

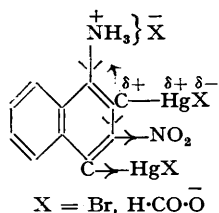
32. *Reactions of 3-Nitro-1-naphthylamine. Part II. Chlorination, Mercuration, Coupling with Diazo-compounds, and the Preparation of some Arsenicals.*

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3-Nitroaceto-1-naphthalide is monochlorinated in position 4, whereas 3-nitro-1-naphthylamine is mercurated initially in position 2 and subsequently in position 4; it couples with certain diazo-compounds also in position 2. The influence of the 3-nitro-group on the deactivation of the 4-position is briefly discussed. The preparation of some arsenicals is described.

THE reaction of chlorine with 3-nitro-1-naphthylamine is very complex, but 3-nitroaceto-1-naphthalide, like 3-nitroacetanilide, is monochlorinated by elementary chlorine in position 4, the constitution of the resulting 4-chloro-3-nitroaceto-1-naphthalide being established by its conversion into 1 : 4-dichloro-2-nitronaphthalene (Hodgson and Crook, J., 1936, 1502). On the other hand, 3-nitro-1-naphthylamine is readily mercurated in position 2 when stoichiometric quantities of the amine and mercuric acetate are boiled together in aqueous alcohol, the resulting 3-nitro-1-naphthylamine-2-mercuriacetate being converted by a solution of iodine in aqueous potassium iodide into 2-iodo-3-nitro-1-naphthylamine, which on deamination gives 3-iodo-2-nitronaphthalene (cf. Cumming and Howie, J., 1931, 3178). By the same procedure with double the amount of mercuric acetate, 3-nitro-1-naphthylamine gives 3-nitro-1-naphthylamine-2 : 4-dimercuriacetate, whose constitution is established by conversion into 2 : 4-diacetoxymercuri-3-nitroaceto-1-naphthalide, from which 2 : 4-dibromo-3-nitroaceto-1-naphthalide (Hodgson and Hathway, J., 1944, 21) is obtained by treatment with bromine.

When 3-nitro-1-naphthylamine-2-mercuriacetate is ground with hydrobromic acid (*d* 1.6), the mercuri-group is replaced by hydrogen with regeneration of 3-nitro-1-naphthylamine, and when 3-nitro-1-naphthylamine-2 : 4-dimercuriacetate is refluxed with 90% formic acid, both mercuri-groups are replaced by hydrogen with formation of 3-nitroformo-1-naphthalide (Hodgson and Birtwell, J., 1944, 75). It would appear, therefore, that the anionid character of both the 2- and the 4-carbon atom is so enfeebled by the combined kationid effects of the 3-nitro-group and salt formation at the amino-group that the kationid mercury is unable to resist anionid attack by either the hydrobromic or formic acid with consequent replacement of the mercuri-group by hydrogen (cf. also Pauling, "Nature of the Chemical Bond," 1941, 199, on the adjacent charge rule).



Diazotised *p*-nitroaniline, *p*-chloroaniline, and aniline couple in acetic acid-ethyl alcohol solution with 3-nitro-1-naphthylamine to give monoazo-compounds in yields of 97%, 50%, and 7% respectively. The fact that in each case the aminoazo-compound can be neither acetylated nor diazotised constitutes evidence in favour of coupling in position 2, since 4-azo-1-naphthylamines are all readily acetylated and

diazotised (cf. Morgan and Jones, *J. Soc. Chem. Ind.*, 1923, 42, 341 r; Hodgson and Turner, J., 1943, 393). The colours of 3-nitro-2-*p*-chlorobenzeneazo-1-naphthylamine with sulphuric acid of different strengths suggest varying salt formation. Also when sodium hydroxide is added to the scarlet solutions of all the dyes in acetone, the colour change to pronounced purple indicates salt formation by the alkali (cf. Chattaway and Clemo, J., 1923, 123, 3041).

Diazo-coupling in position 2 and yield variation of the monoazo-compounds formed in order of the decreasing positivity of the diazo-reagent (cf. Robinson, "Outline of an Electrochemical Theory of the Course of Organic Reactions," Institute of Chemistry, 1932, p. 42) emphasise the enfeebling effect of the 3-nitro-group on the anionid character of the 4-position, a result supported by monomercuration in position 2. The coupling of 3-nitro-1-naphthylamine in position 2 falls into line with the coupling of 1-naphthylamine-3-sulphonic acid in position 2 (Gattermann and Schulze, *Ber.*, 1897, 30, 50; Gattermann and Liebermann, *Annalen*, 1912, 393, 198), and though in some cases mixtures of 2- and 4-coupled compounds are formed, the former preponderate.

3-Nitro-1-naphthylamine is converted by the Bart reaction (*Annalen*, 1922, 429, 95) into 3-nitro-1-naphthylarsonic acid, which is reduced by ferrous hydroxide (Benda, *Ber.*, 1911, 44, 3302) to 3-amino-1-naphthylarsonic acid as shown by diazotisation and subsequent coupling with β -naphthol to give a crimson dye.

The fact that an aqueous solution of sodium bicarbonate decomposes on warming would appear to suggest that sodium carbonate could be used in the sodium sulphide mixture for the mono-reduction of 1 : 3-dinitronaphthalene (Hodgson and Birtwell, J., 1944, 75). When this was done, however, the yield of mixed nitro-naphthylamines fell from 85% to 40%, and 95% of it was 3-nitro-1-naphthylamine, whereas when sodium bicarbonate was used the composition was 84% of 3-nitro-1- and 16% of 4-nitro-2-naphthylamine. The rôle of the bicarbonate as suggested by Hodgson and Birtwell (*loc. cit.*) is thus not only to buffer the reduction mixture throughout the reaction but also to liberate the active reducing agent NaSH according to the equation $\text{NaHCO}_3 + \text{Na}_2\text{S} = \text{NaSH} + \text{Na}_2\text{CO}_3$. Incidentally, carbon dioxide is not evolved when an aqueous solution of sodium bicarbonate and sodium sulphide is heated.

EXPERIMENTAL.

Chlorination of 3-Nitroaceto-1-naphthalide.—A finely divided suspension of 3-nitroaceto-1-naphthalide, formed by refluxing 3-nitro-1-naphthylamine (10 g.) with acetic anhydride (7 c.c.) and glacial acetic acid (120 c.c.) for 15 minutes, was treated with a brisk current of dry chlorine on the boiling water-bath for 90 minutes. 4-Chloro-3-nitroaceto-1-naphthalide (6 g.), which separated on cooling (scratching), crystallised from glacial acetic acid in colourless needles, m. p. 235° (Found : Cl, 13.7. $\text{C}_{12}\text{H}_9\text{O}_3\text{N}_2\text{Cl}$ requires Cl, 13.4%). It was (4.2 g.) refluxed for 3 hours with 50% sulphuric acid (60 c.c.) and ethyl alcohol (75 c.c., charcoal), and the mixture poured into ice-water : 4-chloro-3-nitro-1-naphthylamine (4.2 g.), precipitated by ammonia, crystallised from aqueous ethyl alcohol in yellow needles, m. p. 128° (Found : Cl, 15.7. $\text{C}_{10}\text{H}_7\text{O}_2\text{N}_2\text{Cl}$ requires Cl, 16.0%).

4-Chloro-3-nitroformo-1-naphthalide, prepared by refluxing the above amine with 90% formic acid, crystallised from alcohol in colourless felted needles, m. p. 230° (Found : N, 11.3. $\text{C}_{11}\text{H}_7\text{O}_3\text{N}_2\text{Cl}$ requires N, 11.2%).

Proof of Chlorination in Position 4.—The 4-chloro-3-nitro-1-naphthylamine (1.8 g.), dissolved in glacial acetic acid (15 c.c.), was stirred below 20° into a solution of sodium nitrite (0.8 g.) in sulphuric acid (10 c.c., *d* 1.84), and the mixture stirred after 15 minutes with a suspension of red cuprous oxide (1 g.) in methyl alcohol (50 c.c.); the temperature then rose to 70°. The mixture was poured into ice-water (500 c.c.), and the solid removed, washed free from copper salts, and dried (pump). 1-Chloro-2-nitronaphthalene, extracted from it with boiling alcohol and recovered from the extract by steam-distillation, crystallised from methyl alcohol (charcoal) in pale yellow needles (1 g.), m. p. 76° (Hodgson and

Kilner, J., 1926, 8, give m. p. 76°. Another solution of the diazonium sulphate, prepared as above from the amine (1.8 g.), was stirred into a solution of cuprous chloride (2.5 g.) in hydrochloric acid (10 c.c., *d* 1.18); the precipitated 1:4-dichloro-2-nitronaphthalene (2 g.) was removed, extracted, and crystallised from glacial acetic acid, forming yellow needles, m. p. 117° (Hodgson and Crook, J., 1936, 1502, give m. p. 116.5°).

Monomercuriation of 3-Nitro-1-naphthylamine.—No mercuriacetate could be isolated when a glacial acetic acid solution of 3-nitro-1-naphthylamine and mercuric acetate in stoichiometric proportion was refluxed. Monomercuriation was effected when a solution of mercuric acetate (12.8 g.) in water (50 c.c.) to which glacial acetic acid (2 c.c.) had been added was mixed with a solution of 3-nitro-1-naphthylamine (7.6 g.) in alcohol (100 c.c.), and the mixture boiled until the supernatant liquor gave no reaction with ammonium sulphide for inorganic mercury (*ca.* 1 hour). The liquid was then filtered hot, and the precipitate of 3-nitro-1-naphthylamine-2-mercuriacetate (14 g.) washed with boiling aqueous alcohol; it crystallised from 25% acetic acid in brown micro-needles, which began to decompose at *ca.* 200° (Found: Hg, 45.3. $C_{14}H_{11}O_4N_2Hg$ requires Hg, 45.0%). A finely divided suspension of the monomercuriacetate (4.5 g.) in 20% potassium iodide solution (40 c.c.), to which a little alcohol had been added, was refluxed with 20% potassium iodide solution (40 c.c.) containing iodine (2.7 g.) for 45 minutes. On cooling, the 2-iodo-3-nitro-1-naphthylamine (1 g.) was removed, washed with water and aqueous sodium thiosulphate, and extracted with ethyl alcohol containing charcoal and sodium thiosulphate; it crystallised from the filtered extract in micro-plates, m. p. 100° (Found: I, 40.0. $C_{14}H_{11}O_4N_2I$ requires I, 40.4%). A solution of 2-iodo-3-nitro-1-naphthylamine (1 g.) in glacial acetic acid (10 c.c.) was diazotised by addition below 20° to sulphuric acid (5 c.c., *d* 1.84), in which sodium nitrite (0.35 g.) had been dissolved. The cold solution of the diazonium sulphate was stirred into a suspension of red cuprous oxide (1 g.) in methyl alcohol (20 c.c.) and stirring was continued until the reaction had ceased. The mixture was poured into ice-water (200 g.), the methyl acetate layer removed by evaporation, and the precipitate collected and refluxed with ethyl alcohol containing charcoal and aqueous sodium thiosulphate; after filtration, the 3-iodo-2-nitronaphthalene (0.4 g.) in the filtrate was precipitated by the addition of ice-water, and crystallised from aqueous alcohol, forming rosettes of golden plates, m. p. 92° (Found: I, 42.2. Calc.: I, 42.5%) (Cumming and Howie, J., 1931, 3178, report yellow prisms from alcohol, m. p. 89.5°, after many recrystallisations).

2-Halogenomercuri-3-nitro-1-naphthylamines.—Hot 20% aqueous potassium chloride, bromide, and iodide reacted with the monomercuriacetate to give the following crystalline 2-halogenomercuri-3-nitro-1-naphthylamines:

Compound.	M. p. (decomp.).	Colour.	Crystal form.	% Hg.	
				Found.	Calc.
Chloro-	190°	Rust	Rods	47.1	47.4
Bromo-	214	Tan	Needles	42.5	42.9
Iodo-	204	Red-brown	Squat rods	38.7	39.0

20% Aqueous potassium hydroxide gave 2-hydroxymercuri-3-nitro-1-naphthylamine, which crystallised in long brown needles, m. p. 212° (decomp.) (Found: Hg, 50.0. $C_{14}H_9O_5N_2Hg$ requires Hg, 49.6%).

The action of hydrobromic acid (*d* 1.6) on 3-nitro-1-naphthylamine-2-mercuriacetate was to give 3-nitro-1-naphthylamine hydrobromide, which was basified to give 3-nitro-1-naphthylamine, m. p. and mixed m. p. 136°.

Dimercuriation of 3-Nitro-1-naphthylamine.—A solution of mercuric acetate (13.2 g.) in water (50 c.c.) to which glacial acetic acid (2 c.c.) had been added was added to a solution of 3-nitro-1-naphthylamine (3.8 g.) in alcohol (60 c.c.), and the mixture boiled (*ca.* 3 hours) until the supernatant liquor gave no reaction for inorganic mercury when tested with ammonium sulphide; it was filtered hot, and the precipitate washed with boiling alcohol and extracted with boiling glacial acetic acid. The residue (insoluble in organic solvents) consisted of chestnut felted needles of 3-nitro-1-naphthylamine-2:4-dimercuriacetate (12.5 g.), m. p. 210° (decomp.) (Found: Hg, 56.4. $C_{14}H_{11}O_4N_2Hg_2$ requires Hg, 56.8%). When refluxed with 90% formic acid and filtered, the dimercuriacetate gave 3-nitroformo-1-naphthalide, which separated from the filtrate and recrystallised from ethyl alcohol in fine yellow crystals, m. p. and mixed m. p. with an authentic specimen, 216°. When the dimercuriacetate (4 g.) was refluxed with a mixture of ethyl acetate (60 c.c.) and acetic anhydride (15 c.c.) for 10 hours (the reaction was considered complete when the brown solid had completely dissolved), 2:4-diacetoxymercuri-3-nitroaceto-1-naphthalide (2.5 g.) separated from the liquor in greenish-yellow needles, which had no definite m. p., but decomposed on heating (since mercury was formed in the reaction, the substance was not analysed). This compound (1.9 g.) was converted, when shaken with a solution of bromine (0.85 g.) in aqueous 20% potassium bromide (80 c.c.) and a little alcohol, at 40°, into 2:4-dibromo-3-nitroaceto-1-naphthalide (0.8 g.), which crystallised from glacial acetic acid in colourless needles, m. p. and mixed m. p. 202° (Hodgson and Hathway, *loc. cit.*), and was hydrolysed by refluxing for 3 hours with a mixture of 50% sulphuric acid (10 c.c.) and ethyl alcohol (12 c.c.) to give, on pouring into ice-water, 2:4-dibromo-3-nitro-1-naphthylamine sulphate, which, on basification and crystallisation from ethyl alcohol, gave small bright yellow plates of 2:4-dibromo-3-nitro-1-naphthylamine, m. p. and mixed m. p. 182° (Hodgson and Hathway, *loc. cit.*).

Coupling of 3-Nitro-1-naphthylamine with Diazotised Amines in Acetic Acid.—A chilled solution of *p*-nitroaniline (2.76 g.) in hydrochloric acid (9 g., *d* 1.18) and water (14 c.c.) was diazotised below 5° by aqueous sodium nitrite (1.4 g.), and the filtered solution neutralised with sodium acetate (7 g. in a little water) and stirred dropwise into a solution of 3-nitro-1-naphthylamine (3.76 g.) in ethyl alcohol (200 c.c.) below -5°. As coupling proceeded, aqueous sodium acetate was added so that the medium was never acid to Congo-red paper. The mixture was stirred until coupling was complete. The 3-nitro-2-*p*-nitrobenzeneazo-1-naphthylamine (6.8 g., 97% yield) was removed, washed with water, and dried at 50°; it crystallised from toluene in brick-red micro-needles and from glacial acetic acid in large crimson needles, m. p. 250° (Found: N, 20.7. $C_{18}H_{11}O_4N_5$ requires N, 20.8%), which gave a purple colour with concentrated sulphuric acid, changing to scarlet on dilution. The scarlet solution in acetone changed to indigo-violet on addition of aqueous sodium hydroxide, and warm ethyl-alcoholic potassium hydroxide produced a deep purple solution.

3-Nitro-2-*p*-chlorobenzeneazo-1-naphthylamine, prepared in 50% yield with diazotised *p*-chloroaniline (0.01 g.-mol.) as above and crystallised successively from toluene and glacial acetic acid, formed four-sided orange plates having a steel-blue lustre, m. p. 188° (Found: Cl, 10.8. $C_{18}H_{11}O_4N_4Cl$ requires Cl, 10.9%), which gave a deep scarlet colour with sulphuric acid, changing on dilution with water to purple, thence to scarlet, and finally to bright yellow; the orange solution in acetone became wine-red on addition of aqueous sodium hydroxide, and alcoholic potash afforded a wine-red solution.

3-Nitro-2-benzeneazo-1-naphthylamine was obtained in only 7% yield by coupling diazotised aniline (0.01 g.-mol.) with 3-nitro-1-naphthylamine, as above; crystallised successively from toluene and acetic acid, it formed scarlet micro-needles, m. p. 275° (Found: N, 19.2. $C_{18}H_{13}O_4N_4$ requires N, 19.2%), which gave a purple colour with concentrated sulphuric acid, changing to scarlet on dilution.

Monoreduction of 1:3-Dinitronaphthalene by Sodium Sulphide and Sodium Carbonate.—The amine (13.5 g.), dissolved in boiling methyl alcohol (240 c.c.), was agitated while sodium sulphide (26 g.) and sodium carbonate (4.5 g.) in water (6.3 c.c.) were added during 30 minutes. The mixture was then poured into ice-water (2000 g.), and the precipitate

collected and extracted with 6% hydrochloric acid (600 c.c.) to remove 3-nitro-1- and 4-nitro-2-naphthylamine, which were precipitated from the extract by ammonia. Yield 5.5 g., m. p. 126°, indicating 95% of 3-nitro-1-naphthylamine according to the thermal diagram of Hodgson and Hathway (J., 1944, 386).

Preparation of Arsenicals from 3-Nitro-1-naphthylamine.—*3-Nitro-1-naphthylarsonic acid.* A finely divided suspension of 3-nitro-1-naphthylamine hydrochloride, prepared by rapid cooling of a solution of the base (9.4 g.) in 6% hydrochloric acid (350 c.c.) with vigorous agitation, was treated at 15–20° with an aqueous solution of sodium nitrite (5 g.), and to the clear solution of the diazonium chloride at 0° were added simultaneously (a) a solution of sodium meta-arsenite (20 g.) and a few crystals of copper sulphate in ice-water (1 l.) and (b) 20% aqueous sodium hydroxide (100 c.c.) at such a rate that the resulting solution remained slightly alkaline throughout. The mixture was stirred for several hours, concentrated, and filtered, the filtrate acidified to Congo-red paper, and the precipitate of *3-nitro-1-naphthylarsonic acid* (6 g., 42%) removed, washed, and purified by precipitation with acid from aqueous sodium carbonate solution. It crystallised from water containing a little alcohol in pale orange rods which decomposed on heating (Found: N, 4.7; As, 25.0. $C_{10}H_8O_5NAs$ requires N, 4.7; As, 25.3%).

3-Amino-1-naphthylarsonic acid. 25% Aqueous sodium hydroxide was added to a solution of crystalline ferrous sulphate (27 g.) in water (80 c.c.) until the precipitate after shaking reacted strongly alkaline to litmus; a solution of 3-nitro-1-naphthylarsonic acid (4 g.) in 5% aqueous sodium hydroxide was then added, and the mixture shaken for 10 minutes. The precipitate was removed and washed, the bulked filtrates just acidified with mineral acid to Congo-red paper, and the excess of mineral acid removed by aqueous sodium acetate. *3-Amino-1-naphthylarsonic acid*, extracted from the precipitate with boiling alcohol, crystallised from aqueous alcohol in colourless felted needles, m. p. 252° (decomp.) (Found: As, 27.8. $C_{10}H_{10}O_5NAs$ requires As, 28.1%).

3-Acetamido-1-naphthylarsonic acid crystallised from glacial acetic acid in colourless needles, which decomposed on heating (Found: N, 4.5. $C_{12}H_{12}O_5NAs$ requires N, 4.5%).

1-Arsono-3-p-nitrobenzylidenenaphthylamine was obtained when stoichiometric quantities of the above amino-arsonic acid and *p*-nitrobenzaldehyde were refluxed in acetic acid; it crystallised from glacial acetic acid in yellow needles, which decomposed on heating (Found: N, 7.2. $C_{17}H_{13}O_5N_2As$ requires N, 7.0%).

1-Arsononaphthalene-3-azo- β -naphthol was obtained when a finely divided paste of the above amine (0.35 g.) in glacial acetic acid (4 c.c.) was diazotised by addition below 20° to a solution of sodium nitrite (0.15 g.) in sulphuric acid (2.5 c.c., *d* 1.84), and the solution of the diazonium sulphate added to one of β -naphthol (0.2 g.) in 20% aqueous sodium hydroxide (35 c.c.) and water (17 c.c.) below 20°. After 2 hours' stirring, the dye was precipitated (0.5 g., 90% yield) with hydrochloric acid. It crystallised from acetone in crimson micro-needles which decomposed on heating (Found: N, 6.8. $C_{20}H_{15}O_4N_2As$ requires N, 6.6%), and gave a magenta colour with concentrated sulphuric acid which changed on dilution to scarlet.

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