THE CONSTITUTION OF THE HYDROXY-DERIVATIVES OF DIPHENYLENE OXIDE OBTAINED FROM RESORCINOL.

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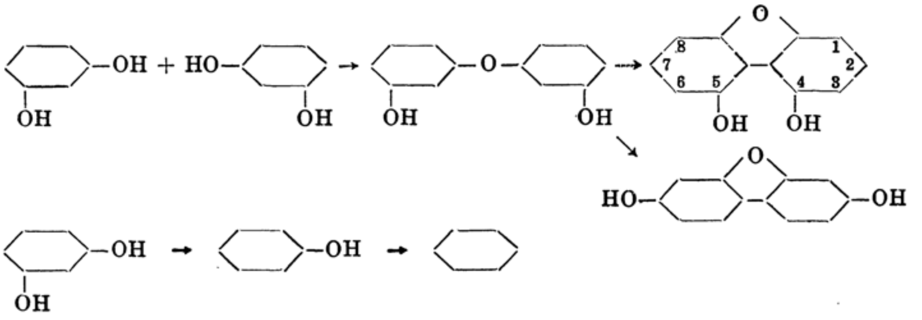
It was previously reported⁽¹⁾ that resorcinol undergoes a certain reduction and condensation under the influence of the blue oxide of tungsten at 500–550°, and gives two substances besides benzene, phenol, and diphenylene oxide. Of the two substances, one melting at 138–138.5° was assumed by Y. Tsuzuki to be 4-hydroxydiphenylene oxide (III) from the observation of its decomposition product as well as of absorption spectra, and the other melting at 241–242° was considered 4,5-dihydroxydiphenylene oxide (I). The process of the reactions giving these two compounds appeared to be represented by the dotted arrows in the scheme shown below:



I

II

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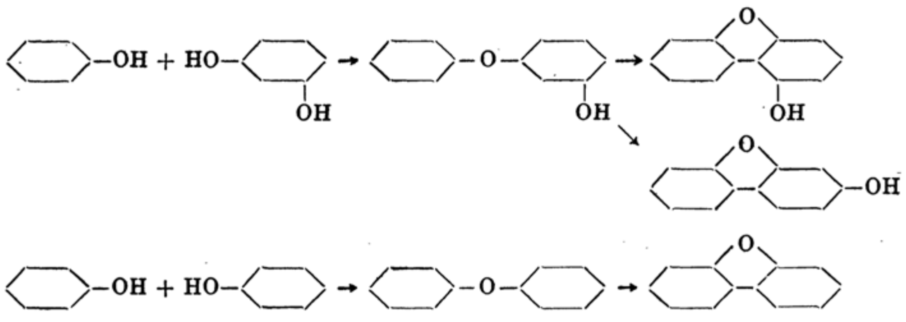
(1) B. Kubota, Y. Fujimura, and K. Akashi, *Scientif. Pap. Inst. Phys. Chem. Research, Japan*, **2** (1925), 185; Y. Tsuzuki, ibid., **6** (1927), 301.



III

IV

With the view of ascertaining the constitutions of these compounds the monohydroxydiphenylene oxide melting at 138–138.5° was again examined. It was compared with 2-hydroxydiphenylene oxide obtained by us from Cullinane's 2-aminodiphenylene oxide[2] by means of the diazo-reaction. The acetyl-, methyl-, and dinitro-derivatives of them were also compared. As shown in Table 1, the melting points of the monohydroxydiphenylene oxide from resorcinol and its derivatives are in good agreement with those of the corresponding compounds obtained from 2-aminodiphenylene oxide, and moreover, the mixed melting point of the two monohydroxydiphenylene oxides gave no depression.

Table 1. Comparison of the Melting Points.

Substance	From resorcinol	From 2-amino-diphenylene oxide
Hydroxydiphenylene oxide	138–138.5°	138–138.5°
Acetyl-derivative	111–111.5°	111–111.5°
Methyl-derivative	93–94°	97–97.5°
Dinitro-derivative	216–217° (decomp.)	216.5–217° (decomp.)

These facts indicate evidently that the compound in question obtained from resorcinol is none other than 2-hydroxydiphenylene oxide (IV), and may naturally suggest that the other substance obtained from resorcinol, melting at 241–242°, is more probably 2,7-dihydroxydiphenylene oxide (II). Although the latter problem is yet under investigation, the main processes of the reactions may be represented by the real arrows in the scheme shown above.

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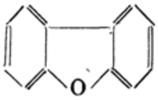
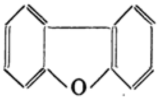
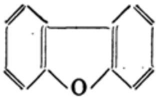
(2) N. M. Cullinane, *J. Chem. Soc.*, **1930**, 2267.

The comparative study of the absorption spectra was the chief ground of the previous arguments concerning the constitutions of these substances. As the previous authors pointed out, the absorption curve of 2-hydroxydiphenylene oxide has a striking resemblance in the form to that of *o*-hydroxydiphenyl but not to that of *p*-hydroxydiphenyl. But it is remarkable that this curve resembles that of 2,4-dihydroxydiphenyl and especially that of diphenylene oxide. As seen from the curves given in the experimental part, the influence of the hydroxyl-group on the absorption spectra is different with the position of the group in the diphenyl ring and also in the diphenylene oxide ring. Thus, if a hydroxyl-group is introduced to diphenyl in the ortho-position with respect to the diphenyl linkage, the absorption spectra are strongly influenced, while the effect of a para-hydroxyl-group is so weak that the form of the curve is hardly affected. From these points of view formula IV is highly probable for the monohydroxydiphenylene oxide melting at 138–138.5°.

Further the constitution of this compound was confirmed by studying its bromination product. Applying Kekulé's formula to the two benzene rings in diphenylene oxide, three formulae (1), (2), and (3), which are conditioned by the two possible arrangements of bonds in each benzene ring, may be considered:


(1)


(2)


(3)

Two of them, (2) and (3), possessing respectively one and two double bonds common to the benzene and the furan rings should be under greater intramolecular strain, because two and four β intravalency angles are respectively included in the furan rings of them, and, therefore, according to Mills's hypothesis,⁽³⁾ considerable distortion of the natural valency directions should be required to approximate these angles to the intravalency angle of the furan ring. In formula (1) in which single bonds only are common to the benzene and the furan rings, four α intravalency angles are brought into the furan ring, and as the α-angle does not differ from the intravalency angle of the furan ring so much as the β-angle does, the molecule of the form (1) should suffer less strain. Thus Mills's hypothesis indicates that the form (1) is the most stable constitution of diphenylene oxide. If our consideration is correct, the most stable form of 2-hydroxy-

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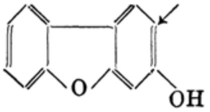
(3) W. H. Mills and I. G. Nixon, *J. Chem. Soc.*, **1930**, 2510.

diphenylene oxide must be (4), and the substitution of bromine should take place mainly at the 3-position as indicated by the arrow :



(4)

We examined accordingly the action of bromine on 2-hydroxydiphenylene oxide, and as expected, the main product was 3-bromo-2-hydroxydiphenylene oxide. The orientation of the bromine atom in the bromo-2-hydroxydiphenylene oxide was established as follows:

The bromo-2-aminodiphenylene oxide, which was obtained by bromination and subsequent hydrolysis of the 2-acetamino-compound prepared from Cullinane's 2-nitrodiphenylene oxide,⁽⁴⁾ was changed into the corresponding bromo-2-hydroxydiphenylene oxide by the diazo-reaction, which was found identical with the bromination product of 2-hydroxydiphenylene oxide. On replacing the amino-group by hydrogen, the bromo-2-aminodiphenylene oxide gave 3-bromodiphenylene oxide of F. Mayer and W. Krieger.⁽⁵⁾ Hence, the position of the bromine atom in the bromo-2-hydroxydiphenylene oxide is either 3 or 6.

2-Acetaminodiphenylene oxide, obtained by acetylation of the 2-amino-compound, gave a nitro-2-aminodiphenylene oxide on nitration and subsequent hydrolysis. This nitro-amino-compound was reduced to a diamino-compound, which proved to be an *o*-diamine, because it combined with benzil and phenanthrene-quinone to close a quinoxaline ring.⁽⁶⁾ Hence, the position of the nitro-group must be either 1 or 3.

On replacing the amino-group by bromine and subsequently reducing the nitro-group, the nitro-2-aminodiphenylene oxide was converted into an amino-2-bromodiphenylene oxide. From this amino-2-bromodiphylene oxide and from the bromo-2-aminodiphenylene oxide mentioned above, Sandmeyer's reaction yielded the same dibromo-compound. Hence the nitro-group in the above-mentioned nitro-2-aminodiphenylene oxide and the bromine atom in the bromo-2-aminodiphenylene oxide, and consequently the bromine atom in the bromo-2-hydroxydiphenylene oxide, must be in the same position, and that in 3. Thus it was established that the main product *of bromination of* 2-hydroxydiphenylene oxide is 3-bromo-2-hydroxy-diphenylene oxide.

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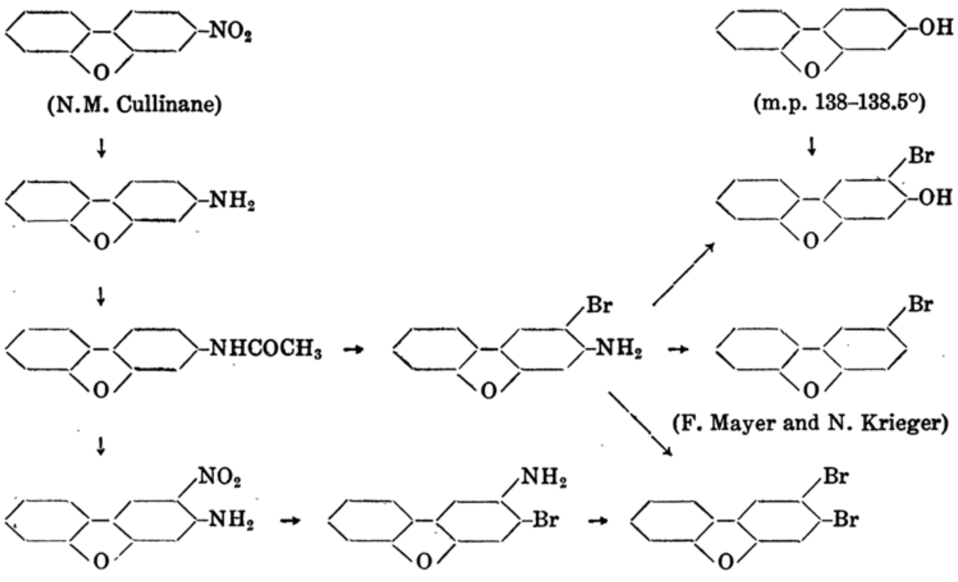
(4) N. M. Cullinane, loc. cit.

(5) *Ber.*, **55** (1922), 1659.

(6) W. Borsche and B. Schacke, *Ber.*, **56** (1923), 2498.

The above-mentioned nitro-2-aminodiphenylene oxide melting at 222° was supposed by Cullinane(7) to possess the nitro-group in the 1-position, but it was thus established that the nitro-group is in the 3-position.



Experimental.

(1) **2-Hydroxydiphenylene oxide.** 2-Nitro-diphenylene oxide is the main product of nitration of diphenylene oxide.(8) It was converted into 2-aminodiphenylene oxide by reducing with stannous chloride in glacial acetic acid saturated with hydrogen chloride. The product crystallized readily from dilute alcohol in colourless needles, m.p. 99–99.5° (W. Borsche and W. Bothe give 94°).

The sulphate of the 2-amino-compound, obtained by heating 2-aminodiphenylene oxide (12 g.) in 5% sulphuric acid (330 c.c.), was diazotized at 0° with sodium nitrite (4.5 g.) in water (12 c.c.), when the diazo-compound gradually separated out in brown yellow needles. After being allowed to stand over night at 0°, the product was gradually put into a boiling 50% copper sulphate solution (400 g.),(9) and the mixture was boiled in a flask with a reflux condenser for two hours. The diazo-compound which was

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(7) N. M. Cullinane, loc. cit.

(8) W. Borsche and W. Bothe, *Ber.*, **41** (1908), 1940.

(9) D. R. P., 167211.

formerly said to be stable,⁽¹⁰⁾ was thus decomposed, and the hydroxy-compound separated out in lustrous crystals. It was recrystallized from dilute alcohol, when it separated out in colourless plates melting at 138–138.5° (Yield 5 g.).

On adding a drop of ferric chloride solution to a solution of the substance, made by dissolving it in a very small quantity of alcohol and then adding water till the solution just began to become turbid, it gave a yellowish green colour, which turned light brown on addition of a dilute soda solution.

The acetyl-derivative, obtained by heating the hydroxy-compound with acetyl chloride, crystallized from concentrated acetic acid in large prisms melting at 111–111.5°.

The monomethyl-derivative, obtained by treating the hydroxy-compound with dimethyl sulphate and caustic soda solution, crystallized from dilute alcohol in plates, m.p. 97–97.5°. It melts somewhat higher than the methyl-derivative of the monohydroxydiphenylene oxide from resorcinol (93–94°).

The dinitro-derivative, obtained by nitration of the hydroxydiphenylene oxide in glacial acetic acid with concentrated nitric acid, crystallized from glacial acetic acid in small yellow prisms melting at 216–217° (decomp.).

These properties of the 2-hydroxydiphenylene oxide are in good agreement with those of the hydroxydiphenylene oxide described by the previous authors.⁽¹¹⁾ Moreover, the mixed melting of the two substances gave no depression, indicating the identity of the two substances.

The absorption curves. The results of a comparative study on the absorption curves of hydroxdiphenylene oxide from resorcinol, its acetyl-derivative, diphenylene oxide, mono- and di-hydroxydiphenyls are shown in the figure. All observations of absorption spectra were made in alcoholic solution.

The curves of the 2-hydroxydiphenylene oxide from the 2-nitro-compound and its acetyl-derivative have not been drawn, for they coincide with the curves of the hydroxydiphenylene oxide from resorcinol and diphenylene oxide respectively.

As already pointed out, the form of the curve of the hydroxy-compound probably depends chiefly upon the diphenylene oxide ring, and the position of the hydroxyl-group is not to be decidedly determined by this result only.

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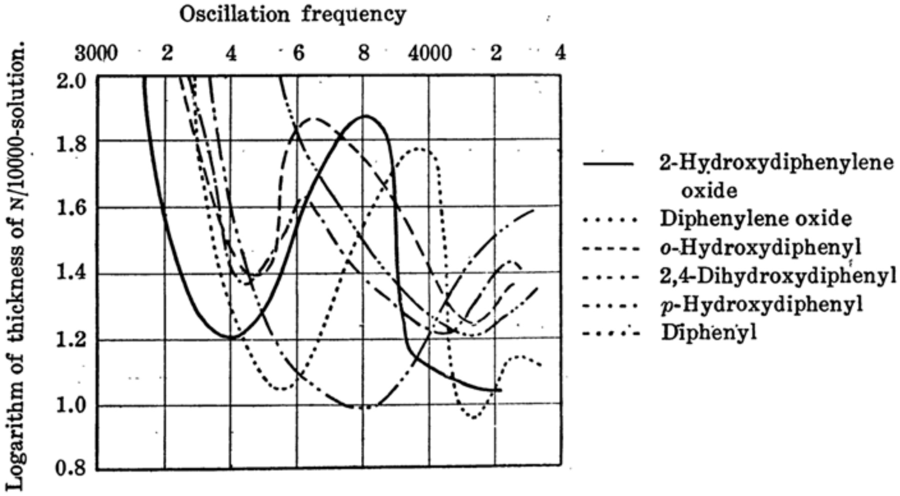
(10) W. Borsche and W. Bothe, loc. cit.

(11) B. Kubota, Y. Fujimura, and K. Akashi, loc. cit.; Y. Tsuzuki, loc. cit.



(2) **3-Bromo-2-hydroxydiphenylene oxide from 2-hydroxydiphenylene oxide.** Bromine (0.5 g.) dissolved in glacial acetic acid (1 c.c.) was added drop by drop at 0° to a solution of 2-hydroxydiphenylene oxide (0.6 g.) in the same solvent, and two hours later a large quantity of water was poured, when a white crystalline precipitate was formed. It was recrystallized from dilute acetone, colourless needles melting at 113°–113.5° (Yield 0.65 g., 70% of the theoretical). Treated with dimethyl sulphate and a caustic soda solution, this compound gave a methyl-derivative melting at 147–148°.

(3) **3-Bromo-2-hydroxydiphenylene oxide from 2-acetaminodiphenylene oxide.** (i) *2-Acetaminodiphenylene oxide.* 2-Nitrodiphenylene oxide was reduced to 2-aminodiphenylene oxide by the action of stannous chloride in acetic acid saturated with hydrogen chloride. The amino-compound (3 g.) was dissolved in absolute alcohol (30 g.) and to this solution acetic anhydride (15 g.) was added. After being kept for half an hour at ordinary temperature, the solvent was evaporated on the water bath. The operation of adding alcohol and evaporating was repeated until a white crystalline mass was obtained. It was recrystallized from dilute alcohol, colourless flat needles melting at 176.5–177° (Yield 3 g.).

(ii) *3-Bromo-2-acetaminodiphenylene oxide.* 2-Acetaminodiphenylene oxide (0.8 g.) was dissolved in glacial acetic acid (15 c.c.) and bromine (0.6 g.) in the same sovent (1.5 c.c.) was added at room temperature, when the colour of bromine soon disappeared and a white crystalline precipitate separated out. After an hour, a sufficient quantity of water (30 c.c.) was added. The crystalline precipitate was collected and well washed with dilute acetic acid. It was recrystallized from dilute acetone, colourless needles, m.p. 195–195.5°. (Yield 0.8 g., 70% of the theoretical. Found: N, 4.56. Calc. for $C_{14}H_{10}O_2NBr$: N, 4.60%.)

(iii) *3-Bromo-2-aminodiphenylene oxide.* 3-Bromo-2-acetaminodiphenylene oxide was boiled with alcoholic potash (2%, 50 c.c.) for one hour, and sufficient water (100 c.c.) was added to the solution, when a white crystalline precipitate was formed. It was recrystallized from dilute alcohol, colourless plates, m.p. 129–130°. (Yield almost theoretical. Found: N, 5.30. Calc. for $C_{12}H_8ONBr$: N, 5.34%.)

(iv) *3-Bromo-2-hydroxydiphenylene oxide.* 3-Bromo-2-aminodiphenylene oxide (0.15 g.) was heated in 10% sulphuric acid (15 c.c.) to obtain its sulphate. The sulphate was diazotized with sodium nitrite (0.05 g.) at 0°. On keeping the reaction mixture over night at 0°, the diazo-compound separated in a yellow crystalline precipitate. It was dissolved in a minimum quantity of water and the solution was added to a 50% solution of copper sulphate (40 g.), the latter being distilled during the addition so as to keep the concentration of copper sulphate constant.(12) After all the diazotized solution was added, the distillation was continued under the addition of water until no more crystals distilled. The crystalline substance was recrystallized from dilute alcohol, colourless needles melting at 113–113.5°. No depression was observed in the mixed melting point of this substance and the bromo-2-hydroxydiphenylene oxide obtained by the direct bromination of 2-hydroxydiphenylene oxide.(2)

(4) **3-Bromodiphenylene oxide.** 3-Bromo-2-aminodiphenylene oxide (0.1 g.) was converted into its hydrochloride by heating with 10% hydrochloric acid (15 c.c.). The hydrochloride was diazotized with sodium nitrite (0.035 g.). After three hours, this solution was made alkaline with caustic soda solution, filtered from reddish brown precipitate, and poured into sodium stannite solution made from stannous chloride (0.1 g.) and an excess of caustic soda solution. Nitrogen was evolved and a white crystalline precipitate separated. After being allowed to stand over night at room temperature, the precipitate was collected and recrystallized from dilute alcohol. It crystallized in colourless plates melting at 107–108°, and gave no depression of the melting point when mixed with 3-bromodiphenylene oxide prepared from diphenylene oxide by direct bromination in carbon disulphide.(13)

(5) **2,3-Dibromodiphenylene oxide from 3-bromo-2-aminodiphenylene oxide.** 3-Bromo-2-aminodiphenylene oxide (0.15 g.) was heated in hy-

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(12) D. R. P., 167211.

(13) F. Mayer and W. Krieger, loc. cit.

drobromic acid (1.5 c.c. of an acid with density 1.38 diluted to 10 c.c.). The hydrobromide thus obtained was diazotized at 0° with sodium nitrite solution. After being kept over night at 0°, it was filtered from some reddish brown precipitate and was poured into cuprous bromide solution (0.2 g. cuprous bromide dissolved in 4 c.c. of hydrobromic acid with density 1.38 and diluted to 10 c.c.), when nitrogen was evolved and some yellow precipitate was obtained. It was recrystallized from 50% alcohol, when it separated out in plates melting at 150–150.5° (Yield 0.02 g.).

(6) **2,3-Dibromodiphenylene oxide from 3-nitro-2-aminodiphenylene oxide.** 3-Nitro-2-aminodiphenylene oxide was obtained from 2-acetaminodiphenylene oxide in a manner just as described by the previous authors.(14)

(i) *3-Nitro-2-bromodiphenylene oxide.* As the basicity of 3-nitro-2-aminodiphenylene oxide is extremely weak and neither its sulphate nor its hydrochloride is stable in water, the diazotation of this compound was carried out by a special method.(15) Sodium nitrite (0.026 g.) was dissolved in well cooled concentrated sulphuric acid (18 c.c.) and to it fine powder of 3-nitro-2-aminodiphenylene oxide was added at 0°. A small quantity of ice (8 g.) was added bit by bit into this solution and after being kept at 0° for one hour, it was poured on ice (70 g.). This diazo-solution was added to a solution of cuprous bromide in hydrobromic acid (1 g. of cuprous bromide dissolved in 18 c.c. of hydrobromic acid with density 1.38 and diluted to 50 c.c. with water), when nitrogen was evolved and a yellow crystalline precipitate separated out. After being allowed to stand over night, it was collected and recrystallized from alcohol, yellow needles melting at 171–172°. (Yield 0.4 g. Found: N, 5.05. Calc. for $C_{12}H_6O_3NBr$: N, 4.79%.)

(ii) *3-Amino-2-bromodiphenylene oxide.* 3-Nitro-2-bromodiphenylene oxide (0.38 g.) was dissolved in a solution of stannous chloride in glacial acetic acid saturated with hydrogen chloride, and after being allowed to stand over night at room temperature, this solution was heated on a water bath for half an hour. By adding an excess of caustic soda solution, the amino-compound was obtained in fine crystals. It was purified by recrystallization from dilute alcohol when it separated out in colourless needles melting at 172–172.5°. (Yield 0.2 g. Found: N, 5.43. Calc. for $C_{12}H_8ONBr$: N, 5.34%.)

(iii) *2,3-Dibromodiphenylene oxide.* 3-Amino-2-bromodiphenylene oxide (0.15 g.) was converted into its sulphate by heating with 10% sulphuric acid (30 c.c.) and the sulphate solution was diazotized with sodium nitrite (0.05 g.). After being allowed to stand over night, the diazo-solution was

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(14) W. Borsche and B. Schacke, loc. cit.

(15) E. Misslin, *Helvetica Chim. Acta*, **3** (1910), 626.

filtered from reddish brown precipitate and poured into a solution of cuprous bromide in hydrobromic acid (0.2 g. of cuprous bromide dissolved in 5 c.c. of hydrobromic acid with density 1.38 and diluted to 15 c.c. with water), when nitrogen was evolved and an orange yellow precipitate separated out. After two hours this was collected and recrystallized from dilute alcohol, colourless plates, m.p. 150.5–151°. No depression was observed in the mixed melting point of this substance and 2,3-dibromodiphenylene oxide obtained from 3-bromo-2-aminodiphenylene oxide (5).

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