substance (10 g.) was stirred into the acid (50 c.c.); dissolution occurred with rise of temperature, and after 24 hours, a precipitate of red needles was obtained (m. p. 219°) which consisted almost entirely (see p. 1151) of 3-chloro-2-nitroaceto-1-naphthalide.

(b) *By concentrated nitric acid.* 10 G., as above, were stirred into nitric acid (100 c.c.; *d* 1·42), the mixture was kept for 1 hour below 30°, and then stirred into cold water (1 l.); the resulting *3-chloro-2-nitroaceto-1-naphthalide* separated from glacial acetic acid in bright brick-red micro-crystals, m. p. 225° (Found : Cl, 13·35. $C_{12}H_9O_3N_2Cl$ requires Cl, 13·4%), identical with the product from (a).

3-Chloro-2-nitro-1-naphthylamine is best prepared by refluxing the acetylated derivative above (20 g.) for 5 hours with a mixture of 50% aqueous sulphuric acid (150 c.c.) and alcohol (150 c.c.); on cooling, the amine separates in deep chrome-yellow needles, m. p. 149° (Found : Cl, 15·9. $C_{10}H_7O_2N_2Cl$ requires Cl, 16·0%); the hydrochloride is formed when the glacial acetic acid solution of the amine (1 g. in 20 c.c.) is treated with concentrated hydrochloric acid (1 c.c.), and separates in colourless crystals which are readily hydrolysed in air (more rapidly in water) to the amine.

If the nitration with nitric acid (b) be conducted above 30°, halogen tends to be eliminated with formation of 2 : *3-dinitroaceto-1-naphthalide*, a replacement which is complete at 85—90°; this product separates from glacial acetic acid in cream-yellow plates, m. p. 275·5° (Found : N, 15·5. $C_{12}H_9O_5N_3$ requires N, 15·3%).

3-Bromo-2-nitroaceto-1-naphthalide, prepared by methods analogous to (a) or (b), crystallised from glacial acetic acid in colourless needles, m. p. 235° (Found : Br, 25·7. $C_{12}H_9O_3N_2Br$ requires Br, 25·9%). Alcoholic acid hydrolysis afforded the *base*, which crystallised from alcohol in deep chrome needles, m. p. 166° (Found : Br, 29·7. $C_{10}H_7O_2N_2Br$ requires Br, 30·0%).

3-Iodo-2-nitroaceto-1-naphthalide crystallised from glacial acetic acid in colourless, feathery needles, m. p. 298° (Found : I, 35·6. $C_{12}H_9O_3N_2I$ requires I, 35·7%); when it (3 g.) was refluxed for 10½ hours with a mixture of 50% sulphuric acid (40 c.c.) and alcohol (30 c.c.), it never went into complete solution but was gradually hydrolysed into red-brown crystals of the *base*, which crystallised from glacial acetic acid in red-brown needles, m. p. 250° (Found : I, 40·3. $C_{10}H_7O_2N_2I$ requires I, 40·4%).

The 3-*Halogeno-*2-*nitronaphthalenes.*

3-Chloro-2-nitronaphthalene.—A solution of 3-chloro-2-nitro-1-naphthylamine (5 g.) in glacial acetic acid (30 c.c.) was added carefully to a cooled solution of sodium nitrite (15 g.) in concentrated sulphuric acid (100 c.c.), the temperature being kept below 20°; the mixture was then poured into alcohol (300 c.c.) and heated for 1 hour on the water-bath. The solid precipitate was filtered off and washed with water, the crude *3-chloro-2-nitronaphthalene* crystallising from alcohol in brownish needles, m. p. 79°, which deepen in colour on keeping and are volatile in steam (0·4 g. per l.; cf. 2 g. per l. for more stable 2-chloro-1-nitronaphthalene), m. p. 94·5° (Found : Cl, 16·9. $C_{10}H_6O_2NCl$ requires Cl, 17·1%). When the diazotisation was carried out at 35°, the water-washed precipitate contained maroon feathery needles, m. p. 145° (Found : Cl, 9·4%), which dissolved in concentrated sulphuric acid to give a deep purple fluorescent solution indicative of an azo-dye due to auto-coupling.

3-Bromo-2-nitronaphthalene, prepared like the chloro-analogue and with the same precaution with regard to temperature, crystallised from alcohol in brown needles, m. p. 84° (Veselý and Chudozilov, *Chem. Listy*, 1925, **19**, 260, give m. p. 82—83°) (Found : Br, 31·7. Calc. : Br, 31·7%), which darken considerably on keeping.

3-Iodo-2-nitronaphthalene, prepared as above, crystallised from 91% formic acid in cream-coloured needles, m. p. 105° (Cumming and Howie, J., 1931, 3178, give m. p. 89—89·5°) (Found : I, 42·3. Calc. : I, 42·5%), which rapidly turn brown and are inappreciably volatile in steam. If the diazotisation be carried out at 30°, a deep purple powder (m. p. 165°) results, which gives a deep purple colour with concentrated sulphuric acid.

The authors thank Imperial Chemical Industries Ltd. (Dyestuffs Group) for various gifts.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, June* 12*th*, 1936.]