## 389. *The Elimination of Halogen during the Nitration of Halogenonaphthylamines.*

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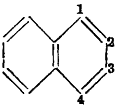
During attempts to prepare 2 : 3-halogenonitronaphthalenes (this vol., p. 1151) we found that the halogen atom in 2-halogeno-*NN'*-diacetyl-1 : 4-naphthylenediamines was eliminated in each of the nitration methods used, and replaced by a nitro-group, whereas in 4-halogeno-*NN'*-diacetyl-1 : 2-naphthylenediamines the chlorine or bromine atom was stable and only iodine was eliminated with the formation of 4-nitro-*NN'*-diacetyl-1 : 2-naphthylenediamine. This work has now been extended to the nitration of 3-*chloro*-NN'-*diacetyl*-1 : 2-*naphthylenediamine*, the three 4-halogeno-2-*N*-acetyl-1 : 2-naphthylenediamines, and the three 2-halogeno-1-*N*-acetyl-1 : 4-naphthylenediamines.

During the preparation of 3-chloro-*NN'*-diacetyl-1 : 2-naphthylenediamine, it was found that, whereas in the attempted diacetylation of 4-halogeno-1 : 2-naphthylenediamines only the 2-amino-group was acetylated (cf. Morgan and Godden, J., 1910, **97**, 1709; Hodgson and Elliott, J., 1935, 1853), 3-*chloro*-1 : 2-*naphthylenediamine* was diacetylated simultaneously in both amino-groups—a reaction in harmony with the formation by this diamine of a *dihydrochloride*, whereas 4-halogeno-1 : 2-naphthylenediamines only form monohydrochlorides.

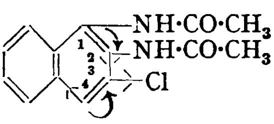
An explanation of the above phenomena may perhaps be found in the Erlenmeyer static formula (inset) for naphthalene, in which, because of the suppression of oscillation and the valency claim made on the double bond shared between the rings, the two nuclei are less aromatic than true benzene rings, and each contains a 1 : 4-conjugated (butadienoid) system with enhanced reactivities at the 1- and the 4-position (cf. Fieser and Lothrop, *J. Amer. Chem. Soc.*, 1935, **57**, 1462). Halogens in the 4-position would thus tend by their inductive (— *I*) effect to restrict the salt-forming affinity of the 1-amino-group in the 1 : 2-diamines, but could only slightly affect that of the 2-amino-group: hence acetylation and hydrochloride formation would occur preferentially at the 2-amino-group. This inductive effect of the halogens (even of iodine) appears sufficient to prevent entirely the reactivity of 4-halogeno-2-*N*-acetyl-1 : 2-naphthylenediamines towards 1-*N*-acetylation and of 4-halogeno-1 : 2-naphthylenediamines towards dihydrochloride formation. Halogens in the 3-position, however, have apparently little effect on either the 1- or the 2-amino-group, both of which in consequence react with acetic anhydride and with hydrochloric acid. These reactions prove that it is not the initial monoacetylation and monohydrochloride formation at the 2-amino-group which inhibit further reactivity at the 1-amino-group, and they constitute further evidence in support of the static Erlenmeyer formula.



Whereas in 2-halogeno-4-*N*-acetyl-1 : 4-naphthylenediamines nitration occurs normally at the 3-position to give 2-halogeno-3-nitro-4-*N*-acetyl-1 : 4-naphthylenediamines (Hodgson and Smith, J., 1935, 674), acetylation of the 4-amino-group produces an entirely different result in that all 2-halogeno-*NN'*-diacetyl-1 : 4-naphthylenediamines have their halogen atom displaced by a nitro-group whatever the conditions of nitration (Hodgson and Elliott, *loc. cit.*). In exactly similar fashion, the halogen atom is replaced by a nitro-group during the nitration of 4-halogeno-2-*N*-acetyl-1 : 2-naphthylenediamines and of 2-halogeno-1-*N*-acetyl-1 : 4-naphthylenediamines.

Replacement of a halogen atom by a nitro-group depends for its first phase on the anionoid character of the carbon atom which is to be attacked by the electron-seeking (electrophilic) reagent, and owing to the prevailing negative inductive (— *I*) effect of chlorine or bromine, this is apparently insufficient in 4-chloro- and 4-bromo-*NN'*-diacetyl-1 : 2-naphthylenediamines for reaction to be initiated at the 4-carbon atom, so that nitration occurs normally at the 3-position as in the ortho-nitration of chlorobenzene. The more amphoteric character of iodine, however, enables this element, under the influence of the electrophilic reagent, to exercise its electromeric (+ *T*) effect, with subsequent attack at the 4-carbon atom by the reagent and replacement of the iodine by a nitro-group. In 4-halogeno-2-*N*-acetyl-1 : 2-naphthylenediamines, the donating 1-amino-group in those molecules where salt formation with the nitric acid has not taken place (cf. the para-nitration of aniline), inhibited perhaps by chelation between the 1-amino- and the 2-acetamido-group, enables the 4-carbon atom to become sufficiently anionoid, by the mechanism of the conjugated 1 : 4-system, for reaction with nitric acid to occur and consequently all the halogens are displaced. In 2-halogeno-1-*N*-acetyl-1 : 4-naphthylenediamines, salt formation at the 4-amino-group will deactivate the 3-position, and thereby render the 2-position the most anionoid, with consequent attack and replacement of all the halogen atoms. As would be anticipated, the nitration of 3- and 4-halogeno-1-*N*-acetyl-1 : 2-naphthylenediamines could not be investigated owing to their great instability under the drastic conditions.

It was reported previously by the authors (*loc. cit.*) that the halogen tended to be eliminated during the nitration of 3-halogenoaceto-1-naphthalides above 35°, the displacement being complete at 90° with the production of 2 : 3-dinitroaceto-1-naphthalide. This reaction has now been found to occur only with the chloro- and the bromo-compound, the nitration of 3-iodoaceto-1-naphthalide at 80—90° giving unexpectedly 3-iodo-2-nitroaceto-1-naphthalide. This apparent anomaly might perhaps find an explanation in chelation between the 3-iodo- and the 2-nitro-group, whereas such co-ordination is improbable between substituent chlorine or bromine and the nitro-group. In 3-chloro-*NN'*-diacetyl-1 : 2-naphthylenediamine (inset), the 4-carbon atom is deactivated by the combined negative inductive (— *I*) effect of the chlorine atom and the negative effect of the second nucleus, whereas the 3-carbon atom will possess greater electronic density owing to the positive (+ *I*) combined inductive effects of the 1 : 2-diacetamido-groups. In consequence the 3-carbon atom will be more anionoid than the 4-carbon atom, with consequent initial attack of the nitric acid and subsequent replacement of the chlorine by the nitro-group.



In view of the analogy of the above eliminations with the straight nitration of aromatic hydrocarbons, electropositive halogens being displaced in like manner to electropositive hydrogen, support would appear to be given to Michael's aldolisation theory of nitration (cf. *J. Amer. Chem. Soc.*, **1935**, **57**, 1268). The elimination would then appear as a three-phase mechanism, *viz.*, the initial attack of the electrophilic nitric acid polarised as $\overset{+}{\mathrm{N}}\mathrm{O_2}\overset{-}{\mathrm{O}}\mathrm{H}$, succeeded by the expulsion of positive halogen with formation of the very unstable group —NO(OH)(OHal.), and finally the scission of hypohalogenous acid.

## EXPERIMENTAL.

*Preparation of 3-Chloro-*NN'*-diacetyl-*1 : 2*-naphthylenediamine.*—3-Chloro-2-nitroaceto-1-naphthalide (8 g.) (Hodgson and Elliott, this vol., p. 1152), intimately mixed with stannous chloride (60 g.), was added to a mixture of alcohol (15 c.c.) and hydrochloric acid (50 c.c., *d* 1·16) and very gradually heated with agitation until the reaction commenced. Reduction proceeded vigorously and after its completion *3-chloro-*1-N-*acetyl-*1 : 2-*naphthylenediamine stannichloride* separated, on cooling, as a pink crystalline powder [Found : Cl, 35·5. $(C_{12}H_{12}ON_2Cl)_2SnCl_6$ requires Cl, 35·4%]. A suspension of the stannichloride (5 g.) in cold water (100 c.c.), on rapid addition with stirring of aqueous ammonia (5 c.c., *d* 0·880), gave *3-chloro-*1-N-*acetyl-*1 : 2-*naphthylenediamine*, which quickly oxidised superficially and acquired a deep blue colour. It was rapidly filtered off, washed with a little 5% aqueous alcohol to remove admixed ammonia, and crystallised from hot water, forming cream-coloured plates, m. p. 161° (Found : Cl, 15·0. $C_{12}H_{11}ON_2Cl$ requires Cl, 15·1%). Such washing procedure has been found very efficacious after the liberation of readily oxidisable bases. The above base, in solution in 20% acetic acid, was rapidly acetylated when shaken with acetic anhydride, giving *3-chloro-*NN'*-diacetyl-*1 : 2-*naphthylenediamine*, which crystallised from glacial acetic acid in almost colourless plates, m. p. 317·5° (Found : Cl, 12·7. $C_{14}H_{13}O_2N_2Cl$ requires Cl, 12·8%).

*Nitration of 3-Chloro-*NN'*-diacetyl-*1 : 2*-naphthylenediamine.*—The finely powdered diamine (2 g.), when stirred into cold nitric acid (10 c.c., *d* 1·42), dissolved immediately. After 30 seconds, the solution was stirred rapidly into cold water (100 c.c.) and the pale yellow precipitate of *3-nitro-*NN'*-diacetyl-*1 : 2-*naphthylenediamine* was collected and crystallised from glacial acetic acid, forming pale yellow, feathery needles, m. p. 303° (Found : N, 14·9. $C_{14}H_{13}O_4N_3$ requires N, 14·6%).

*Preparation of* 3-*Chloro*-1 : 2-*naphthylenediamine*.—Reduction of 3-chloro-2-nitro-1-naphthylamine (5 g.) (Hodgson and Elliott, *loc. cit.*) by the standard acid stannous chloride procedure adopted in these investigations gave 3-*chloro*-1 : 2-*naphthylenediamine dihydrochloride*, which crystallised from dilute hydrochloric acid in light sandy nodules (Found: Cl, 40·2. $C_{10}H_9N_2Cl,2HCl$ requires Cl, 40·0%). Basification by ammonia liberated 3-*chloro*-1 : 2-*naphthylenediamine*, m. p. 136° (Found: Cl, 18·2. $C_{10}H_9N_2Cl$ requires Cl, 18·4%), which, however, rapidly oxidised in the air. 3-Chloro-*NN'*-diacetyl-1 : 2-naphthylenediamine was readily prepared from the liberated base by shaking it with a mixture of dilute acetic acid and acetic anhydride; the product crystallised from glacial acetic acid in almost colourless plates, m. p. 317·5°, identical with the product obtained as above.

*Attempted Nitration of* 4-*Halogeno*-1 : 2-*naphthylenediamines*.—(a) 4-Chloro-, 4-bromo-, and 4-iodo-1 : 2-naphthylenediamine (1 g.) (Hodgson and Elliott, J., 1935, 1853) were dissolved each in glacial acetic acid (20 c.c.) and treated with nitric acid (3 c.c., *d* 1·42), and the mixtures gradually heated to 90°; nitration then occurred, the temperature remained constant for *ca.* 2 minutes, and the colour of the solutions changed from olive-green to deep red-brown. After 10 minutes, water (50 c.c.) was added with stirring. The deep yellow precipitates of 4-*nitro*-2-N-*acetyl*-1 : 2-*naphthylenediamine* were filtered off after 1 hour and recrystallised once from glacial acetic acid and once from 85% formic acid, pale golden-yellow needles, m. p.'s and mixed m. p.'s 245°, being obtained (Found: N, 17·3. $C_{12}H_{11}O_3N_3$ requires N, 17·1%).

(b) Each of the 4-halogeno-2-*N*-acetyl-1 : 2-naphthylenediamines (1 g.) was suspended in cold water (30 c.c.) and treated with nitric acid (25 c.c., *d* 1·42): nitration occurred and the temperature rose to 60°. After 1 minute, the mixtures were poured into water (50 c.c.) and the bright yellow precipitates of 4-nitro-2-*N*-acetyl-1 : 2-naphthylenediamine were filtered off and worked up as under (a); m. p. and mixed m. p. with the products from (a), 245°.

The displaced halogens were identified in both the (a) and the (b) filtrates. Oxidation of the nitration products from (a) and (b) afforded unsubstituted phthalic acid, showing that nitration had not occurred in the second nucleus. In all the nitrations there were diminished yields due to oxidation as in the nitration of 2-nitro-*NN'*-diacetyl-1 : 4-naphthylenediamine (Hodgson and Elliott, this vol., p. 1153).

*Nitration of* 2-*Halogeno*-1-N-*acetyl*-1 : 4-*naphthylenediamines*.—2-Chloro-, 2-bromo-, and 2-iodo-1-*N*-acetyl-1 : 4-naphthylenediamine (5 g.), prepared by reduction of the 2-halogeno-4-nitroaceto-1-naphthalides (Hodgson and Elliott, J., 1935, 1851), were separately suspended in water (50 c.c.) and treated with nitric acid (50 c.c., *d* 1·42). The solutions became purple and then brown, hydrogen chloride and hydrogen bromide being freely evolved from the respective chloro- and bromo-compound. After *ca.* 1 minute, the solutions were poured into cold water (500 c.c.), and the sandy brown precipitates of 2-*nitro*-1-N-*acetyl*-1 : 4-*naphthylenediamine* filtered off. This product crystallised from glacial acetic acid in yellowish-brown nodules, m. p. 164° (Found: N, 17·3. $C_{12}H_{11}O_3N_3$ requires N, 17·1%). The displaced halogens were identified in the respective filtrates above, together with much phthalic acid produced by concurrent oxidation. Acetylation readily occurred when the product was shaken with a mixture of acetic anhydride and dilute acetic acid, giving 2-nitro-*NN'*-diacetyl-1 : 4-naphthylenediamine, which after crystallisation from glacial acetic acid had m. p. and mixed m. p. with an authentic specimen, 310·5° (Hodgson and Elliott, *loc. cit.*, give m. p. 309°, and previous literature 295°) (Found: N, 14·7. Calc.: N, 14·6%). The yield from 2-bromo-1-*N*-acetyl-1 : 4-naphthylenediamine was very poor, indicating that preferential oxidation had occurred in this reaction.

*Reduction of* 4-*Nitro*-1-*naphthylamine and of* 4-*Nitroaceto*-1-*naphthalide*.—4-Nitro-1-naphthylamine, when treated by the standard stannous chloride reduction procedure, gave 1 : 4-naphthylenediamine dihydrochloride, which, after basification with ammonia and acetylation, afforded *NN'*-diacetyl-1 : 4-naphthylenediamine. This product after crystallisation from glacial acetic acid had m. p. 319° (Kleeman, *Ber.*, 1886, **19**, 334, gives m. p. 303—304°), and was nitrated readily in 50% nitric acid, giving 2-nitro-*NN'*-diacetyl-1 : 4-naphthylenediamine, m. p. 310·5°.

Reduction of 4-nitroaceto-1-naphthalide by the same procedure afforded N-*acetyl*-1 : 4-*naphthylenediamine stannichloride*, which crystallised in colourless needles [Found: Cl, 28·9. $(C_{12}H_{13}ON_2)_2SnCl_6$ requires Cl, 29·0%]. The free base was unstable, but was acetylated readily in solution to give a diacetyl compound identical with the above, m. p. and mixed m. p. 319°.

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