Studies on the Derivatives of Biphenylene Oxide. VII. The Influence of Substitution on the Opening and Closing of the Furan-ring of Biphenylene Oxide.

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It was communicated by the present author in Part IV⁽¹⁾ that when the nitro derivatives of 2,2′-diacetoxydiphenyl were melted in the presence of dry carbonate of barium or sodium, they converted mainly into the corresponding derivatives of biphenylene oxide, while 2,2′-diacetoxydiphenyl itself was converted by the same treatment exclusively into *o,o′*-biphenol, and, therefore, the formation of the furan-ring of this type may require the presence of some negative groups in the derivatives of 2,2′-diacetoxydiphenyl. Now, if this be the case, changes in the number and negativities of the substituents of the substitution products of 2,2′-diacetoxydiphenyl must show parallel changes in the yields of the derivatives of biphenylene oxide. With this in view, the nitro groups of the nitro derivatives of 2,2′-diacetoxydiphenyl were replaced step by step by the less negative bromine atoms, and then the bromonitro and bromo derivatives thus obtained were submitted to the tests of the formation of the furan-ring in comparison with the case of the corresponding nitro compounds. And in that case, it might be expected, of course, that the positions, at which the substitutions were to take place, would give certain effects to the formation of the furan-ring. For the purpose of making a complete test of this effect exerted by the nitro group, 4,4′-dinitro- and 4,4′,6,6′-tetranitro-2,2′-diacetoxydiphenyls were also prepared.

Among the derivatives of *o,o′*-biphenol which were submitted to the tests, 3-bromo-5,5′-dinitro-(II), 3,3′-dibromo-5,5′-dinitro-(III), 3-bromo-3′,5,5′-trinitro-(IV), 5-bromo-3,5′-dinitro-(VI), 3,5′-dibromo-3′,5-dinitro-(VII), 5-bromo-3,3′,5′-trinitro-(IX), 5,5′-dibromo-3,3′-dinitro-(XI), 4,4′-dinitro-(XIV), and 4,4′,6,6′-tetranitro-(XVII)-2,2′-dihydroxydiphenyls were newly obtained by the present author in the scheme shown below, in which the reactions that proceeded smoothly are repersented by the arrows in full line, and those which were brought about unsuccessfully, by the arrows in dotted line.

On the preparation of 3,3′-dibromo-5,5′-dinitro-2,2′-dihydroxydiphenyl R. W. Robertson and H. V. A. Briscoe⁽²⁾ reported that it was obtained either by nitration of 5,5′-dibromo-2,2′-dihydroxydiphenyl or by bromination of 5,5′-dinitro-2,2′-dihydroxydiphenyl, and that both products melting at 201° would be identical. The present author, however, considered that their report was unreasonable to be accepted as it is, and prepared 3,3′-dibromo-5,5′-dinitro-2,2′-dihydroxydiphenyl melting at 314–315° (corr.) by bromination of 5,5′-dinitro-2,2′-dihydroxydiphenyl. 3,3′-Dinitro-2,2′-

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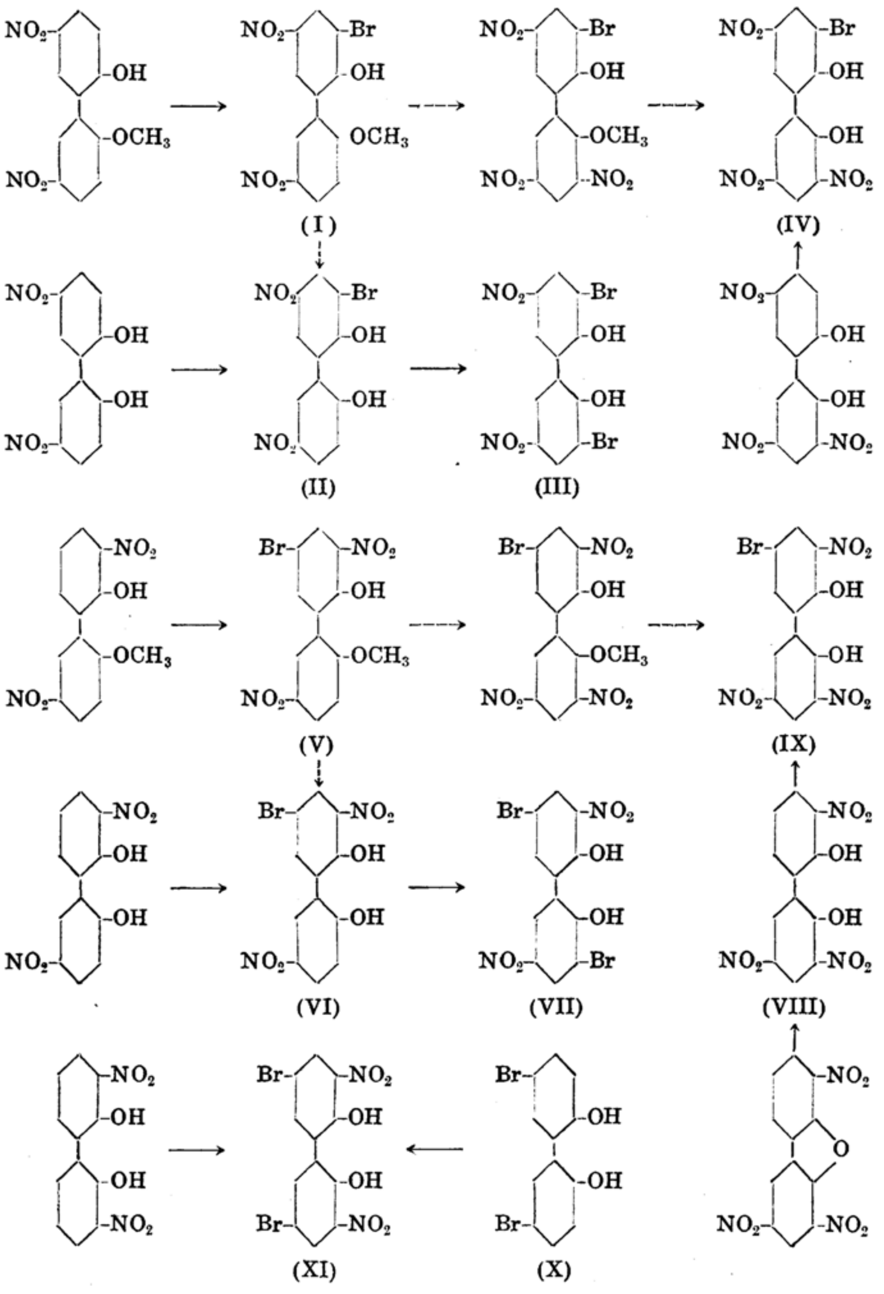
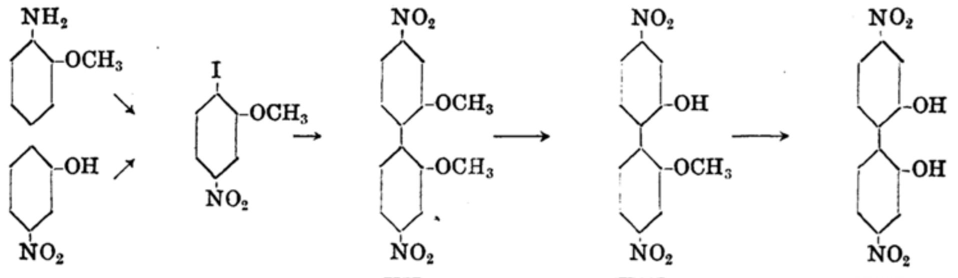
(1) S. Yamashiro, *J. Chem. Soc. Japan*, **59** (1938), 945.

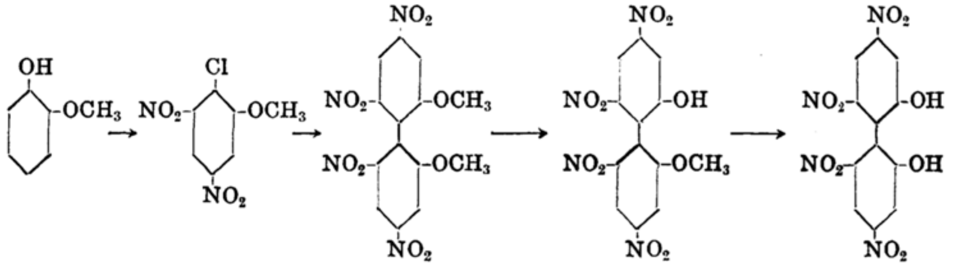
(2) P. W. Robertson and H. V. A. Briscoe, *J. Chem. Soc.*, **101** (1912), 1974.

dihydroxydiphenyl, which was hardly brominated by the preceding investigators, was converted by the present author into 5,5′-dibromo-3,3′-dinitro-2,2′-dihydroxydiphenyl melting at 207–208° (corr.), which was also obtained by nitration of 5,5′-dibromo-2,2′-dihydroxydiphenyl to the confirmation of its constitution. In consequence the dibromodinitrobiphenol obtained by Robertson and his coworker should be 5,5′-dibromo-3,3′-dinitro-2,2′-dihydroxydiphenyl.





(XII) (XIII) (XIV)



(XV) (XVI) (XVII)

In the courses of these reactions it was found that the brominations of the derivatives of *o,o′*-biphenol and its monomethyl ether took place in the lower boiling solvents, such as chloroform, carbon bisulphide and carbon tetrachloride, principally at the *p*-position to the hydroxyl group, while in the higher boiling solvent such as acetic acid, at both of the *o*- and *p*-positions to the same hydroxyl group; but the same reaction took place neither at the *o*-position nor at the *p*-position relative to the methoxyl group, even when the methoxyl compounds were heated for a long time with a large excess of bromine in glacial acetic acid.

5,5′-Dibromo-(X) and 3,3′,5,5′-tetrabromo-2,2′-dihydroxydiphenyls, which have been submitted to the test of the closing of furan-ring, were obtained from *o,o′*-biphenol after the method communicated by O. Diels and his coworker.⁽³⁾ And, as to these bromo compounds, the former converted into 3,6-dibromobiphenylene oxide when heated in a sealed tube with hydrobromic acid in the presence of red phosphorus, and the latter gave none other than an oily matter in the same treatment.

4,4′,6,6′-Tetranitro-2,2′-dimethoxydiphenyl (XV) was prepared after the method described by J. van Alphen,⁽⁴⁾ viz., by taking guaiacol as a starting material, changing it into 3,5-dinitroguaiacol and 2-chloro-3,5-dinitroanisol in succession, and then condensing the last compound into the tetranitrodianisol.

Now, *o,o′*-biphenol and its sixteen derivatives were converted into the corresponding diacetoxy compounds by heating them with acetic anhydride in presence of a little sulphuric acid, and then the diacetoxy compounds thus obtained were submitted to the tests of the formatiton of furan-ring.

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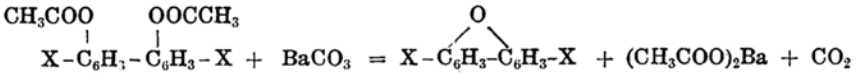
(3) O. Diels and A. Bibergeil, *Ber.*, **35** (1902), 306.
(4) J. van Alphen, *Rec. trav. chim.*, **51** (1932), 453-459.
(5) W. Borsche, *Ber.*, **50** (1917), 1347.

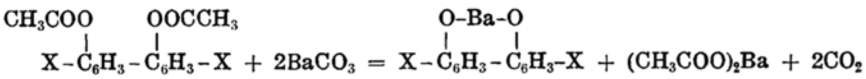
As shown in Part IV by the present author, the reactions between the *o,o'*-diacetoxydiphenyl compounds and the dry carbonate of barium or sodium will proceed in two ways, producing biphenylene oxides and o,o'-biphenolates.

(i)



$$X-\overset{CH_3COO}{C_6H_3}-\overset{OOCCH_3}{C_6H_3}-X + BaCO_3 = X-\overset{O}{\widehat{C_6H_3-C_6H_3}}-X + (CH_3COO)_2Ba + CO_2$$

(ii)



$$X-\overset{CH_3COO}{C_6H_3}-\overset{OOCCH_3}{C_6H_3}-X + 2BaCO_3 = X-\overset{O-Ba-O}{C_6H_3-C_6H_3}-X + (CH_3COO)_2Ba + 2CO_2$$

From the comparison of the yields of the reaction products given in Tables 3 and 4, it is realized that the predominance of one of these two reactions depends upon the nature and the position of the substituents introduced into the phenylene residues; namely.

(1) The introduction of the nitro group facilitates generally the removal of the acetyl groups from the derivatives of *o,o'*-diacetoxydiphenyl. This facilitating tendency can be represented in the order of the positions of the nitro groups introduced, i.e., ortho>para>meta relative to the acetoxyl groups, because it was found from the comparison of the experimental results (Tables 2, 3 and 4 in Part IV, and Table 3 in this report) that the velocities of the removal of the acetyl groups of dinitrodiacetoxydiphenyls can be represented in the order of these compounds, i. e., 3,3'->3,5'->5,5'->4,4'-dinitro-2,2'-diacetoxydiphenyl.

The *m*-nitrosubstitution relative to the acetoxyl groups does not induce the reaction (i), while the *o*- and *p*-nitrosubstitutions, especially the former, promote the reaction (i). The increase in the number of the nitro groups introduced in the latter two substitutions increases appreciably the yields of the resulting biphenylene oxides, although the yield of 1,3,6-trinitrobiphenylene oxide has come out exceptionally smaller than those of 1,6- and 3,6-dinitrobiphenylene oxides.

(2) The introduction of bromine into the nitro derivatives of *o,o'*-diacetoxydiphenyl hinders somewhat the removal of the acetyl groups, and reduces the reaction (i), increasing the yields of the biphenols. The last effect of bromine comes out remarkably when the bromination takes place at the *o*-position relative to the acetoxyl groups.

(3) The bromo derivatives of *o,o'*-diacetoxydiphenyl resist strongly against the action of barium carbonate, although they react readily with sodium carbonate. The reactions between the bromo compounds and these carbonates take place always in accordance with the reaction formula (ii), giving none of the bromo derivatives of biphenylene oxide.

In summarizing, so far as is concerned with the removal of the acetyl groups and the formation of the biphenylene oxides from the *o,o'*-diacetoxydiphenyls, the effects of bromine and the nitro group are unexpectedly opposite to each other. The velocity of the removal of the acetyl groups will be proportional to the thermal dissociation degrees of the acetoxyl groups of the diacetoxydiphenyls.

In order to compare the influence of substitution exerted on the opening of the furan-ring with that exerted on the formation of the same ring, eleven nitro derivatives of biphenylene oxide were submitted to the tests of the ring-opening. The tests were carried out by heating the finely powered biphenylene oxides for two hours with 5% solution of caustic soda at constant temperatures (20°, 40°, 60°, 80°, and 100°C.), and it was found from the experimental results (Table 6) that (1) the increase in the number of the nitro groups introduced into the phenylene residues of biphenylene oxide facilitates the ring-opening, (2) the favourable influence exerted by the nitro group on the ring-opening of this type depends upon the position of this group relative to the oxygen atom of the furan-ring, the order of the favourable positions being ortho>para>meta.

The tendency of the ring-opening of the nitrobiphenylene oxides in caustic soda solution will be proportional to the electrolytic dissociation degrees of the corresponding nitrobiphenols and again to those of the nitrophenols, of which the nitrobiphenols are composed. And it is because the yields of the nitrobiphenols obtainable from the nitrobiphenylene oxides (Table 6) and the electrolytic dissociation constants K⁽⁶⁾ of the nitrophenols can be represented in the orders of the nitrobiphenylene oxides and the nitrophenols respectively as follows:

1,3,6,8-Tetranitro- > 1,3,6,7-tetranitro- > 1,3,8-trinitro- > 2,3,6,7-tetranitro- > 1,3,6-trinitro- > 2,3,6-trinitro- > 1,8-dinitro- > 1,6-dinitro- > 3,6-dinitro- > 2,6-dinitro- > 2,7-dinitro-biphenylene oxide;

Components,	2,4-dinitro->	3,4-dinitro->	2-nitro->	4-nitro->	3-nitro-phenol.
$K_{25°}\times 10^{-6}$	10000	430	6.8	6.5	1.0

Among the nitrobiphenols obtainable from the above-mentioned nitrobiphenylene oxides, 4,4′,5,5′-tetranitro-2,2′-dihydroxydiphenyl has not been isolated in the pure crystalline form, because the reaction product obtained from 2,3,6,7-tetranitrobiphenylene oxide was liable to separate as a brown amorphous substance.

Experimental.

3-*Bromo*-5,5′-*dinitro*-2-*hydroxy*-2′-*methoxydiphenyl* (I). 5,5′-Dinitro-2-hydroxy-2′-methoxydiphenyl (2.9 g.) was heated for four hours with bromine (3 g.) in boiling acetic acid (30 c.c.), when the colour of bromine disappeared. The reaction product separated out on diluting; the reaction mixture was recrystallized from acetone-ethanol into colourless needles or prisms, m.p. 242–243° (corr.) with decomposition (Yield 3.6 g., 95%. Found: N, 7.72; Br, 21.81. Calc. for $C_{12}H_5OH(OCH_3)(NO_2)_2Br$: N, 7.59; Br, 21.66%.). It is readily soluble in acetone and ethyl acetate, moderately in ethanol, and sparingly in benzene, chloroform, carbon tetrachloride, ether, ligroin, methanol and acetic acid.

3-Bromo-5,5′-dinitro-2-hydroxy-2′-methoxydiphenyl (2 g.) was dissolved in cold fuming nitric acid ($d=1.52$; 20 c.c.) in the hope of obtaining 3-bromo-3′,5,5′-trinitro-2-hydroxy-2′-methoxydiphenyl, and the reaction mixture was poured into ice, separating yellow precipitates. The reaction product, however, readily decomposed into a brown mass, even when it was dried below 100°C., and gave no crystalline substance in the ordinary method of recrystallization.

3-*Bromo*-5,5′-*dinitro*-2,2′-*dihydroxydiphenyl* (II). (i) 5,5′-Dinitro-2,2′-dihydroxydiphenyl (8.28 g.) was dissolved in boiling glacial acetic acid (250 c.c.) and

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(6) A. F. Holleman and R. Herwig, *Rec. trav. chim.*, **21** (1902), 444.

brominated at this temperature by the gradual addition of bromine (4.8 g.) diluted with ten times its weight of acetic acid. When the colour of bromine disappeared, acetic acid was distilled off, the residue was diluted with water, and the reaction product separated out was extracted with ether after drying to remove the sparingly soluble dibromo derivative. The extract was evaporated to dryness and the residue was recrystallized from acetic acid into colourless needles, m.p. 302–303°C. (corr.) with decomposition (Yield 11 g., 85.5%. Found: N, 7.85; Br, 28.83. Calc. for $C_{12}H_5(OH)_2(NO_2)_2Br$: N, 7.89; Br, 22.51%.). It is readily soluble in alcohols, acetone, ether and ethyl acetate, fairly in acetic acid, and sparingly in benzene, chloroform, carbon tetrachloride and ligroin.

(ii) 3-Bromo-5,5′-dinitro-2-hydroxy-2′-methoxydiphenyl (3 g.) was heated for sixteen hours with hydrobromic acid ($d=1.49$; 40 c.c.) in boiling acetic acid (200 c.c.), and, after concentrating the reaction mixture, the residue was diluted with water, when dark brown precipitates separated out. The reaction product was extracted with dilute caustic soda solution, the extract was acidified separating out yellow precipitates, and the last product was then recrystallized from acetone-ethanol, when none other than 3-bromo-5,5′-dinitro-2-hydroxy-2′-methoxydiphenyl (1 g.) was isolated. The other part of the starting material decomposed into dark brown tarry matter.

3,3′-*Dibromo*-5,5′-*dinitro*-2,2′-*dihydroxydiphenyl* (III). 5,5′-Dinitro-2,2′-dihydroxydiphenyl (5.52 g.) was heated for four hours with bromine (6.4 g.) in acetic acid (100 c.c.), when the colour of bromine disappeared. The reaction mixture was concentrated and the reaction product separated out on cooling the mixture was recrystallized from dilute ethanol into small colourless needles, d.p. 314–315°C. (corr.) (Yield 7.93 g., 91.4%. Found: N, 6.53; Br, 36.99. Calc. for $C_{12}H_4(OH)_2(NO_2)_2Br_2$: N, 6.46; Br, 36.83%.). It is readily soluble in acetone, alcohols and ethyl acetate, and sparingly in acetic acid, benzene, chloroform, carbon tetrachloride, ether and ligroin.

3-*Bromo*-3′,5,5′-*trinitro*-2,2′-*dihydroxydiphenyl* (IV). 3,5,5′-Trinitro-2,2′-dihydroxydiphenyl (3.31 g.) was heated for four hours with bromine (1.7 g.) in boiling acetic acid (50 c.c.), and, after the same treatment as in the case of the compound (III), the reaction product was recrystallized from dilute ethanol into small yellow rectangular plates melting at 224–226°C. (corr.) with decomposition (Yield 3.9 g., 97.5 %. Found: N, 10.49; Br, 20.04. Calc. for $C_{12}H_4(OH)_2(NO_2)_3Br$: N, 10.51; Br, 19.98%.). It is readily soluble in acetone, alcohols, acetic acid and ethyl acetate, fairly in benzene, chloroform and ether, and sparingly in carbon tetrachloride and ligroin.

5-*Bromo*-3,5′-*dinitro*-2-*hydroxy*-2′-*methoxydiphenyl* (V). 3,5′-Dinitro-2-hydroxy-2′-methoxydiphenyl (5.8 g.) was brominated just as in the case of the preparation of 3-bromo-5,5′-dinitro-2-hydroxy-2′-methoxydiphenyl (I) and the reaction product was recrystallized from acetone-ethanol into small yellow needles, m.p. 219–220°C. (corr.) (Yield 7.27 g., 98.5%. Found: N, 7.63; Br, 21.79. Calc. for $C_{12}H_5OH(OCH_3)(NO_2)_2Br$: N, 7.59; Br, 21.66%.). It is readily soluble in acetone, benzene, chloroform, carbon tetrachloride and ethyl acetate, moderately in acetic acid, and sparingly in alcohols, ether and ligroin.

5-*Bromo*-3,5′-*dinitro*-2,2′-*dihydroxydiphenyl* (VI). (i) 3,5′-Dinitro-2,2′-dihydroxydiphenyl (1.38 g.) was treated with bromine (0.8 g.) just as in the preparation of 3-Bromo-5,5′-dinitro-2,2′-dihydroxydiphenyl. The reaction product was extracted with carbon tetrachloride to remove the more soluble dibromo derivative, and the residue was recrystallized from methanol into small yellow prisms, m.p. 216–217°C. (corr.) (Yield 0.75 g., 42%. Found: N, 6.58; Br, 36.76. Calc. for $C_{12}H_5(OH)_2(NO_2)_2Br$: N, 6.46; Br, 36.83%.). It is readily soluble in acetone, acetic acid, benzene, chloroform, ethanol, ether and ethyl acetate, moderately in methanol, and sparingly in carbon tetrachloride and ligroin. This product must be the 5-bromo-derivative, because the bromination of *o′o′*-biphenol takes place more readily at the *p*-position than at the *o*-one relative to the hydroxyl groups.

The carbon tetrachloride extract was evaporated to dryness and then recrystallized from methanol, isolating 3′,5-dibromo-3,5′-dinitro-2,2′-dihydroxydiphenyl melting at 203–204°C. (corr.) (Yield 0.5 g., 23%.).

(ii) 5-Bromo-3,5′-dinitro-2-hydroxy-2′-methoxydiphenyl (2.5 g.) was treated with hydrobromic acid just as in the case of 3-bromo-5,5′-dinitro-2-hydroxy-2′-methoxydiphenyl. From the reaction product, however, none of 5-bromo-3,5′-dinitro-2,2′-dihydroxydiphenyl was obtained.

3,5′-*Dibromo*-3′5-*dinitro*-2,2′-*dihydroxydiphenyl* (VII). 3,5′-Dinitro-2,2′-dihydroxydiphenyl (2.76 g.) was brominated just as in the preparation of 3,3′-dibromo-5,5′-dinitro-2,2′-dihydroxydiphenyl. The reaction product was recrystallized from methanol into yellow needles melting at 203–204°C. (corr.) with decomposition (Yield 4.21 g., 97%. Found: N, 6.55; Br, 36.78. Calc. for $C_{12}H_4(OH)_2(NO_2)_2Br_2$: N, 6.46; Br, 36.83%.). It is readily soluble in acetone, benzene, chloroform, carbon tetrachloride, ethanol, ether and ethyl acetate, moderately in acetic acid and methanol, and sparingly in ligroin.

3,3′,5-*Trinitro*-2,2′-*dihydroxydiphenyl* (VIII). 1,3,8-Trinitrobiphenylene oxide (3.03 g.) was dissolved in a hot dilute solution of caustic soda, and the reaction product separated out on acidifying the solution was recrystallized from ethanol into yellow rhombic plates, m.p. 156–157°C. (corr.) (Yield 3.0 g., 93.5%. Found: N, 13.14. Calc. for $C_{12}H_5(OH)_2(NO_2)_3$: N, 13.09%.). It is readily soluble in acetone, acetic acid, benzene, chloroform and ethyl acetate ,moderately in ethanol, and sparingly in carbon tetrachloride, ether, ligroin and methanol.

5-*Bromo*-3,3′,5-*trinitro*-2,2′-*dihydroxydiphenyl* (IX). 3,3′,5-*Trinitro*-2,2-*dihydroxydiphenyl* (1.605 g.) was brominated just as in the preparation of 3,3′-dibromo-5,5′-dinitro-2,2′-dihydroxydiphenyl, and the reaction product was recrystallized from methanol into yellow prisms, m.p. 191–192°C. (corr.) (Yield 1.94 g., 97%. Found: N, 10.64; Br, 19.86. Calc. for $C_{12}H_4(OH)_2(NO_2)_3Br$: N, 10.51; Br, 19.98%.). It is readily soluble in acetone, acetic acid, benzene, chloroform, ethanol and ethyl acetate, fairly in carbon tetrachloride and methanol, and sparingly in ether and ligroin.

5,5′-*Dibromo*-3,3′-*dinitro*-2,2′-*dihydroxydiphenyl* (XI). (i) 3,3′-Dinitro-2,2′-dihydroxydiphenyl (2.76 g.) was brominated as in the preparation of 3,3′-dibromo-5,5′-dinitro-2,2′-dihydroxydiphenyl and the reaction product was recrystallized from acetone-ethanol into yellow needles, m.p. 207–208°C. (corr.) (Yield 3.95 g., 91%. Found: N, 6.55; Br, 36.69. Calc. for $C_{12}H_4(OH)_2(NO_2)_2Br_2$: N, 6.46; Br, 36. 83%.). It is readily soluble in acetone, benzene, chloroform, carbon tetrachloride, ether and ethyl acetate, moderately in alcohols and acetic acid, and sparingly in ligroin.

(ii) 5,5′-*Dibrmo*-2,2′-*dihydroxydiphenyl* (3.44 g.) was dissolved in glacial acetic acid (35 c.c.), fuming nitric acid ($d=1.52$; 2.1 g.) was added and the mixture was heated on the water bath. The reaction product separated out on diluting the reaction mixture was recrystallized from ethanol into yellow needles, m.p. 207–208°C. (corr.) (Yield 4.15 g., 95.6%.). It is identical in all respects with the corresponding compound obtained from 3,3′-dinitro-2,2′-dihydroxydiphenyl.

3,6-Dibromobiphenylene oxide from 5,5′-dibromo-2,2′-dihydroxydiphenyl. A dibromo-2,2′-dihydroxydiphenyl (0.5 g.) melting at 191–192° (corr.), which was obtained by bromination of o,o′-biphenol in chloroform(3) and for the confirmation of its constitution, it was heated for 6 hours, at about 190–200° in a sealed tube with hydrobromic acid ($d=1.49$; 5 c.c.) and a small proportion of red phosphorus, when a pale brown oily mass was obtained. This reaction product was extracted with caustic soda solution, and the residue was repeatedly recrystallized from ethanol and then from acetic acid into colourless rectangular plates, m.p. 199–200° (corr.). It is identical in all respects with 3,6-dibromobiphenylene oxide obtained by bromination of biphenylene oxide.

4,4′-*Dinitro*-2,2′-*dimethoxydiphenyl* (XII). 6-Iodo-3-nitroanisol was first obtained from *o*-anisidine in the usual way (by means of acetylation, nitration, hydrolysis and diazo-reaction in succession), and also from *m*-nitrophenol by means of iodination(7) (Yield of 6-iodo-3-nitrophenol, 40%, and that of 2-iodo-3-nitrophenol, 10%) and subsequent methylation.(8) The iodonitroanisol (55.8 g.) thus obtained was heated for 2 hours at about 210–220° with copper bronze (20 g.) and nitrobenzene (30 c.c.) with constant stirring, in the atmosphere of carbon dioxide. The reaction mixture was submitted to a steam distillation, and the residue was pulverized after drying and then extracted with ether and benzene in succession. The benzene extract was concentrated and the condensation product separatd out was recrystallized from the same solvent into pale yellow needles, m.p. 257–258° (corr.) (Yield 25.3 g., 83%. Found: N, 9.28. Calc. for $C_{12}H_6(OCH_3)_2(NO_2)_2$: N, 9.21%). It is sparingly soluble in acetone, alcohols, carbon tetrachloride, ether and ligroin, and fairly in acetic acid, benzene, chloroform and ethyl acetate.

4,4′-Dinitro-2-hydroxy-2′-methoxydiphenyl (XIII) and *4,4′-dinitro-2,2′-dihydroxydiphenyl* (XIV) from *4,4′-dinitro-2,2′-dimethoxydiphenyl.* 4,4′-Dinitro-2,2′-dimethoxydiphenyl (30.4 g.) was heated for 20 hours with hydrobromic acid (d=1.49, 300 c.c.) in a boiling mixture of acetic acid (200 c.c.) and acetic anhydride (200 c.c.), the reaction mixture was after concentration diluted with water, and the reaction product which separated out was after filtration extracted with caustic soda solution for the purpose of removing the unchanged dinitrodianisol (6 g.) and the carbonized product. The extract was neutralized, the precipitates separated out were after drying extracted with benzene, and the residue was recrystallized from ethanol into yellow needles melting at 253–254° (corr.) with decomposition (Yield 13 g. Found: N, 10.22. Calc. for $C_{12}H_6(OH)_2(NO_2)_2$: N, 10.14%). The benzene extract was evaporated to dryness, and the residue was recrystallized from methanol into yellow needles, m.p. 206–207° (corr.) (Yield 7 g. Found: N, 9.72. Calc. for $C_{12}H_6(OH)(OCH_3)(NO_2)_2$: N, 9.66%). The higher melting product is readily soluble in acetone, alcohols, acetic acid, ether and ethyl acetate, and sparingly in benzene, chloroform, carbon tetrachloride and ligroin. The lower melting one dissolves similarly in those solvents except benzene and chloroform, in which it dissolves readily. The lower melting product was conveted into the higher melting one by a further treatment with hydrobromic acid.

4,4′,6,6′-Tetranitro-2-hydroxy-2′-methoxydiphenyl (XVI) and *4,4′,6,6′-tetranitro-2,2′-dihydroxydiphenyl* (XVII) from 4,4′, *6,6′-tetranitro-2,2′-dimethoxydiphenyl* (XV). 4,4′, 6,6′-Tetranitro-2,2′-dimethoxydiphenyl (7.88 g.), which was prepared after the method described by J. van Alphen(4) from 2-chloro-3,5-dinitronanisol obtained from guaiacol, was heated for 20 hours with hydrobromic acid (d=1.49, 150 c.c.) in boiling glacial acetic acid (150 c.c.), and the reaction mixture was after concentration diluted with water, when a dark brown crystalline mass separated out along with yellow hexagonal-prismatic crystals which have double-melting points, i.e. 95–98° and 228–229° (uncorr.). The reaction product was dissolved in caustic soda solution, and, after the removal of the insoluble part, it was reprecipitated by acidifying the solution. The precipitates were extracted with hot water, and the residue was then recrystallized from benzene into reddish yellow rectangular plates, m.p. 208–209° (corr.) (Yield 1.4 g. Found: N, 14.88. Calc. for $C_{12}H_4(OH)(OCH_3)(NO_2)_4$: N, 14.75%). The aqueous extract was evaporated to dryness and then the residue was recrystallized from benzene into yellow prisms, m.p. 235—236° (corr.) (Yield 4.6 g., 63%. Found: N, 15.33. Calc. for $C_{12}H_4(OH)_2(NO_2)_4$: N, 15.31%). The lower melting product was converted into the higher melting one by a further treatment with hydrobromic acid as described above. Both products are readily soluble in acetone, alcohols, acetic acid, chloroform, ether and ethyl acetate, fairly in benzene, and sparingly in carbon tetrachloride; but the higher melting product is much more readily soluble in hot water than the lower melting one.

Formation of the bromo-, bromonitro- and nitro-derivatives of 2,2′-diacetoxy-

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(7) F. W. Schlieper, *Ber.*, **26** (1893), 2467.

(8) R. Meldola and J. V. Eyre, *Proc. Chem. Soc.*, **238**.

diphenyl and 2-acetoxy-2′-methoxydiphenyl, from the corresponding derivatives of 2,2′-dihydroxydiphenyl and its monomethyl ether. The bromo-, bromonitro- and nitro-biphenols and their monomethyl ethers were boiled for a few minutes with ten times their weights of acetic anhydride in the presence of a little sulphuric acid, the reaction mixtures were treated with hot water to the decomposition of the excess of

Table

Derivatives of biphenol	Derivatives of 2,2′-diacetoxydiphenyl					Crystals and (their crystallizing solvents)
		M.p., (corr.)	Yield, %	Found, %	Calc., %	
II →	II′ 3-Bromo-5,5′-dinitro-derivative	186-187°	95.7	N, 6.35	6.38	Colourless small needles (acetic-acid)
III →	III′ 3,3′-Dibromo-5,5′-dinitro- ,,	194-195°	99.8	N, 5,48	5.41	Pale yellow small needles (ethanol)
IV →	IV′ 3-Bromo-3′,5,5′-trinitro- ,,	142-143°	99.7	N, 8.73	8.68	Colourless small needles (methanol)
VI →	VI′ 5-Bromo-3,5′-dinitro- ,,	113-114°	100	N, 6.41	6.38	Colourless granules (ether-ligroin)
VII →	VII′ 3,5′-Dibromo-3′,5-dinitro- ,,	147-148°	99.9	N, 5.44	5.41	Pale yellow rectangular plates (methanol)
IX →	IX′ 5-Bromo-3.3′5′,-trinitro- ,,	154-155°	98.2	N, 8.71	8.68	Pale yellow rectangular plates (methanol)
X →	X′ 5,5′-Dibromo- ,,	102-103°	100	Br, 37.21	37.34	Colourless needles (ethanol)
XI →	XI′ 5,5′-Dibromo-3,3′-dinitro- ,,	120-121°	100	N, 5.45	5.41	Colourless rectangular plates (ligroin)
XIV →	XIV′ 4,4′-Dinitro- ,,	155-156°	86.6	N, 7.83	7.78	Pale yellow rhombic plates (methanol)
XVII →	XVII′ 4,4′,6,6′-Tetranitro- ,,	165-166°	96.0	N, 12.50	12.45	Pale yellow rhombic plates (acetone-ethanol)

Table

Mono-methyl ethers	Derivatives of 2,2′-acetoxymethoxydiphenyl					Crystals and (their crystallizing solvents)
		M.p., (corr.)	Yield, %	Found, %	Calc., %	
I →	I′ 3-Bromo-5,5′-dinitro-derivative	160-161°	100	N, 6.94	6.82	Colourless needles (methanol)
V →	V′ 5-Bromo-3,5′-dinitro- ,,	170-171°	100	N, 6.99	6.82	Colourless rectangular plates (ethanol)
XIII →	XIII′ 4,4′-Dinitro- ,,	183-184°	98	N, 8.47	8.44	Pale yellow rhombic plates (methanol)
XVI →	XVI′ 4,4′,6,6-Tetranitro- ,,	157-158°	95	N, 13.25	13.28	Colourless small prisms (dilute ethanol)

acetic anhydride, and the reaction products separated out were washed with a cold dilute solution of caustic soda and then recrystallized from the suitable solvents. Among the experimental results thus obtained, those concerning the newly obtained compounds from the above-mentioned derivatives of biphenol and its monomethyl ether are as shown here in Tables 1 and 2.

1.

Solubility (e: easily soluble, m: moderately soluble, d: difficultly soluble: e > m > d.)									
Ligroin	Ether	Carbon tetra-chloride	Chloro-form	Benzene	Methanol	Ethanol	Acetone	Acetic acid	Ethyl acetate
d	d	e	e	e	m	m	e	m	e
d	d	e	e	e	m	m	e	e	e
d	d	m	e	e	m	m	e	e	e
d	e	e	e	e	e	e	e	e	e
d	e	e	e	e	m	m	e	e	e
d	d	e	e	e	m	e	e	e	e
d	e	e	e	e	m	m	e	e	e
d	e	e	e	e	e	e	e	e	e
d	m	e	e	e	e	m	m	e	e
d	d	d	e	e	d	d	e	e	e

2.

Solubility (e: easily soluble, m: moderately soluble, d: difficultly soluble: e > m > d.)									
Ligroin	Ether	Carbon tetra-chloride	Chloro-form	Benzene	Methanol	Ethanol	Acetone	Acetic acid	Ethyl acetate
d	m	e	e	e	m	m	e	e	e
d	d	e	e	e	m	m	e	e	e
d	d	m	e	e	m	m	e	m	e
d	m	e	e	e	m	m	e	e	e

Formation of the biphenylene oxides from the diacetoxydiphenyls. With the exception of 4,4′, 6,6′-tetranitro-2,2′-dihydroxydiphenyl, which was kept at about 170–180° on account of its unstability at higher temperature, the nitro and bromonitro derivatives of diacetoxydiphenyls were heated for 4 hours at about 200–210°, in mixing with dry barium carbonate; while diacetoxydiphenyl itself and its bromo derivatives were treated under the same condition with dry sodium carbonate because of their stability towards barium carbonate. The reaction products were treated with cold dilute hydrochloric acid, washed well with water and extracted with cold dilute solution of caustic soda, the biphenols formed being recovered. The residues were hydrolysed with hydrochloric acid in boiling acetone and again extracted with dilute caustic soda solution in order to remove the unacted diacetoxy compounds from the biphenylene oxides formed. The last compounds were recrystallized from suitable solvents. The experimental results thus obtained are as shown below in Tables 3, 4 and 5.

Tests of the opening of the furan-ring of the nitrobiphenylene oxides. The nitro derivatives of biphenylene oxide (0.3 g.) were finely pulverized, made into a paste with water and then suspended in a 5% solution of caustic soda (20 c.c.). These suspensions were treated for two hours under constant stirring at constant temperatures (20°, 40°, 60°, 80° and 100°), and the undissolved parts were filtered through

Table 3 (Acid-fixer: $BaCO_3$).

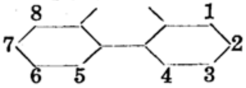
Nature and positions of substituents 	Diacetoxydiphenyls (unchanged) Yield (%)	Biphenols (formed) Yield (%)	Biphenylene oxides (formed) Yield (%)
2,4,5,6-Tetranitro-	XVII′ 0	XVII 100	0
1,3,6,8-Tetranitro-	0	0	99.1
1,3,6-Trinitro-	0	20.0	79.5
1,8-Dinitro-	0	1.0	98.5
1,6-Dinitro-	0	1.0	98.1
3,6-Dinitro-	0	3.6	95.1
2,7-Dinitro-	XIV′ 56.4	XIV 43.0	0
6-Bromo-1,3,8-trinitro-	IX′ 0	IX 0.6	IX″ 98.5
8-Bromo-1,3,6-trinitro-	IV′ 0	IV 9.8	IV″ 89.6
3-Bromo-1,6-dinitro-	VI′ 0	VI 2.6	VI″ 96.9
1-Bromo-3,6-dinitro-	II′ 0	II 20.4	II″ 79.0
3,6-Dibromo-1,8-dinitro-	XI′ 0	XI 5.9	XI″ 93.4
3,8-Dibromo-1,6-dinitro-	VII′ 0	VII 31.5	VII″ 67.7
1,8-Dibromo-3,6-dinitro-	III′ 0	III 79.4	III″ 19.8
1,3,6,8-Tetrabromo-	99.9	trace	0
3,6-Dibromo-	98.5	1.3	0
Unsubstituted	57.0	43.0	0

Table 4 (Acid-fixer: Na_2CO_3).

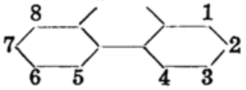
Nature and positions of substituents 	Diacetoxydiphenyls (unchanged) Yield (%)	Biphenols (formed) Yield (%)	Biphenylene oxides (formed) Yield (%)
1,3,6,8-Tetrabromo-	0	100	0
3,6-Dibromo-	0	100	0
Unsubstituted	0	100	0

Table 5. The properties of the bromonitrobiphenylene oxides.

Compounds	Crystals and (their crystallizing solvents)	M. p. (corr.)	N, %. Found,	N, %. Calc.	Br, %. Found,	Br, %. Calc.
IX″	Almost colourless rectangular plates (acetone-methanol)	264-265°	11.18	11.00	20.89	20.92
IV″	Almost colourless hexagonal plates (acetone-methanol)	295-296°	11.13	11.00	21.00	20.92
VI″	Almost colourless needles (acetone-methanol)	229-230°	8.42	8.31	23.99	23.71
II″	Colourless small hexagonal plates (acetone-ethanol)	297-298°	8.29	8.31	24.02	23.71
XI″	Colourless small rectangular plates (acetone)	317-318°	6.81	6.75	38.23	38.42
VII″	Almost colourless rectangular plates (acetone-methanol)	226-227°	6.88	6.75	38.57	38.42
III″	Colourless rectangular plates (acetone)	302-303°	6.66	6.75	38.72	38.42

Compounds	Solubility (e: easily soluble, m: moderately soluble, d: difficultly soluble: e > m > d.)									
	Ligroin	Ether	Carbon tetrachloride	Chloroform	Benzene	Methanol	Ethanol	Acetone	Acetic acid	Ethyl acetate
IX″	d	d	d	e	e	d	d	e	m	e
IV″	d	d	d	d	m	d	d	e	m	e
VI″	d	d	m	e	e	d	d	e	m	e
II″	d	d	m	e	e	d	d	e	m	e
XI″	d	d	d	d	d	d	d	d	d	d
VII″	d	d	d	e	e	d	d	e	e	e
III″	d	d	d	m	m	d	d	m	d	m

a glass filter, washed well with hot water, dried and weighed. The filtrates were acidified with hydrochloric acid, precipitating the corresponding nitro derivatives of *o,o′*-biphenol or their decomposition products. This alkaline treatment of the nitrobiphenylene oxides at lower temperature brought about no colour change of their undissolved parts, but the same treatment at higher temperature changed the undissolved parts of some compounds into pale orange substances. In consequence, the precipitates recovered from the dissolved parts of the nitrobiphenylene oxides are not always the corresponding nitrobiphenols. The quantitative estimation of such compounds, therefore, must be carried out at a comparatively lower temperature. The experimental results obtained are as shown here in Table 6.

Table 6.

Nitro-derivatives of biphenylene oxide	Percentages of the dissolved parts yielding the biphenols				
	at 20°C.	40°C.	60°C.	80°C.	100°C.
1,3,6,8-Tetranitro-	1.2	11.2	49.6	100	—
1,3,6,7-Tetranitro-	0.9	3.3	11.3	99.7	—
2,3,6,7-Tetranitro-	0.5	2.6	6.5	23.3	—
1,3,8-Trinitro-	0.7	3.0	10.0	43.4	—
1,3,6-Trinitro-	0.3	1.0	4.8	20.9	—
2,3,6-Trinitro-	0.1	0.4	1.0	4.0	35.7
1,8-Dinitro-	—	—	—	1.0	3.8
1,6-Dinitro-	—	—	—	0	2.1
3,6-Dinitro-	—	—	—	0	1.3
2,6-Dinitro-	—	—	—	0	0.9
2,7-Dinitro-	—	—	—	0	0.5

Summary.

(1) The influence of substitution on the formation of a furan-ring has been compared among *o′,o′*-biphenol and its nitro, bromonitro and bromo derivatives, the following results being obtained in the case of reactions between dry carbonate of barium or sodium and the diacetoxydiphenyls derived from those biphenols.

(i) The introduction of nitro groups into the diacetoxydiphenyls facilitates the removal of acetyl groups of those compounds and also the formation of the furan-ring. This facilitating effect varies with the relative position of the nitro group and the acetoxyl group, the order of the effect being ortho>para>meta; but the *m*-nitrosubstitution induces no ring-formation, giving exclusively nitrobiphenols.

(ii) The introduction of bromine into the diacetoxydiphenyls hinders the removal of the acetyl groups and also the formation of the furan-ring, no bromobiphenylene oxide being obtained. This effect is more remarkable in the case of *o*-substitution than in that of *p*-one relative to the acetoxyl groups.

(2) The effect of nitrosubstitution on the opening of the furan-ring of biphenylene oxide in caustic soda solution was also studied, and it was found that the introduction of the nitro groups facilitates the ring-opening, and this facilitating effect varies with the relative position of the nitro group and the oxygen atom of biphenylene oxide, the order of the effect being ortho>para>meta. This effect appears to be proportional to the electrolytic dissociation degree of nitrobiphenols obtainable from the nitrobiphenylene oxides.

(3) In the course of these experiments, two nitrobiphenols and seven bromonitrobiphenols were newly prepared.

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