

195. *The Elimination of Sulphur in certain Reductions of the 2 : 2' : 4 : 4'-Tetranitrodiphenyl Mono- and Di-sulphides, and an Alternative Route to the Preparation of Some 5-Substituted Benz-1-thia-2 : 3-diazoles.*

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2 : 2' : 4 : 4'-Tetranitrodiphenyl sulphide is found to be best prepared by a two stage process of the Twiss reaction of sodium thiosulphate on 1-chloro-2 : 4-dinitrobenzene, and the disulphide by interaction of the last compound with sodium disulphide at as low a temperature as possible, both reactions being carried out in aqueous ethanol. Attempted reduction with iron replaced sulphur by hydrogen and afforded *m*-phenylenediamine from both the mono- and the di-sulphide. The disulphide was reduced by zinc and 90% aqueous acetic acid, but the monosulphide only gave a blue compound of high m. p. The 2 : 4-diamino-thiol produced from the disulphide gave with nitrous acid a benz-1-thia-2 : 3-diazole-5-diazonium salt which was converted into various 5-substituted benz-1-thia-2 : 3-diazoles; the overall yields of the 5-halogeno-compounds were somewhat higher than *via* 5-nitrobenz-1-thia-2 : 3-diazole.

Twiss found (*J.*, 1914, **105**, 1678) that when 1-chloro-2 : 4-dinitrobenzene reacted with sodium thiosulphate in aqueous ethanol a mixture of 2 : 2' : 4 : 4'-tetranitrodiphenyl mono- and di-sulphides was formed in which the former greatly preponderated. It has now been found that the yield of the monosulphide is improved by the addition of the sodium thiosulphate in two batches. Alternatively, a somewhat increased yield is obtained by the action of sodium sulphide on 1-chloro-2 : 4-dinitrobenzene in aqueous ethanol. For the preparation of the disulphide, a somewhat modified method of Claas (*Ber.*, 1912, **45**, 753) has been adopted whereby 1-chloro-2 : 4-dinitrobenzene is treated with sodium disulphide in aqueous ethanol at as low a temperature as possible; this involves a much greater dilution than that employed by Claas, but the product at the minimum temperature was much lighter yellow than that at higher temperatures.

The reduction of both the mono- and the di-sulphide varied according to the reagent employed. The neutral iron powder method of Hodgson and Marsden (*J.*, 1944, **398**) proved difficult to manipulate owing to the resistance offered to wetting by the organic nitro-compound, and the usual Béchamp process of iron and dilute sulphuric acid resulted in complete removal of sulphur from both the mono- and the di-sulphide with replacement by hydrogen and formation of *m*-phenylenediamine. The fate of the sulphur was not investigated, but, although the yields of *m*-phenylenediamine did not account for the whole of the tetranitro-compound, no trace of an organic sulphur compound could be found. Reduction by stannous chloride in hydrochloric acid solution also resulted in the removal of sulphur. This scission of sulphur linkages is a known but little investigated phenomenon, and, in the so-called "sweetening" practice in petroleum refining, sulphur is removed by treatment of the oil with iron or a similar metal at high temperatures, a process which in some cases may involve catalytic reduction. Lankelma and Knauf (*J. Amer. Chem. Soc.*, 1931, **53**, 309) also found that in the reduction of 4 : 4'-dichloro-2 : 2'-dinitrodiphenyl disulphide with tin and hydrochloric acid there was considerable elimination of sulphur particularly at boiling temperatures, and in consequence the reaction had to be carried out at about 70° (cf. Baxter and Spring, *Ann. Reports*, 1945, **42**, 99—101).

Finally, zinc dust in glacial acetic acid, containing a small quantity of water to avoid the possibility of concurrent acetylation, was found to be the most satisfactory method for the reduction of 2 : 2' : 4 : 4'-tetranitrodiphenyl disulphide; the only disadvantage was the comparatively large amount of acetic acid required for good filtration. Reduction with sodium dithionite (hydrosulphite) was less convenient and not more efficient.

From 2 : 2' : 4 : 4'-tetranitrodiphenyl monosulphide a blue compound containing nitrogen and sulphur—probably a highly complex mixture of thiazine-like compounds—was obtained. This recalls the similar observation by Leigh (Thesis, University of London, Nov., 1939, p. 16) that attempts to reduce 4 : 4'-dinitro-1 : 1'-dinaphthyl sulphide gave only an unidentifiable insoluble deep blue substance.

The 2 : 4-diaminophenylthiol, obtained by reduction of the disulphide as above, was characterised by its *dihydrochloride* and its *triacetyl* derivative, and was converted by diazotisation (Hodgson and Walker, *J.*, 1933, 1620) followed by the usual procedures into 5-chloro-, 5-bromo-, 5-iodo-, and 5-hydroxy-benz-1-thia-2 : 3-diazole, and (in 65% yield) into benz-1-thia-2 : 3-diazole-5-azo- β -naphthol. The overall yields of the 5-substituted benz-1-thia-2 : 3-diazoles (*ca.* 30%), prepared in this way from 1-chloro-2 : 4-dinitrobenzene as initial material, are greater than by the processes already described by Hodgson and Dodgson (this vol., p. 870) from 5-nitrobenz-1-thia-2 : 3-diazole (*ca.* 12% from the same initial material) by virtue of the

fewer stages involved. Further, the solid benz-1-thia-2 : 3-diazole-5-diazonium sulphate was isolated by the method of Hodgson and Mahadevan (*J.*, 1947, 325), and thereby facilitates the preparation of the numerous compounds for which diazo-compounds are used as intermediates.

2 : 4-Diaminophenylthiol has been mentioned previously but not isolated or identified (Pollack, Riesz, and Riesz, *Monatsh.*, 1931, 58, 129).

EXPERIMENTAL.

2 : 2' : 4 : 4'-Tetranitrodiphenyl Sulphide.—(a) *Thiosulphate process.* To a solution of 1-chloro-2 : 4-dinitrobenzene (40.5 g., 0.2 g.-mol.) in ethanol (350 c.c.) was added one of sodium thiosulphate (50 g., 0.2 g.-mol.) in water (200 c.c.), and the mixture was refluxed for an hour. The yellow crystalline sulphide was filtered off from the hot solution, and sodium thiosulphate (20 g.) was added to the filtrate which was again refluxed for 30 minutes. After cooling, the second precipitate of sulphide was removed and added to the first; total yield, 28 g. (76%), m. p. 193—195° raised to 197° on recrystallisation from glacial acetic acid (Twiss, *loc. cit.*, gives m. p. 193°) (Found : S, 9.0. Calc. for $C_{12}H_6O_8N_4S$: S, 8.7%).

(b) *Sodium sulphide process.* To a stirred solution of 1-chloro-2 : 4-dinitrobenzene (40.5 g.) in ethanol (400 c.c.) was added one of sodium sulphide nonahydrate (24 g., 0.1 g.-mol.) in ethanol (60 c.c.) and water (40 c.c.); when the red colour produced had disappeared, this being hastened by moderate heating towards the end of the reaction, the crystalline sulphide was filtered off and washed in sequence with 5% aqueous sodium hydroxide, water, 5% hydrochloric acid, and water; yield, 29 g. (79%) of a product somewhat browner than that from (a), especially when the reaction was carried out at higher temperatures; this colour was difficult to remove.

2 : 2' : 4 : 4'-Tetranitrodiphenyl Sulphoxide.—2 : 2' : 4 : 4'-Tetranitrodiphenyl sulphide (0.9 g.) was oxidised by keeping it for an hour at room temperature in nitric acid (10 c.c., *d* 1.5). On dilution with water, the precipitate of the sulphoxide crystallised from ethanol in long pale yellow prisms, m. p. 190° (mixed m. p. with initial material, 170—189°) (Found : S, 8.5. $C_{12}H_6O_9N_4S$ requires S, 8.4%).

Reduction of 2 : 2' : 4 : 4'-Tetranitrodiphenyl Sulphide.—(a) *With iron powder and sulphuric acid.* The sulphide (3.66 g.) was made into a paste with iron powder (14 g., pin dust) and 5% aqueous sulphuric acid (5 c.c.), and, when frothing had ceased, ethanol (3 c.c.) was added and the mixture refluxed on an oil-bath for 3 hours with occasional stirring. Charcoal and ethanol (15 c.c.) were then added, the heating continued for a further 30 minutes, ammonia (2.5 c.c., *d* 0.88) added, and the stirred mixture cooled and filtered. The residue was extracted with boiling ethanol (30 c.c.), the extract added to the previous filtrate, followed by hydrochloric acid (4 c.c., *d* 1.18). After concentration to 10 c.c. and cooling, the dihydrochloride of *m*-phenylenediamine (2.25 g.) crystallised and was identified by its diacetyl and tribromo-derivatives, and also by bisdiazotisation and conversion into 1 : 3-di-iodobenzene.

(b) *With stannous chloride and hydrochloric acid.* The sulphide (18.3 g.) was added portionwise to a solution of crystallised stannous chloride (120 g.) in concentrated hydrochloric acid (125 c.c., *d* 1.18) at 70°. Each batch dissolved readily with no appreciable colour change, and, after complete dissolution, the tin was removed from the solution by hydrogen sulphide, the volume reduced to 10 c.c., and the dihydrochloride of *m*-phenylenediamine (2.5 g.) which separated was removed and identified as above.

(c) *With zinc dust and acetic acid.* A mixture of the finely powdered sulphide (7.3 g.) and zinc dust (24 g.) was carefully stirred with 90% aqueous acetic acid (150 c.c.) added gradually; an intense blue colour appeared immediately and the liquid boiled vigorously. When the boiling had ceased, the mixture was filtered, the filtrate made alkaline with ammonia, and the blue precipitate collected; it contained nitrogen and sulphur and did not melt below 300°. This complex was very sparingly soluble in the usual solvents and in dilute hydrochloric acid; its solution in concentrated sulphuric acid was intense blue, changing to maroon on dilution with water.

2 : 2' : 4 : 4'-Tetranitrodiphenyl Disulphide.—(a) *Thiosulphate process.* After removal by filtration of the monosulphide (see above), air was bubbled through the filtrate until the disulphide (2.5 g., 6.5%) was completely precipitated.

(b) *Sodium disulphide process.* A stirred solution of 1-chloro-2 : 4-dinitrobenzene (40.5 g.) in ethanol (250 c.c.) below 30° was treated gradually with a solution of crystallised sodium sulphide (24 g., 0.1 g.-mol.) and sulphur (3.2 g., 0.1 g.-mol.). At each addition the mixture became transitorily red, and a yellow-brown precipitate rapidly formed. A small amount of heat was evolved, and on completion of the addition the mixture was heated on the water-bath until no red colour remained; it was then filtered, and the light yellow residue of the crude disulphide was extracted with hot glacial acetic acid and then washed in sequence with water, hot 5% aqueous hydrochloric acid, water, hot 5% aqueous sodium hydroxide, and hot water; yield, 33 g., 83%. It crystallised from hot pyridine or aniline, but for all experimental purposes the crude product was sufficiently pure; it exploded at *ca.* 300° (Claas, *Ber.*, 1912, 45, 753, gives 303°). Reaction at initial boiling temperatures is more rapid, but the product is browner (Found : S, 15.7. Calc. for $C_{12}H_6O_8N_4S_2$: S, 16.1%).

Reduction of 2 : 2' : 4 : 4'-Tetranitrodiphenyl Disulphide.—(a) *By iron powder and sulphuric acid, and* (b) *by stannous chloride and hydrochloric acid.* Experimental details are as for the monosulphide. In each process sulphur was eliminated with formation of *m*-phenylenediamine, which was identified as above.

(c) *By sodium dithionite (hydrosulphite).* The disulphide (4 g.), suspended in hot 15% aqueous sodium hydroxide (100 c.c.) was treated gradually with sodium dithionite (64 g.), and the mixture then refluxed for 30 minutes, cooled, and treated with sulphuric acid (25 c.c., *d* 1.84); after 30 minutes the precipitated sulphur was filtered off and the filtrate stirred gradually into a solution of sodium nitrite (3 g.) in sulphuric acid (20 c.c., *d* 1.84) maintained below 10°. After an hour, the solution was poured into cold hydrochloric acid (160 c.c., *d* 1.18) containing cuprous chloride (16 g.), and, when reaction had ceased, the mixture was diluted with water and steam distilled. Yield of 5-chlorobenz-1-thia-2 : 3-diazole, 0.8 g. (24%).

(d) *By zinc dust and acetic acid.* A mixture of the disulphide (4 g.) and zinc dust (12.8 g.) was stirred into 90% aqueous acetic acid (100 c.c.), and, after the initial evolution of heat had ceased, the whole was carefully raised to the boil, refluxed for 30 minutes, filtered hot, and the residue washed with hot 90% acetic acid (50 c.c.). The two filtrates were combined, and saturated at 0° with dry hydrogen chloride, after which ether (400 c.c.) was added at 0°; a white precipitate of 2:4-diaminophenylthiol dihydrochloride (3 g., 71% yield) formed gradually. This was filtered off, washed with ether, dissolved in the minimum amount of water (15 c.c.), reprecipitated by saturation of the ice-cold solution with hydrogen chloride, filtered off, washed with ether, and dried. The pale yellow compound was readily soluble in water, less so in ethanol, and quite stable in air; m. p. > 300° (Found: S, 14.7. $C_6H_8N_2S_2 \cdot 2HCl$ requires S, 15%).

γ : 4-Diacetamidophenyl thiolacetate was obtained when a solution of the above hydrochloride (1 g.) in pyridine (2 c.c.) was heated with acetic anhydride (2 c.c.) on the water-bath for 30 minutes, cooled, and stirred into 4% aqueous hydrochloric acid (20 c.c.). After several days, with periodic scratching, the colourless triacetyl compound separated; it crystallised from ethanol in silvery plates, m. p. 245° (decomp.) (Found: S, 12.3. $C_{12}H_{14}O_3N_2S$ requires S, 12.0%), which were readily soluble in the usual organic solvents, slightly soluble in hot water, but insoluble in cold aqueous sodium hydroxide.

Reactions of 2:4-Diaminophenylthiol.—The hydrochloride (1 g.) was suspended in glacial acetic acid (5 c.c.) and the mixture stirred gradually into a solution of sodium nitrite (0.7 g.) in sulphuric acid (4 c.c., *d* 1.84) maintained below 10°; some hydrogen chloride was evolved at this stage, but did not interfere with the reaction. The acid solution was next poured on ice (20 g.), and the free nitrous acid removed by urea (0.3 g.), after which potassium iodide (3.3 g.) was added, the mixture subsequently made alkaline with aqueous sodium hydroxide, and steam distilled. The 5-iodobenz-1-thia-2:3-diazole, which passed over, crystallised from 80% aqueous methanol in small cubes, m. p. and mixed m. p. with authentic specimen (Hodgson and Dodgson, *loc. cit.*) 103°.

Diazotisation of the Zinc-Acetic Acid Reduction Liquor Above.—Batches of 2:2':4:4'-tetranitrodiphenyl disulphide (4 g.) were reduced and the mixtures filtered as above; sulphuric acid (6 c.c., *d* 1.84) was added to each mixture which was then cooled to ca. 10°, at which point solidification began, and stirred into a solution of sodium nitrite (3 g.) in sulphuric acid (14 c.c., *d* 1.84) below 10°. The resulting mixtures were treated as follows: (a) Coupled with β -naphthol after dilution with water, to give benz-1-thia-2:3-diazole-5-azo- β -naphthol (4.1 g., 67%). (b) Added separately to solutions of cuprous chloride (12 g.) in hydrochloric acid (120 c.c., *d* 1.18), and cuprous bromide (17 g.) in hydrobromic acid (120 c.c., *d* 1.7), which were then steam distilled to give 5-chloro- (1 g., 30%) and 5-bromo- (1 g., 23%) benz-1-thia-2:3-diazole respectively; also diluted with ice-water, free nitrous acid removed by urea (1.5 g.), potassium iodide added (6.6 g.), and the mixture steam distilled for 5-iodobenz-1-thia-2:3-diazole to pass over. (c) Diluted with ice-water until all the salts had dissolved, kept overnight, then gradually heated to boiling, cooled, and extracted with ether; the extract was washed with aqueous sodium hydrogen carbonate to remove acidity, and then shaken with 10% aqueous sodium hydroxide (10 c.c.) to remove the 5-hydroxybenz-1-thia-2:3-diazole (0.8 g., 26% yield) which was precipitated from the alkaline extract on acidification and recrystallised from hot water in yellow needles, m. p. and mixed m. p. with authentic specimen (Hodgson and Dodgson, *loc. cit.*) 161°.

Before addition of the acetic acid solution of the amine to the nitrosylsulphuric acid it was concentrated to 60 c.c., and, after diazotisation, the acid solution was treated with ether (200 c.c.); after an hour the yellow benz-1-thia-2:3-diazole-5-diazonium sulphate was collected and washed with ether; it only slowly turned brown in air, and on addition to 10% aqueous sodium hydroxide (200 c.c.) containing β -naphthol (4 g.), gave a precipitate of benz-1-thia-2:3-diazole-5-azo- β -naphthol (0.7 g., 11%) which was crystallised and identified (cf. Hodgson and Dodgson, *loc. cit.*).

A solution of *m*-phenylenediamine (2.16 g.) in glacial acetic acid (15 c.c.) was stirred gradually into one of sodium nitrite (3.2 g.) in sulphuric acid (32 c.c., *d* 1.84) below 30°. When diazotisation was complete, the mixture was poured into sufficient ice-water to give a clear solution, which was filtered and then stirred into 20% aqueous sodium hydroxide (400 c.c.) containing β -naphthol (10 g.) and ice (200 g.). After being kept at 0° until coupling was complete, the mixture was heated to 50° to coagulate the precipitate of the benzene-1:3-bisazo- β -naphthol, which was removed and washed with hot 2% aqueous sodium hydroxide and water; it crystallised from glacial acetic acid (charcoal) in very dark green crystals (red in transmitted light), m. p. 265° (Schoutissen, *Rec. Trav. chim.*, 1935, 54, 381, gives m. p. 251°) (Found: N, 13.6. Calc. for $C_{26}H_{18}O_2N_4$: N, 13.4%).

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