

207. *The Preferential Reduction of Nitro Groups in Polynitro-compounds. Part IV. The Preparation of 4 : 5-Dinitro-2-naphthylamine from 1 : 3 : 8-Trinitronaphthalene and a Comparison of Sodium Sulphide Reductions of Available Dinitronaphthalenes.*

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Methanolic sodium sulphide in the presence of sodium bicarbonate reduced 1 : 3 : 8-trinitronaphthalene to 4 : 5-dinitro-2-naphthylamine, and variation in amount of bicarbonate had considerable effect on the yields obtained. By this method 1 : 3-, 1 : 5-, 1 : 6-, and 2 : 7-dinitronaphthalenes gave yields of almost pure mono-nitro-amines of 85%, 50%, 55%, and 82% respectively; whereas 1 : 8-dinitronaphthalene was converted entirely to sulphide dyes.

MONOREDUCTION of 1 : 3 : 8-trinitronaphthalene by Hodgson and Birtwell's method (*J.*, 1944, 75) succeeds only if the amount of sodium bicarbonate is increased, otherwise alkali soluble dyes are formed. Reduction of the β -nitro-group took place and the constitution of the 4 : 5-dinitro-2-naphthylamine produced was established by its deamination to 1 : 8-dinitronaphthalene. Reduction in the absence of alcohol gave sulphide dyes only, while reductions by hydrogen sulphide in pyridine or aqueous alcoholic ammonia gave tars. 1 : 3 : 8-Trinitronaphthalene is more readily reduced, as would be expected, than any of the dinitronaphthalenes yet examined with the exception of 1 : 8-dinitronaphthalene (see below). This preferential reduction of the 3-nitro-group in 1 : 3 : 8-trinitronaphthalene is in striking contrast with the reactivity of 1 : 3-dinitronaphthalene, which reduces mainly at the 1-nitro-group, and the difference in behaviour must be ascribed to the mutual interactions of the 1 : 8-dinitro groups, which in aqueous medium in the case of 1 : 8-dinitronaphthalene, are sufficient to resist attack by sodium sulphide (cf. Hodgson and Walker, *J.*, 1933, 1346).

4 : 5-Dinitro-2-naphthylamine would be expected to give reactions similar to 4-nitro-2-naphthylamine (cf. Hodgson and Hathway, *J.*, 1944, 385; this vol., p. 453), but whereas it is only monobrominated, even with excess of bromine, to give 1-bromo-4 : 5-dinitro-2-naphthylamine, as shown by deamination of the latter to the known 1-bromo-4 : 5-dinitronaphthalene (Ullmann and Consonno, *Ber.*, 1902, 35, 2803), it failed to give a *p*-toluenesulphonyl derivative after many variations of procedure; this is in contrast to the formation of a di-*p*-toluenesulphonyl derivative by 4-nitro-2-naphthylamine (Hodgson and Hathway, *loc. cit.*). 1-Bromo-4 : 5-dinitro-2-naphthylamine was only monoacetylated with difficulty, but it was diazotised readily by the Hodgson and Walker method (*J.*, 1933, 1620), and was converted into 1 : 2-dibromo-4 : 5-dinitronaphthalene by subsequent Sandmeyer procedure. 4 : 5-Dinitro-2-naphthylamine also diazotised readily by the same process, and the diazonium sulphate was converted by the Sandmeyer reaction to 2-chloro-4 : 5-dinitronaphthalene, a compound which appears to be identical with the previously unorientated monochloro-derivative obtained by Pollak (*G.P.*, 134,306; *Chem. Zentr.*, 1902, 918) from the direct chlorination of 1 : 8-dinitronaphthalene. Since both 1-chloro- and 3-chloro-4 : 5-dinitronaphthalenes are known, the additional monochloro-4 : 5-dinitronaphthalene having m. p. 132° reported by Pollak would appear to be a mixture.

1 : 5-, 1 : 6-, and 1 : 8-Dinitronaphthalenes have also been reduced by the Hodgson and Birtwell procedure (*loc. cit.*), and comparative data are tabulated below. The reduction was rapidly completed for the 1 : 5- and 1 : 6-compounds and the crude nitro-amines obtained were pure and free from the tarry material which usually accompanies reduction in aqueous medium. Whereas 1 : 8-dinitronaphthalene is scarcely attacked by aqueous sodium sulphide even at 90° (cf. Hodgson and Walker, *loc. cit.*) nevertheless, in methanol, it is rapidly converted to a sulphide dye at 60°. The yield of 5-nitro-1-naphthylamine was less than that of the other isomerides, and the difference is not accounted for by further reaction with the sodium thiosulphate formed during the reduction, since both 1 : 5-dinitronaphthalene and 5-nitro-1-naphthylamine remain unchanged when boiled with alkaline sodium thiosulphate; the yield of 5-nitro-1-naphthylamine is actually decreased by further addition of sodium bicarbonate to the reduction medium.

EXPERIMENTAL.

Preparation of 4 : 5-Dinitro-2-naphthylamine.—Finely powdered 1 : 3 : 8-trinitronaphthalene (10 g.), suspended in boiling methanol (150 c.c.), was treated with sodium bicarbonate (2 g.) which caused a red colour to develop immediately; it was reduced by the dropwise addition of a solution of crystalline sodium sulphide (24 g.) and sodium bicarbonate (7.5 g.) in water (40 c.c.) and methanol (63 c.c.). The mixture was vigorously agitated and further sodium bicarbonate (2 g.) was added when half the previous solution was added; the solution was cooled, ice and water added in quantity; after 1 hour, the precipitated crude 4 : 5-dinitro-2-naphthylamine with some unchanged trinitro-compound was separated, washed with water, extracted twice with boiling hydrochloric acid (300 c.c., 8%) and the solution filtered; part of the hydrochloride of the base separated as a flocculent yellow precipitate which was only sparingly soluble in boiling hydrochloric acid; ammonia (*d* 0.88) was then stirred gradually into the mixture at 0° and the crude 4 : 5-dinitro-2-naphthylamine (2.2 g., 25%) separated as a flocculent orange-yellow precipitate, m. p. 224—227°. This, after separation, washing and

drying, crystallised from 50% aqueous pyridine (charcoal) in orange rods, m. p. 232° (Found: N, 18.2. $C_{10}H_{17}O_4N_3$ requires N, 18.0%) which are almost insoluble in cold but more soluble in hot ethanol and glacial acetic acid, and readily soluble in cold acetone and pyridine. Alternatively, if, after the addition of water to the reaction mixture above, hydrochloric acid be added until the solution is almost neutral, the precipitate is more easily manipulated in spite of the fact that it is accompanied with sulphur. If the amount of sodium bicarbonate added initially and after 5 minutes is diminished by 50%, the yield falls to *ca.* 20%, and without sodium bicarbonate the yield is only 2%. When the filtrate from the ammonia neutralisation is extracted with ether and the extract treated with hydrochloric acid gas, a colourless hydrochloride is precipitated and the reddish orange base from this had m. p. 145–160°; it was insufficient in quantity for further investigation.

4 : 5-Dinitroaceto-2-naphthalide was obtained when the above amine (0.3 g.) was boiled for 2 minutes with acetic anhydride (1 c.c.) in glacial acetic acid (10 c.c.); it separated from the hot mixture, and crystallised from 50% aqueous pyridine in yellow needles, m. p. 296°, which are almost insoluble in boiling ethanol (Found: N, 15.4. $C_{12}H_9O_5N_2$ requires N, 15.3%).

Diazotisation and Deamination of 4 : 5-Dinitro-2-naphthylamine.—A solution of the amine (0.6 g.) in glacial acetic acid (8 c.c.) was stirred into one of sodium nitrite (0.3 g.) in sulphuric acid (3 c.c., *d* 1.84) below 20°, kept 1 hour, and the mixture stirred rapidly into a suspension of cuprous oxide (5 g.) in ethanol (50 c.c.), the temperature rising to 70°; after stirring for a further 15 minutes, the mixture was added to water (500 c.c.), kept overnight, the precipitate separated, dried at 100° and extracted with toluene; after removal of toluene from the filtered extract, the residue of 1 : 8-dinitronaphthalene, after crystallisation from ethanol (charcoal), had m. p. 168° and was identified as 1 : 8-dinitronaphthalene, (Found: N, 13.0. Calc. for $C_{10}H_6O_4N_2$: N, 12.8%); it was not 1 : 6-dinitronaphthalene, m. p. 165°. It gave an intense violet colour when a trace in boiling methanol was treated with a small quantity of sodium sulphide, whereas the 1 : 3- and 1 : 6-isomerides gave brown colours; it was only slowly attacked by boiling sodium sulphite solution giving a brown solution (the 1 : 3-isomeride gives an immediate violet colour, while 1 : 6-dinitronaphthalene only slowly gives a brown colour).

2-Chloro-4 : 5-dinitronaphthalene.—A solution of the above amine (1.2 g.) in sulphuric acid (5 c.c., *d* 1.84) was added to sodium nitrite (0.6 g.) in sulphuric acid (5 c.c., *d* 1.84) and the solution stirred into glacial acetic acid (15 c.c.) below 20°; the mixture, after 1 hour, was stirred into a solution of cuprous chloride (2 g.) in hydrochloric acid (15 c.c., *d* 1.18) and kept overnight. The crude 2-chloro-4 : 5-dinitronaphthalene was separated, washed with water and dried at 100°; it was extracted with the minimum amount of pyridine, the extract boiled (charcoal), cooled, water added in equal volume, the mixture again boiled, and from the filtered solution the chloro-compound separated in pale yellow rods (70%), m. p. 163° (Found: N, 11.4. $C_{10}H_5O_4N_2Cl$ requires N, 11.1%).

Bromination of 4 : 5-Dinitro-2-naphthylamine.—A suspension of 4 : 5-dinitro-2-naphthylamine (0.8 g.) in chloroform (25 c.c.) was stirred at 5° with bromine (0.45 c.c.) in chloroform (4 c.c.); a yellow-white precipitate of 1-bromo-4 : 5-dinitro-2-naphthylamine hydrobromide was produced and, after a part of the chloroform had been removed the precipitate was separated and treated with dilute ammonia; the 1-bromo-4 : 5-dinitro-2-naphthylamine crystallised from 50% aqueous pyridine (charcoal) in clusters of yellow needles (1.0 g.), m. p. 176° (Found: N, 13.8. $C_{10}H_5O_4N_2Br$ requires N, 13.6%). The substance was almost insoluble in cold ethanol and glacial acetic acid but rather more soluble in these solvents when hot; it was readily soluble in cold pyridine and acetone and it gave an intense violet colour when boiled with ethanol and a trace of sodium sulphide.

1-Bromo-4 : 5-dinitroaceto-2-naphthalide. This was obtained when the above amine (0.2 g.) was boiled with acetic anhydride (2 c.c.); the acetyl derivative crystallised from 50% aqueous acetic acid in yellow needles, m. p. 260° (Found: N, 12.0. $C_{12}H_9O_5N_2Br$ requires N, 11.8%).

1-Bromo-4 : 5-dinitronaphthalene was prepared by diazotisation of 1-bromo-4 : 5-dinitro-2-naphthylamine (0.5 g.) as above, and decomposition of the diazonium sulphate by stirring the solution into a suspension of cuprous oxide (5 g.) in ethanol (50 c.c.), the temperature rising to 70°. The bromo-compound was obtained as in the deamination of 4 : 5-dinitro-2-naphthylamine and crystallised (0.2 g.) from alcohol (charcoal) in yellow needles, m. p. 170°, identified as 1-bromo-4 : 5-dinitronaphthalene (Ullmann and Consonno, *Ber.*, 1902, 35, 2805, give m. p. 170°) (Found: N, 9.6. Calc. for $C_{10}H_5O_4N_2Br$: N, 9.4%).

1 : 2-Dibromo-4 : 5-dinitronaphthalene was prepared when a solution of 1-bromo-4 : 5-dinitro-2-naphthylamine (0.5 g.) in sulphuric acid (2.5 c.c., *d* 1.84) was added to one of sodium nitrite (0.2 g.) in sulphuric acid (1.5 c.c., *d* 1.84) and the mixture stirred into glacial acetic acid (6 c.c.) below 20°, kept for 1 hour, and then stirred into a solution of cuprous bromide (1 g.) in hydrobromic acid (5 c.c., *d* 1.7). After some hours, the mixture was poured on to ice, the precipitate of crude 1 : 2-dibromo-4 : 5-dinitronaphthalene separated and extracted with boiling alcohol (charcoal) from which it separated on cooling in clusters of pale yellow polyhedra, m. p. 161°, readily soluble in cold pyridine (Found: N, 7.7. $C_{10}H_4O_4N_2Br_2$ requires N, 7.4%); it developed rapidly an intense violet colour when a trace was boiled with ethanol containing sodium sulphide.

A Comparative Experimental Survey of the Monoreduction of Available Dinitronaphthalenes by Sodium Sulphide. General Procedure.—The finely divided dinitronaphthalene (10 g.) suspended in boiling methanol (150 c.c.) was reduced by dropwise addition during 15 minutes of a previously heated solution of crystallised sodium sulphide (16 g.) and sodium bicarbonate (5 g.) in water (40 c.c.) with vigorous agitation throughout. (The presence of excess sodium sulphide was tested by ferrous sulphate paper.) The mixture was then rapidly cooled, ice added and then water added to 1 l. The precipitated nitroamine was separated and extracted twice with boiling hydrochloric acid (300 c.c.; 8%). In some cases the amine separated in finely divided form and was difficult to filter, in which case hydrochloric acid was added to the reaction mixture above in amount nearly sufficient to neutralise it; the precipitate then coagulated rapidly and the presence of sulphur did not interfere greatly with the extraction or purity of the final product. The hydrochloric extract was treated at 0° with excess ammonia, the precipitated amine separated and recrystallised from a suitable solvent (pyridine, acetic acid, or alcohol with charcoal); all the crude products had a high degree of purity and were free from the tarry matter usually obtained in aqueous reductions. About 1.8 g.-mol. of reducing agent (sodium hydrosulphide) was used per g.-mol. dinitro-compound. The following are the summarised results:

Dinitronaphthalene (10 g.).	Yield, %.	Composition of product.
1 : 3	85	Mixture of 3-nitro-1- and 4-nitro-2-naphthylamine (Hodgson and Birtwell, <i>loc. cit.</i>).
1 : 5	50	5-Nitro-1-naphthylamine, m. p. 122° (Hodgson and Birtwell, <i>loc. cit.</i> , give m. p. 119°).
1 : 6	55	5-Nitro-2-naphthylamine.
2 : 7	82	7-Nitro-2-naphthylamine (Hodgson and Ward, this vol., p. 590).
1 : 8	—	Only sulphide dyes.

To ascertain whether the yield of 5-nitro-1-naphthylamine would be improved by further addition of sodium bicarbonate, 1 g. was added to the original mixture and a further 1 g. after 7½ minutes of reduction, but the yield actually decreased

to 45%. 1:5-Dinitronaphthalene (1 g.) and 5-nitro-1-naphthylamine (1 g.) were separately refluxed for 20 minutes with a solution of sodium thiosulphate (0.5 g.) and sodium hydroxide (0.2 g.) in water (4 c.c.), but both compounds were recovered unchanged.

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