266. *Investigations in the Diphenylene Oxide Series. Part V.*

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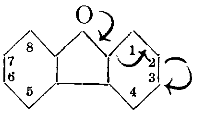
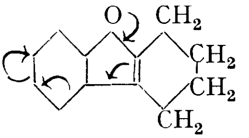
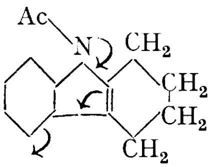
When diphenylene oxide is halogenated, the halogen atom is substituted in the para-position to the oxygen atom (Mayer and Krieger, *Ber.*, 1922, **55**, 1660; cf. Cullinane, J., 1932, 2367), as is to be expected from the electronic theory (I). Nitration, however, occurs mainly at position 2(= 7), and Robinson accounts for this unexpected result by assuming that in this case the route taken by the electromeric changes is different (see Cullinane, *loc. cit.*). The nitration of 1 : 2 : 3 : 4-tetrahydrodiphenylene oxide also furnishes the 7-nitro-derivative (Gilman, Brown, Bywater, and Kirkpatrick, *J. Amer. Chem. Soc.*, 1934, **56**, 2477), and a similar explanation may be advanced to explain this result (II). Nitration of 9-acetyltetrahydrocarbazole takes place at position 5 (III), which can be regarded as meta to the nitrogen atom, although nitration of tetrahydrocarbazole itself yields the 6-nitro-derivative in the normal way (IV) (Perkin and Plant, J., 1923, **123**, 676).



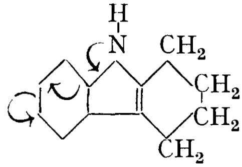
(I.)



(II.)



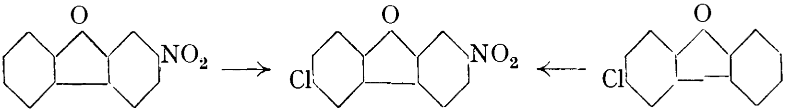
(III.)



(IV.)

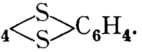
Now the comparison of tetrahydrodiphenylene oxide with tetrahydrocarbazole is analogous to that of acetylated tetrahydrocarbazole with tetrahydrocarbazole, because in each case the hetero-atom suffers a diminution in the availability for electromeric changes of its unshared electrons, *i.e.*, NH>N·COR and NH>O.

When a second substituent is introduced into the 2-nitrodiphenylene oxide molecule, owing to the presence of the deactivating nitroxyl group substitution must rely on direct activation of the substituted nucleus by the oxygen atom; hence a second nitro-group (Cullinane, *loc. cit.*), or a chlorine atom, enters the molecule at the normal position 6 (see V). In the absence of the deactivating nitroxyl group the conditions obtaining in the case of diphenylene oxide itself apply, and therefore nitration of 6-chlorodiphenylene oxide yields 6-chloro-2-nitrodiphenylene oxide (V). Analogous results are obtained for bromine derivatives (Cullinane, Davey, and Padfield, J., 1934, 717).



(V.)

1 : 2 : 3 : 4-Tetrahydrodiphenylene oxide (II) was prepared by reduction of diphenylene oxide by means of sodium and *cyclo*hexanol, and in almost quantitative yield by means of hydrogen in the presence of platinum-black. Dehydrogenation of the tetrahydride to diphenylene oxide was effected by means of sulphur, selenium, or potassium permanganate.

The dry distillation of litharge and phenol (Cullinane, J., 1930, 2268) furnished diphenylene oxide together with a small quantity of diphenyl ether. When phenol was replaced by thiophenol, the products of distillation were diphenylene sulphide, diphenyl sulphide, diphenyl disulphide, Ph•S•S•Ph, and diphenylene disulphide (thianthren),  $C_6H_4{<}\begin{smallmatrix}S\\S\end{smallmatrix}{>}C_6H_4$.

Experimental.

Chlorination of 2-Nitrodiphenylene Oxide.—Dry chlorine was rapidly passed for 45 minutes into a warm solution of 2-nitrodiphenylene oxide (2 g.) in glacial acetic acid (40 c.c.). A pale yellow solid was deposited. The product was kept at room temperature for 12 hours, water added, and the precipitate washed with water and recrystallised from acetic acid or acetone–alcohol. Pale yellow needles (2 g.) were obtained, m. p. 226°, undepressed by admixture with a specimen of 6-chloro-2-nitrodiphenylene oxide (kindly supplied by Dr. H. A. Scarborough) prepared from 4-chloro-5′-nitro-2′-aminodiphenyl ether by diazotisation and ring closure (McCombie, Macmillan, and Scarborough, J., 1931, 534).

Nitration of 6-Chlorodiphenylene Oxide.—Chlorination of diphenylene oxide in glacial acetic acid with 1 mol. of chlorine gave a mixture of 6-chloro- and 3 : 6-dichloro-diphenylene oxides. However, when 0·5 mol. of chlorine was employed, the 6-chloro-derivative, composed of colourless leaflets, m. p. 103°, was formed. The constitution of this substance was established by Gilman, Brown, Bywater, and Kirkpatrick (*loc. cit.*, p. 2476).

Nitric acid (5·6 c.c.; *d* 1·5) was added dropwise to a warm solution of 6-chlorodiphenylene oxide (2 g.) in glacial acetic acid (14 c.c.). The product was kept at room temperature for 2 hours and then heated on the water-bath for 1½ hours. The crystalline deposit formed on cooling was washed with water and recrystallised from acetone–alcohol, giving pale yellow needles (2 g.), m. p. 228°, of 6-chloro-2-nitrodiphenylene oxide (identified by a mixed m. p.).

Action of Bromine on 2-Bromodiphenylene Oxide.—2-Aminodiphenylene oxide (4 g.),* m. p. 99° (Cullinane, J., 1930, 2268), was diazotised at 0°; the diazo-solution was run gradually into a 10% solution of cuprous bromide (20 c.c.), heated under reflux for 15 minutes, and then distilled in steam. Recrystallisation from alcohol furnished colourless scales (1·5 g.), m. p. 116°, of 2-bromodiphenylene oxide.

* The acetyl derivative of this amine on nitration and subsequent hydrolysis furnished a nitroamino-compound, which was reduced to an *o*-diamine. This was stated (Cullinane, J., 1930, 2267) to be 1 : 2-diaminodiphenylene oxide on the basis of a statement by Borsche and Schacke (*Ber.*, 1923, **56**, 2500) that elimination of the amino-group from the above nitroamino-derivative gave a nitrodiphenylene oxide of m. p. 110°. However, this compound has been shown by Brumberg in a memoir only recently available (Diss., Göttingen, 1925, p. 22) to melt at 152°. Its constitution was established as follows : The amine formed on reduction was diazotised at 0°, and the diazo-compound treated with cuprous cyanide. The crude nitrile obtained was heated under reflux for several hours with alcoholic potassium hydroxide, yielding an acid, consisting of colourless needles, m. p. 246°, identical with the 3-carboxydiphenylene oxide prepared by Mayer and Krieger (*loc. cit.*) by the oxidation of 3-methyldiphenylene oxide. Its identity was further confirmed by reducing it to the amine and converting this compound into 3-bromodiphenylene oxide (Cullinane, J., 1932, 2367; cf. Gilman, Brown, Bywater, and Kirkpatrick, *loc. cit.*; Tatematsu and Kubota, *Bull. Chem. Soc. Japan*, 1934, **9**, 452).

2-Bromodiphenylene oxide (3·2 g.) was dissolved in glacial acetic acid (20 c.c.), and bromine (2 c.c.) was added dropwise to the hot solution. Evolution of hydrogen bromide was observed and a pale yellow precipitate was formed on cooling. The mixture was kept for 12 hours and then heated on the water-bath for 3 hours. The product was washed with water and recrystallised from light petroleum (b. p. 60—80°), followed by acetone, yielding pale yellow needles, m. p. 174° (Found : Br, 48·9. Calc. for $C_{12}H_6OBr_2$: Br, 49·05%). The constitution of this substance has not yet been established.

Nitration of 2-*Chlorodiphenylene Oxide.*—2-Chlorodiphenylene oxide (2 g.) was dissolved in glacial acetic acid (20 c.c.), and nitric acid (6 c.c.; *d* 1·5) added gradually with cooling; during 2 hours' standing, a precipitate formed. The mixture was then heated on the water-bath for 2 hours, a solid cake separating. The product on recrystallisation from glacial acetic acid (in which it was fairly readily soluble in the heat and sparingly in the cold) yielded pale yellow needles (2 g.), m. p. 253° (Found : N, 5·8. $C_{12}H_6O_3ClN$ requires N, 5·7%). The constitution of this compound has not yet been established, but it is probably 2-chloro-7-nitrodiphenylene oxide.

Courtot, Nicolas, and Liang (*Compt. rend.*, 1928, **186**, 1624) state that thionyl chloride converts nitrodiphenylene sulphide in the cold into the corresponding chloro-compound. However, treatment of 2-nitrodiphenylene oxide with excess of boiling thionyl chloride for several hours was without effect, the original substance being all recovered unchanged.

Conversion of Diphenylene Oxide into 1 : 2 : 3 : 4-*Tetrahydrodiphenylene Oxide.*—The tetrahydride was first obtained in unstated yield by Hönigschmid (*Monatsh.*, 1901, **22**, 563; **23**, 829) by treatment of diphenylene oxide with sodium and absolute alcohol. In the present work sodium and *cyclo*hexanol were used, the yield of product being 70% (Mayer and Krieger, *loc. cit.*, p. 1665). A still better yield (97%) was obtained by the following method.

Into a mechanically agitated solution of diphenylene oxide (5 g.) in pure dry glacial acetic acid (75 c.c.) containing platinum-black (2 g.), dry hydrogen (obtained by the electrolysis of acidified water) was slowly passed. When 1558 c.c. (corresponding to 2·2 mols. at *N.T.P.*) had been taken up, the liquid was filtered, the residue washed with acetic acid, and the filtrate and washings mixed and made alkaline with sodium carbonate. The oil which separated was extracted with ether, dried over calcium chloride, recovered, and distilled (Found : C, 83·4; H, 7·1. Calc. for $C_{12}H_{12}O$: C, 83·7; H, 7·0%). A still purer product was obtained by mixing hot solutions containing equimolecular proportions of the tetrahydride and picric acid in the minimum quantities of alcohol. The additive compound deposited, on cooling, in orange-yellow needles, m. p. 91°, was decomposed with excess of aqueous ammonia (*d* 0·880), and the product extracted with ether and distilled.

Tetrahydrodiphenylene oxide is a heavy colourless oil with a characteristic odour, b. p. 270°/ordinary press., 170°/40 mm., and 151°/20 mm. It is insoluble in water, but soluble in the ordinary organic solvents. With concentrated sulphuric acid it gives a purplish-red coloration. The intention to nitrate it and investigate the constitution of the nitro-derivative was abandoned in view of the results of Gilman and his collaborators (*loc. cit.*, p. 2477).

Attempt to prepare Dihydrodiphenylene Oxide.—Hönigschmid (*loc. cit.*), using half the quantity of sodium and absolute alcohol required to prepare the tetrahydro-compound, claimed to have obtained a dihydrodiphenylene oxide. This appears doubtful, for an attempt made by the present authors to reduce the oxide to the dihydride by employing 1·1 mols. of hydrogen in the presence of platinum-black yielded only unchanged oxide together with some tetrahydride.

Conversion of Tetrahydrodiphenylene Oxide into Diphenylene Oxide.—(a) *By the action of sulphur or selenium.* An intimate mixture of tetrahydrodiphenylene oxide (2 g.) and sulphur (0·8 g.; 2·2 mols.) or selenium powder was heated gradually to 260°. Hydrogen sulphide was evolved and, when the evolution of the gas had ceased, the dark-coloured mass was allowed to cool and then extracted with boiling alcohol. Recrystallisation of the solid obtained by evaporation of the alcohol afforded pure diphenylene oxide (0·9 g.), m. p. 87°.

(b) *By the action of potassium permanganate.* Little or no diphenylene oxide was isolated when the tetrahydride was treated with boiling 5% potassium permanganate solution, even in presence of magnesium sulphate.

To a boiling stirred mixture of magnesium sulphate solution (25 g. in 25 c.c. of water) and tetrahydrodiphenylene oxide (2 g.), a 20% solution of potassium permanganate (130 c.c.) was added in small portions. After cooling and filtration, ether extracted from the residue an oil, from which about 0·1 g. of diphenylene oxide was isolated.

The action of mercuric acetate upon tetrahydrodiphenylene oxide failed to yield diphenylene oxide (compare tetrahydrocarbazole derivatives; Perkin and Plant, J., 1921, **119**, 1838).

The Action of Litharge on Thiophenol.—A mixture of thiophenol (30 g.) and litharge (40 g.)

was heated at 160° for 7 hours in a flask fitted with an air condenser, orange-red crystals of lead thiophenoxide being formed. Distillation under atmospheric pressure removed thiophenol (5 g.), which was mixed with diphenyl disulphide (0·5 g.), m. p. 61°. The residue was fractionally distilled under 11 mm. pressure. Thianthren (2 g.), colourless needles, m. p. 155°, was isolated. Diphenylene sulphide (1·5 g.), m. p. 99°, was also obtained, and identified by comparison with a specimen prepared synthetically. The synthesis adopted was that employed by Courtot (*Compt. rend.*, 1932, **195**, 1660), but more prolonged heating (15 hours) of the diphenyl sulphoxide with powdered sodamide improved the yield. In addition, diphenyl sulphide (4 g.) was separated, and was characterised by conversion into the sulphone, m. p. 129°.

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