THE FORMATION OF OXY-DERIVATIVES OF DIPHENYLENE OXIDE FROM RESORCIN.

By Yojiro TSUZUKI.

Received January 29, 1927. Published March 28, 1927.

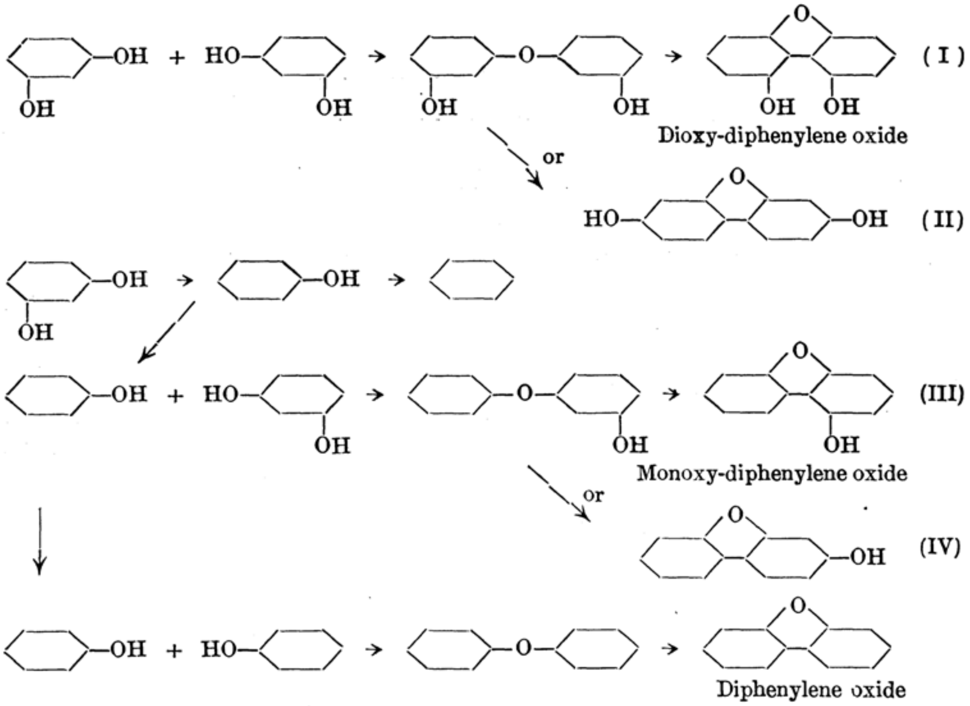
It was reported(1) that resorcin undergoes a certain reduction and condensation under the influence of blue oxide of tungsten between 500° and 550°, giving rise to the formation of a new compound which was supposed to be 2,6-dioxydiphenyl. With the view of ascertaining this constitution and whether there is any other product or not, and also of inquiring into the mechanism of this formation, this reaction was further examined by the suggestion of Professor B. Kubota.

The reaction was carried out exactly in the same manner as described in the previous paper. After the whole of the reaction products was subjected to steam distillation until no crystalline substance deposited in the condenser and the distillate showed no marked phenolic reaction, the remainder in the distilling flask was made strongly acidic with hydrochloric acid and the steam distillation was continued. By means of this steam distillatin it was found that there existed two products, one of which distils with steam though it goes on very slowly, and the other remains in the residual liquid. The former, melting at 138–138°.5, gave a monomethoxy-derivative $C_{12}H_7O(OCH_3)$ by being treated with sodium hydroxide and dimethylsulphate, whilst when heated with zinc dust diphenylene oxide was produced. The latter, melting at 241–242°, gave a dimethoxy-derivative $C_{12}H_6O(OCH_3)_2$ and diphenylene oxide by being treated in the same way. These facts lead us to suppose that the one compound melting at 138–138°.5 is evidently a monoxy-diphenylene oxide which contains two hydrogen atoms less than dioxy-diphenyl in the previous paper and the other melting at 241–242° a dioxy-diphenylene oxide.

Thus it seems to me that the production of benzene, phenol, diphenylene oxide, monoxy- and dioxy-diphenylene oxide may be regarded as the result of the normal action (dehydration) of the catalyst, accompanied by its secondary action (reduction), the processes of which being represented by the following schemes:

---

(1) Kubota, Fujimura and Akashi, *Scientific Papers of the Institute of Physical and Chemical Research*, 2 (1925), 185.



The well known formation of diphenylene oxide from phenol by means of lead oxide(1) or aluminium oxide(2) and also from diphenyl ether by means of heating(3) is suggestive of a remarkable tendency of the newly combining phenyl groups occupying ortho position with respect to the bridge oxygen atom. On the other hand, absorption curves show in their forms much resemblance to those of o-oxy-derivatives of diphenyl but not to those of p-oxy-derivatives(4), and those of acetyl derivatives are in good agreement with that of diphenylene oxide. Besides, it has been shown(4) that phenyl malonic acid was produced on oxidising the hexahydro-derivative of the compound melting at 138–138°.5. From this fact it is clear that the compound melting at 138–138°.5 is 2-oxydiphenylene oxide (formula III). From this point of view the formula I (2,2′-dioxydiphenylene oxide) becomes highly probable as that of the dioxy-diphenylene oxide) becomes highly probable as that of the dioxy-diphenylene oxide.

---

(1) Graebe, *Ber.*, 7 (1874), 396.

(2) Sabatier and Maihe, *Compt. rend.*, 151 (1910), 429; *Bull. soc. Chim.*, 11 (1912), 843; *Compt. rend.*, 155 (1912), 260; 158 (1914), 608.

(3) Graebe u. Ullmann, *Ber.*, 29 (1896), 1876.

(4) Kubota, Fujimura and Akashi, loc. cit.

Experimental.

Monoxy-diphenylene Oxide. *The Methoxy-derivative.* Oxydiphenylene oxide (0.1 gr.) obtained by passing resorcin vapour over blue oxide of tungsten at 500–550° as descrived in the paper cited above, was dissolved in a sodium hydroxide solution and a drop of dimethyl sulphate was added. The solution was warmed, when some white crystals separated out. Being recrystallised from dilute alcohol, it separated out in small plates melting at 93–94.° Yield 0.08 gr. It is soluble in alcohol and ether, but insoluble in water. 2.503 mg. and 2.398 mg. substance gave 3.086 mg. and 2.862 mg. AgI. (Found: $-OCH_3=16.29$ and 15.77. $C_{12}H_7O(OCH_3)$ requires $-OCH_3=15.66\%$.)

From this result the formula $C_{12}H_7O(OH)$ becomes more probable as that of the compound melting at 138–138°.5 than $C_{12}H_8(OH)_2$ which was reported in the previous paper.

Nitro-derivative. Oxy-diphenylene oxide (16 mg.) was dissolved in glacial acetic acid and some drops of concentrated nitric acid were added. The solution on being warmed on the water bath yielded 10 mg. of fine yellow crystals. Upon recrystallisation from hot petroleum ether, it separated out in small prisms becoming dark brown at about 200° and melting with decomposition at 216–217°. 1.300 mg. gave 0.112 c.c. of N_2(20°, 754 mm.). (Found: $N=9.87$, $C_{12}H_6N_2O_6$ requires $N=10.22\%$). It is soluble in alcohol and in almost all other organic solvents, but insoluble in water. This substance appears to be 3,5-dinitro-oxydiphenylene oxide.

Dioxy-diphenylene Oxide. The reaction products which were obtained by passing resorcin vapour over the catalyst at 500–550° were subjected to steam distillation until no crystalline substance deposited in the condenser and the distillate showed no marked phenolic reaction. The remainder in the distilling flask was made strongly acidic with hydrochloric acid and the steam distillation was continued so long as oxy-diphenylene oxide came out. The residual liquid was filtered from a tarry matter while still hot and was allowed to stand a mean while, when some brown prisms separated out. These were dissolved in hot water, treated with animal charcoal and recrystallised, but the faint brown colour was not removed off. It is soluble in alcohol, ether and hot water, but scarcely soluble in cold water, thuogh it is more soluble than oxy-diphenylene oxide. With a ferric chloride solution it gives a green colour turning to a light brown on the addition of sodium carbonate solution. It becomes almost colourless at 100° and melts at 241–242°. On being dehydrated over P_2O_5 at 100° under a diminished pressure, 5.31 mg. of the substance lost 0.22 mg. of water. (Found: $H_2O=4.31$; $C_{12}H_8O_3 1/2H_2O$ requires $H_2O=4.15\%$).

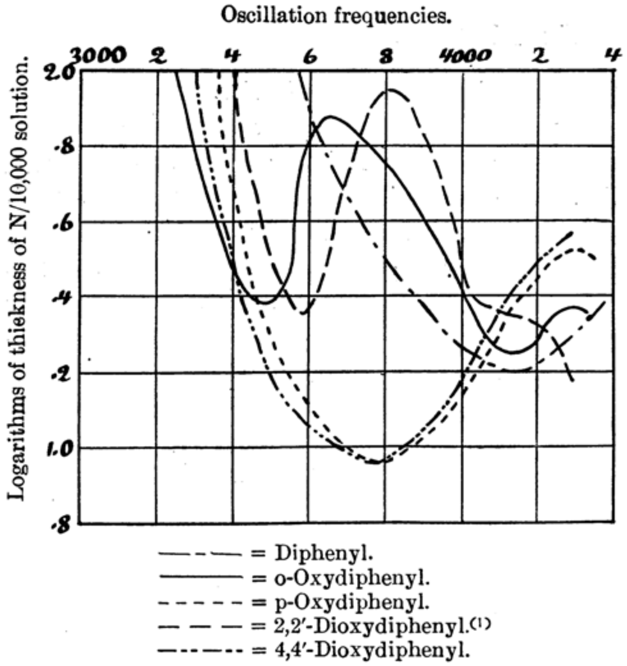


Fig. 1.

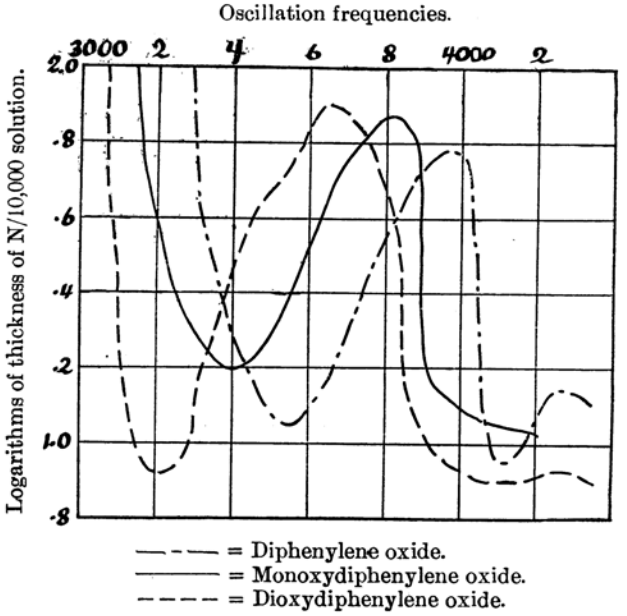


Fig. 2.

Molecular weight was determined by K. Rast's method. 0.14 mg. of substance in 1.94mg. of camphor gave $\Delta t = -13.°0$. (Found: M=210. $C_{12}H_8O_3$ requires M=200.)

The Dimethoxy-derivative. The dioxy-diphenylene oxide was treated with sodium hydroxide and dimethyl sulphate as described in the case of oxy-diphenylene oxide, when fine crystals were obtained. It was recrystallised from dilute alcohol, when it separated out in small plates melting at 150°. It is soluble in alcohol and ether, but insoluble in water. 2.123 mg. of substance gave 4.348 mg. AgI. (Found: $-OCH_3 = 27.06$. $C_{12}H_6O(OCH_3)_2$ requires $-OCH_3 = 27.20\%$).

The Acetyl-derivative. The dioxy-diphenylene oxide was warmed on the water bath with an excess of acetyl chloride, and that part of acetyl chloride, which was not used in the acetylation was for the most part driven off by diminishing pressure while still hot, when a residue consisting

---

(1) In practice, its dimethoxy derivative was observed, for dioxydiphenyl was not easily obtained.

of fine crystals was obtained. It was recrystallised from dilute acetic acid, when it separated out in small plates melting at 138°. 0.190 mg. of substance in 2.682 mg. of camphor gave $\Delta t = -10^\circ.0$. (Found: M=283. $C_{12}H_6O(OCOCH_3)_2$ requires M=284.)

The Zinc Dust Distillation. The dioxy-diphenylene oxide was intimately mixed with zinc dust and was gradually heated in a small test tube, when a colourless oil solidifying to a crystalline state in the upper part of the tube was found to distil off. This product was washed with sodium hydroxide solution and was recrystallised from dilute alcohol, when it separated out in scaly crystals melting at 80–81°. Its properties were found in good agreement with those of diphenylene oxide.

Absorption Curve. The results of a comparative study of the absorption curves of diphenylene oxide, oxy-diphenylene oxide, dioxy-diphenylene oxide and their acetyl derivatives are shown in the figures which, as already pointed out, give an indication of the fact that the compound meltings at 138–138°,5 and at 241–242° are both derivatives of diphenylene oxide whose hydroxyl groups are attached to the ortho position with respect to the other phenyl group. The curves of the two acetyl derivatives of oxy-diphenylene oxides are not especially drawn in the diagram as they are superposed on that of diphenylene oxide. All observations of absorption spectra were made in alcoholic solutions.

The author's best thanks are due to Professor B. Kubota under whose kind guidance the present investigations were carried out.

Summary.

The substance which was formerly supposed as 2,6-dioxydiphenyl was shown to be 2-oxydiphenylene oxide (III).

A new phenol was obtained, the formula of which was shown to be dioxydiphenylene oxide $C_{12}H_6O(OH)_2$. Two hydroxy groups seem to be in 2 and 2′ positions from the mechanism of its formation and its absorption spectrum.

The Institute of Physical and Chemical Research,
Hongo, Tokyo.