# 4. *Preparation of 6-Nitro-1-naphthol, Improved Methods for the Decomposition of Diazo-naphthols, and New Reactions of Nitronaphthols.*

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6-Nitro-1-naphthol, 6-bromo-1-naphthol, and 4 : 5-dinitro-2-naphthol have been prepared from the corresponding diazonaphthols by improved methods of decomposition. The electronic effect of the 6-nitro-group on position 2 is greater than that of the 6-bromo-substituent. 2 : 4-*Dibromo-6-nitro-1-naphthol* has been obtained from one molecule each of bromine and 6-nitro-2-diazo-1-naphthol. Monobromination and monomercuration of 6-nitro-1-naphthol occur in position 4.

The replacement of diazo-nitrogen in a diazo-naphthol by hydrogen by Morgan and Evens's method (J., 1919, **115**, 1126) is accomplished by boiling with ethyl alcohol in the presence of a metallic powder or hypophosphorous acid. The reaction is very slow; *e.g.*, 4-nitro-1-diazo-2-naphthol requires 32 hours with aluminium powder. When precipitated copper is added, however, the time is reduced to 12 hours and the yield (45—50%) is larger than that obtained (38%) when aluminium is used alone. Similarly, 4 : 5-*dinitro-1-diazo-2-naphthol* is readily reduced by the copper–aluminium mixture.

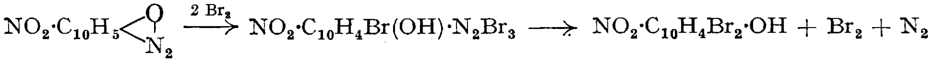
The decomposition of 6-nitro-2-diazo-1-naphthol could not be effected by Morgan and Evens's method even after 34 hours' boiling, but was accomplished in 30 minutes when its solution in glacial acetic–concentrated sulphuric acid was added to a suspension of yellow precipitated cuprous oxide in ethyl alcohol (cf. Hodgson and Turner, J., 1943, 86).

6-Nitro-2-diazo-1-naphthol is also non-reactive towards concentrated aqueous potassium iodide, even when cuprous iodide is added, and towards a suspension of cuprous iodide in hydriodic acid, but reacts immediately when its solution in glacial acetic–sulphuric acid is added to a suspension of precipitated copper powder in saturated aqueous potassium iodide: the reactivity may be due to the diazonium salt re-formed by the sulphuric acid. In a neutral or a weakly acid medium (ethyl alcohol and acetic acid) this diazo-oxide is stable towards the usual reagents for diazo-compounds.

In the preparation of 6-*bromo-2-diazo-1-naphthol*, *p*-toluenesulphon-2-naphthalide is brominated in glacial acetic acid at 90—100°; after the mixture of 1 : 6-dibromo-*p*-toluenesulphon-2-naphthalide and 1 : 6-dibromo-2-naphthylamine hydrobromide obtained has been basified, hydrolysed, and diazotised in sulphuric–glacial acetic acid, the removal of mineral acid by sodium acetate brings about the formation of the diazo-oxide in 84·5% yield.

6-Nitro-1-naphthol, hitherto difficultly accessible (cf. Veselý and Dvořak, *Bull. Soc. chim.*, 1923, **33**, 319), has now been prepared in good yield from 6-nitro-2-diazo-1-naphthol, itself readily obtained from 1 : 6-dinitro-*p*-toluenesulphon-2-naphthalide (Hodgson and Turner, *loc. cit.*).

The reaction between equivalent amounts of bromine and 6-nitro-2-diazo-1-naphthol produces 2 : 4-*dibromo-6-nitro-1-naphthol* without evolution of hydrogen bromide, possibly as follows:



$$\mathrm{NO_2{\cdot}C_{10}H_5}\!<\!\begin{smallmatrix}\mathrm{O}\\ \mathrm{N_2}\end{smallmatrix} \xrightarrow{2\,\mathrm{Br_2}} \mathrm{NO_2{\cdot}C_{10}H_4Br(OH){\cdot}N_2Br_3} \longrightarrow \mathrm{NO_2{\cdot}C_{10}H_4Br_2{\cdot}OH + Br_2 + N_2}$$

6-Nitro-1-naphthol is monobrominated and monomercurated in position 4, like 6-nitro-1-naphthylamine (Hodgson and Turner, J., 1943, 391). The *mercuriacetate* is readily converted into 4-*iodo-6-nitro-1-naphthol*. The 4-halogeno-derivatives were oriented by their difference from the only possible alternatives, the 2-halogeno-derivatives, which were synthesised from 6-nitro-2-diazo-1-naphthol.

## EXPERIMENTAL.

All m. p.'s are corrected.

6-*Nitro*-2-*diazo*-1-*naphthol*.—1 : 6-Dinitro-*p*-toluenesulphon-2-naphthalide (50 g.) was hydrolysed and diazotised (Hodgson and Turner, this vol., p. 86), and the diazonium solution poured into ice-water (6 l.). After 12 hours, the diazo-naphthol was collected, washed with water, and dried at 60°; yield, 26·6 g. (95·5%). It crystallised from glacial acetic acid in yellow-brown needles, which exploded at 150—151° (Gaess and Ammelburg, *Ber.*, 1894, **27**, 2211, give expl. p. 142—145°; Scheid, *Ber.*, 1901, **34**, 1816, gives 151—157°) (Found : N, 19·6. Calc. : N, 19·5%).

6-*Nitro*-1-*naphthol*.—The above diazo-naphthol (10 g.) was dissolved in a mixture of glacial acetic acid (75 c.c.) and sulphuric acid (75 c.c., *d* 1·84) below 20°, and the solution added during 15 minutes to a well-stirred suspension of precipitated cuprous oxide (25 g.) in alcohol (200 c.c.), initially at 55°; nitrogen was evolved and the temperature rose to 82°. A further quantity (7 g.) of cuprous oxide was then added, and stirring continued at 80° for 30 minutes. The solid was collected and washed with a little boiling alcohol and the combined filtrate and washings were stirred into a mixture of ice and water (1 l.). After 12 hours, the precipitate was collected and dissolved in warm 2% aqueous sodium hydroxide (200 c.c.), the deep red solution filtered and acidified with dilute hydrochloric acid, and the precipitated 6-nitro-1-naphthol (5·2—6·0 g.; 60—70% yield) collected, washed, dried, and crystallised from glacial acetic acid, forming yellow elongated plates, m. p. 181—182° (Veselý and Dvořák, *loc. cit.*, give m. p. 179°) (Found : N, 7·5. Calc : N, 7·4%).

6-*Nitro*-1-*naphthyl acetate*, formed from 6-nitro-1-naphthol (1·0 g.) in boiling acetic anhydride (5 c.c.) and glacial acetic acid (5 c.c.), crystallised from dilute acetic acid (charcoal) in slender cream needles, m. p. 121° (Found : N, 6·3. $C_{12}H_9O_4N$ requires N, 6·1%). 6-*Nitro*-1-*naphthyl benzoate*, prepared by the Schotten–Baumann method, crystallised from ethylene dichloride in cream needles, m. p. 147·5—148° (Found : N, 4·6. $C_{17}H_{11}O_4N$ requires N, 4·8%).

2-*Chloro*-6-*nitro*-1-*naphthol*.—The paste made from 6-nitro-2-diazo-1-naphthol (2·0 g.), hydrochloric acid (20 c.c., *d* 1·16), water (10 c.c.), and cuprous chloride (2·0 g.) was heated on the water-bath until nitrogen ceased to be evolved (2 hours). After dilution with water, the solid (2·1 g.) was collected, washed with dilute hydrochloric acid and with water, and dried. 2-*Chloro*-6-*nitro*-1-*naphthol* crystallised from glacial acetic acid in chrome-yellow needles, m. p. 179—180°) (Found : N, 6·5. $C_{10}H_6O_3NCl$ requires N, 6·3%).

2-*Chloro*-4-*bromo*-6-*nitro*-1-*naphthol* was formed when 2-chloro-6-nitro-1-naphthol (0·95 g.), dissolved in glacial acetic acid (20 c.c.), was treated with a 25% (w./v.) solution of bromine in glacial acetic acid (2·8 c.c.) at 60°, the mixture heated at 90° for 5 minutes, and the volume then reduced to 10 c.c.; on cooling, primrose-yellow needles separated, m. p. 199° and after recrystallisation from glacial acetic acid (Found : N, 5·0. $C_{10}H_5O_3NClBr$ requires N, 4·7%).

2-*Bromo*-6-*nitro*-1-*naphthol* was formed when 6-nitro-2-diazo-1-naphthol (5·0 g.) was added to a solution of cuprous bromide (5·0 g.) in hydrobromic acid (50 c.c., 30%) and the mixture heated on the water-bath for 4 hours. 5% Hydrochloric acid was added, and the bromonitronaphthol (7·2 g.) crystallised from 70% acetic acid (charcoal), forming mustard-yellow needles, m. p. 164·5—165·5° (Found : N, 5·4. $C_{10}H_6O_3NBr$ requires N, 5·2%).

4-*Bromo*-6-*nitro*-1-*naphthol* was obtained when a solution of 6-nitro-1-naphthol (6·2 g.) in glacial acetic acid (40 c.c.) was shaken with a mixture of glacial acetic acid (10 c.c.) and a 20% solution of bromine in glacial acetic acid (8·5 c.c.), added gradually. After 2 hours, the solution was heated on the water-bath for 1 hour, evaporated to small bulk with charcoal, filtered, and allowed to crystallise; the bromonitronaphthol crystallised from 80% acetic acid in orange needles, m. p. 238° (Found : N, 5·5. $C_{10}H_6O_3NBr$ requires N, 5·2%).

2 : 4-*Dibromo*-6-*nitro*-1-*naphthol* was formed when 6-nitro-1-naphthol (1 g.), dissolved in glacial acetic acid (15 c.c.), was heated on the water-bath for 30 minutes with the above solution of bromine (8·5 c.c.); after concentration to 10 c.c. (charcoal) and filtration, the filtrate deposited the dibromonitronaphthol in greenish-yellow needles, m. p. 210° after recrystallisation from glacial acetic acid (Found : N, 4·2. $C_{10}H_5O_3NBr_2$ requires N, 4·0%). Alternatively, 6-nitro-2-diazo-1-naphthol (5·0 g.), dissolved in glacial acetic acid (65 c.c.) at 110°, was shaken with a solution of bromine (1·2 c.c.) in glacial acetic acid (3 c.c.), nitrogen only being evolved. The dibromonitronaphthol (5·1 g.) separated on cooling; recrystallised from glacial acetic acid, it formed greenish-yellow needles, m. p. and mixed m. p. 210° (Found : N, 4·2%).

2-*Iodo*-6-*nitro*-6-*naphthol*.—A solution of 6-nitro-2-diazo-1-naphthol (2·6 g.) in a cold mixture of glacial acetic acid (15 c.c.) and sulphuric acid (15 c.c., *d* 1·84) was stirred into aqueous potassium iodide (30 g. in 25 c.c.) at 95° in which copper powder (4·0 g.) was suspended. When the vigorous evolution of nitrogen had ceased, the mixture was diluted to 150 c.c., aqueous sodium thiosulphate added to remove free iodine, and the solid collected, washed with water, dried, and extracted with boiling acetone (50 c.c.). The extract afforded 2-*iodo*-6-*nitro*-1-*naphthol* (1·4 g.), which crystallised from glacial acetic acid (charcoal) in brass-yellow elongated plates, m. p. 214—215° (decomp. and evolution of iodine after discoloring above 200°) (Found : N, 4·5. $C_{10}H_6O_3NI$ requires N, 4·45%).

6-*Nitro*-1-*naphthol*-4-*mercuriacetate* was obtained when a mixture of 6-nitro-1-naphthol (3·0 g.), glacial acetic acid (20 c.c.), and mercuric acetate (6·0 g.) was boiled to effect solution, heated on the water-bath for 1 hour, and kept overnight. The dense, yellow, crystalline solid (5·4 g.) which separated was washed with glacial acetic acid and alcohol, dried, and recrystallised from glacial acetic acid, forming cream-coloured, almost colourless, lustrous, feathery needles, m. p. above 360° (shrinking at 300°) (Found : Hg, 44·1. $C_{12}H_9O_5NHg$ requires Hg, 44·7%).

4-*Iodo*-6-*nitro*-1-*naphthol*.—The above mercuriacetate (1·8 g.), suspended in 20% aqueous potassium iodide (20 c.c.) at 90°, was heated with a solution of iodine (0·92 g.) in hot 30% aqueous potassium iodide for 5 minutes on the water-bath, the mixture cooled and treated with sodium thiosulphate, and the 4-*iodo*-6-*nitro*-1-*naphthol* crystallised from glacial acetic acid, forming light brownish-yellow needles, m. p. 214—216° (without noticeable decomp.; cf. the 2-iodo-isomeride above); mixed m. p. with 2-iodo-6-nitro-1-naphthol, 192—198° (Found : N, 4·4. $C_{10}H_6O_3NI$ requires N, 4·45%).

4 : 5-*Dinitro*-1-*diazo*-2-*naphthol*.—2 : 4 : 5-Trinitro-*p*-toluenesulphon-1-naphthalide (7·2 g.) (Hodgson and Turner, J., 1942, 724) was dissolved in sulphuric acid (20 c.c., *d* 1·84), below 20°, mixed with a solution of sodium nitrite (2·0 g.) in sulphuric acid (15 c.c., *d* 1·84), and stirred into glacial acetic acid (40 c.c.) below 20°. After 1 hour the diazo-solution was run into ice-water (1 l.), and a slight excess of sodium acetate added to neutralise the free sulphuric acid. After 12 hours, the 4 : 5-*dinitro*-1-*diazo*-2-*naphthol* (4·2 g.; 97%) was removed, washed, and dried in a vacuum; it crystallised from glacial acetic acid in yellow needles, which decomposed slowly when heated gradually, but exploded at 160° when heated rapidly (Found : N, 21·3. $C_{10}H_4O_5N_4$ requires N, 21·5%).

4 : 5-*Dinitro*-2-*naphthol*.—When the above diazo-naphthol (1 g.) in alcohol (25 c.c.) was refluxed with aluminium powder (0·2 g.) on a water-bath for 4 hours (cf. Morgan and Evens, *loc. cit.*), little reaction occurred, but when precipitated copper (0·05 g.) was added, the rate of decomposition was greatly accelerated and, after refluxing for a further 2¼ hours, the solution gave no coupling colour with alcoholic alkaline resorcinol. After filtration, the pale purple filtrate was evaporated to dryness on the water-bath, and the residue extracted repeatedly with boiling water (in 60 c.c. portions). 4 : 5-Dinitro-2-naphthol, which crystallised from the combined extracts on cooling, separated from 50% aqueous alcohol in deep yellow, micro-lenticular crystals, m. p. 237—238° (Bell, J., 1933, 288, gives m. p. *ca.* 230°) (Found : N, 12·1. Calc. : N, 11·95%).

1-*Bromo*-4 : 5-*dinitro*-2-*naphthol* was formed when 4 : 5-dinitro-1-diazo-2-naphthol (1·0 g.), made into a paste with hydrobromic acid (5 c.c., 30%), was treated with a solution of cuprous bromide (2·0 g.) in hydrobromic acid (10 c.c., 30%)

and heated on the water-bath for 2 hours. After dilution with water, the bromodinitronaphthol was collected, washed, dried, and twice crystallised from dilute acetic acid, forming light lemon-yellow needles, m. p. 218—220° (Found : N, 9·3. $C_{10}H_5O_5N_2Br$ requires N, 9·4%).

6-*Bromo*-2-*diazo*-1-*naphthol*.—A solution of *p*-toluenesulphon-2-naphthalide (40 g.) in glacial acetic acid (100 c.c.) was treated at 90° with one of bromine (13·6 c.c.) in glacial acetic acid (50 c.c.). After 5 minutes the pasty mass of cream needles was cooled, washed, after filtration, with a little glacial acetic acid, and dried in a vacuum. The product was suspended in water and rendered faintly alkaline with dilute sodium carbonate solution, and the solid was collected, washed, dried in a vacuum, dissolved in cold sulphuric acid (90 c.c., *d* 1·84) and treated with a solution of sodium nitrite (9·0 g.) in sulphuric acid (65 c.c., *d* 1·84). The diazo-solution was stirred into glacial acetic acid (220 c.c.) below 20°, and the mixture added after 30 minutes to ice-water (6 l.) containing sufficient sodium acetate to neutralise the mineral acid. After 14 days the precipitate (18·5 g.) of 6-*bromo*-2-*diazo*-1-*naphthol* was collected, washed, and dried in a vacuum; it crystallised from glacial acetic acid in stout brownish needles and from acetone in slender, matted, yellow needles, m. p. 214° (decomp.) after darkening at about 145° and shrinking at about 160° (Found : N, 11·2. $C_{10}H_5ON_2Br$ requires N, 11·2%).

6-*Bromo*-1-*naphthol*.—A mixture of the above diazo-naphthol (10 g.), alcohol (125 c.c.), aluminium powder (1·0 g.), copper powder (1·0 g.), and Devarda's alloy (4·0 g.) was refluxed for 10½ hours. After filtration, the liquid was evaporated to dryness on the water-bath, and the residue boiled repeatedly with water until the filtered extracts no longer deposited 6-bromo-1-naphthol on cooling. The colourless needles obtained had m. p. 128·5—129·5° (Fuson, *J. Amer. Chem. Soc.*, 1925, **47**, 516, gives m. p. 129—130°).

1 : 6-*Dinitronaphthalene*-2-*azo*-β-*naphthol* was obtained when 1 : 6-dinitro-*p*-toluenesulphon-2-naphthalide (5·0 g.) was hydrolysed and diazotised as above, and the diazo-solution diluted with ice-water (100 c.c.) and added *at once* to a solution of β-naphthol (1·9 g.) in 20% aqueous sodium hydroxide (100 c.c.) and water (100 c.c.) below 10°. The precipitated, washed, and dried dye crystallised from tetrachloroethane in deep red, prismatic needles, m. p. 310° (Found : N, 14·3. $C_{20}H_{12}O_5N_4$ requires N, 14·4%); it also crystallised readily from nitrobenzene, ethylene dichloride, chloroform, tetralin, pyridine, and diethylaniline.

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