199. *Some Reactions and Derivatives of* 6- *and* 7-*Nitro*-2-*naphthylamines. Part II. Nitration and Diazo-coupling.*

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The acetyl and toluene-*p*-sulphonyl derivatives of 6- and 7-nitro-2-naphthylamines nitrate in the 1-position, and the dinitro-compounds are highly resistant to further nitration. 6- and 7-Nitro-2-naphthylamines couple in the 1-position, and the resulting *o*-aminoazo-compounds are oxidised to triazoles. Replacement of the amino- by the acetoxy-group in 6- and 7-nitro-*p*-nitrobenzeneazo-2-naphthylamines readily occurs by heating in glacial acetic acid with sodium nitrite.

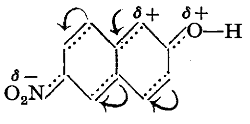
Further nitration of both the acetyl and the toluene-*p*-sulphonyl derivatives of 6- and 7-nitro-2-naphthylamines occurs in the 1-position only, and absence of nitration in the 3-position, as pointed out by Bell (*J.*, 1929, 2784) for the corresponding derivatives of β-naphthylamine, is now further emphasised.

It may be noted that the further nitration of six of the eight possible heteronuclear mononitrotoluene-*p*-sulphon-naphthalides has now been investigated, and whereas the four heteronuclear mononitro-2-naphthalides are only mononitrated in acetic acid medium with fuming nitric acid, both 5- and 6-nitro-1-naphthalides are simultaneously dinitrated. This is in contrast to the simultaneous dinitration of the unsubstituted 1- and 2-toluene-*p*-sulphonnaphthalides. Incidentally, however, the *m*-nitrobenzenesulphonyl derivatives of 8-nitro- and 1 : 6-dinitro-2-naphthylamines both afforded the 1 : 6 : 8-trinitro-derivative on further nitration (Bell, *loc. cit.*).

The constitutions of the 1 : 7-*dinitroaceto*- and 1 : 7-*dinitrotoluene*-p-*sulphon*-2-*naphthalides* were established by hydrolysis to the amine followed by its diazotisation and deamination to the known 1 : 7-dinitronaphthalene (cf. Hodgson and Birtwell, *J.*, 1943, 433).

6- and 7-Nitro-2-naphthylamines, used as second components, both couple in alcoholic acetic acid with diazotised amines in the 1-position as shown by oxidation of the resulting *o*-aminoazo-compounds to triazoles, by their resistance to acetylation, and by their diazotisation and conversion into a mixture of *o*-azonaphthol and *o*-azonaphthyl acetate by the sodium nitrite–glacial acetic procedure of Hodgson and Foster (*J.*, 1942, 435) [cf. also Morgan and Chazan (*J. Soc. Chem. Ind.*, 1922, **41**, 1T) and Morgan and Gilmour (*ibid.*, p. 61T) who showed similarly that 5- and 8-nitro-2-naphthylamines coupled in the 1-position]. 6- and 7-*Nitro*-p-*nitrobenzeneazo*-2-*naphthylamines* behaved somewhat differently towards the Hodgson and Foster procedure (*loc. cit.*), the former being hydrolysed more readily to give predominant naphthol in the mixture of naphthol and naphthyl acetate obtained, whereas the latter afforded a good yield of the 7-*nitro*-1-p-*nitrobenzeneazonaphthyl acetate.* It is noteworthy that tar was absent in these decompositions, indicating ease of replacement of the amine by the acetoxy-group. Previously, Hodgson and Foster (*loc. cit.*) had found, for azo-dyes with unsubstituted β-naphthylamine as second component, that meta-directing groups in the first component promoted this replacement, so that evidence is now to hand of the same effect by the meta-directing 6- and 7-nitro-groups in the β-naphthylamine component.

In connection with the transmissions of effects from the 6- to the 2-position (cf. Robinson and Thompson, *J.*, 1932, 2015), it is of interest that 6-nitro-2-naphthol would not couple with diazotised *p*-nitroaniline in either ethanol or aqueous sodium carbonate solution, showing the deactivating effect of the 6-nitro- on the phenolic group, in the potential ionic quinonoid structure, in which the 1-position, instead of acquiring the anionoid activity requisite for coupling, becomes kationoid.



The claim of Friedländer and Littner (*Ber.*, 1915, **48**, 330) to have prepared some 5-nitroaceto-2-naphthalide from β-acetonaphthalide, and since disproved by Veselý and Jakeš (*Bull. Soc. chim.*, 1923, **33**, 942), has erroneously been repeated in *Org. Synth.*, 1933, **13**, 73.

Experimental.

Nitration of 7-*Nitro*-2-*acetonaphthalide.*—7-Nitro-2-naphthylamine (3 g.) was refluxed with glacial acetic acid (12 c.c.) and acetic anhydride (3 c.c.) for 10 minutes; on cooling, an almost quantitative separation of 7-nitro-2-acetonaphthalide was obtained, which, after recrystallisation from 50% ethanol, had m. p. 221°. This acetyl compound (3 g.) was added gradually to nitric acid (12 c.c., *d* 1·5) during 15 minutes (the temperature being kept below 20°), and, after being stirred for a further 15 minutes, the mixture was poured on ice and the precipitate of 1 : 7-*dinitro*-2-*acetonaphthalide* (3·5 g.) removed, washed with water, and dried; it crystallised from glacial acetic acid in pale yellow needles, m. p. 222°

(Found : N, 15·1. $C_{11}H_9O_5N_3$ requires N, 15·3%). Should the temperature be allowed to rise during nitration even as high as 60° for 5—10 minutes, some oxidation occurs although the final product is mainly 1 : 7-dinitro-2-acetonaphthalide.

1 : 7-*Dinitro*-2-*naphthylamine* was obtained when the acetyl derivative above (2·5 g.) was hydrolysed by refluxing with a solution of ethanol (25 c.c.) and 50% aqueous sulphuric acid (25 c.c.) for 45 minutes; after cooling, the separated 1 : 7-dinitro-2-naphthylamine (2 g.) was filtered off, washed with ethanol, and dried; it crystallised from 50% aqueous pyridine in golden yellow needles, m. p. 248—249° (Found : N, 18·1. $C_{10}H_7O_4N_3$ requires N, 18·0%). Deamination of the amine (1·5 g.) occurred when its solution below 20° in sulphuric acid (8 c.c., *d* 1·84) containing sodium nitrite (0·6 g.) was stirred gradually into glacial acetic acid (20 c.c.), the stirring continued for 30 minutes, red copper oxide (2—3 g.) added portionwise during 15 minutes, and the temperature allowed to rise to 40°. After being stirred for a further 1 hour, the mixture was poured on ice, the precipitate of 1 : 7-dinitronaphthalene filtered off, washed with water, dried, extracted with boiling ethylene dichloride, the solvent removed from the extract, and the 1 : 7-dinitronaphthalene purified by sublimation at 190—200°/15 mm.; m. p. and mixed m. p. with an authentic specimen, 156° (Veselý and Dvořak, *Bull. Soc. chim.*, 1923, **33**, 319, give m. p. 156°).

Nitration of 7-*Nitrotoluene*-p-*sulphon*-2-*naphthalide*.—A solution of the naphthalide (2·5 g.) in glacial acetic acid (20 c.c.) at 60° was treated first with a crystal of sodium nitrite and then with 7·5 c.c. of a solution made up of nitric acid (1 c.c., *d* 1·5) in glacial acetic acid (9 c.c.); nitration began when the temperature was raised to 65°, and for completion the mixture was kept at 90° for 5 minutes; on cooling, 1 : 7-*dinitro*-p-*toluenesulphon*-2-*naphthalide* (1·7 g.) crystallised out; after removal, it was washed with glacial acetic acid and ether, and dried. It crystallised from glacial acetic acid in bright yellow rectangular plates, m. p. 165—166° (Found : N, 11·0. $C_{17}H_{13}O_6N_3S$ requires N, 10·8%). On hydrolysis by dissolution (1 g.) in sulphuric acid (10 c.c., *d* 1·84) and heating for 5 minutes at 40°, 1 : 7-dinitro-2-naphthylamine was obtained and precipitated by pouring the mixture on ice, with subsequent treatment as above. Alternatively, the 1 : 7-dinitro-*p*-toluenesulphon-2-naphthalide was converted directly into 1 : 7-dinitronaphthalene by the Hodgson and Birtwell procedure (*loc. cit.*), but diazotisation had to be carried out carefully since hydrolysis and diazotisation followed rapidly.

Coupling with Diazo-compounds.—To a solution of the naphthylamine (0·01 g.-mol.) in ethanol (400 c.c.) containing sufficient sodium acetate for the replacement by acetic acid of all mineral acid involved, was added an aqueous solution of the diazonium salt (chloride or sulphate, 0·01 g.-mol.), prepared from *p*-nitroaniline, *p*-chloroaniline, or *p*-toluidine, from which free nitrous acid had been removed by urea. The mixture was stirred for 1 hour, and the azo-dye filtered off, washed with cold ethanol (50 c.c.) and hot water, dried, and crystallised from nitrobenzene (charcoal). All the azo-dyes now described were moderately soluble in boiling acetic anhydride or boiling glacial acetic acid, and resisted acetylation thereby even at 100°; they were only slightly soluble in boiling toluene or ethanol. The sequence of colours produced by concentrated sulphuric acid and subsequent dilution with water are recorded immediately after the m. p. The large amount of ethanol used for the couplings is necessary to prevent uncoupled amine from separating with the azo-dye.

6-*Nitro*-p-*nitrobenzeneazo*-2-*naphthylamine* formed micro-needles, m. p. 304° (sintered at 290°; blood-red, salmon-pink, brownish-red precipitate) (Found : N, 21·1. $C_{16}H_{11}O_4N_5$ requires N, 20·8%). 6-*Nitro*-1-p-*chlorobenzeneazo*-2-*naphthylamine* formed orange-red micro-needles, m. p. 261° (sintered at 245°; magenta, red to yellow-brown) (Found : N, 17·4. $C_{16}H_{11}O_2N_4Cl$ requires N, 17·15%). 6-*Nitro*-1-p-*tolylazo*-2-*naphthylamine* formed orange red micro-plates, m. p. 234° (mauve, magenta, reddish-brown, orange) (Found : N, 18·5. $C_{17}H_{14}O_2N_4$ requires N, 18·3%). 7-*Nitro*-1-p-*chlorobenzeneazo*-2-*naphthylamine* formed felted scarlet needles, m. p. 199° (magenta, purple, brown precipitate) (Found : N, 17·4. $C_{16}H_{11}O_2N_4Cl$ requires N, 17·15%). 7-*Nitro*-1-p-*nitrobenzeneazo*-2-*naphthylamine* formed very dark red almost black needles, m. p. 265—266° (crimson, reddish-blue) (Found : N, 21·1. $C_{16}H_{11}O_4N_5$ requires N, 20·8%).

Oxidation of Azo-dyes to Triazoles.—The dye (0·5 g.) was dissolved in boiling glacial acetic acid (30 c.c.), and a solution of chromium trioxide (0·5 g.) in water (1 c.c.) was added with caution to the stirred boiling mixture; the red colour disappeared, to be replaced by a white precipitate. On cooling and dilution with water, the triazole separated; it was filtered off, washed with hot water until the filtrate was colourless, dried at 100°, and recrystallised from hot nitrobenzene.

6-*Nitro*-1 : 2-*naphtho*-p-*nitrophenyltriazole* crystallised in flesh-coloured micro-plates, m. p. 288° (Found : N, 21·3. $C_{16}H_9O_4N_5$ requires N, 20·9%). 7-*Nitro*-1 : 2-*naphtho*-p-*nitrophenyltriazole* crystallised in flesh-coloured plates, m. p. 311—312° (sintered at 300°) (Found : N, 21·3. $C_{16}H_9O_4N_5$ requires N, 20·9%).

Reactions of 6- *and* 7-*Nitro*-1-p-*nitrobenzeneazo*-2-*naphthylamines with Sodium Nitrite in Glacial Acetic Acid*.—(*a*) The 6-nitro-compound (1·0 g.) was dissolved in hot glacial acetic acid (350 c.c.) at 70°, and treated portionwise with finely powdered sodium nitrite (1 g.); nitrogen was briskly evolved, and, when the evolution had ceased, the solution was raised to the boil for 15 minutes. On cooling, no separation occurred, so water was added to precipitate the reaction product which was a mixture of difficultly separable 6-nitro-1-*p*-nitrobenzeneazo-2-naphthol and its acetate. When the precipitate (0·25 g.) was refluxed with ethanol (50 c.c.) containing hydrochloric acid (2 c.c., *d* 1·18) for 30 minutes, complete hydrolysis occurred, and the 6-*nitro*-1-p-*nitrobenzeneazo*-2-*naphthol* separated on cooling and was removed, washed, and dried; it crystallised from boiling glacial acetic acid in pillar-box red microcrystals, m. p. 314° (sintered at 305°; reddish salmon pink, orange-red) (Found : N, 16·7. $C_{16}H_{10}O_5N_4$ requires N, 16·5%), which were only slightly soluble in hot glacial acetic acid, almost insoluble in boiling ethanol, and readily soluble in boiling nitrobenzene. Alternatively, the dye (0·5 g.) was added gradually to a solution of sodium nitrite (0·15 g.) in sulphuric acid (4 c.c., *d* 1·84) at 0°, followed by the gradual addition of glacial acetic acid (5 c.c.) over 15 minutes below 20°. After a further 15 minutes ice chips were added and stirring maintained until evolution of nitrogen had ceased; on dilution with water 6-nitro-1-*p*-nitrobenzeneazo-2-naphthol separated.

(*b*) The 7-nitro-compound (1 g.) was dissolved in glacial acetic acid (200 c.c.), in which it is more soluble than the 6-nitro-isomeride, and treated as above so far as the boiling operation, when on cooling there separated 7-*nitro*-1-p-*nitrobenzeneazo*-2-*naphthyl acetate*, which crystallised from boiling acetic acid in orange red needles, m. p. 233° (red violet, orange) (Found N, 15·0. $C_{18}H_{12}O_6N_4$ requires N, 14·7%). 7-*Nitro*-1-p-*nitrobenzeneazo*-2-*naphthol* was obtained by hydrolysis as above, and crystallised from boiling nitrobenzene in red micro-crystals, m. p. 310° (decomp.) (Found : N, 16·7. $C_{16}H_{10}O_5N_4$ requires N, 16·5%).

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