77. *Reactions of Aromatic Nitro-compounds with Alkaline Sulphides. Part IV.* Disulphide Formation.*

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From a study of the reactions of *o*-dinitrobenzene with alkaline sulphides it is concluded that some diaryl disulphides may be formed from aromatic compounds containing labile nitro-groups by way of the aryl thiol or aryl thiophenoxide which is then oxidised by concurrently liberated nitrous acid or sodium nitrite. Alternative reaction mechanisms are discussed. The behaviour of 3 : 4- and 2 : 5-dinitrotoluenes with alkaline sulphides has been examined.

Hodgson and Ward (*J.*, 1949, **1316**) suggested that the formation of 2 : 2′-dinitrodiphenyl disulphide from *o*-dinitrobenzene by the action of sodium hydrogen sulphide was accounted for by the oxidation of the primary reaction product, *o*-nitrothiophenol, by concurrently liberated sodium nitrite. We now find this suggestion, with certain modifications, to be correct. These reactions constitute one possible general mode of formation of diaryl disulphides from aromatic compounds containing labile nitro-groups.

Pure sodium hydrogen sulphide in reaction with *o*-dinitrobenzene will liberate sodium nitrite and free nitrous acid (the latter unstable at the usual reaction temperatures). We have found that sodium nitrite or, more readily, free nitrous acid oxidises *o*-nitrothiophenol to 2 : 2′-dinitrodiphenyl disulphide. This reaction may proceed by way of the *S*-nitrosothiophenol, the formation of such compounds from thiophenols by nitrites, and their oxidation to the disulphides having been studied by Rheinboldt *et al.* (*Ber.*, 1926, **59**, 1311; 1927, **60**, 184; *J. pr. Chem.*, 1931, **130**, 133; B.P. 374 594). The intense colours formed during the reaction of alkaline sulphides with aromatic compounds containing labile nitro-groups support this idea, the colour of nitroso-thiols having been claimed as their most striking property (Lecher and Siefken, *Ber.*, 1926, **59**, 2594).

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* Part III, *J.*, 1949, **1316**.

Furthermore, disulphide formation from *o*-dinitrobenzene is almost completely suppressed by removal of nitrite ions from the reaction mixture, *e.g.*, by urea or ammonium salts, and it is largely suppressed by appreciable amounts of free alkali. Thus, whereas only the diaryl disulphide is formed by passing hydrogen sulphide into a solution of *o*-dinitrobenzene in hot methanol (whereby only nitrous acid is liberated), both the di- and the mono-sulphide are formed by sodium hydrogen sulphide; in the latter case reaction is due to both nitrous acid and the less reactive sodium nitrite, and is in competition with that between *o*-dinitrobenzene and *o*-nitrothiophenol which is favoured by the more alkaline medium. The effect of using varying molecular quantities of sodium hydrogen sulphide (Hodgson and Ward, *loc. cit.*) is thus accounted for.

An alternative possibility, that of direct sulphurisation of the 2 : 2′-dinitrodiphenyl sulphide by sodium hydrogen sulphide, has been found not to occur (cf. Fuson and Melamed, *J. Org. Chem.*, 1948, **13**, 690).

Parallel experiments with 3 : 4-dinitrotoluene were inconclusive. Sodium hydrogen sulphide gave a mixture, but sodium disulphide in boiling methanol produced only the disulphides (a mixture, owing to the lability of both nitro-groups), as was the case also with *o*-dinitrobenzene. It seems possible that in the disulphide reactions intermediate nitrothiophenoxides are not formed. However, 1 : 2-dinitronaphthalene and sodium disulphide give only the sulphide (and free sulphur), presumably by way of the thiol. That disulphides are formed by way of compounds of the type Ar·S·SH is not to be completely disregarded although the existence of such compounds is controversial. The same mixture of disulphides was obtained from 3 : 4-dinitrotoluene with sodium tetrasulphide, but under relatively strongly alkaline conditions some reduction to the isomeric nitrotoluidines also occurred. It is important that under none of our varied reaction conditions was 4-amino-3-nitrobenzaldehyde formed (cf. the analogous formation of *p*-aminobenzaldehyde from *p*-nitrotoluene; Hodgson and Beard, *J.*, 1944, 708).

Whilst one mode of formation of diaryl disulphides from aromatic polynitro-compounds by sodium hydrogen sulphide may be as suggested above, other mechanisms are also possible. One such we have already indicated for sodium disulphide, where there are complications caused by its ability to function in several ways (cf. Blanksma, *Rec. Trav. chim.*, 1901, **20**, 141), *e.g.*, by hydrolysis to sodium hydrogen sulphide and sodium hydroxide. This hydrolysis would account for the exclusive formation of diaryl monosulphides by this reagent in certain cases. It also must be borne in mind that according to Bullock and Forbes (*J. Amer. Chem. Soc.*, 1933, **55**, 232; cf. Raschevskaja, *J. Gen. Chem. Russia*, 1940, **10**, 1089), disulphide ions may arise in any reaction of aromatic nitro-compounds with any alkaline sulphide if reduction occurs simultaneously.

Blanksma (*Rec. Trav. chim.*, 1901, **20**, 121) failed to convert 2 : 2′-dinitrodiphenyl sulphide into the disulphide by sulphur in alcohol. Fuson and Melamed (*loc. cit.*) suggested that this could be accomplished by alkaline sulphides but they relied on an isolated observation that 4 : 4′-dinitrodiphenyl sulphide with sodium disulphide gave a mixture of the disulphide, *p*-nitrothiophenol, and *p*-aminothiophenol [cf. Lukashevich and Sergeeva, *Doklady Akad. Nauk. S.S.S.R.*, 1949, **67**, 1041 (*Chem. Abs.*, 1950, **44**, 1921); *Zhur. Obscheĭ Khim.*, 1949, **19**, 1493 (*Chem. Abs.*, 1950, **44**, 3456)].

There are moreover further complications, such as the reaction of nitrous acid or nitrites with the sulphides of sodium, or with sodium thiosulphate which may also be present when alkaline sulphides react with aromatic nitro-compounds. Much remains to be done to clarify alternative mechanisms of disulphide formation.

2 : 5-Dinitrotoluene with sodium hydrogen sulphide or sodium polysulphides yields 5-nitro-*o*-toluidine, 6-nitro-*m*-toluidine, and large amounts of unidentified amorphous material. There was no evidence of replacement of nitro-groups by arylthio-groups.

EXPERIMENTAL

Analyses are by Drs. Weiler and Strauss, Oxford.

Aqueous-methanolic sodium hydrogen sulphide was prepared by Hodgson and Ward's method (*J.*, 1948, 242). All the experiments were carried out under reflux, a rapid stream of nitrogen serving to exclude air and to provide efficient agitation.

Reaction of o-*Nitrothiophenol with Sodium Nitrite.*—*o*-Nitrothiophenol (1 g.) in ethanol (10 c.c.) was allowed to react with sodium nitrite (0·1 g.) for 15 minutes. After cooling, 2 : 2′-dinitrodiphenyl disulphide (0·65 g., 65%), m. p. 194—196° (Hodgson and Ward, *loc. cit.*, give 196—198°), was precipitated. Oxidation of the filtrate with potassium ferricyanide gave a yellow product (0·35 g.), m. p. 95—112°.

Reaction of o-*Nitrothiophenol with Nitrous Acid.*—The above experiment, with the addition of one equivalent of sodium hydrogen sulphate to liberate nitrous acid, gave 2 : 2′-dinitrodiphenyl disulphide (0·9 g., 91%), m. p. 192—195°. The filtrate on oxidation gave 0·05 g. of material, m. p. 98—113°.

Experiments with 2 : 2′-Dinitrodiphenyl Disulphide.—This was recovered unchanged after being boiled with aqueous sodium nitrite for 15 minutes and was only slightly affected by boiling aqueous sodium hydrogen sulphide (*ca.* 1 mol.) during 15 minutes.

Reactions of o-*Dinitrobenzene.*—(*a*) *o*-Dinitrobenzene (2 g.) in methanol (20 c.c.) was treated with a rapid stream of hydrogen sulphide during 25 minutes. The solution slowly darkened and a precipitate was formed. After cooling, the latter was removed, washed with water, and dried (0·8 g.). After extraction with cold carbon disulphide it afforded crude 2 : 2′-dinitrodiphenyl disulphide, m. p. 194° (from acetone), not depressed on admixture with an authentic specimen.

(*b*) *o*-Dinitrobenzene (2 g.) and urea (1 g.) in methanol (20 c.c.) were treated with sodium hydrogen sulphide (15 c.c.; *ca.* 0·75 mol.) during 5 minutes and the whole was heated for a further 10 minutes. After cooling, the solid product was collected, washed with a little cold methanol, dried, and extracted with cold carbon disulphide, affording crude 2 : 2′-dinitrodiphenyl sulphide, m. p. 94—99° (Found : S, 11·6. Calc. for $C_{12}H_8O_4N_2S$: S, 11·6%). Similar results were obtained with ammonium acetate in place of urea.

(*c*) *o*-Dinitrobenzene (2 g.) in methanol (20 c.c.) was treated with aqueous sodium sulphide (0·75 g., 0·8 mol.; 5 c.c.) as in (*b*). The sole product was pure monosulphide (0·8 g.), m. p. 119—122°.

(*d*) The previous experiment was repeated with the addition of sodium hydrogen carbonate (0·5 g.) and treatment with sodium hydrogen sulphide (1 mol.). The product was almost pure monosulphide (1·5 g.), m. p. 116—121° (Found : S, 11·3. Calc. for $C_{12}H_8O_4N_2S$: S, 11·6%).

Reactions of 3 : 4-Dinitrotoluene.—(*a*) 3 : 4-Dinitrotoluene was unaffected when a rapid stream of hydrogen sulphide was passed into a solution of it in boiling methanol.

(*b*) 3 : 4-Dinitrotoluene (2 g.) in methanol 20 c.c.) was treated with sodium hydrogen sulphide (30 c.c.; 1·5 mols.) for 5 minutes and the whole heated for a further 10 minutes. Cooling and acidification by dilute hydrochloric acid afforded an oil which solidified (1·4 g.). This was extracted by cold carbon disulphide and recrystallised from acetone, giving light yellow needles, m. p. 145—153° (Found : S, 16·2. Calc. for $C_{14}H_{12}O_4N_2S$: S, 10·5. Calc. for $C_{14}H_{12}O_4N_2S_2$: S, 19·0%). The acetone mother-liquors on evaporation to dryness gave a dark red product of low m. p. which could not be crystallised.

(*c*) The foregoing experiment was repeated with the addition of urea (1·0 g.). The main yellow product could not be obtained in a satisfactory crystalline form and appeared to contain sulphur.

(*d*) 3 : 4-Dinitrotoluene (2 g.) in ethanol (12 c.c.) was treated with aqueous sodium tetrasulphide (12 c.c., 0·33 mol.) containing sodium hydroxide (0·75 g.) (cf. Hodgson and Beard, *loc. cit.*) for 45 minutes and steam was then passed into the mixture. The orange-coloured distillate, collected after removal of alcohol, afforded by ether-extraction mixed nitrotoluidines (0·2 g.). After purification these had m. p. 77—78° (Found : N, 18·3. Calc. for $C_7H_8O_2N_2$: N, 18·4%). The residue in the flask consisted of tar and a red water-soluble compound which could not be identified. Reactions with sodium disulphide or tetrasulphide in methanol without the addition of alkali afforded, apparently, mixtures of disulphides containing small amounts of free sulphur.

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