155. *Investigations in the Diphenylene Oxide Series. Part IV.*

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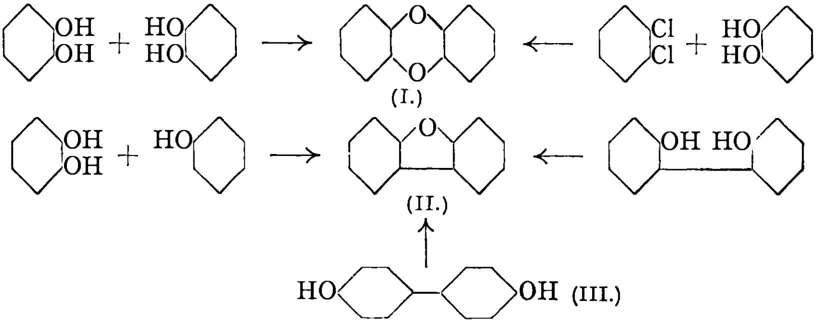
The diphenylene oxide used was prepared by the destructive distillation of litharge and phenol (Cullinane, J., 1930, 2268). The product was readily obtained, but the yield was not large (20%). However, the condensation of catechol and phenol, either without the use of a dehydrating agent or in the presence of phosphoric oxide, gave a still smaller yield of the ether, and in this experiment diphenylene dioxide (I) also. The latter was evidently formed by the condensation of two molecules of catechol, for this substance also, when heated with phosphoric oxide in a sealed tube, was converted into the dioxide. The product was identified by comparison with the compound obtained by the action of heat under pressure on sodium *o*-chlorophenoxide (Bayer and Co., D.R.-P. 223,367; compare Ullmann and Stein, *Ber.*, 1906, **39**, 624) or by the condensation of catechol with *o*-dichlorobenzene.



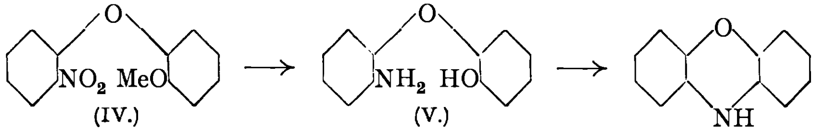
(I.)

(II.)

(III.)

When the two amino-groups of 2 : 2′-diaminodiphenyl were diazotised and the product was boiled with water, the dihydroxy-compound passed immediately into diphenylene oxide (II). Hot water, anhydrous zinc chloride, or 50% sulphuric acid was without action on 4 : 4′-dihydroxydiphenyl (III); this, however, was converted by phosphoric oxide into diphenylene oxide as sole product, a wandering of the link between the two phenyl nuclei to meta-positions having occurred.

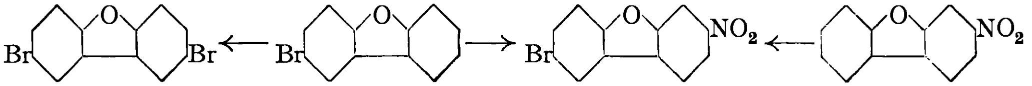
2-*Nitro*-2′-*methoxydiphenyl ether* (IV) was prepared from *o*-chloronitrobenzene and guaiacol. An attempt to demethylate this with hydrobromic acid failed, and hydriodic acid gave, not the expected 2-nitro-2′-hydroxydiphenyl ether, but 2-*amino*-2′-*hydroxydiphenyl ether* (V). The amino-group was diazotised, and the product treated with copper sulphate solution, followed by 50% sulphuric acid, yielding diphenylene dioxide. The action of heat under pressure on the aminohydroxy-derivative (V) gave a small yield of phenoxazine (VI), which Bernthsen (*Ber.*, 1887, **20**, 943) had obtained by heating *o*-aminophenol and catechol in a sealed tube.



(IV.) (V.) (VI.)

2-Nitrodiphenylene oxide on monobromination gave the same compound as was obtained by the mononitration of 3-bromodiphenylene oxide. On the assumption that the bromine atom was not substituted in the ortho-position to the nitro-group the product was 6-*bromo*-2-*nitrodiphenylene oxide* (VII). The action of bromine on 3-bromodiphenylene oxide afforded the 3 : 6-dibromo-derivative (VIII), obtained by Hoffmeister (*Annalen*, 1871, **159**, 215) and oriented by McCombie, Macmillan, and Scarborough (J., 1931, 536).

The above results are of interest from the point of view of the modern electronic theory (compare Cullinane, Part III, J., 1932, 2365). The result obtained by the bromination of 2-nitrodiphenylene oxide can be explained by stating that the positive field of the nitro-group inhibits any electromeric change from passing out of the nucleus containing it. Hence bromination of this compound must rely on direct activation of the substituted nucleus by the oxygen atom. The results obtained on nitration and on further bromination of 3-bromodiphenylene oxide can be accounted for in this way. In the absence of the deactivating nitroxyl group the conditions obtaining in the case of diphenylene oxide itself apply (Cullinane, Part III, *loc. cit.*), and hence the nitro-group enters the ring at position 7, and the second bromine atom at position 6.



(VIII.) (VII.)

EXPERIMENTAL.

Condensation of Catechol and Phenol.—2·6 G. (1 mol.) of phenol and 3 g. (1 mol.) of catechol were heated in a sealed tube for 30 hours at 240°. The dark oily product was extracted with warm dilute sodium hydroxide solution, and the residue washed with water and extracted with hot alcohol, evaporation of which left a small quantity of diphenylene oxide, m. p. 87° after recrystallisation.

The same weights as above of phenol and catechol together with 5 g. of phosphoric oxide were heated in a sealed tube for 10 hours at 250—260°. The product was extracted with sodium hydroxide solution and with alcohol as before. Recrystallisation from alcohol afforded colourless needles (0·1 g.), m. p. 119°, undepressed by admixture with diphenylene dioxide prepared from sodium *o*-chlorophenoxide (D.R.-P. 223,367). The blue colour which it gave with concentrated sulphuric acid also served as identification. From the solid obtained by evaporation of the alcoholic mother-liquor, diphenylene oxide (0·1 g.) was isolated by recrystallisation from alcohol.

Action of Phosphoric Oxide on Catechol.—3 G. of catechol and 3 g. of phosphoric oxide were heated in a sealed tube for 24 hours at 250—260°. The dark-coloured product was extracted with hot dilute sodium hydroxide solution, washed with water, and recrystallised from alcohol. Colourless crystals (0·15 g.) of diphenylene dioxide, m. p. 119°, were obtained.

Condensation of Catechol and o-*Dichlorobenzene.*—To the clear melt obtained by heating potassium hydroxide (2·24 g.; 2·2 mols.) and water (0·72 g.; 2·2 mols.), catechol (2 g.; 1 mol.) was added with stirring. *o*-Dichlorobenzene (2·67 g.; 1 mol.) was quickly added, and the mixture heated in a sealed tube at 220° for 10 hours. The product was treated with excess of sodium hydroxide solution and then distilled with superheated steam. The distillate contained a little unchanged dichlorobenzene together with a white solid. After extraction with ether the solvent and the dichlorobenzene were evaporated. The solid residue, crystallised from alcohol, gave diphenylene dioxide (0·2 g.), m. p. 119°.

The yield of dioxide was still further reduced when catechol and dichlorobenzene were heated for 24 hours at 150°.

2-*Nitro*-2′-*methoxydiphenyl Ether.*—Potassium hydroxide (6·7 g.) was heated with water (1·5 c.c.) until a clear melt was obtained. When incipient crystallisation occurred, guaiacol (19 g.) was added rapidly with vigorous stirring, followed by *o*-chloronitrobenzene (14 g.). The mixture was heated at 190—195° (oil-bath temperature) for 1½ hours, and the product extracted with warm sodium hydroxide solution until the odour of guaiacol had disappeared. The oily residue solidified and was then recrystallised from alcohol, giving pale yellow leaflets (16·3 g.; 75% yield) of 2-*nitro*-2′-*methoxydiphenyl ether*, m. p. 71° (Found: N, 5·8. $C_{13}H_{11}O_4N$ requires N, 5·7%). The product was soluble in warm benzene, alcohol, or acetic acid, and very easily soluble in acetone.

The compound obtained by Bouveault (*Bull. Soc. chim.*, 1897, **17**, 944) by heating *o*-bromonitrobenzene and guaiacol in alcoholic solution melted at 55°.

An attempt to prepare 1-nitrodiphenylene oxide by treatment of 2-nitro-2′-methoxydiphenyl ether with aluminium chloride, followed by 50% sulphuric acid, was unsuccessful.

2-*Amino*-2′-*hydroxydiphenyl Ether.*—2-Nitro-2′-methoxydiphenyl ether (2 g.) was heated under reflux for 3 hours with hydriodic acid (25 c.c.; *d* 1·7), the deep red product poured into dilute aqueous sodium hydroxide, and sulphur dioxide passed in until the solution became yellow. Excess of concentrated hydrochloric acid was added, and the solution made neutral with aqueous ammonia. The colourless crystalline precipitate was collected, washed with a little cold water, and recrystallised from dilute alcohol, forming colourless plates, m. p. 116° (1·5 g.; yield, 94%) (Found: C, 71·2; H, 5·5; N, 7·1. $C_{12}H_{11}O_2N$ requires C, 71·6; H, 5·5; N, 7·0%). The *amine* was soluble in hydrochloric acid, sodium hydroxide solution, and the usual organic solvents, and slightly soluble in hot water.

Conversion of 2-*Amino*-2′-*hydroxydiphenyl Ether into Diphenylene Dioxide.*—The ether (2 g.) was diazotised in dilute hydrochloric acid (30 c.c.) at 0° with sodium nitrite (1 g.) in water (10 c.c.), the solution poured gradually into a hot 30% solution of copper sulphate (30 c.c.), and the mixture boiled for 15 minutes. Sulphuric acid was added until the concentration of acid was 50%, and the product was again heated under reflux for 3 hours and was then subjected to distillation with superheated steam. The solid distillate was crystallised from alcohol, yielding a small quantity of diphenylene dioxide.

Conversion of 2-*Amino*-2′-*hydroxydiphenyl Ether into Phenoxazine.*—The ether (2 g.) was heated in a sealed tube at 270—280° for 40 hours, the dark-coloured product extracted with ether in a Soxhlet apparatus, and the extract washed with dilute sodium hydroxide solution.

The ether on evaporation deposited a dark brown, oily solid, from which phenoxazine (0·22 g.) was isolated with difficulty in colourless leaflets, m. p. 156°, by recrystallisation from alcohol. The compound gave a violet-red coloration with concentrated sulphuric acid and a dirty blue-green colour with alcoholic ferric chloride. The acetyl derivative formed colourless prisms, m. p. 141° (Kehrmann and Saager, *Ber.*, 1903, **36**, 477, give m. p. 142°).

Conversion of 2 : 2′-*Diaminodiphenyl into Diphenylene Oxide.*—2 : 2′-Dinitrodiphenyl (Ullmann and Bielecki, *Ber.*, 1901, **34**, 2176; Ullmann and Frentzel, *Ber.*, 1905, **38**, 725) was reduced by means of tin and hydrochloric acid to the diamine (yield, 70%), which (5·5 g.) was diazotised in dilute hydrochloric acid at 0°. The solution was kept at room temperature for 12 hours, warmed on the water-bath for 15 minutes, and then distilled with steam. The colourless solid distillate, recrystallised from alcohol, afforded pure diphenylene oxide (3·8 g.), m. p. 87° (compare Täuber and Halberstadt, *Ber.*, 1892, **25**, 2745).

Action of Phosphoric Oxide on 4 : 4′-*Dihydroxydiphenyl.*—A mixture of 4 : 4′-dihydroxydiphenyl (6 g.) and phosphoric oxide (1·6 g.) was heated rapidly. A small quantity of diphenylene oxide distilled and solidified; m. p. 87° (picrate, m. p. 102°).

2 : 2′-*Dinitrodiphenyl Ether.*—The yield of this compound obtained by heating *o*-chloronitrobenzene and potassium *o*-nitrophenoxide at 140° (Häussermann and Bauer, *Ber.*, 1896, **29**, 2084) is ~~very small. At a higher temperature (240°) the mixture tends to decompose violently. The follow~~ing method gives a yield of 6%, but the unchanged initial materials can be recovered and used again. Potassium hydroxide (28 g.) was heated with water (10 c.c.) until a clear melt was obtained. *o*-Nitrophenol (70 g.) was quickly mixed with this, and the resulting mass was dried in an air-oven at 140°. The phenoxide was then heated with *o*-chloronitrobenzene (70 g.), *o*-nitrophenol (35 g.), and pyridine (10 c.c.) at 220° (oil-bath temperature) for 2 hours. The product was extracted with hot dilute potassium hydroxide solution, from which unchanged *o*-nitrophenol was recovered, and the undissolved portion was distilled with steam, which removed *o*-chloronitrobenzene. 2 : 2′-Dinitrodiphenyl ether was extracted from the residue with acetone and recrystallised from alcohol, forming pale yellow needles, m. p. 116°.

2′-*Nitro*-2-*aminodiphenyl Ether.*—The dinitro-compound (10 g.) was reduced in alcohol (100 c.c.) and aqueous ammonia (10 c.c.; *d* 0·880) with hydrogen sulphide and after 1 hour the solvent was distilled off and the residue extracted with boiling dilute hydrochloric acid. Addition of aqueous ammonia to the filtrate precipitated an oil, which was dried and crystallised from alcohol, yielding the *nitroamino*-compound in yellow needles (5 g.), m. p. 56° (Found : N, 12·4. $C_{12}H_{10}O_3N_2$ requires N, 12·2%). Reduction with hydrogen chloride–stannous chloride–glacial acetic acid gave the same result.

Action of Bromine on 2-*Nitrodiphenylene Oxide.*—A solution of the oxide (2 g.) in glacial acetic acid (40 c.c.) was slowly treated with bromine [2·2 c.c.; 3 mols. (the use of only 1·2 mols. was unsatisfactory)] and boiled under reflux for 6 hours. The solid obtained on cooling was washed with acetic acid and recrystallised from boiling acetone, giving pale yellow needles (2·9 g.) of 6-*bromo*-2-*nitrodiphenylene oxide*, m. p. 248° [Found : Br, 27·2. $C_{12}H_6O_3NBr$ requires Br, 27·4%. In the estimation (Carius) the tube had to be heated at 340° for 20 hours in order to ensure complete decomposition of the bromo-compound], fairly soluble in hot acetone, but not very soluble in acetic acid, alcohol, benzene, or chloroform.

Action of Nitric Acid on 3-*Bromodiphenylene Oxide.*—Into a solution of the oxide (5 g.) in glacial acetic acid (30 c.c.), nitric acid (12·5 c.c.; *d* 1·5) was dropped with water-cooling; the whole was kept at room temperature for 2 hours and then heated on the water-bath for 1½ hours. The crystals obtained on cooling were washed with acetic acid and recrystallised from acetone, giving pale yellow needles (3 g.) of 6-bromo-2-nitrodiphenylene oxide, m. p. 248°, identical with the preceding compound.

3 : 6-*Dibromodiphenylene Oxide.*—When bromine (3·4 g.) was dropped with stirring into a hot solution of 3-bromodiphenylene oxide (2 g.) in glacial acetic acid (12 c.c.), vigorous evolution of hydrogen bromide occurred and a yellow precipitate was deposited. The mixture was kept at room temperature for 24 hours and then warmed on the water-bath for 3 hours. After cooling, the yellow crystals were collected, washed with a little acetic acid, and recrystallised from alcohol–acetone, giving colourless leaflets (2·4 g.) of the 3 : 6-dibromo-compound, m. p. 195°.

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