107. *The Further Nitration of* 1 : 3-, 1 : 6-, 2 : 6-, *and* 2 : 7-*Dinitronaphthalenes, and the Preparation of* 1 : 3 : 6-*Trinitronaphthalene.*

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1 : 3- and 1 : 6-Dinitronaphthalenes both afford 1 : 3 : 8-trinitro- and 1 : 3 : 6 : 8-tetranitro-naphthalenes when further nitrated under the conditions employed by Hodgson, Ward, and Whitehurst (*J.*, 1945, 450) for 1 : 8-dinitronaphthalene. The 1-nitro-group appears to direct nitration to the 8-position exclusively. 2 : 6- and 2 : 7-Dinitronaphthalenes dinitrate readily to give mainly 1 : 3 ; 5 : 7- and 1 : 3 : 6 : 8-tetranitronaphthalenes respectively. Mononitration of 2 : 7-dinitronaphthalene to 1 : 3 : 6-*trinitronaphthalene* requires special conditions. The 2-nitro-group appears to direct nitration mainly to the 4-position, and when two β-nitro-groups are present there is simultaneous dinitration to the corresponding *meta* α-positions. The preparation of 2 : 6-dinitronaphthalene from 6-nitro-2-naphthylamine is readily effected by Hodgson and Marsden's method (*J.*, 1944, 22).

When nitrated under conditions identical with those employed for the mono- and di-nitration of 1 : 8-dinitronaphthalene (Hodgson, Ward, and Whitehurst, *J.*, 1945, 450), 1 : 3- and 1 : 6-dinitronaphthalenes both afford 1 : 3 : 8-trinitro- and 1 : 3 : 6 : 8-tetranitro-naphthalenes (cf. Chatt and Wynne, *J.*, 1943, **33**, who mononitrated 1 : 3-dinitronaphthalene to 1 : 3 : 8-trinitronaphthalene under different conditions). It is noteworthy that the mono-nitration of both 1 : 3- and 1 : 6-dinitronaphthalenes takes place in the 8-position and not at all in 5- and 3-positions which are *meta* to the existing nitro-groups. This nitration in the *peri* position recalls the predominant nitration of 1-nitronaphthalene in the 8-position, and it would appear that the directing influence in all cases of further nitration of a dinitronaphthalene which contains a 1-nitro-group is exerted by this particular nitro-group (cf. Chatt and Wynne, *loc. cit.*).

In contrast with the above directed mono-nitrations, 2 : 6- and 2 : 7-dinitronaphthalenes both dinitrate very readily to give mainly 1 : 3 : 5 : 7-tetranitronaphthalene and wholly 1 : 3 : 6 : 8-tetranitronaphthalene respectively, thereby indicating the powerful and independent influence of each 2-nitro-group in directing the entering nitro-groups simultaneously into the relevant *meta* positions to them. Owing to the great ease of dinitration, special conditions are necessary for the mononitration of 2 : 7-dinitronaphthalene to 1 : 3 : 6-*trinitronaphthalene*, and we have been unable to isolate a mono-nitrated derivative of 2 : 6-dinitronaphthalene at all, since, even with a deficiency of nitrating acid under varied temperature control, dinitration always occurred. The constitution of 1 : 3 : 6-trinitronaphthalene follows from its conversion by further nitration to 1 : 3 : 6 : 8-tetranitronaphthalene.

A consideration of the possible resonance forms of 2 : 6- and 2 : 7-dinitronaphthalenes indicates that the 4 : 8- and 4 : 5-positions respectively are those which will be the least deactivated by the resonance of the two initial nitro-groups into the various quinonoid positions available (cf. Veselý and Jakes, *Bull. Soc. chim.*, 1923, **33**, 955; Hodgson and Hathway, *J. Soc. Dyers and Col.*, 1945, **61**, 283), and it is in these positions that further nitration occurs.

The preparation of 2 : 6-dinitronaphthalene in *ca.* 50% yield from 6-nitro-2-naphthylamine by Hodgson and Marsden's cobaltinitrite procedure (*J.*, 1944, 22) provides a facile method for obtaining this compound.

Experimental.

Nitration of 1 : 3- *and* 1 : 6-*Dinitronaphthalenes*.—The procedure for the corresponding nitrations of 1 : 8-dinitronaphthalene was followed (Hodgson, Ward, and Whitehurst, *loc. cit.*). In the mononitrations only small amounts of 1 : 3 : 8-trinitronaphthalene separated from the nitration mixture on cooling, and this product, in over 70% yield, was precipitated by pouring on to ice; crystallisation from glacial acetic acid afforded pure 1 : 3 : 8-trinitronaphthalene as established by mixed m. ps. with an authentic specimen. In the dinitrations *ca.* 50% yields of 1 : 3 : 6 : 8-tetranitronaphthalene were obtained, which, in successive crystallisations from glacial acetic acid and acetone, had m. p. 208° (cf. Hodgson, Ward, and Whitehurst, *loc. cit.*, who reported m. p. 207°) (Found : N, 18·4. Calc. for $C_{10}H_4O_8N_4$: N, 18·2%). There remained a small amount of a substance insoluble in acetone, which had m. p. >300°, and appeared to be highly nitrated but not sulphonated since, while it reacted with cold sodium sulphite after the manner of polynitronaphthalenes, it was soluble in hot sodium carbonate but contained no sulphur; it is probably a polynitrohydroxy-compound.

Attempted Mononitration of 2 : 6-*Dinitronaphthalene*.—The 2 : 6-dinitronaphthalene (3 g., m. p. 275°) was suspended in sulphuric acid (8 c.c., *d* 1·84), cooled to 0°, and then treated dropwise below 10°, using vigorous agitation, with a solution of nitric acid (0·85 c.c., *d* 1·42) in sulphuric acid (4 c.c., *d* 1·84), after which the temperature was raised to 30° when nitration commenced and eventually to 75° where it was kept for 5 minutes and then allowed to fall to room temperature. No frothing or oxidation occurred even at 75°. 1 : 3 : 5 : 7-Tetranitronaphthalene (see below) separated during cooling and was the only isolable product.

Dinitration of 2 : 6-*Dinitronaphthalene*.—The dinitro-compound (2 g., m. p. 275°) suspended in sulphuric acid (12 c.c., *d* 1·84) was treated gradually with nitric acid (1·5 c.c., *d* 1·42) in sulphuric acid (1·5 c.c., *d* 1·84) when it passed into solution to reappear after nitration as 1 : 3 : 5 : 7-tetranitronaphthalene. The temperature was allowed to attain 80°, after which the mixture was cooled, and the 1 : 3 : 5 : 7-tetranitronaphthalene filtered off, washed successfully with small amounts of 98% and 50% sulphuric acid, then with water, dried at 100°, and crystallised twice from glacial acetic acid (charcoal), when it melted at 260° (Chatt and Wynne, *loc. cit.*, give m. p. 260°) (Found : N, 18·4. Calc. for $C_{10}H_4O_8N_4$: N, 18·2%). It gave a red-violet solution in hot but not in cold aqueous sodium sulphite (cf. the similar behaviour of 1 : 3 : 8- and 1 : 3 : 6 : 8-tetranitronaphthalenes, Hodgson, Ward, and Whitehurst, *loc. cit.*); the filtrate was rejected.

Mononitration of 2 : 7-*Dinitronaphthalene*.—The dinitro-compound (3 g., m. p. 234°) was suspended in sulphuric acid (14 c.c., *d* 1·84) at 5°, vigorously stirred, and treated dropwise with nitric acid (0·9 c.c., *d* 1·42) in sulphuric acid (3·6 c.c., *d* 1·84) below 10°. The temperature was allowed to rise to 25° when nitration commenced with further rise to 45°, after which the mixture was heated to 80° without any signs of frothing or oxidation. At 70° crystals of 1 : 3 : 6-*trinitronaphthalene* appeared; after the mixture had been cooled to room temperature, these were filtered off, washed, and dried as above; the compound, recrystallised successively from toluene and 80% aqueous acetone, was obtained in rectangular prisms with facets, m. p. 186° depressed to 158—170° by 1 : 3 : 6 : 8-tetranitronaphthalene (Found: N, 16·2. $C_{10}H_5O_6N_3$ requires N, 16·0%). The filtrate was poured on to ice, and the dark yellow precipitate (2 g.) afforded a further quantity of 1 : 3 : 6-trinitronaphthalene when crystallised from 50% aqueous acetone, the later fractions being unchanged 2 : 7-dinitronaphthalene. 1 : 3 : 6-Trinitronaphthalene readily dissolves in hot aqueous sodium sulphite to an intense red solution, and in acetone it gives a red colour with 10% aqueous potassium hydroxide but only a feeble orange-red colour with boiling sodium carbonate; it is readily soluble in cold toluene in which it tends to form supersaturated solutions, in acetone (in which, however, it is less soluble than 1 : 3 : 6 : 8-tetranitronaphthalene thereby resembling 1 : 3 : 8-trinitronaphthalene), and in hot glacial acetic acid; it is only slightly soluble in hot alcohol.

Dinitration of 2 : 7-*Dinitronaphthalene.*—A suspension of 2 : 7-dinitronaphthalene (5 g.) in cold sulphuric acid (30 c.c., *d* 1·84; it is less soluble in sulphuric acid than the 1 : 8-, 1 : 3-, and 1 : 6-isomers) was nitrated by the procedure employed for 1 : 8-dinitronaphthalene (*loc. cit.*). On addition of the nitrating acid, the temperature rose rapidly but was not allowed to exceed 75°. The 2 : 7-dinitronaphthalene passed into solution; separation subsequently occurred of an intermediate nitration product which itself was redissolved as the temperature increased; on cooling, 1 : 3 : 6 : 8-tetranitronaphthalene separated, and was filtered off, a further quantity being obtained in a less pure condition when the filtrate was poured on to ice. Total yield of pure 1 : 3 : 6 : 8-tetranitronaphthalene, *ca.* 60%. When the nitration was repeated with only 30% excess of nitrating acid over that required for dinitration, the resulting product was mainly 1 : 3 : 6-trinitronaphthalene, the nitration being less violent than in the previous experiment.

Preparation of 2 : 6-*Dinitronaphthalene.*—6-Nitro-2-naphthylamine (7·6 g., 0·05 g.-mol.) was boiled with sulphuric acid (3·5 c.c., *d* 1·84) and water (50 c.c.), the mixture chilled to obtain fine crystals, and then stirred vigorously with a solution of sodium nitrite (3·5 g.) in water (15 c.c.) below 0°. When diazotisation was complete, the solution was stirred into a mixture of finely powdered calcium carbonate (4·5 g.) and crushed ice, a little ether added to remove froth, the liquid filtered, and the filtrate of the neutral 6-nitro-2-naphthalenediazonium sulphate stirred with finely powdered sodium cobaltinitrite (6 g.). A yellow cobaltinitrite complex separated slowly during 20 minutes; it was filtered off and washed with water and ether at the pump (being almost insoluble in either; cf. Hodgson and Marsden, *loc. cit.*). The cobaltinitrite complex reddened rapidly in bright sunlight but could be kept in the dark for at least 24 hours; it was, however, immediately stirred into a solution of sodium nitrite (10 g.) and copper sulphate crystals (10 g.) in water (60 c.c.) containing a suspension of finely divided and freshly prepared cuprous oxide (4 g.). Decomposition was slow at room temperature, so the mixture was raised to 60° and maintained there with stirring for 1 hour, after which it was kept overnight. Water (400 c.c.) was then added, and the precipitate filtered off and washed with water until free from soluble copper salts, dried at 100°, and extracted twice with boiling ethylene dichloride (200 c.c.). The extract was concentrated to very small bulk, and the separated 2 : 6-dinitronaphthalene recrystallised from glacial acetic acid or toluene and purified by sublimation at 230°/15 mm.; it had m. p. 278° (Chatt and Wynne, *loc. cit.*, give m. p. 279°; Veselý and Jakes, *loc. cit.*, give m. p. 268°) (Found: N, 13·0. Calc. for $C_{10}H_6O_4N_2$: N, 12·8%). Yield of pure 2 : 6-dinitronaphthalene, *ca* 50%. 1 : 7-Dinitronaphthalene can be similarly prepared from 8-nitro-2-naphthylamine.

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