258. *Reactions of Aromatic Nitro-compounds with Alkaline Sulphides. Part III. Dinitronaphthalenes.*

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A dinitronaphthalene reacts with alkali sulphides, and in particular with sodium hydrogen sulphide to form, mainly, a monoamine by reduction, and a sodium mercaptide by replacement of a nitro- with a sodium-thio- (SNa-)group, the ratio of these products varying according to the electropositivity of the carbon atom to which the reactive nitro-group is attached. 1 : 2- or 1 : 8-Dinitronaphthalene gives only mercaptan, whereas the 1 : 3-, 1 : 5-, 1 : 6-, and 2 : 7-isomers give mainly the amine. 1 : 4-Dinitronaphthalene behaves like the 1 : 2-isomer, except that *ca.* 4% of monoamine is also formed. The results are in accord with Hodgson's theory of sulphide reduction and with the previous conclusions of the present authors.

In former reductions of dinitronaphthalenes with alkaline sulphides, the low yield of amine which generally occurred was thought to be due to the formation of sulphur dyes or of similar complexes (cf. Hodgson and Ward, *J.*, 1945, 663, 794), but it has now been established that these by-products are produced only in traces, if at all, when pure reagents are used and, in particular, the pure sodium hydrogen sulphide of Hodgson and Ward (*J.*, 1948, 242). Reactions of various alkaline sulphides with numerous dinitronaphthalenes are now reported, together with supplementary information from similar experiments with α- and β-nitronaphthalene, α- and β-naphthylhydroxylamine, αα'-azoxynaphthalene, and 1 : 3 : 8-trinitro- and 1 : 3 : 6 : 8-tetranitro-naphthalene.

In addition to the direct reduction of a nitro- to an amino-group, there occurs a considerable replacement of the nitro- by the sodium-thio- (SNa-)group, the extent of this replacement varying according to the electropositivity of the carbon atom to which the nitro-group is attached; for example, there is only replacement of the nitro-group in 1 : 2-dinitronaphthalene, in which C_1 has the higher positivity, very largely owing to the combined electron-attracting effects of the 2-nitro-group and the negative inductive ($-I$) effect (Hodgson and Elliott, *J.*, 1935, 1850; *J. Soc. Dyers and Col.*, 1938, **54**, 264) of the second nucleus. In many cases, owing to the labile character of the sodium mercaptide formed, it has proved very difficult to isolate this or the disulphide obtained from it by oxidation. The replacement occurs in both the poly- and mono-nitronaphthalene series.

In most of the work now described, sodium hydrogen sulphide (Hodgson and Ward, *loc. cit.*) was caused to react in just definite excess with the dinitro- or other nitro-naphthalene in solution or suspension in aqueous methanol. The insoluble part of the product usually contained an amine, organic sulphide, and unchanged reactant; the solution contained a mercaptide which, in most cases, immediately began to oxidise to disulphide, a process doubtless aided by the sodium nitrite liberated by the replacement reaction. The stability of the mercaptide depends on the position of the remaining nitro-group in the nucleus. *E.g.*, that from 1 : 2-dinitronaphthalene is stable for a comparatively long time, and that from the 1 : 5-isomer was more stable than that from 1 : 6-dinitronaphthalene; these results are in accord with the quinonoid hypothesis of Veselý and Jakes (*Bull. Soc. chim.*, 1923, **33**, 955), amplified by Hodgson and Hathway (*J. Soc. Dyers and Col.*, 1945, **61**, 283; 1946, **62**, 241) and by Hodgson and Ward (*ibid.*, 1947, **63**, 141, 177), for this predicts that the 2- and 5-nitro-groups should cause greater electronic attraction at C_1 (*i.e.*, pronounced positive character of the carbon atom to which the sodium-thio-group is attached) than does the 6-nitro-group in a non-quinonoid position.

The sulphur compounds associated with the amine are usually a disulphide, formed by oxidation during manipulation, and a monosulphide formed by interaction of the reactive nitro-group of the initial material with the mercaptan produced by replacement.

Strong evidence for mercaptide formation, *e.g.*, with 1 : 8- and 2 : 7-dinitronaphthalene, is provided, when isolation is difficult, by computation of the amounts of sodium hydrogen sulphide used for reduction and replacement, respectively, in comparison with the actual amount consumed. Direct proof has also been obtained in several cases by oxidation to the disulphide and isolation of the thiolacetate (SAc) derivative. The following table summarises the results of the reactions of sodium hydrogen sulphide with seven dinitronaphthalenes.

Dinitro-naphthalene.	Products formed.
1 : 2-	2 : 2′-Dinitro-1 : 1′-dinaphthyl sulphide, and 2-nitro-1-naphthalenethiol. Sodium disulphide also gave the monosulphide (with sulphur).
1 : 3-	A mixture (82%) of 3-nitro-1-naphthylamine and 4-nitro-2-naphthylamine (cf. Hodgson and Birtwell, *J.*, 1944, 75).
1 : 4-	4 : 4′-Dinitro-1 : 1′-dinaphthyl sulphide, 4-nitro-1-naphthalenethiol, 4-nitro-1-naphthylamine (4—5%), and sulphur.
1 : 5-	5-Nitro-1-naphthylamine (55—58%); remainder was mainly 5-nitro-1-naphthalenethiol (oxidised to 5 : 5′-*dinitro*-1 : 1′-*dinaphthyl disulphide*; converted into 5-*nitro*-1-*naphthyl thiolacetate*).
1 : 6-	5-Nitro-2-naphthylamine (60—62%); remainder mainly 5-nitro-2-naphthalenethiol (converted into 5-*nitro*-2-*naphthyl thiolacetate*).
1 : 8-	The filtered solution, after reaction with insufficient reagent, exhibited the oxidation behaviour of a thiol, which computation indicated to be present (agreement within 5%).
2 : 7-	7-Nitro-2-naphthylamine (80%); remainder mercaptan, as indicated by oxidation to 7 : 7′-*dinitro*-2 : 2′-*dinaphthyl disulphide* and confirmed by computation.

The relative ease of amine-formation, *viz.*, 2 : 7- > 1 : 6- > 1 : 5- > 1 : 4- > 1 : 2-, is in accord with the theory of Hodgson (*J. Soc. Dyers and Col.*, 1943, **59**, 246; cf. Hodgson and Turner, *J.*, 1943, 318) that the reduction of the nitro-group by alkali sulphides is to be regarded as oxidation of the sulphide by the nitro-group; consequently the isomers capable of resonance into quinonoid forms, *viz.*, the 1 : 5-, 1 : 4-, and 1 : 2-dinitronaphthalenes, are in the order of increasing restraint due to the ease of mutual interaction between the nitro-groups, but the 2 : 7-, 1 : 3-, and 1 : 6-dinitronaphthalenes are in the decreasing order of independent easy resonance, since a β-group exceeds an α-group in this respect. The oxidising power of any particular nitro-group will be enhanced by its freedom from restraint and its ease of resonance.

EXPERIMENTAL.

(Analyses are by Drs. Weiler and Strauss, Oxford.)

General Procedure.—A stirred solution or suspension of the dinitronaphthalene (10 g.) in methanol (80 c.c.), heated on the water-bath under reflux, is treated dropwise during *ca.* 15 minutes with a solution of sodium hydrogen sulphide. This solution, henceforward styled the "reagent," is prepared by treating 13% aqueous sodium sulphide (100 c.c.) with sodium hydrogen carbonate (14 g.) and then adding methanol (100 c.c.), filtering, and washing the residue on the filter with methanol, to afford a reagent (*ca.* 250 c.c.) containing sodium hydrogen sulphide (3·6—3·7 g. per 100 c.c.). After heating the reaction mixture for a further 15 minutes (25 minutes for the 2 : 7-isomer), ice is added to the hot solution which is then poured into ice-water (*ca.* 1 l.); the mixture is filtered rapidly, and the residue washed with water and extracted with boiling 8—10% hydrochloric acid to dissolve out the nitronaphthylamine. The insoluble residue contains unchanged dinitro-compound and aromatic sulphides. It is important that the " reagent " be added until present in permanent (calculated) excess, the amount required varying according to the compound examined.

Dinitronaphthalenes.

1 : 2-*Dinitronaphthalene.*—(*a*) The compound (2·5 g.) in methanol (20 c.c.) was treated with the reagent (1·5 g.-mols.) during 10 minutes; the red colour, at first transitory, became permanent when *ca.* half of the reagent had been added. On dilution as above 2 : 2′-dinitro-1 : 1′-dinaphthyl sulphide (0·75 g.) was precipitated, filtered off, and crystallised from hot glacial acetic acid; pale yellow parallelepipeds, m. p. and mixed m. p. 204° (Hodgson and Leigh, *J.*, 1937, 1352, give m. p. 205°; Hoogeveen, *Rec. Trav. chim.*, 1901, **20**, 141, gives m. p. 204°) (Found: S, 8·7. Calc. for $C_{20}H_{12}O_4N_2S$: S, 8·5%). A specimen prepared from the sodium salt of 2-nitro-1-naphthalenethiol and 1-chloro-2-nitronaphthalene had m. p. 207°. The filtrate from the reduction, when treated with acetic acid, afforded bright yellow 2-nitro-1-naphthalenethiol, m. p. 205°; this dissolved readily in 3% aqueous sodium hydroxide or sodium carbonate. to give a solution which was more stable in air than the corresponding solutions from 1 : 5- and 1 : 6-dinitronaphthalenethiol; when stirred with excess of acetic anhydride and then kept overnight, it yielded a precipitate of 2-*nitro*-1-*naphthyl thiolacetate* which separated from 50% aqueous acetic acid in almost colourless crystals, m. p. 103° (Found: S, 12·8. $C_{12}H_9O_3NS$ requires S, 12·9%); a sample prepared from 1-chloro-2-nitronaphthalene had m. p. and mixed m. p. 102°. No amine formation could be detected.

(*b*) With quantities as in (*a*) but 0·75 g.-mol. of the reagent, the monosulphide (1·75 g.) was isolated, and there was a negligible amount of mercaptan.

(*c*) A solution of 1-chloro-2-nitronaphthalene (2 g.) in methanol (30 c.c.) was heated under reflux with the reagent (16 c.c.) for 30 minutes, the mixture worked up as in (*a*), and the considerable amount of mercaptan formed was converted into the acetyl derivative.

(*d*) 1 : 2-Dinitronaphthalene (0·5 g.) in methanol (10 c.c.) was treated dropwise during 5 minutes with sodium disulphide (0·5 g.-mol.) in water (8 c.c.); the initial red colour gave place to a yellow precipitate (0·4 g.) of crude 2 : 2′-dinitrodinaphthyl sulphide, m. p. 185—193°, containing sulphur.

1 : 4-*Dinitronaphthalene.*—From this compound (1·0 g.-mol.) and the reagent (0·5 g.-mol.), the product was 4 : 4′-dinitro-1 : 1′-dinaphthyl sulphide (identified by comparison with an authentic specimen), but from 1·0 g.-mol. of the reagent the main product was 4-nitro-1-naphthalenethiol with *ca.* 4—5% of 4-nitro-1-naphthylamine. Reduction with sodium disulphide appeared to form first the mercaptan and then the monosulphide, but all the products were so contaminated with sulphur that attempts at purification were frustrated.

1 : 5-*Dinitronaphthalene.*—The procedure used in (*a*) above gave 5-nitro-1-naphthylamine (55—58%). 5-*Nitro*-1-*naphthyl thiolacetate,* prepared from the alkaline filtrate by precipitating the orange-red 5-nitro-1-naphthalenethiol with acetic acid and subsequently acetylating its sodium salt, crystallised from boiling glacial acetic acid in pale yellow hair-like needles, m. p. 181—182° (Found: S, 12·7. $C_{12}H_9O_3NS$ requires S, 12·95%), which were readily soluble in cold acetone and moderately soluble in hot glacial acetic acid, but only slightly soluble in either hot or cold ethanol. 5 : 5′-*Dinitro*-1 : 1′-*dinaphthyl disulphide,* obtained by aërial or potassium ferricyanide oxidation of an alkaline solution of the above thiol, separated from boiling glacial acetic acid in small yellow crystals, m. p. 231—233° (Found: S, 15·6. $C_{20}H_{12}O_4N_2S_2$ requires S, 15·7%). The product formed by heating a mixture of 1-chloro-5-nitronaphthalene with sodium disulphide [prepared by dissolution together of sodium monosulphide nonahydrate (3 g.) and sulphur (0·5 g.)] in boiling ethanol for 8 hours afforded, after repeated extraction with boiling ethanol, a crystalline product, m. p. 190—230° (Found: S, 17·6%), which on further crystallisation melted sharply at 198° (Found: S, 18·2%); when the reduction was carried out in acetone by the general procedure, the final liquor had a very dark reddish-brown colour, and the yield of 5-nitro-1-naphthylamine decreased to 40%.

1 : 6-*Dinitronaphthalene.*—The main product was 5-nitro-2-naphthylamine (60—62%). 5-*Nitro*-2-*naphthyl thiolacetate,* obtained from the yellow 5-nitro-2-naphthalenethiol, crystallised from hot 50% aqueous acetic acid in pale yellow plates, m. p. 193—196° (Found: S, 12·7. $C_{12}H_9O_3NS$ requires S, 12·9%). When 1-chloro-6-nitronaphthalene was heated under reflux in ethanol with sodium disulphide for 8 hours, the yield of sulphur compounds was negligible.

1 : 8-*Dinitronaphthalene.*—The violet solution, obtained when insufficient of the reagent was used and the excess of 1 : 8-dinitronaphthalene filtered off, oxidised rapidly in the cold, either in air or with potassium ferricyanide, and was decolorised by acetic acid with production of a gelatinous precipitate. These reactions would appear to indicate replacement of a nitro- by the SNa-group.

2 : 7-*Dinitronaphthalene.*—The main product was 7-nitro-2-naphthylamine (80%); the violet filtrate obtained by the general procedure afforded 7 : 7′-*dinitro*-2 : 2′-*dinaphthyl disulphide* on oxidation with potassium ferricyanide; this disulphide separated from boiling acetic acid in reddish-orange crystals, m. p. 264—265° (Found: S, 15·75. $C_{20}H_{12}O_4N_4S_2$ requires S, 15·7%). The acetyl derivative of the thiol, obtained as above, contained some dark green substance which could not be entirely removed by repeated crystallisation from acetic acid (charcoal); the crude 7-nitro-2-naphthyl thiolacetate had m. p. 185°, but the sulphur content was low and indicated that the admixed impurity did not contain sulphur.

Miscellaneous Reductions.

α-*Nitronaphthalene.*—(*a*) When treated by the Hodgson–Birtwell reagent (*loc. cit.*), this (2·5 g.) reacted slowly in the cold. (*b*) When heated under reflux with a slight excess of reagent for 2 hours, it (2·5 g.) gave α-naphthylamine (0·8 g., *ca.* 40%) and unchanged material (1·5 g.), but no sulphur dyes; α-naphthylhydroxylamine was probably also present. After longer heating with excess of reagent, the yield of α-naphthylamine increased to *ca.* 75%, only 2—4% of unchanged material being recovered. (*c*) Treatment with aqueous sodium sulphide–sodium hydroxide at 90° for 3½ hours gave only indeterminate products.

β-Nitronaphthalene.—When treated as above, the β-isomer gave a small amount of β-naphthylamine and no sulphur dyes, but, since only a small amount of the initial substance remained unchanged, the reduction must have proceeded mainly to intermediate stages.

αα′-Azoxynaphthalene.—Prepared by the method of Cumming and Steel (*J.*, 1923, 2464), this was mainly unchanged by the Hodgson–Birtwell procedure, although a very small amount of α-naphthylamine was formed; similar non-reactivity was observed towards hot aqueous solutions of alkaline sodium sulphide.

α-Naphthylhydroxylamine.—Prepared according to the directions of Willstätter and Kubli (*Ber.*, 1908, **41**, 1936), this gave α-naphthylamine (50%) by the Hodgson–Birtwell procedure (*loc. cit.*).

β-Naphthylhydroxylamine.—Prepared as for the α-isomer (cf. also Baudisch and Furst, *Ber.*, 1917, **50**, 324) this afforded β-naphthylamine (50—55%) by the same method.

In the four preceding reactions some replacement of nitro- by SNa-groups occurs, since the filtered solutions give bright yellow precipitates on acidification; also, the solutions of the naphthylamines, obtained by steam-distillation of the acidified (acetic acid) reduction mixtures, when diazotised, afford intense green colours which indicate the presence of a volatile thiol and are due to nitroso-compound formation between the thiol and nitrous acid (cf. also Veselý and Chudozilov, *Rec. Trav. chim.*, 1925, **44**, 352).

1 : 3 : 8-*Trinitro- and* 1 : 3 : 6 : 8-*Tetra-nitronaphthalene.*—Reduction by the general procedure occurs rapidly, even in the cold, to give dark red solutions which contain sodium nitrite formed by displacement of nitro-groups. The filtrates, after separation of the insoluble material, were oxidised rapidly in air to give yellow products which, however, could not be purified.

Evidence for Thiol Formation by Calculation.—10 G. of a dinitronaphthalene requires 3·85 g. of NaSH for complete conversion into a nitronaphthylamine (8·624 g.), and 2·57 g. of NaSH for replacement of one nitro-group by SNa to give a nitronaphthalenethiol (9·42 g.).

1 : 6-Dinitronaphthalene (10 g.) was reduced by NaSH (3·5 g., determined by iodine titration) to give amine (minimum yield, 60%) and thiol (assumed 40% by difference). The amine would consume 2·31 g. of NaSH and the thiol 1·02 g., *i.e.*, a total of 3·32 g. If the real yield of amine (when loss incurred during manipulation and determination as azo-β-naphthol is taken into account) is assumed to be 65% and that of thiol 35%, the total NaSH required is 3·4 g. Since a slight excess of NaSH is always used in these reductions, the calculated and experimental results show reasonable agreement on the probable assumption that the thiol is substantially the only by-product formed.

1 : 5-Dinitronaphthalene (10 g.), yielding 55% of amine and 45% of thiol, similarly gives a calculated value of 3·3 g. of NaSH, compared with 3·5 g. actually used.

2 : 7-Dinitronaphthalene, yielding 80% of amine, gives a calculated value of 3·58 g. of NaSH used.

1 : 8-Dinitronaphthalene (10 g.) would require 2·57 g. for thiol replacement only; by using a deficiency of NaSH and basing calculations on the amount used, the agreement between the calculated and actual amounts was within 5%.

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