117. *The Preferential Reduction of Nitro-groups in Polynitro-compounds. Part II. The Preparation of* 3 : 6-*Dinitro*-1 : 8-*naphthylenediamine from* 1 : 3 : 6 : 8-*Tetranitronaphthalene.*

By Herbert H. Hodgson, Edward R. Ward, and John S. Whitehurst.

A solution of stannous chloride in glacial acetic acid saturated by hydrogen chloride reduces 1 : 3 : 6 : 8-tetranitronaphthalene to 3 : 6-*dinitro*-1 : 8-*naphthylenediamine*. Improved procedures are given for the preparations of 1 : 3 : 6 : 8-tetra- and 1 : 3 : 8-tri-nitronaphthalene.

Will's method (*Ber.*, 1895, **28**, 519) for the preparation of 1 : 3 : 6 : 8-tetranitronaphthalene has proved unserviceable, and his statement that further nitration of 1 : 3 : 8-trinitronaphthalene takes place in the cold could not be substantiated : a mixture of nitric acid (*d* 1·52) and oleum (26% SO_3) when kept for 6 months afforded mainly unchanged trinitro-compound.

Dhar (J., 1920, **117**, 1001) claimed to have isolated both 1 : 2 : 6 : 8- and 1 : 3 : 6 : 8-tetranitronaphthalene by treating a solution of 1 : 8-dinitronaphthalene in concentrated sulphuric acid with fuming nitric acid and then heating the mixture at *ca.* 100° for 4 hrs.; the 1 : 2 : 6 : 8-tetranitronaphthalene was said to separate, leaving the 1 : 3 : 6 : 8-isomeride in solution. Dhar's experimental details were insufficient for us to obtain the 1 : 2 : 6 : 8-tetranitronaphthalene by his procedure, and Chatt and Wynne (J., 1943, 33), by dinitration of 2 : 6-dinitronaphthalene, obtained the 1 : 2 : 6 : 8-tetranitro-compound, which differed from that described by Dhar. Details are now given of the dinitration of 1 : 8-dinitro- to 1 : 3 : 6 : 8-tetranitro-naphthalene by a modification of Dhar's procedure, and similarly 1 : 3 : 8-trinitronaphthalene has been mononitrated to produce the same compound. Mononitration of 1 : 8-dinitronaphthalene is rapid, but dinitration only occurs above 80° and is accompanied by appreciable oxidation; the same conditions hold for the mononitration of 1 : 3 : 8-trinitronaphthalene.

1 : 3 : 6 : 8-Tetranitronaphthalene is partly reduced to 3 : 6-dinitro-1 : 8-naphthylenediamine by a solution of stannous chloride in glacial acetic acid saturated with hydrogen chloride. The preferential reduction of nitro-groups in the α-positions by this reagent (cf. J., 1943, 318, which is to be regarded as Part I) now receives strong support, since two α- and two β-nitro-groups are involved in the tetranitro-compound. The constitution of the diamine was established by (*a*) tetrazotisation according to Hodgson and Walker (cf. J., 1933, 1620; J., 1943, 86, 433) and subsequent Sandmeyer reactions to give dichloro- and dibromo-compounds, thereby establishing that two nitro-groups had been reduced; (*b*) reaction with acetone to give 5 : 8-*dinitrodimethydihydroperimidine*, a proof that the amino-groups are in the 1 : 8-positions; (*c*) deamination to 2 : 7-dinitronaphthalene, thereby confirming the 3 : 6-positions for the unreduced nitro-groups.

Will (*loc. cit.*) made many attempts at partial reduction of 1 : 3 : 6 : 8-tetranitronaphthalene, but obtained only insoluble, brown, amorphous powders.

Experimental.

Preparation of 1 : 3 : 6 : 8-*Tetranitronaphthalene*.—(a) *From* 1 : 8-*dinitronaphthalene*. To a stirred solution of 1 : 8-dinitronaphthalene (25 g., m. p. 168—172°) in sulphuric acid (125 c.c., *d* 1·84) at 20°, nitric acid (125 c.c., *d* 1·5) was gradually added, the temperature being kept below 75°; the evolution of heat decreased considerably after about half the acid had been added, and the precipitate which appeared at this stage gradually redissolved as the temperature was raised to 80°. Frothing became serious above 80°, and the temperature was then kept below 90° until this subsided (if the reaction gets out of control carbonaceous matter is formed, sometimes with explosive violence). The mixture was finally heated on the water-bath for 2½ hrs., and 1 : 3 : 6 : 8-tetranitronaphthalene was precipitated at first as an oil, subsequently solidifying. The hot suspension was filtered through asbestos, and the faintly pink solid was washed successively with small portions of sulphuric acid (*d* 1·84), 25% aqueous sulphuric acid, water, aqueous sodium carbonate (which intensified the pink colour), and water (which removed the pink colour), and dried at 100° (15 g., *ca.* 45% yield). On recrystallisation from boiling toluene, the 1 : 3 : 6 : 8-tetranitronaphthalene was obtained in colourless micro-needles, m. p. 207°, depressed by 1 : 3 : 8-trinitronaphthalene to 180° (Will, *loc. cit.*, gives m. p. 203°) (Found : N, 18·3. Calc. : N, 18·1%). It was slightly soluble in cold but readily soluble in hot alcohol, toluene, benzene, or acetic acid, and gave an intense bluish-red colour in cold acetone solution with 10% aqueous alkalis.

The filtrate from the nitration was deep red and stained the skin (cf. Chatt and Wynne, *loc. cit.*, who ascribed similar phenomena to the formation of polynitronaphthols during the nitration of 2 : 6-dinitronaphthalene; these substances may be intermediates in the oxidation sequence). This filtrate was poured on ice, and the flocculent pink separation was washed successively with small portions of water, dilute sodium carbonate, and water, and then dried in a vacuum (yield, 6·5 g., m. p. 140—160°); it separated (3 g.) from toluene (50 c.c.) in colourless crystals of a mixture, m. p. 180—200°.

(b) *From* 1 : 3 : 8-*trinitronaphthalene*. The initial compound was prepared by dissolution of 1 : 8-dinitronaphthalene (85 g.) in sulphuric acid (450 c.c., *d* 1·84) and treatment at 20° with a mixture of nitric acid (60 c.c., *d* 1·5) and sulphuric acid (60 c.c., *d* 1·84), the temperature being kept below 75°, for oxidation and frothing set in at about 80°. The mixture was cooled to 0°, filtered through asbestos, and the solid worked up as above (yield, 60 g.; *ca.* 60%). The 1 : 3 : 8-trinitronaphthalene separated from boiling toluene or glacial acetic acid in crystals, m. p. 212—218°, which recrystallised from acetone in fine, very pale yellow needles, m. p. 223° (Rindl, J., 1913, **103**, 1914, gives m. p. 212°; Chatt and Wynne, *loc. cit.*, give m. p. 216—220°); it crystallised from acetic anhydride in very pale yellow rhombs (Found : N, 16·1. Calc. : N, 16·0%). The filtrate from the solid (above), when poured on ice, gave a crude mixture (15 g.) of low m. p.

1 : 3 : 8-Trinitronaphthalene differs from 1 : 3 : 6 : 8-tetranitronaphthalene in its sparing solubility in cold acetone; the solution, however, gives an intense bluish-red colour with aqueous alkalis. The further nitration was carried out as follows : 1 : 3 : 8-trinitronaphthalene (25 g.) was stirred with sulphuric acid (125 c.c., *d* 1·84) and nitric acid (100 c.c., *d* 1·5) at 20°, and gradually passed into solution when cautiously heated to 80—90°, the phenomena noted in (a) occurring; after abatement of frothing, the nitration was completed by heating on the water-bath for 1½ hours; 1 : 3 : 6 : 8-tetranitronaphthalene separated and was treated as in (a); yield 13 g.

Preparation of 3 : 6-*Dinitro*-1 : 8-*naphthylenediamine*.—A suspension of 1 : 3 : 6 : 8-tetranitronaphthalene (10 g.) in glacial acetic acid (40 c.c.) at 20° was treated dropwise with a solution of hydrated stannous chloride (48·4 g., 10% excess) in glacial acetic acid (180 c.c.) saturated at 0° with dry hydrogen chloride (cf. Hodgson and Turner, *loc. cit.*); the temperature was kept at 35—40°, and stirring continued for 15 mins. after the addition. The smell of ethyl acetate was observed during the experiment. The nitro-compound gradually passed into a reddish-brown solution, which was filtered from inorganic matter and poured into water (2 l.). The resulting red flocculent precipitate (4 g.) of 3 : 6-*dinitro*-1 : 8-*naphthylenediamine* was filtered off, repeatedly washed with water, and dried in a vacuum. It crystallised from hot glacial acetic acid in deep reddish-orange prisms which decomposed when heated above 220° (Found : N, 22·8. $C_{10}H_8O_4N_4$ requires N, 22·6%) and were sparingly soluble in the usual solvents. The hydrochloride, formed by passage of dry hydrogen chloride into an ethereal or benzene solution of the diamine, was decomposed by moisture.

5 : 8-*Dinitro*-2 : 2-*dimethyl*-1 : 3-*dihydroperimidine* was formed in almost quantitative yield when the above dinitrodiamine was dissolved in acetone, from which it crystallised in scarlet needles, m. p. 241° (decomp.) (Found : N, 19·6. $C_{13}H_{12}O_4N_4$ requires N, 19·4%), which were readily soluble in cold acetone, ether, and glacial acetic acid.

Diazotisation and Sandmeyer Reactions with 3 : 6-*Dinitro*-1 : 8-*naphthylenediamine*.—The diamine (1·75 g.), dissolved in sulphuric acid (25 c.c., *d* 1·84), was treated with a solution of sodium nitrite (2 g.) in sulphuric acid (15 c.c., *d* 1·84), the mixture stirred below 20° into glacial acetic acid (40 c.c.), and the solution of the diazonium salt added to one of cuprous chloride (5 g.) in hydrochloric acid (50 c.c., *d* 1·18); the precipitated 1 : 8-*dichloro*-3 : 6-*dinitronaphthalene* (1·4 g.) was removed, washed with water and aqueous sodium hydroxide to remove any nitronaphthols, and extracted with toluene, from which it crystallised; it recrystallised from glacial acetic acid in yellow-orange rods, m. p. 222° (Found : N, 9·5. $C_{10}H_4O_4N_2Cl_2$ requires N, 9·7%). 1 : 8-*Dibromo*-3 : 6-*dinitronaphthalene* (1 g.), prepared similarly by use of cuprous bromide (2 g.) and hydrobromic acid (10 c.c.), crystallised from glacial acetic acid in yellow-orange rods, m. p. 210° (Found : N, 7·6. $C_{10}H_4O_4N_2Br_2$ requires N, 7·4%).

2 : 7-Dinitronaphthalene was formed in very small quantities when the diazonium solution (above) was poured gradually into a suspension of cuprous oxide (10 g.) in ethyl alcohol (150 c.c.), the temperature allowed to rise to 70°, and the mixture stirred for one hour after the addition was completed; the mixture was poured into water (2 l.), filtered, the solid washed with water, dried in a vacuum, and repeatedly extracted with ether; the ethereal solution when evaporated to dryness gave a bright yellow residue of crude 2 : 7-dinitronaphthalene (m. p. 210—220°), which crystallised from 50% aqueous acetic acid in yellow needles, m. p. 232°, not depressed by an authentic specimen (m. p. 234°) made according to Rule and Brown (J., 1934, 171) (Found : N, 13·0. Calc. : N, 12·8%).

The authors thank the Charles Brotherton Trust for Research Scholarships (to E. R. W. and J. S. W.), and Imperial Chemical Industries Ltd. (Dyestuffs Division) for gifts of chemicals.

THE TECHNICAL COLLEGE, HUDDERSFIELD.

[*Received, May* 18*th*, 1945.]