63. *Some Reactions and Derivatives of* 6- *and* 7-*Nitro*-2-*naphthylamines. Part I. Bromination, Halogeno-derivatives, and the Preparation of the New* 7-*Nitro*-2-*naphthol.*

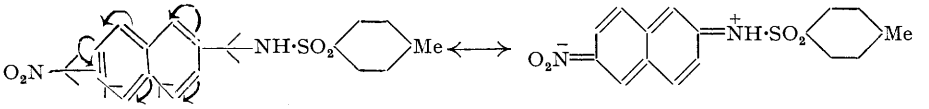
By Herbert H. Hodgson and Edward R. Ward.

The direct bromination of 6- and 7-nitro-2-naphthylamines and of their *p*-toluenesulphonyl derivatives takes place in the 1-position only, in contrast with the tribromination of β-naphthylamine in chloroform and its dibromination in pyridine solution. 6- and 7-Nitro-2-naphthylamines readily form mono- but only with difficulty di-toluene-*p*-sulphonamides. All the 2-halogeno-6- and -7-nitronaphthalenes and the 6- and 7-halogeno-2-naphthylamines have been prepared from a common source. The new 7-nitro-2-naphthol has been prepared, and the difference noted between decompositions of aqueous solutions of 6- and 7-nitronaphthalene-2-diazonium sulphates when dropped into boiling 20% sulphuric acid with production of naphthol, or, when boiled *in situ*, with resultant azo-compound formation.

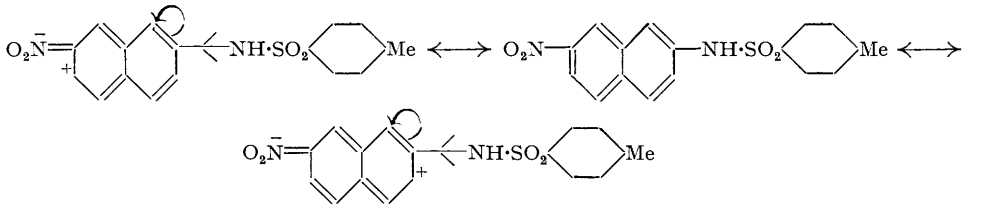
The direct bromination of 6- and 7-nitro-2-naphthylamines and of their toluene-*p*-sulphonyl derivatives occurred only in the 1-position whether in chloroform or pyridine solution, and a great excess of bromine had no further effect. This is in striking contrast with the bromination of β-naphthylamine, which Franzen and Stäuble (*J. pr. Chem.*, 1922, **103**, 352) found to take place successively in the order 1, 6, and 3, giving 1 : 3 : 6-tribromo-2-naphthylamine as the final product—a result similar to that in the bromination of β-naphthol, where 1 : 3 : 4 : 6-tetrabromo-2-naphthol is ultimately formed; also, Bell (*J.*, 1932, 2732) found that the bromination of toluene-*p*-sulphon-2-naphthalide in chloroform solution gave the 1 : 6-dibromo-derivative in analogy with its nitration (cf. Morgan and Micklethwait, *J.*, 1912, **101**, 148), but that in pyridine solution this naphthalide would not brominate further than the 1 : 3-derivative, although the toluene-*p*-sulphon-1 : 3 : 6-tribromo-2-naphthalide was formed in the chloroform solution of the 1 : 3-dibromo-compound, and toluene-*p*-sulphon-1 : 6-dibromo-2-naphthalide was readily converted into the 1 : 3 : 6-tribromo-compound in pyridine solution.

The unique monobromination of 6-nitro-2-naphthylamine and of its toluene-*p*-sulphonyl derivative must therefore be ascribed to the deactivation of the 3-position by the 6-nitro-group, which, by resonance with the amino- and toluene-*p*-sulphonamido-groups (cf. Robinson and

Thompson, *J.*, 1931, 2015, for ready transmission of effects between the 2- and the 6-position), causes the nitrogen to become kationoid (electrophilic) in the contributing 2 : 6-quinonoid structure of the resonance hybrid :



Similarly, in 7-nitro-2-naphthylamine and its toluene-*p*-sulphonyl derivative there is resonance into the 3 : 7-ionic quinonoid structure whereby the 3-position is deactivated :



In both cases activation is restricted to the 1-position of the contributing benzenoid structure of the resonance hybrid, and only monobromination takes place.

With a nitro-group in the 1-position, toluene-*p*-sulphon-1-nitro-2-naphthalide was shown to brominate readily in the 3-position in pyridine solution by Consden and Kenyon (*J.*, 1935, 1592), who explained this by salt formation of the sulphonamido-group with pyridine. A similar claim was made for toluene-*p*-sulphon-1 : 6-dinitro-2-naphthalide, although the fact of 3-bromination could not be definitely proved by them and their claim rests upon analogy. It is possible, however, that bromination could have occurred elsewhere, since the 6-nitro-group could restrain salt formation by pyridine at the toluene-*p*-sulphonamido-group as in the case of toluene-*p*-sulphon-6-nitro-2-naphthalide.

Earlier, Veselý and Dvorák (*Chem. Listy*, 1923, **17**, 163) had found that bromination of 4-, 5-, 6-, and 8-nitroaceto-2-naphthalides occurred exclusively in the 1-position; this can be readily explained as above.

On analogy with the effect of the nitro-group on halogenation, the similar electrophilic effect of the sulphonic acid group likewise directs and restricts halogenation to the 1-position; *e.g.*, aceto-2-naphthalide-6-sulphonic acid is chlorinated in the 1-position only (Steiger, G.P. 536,995; *Chem. Abstr.*, 1932, **26**, 2747), and the 5-, 6-, and 7-sulphonic acids of β-naphthylamine all brominate exclusively in the 1-position (Heller, Arnold, and Schmidt, *Z. angew. Chem.*, 1930, **43**, 1132).

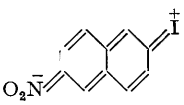
Proof of the constitution of 1-bromo-6-nitro-2-naphthylamine was given by deamination to the known 1-bromo-6-nitronaphthalene, and by conversion, *via* the Sandmeyer reaction, into the known 1 : 2-dibromo-6-nitronaphthalene (Hodgson and Turner, *J.*, 1943, 579). *1-Bromo-7-nitro-2-naphthylamine* was orientated by conversion *via* the Sandmeyer reaction into 1 : 2-*dibromo*-7-*nitronaphthalene*, followed by reduction to 7 : 8-*dibromo*-2-*naphthylamine* by the iron-powder method of Hodgson and Marsden (*J.*, 1944, 398), and deamination to the known 1 : 2-dibromonaphthalene.

Toluene-p-*sulphon*-1-*bromo*-6- and -7-*nitro*-2-*naphthalides* were readily hydrolysed by concentrated sulphuric acid to the free amines and so orientated.

Probably as a result of easy resonance with consequent partial inhibition of the anionoid reactivity of the 2-amino-group, 6- and 7-nitro-2-naphthylamines, while forming mono-toluene-*p*-sulphonyl derivatives with ease, were converted only with difficulty into the di-derivatives, even when a large excess of toluene-*p*-sulphonyl chloride in pyridine was used, although the reaction proceeded a little more readily in water (cf. Hodgson and Turner, *J.*, 1943, 391; Hodgson and Hathway, *J.*, 1944, 538; 1945, 453). The further weakening of the anionoid reactivity above by the presence of bromine in the 1-position appears to prevent toluene-*p*-sulphonation altogether, and the toluene-*p*-sulphon-1-bromo-6- and -7-nitro-2-naphthalides had to be prepared by bromination of toluene-*p*-sulphon-6- and -7-nitro-2-naphthalides.

All the possible 2-halogeno-6- and -7-nitronaphthalenes have been prepared from a common source, and also 6- and 7-halogeno-2-naphthylamines; of these compounds only 2-bromo-6-nitronaphthalene and 6-bromo-2-naphthylamine have been prepared before.

2-*Iodo*-6-*nitronaphthalene* could not be reduced by the methyl alcoholic–alkaline sulphide procedure of Hodgson and Birtwell (*J.*, 1944, 75), the nitro-compound being recovered unchanged; this resistance to sulphide reduction may well be a result of facile resonance between the iodine and nitro-group (annexed), owing to the amphoteric character of the iodine, whereby the reactivity of the nitro-group is so decreased as to resist further acceptance of electrons from the reducing agent. In this respect the iodine is resonating like an amino-group; analogously, 6-nitro-2-naphthylamine also resists further reduction with alkaline sulphides, as do other nitronaphthylamines.



The new 7-*nitro*-2-*naphthol* as well as the known 6-nitro-2-naphthol have been readily obtained by decomposition of the corresponding 6- and 7-nitronaphthalene-2-diazonium sulphates when added to boiling 20% sulphuric acid (cf. Hodgson, E.P. 200,714). When solutions of the above diazonium sulphates were boiled *in situ*, almost quantitative yields were obtained of 6- and 7-*nitronaphthalene*-2 : 1′-*azo*-6′- and -7′-*nitro*-2′-*naphthols* (cf. the corresponding preparation of *m*-chlorophenol by the same device, and the complete conversion into azo-compound by heating *m*-chlorobenzenediazonium sulphate *in situ*).

6- and 7-Nitronaphthylamines form stable *anils* with *p*-nitrobenzaldehyde in glacial acetic acid solution.

Experimental.

Bromination of 6- *and* 7-*Nitro*-2-*naphthylamines.*—A solution of the requisite amine (1 g.) in dry chloroform (50 c.c.) was treated at 50° with 3 c.c. of a solution of bromine (1 c.c.) in dry chloroform (9 c.c.); the hydrobromide of 1-bromo-6-nitro- or 1-bromo-7-nitro-2-naphthylamine was then immediately precipitated, and was filtered off after cooling to room temperature. The hydrobromides could be basified by dilute ammonia or even by trituration with water, and the free bases were then crystallised from boiling glacial acetic acid or pyridine; yield of each, 1·25 g. (*ca.* 90%). Further small amounts were obtainable by concentrating the chloroform solutions.

1-Bromo-6-nitro-2-naphthylamine separated from pyridine in orange rods, m. p. 225—226° (Vesely and Dvorăk, *loc. cit.*, give m. p. 222—223°) (Found: N, 7·4. Calc. for $C_{10}H_7O_2N_2Br$: N, 7·35%); the hydrochloride is stable only in hot concentrated hydrochloric acid and, like the hydrobromide, is hydrolysed by water. Deamination to 1-bromo-6-naphthalene was effected by adding a solution of the amine (2·5 g.) in sulphuric acid (5 c.c., *d* 1·84) to one of sodium nitrite (1 g.) in sulphuric acid (5 c.c., *d* 1·84), and then stirring the whole into glacial acetic acid (20 c.c.) below 20°; the mixture was kept for 30 minutes to complete the diazotisation and then stirred with red cuprous oxide (3 g.), added gradually over 15 minutes, during which time the temperature was allowed to rise to 40°; stirring was continued for a further 1 hour, after which the mixture was poured on ice and the precipitate containing 1-bromo-6-nitronaphthalene removed, washed in sequence with water, aqueous sodium carbonate, and water, and then extracted with ethanol (50 c.c.); on concentration of the extract 1-bromo-6-nitronaphthalene separated; it crystallised from aqueous pyridine in pale yellow micro-plates, m. p. and mixed m. p. with an authentic specimen prepared by Hodgson and Turner (*loc. cit.*) 130—131° (Found: N, 5·7. Calc. for $C_{10}H_6O_2NBr$: N, 5·5%). When 1-bromo-6-nitro-2-naphthylamine was diazotised as above and the solution added to one of cuprous bromide (5 g.) in hydrobromic acid (20 c.c., *d* 1·7), the mixture stirred for 3 hours, kept overnight, and then poured on ice, 1 : 2-dibromo-6-nitronaphthalene was precipitated; it crystallised from methanol–acetone in cream-coloured needles, m. p. 175° (Hodgson and Turner, *loc. cit.*, give m. p. 175°).

1-*Bromo*-7-*nitro*-2-*naphthylamine* crystallised from pyridine in orange-red rods which were redder and somewhat more soluble in organic solvents than the 6-nitro-isomeride above, and had m. p. 228° (Found: N, 10·6; Br, 30·0. $C_{10}H_7O_2N_2Br$ requires N, 10·4; Br, 30·0%). Diazotisation of the amine (2·5 g.) followed by treatment as above gave 1 : 2-*dibromo*-7-*nitronaphthalene* (2·9 g.) which crystallised from 80% pyridine in cream-coloured micro-needles, m. p. 147° (Found: N, 4·4. $C_{10}H_5O_2NBr_2$ requires N, 4·2%), which were very soluble in hot or cold pyridine and in ethylene chloride, soluble in chloroform, but only slightly soluble in cold ethanol.

7 : 8-*Dibromo*-2-*naphthylamine* was formed when finely powdered 1 : 2-dibromo-7-nitronaphthalene (2 g.) was refluxed for 3 hours with a mixture of iron powder (pin dust, 6 g.), ferrous sulphate (1 g.), and water (50 c.c.); the mixture was filtered cold, the solid washed with cold water, dried, and extracted with boiling ethanol, and the solvent removed from the crude 7 : 8-dibromo-2-naphthylamine which crystallised from 50% aqueous ethanol in scimitar-like clusters of colourless needles or from ethanol in similar clusters of colourless needles, m. p. 103—104° (Found: N, 4·8. $C_{10}H_7NBr_2$ requires N, 4·65%); the filtrate above yields only a very small additional amount when extracted by chloroform. On deamination as above, 1 : 2-dibromonaphthalene was obtained which crystallised from methanol in colourless needles, m. p. and mixed m. p. with authentic specimen 68° (Meldola and Streatfeild, *J.*, 1893, **63**, 1054, give m. p. 68°).

Action of Toluene-p-*sulphonyl Chloride on* 6- *and* 7-*Nitro*-2-*naphthylamines.*—The amine (2 g.) was ground with toluene-*p*-sulphonyl chloride (3 g.), added to pyridine (15 c.c.), the mixture heated on the water-bath for 2—3 hours with addition of a little sodium carbonate, then cooled and stirred into 10% hydrochloric acid; the precipitate of the sulphonamide was washed with water and extracted with 5% aqueous sodium hydroxide (500 c.c.), and the filtered extract cooled and neutralised with dilute hydrochloric acid; the precipitated monosulphonamide was then filtered off, washed with water, dried at 100°, and crystallised from glacial acetic acid. The alkali-insoluble residue of the sulphonamide was washed with water and crystallised from acetone. Only a very small yield of the disulphonamide was

obtained, and this was not appreciably increased even when a five-fold excess of toluene-*p*-sulphonyl chloride was used. With water instead of pyridine, and several equivalents of toluene-*p*-sulphonyl chloride, the yield of disulphonamide was somewhat improved.

Toluene-p-*sulphon*-6-*nitro*-2-*naphthalide* crystallised from ethanol in star-like clusters of colourless needles, m. p. 192° (Found: N, 8·4. $C_{17}H_{14}O_4N_2S$ requires N, 8·5%). *Bistoluene*-p-*sulphonyl*-6-*nitro*-2-*naphthylamine* crystallised from acetone or 50% aqueous acetone in colourless needles, m. p. 249° (Found: N, 5·8. $C_{24}H_{20}O_6N_2S_2$ requires N, 5·65%), which were readily soluble in ethanol.

Toluene-p-*sulphon*-7-*nitro*-2-*naphthalide* crystallised from ethanol in colourless needles, m. p. 176° (Found: N, 8·8. $C_{17}H_{14}O_4N_2S$ requires N, 8·55%); the sodium salt was only sparingly soluble in hot 5% aqueous sodium hydroxide and crystallised readily from the hot solution on cooling. *Bistoluene*-p-*sulphonyl*-7-*nitro*-2-*naphthylamine* crystallised from acetone in colourless needles, m. p. 231° (Found: N, 5·8. $C_{24}H_{20}O_6N_2S_2$ requires N, 5·65%).

Bromination of Toluene-p-*sulphon*-6- *and* -7-*nitro*2-*naphthalides*.—The naphthalide (1 g.) was dissolved in hot pyridine (10 c.c.) and the cold solution stirred with 1 c.c. of a solution of bromine (1 c.c.) in pyridine (9 c.c.); after 12 hours the mixture was stirred into 10% hydrochloric acid and the precipitate was removed, washed with water, dried, and crystallised from hot acetone or hot glacial acetic acid. No further bromination could be effected even with a great excess of the bromine solution.

Toluene-p-*sulphon*-1-*bromo*-6-*nitro*-2-*naphthalide* crystallised from hot acetone in cream coloured prisms, m. p. and mixed m. p. with authentic specimen (Hodgson and Turner, *loc. cit.*) 197—198°, which were hydrolysed by dissolution in sulphuric acid (*d* 1·84) at 40°, and the free amine identified with the 1-bromo-6-nitro-2-naphthylamine prepared by direct bromination.

Toluene-p-*sulphon*-1-*bromo*-7-*nitro*-2-*naphthalide* crystallised from boiling acetic acid in light yellow needles, m. p. 171—172° (Found: N, 6·8. $C_{17}H_{13}O_4N_2Br$ requires N, 6·65%), which were moderately soluble in pyridine and readily hydrolysed by dissolution in sulphuric acid (*d* 1·84) at 40° to 1-bromo-7-nitro-2-naphthylamine. Attempts to prepare these naphthalides by treating solutions of the respective amines in pyridine with toluene-*p*-sulphonyl chloride were unsuccessful, the free amines being recovered unchanged.

Anil Formation.—6- or 7-Nitro-2-naphthylamine (0·5 g.) and *p*-nitrobenzaldehyde (0·3 g.) were separately dissolved in minimum amounts of glacial acetic acid, and the mixed solutions refluxed for 1 hour. On cooling the anil separated; it was removed, washed with pyridine, and crystallised from hot ethanol or pyridine. 6 : 4′-*Dinitrobenzylidene*-2-*naphthylamine* crystallised from pyridine in yellow micro-needles, m. p. 258° (Found: N, 13·4. $C_{17}H_{11}O_4N_3$ requires N, 13·1%). 7 : 4′-*Dinitrobenzylidene*-2-*naphthylamine* crystallised from pyridine in yellow micro-needles, m. p. 193° (Found: N, 13·3. $C_{17}H_{11}O_4N_3$ requires N, 13·1%).

Halogeno-derivatives from 6- *and* 7-*Nitro*-2-*naphthylamines*.—*General diazotisation procedure.* The amine (2·5 g.) was boiled with hydrochloric acid (5 c.c., *d* 1·18) and water (25 c.c.), the mixture rapidly chilled, and treated at 0° with a solution of sodium nitrite (1 g.) in water (3 c.c.).

2-*Chloro*-6-*nitronaphthalene* was obtained when the 6-nitro-2-naphthylamine, diazotised as above, was added to a solution of cuprous chloride (5 g.) in hydrochloric acid (50 c.c., *d* 1·18) at 60°; when the reaction had ceased, the mixture was filtered cold and the precipitate was washed, dried, and extracted with ethanol (150 c.c., charcoal); from the concentrated extract almost pure 2-chloro-6-nitronaphthalene separated on cooling and was further purified by sublimation at 180—190°/15 mm.; lemon-yellow needles, m. p. 170° (Found: N, 6·9. $C_{10}H_6O_2NCl$ requires N, 6·7%). 2-Bromo-6-nitronaphthalene was obtained similarly, but by the use of hydrobromic instead of hydrochloric acid; it sublimed in lemon-yellow needles, m. p. 190° (McLeish and Campbell, *J.*, 1937, 103, give m. p. 190°) (Found: N, 5·6. Calc. for $C_{10}H_6O_2NBr$: N, 5·5%). 2-*Iodo*-6-*nitronaphthalene* was obtained from the diazo-solution above when, after removal of excess of nitrous acid by urea, it was treated with a solution of potassium iodide (10 g.) in the minimum amount of water; the precipitate was filtered off, washed successively with water, aqueous sodium thiosulphate, and water, dried, extracted with boiling ethanol (400 c.c.), the extract concentrated, and the separated 2-iodo-6-nitronaphthalene (2·6 g.) purified by sublimation at 190—200°/15 mm. to give very pale yellow rods, m. p. 231° (Found: N, 5·0. $C_{10}H_6O_2NI$ requires N, 4·7%), which were only sparingly soluble in boiling ethanol.

The 7-nitro-analogues were prepared and purified in like manner. 2-*Chloro*-7-*nitronaphthalene* (2·1 g.) sublimed in pale yellow needles, m. p. 136° (Found: N, 7·0. $C_{10}H_6O_2NCl$ requires N, 6·7%). 2-*Bromo*-7-*nitronaphthalene* (2·2 g.) sublimed in very pale yellow needles, m. p. 147—148° (Found: N, 5·7. $C_{10}H_6O_2NBr$ requires N, 5·55%). 2-*Iodo*-7-*nitronaphthalene* (2·4 g.) sublimed in almost colourless needles, m. p. 122° (Found: N, 5·0. $C_{10}H_6O_2NI$ requires N, 4·7%).

Reduction of the 2-*Halogeno*-6- *and* -7-*nitronaphthalenes*.—The halogeno-nitro-compound (1 g.) was suspended in hot ethanol (60 c.c.) and treated gradually with a solution of sodium hyposulphite (3·5 g.) in water (16 c.c.). The mixture was refluxed for 1 hour and filtered cold to remove most of the inorganic matter, water was added to the filtrate to increase the volume three- to four-fold, and the precipitate which appeared was redissolved by heating and the solution filtered hot. The almost pure halogeno-amine separated on cooling, and recrystallised from 40% aqueous pyridine in silvery micro-plates which were readily soluble in cold pyridine or ethanol. Yields were almost quantitative.

6-*Chloro*-2-*naphthylamine* had m. p. 123° (Found: N, 8·1. $C_{10}H_8NCl$ requires N, 7·8%). 6-Bromo-2-naphthylamine had m. p. 127° (Franzen and Stäuble, *loc. cit.*, give m. p. 128°) (Found: N, 6·4. Calc. for $C_{10}H_8NBr$: N, 6·3%). 6-*Iodo*-2-*naphthylamine* had m. p. 138° (Found: N, 5·3. $C_{10}H_8NI$ requires N, 5·2%). 7-*Chloro*-2-*naphthylamine* had m. p. 118—119° (Found: N, 7·9%). 7-*Bromo*-2-*naphthylamine* had m. p. 130° (Found: N, 6·4%). 7-*Iodo*-2-*naphthylamine* had m. p. 116° (Found: N, 5·1%).

Preparation of 6- *and* 7-*Nitro*-2-*naphthols*.—6- or 7-Nitro-2-naphthylamine (2 g.) was stirred with sulphuric acid (1·5 c.c., *d* 1·84) and water 20 c.c., and the mixture heated, chilled to obtain the sulphate in fine suspension, and then diazotised at 0° with sodium nitrite (1 g.) dissolved in the minimum amount of water. The solution of the diazonium sulphate was then dropped gradually into boiling 20% sulphuric acid (50 c.c.). A small amount of tar then formed. After evolution of nitrogen had ceased, charcoal

(2 g.) was added, and the mixture boiled for 2 minutes and rapidly filtered hot; the filtrate was cooled to 0°, and the almost pure nitronaphthol (*ca.* 0·4 g.) was collected and recrystallised from boiling water.

6-Nitro-2-naphthol was obtained in felted yellow needles, m. p. 155° (Gaess, *J. pr. Chem.*, 1892, **45**, 616; **46**, 160, gives m. p. 156—158°) (Found : N, 7·5. Calc. for $C_{10}H_7O_3N$: N, 7·4%). *6-Nitro-2-naphthyl acetate* was formed when 6-nitro-2-naphthol (0·2 g.) was heated with acetic anhydride (1 c.c.) and glacial acetic acid (1 c.c.) for 10 minutes. The cooled mixture was treated with water; the precipitated acetate crystallised from hot glacial acetic acid in colourless micro-needles, m. p. 147° (Found : N, 6·3. $C_{12}H_9O_4N$ requires N, 6·1%).

7-Nitro-2-naphthol crystallised in felted yellow needles, m. p. 159° (Found : N, 7·6. $C_{10}H_7O_3N$ requires N, 7·4%), which sublimed readily, were soluble in ethanol and slightly soluble in cold water, and gave no colour with ferric chloride. *7-Nitro-2-naphthyl acetate*, prepared like the 6-nitro-isomeride, crystallised from hot glacial acetic acid in colourless needles, m. p. 124° (Found : N, 6·4. $C_{12}H_9O_4N$ requires N, 6·1%).

When either of the diazo-solutions above was freed from excess of nitrous acid by urea and then boiled, the main product was a nitronaphthaleneazonitronaphthol with only a small amount of admixed nitronaphthol; the azo-compound was filtered off, washed repeatedly with boiling water to remove the nitronaphthol, and crystallised from nitrobenzene. The yields were almost quantitative. *6-Nitronaphthalene-2 : 1′-azo-6′-nitro-2′-naphthol* formed red micro-needles, m. p. 296° (Found : N, 14·7. $C_{20}H_{12}O_5N_4$ requires N, 14·4%), which gave a magenta colour with sulphuric acid changing to a bluish-red and then to a brown precipitate on dilution. *7-Nitronaphthalene-2 : 1′-azo-7′-nitro-2′-naphthol* formed red micro-needles, m. p. 317° (decomp.) (Found : N, 14·6%), which gave a magenta colour with sulphuric acid changing to a bluish-red and then to a brown precipitate on dilution.

When 7-nitro-2-naphthylamine was boiled with 5% aqueous sodium hydroxide for 6 hours it was recovered unchanged, as also was its acetyl derivative, which resisted replacement of the acetamido-group by the hydroxyl group even with boiling 20% aqueous sodium hydroxide.

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