Studies on the Derivatives of Biphenylene Oxide. VIII. Bromonitro-derivatives of Biphenylene Oxide.

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As to the bromonitro-derivatives of biphenylene oxide, four of them, i.e. 2-bromo-3-nitro-,(1) 3-bromo-2-nitro-, 6-bromo-2-nitro- and 7-bromo-2-nitro-biphenylene oxides,(2) were already obtained several years ago, and the present author also had recently the pleasure of adding ten more derivatives to them as discribed in Parts VI and VII,(3) namely the three of them i.e. 6-bromo-1-nitro-, 6-bromo-3-nitro- and 6-bromo-4-nitro-biphenylene oxides, were obtained by the direct bromination of the corresponding nitro compounds, and the rest, i.e. 1-bromo-3,6-dinitro-, 3-bromo-1,8-dinitro-, 1,8-dibromo-3,6-dinitro-, 3,6-dibromo-1,8-dinitro-, 3,8-dibromo-1,6-dinitro-, 6-bromo-1,3,8-trinitro- and 8-bromo-1,3,6-trinitro-biphenylene oxides, by the intramolecular furan-ring-formation in the corresponding bromonitrobiphenols.

Now, with a view to extend the research on the tendency of the nitro-substitution and, at the same time, to supplement the bromonitro-derivatives which could hardly be obtained either by the direct bromination of nitrobiphenylene oxides or by the intramolecular furan-ring-formation in the corresponding bromonitrobiphenols, the present author nitrated bromobiphenylene oxides and their lower nitro derivatives in the following schemes. Of the newly obtained derivatives, twenty-seven compounds (I～XXVII) are reported in this paper. They are:

6-Bromo-2,7-dinitro-	biphenylene	oxide	(I)	M.p. (corr.)	254–255°
6-Bromo-2,3,7-trinitro-	"	"	(II)	"	254–255°
6-Bromo-2,3,5,7-tetranitro-	"	"	(III)	"	278–279°
6-Bromo-3,7-dinitro-	"	"	(IV)	"	216–217°
6-Bromo-1,3,7-trinitro-	"	"	(V)	"	251–252°
6-Bromo-1,3,5,7-tetranitro-	"	"	(VI)	"	285–286°
6-Bromo-4,7-dinitro-	"	"	(VII)	"	198–199°
6-Bromo-2,4,5,7-tetranitro-	"	"	(VIII)	D.p. (corr.)	329°
7-Bromo-2,6-dinitro-	"	"	(IX)	M.p. (corr.)	223–224°
7-Bromo-3,6-dinitro-	"	"	(X)	"	254–255°
7-Bromo-2,3,6-trinitro-	"	"	(XI)	"	248–249°
3,6-Dibromo-2-nitro-	"	"	(XII)	"	190–191°
3,6-Dibromo-2,7-dinitro-	"	"	(XIII)	"	297–298°
3,6-Dibromo-4-nitro-	"	"	(XIV)	"	245–247°
3,6-Dibromo-4,7-dinitro-	"	"	(XV)	"	273–274°

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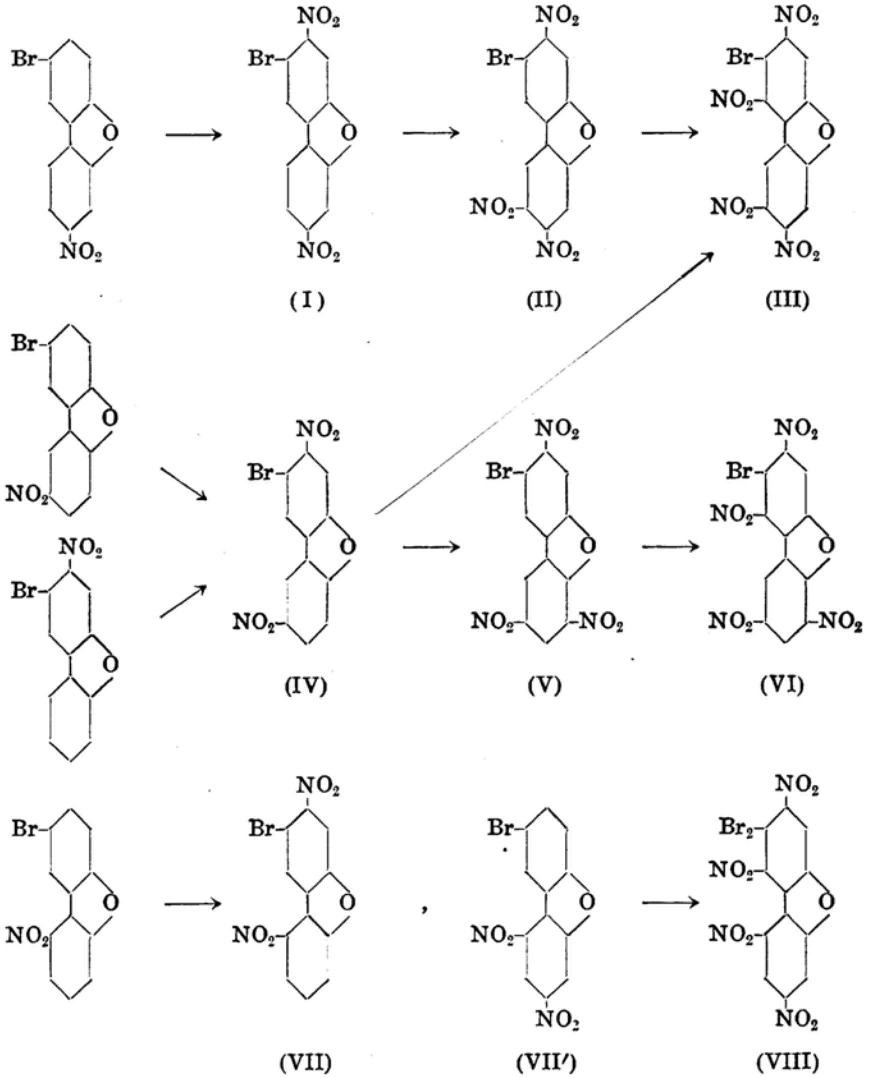
(1) K. Tatematsu and B. Kubota, *This Bulletin*, **9** (1934), 456.

(2) H. Gilman, G. E. Brown, W. G. Bywater and W. H. Kirkpatrick, *J. Am. Chem. Soc.*, **56** (1934), 3473–7.

(3) S. Yamashiro, *This Bulletin*, **16** (1941), 68; **17** (1942), 10.

3,6-Dibromo-2,4,7-trinitro-	"	"	(XVI)	"	275–276°
3,6-Dibromo-2,4,5,7-tetranitro-	"	"	(XVII)	"	*352–354°
3,6-Dibromo-1,2,8-trinitro-	"	"	(XVIII)	"	334–334.5°
2,6-Dibromo-3-nitro-	"	"	(XIX)	"	205–206°
2,6-Dibromo-7-nitro-	"	"	(XX)	"	209–210°
2,6-Dibromo-3,7-dinitro-	"	"	(XXI)	"	262–263°
2,6-Dibromo-3,5,7-trinitro-	"	"	(XXII)	"	257–258°
1,8-Dibromo-2,3,6-trinitro-	"	"	(XXIII)	"	297–298°
2,3,6-Tribromo-4,7-dinitro-	"	"	(XXIV)	"	256–257°
2,3,6,7-Tetrabromo-4,5-dinitro-	"	"	(XXV)	"	*364–365°
1,3,6,7-Tetrabromo-2,5-dinitro-	"	"	(XXVI)	"	329–330°
1,3,6,7-Tetrabromo-2,8-dinitro-	"	"	(XXVII)	"	297–298°



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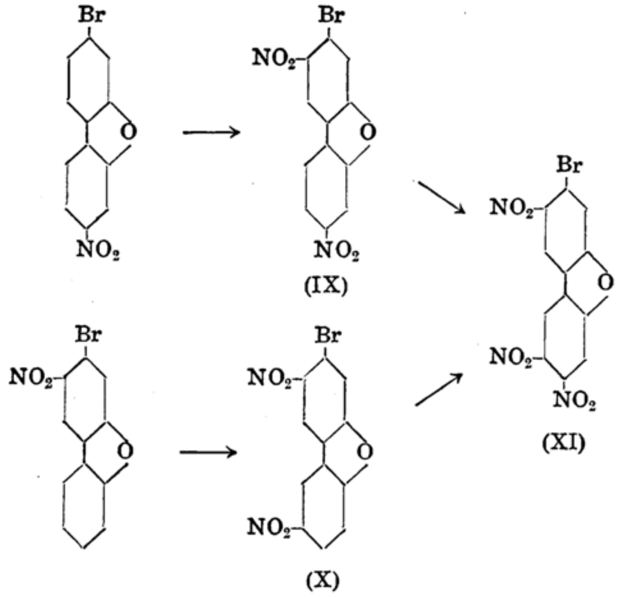
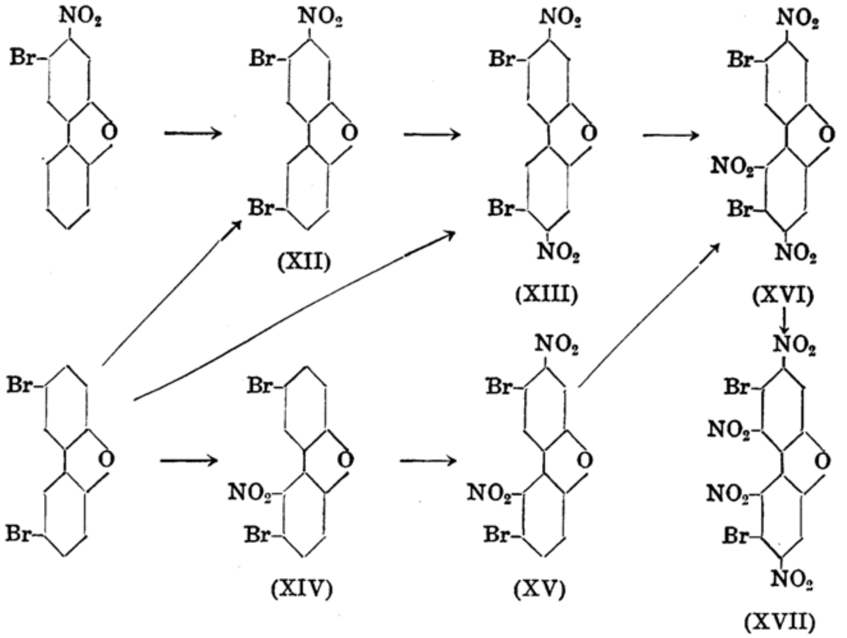
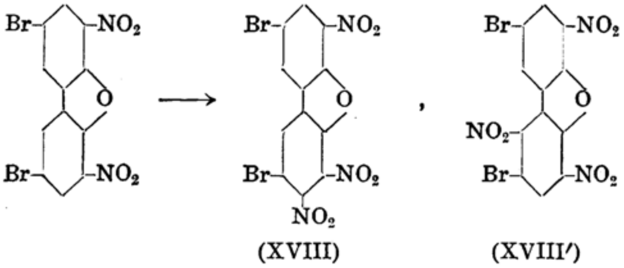
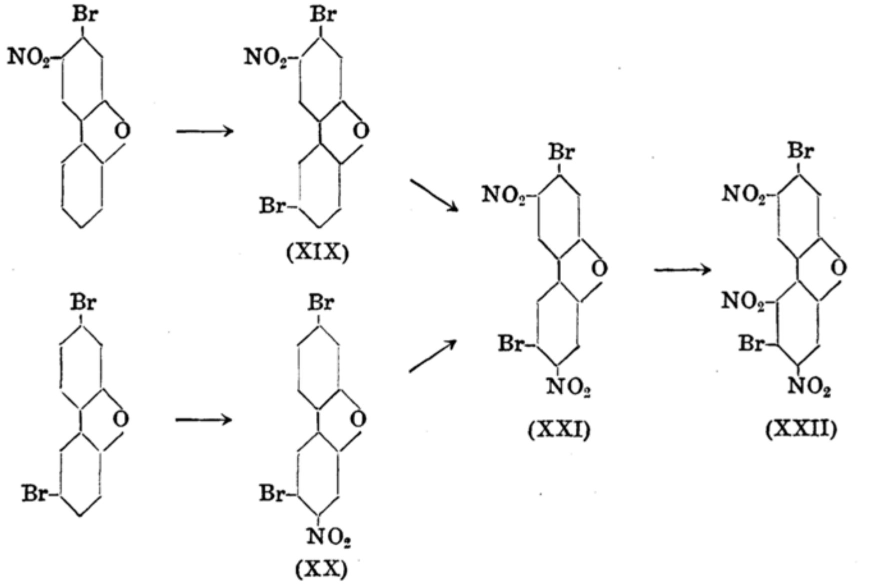
* With decomp.


Br
NO2
O
(IX)
(X)
(XI)


NO2
Br
O
(XII)
(XIII)
(XIV)
(XV)
(XVI)
(XVII)


Br
NO2
O
(XVIII)
(XVIII′)

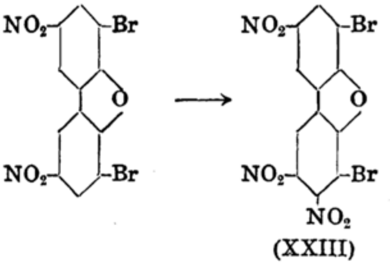


(XIX)

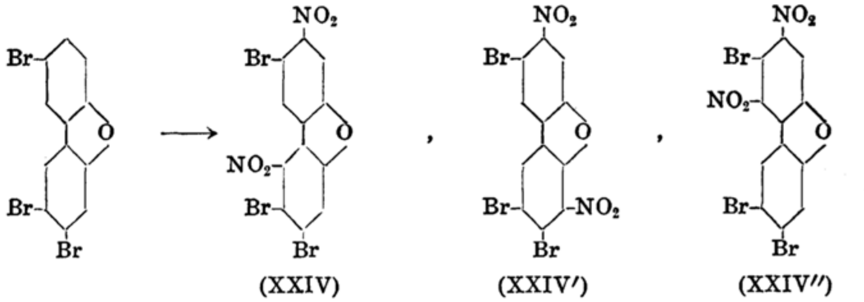
(XX)

(XXI)

(XXII)



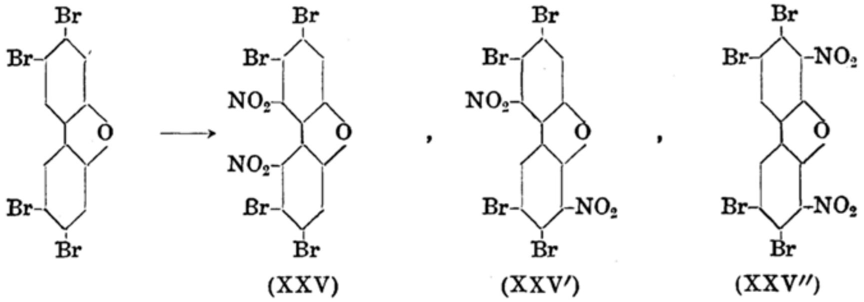
(XXIII)



(XXIV)

(XXIV′)

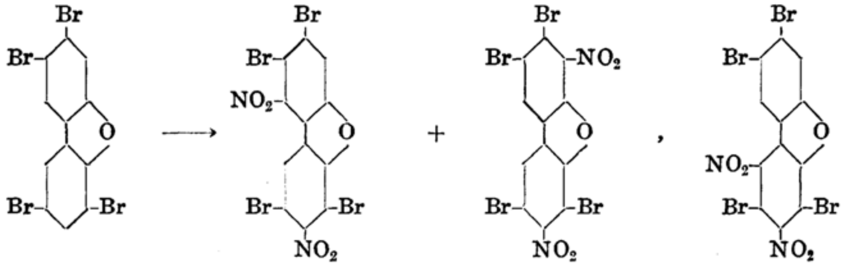
(XXIV″)



(XXV)

(XXV′)

(XXV″)



(XXVI) (XXVII) (XXVII′)

The constitutions of these compounds were mainly established by the following facts:

(1) Of the positions of biphenylene oxide, 2(7) and 3(6) are more active than 1(8) and 4(5) for the introduction of nitro groups. This fact excludes the formula XVIII′.

(2) The nitro groups and the nitro- or bromonitro-phenylene residues of the nitro- or bromonitro-biphenylene oxides exert generally the *m*-directing influence on the further introduction of nitro groups, while bromine and the bromophenylene residues of the bromo- or bromonitro-biphenylene oxides, the *o,p*-directing influence on the introduction of the same groups. And it must be noticed that this fact occurs only when it is compatible with the fact (1).

(3) The nitro groups introduced are found, in many cases, to be distributed evenly between both phenylene residues of biphenylene oxide. This fact excludes the formulas VII′, XXIV″ and XXVII′.

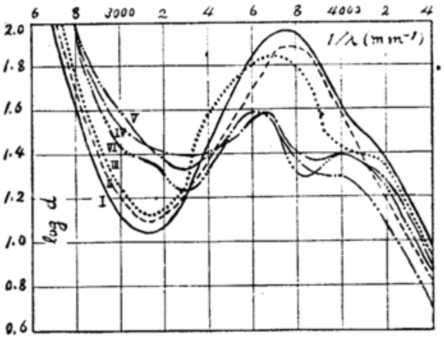
(4) When the nitro group already occupies the position 2 or 3, the further nitro-substitution does not take place at the position 1 or 4 respectively in correspondence with that 2 or 3. And when the nitro groups already occupy the positions 1 and 3, the further introduction of the same group does not occurs at the position 2, though it takes place at the same position when the position 3 alone is already occupied by the nitro group.

(5) The nitro-substitution hardly takes place at the position 1 of the 2-bromo-3-nitrophenylene residue, whereas the same reaction occurs without too much difficulty at the position 4 of the 3-bromo-2-nitrophenylene residue, even though they contradict to the general rule (2), it is because of the compound XI which did not give any higher nitro derivative, while the compounds II, V and XIII gave the compounds III, VI and XVIII respectively as the higher nitro derivatives. This fact admits no dispute about the formula XXII, and also enables us to infer that the nitro-substitution will occur more readily at the position 4 than at the position 1 of the 2,3-dibromophenylene residue. From this reason the formulas XXIV′ and XXV″ are excluded.

Of the dinitro derivatives of 1,3,6,7-tetrabromobiphenylene oxide, the higher melting one should be the 2,5-dinitro compound XXVI, and the lower melting one, the 2,8-dinitro compound XXVII, because the former is the main product and the latter, a by-product.

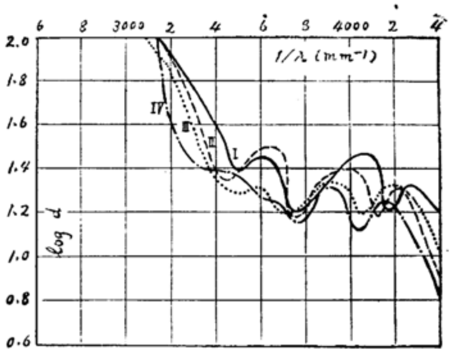
For the benefit of the confirmation of the constitutions of those bromo-nitrobiphenylene oxides, the absorption curves of those compounds were compared with those of the corresponding nitro compounds and the related bromo-nitrobiphenylene oxides as in Figs. 1~15.

Absorption curves of the derivatives of biphenylene oxide.
M/10000 alcoholic solutions.



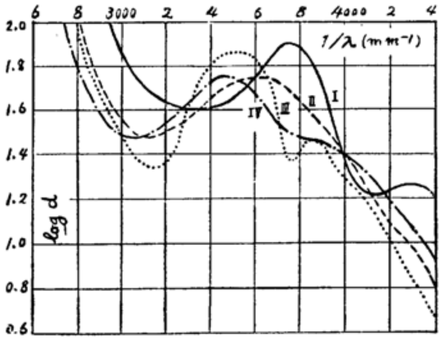
I 2-Nitro derivative.
II 6-Bromo-2-nitro derivative.
III 7-Bromo-2 nitro derivative.
IV 3-Bromo-2-nitro derivative.
V 3,6-Dibromo-2-nitro derivative.
VI 3,7-Dibromo-2-nitro derivative.

Fig. 1.



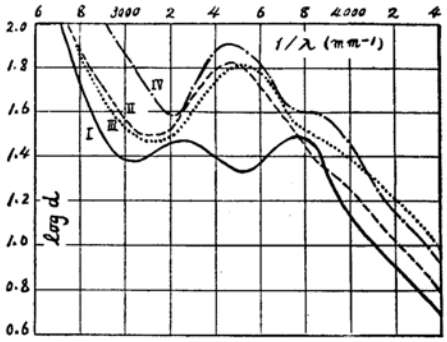
I 3-Nitro derivative.
II 6-Bromo-3-nitro derivative.
III 2-Bromo-3-nitro derivative.
IV 2,6-Dibromo-3-nitro derivative.

Fig. 2.



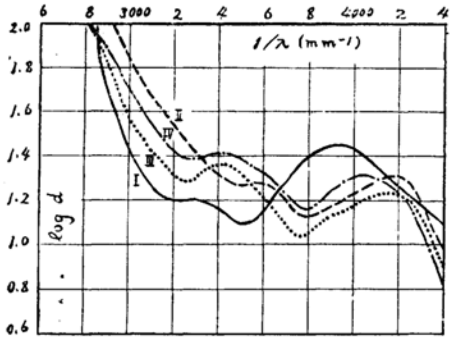
I 1,8-Dinitro derivative.
II 3,6-Dibromo-1,8-dinitro derivative.
III 2,3,6,7-Tetrabromo-4,5-dinitro ,, .
IV 3,6-Dibromo-1,2,8-trinitro ,, .

Fig. 3.



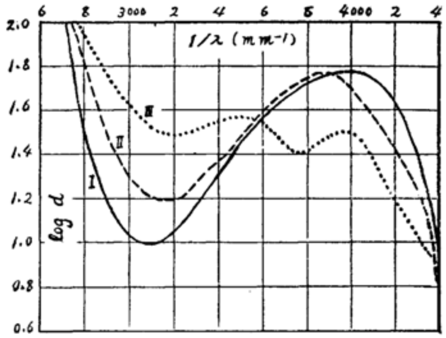
I 6-Bromo-4,7-dinitro derivative.
II 3,6-Dibromo-4,7-dinitro derivative.
III 2,3,6-Tribromo-4,7-dinitro derivative.
IV 2,3,6,8-Tetrabromo-4,7-dinitro ,, .

Fig. 4.



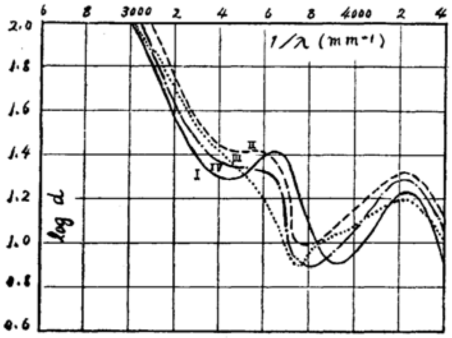
I 2,6-Dinitro derivative.
II 3-Bromo-2,6-dinitro derivative.
III 7-Bromo-2,6-dinitro derivative.
IV 3,7-Dibromo-2,6-dinitro derivative.

Fig. 5.



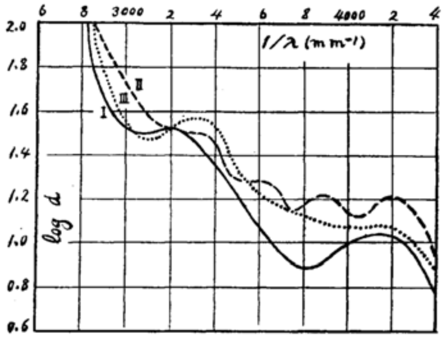
I 2,7-Dinitro derivative.
II 6-Bromo-2,7-dinitro derivative.
III 3,6-Dibromo-2,7-dinitro derivative.

Fig. 6.



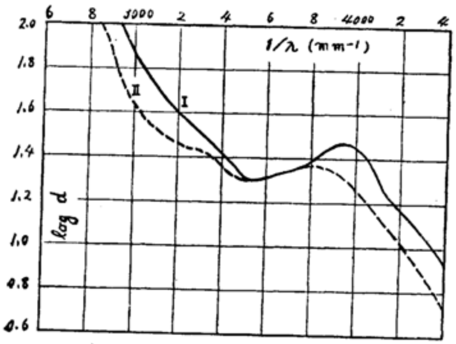
I 3,6-Dinitro derivative.
II 1-Bromo-3,6-dinitro derivative.
III 7-Bromo-3,6-dinitro derivative.
IV 1,8-Dibromo-3,6-dinitro derivative.

Fig. 7.



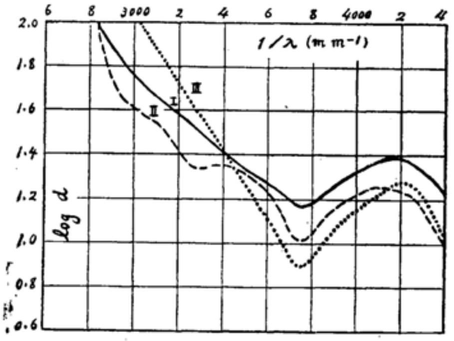
I 1,3,6,7-Tetranitro derivative.
II 6-Bromo-1,3,7-trinitro derivative.
III 6-Bromo-1,3,5,7-tetranitro derivative.

Fig. 8.



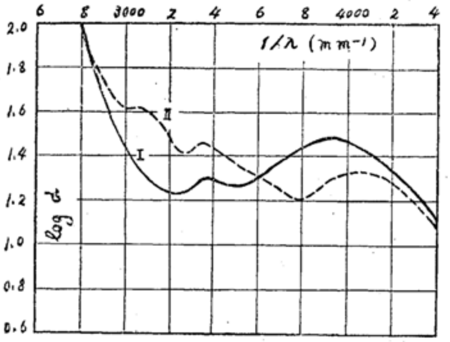
I 1,3,8-Trinitro derivative.
II 6-Bromo-1,3,8-trinitro derivative.

Fig. 9.



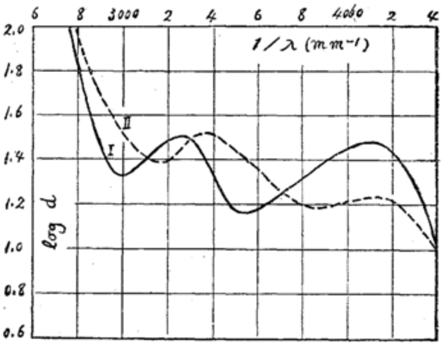
I 2,3,6-Trinitro derivative.
II 7-Bromo-2,3,6-trinitro derivative.
III 1,8-Dibromo-2,3,6-trinitro derivative.

Fig. 10.



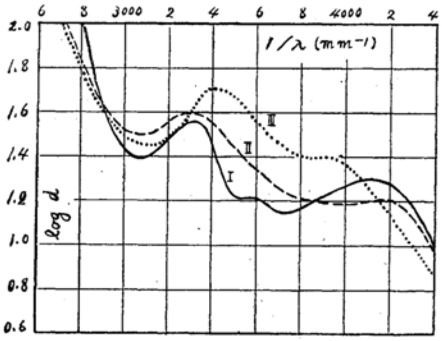
I 2,3,7-Trinitro derivative.
II 6-Bromo-2,3,7-trinitro derivative.

Fig. 11.



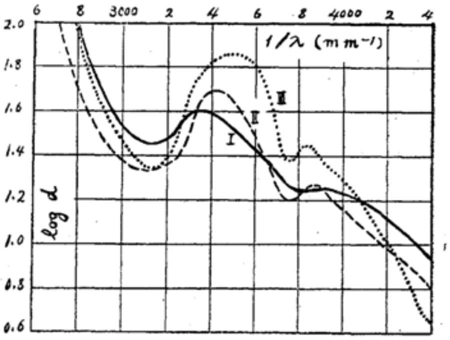
I 3,5,7-Trinitro derivative.
II - 2,6-Dibromo-3,5,7-trinitro derivative.

Fig. 12.



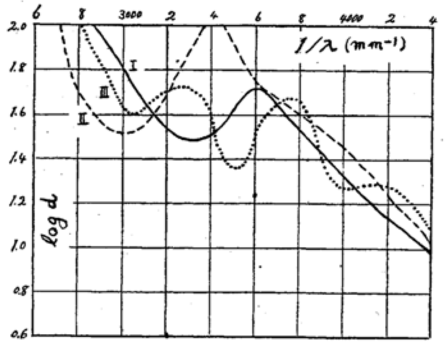
I 2,4,6,7-Tetranitro derivative.
II 3-Bromo-2,4,6,7-tetranitro derivative.
III 3,6-Dibromo-2,4,7-trinitro derivative.

Fig. 13.



I 6-Bromo-2,4,5,7-tetranitro derivative.
II 3,6-Dibromo-2,4,5,7-tetranitro ,, .
III 2,3,6,7-Tetrabromo-4,5-dinitro ,, .

Fig. 14.



I 3,6-Dibromo-4-nitro derivative.
II 6-Bromo-4-nitro derivative.
III 6-Bromo-1-nitro derivative.

Fig. 15.

The absorption curves of 1,6-dinitro- and 1,3,6-trinitro-biphenylene oxides have already been compared in Part V with those of their bromo-derivatives.

From the comparison among the curves in Figs. 1 and 2, especially in the former, it may be found that the bromo-substitution in the nitro-biphenylene oxides shifts and deforms the curves of the parent compounds, and that those effects of bromine are greater when the substitution takes place in the nitro-phenylene residues, than when it does in the phenylene residues which have no nitro group. These effects, however, are not so remarkable as to change completely the curves of the parent compounds, therefore, the curves in each of the above figures are liable to resemble to each other in some degree. In fact, the curve of the compound XIV, which was regarded as 3,6-dibromo-4-nitrobiphenylene oxide, resembles more closely to that of 6-bromo-4-nitrobiphenylene oxide, than to that of 6-bromo-1-nitrophenylene oxide in Fig. 15. And the curve of the compound XXV, which was regarded as 2,3,6,7-tetrabromo-4,5-dinitrobiphenylene oxide, resembles indeed more closely to those of the derivatives of 4,5-dinitrobiphenylene oxide in Fig. 14, rather than to those of the derivatives of 1,8-dinitrobiphenylene oxide in Fig. 3.

As seen from the comparison of the curves in Figs. 4 and 6, 6-bromo-4,7-dinitro and 3,6-dibromo-2,7-dinitro-biphenylene oxides have exceptionally special curves. But a certain resemblance can be found when both of these curves are compared with that of 3-bromo-2-nitrobiphenylene oxide, a parent compound, in Fig. 1.

Experimental.

(1) **Nitro-derivatives of 3-bromobiphenylene oxyde.** 6-*Bromo*-2,7-*dinitrobiphenylene oxide* (I). 6-Bromo-2-nitrobiphenylene oxide (5.28 g.) was dissolved in hot fuming nitric acid (d=1.45; 200 c.c.), and after being kept on standing 20 minutes the reaction mixture was poured into ice, when pale yellow precipitates separated out. The reaction product (6.67 g.) was recrystallized from acetic acid, into pale yellow needles, m.p. 254–255° (corr.) (Yield 4.45 g. Found: N, 8.25; Br, 23.58. Calc. for $C_{12}H_5OBr(NO_2)_2$: N, 8.31; Br, 23.71%). It is readily soluble in acetone and chloroform, and fairly in benzene, acetic acid and ethyl acetate, and sparingly in alcohols, carbon tetrachloride, ether and ligroin.

6-*Bromo*-2,3,7-*trinitrobiphenylene oxide* (II). 6-Bromo-2,7-dinitrobiphenylene oxide (2 g.) was dissolved in warm fuming nitric acid (d=1.52; 10 c.c.), and when the reaction mixture was diluted with ice, pale yellow precipitates separated out. The reaction product (2.42 g.) was extracted with ethanol, and the residue was recrystallized from acetic acid into pale yellow short needles, m.p. 254–255° (corr.) (Yield 1.2 g. Found: N, 11.14; Br, 20.97. Calc. for $C_{12}H_4OBr(NO_2)_3$: N, 11.00; Br, 20.92%). It is readily soluble in acetone, fairly in benzene, acetic acid and ethyl acetate, and sparingly in alcohols, chloroform, carbon tetrachloride, benzene, ether and ligroin.

6-*Bromo*-2,3,5,7-*tetranitrobiphenylene oxide* (III). 6-Bromo-2,3,7-trinitrobiphenylene oxide (1 g.) was heated for one hour with fuming nitric acid (d=1.52; 10 c.c.) on the water-bath, and when the reaction mixture was poured into ice, white precipitates separated out. The reaction product (0.9 g.) was recrystallized from acetone into almost colourless hexagonal plates, m.p. 278–279° (corr.) (Yield 0.7 g. Found: N, 13.21; Br, 16.84. Calc. for $C_{12}H_3OBr(NO_2)_4$: N, 13.12; Br, 16.93%). The same compound was also isolated from the nitration products of 6-bromo-3,7-dinitrobiphenylene oxide. It is readily soluble in acetone and ethyl acetate, fairly in benzene and acetic acid, and sparingly in alcohols, chloroform, carbon tetrachloride, ether and ligroin.

6-*Bromo*-3,7-*dinitro*-(or 3-*bromo*-2,6-*dinitro*-) *biphenylene oxide* (IV). (i) 6-Bromo-3-nitrobiphenylene oxide (4 g.) was dissolved in warm nitric acid (d=1.45; 100 c.c.), and the reaction product separated out on dilution was recrystallized from acetic acid into pale yellow needles, m.p. 216–217° (corr.) (Yield 4.2 g. Found: N, 8.33; Br, 23.76. Calc. for $C_{12}H_5OBr(NO_2)_2$: N, 8.31; Br, 23.71%). It is readily soluble in acetone, acetic acid, benzene, chloroform and ethyl acetate, and fairly in alcohols, carbon tetrachloride, ether and ligroin.

(ii) 3-Bromo-2-nitrobiphenylene oxide (2 g.), which was obtained from 3-amido-2-nitrobiphenylene oxide by the Sandmeyer's diazo-reaction, was dissolved in warm nitric acid (d=1.45; 30 c.c.), and the reaction product, separated out on dilution, was recrystallized from acetic acid into pale yellow needles melting at 216–217° (corr.) (Yield 2.1 g.). No depression of its melting point was observed when it was mixed with the bromodinitrobiphenylene oxide obtained from 6-bromo-3-nitrobiphenylene oxide.

6-*Bromo*-1,3,7-*trinitro*- (V) and 6-*bromo*-2,3,5,7-*tetranitro* (or 3-*bromo*-2,4,6,7-*tetranitro*)- (III)-*biphenylene oxides*. 6-Bromo-3,7-dinitrobiphenylene oxide (3 g.) was heated for one hour on the water-bath with nitric acid (d=1.52; 30 c.c.), and the reaction product (2.9 g.) separated out on dilution was recrystallized from acetic acid into colourless small prismatic needles, m.p. 251–252° (corr.) (Yield 0.2 g. Found: N, 10.91; Br, 20.78. Calc. for $C_{12}H_4OBr(NO_2)_3$: N, 11.00; Br, 20.92%). It is readily soluble in acetone, benzene and ethyl acetate, fairly in alcohols and acetic acid, and sparingly in chloroform, carbon tetrachloride, ether and ligroin. The dissolved part was recovered from the acetic mother-liquor and extracted with ethanol and cloroform. And the residue was recrystallized from a mixture of acetone and ethanol, colourless plates melting at 278–279° (corr.) (Yield 0.6 g.). The latter compound is identical in all respects with the bromotetranitrobiphenylene oxide obtained from 6-bromo-2,3,7-trinitrobiphenylene oxide as above described.

6-*Bromo*-1,3,5,7-*tetranitrobiphenylene oxide* (VI). 6-Bromo-1,3,7-trinitrobiphenylene oxide (0.2 g.) was heated for 2 hours with a large excess of nitric acid (d=1.52). The reaction product (0.21 g.) separated out on dilution was recrystallized from benzene into colourless micro rectangular plates, m.p. 285–286° (corr.) (Yield 0.18 g. Found: N, 13.22; Br, 16.89. Calc. for $C_{12}H_3OBr(NO_2)_4$: N, 13.12; Br, 16.93%). It is readily soluble in acetone and ethyl acetate, fairly in benzene and acetic acid, and sparingly in alcohols, chloroform, carbon tetrachloride, ether and ligroin.

6-*Bromo*-4,7-*dinitrobiphenylene oxide* (VII). When 6-Bromo-4-nitrobiphenylene oxide (2 g.) was treated for 1 hour with a large excess of warm nitric acid (d=1.45), the large crystals of this oxide perfectly changed into micro needles. These needle crystals were separated from the reaction mixture on cooling, and extracted with carbon tetrachloride to the removal of higher nitro-derivatives. The extract was evaporated to dryness and the residue was recrystallized from acetone-ethanol into pale yellow needles, m.p. 198–199° (corr.) (Yield 1.6 g. Found: N, 8.58; Br, 23.53. Calc. for $C_{12}H_5OBr(NO_2)_2$: N, 8.31; Br, Br, 23.71%). It is readily soluble in acetone, benzene, chloroform and ethyl acetate, fairly in acetic acid, carbon tetrachloride and ethanol, and sparingly in ether, ligroin and methanol.

6-*Bromo*-2,4,5,7-*tetranitrobiphenylene oxide* (VIII). 6-Bromo-4,7-dinitrobphenylene oxide (1.5 g.) was strongly nitrated by being heated for 1 hour with fuming nitric acid (d=1.52; 15 c.c.), and the reaction product (1.3 g.) separated out on dilution was recrystallized from acetone into colourless rectangular plates, d.p. 329° (corr.) (Yield 0.9 g. Found: N, 13.29; Br, 16.88. Calc. for $C_{12}H_3OBr(NO_2)_4$: N, 13.12; Br, 16.93%). It is sparingly soluble in the ordinary organic solvents except acetone and ethyl acetate which dissolve it fairly.

(2) Nitro-derivatives of 2-bromobiphenylene oxide. 7-*Bromo*-2,6-*dinitrobiphenylene oxide* (IX). 7-Bromo-2-nitrobiphenylene oxide (2 g.) was dissolved in warm nitric acid (d=1.45; 20 c.c.), and the crystals of the reaction product separated on cooling and recrystallized from acetic acid into pale yellow needles melting at 223–224° (corr.) (Yield 1.9 g. Found: N, 8.27; Br, 23.62. Calc. for $C_{12}H_5OBr(NO_2)_2$: N, 8.31; Br, 23.71%). It is readily soluble in acetone, benzene, chloroform and ethyl acetate, fairly in alcohols, acetic acid and carbon tetrachloride, and difficultly in ether and ligroin.

7-Bromo-3,6-dinitrobiphenylene oxide (X). 2-Bromo-3-nitrobiphenylene oxide (2 g.), which was obtained from 2-amido-3-nitrobiphenylene oxide by the Sandmeyer's reaction according to B. Kubota and his co-worker(1), was treated for half an hour with warm nitric acid (d=1.45; 20 c.c.), and the reaction product (2.15 g.) separated out on dilution was recrystallized from acetone-ethanol into yellow needles melting at 254–255° (corr.) (Yield 1.2 g. Found: N, 8.36; Br, 23.59. Calc. for $C_{12}H_5OBr(NO_2)_2$: N, 8.31; Br, 23.71%). It is readily soluble in acetone, benzene, chloroform and ethyl acetate, and sparingly in alcohols, acetic acid, carbon tetrachloride, ether and ligroin.

7-Bromo-2,3,6-trinitrobiphenylene oxide (XI). (i) 7-Bromo-2,6-dinitrobiphenylene oxide (2.5 g.) was dissolved in warm nitric acid (d=1.52; 25 c.c.), and, after being kept on standing for 1 hour, the reaction mixture was poured into water. The reaction product (2.4 g.) was separated and recrystallized from acetic acid into pale yellow prismatic needles melting at 248–249° (corr.) (Yield 1.1 g. Found: N, 11.24; Br, 20.74. Calc. for $C_{12}H_4OBr(NO_2)_3$: N, 11.00; Br, 20.92%). It is readily soluble in acetone, benzene, chloroform and ethyl acetate, fairly in alcohols and acetic acid, and sparingly in ether, ligroin and carbon tetrachloride. This bromotrinitro compound gives no higher nitro derivative even when it is boiled with a large excess of fuming nitric acid (d=1.52).

(ii) 7-Bromo-3,6-dinitrobiphenylene oxide (1 g.) was strongly nitrated with fuming nitric acid (d=1.52), and the reaction product (1.1 g.) separated out on dilution was recrystallized from acetic acid into pale yellow prismatic needles melting at 248–249° (corr.) (Yield 0.9 g.). When it was mixed with the corresponding compound obtained from 7-bromo-2,6-dinitrobiphenylene oxide no depression of its melting point was observed.

(3) Nitro-derivatives of 3,6-dibromobiphenylene oxide. *3,6-Dibromo-2-nitrobiphenylene oxide* (XII). When 3-Bromo-2-nitrobiphenylene oxide (1 g.) was heated for 12 hours with a large excess of bromine (2 g.) in boiling acetic acid (20 c.c.) the colour of bromine disappeared. The reaction product (1.25 g.) separated out on dilution was recrystallized from acetic acid into pale yellow needles, m.p. 190–191° (corr.) (Yield 1.1 g. Found: N, 3.84; Br, 42.87. Calc. for $C_{12}H_5OBr_2NO_2$: N, 3.78; Br, 43.08%). It is readily soluble in acetone, benzene, chloroform and ethyl acetate, fairly in acetic acid and carbon tetrachloride, and sparingly in alcohols, ether and ligroin. It can also be obtained as below from 3,6-dibromobiphenylene oxide.

3,6-Dibromo-2,7-dinitrobiphenylene oxide (XIII). (i) 3,6-Dibromo-biphenylene oxide (3 g.) was treated for 1 hour with a large excess of warm nitric acid (d=1.45). The undissolved part of the reaction product was separated on cooling from the reaction mixture and extracted with acetone-alcohol to the removal of the unacted dibromo-compound. The residue was then recrystallized from acetic acid into pale yellow prisms, m.p. 297–298° (corr.) (Yield 2.5 g. Found: N, 6.53; Br, 38.59. Calc. for $C_{12}H_4OBr_2(NO_2)_2$: N, 6.74; Br, 38.42%.). It is fairly soluble in acetone, benzene, chloroform and ethyl acetate, and sparingly in alcohols, acetic acid, carbon tetrachloride, ether and ligroin.

(ii) 3,6-Dibromo-2-nitrobiphenylene oxide (0.5 g.) was treated for half an hour with a large excess of warm nitric acid (d=1.45). The undissolved part (0.35 g.) of the reaction product was separated on cooling and extracted with carbon tetrachloride to the removal of the unacted dibromonitro-compound, and the residue was successively recrystallized from acetone and acetic acid into pale yellow prisms, m.p. 297–298° (corr.). It is identical in all respects with the corresponding compound obtained from 3,6-dibromobiphenylene oxide.

3,6-*Dibromo-2-nitro* (XII)- and 3,6-*dibromo-4-nitro* (XIV)-*biphenylene oxides.* Finely pulverized 3,6-dibromobiphenylene oxide (22 g.) was treated for 1 hour at about 50° with warm nitric acid (d=1.45; 50 c.c.), and the undissolved part (25.7 g.) of the reaction product was fractionated by the successive extractions with acetone. The readily soluble part was again extracted with acetic acid, and the dissolved part was recrystallized from the same solvent into pale yellow needles melting at 190–191° (corr.) (Yield 12 g.). It is identical with the corresponding compound obtained by the bromination of 3-bromo-2-nitrobiphenylene oxide, and, therefore, it must be 3,6-dibromo-2-nitrobiphenylene oxide. The sparingly soluble part (1.5 g.) of the reaction product was recrystallized from benzene into pale yellow needles, m.p. 245–247° (corr.) (Yield 1.03 g. Found: N, 3.55; Br, 44.05. Calc. for $C_{12}H_5OBr_2NO_2$: N, 3.78; Br, 43.08%). It is sparingly soluble in the ordinary organic solvents except benzene and chloroform which dissolve it fairly. The latter product should be 3,6-dibromo-4-nitrobiphenylene oxide, but not 3,6-dibromo-1-nitrobiphenylene oxide, because the product gives 3,6-dibromo-2,4,7-trinitrobiphenylene oxide on further nitration.

3,6-*Dibromo-4,7-dinitrobiphenylene oxide* (XV). 3,6-Dibromo-4-nitrobiphenylene oxide (0.7 g.) was heated for half an hour on the water-bath with a large excess of nitric acid (d=1.45), and the reaction product was recrystallized from acetone into colourless rectangular plates, m.p. 273–274° (corr.) (Yield 0.5 g. Found: N, 6.71; Br, 38.47. Calc. for $C_{12}H_4OBr_2(NO_2)_2$: N, 6.75; Br, 38.42%).

3,6-*Dibromo-2,4,7-trinitrobiphenylene oxide* (XVI). (i) 3,6-Dibromobiphenylene oxide (3.26 g.) was dissolved in warm nitric acid (d=1.52; 40 c.c.), and, after being kept on standing half an hour, the reaction mixture was diluted with water, then the colourless precipitates separated out. The reaction product (4.66 g.) was repeatedly recrystallized from acetone-methanol into colourless small hexagonal plates, m.p. 275–276° (corr.) (Yield 2.9 g. Found: N, 9.01; Br, 34.73. Calc. for $C_{12}H_3OBr_2(NO_2)_3$: N, 9.12; Br, 34.67%). It is readily soluble in acetone, benzene, chloroform and ethyl acetate, fairly in acetic acid and carbon tetrachloride, and sparingly in alcohols, ether and ligroin.

(ii) When 3,6-Dibromo-2,7-dinitrobiphenylene oxide (1 g.) was dissolved in warm nitric acid (d=1.52; 10 c.c.), and the reaction mixture was diluted with water, the colourless precipitates separated out. The reaction product (1.1 g.) was recrystallized from acetone-methanol into colourless hexagonal plates melting at 275–276° (corr.) (Yield 0.8 g. Found: N, 9.27; Br, 34.49. Calc. for $C_{12}H_3OBr_2(NO_2)_3$: N, 9.12; Br, 34.67%). It is identical in all respects with the corresponding compound obtained as described above by the direct nitration of 3,6-dibromobiphenylene oxide.

(iii) 3,6-Dibromo-4,7-dinitrobiphenylene oxide was dissolved in a large excess of warm nitric acid (d=1.52), and the reaction mixture was treated as in the case (i). The reaction product recrystallized from acetone-methanol is identical in all respects with the dibromotrinitrobiphenylene oxide which was obtained from 3,6-dibromo-2,7-dinitrobiphenylene oxide.

3,6-*Dibromo-2,4,5,7-tetranitrobiphenylene oxide* (XVII). 3,6-Dibromo-2,4,7-trinitrobiphenylene oxide (1 g.) was heated for 1 hour on the water-bath with nitric acid (d=1.52; 10 c.c.), and the reaction product (0.7 g.) separated out on dilution was recrystallized from acetone-ethanol into colourless needles melting at 352–354° (corr.) with decomposition, (Yield 0.5 g. Found: N, 10.95; Br, 31.42. Calc. for $C_{12}H_2OBr_2(NO_2)_4$ N, 11.07; Br, 31.59%). It is readily soluble in acetone, benzene and ethyl acetate, and sparnigly in the other ordinary organic solvents.

3,6-*Dibromo-1,2,8-trinitrobiphenylene. oxide* (XVIII). 3,6-Dibromo-1,8-dinitrobiphenylene oxide (1 g.) was dissolved in a large excess of warm nitric acid (d 1.52; 20 c.c.), and the reaction product (1.07 g.) separated out on dilution was recrystallized from acetone into colourless leaflets melting at 334–334.5° (corr.) with decomposition (Yield 1.0 g. Found: N, 8.99; Br, 34.79. Calc. for $C_{12}H_3OBr_2(NO_2)_3$: N, 9.12; Br, 34.67%). It is sparingly soluble in the ordinary organic solvents except acetone which dissolves it fairly.

(4) Nitro-derivatives of 2,6-dibromobiphenylene oxide. 2,6-*Dibromo*-3-*nitrobiphenylene oxide* (XIX). When 2-Bromo-3-nitrobiphenylene oxide (2.92 g.) was heated for 20 hours with a large execss of bromine (4 g.) in boiling acetic acid (30 c.c.), the colour of bromine disappeared. The reaction product separated out on dilution was recrystallized from acetone-ethanol into yellow prisms melting at 205–206° (corr.) (Yield 3.5 g. Found: N, 3.75; Br, 43.20. Calc. for $C_{12}H_5OBr_2NO_2$: N, 3.78; Br, 43.08%). It is sparingly soluble in alcohols, and readily in the other ordinary organic solvents.

2,6-*Dibromo*-7-*nitrobiphenylene oxide* (XX). 2,6-Dibromobiphenylene oxide (1.63 g.) was dissolved in glacial acetic acid (25 c.c.), and, after addition of nitric acid (d=1.52; 2.5 c.c.), the mixture was heated on the water-bath. The reaction product separated out on dilution was recrystallized from ethanol into pale yellow needles melting at 209–210° (corr.) (Yield 0.9 g. Found: N, 3.80; Br, 43.21. Calc. for $C_{12}H_5OBr_2NO_2$: N, 3.78; Br, 43.08%). It is readily soluble in acetone, acetic acid, benzene, chloroform, carbon tetrachloride, ether and ethyl acetate, and fairly in alcohols and ligroin. When it was mixed with the dibromonitro-compound obtained by the bromination of 2-bromo-3-nitrobiphenylene oxide, its melting point was exceedingly depressed.

2,6-*Dibromo*-3,7-*dinitro* (or 3,7-*dibromo*-2,6-*dinitro*)-*biphenylene oxide* (XXI). (i) When 2,6-Dibromo-3-nitrobiphenylene oxide (1 g.) was treated for 10 minutes with warm nitric acid (d=1.45 c.c.), the crystalline form of the oxide completely changed. The reaction product was recrystallized from acetone into pale yellow hexagonal plates, m.p. 262–263° (corr.) (Yield 0.75 g. Found: N, 6.76; Br, 38.38. Calc. for $C_{12}H_4OBr_2(NO_2)_2$: N, 6.74; Br, 38.42%). It is fairly soluble in acetone, acetic acid, benzene, chloroform and ethyl acetate, and sparingly in alcohols, carbon tetrachloride, ether and ligroin.

(ii) 2,6-Dibromo-7-nitrobiphenylene oxide (0.6 g.) was heated for 3 hours on the water-bath with nitric acid (d=1.45; 10 c.c.), and the reaction product separated out on dilution was recrystallized from acetone into pale yellow hexagonal plates, m.p. 262–263° (corr.) (Yield 0.4 g.). It is identical with the corresponding compound obtained from 2,6-dibromo-3-nitrobiphenylene oxide.

2,6-*Dibromo*-3,5,7-*trinitrobiphenylene oxide* (XXII). 2,6-Dibromo-3,7-dinitrobiphenylene oxide (0.8 g.) was warmed with nitric acid (d=1.52; 10 c.c.) for 10 minutes on the water-bath, and the reaction product separated out on dilution was recrystallized from acetone-ethanol into colourless needles, m.p. 257–258° (corr.) (Yield 0.83 g. Found: N, 9,07; Br, 34.49. Calc. for $C_{12}H_3OBr_2(NO_2)_3$: N, 9.12; Br, 34.67%). It is readily soluble in acetone, fairly in acetic acid, benzene, chloroform and ethyl acetate, and sparingly in alcohols, carbon tetrachloride, ether and ligroin. This dibromotrinitro-compound hardly gives any higher nitro-derivative, even when it is boiled with fuming nitric acid (d 1.52).

(5) Nitro-derivative of 1,8-dibromobiphenylene oxide. 1,8-*Dibromo*-2,3,6-*trinitrobiphenylene oxide* (XXIII). 1,8-Dibromo-3,6-dinitrobiphenylene oxide (0.5 g.) was treated for 1 hour with warm nitric acid (d=1.52; 10 c.c.), and the reaction mixture was diluted with water, and then colourless precipitates separated out. The reaction product (0.51 g.) was recrystallized from acetone-methanol into colourless rectangular plates, m.p. 297–298° (corr.) (Yield 0.45 g. Found: N, 9.03; Br, 34.52. Calc. for $C_{12}H_3OBr_2(NO_2)_3$: N, 9.12; Br, 34.67%). It is readily soluble in acetone, fairly in benzene and ethyl acetate, and sparingly in alcohols, acetic acid, chloroform, carbon tetrachloride, ether and ligroin.

(6) Nitro-derivative of 2,3,6-tribromobiphenylene oxide. 2,3,6-*Tribromo*-4,7-*dinitrobiphenylene oxide* (XXIV). 2,3,6-Tribromobiphenylene oxide (3 g.) was dissolved in hot nitric acid (d=1.45), and the reaction product separated out on cooling was recrystallized from acetone ethanol into colourless needles or rhombic plates, m.p. 256–257° (corr.) (Yield 1.8 g. Found: N, 5.65; Br, 48.38. Calc. for $C_{12}H_3OBr_3(NO_2)_2$: N, 5.66; Br, 48.44%). It is readily soluble in acetone, benzene and ethyl acetate, fairly in acetic acid and chloroform, and sparingly in alcohols, carbon tetrachloride, ether and ligroin.

(7) **Nitro-derivative of 2,3,6,7-tetrabromobiphenylene oxide.** 2,3,6,7-*Tetrabromo-4,5-dinitrobiphenylene oxide* (XXV). Finely pulverized 2,3,6,7-tetrabromobiphenylene oxide (1 g.) was treated for 1 hour with a large excess of boiling nitric acid (d=1.52) and the reaction product (1.18 g.) separated out on dilution was recrystallized from a large quantity of acetone into colourless rhombic plates or needles, m.p. 364–365° (corr.) with decomposition, (Yield 0.9 g. Found: N, 4.86; Br, 55.54. Calc. for $C_{12}H_2OBr_4(NO_2)_2$: N, 4.88; Br, 55.69%). It is sparingly soluble in the ordinary organic solvents except acetone, benzene and ethyl acetate which dissolve it fairly.

(8) **Nitro-derivatives of 1,3,6,7-tetrabromobiphenylene oxide.** 1,3,6,7-*Tetrabromo-2,5-dinitro* (or 2,3,6,8,-*tetrabromo-4,7-dinitro*)- and 1,3,6,7-*tetrabromo-2,8-dinitro-biphenylene oxides* (XXVI) and XXVII). When 1,3,6,7-Tetrabromobiphenylene oxide (0.7 g.) was treated for half an hour with warm nitric acid (d=1.52; 10 c.c.), the crystalline form of this compound completely changed. The reaction product was separated from the reaction mixture and extracted with acetone-ethanol. The residue was recrystallized from acetone, and two kinds of crystals were isolated by decantation. The one is colourless needles melting at 329–330° (corr.) (Yield 0.3 g. Found: N, 4.97; Br, 55.51. Calc. for $C_{12}H_2OBr_4(NO_2)_2$: N, 4.88; Br, 55.69%), and the other is pale yellow compact prisms melting at 297–298 (corr.) (Yield 0.15 g. Found: N, 5.05; Br, 55.47%). Both of these derivatives are sparingly soluble in the ordinary organic solvents.

Summary.

(1) Twenty seven higher nitro-derivatives of 2- and 3-bromo-, 2,6-, 3,6- and 1,8-dibromo-, 2,3,6-tribromo-, and 1,3,6,7- and 2,3,6,7-tetrabromobiphenylene oxides were newly obtained by nitrating the corresponding lower nitro-derivatives, and their constitutions were established.

(2) The absorption curves of those bromonitro-compounds were compared with each other, and also with those of the corresponding nitrobiphenylene oxides, to the confirmation of their constitutions as a consequence.

(3) In the nitration of the bromo- and bromonitro-biphenylene oxides, it was found that when the relative arrangements of the substituents at the 2- and 3-positions to the 1-position are the same as those of the same substituents at the 3- and 2-positions to the 4-position, the introduction of the nitro group more readily takes place at the 4-position than at the 1-position.

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