78. *A Case of Simple Substitution in the 3-Position of a 1 : 2-Disubstituted Naphthalene.*

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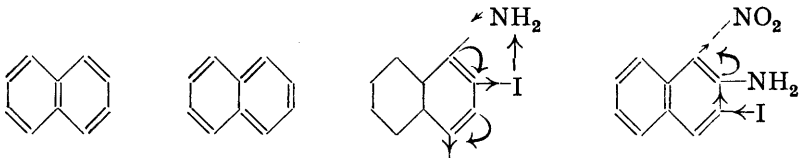
Mercuration of 1-nitro-2-naphthylamine takes place in the 3-position, for the *mercuriacetate* produced is convertible into 3-iodo-1-nitronaphthalene. 3-*Iodo*-1-*nitro*-2-*naphthylamine* is readily acetylated by acetic anhydride and 2-chloro-4-nitro-1-naphthylamine is easily converted into 1 : 2-*dichloro*-4-*nitronaphthalene* by the Sandmeyer reaction.

To the very few recorded examples (see McLeish and Campbell, J., 1937, 1103) of direct substitution in the 3-position of 1 : 2-naphthalene derivatives, mercuration of 1-nitro-2-naphthylamine is to be added. It is another case, this time without a special medium such as pyridine (cf. Bell, J., 1932, 2732), where the symmetrical Erlenmeyer formula (I) can be changed by a reagent into the asymmetrical structure (II). Proof of the orientation

was obtained by conversion of the 1-*nitro*-2-*naphthylamine*-3-*mercuriacetate* into 3-iodo-1-nitronaphthalene (Hodgson and Elliott, J., 1934, 1705).



(I.) (II.) (III.) (IV.)

2-Iodo-4-nitro-1-naphthylamine (Hodgson and Elliott, J., 1935, 1850) is not acetylated under standard conditions, but 3-*iodo*-1-*nitro*-2-*naphthylamine* is readily attacked by acetic anhydride. A probable explanation of the anomaly is the powerful chelation of the iodine with the amino-group in (III) consequent on its greatly decreased anionoid activity, and the reduced intensity or absence of chelation in (IV), both causes being due to the positional effect of the nitro-group and the ready adaptability of iodine. This result recalls the formation of a dihydrochloride and the simultaneous acetylation of both amino-groups in 3-chloro-1 : 2-naphthylenediamine in contrast with the formation of a monohydrochloride and the monoacetylation of the 2-amino-group in the case of 4-halogeno-1 : 2-naphthylenediamines.

The Sandmeyer reaction converts 2-chloro-4-nitro-1-naphthylamine normally into 1 : 2-*dichloro*-4-*nitronaphthalene*, but pursues a different course with 4-chloro-2-nitro-1-naphthylamine, giving an amorphous product of low chlorine content.

Experimental.

1-*Nitro*-2-*naphthylamine*-3-*mercuriacetate*.—1 Nitro-2-naphthylamine (10 g.) was dissolved in boiling glacial acetic acid (50 c.c.) and added to a boiling solution of mercuric acetate (20 g.) in glacial acetic acid (35 c.c.); the mixture was kept for 12 hours and the long colourless needles of the *mercuriacetate* which separated were recrystallised from glacial acetic acid (Found: Hg, 44·7. $C_{12}H_{10}O_4N_2Hg$ requires Hg, 44·8%).

3-*Iodo*-1-*nitro*-2-*naphthylamine*.—The above product (5 g.) was added to a boiling solution of iodine (3 g.) in 10% aqueous potassium iodide (50 c.c.), and the boiling continued for 10 minutes; solid sodium thiosulphate was then added and the precipitate of 3-*iodo*-1-*nitro*-2-*naphthylamine* was collected and recrystallised from alcohol, forming orange-yellow needles, m. p. 174° (Found: I, 40·3. $C_{10}H_7O_2N_2I$ requires I, 40·4%). Deamination by the process of Hodgson and Elliott (*loc. cit.*) gave 3-iodo-1-nitronaphthalene, m. p. 108° (Found: I, 42·2. Calc.: I, 42·5%).

3-*Iodo*-1-*nitroaceto*-2-*naphthalide*, obtained by acetylation of the above amine with acetic anhydride, crystallised from glacial acetic acid in pale orange-yellow needles, m. p. 196° (Found: I, 35·5. $C_{12}H_9O_3N_2I$ requires I, 35·7%). On reduction by the process of Hodgson and Elliott (J., 1935, 1850), colourless crystals of the *stannichloride* of 3-iodo-2-acetamido-1-naphthylamine were formed [Found: Cl + I, 47·2. $(C_{12}H_{11}ON_2I)_2,H_2SnCl_6$ requires Cl + I, 47·4%].

1 : 2-*Dichloro*-4-*nitronaphthalene*.—2-Chloro-4-nitro-1-naphthylamine (10 g.), diazotised by Hodgson and Walker's method (J., 1933, 1620), was gradually added, after removal of the excess of nitrous acid, to a solution of cuprous chloride (14 g.) in concentrated hydrochloric acid (130 c.c.); the mixture was kept for 6 hours, then diluted with water (1 l.), and kept overnight. The precipitated 1 : 2-*dichloro*-4-*nitronaphthalene* crystallised from alcohol in brown nodules, m. p. 119° (Found: Cl, 29·1. $C_{10}H_5O_2NCl_2$ requires Cl, 29·3%).

The above process carried out with 4-chloro-2-nitro-1-naphthylamine afforded a brownish-yellow precipitate, which separated from alcohol as a bright yellow, amorphous powder, m. p. 102° (Found: Cl, 20·4%), which was not identified.

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