309. *Substitution Derivatives of Diphenylene Sulphide and Diphenylenesulphone.*

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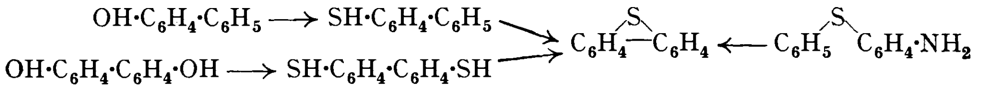
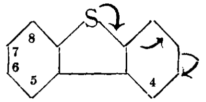
Diphenylene sulphide was prepared (1) from 2-nitrodiphenyl sulphide by the usual reduction and diazotisation process; (2) by the action of heat on a mixture of 2-hydroxydiphenyl and phosphorus pentasulphide under pressure, the intermediate thiol being oxidised readily to the cyclic sulphide; (3) by treatment of 2 : 2′-dihydroxydiphenyl with phosphorus pentasulphide or sulphur :

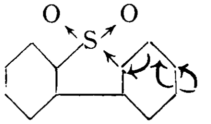


$$\left.\begin{array}{l} OH\cdot C_6H_4\cdot C_6H_5 \longrightarrow SH\cdot C_6H_4\cdot C_6H_5 \\ OH\cdot C_6H_4\cdot C_6H_4\cdot OH \longrightarrow SH\cdot C_6H_4\cdot C_6H_4\cdot SH \end{array}\right\} \longrightarrow C_6H_4\overset{S}{\text{—}}C_6H_4 \longleftarrow C_6H_5\overset{S}{\ }C_6H_4\cdot NH_2$$

Nitration of diphenylene sulphide afforded the 3-*nitro*-derivative, the sulphur atom being here *op*-directing (I) (diphenylene oxide yields the 2-nitro-compound; Cullinane, J., 1930, 2267). The constitution of the nitrodiphenylene sulphide was established by its synthesis from 2 : 4-dinitrodiphenyl sulphide by reduction to 4-nitro-2-aminodiphenyl sulphide, followed by diazotisation and treatment with 50% sulphuric acid. The action of bromine on diphenylene sulphide gave the expected 3-*bromo*-derivative (as in the case of diphenylene oxide; Mayer and Krieger, *Ber.*, 1922, **55**, 1661). The bromo-compound was identical with the product obtained from 3-nitrodiphenylene sulphide by reduction, followed by the Sandmeyer process.

(I.)





(II.)

Diphenylenesulphone was readily prepared by oxidation of the sulphide. The sulphone group being strongly meta-directive, both nitration and bromination afforded as sole products the 2 : 7-disubstitution derivatives. The general electric effect of the sulphone group is indicated in (II) (the electromeric effect being exercised in the same direction), resulting in deactivation of the benzene ring, this effect being least pronounced in the meta-position, as shown by the arrow, and hence substitution took place at this point (compare Robinson, *J. Soc. Dyers and Colourists*, 1934, 70). Owing to the deactivating effect of the nitro-group and the bromine atom on the nucleus containing them, the second substituent entered the other benzene ring in each case. Similar results were observed with diphenylene sulphide and diphenylene oxide.

Very vigorous methods were needed for the preparation of the substitution derivatives of diphenylenesulphone : the *dinitro*-derivative was obtained by heating a mixture of the sulphone with a large excess of fuming nitric and concentrated sulphuric acids, and the *dibromo*-compound could only be prepared by heating the sulphone under reflux with several molecular proportions of bromine.

The constitution of the dinitro-compound was established by reduction to benzidine-sulphone. Diazotisation, followed by the Sandmeyer reaction, afforded a dibromo-derivative identical with the compound formed by the action of bromine on diphenylene-sulphone.

Experimental.

Diphenylene Sulphide.—(a) A mixture of 2-hydroxydiphenyl (20 g.) and phosphorus pentasulphide (6 g.) was boiled for 10 hours, excess of aqueous sodium hydroxide added, and the product distilled in steam. The solid in the distillate was washed with sodium hydroxide solution and with water and crystallised from alcohol, affording colourless needles (4 g.) of diphenylene sulphide, m. p. 99°.

(b) A mixture of 2 : 2′-dihydroxydiphenyl (30 g.) and phosphorus pentasulphide (20 g.)

was heated at 350° for 15 hours in carbon dioxide in an autoclave; hydrogen sulphide was formed. The product was extracted with hot acetone, the solvent removed, and the residue washed with warm aqueous sodium hydroxide and water and distilled under reduced pressure, giving diphenylene oxide (small quantity), diphenylene sulphide, and a gummy material; the cyclic sulphide (4 g.) had b. p. 182°/10 mm.

A mixture of 2 : 2′-dihydroxydiphenyl (22·5 g.) and sulphur (8 g.), similarly treated, gave 3 g. of diphenylene sulphide.

2 : 4-*Dinitrodiphenyl Sulphide.*—Bogert and Evans (*J. Ind. Eng. Chem.*, 1926, **18**, 301) obtained a 31% yield of this compound by grinding together 2 : 4-dinitrochlorobenzene and potassium thiophenoxide. The following method gave an 80% yield. The clear melt obtained by heating potassium hydroxide (28 g.) and water (10 c.c.) was added in small portions to thiophenol (55 g.) maintained somewhat below its b. p., and the mixture stirred until solidification occurred. The product was dried at 140° for 4 hours. 2 : 4-Dinitrochlorobenzene (46 g.) was melted in a dish heated by a small flame, and powdered potassium thiophenoxide (34 g.) added gradually with stirring; the brownish mass formed was stirred for a further 30 minutes and then extracted with warm sodium hydroxide solution. The residue was washed with alkali and water and extracted with hot acetone. Recrystallisation from alcohol (charcoal) afforded yellow plates, m. p. 121°.

3-*Nitrodiphenylene Sulphide.*—To a solution of 2 : 4-dinitrodiphenyl sulphide (5·5 g.) in glacial acetic acid (22 c.c.) at about 80° was added in several portions a solution containing stannous chloride (12·5 g.) in glacial acetic acid (33 c.c.) into which hydrogen chloride had been passed until almost all the tin salt had dissolved. The product was poured into 6 vols. of water and the oily solid obtained was collected, washed with water, and extracted with much boiling dilute hydrochloric acid. Addition of concentrated aqueous ammonia to this extract precipitated a small quantity of the nitroamino-compound as a brownish oily solid.

Sodium nitrite (0·65 g.) was added with cooling to concentrated sulphuric acid (5·2 c.c.), and the solution warmed slowly to 70°, maintained at this temperature until the solid had completely dissolved, and then cooled. The crude nitroamino-compound (2 g.) was dissolved in glacial acetic acid (24 c.c.), and the cold solution added gradually below 20° to the nitrite solution. The diazo-mixture was made up to 100 c.c. with sulphuric acid so that the ultimate concentration of the acid was 50%, boiled under reflux for 8 hours, and distilled with steam. The distillate was made alkaline with aqueous sodium hydroxide, and the solid deposit recrystallised from alcohol, from which pale yellow needles of 3-*nitrodiphenylene sulphide* (0·3 g.), m. p. 186°, separated (Found : S, 14·0. $C_{12}H_7O_2NS$ requires S, 14·0%).

Nitration of Diphenylene Sulphide.—Treatment of diphenylene sulphide with nitric acid (90%; 1½ mols.) under the conditions specified by Courtot and Pomonis (*Compt. rend.*, 1926, **182**, 894) gave mostly diphenylene sulphoxide together with unchanged initial material. The following method gave a 40% yield of nitro-compound and a similar yield of sulphoxide. Diphenylene sulphide (10 g.) was dissolved in glacial acetic acid (80 c.c.), the solution allowed to cool to about 30°, and nitric acid (10 c.c.; *d* 1·5) added drop by drop; after a few minutes' warming, a copious yellow precipitate formed. The mixture was shaken for an hour and poured into water and the precipitate was washed with water and treated with small amounts of boiling alcohol (to remove the sulphoxide) until the m. p. of the residue was about 180°. Recrystallisation from alcohol or benzene furnished 3-nitrodiphenylene sulphide, m. p. 186°, identified by means of a mixed m. p. with the synthetic product.

3-*Aminodiphenylene Sulphide.*—The reduction of the nitro-derivative can be effected by means of zinc and alcoholic ammonia solution (Courtot and Pomonis, *loc. cit.*) or (better) by treating the powdered substance (8 g.) with iron filings (12 g.) and water (8 g.), followed by ferric chloride (0·12 g.). The product was extracted with much boiling dilute hydrochloric acid, from which colourless needles (5·6 g.) of the amine hydrochloride separated on cooling. The base, liberated by addition of sodium hydroxide solution and crystallised from methyl alcohol, formed white needles, m. p. 133°.

3-*Hydroxydiphenylene Sulphide.*—The amine hydrochloride (2·4 g.) in finely divided suspension in dilute hydrochloric acid (40 c.c.) was diazotised at 0°, the diazo-compound being precipitated in fine yellow crystals. The mixture was shaken for an hour and then warmed gradually to 70° with shaking for 30 minutes, after which it was boiled under reflux for a further ½ hour, and the product distilled with superheated steam. The distillate crystallised from ligroin in colourless needles (0·5 g.), m. p. 159°, of 3-hydroxydiphenylene sulphide, identified by a mixed m. p. with a specimen of this compound (for which we are indebted to I. G. Farbenindustrie A.G.) obtained by Muth, Pützer, and Carl (D.R.-P. 591,213) by diazotising 3-aminodiphenylene sulphide in orthophosphoric acid and heating the product with the same acid to 200°.

3-*Bromodiphenylene Sulphide.*—The diazo-mixture obtained from the amine hydrochloride (2·4 g.) was added gradually to a 10% solution of cuprous bromide (50 c.c.), and the whole boiled under reflux for 20 minutes and then distilled with steam. The solid was extracted with hot acetone and recrystallised from alcohol, colourless plates of 3-*bromodiphenylene sulphide* (about 1 g.), m. p. 127°, being deposited (Found : S, 12·3; Br, 30·3. $C_{12}H_7BrS$ requires S, 12·2; Br, 30·4%).

To a cold solution of diphenylene sulphide (5 g.) in dry carbon disulphide or chloroform (28 c.c.), bromine (4·4 g.) was added dropwise with agitation; hydrogen bromide was evolved. After standing at room temperature for 12 hours, the solution was boiled under reflux for 3 hours. The solvent was then evaporated, and the residue crystallised from alcohol; crystals (5·5 g.) identical with the 3-bromodiphenylene sulphide described above were obtained.

2 : 7-*Dinitrodiphenylenesulphone.*—To a cold solution of diphenylenesulphone (3 g.) in concentrated sulphuric acid (10·5 c.c.), nitric acid (9 c.c.; *d* 1·5) was added dropwise with shaking; the temperature rose to 60—70°. The product was heated on a boiling water-bath for 40 minutes, cooled, and poured into ice-water. The white precipitate formed was washed with water, dried, and crystallised from acetone, giving long, pale yellow prisms (2·5 g.), m. p. 290° (slight decomp.) (Found : S, 10·4. $C_{12}H_6O_6N_2S$ requires S, 10·45%).

2 : 7-*Diaminodiphenylenesulphone* (*Benzidinesulphone*).—The above dinitro-compound (4 g.) was reduced with iron filings (16 g.), water (10 c.c.), and ferric chloride (0·16 g.). The product was extracted with boiling dilute hydrochloric acid, excess of alkali added to the extract, and the precipitate taken up with hot acetone. Recrystallised from the same solvent, it afforded pale yellow needles (2·5 g.), identified by a mixed m. p. as benzidinesulphone, m. p. 327°.

2 : 7-*Dibromodiphenylenesulphone.*—Benzidinesulphone (5 g.), made into a paste with concentrated hydrochloric acid (20 c.c.) and water (7 c.c.), was treated at 0° with sodium nitrite (3·37 g.) in water (10 c.c.), giving a clear solution of the tetrazo-compound. This was added to a 10% solution of cuprous bromide (150 c.c.), heated gradually to the b. p., boiled under reflux for 30 minutes, and then poured into water. The precipitate was washed with water and extracted with chloroform, from which crystals separated on cooling. Recrystallisation from acetone furnished the *dibromo*-derivative (5·5 g.) in pale yellow plates, m. p. 312° (Found : S, 8·8; Br, 41·8. $C_{12}H_6O_2Br_2S$ requires S, 8·6; Br, 42·8%).

The same dibromo-compound (2 g.) was obtained when finely powdered diphenylenesulphone (4 g.) was boiled with bromine (20 g.) for 4 hours under a long reflux condenser; the residue obtained after evaporation to dryness was extracted with sulphurous acid, and the solid crystallised from chloroform.

3-*Nitrodiphenylenesulphone.*—3-Nitrodiphenylene sulphide (4 g.) was boiled under reflux for 5 hours with potassium dichromate (9·6 g.), concentrated sulphuric acid (32 c.c.), and water (32 c.c.), the mixture poured into much water, and the precipitate recrystallised from acetone. Pale yellow plates (4 g.), m. p. 258° (slight decomp.), separated (Found : N, 5·4. $C_{12}H_7O_4NS$ requires N, 5·4%). A similar yield was obtained by adding perhydrol (32 g.) at 42° to a solution of 3-nitrodiphenylene sulphide (4 g.) in glacial acetic acid (80 c.c.) and boiling the mixture under reflux for 2 hours.

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