219. *The Preparation of 2 : 2′-Dichloro-4 : 4′-dinitrodiphenyl Sulphide and 2′-Chloro-4 : 4′-dinitro-2-aminodiphenyl Sulphide, with Some Derivatives and Attempts at Cyclisation to Thiazines.*

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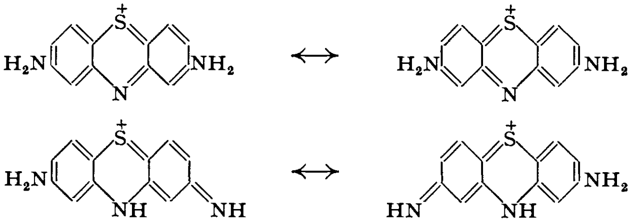
The above preparations had for their objective the ultimate formation of 2 : 8-diaminothiodiphenylamine (2 : 8-diaminophenothiazine) in which, on oxidation, the thiazine ring would play the reversed rôle to that in Lauth's violet and methylene-blue. Attempted cyclisations by an imino-bridge, however, failed, and this is tentatively attributed to lack of co-planarity of the benzene rings in the various sulphides used.

The work now reported had for its objective the preparation of thiazine compounds by cyclisation of *oo*′-disubstituted diphenyl sulphides, where, in the dyes therefrom, the sulphur, now in the *o*- and *p*-positions to the nitrogen, would play the predominant chromophoric rôle, *i.e.*, it would be a constituent of all the quinonoid structures possible, *e.g.*:



When the starting compound is a substituted diphenylamine derivative, cyclisation by thionation readily takes place, as indicated by the direct thionation of diphenylamine itself when heated with sulphur alone at 250—300° (Bernthsen, *Annalen*, 1885, **230**, 77) or with sulphur and aluminium chloride at 135—160° (Ackermann, D.R.-P. 222879; Friedländer, **10**, p. 144), or in the various syntheses of methylene-blue. Unexpected difficulties, however, occurred when a diphenyl sulphide was the initial material, and so far the cyclisation objective has not been achieved. The following modes of approach have been tried: In the attempted preparation of 2 : 2′ : 4 : 4′-tetraminodiphenyl sulphide from 2 : 2′ : 4 : 4′-tetranitrodiphenyl sulphide by various reducing agents with possible cyclisation *en route*, the great ease of elimination of sulphur, especially in iron and tin reductions, became very evident, with *m*-phenylenediamine as the reaction-product instead of the expected 2 : 8-diaminothiodiphenylamine (cf. Hodgson and Dodgson, in the press). The reduction with zinc and acetic acid gave blue sulphur-containing complexes, whereas stannous chloride in acetic acid appeared to avoid both complex formation and elimination of sulphur. Attempts to produce the imino-bridge by heating the newly prepared 2 : 2′-*dichloro*-4 : 4′-*dinitrodiphenyl sulphide*, with ammonia under pressure at 200°, or for 10 hours with potassium phthalimide at 200°, left the initial material unchanged in both cases. Unsuccessful cyclisation attempts from 4 : 4′-dinitro-2 : 2′-diaminodiphenyl sulphide are also recorded in the experimental section.

Ammonium sulphide appears to convert 2 : 2′ : 4 : 4′-tetranitrodiphenyl sulphide into the disulphide, possibly by air oxidation of the thiol produced by a process of hydrosulpholysis, $R_2S + H_2S \longrightarrow 2R{\cdot}SH$, analogous to hydrolysis, which seems to have occurred. Attempts at the cyclisation of this compound may therefore involve far more deep-seated changes than were expected.

It is of interest that Matsumura (*J. Amer. Chem. Soc.*, 1930, **52**, 3199) found that 2 : 2′ : 4 : 4′-tetra-aminodiphenyl ether could not be cyclised by heating the hydrochloride either alone or in the presence of zinc chloride in an atmosphere of carbon dioxide for 20 hours at 200°, while in the preparation of the tetra-amine, by reduction of the tetranitro-compound with stannous chloride, an appreciable amount of oxygen was liberated corresponding to the analogous elimination of sulphur from the sulphide analogue (*loc. cit.*). In striking contrast, there is the ready cyclisation of 2 : 2′-diaminodiphenyl to carbazole by heating it with an excess of 25% sulphuric or 15% hydrochloric acid in a sealed tube for 15 hours at 200° (Tauber, *Ber.*, 1891, **24**, 197), and the conversion of 2 : 2′-diaminodiphenylamine into phenazine by such simple oxidising agents as ferric chloride, hydrogen peroxide, or potassium permanganate (Eckert and Steiner, *Monatsh.*, 1914, **35**, 1153). These results would appear to indicate non-coplanarity of the benzene rings in the sulphide and ether above. Support for this view comes from the non-substantivity to cotton of the bisazo-dyes from 4 : 4′-diaminodiphenyl sulphide as compared with the affinity for cotton of those from 4 : 4′-diaminodiphenylamine (cf. Hodgson and Marsden, *J. Soc. Dyers and Col.*, 1944, **60**, 210, for coplanarity as a factor for substantivity). Further, while resonance of the whole molecule will account for coplanarity in a diphenylamine, it is prevented in an *oo*′-diaminodiphenyl sulphide, so that cyclisation with sulphur will be facilitated in the former and elimination of ammonia will be frustrated in the latter type of compound.

Finally, the preparation is now reported of 2-*chloro*-4 : 4′-*dinitro*-2′-*aminodiphenyl sulphide*, and an attempt was made to cyclise the acetyl derivative, with the object of effecting a diphenylamine-type of synthesis (Goldberg, *Ber.*, 1907, **40**, 4541), by heating it in nitrobenzene solution with potassium carbonate and cuprous chloride at 180° for 7 hours. None of the initial compound was left, but the brown unidentifiable substance gave an olive-green colour with concentrated sulphuric acid, thereby indicating some salt-forming character.

EXPERIMENTAL.

2 : 2′-*Dichloro*-4 : 4′-*dinitrodiphenyl Sulphide*.—*o*-Dichlorobenzene (11·3 c.c., b. p. 174·5°), prepared by the Sandmeyer reaction from *o*-chloroaniline, was dissolved in sulphuric acid (25 c.c., *d* 1·84), and powdered potassium nitrate (11 g.) then stirred gradually into the solution at 0°. When the addition was complete, the mixture was stirred for an hour without external cooling and poured on ice. The oily layer of 2 : 3- and 3 : 4-dichloronitrobenzene was separated and cooled to − 10°, after which the oily paste was drained at the pump to leave a colourless crystalline 3 : 4-dichloronitrobenzene. Alternatively, *o*-dichlorobenzene (7 c.c.) was stirred during 4 hours into a mixture of nitric acid (7 c.c., *d* 1·5) and sulphuric acid (9 c.c., *d* 1·84) at 0°; almost solid 3 : 4-dichloronitrobenzene then separated, and was worked up as above. The 3 : 4-dichloronitrobenzene crystallised from methanol in silky colourless needles, m. p. 43° (Beilstein and Kurbatov, *Annalen*, 1875, **176**, 41, give m. p. 43°). For the preparation of the sulphide, the solution of 3 : 4-dichloronitrobenzene (9·6 g.) in ethanol (70 c.c.) was mixed with one of sodium sulphide nonahydrate (6 g.) in ethanol (10 c.c.) and water (10 c.c.); the mixture, which immediately turned red, was refluxed for 2 hours, filtered hot, and the solid 2 : 2′-*dichloro*-4 : 4′-*dinitrodiphenyl sulphide* (6 g., 70% yield) washed with ethanol (50 c.c.) and water (100 c.c.), after which it crystallised from 80% acetic acid (charcoal) in long yellow needles, m. p. 166° (Found : Cl, 20·3. $C_{12}H_6O_4N_2Cl_2S$ requires Cl, 20·6%). Alternatively, 3 : 4-dichloronitrobenzene (2 g.), dissolved in ethanol (15 c.c.), was added to a hot solution of sodium sulphide nonahydrate (1·5 g.) in ethanol (7 c.c.), the mixture refluxed for 10 hours, and the 2 : 2′-dichloro-4 : 4′-dinitrodiphenyl sulphide filtered off and recrystallised as above; the filtrate from this experiment, on dilution with water, afforded 2-chloro-4-nitrophenetole (0·2 g.), 3 : 4-dichloroaniline (0·2 g., determined as 3 : 4-dichlorobenzeneazo-β-naphthol), and unchanged 3 : 4-dichloronitrobenzene (0·2 g.). When heated in a sealed tube with ethyl-alcoholic ammonia at 200° for 12 hours no amination occurred.

2 : 2′-*Dichloro*-4 : 4′-*dinitrodiphenyl sulphoxide* was obtained when the above sulphide was stirred at room temperature with nitric acid (*d* 1·5) for 30 minutes; it crystallised from glacial acetic acid on addition of water in pale buff needles, m. p. 184° (Found : S, 9·1. $C_{12}H_6O_5N_2Cl_2S$ requires S, 8·9%).

2 : 2′-*Dichloro*-4 : 4′-*dinitrodiphenyl sulphone* was formed when a solution of the sulphide above in the minimum of acetic anhydride was heated on the water-bath for 12 hours with a large excess of 30% hydrogen peroxide; it separated from 80% acetic acid in stellate clusters of colourless needles, m. p. 169° (Found : S, 8·6. $C_{12}H_6O_6N_2Cl_2S$ requires S, 8·5%).

2′-*Chloro*-4 : 4′-*dinitro*-2-*aminodiphenyl sulphide* was produced when a solution of 2-chloro-5-nitroaniline

(1·725 g.) in ethanol (30 c.c.) was treated with one of sodium sulphide nonahydrate (3·6 g.) and sodium hydrogen carbonate (1·26 g.) in water (20 c.c.), and the mixture heated on the water-bath under the reflux for 1 hour; a further addition of sodium hydrogen carbonate (1·26 g.) dissolved in ethanol (10 c.c.) and water (10 c.c.) was made, and the refluxing continued for 5 minutes, after which a solution of 3 : 4-dichloronitrobenzene (1·92 g.) in ethanol (20 c.c.) was added and the refluxing continued for 2 hours. After cooling, the solid was filtered off, washed with ethanol (50 c.c.) and water, and dried; it crystallised from glacial acetic acid (charcoal) in short yellow needles, m. p. 211° (Found : N, 13·1. $C_{12}H_8O_4N_3ClS$ requires N, 12·9%), which were quite insoluble in dilute or concentrated hydrochloric acid. On acetylation 2 -*chloro*-4 : 4-*dinitro*-2-*acetamidodiphenyl sulphide* was obtained; this crystallised from glacial acetic acid in pale yellow prisms, m. p. 187° (Found : N, 11·6. $C_{14}H_{10}O_5N_3ClS$ requires N, 11·4%).

Attempts to Cyclise 4 : 4′-*Dinitro*-2 : 2′-*diaminodiphenyl Sulphide*.—The following treatments were found to be ineffective. (*a*) Boiling with excess of concentrated hydrochloric acid for 3 hours. (*b*) Heating with excess of aqueous sulphuric acid (33% by vol.) on a water-bath for 3 hours, or with excess of aqueous acid (25% by vol.) at the boiling point for 2 hours. In the next experiments the initial material was charred completely. (*c*) Heating with excess of zinc chloride in an oil-bath at 200° for 30 minutes. (*d*) Heating with excess of sulphuric acid (67% by vol.) for 3 hours in an oil-bath at 200°. With conditions intermediate between these extremes, only indications of products that gave colour reactions were obtained. (*e*) Heating with aqueous sulphuric acid (50% by vol.) for 2 hours at the boiling point charred most the material, but dilution of the filtrate did not precipitate any initial substance. The sulphuric acid solutions, however, had a red colour, which was discharged by reduction with zinc but restored by subsequent addition of ferric chloride.

Action of Ammonia and Hydrogen Sulphide on 2 : 2′ : 4 : 4′-*Tetranitrodiphenyl Sulphide*.—The monosulphide (1 g.) was suspended in ethanol (35 c.c.), saturated with ammonia gas, and the mixture treated with hydrogen sulphide until dissolution occurred. The deep red solution was heated on the water-bath for 15 minutes, filtered, acidified, and the pale yellow precipitate extracted with glacial acetic acid; the residue was 2 : 2′ : 4 : 4′-tetranitrodiphenyl disulphide, which crystallised from pyridine or aniline in light yellow micro-crystals that exploded at *ca.* 300° (Claas, *Ber.*, 1912, **45**, 753, gives explosion point, 303°).

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