Studies on the Derivatives of Biphenylene Oxide. V. Bromo-derivatives of Biphenylene Oxide.

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Among the bromo-derivatives of biphenylene oxide, although all isomers of the monobromo-compounds and three dibromo-compounds (2,3-,(1) 2,6-(2) and 3,6(3)-dibromobiphenylene oxides) are already prepared by many investigators, yet nothing has been reported to this day about the tri- and tetra-bromo compounds.

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

(2) H. McCombie, W. G. Macmillan and H. A. Scarborough, *J. Chem. Soc.*, **1913**, 536.

(3) O. Hoffmeister, *Ann.*, **159** (1871), 215; H. McCombie, W. G. Macmillan and H. A. Scarborough, *J. Chem. Soc.*, **1913**, 536; N. M. Cullinane, H. G. Davey and H. J. H. Padfield, *J. Chem. Soc.*, **1934**, 719; H. Gilman, H. B. Willis and J. Swislowsky, *J. Am. Chem. Soc.*, **61** (1939), 1372.

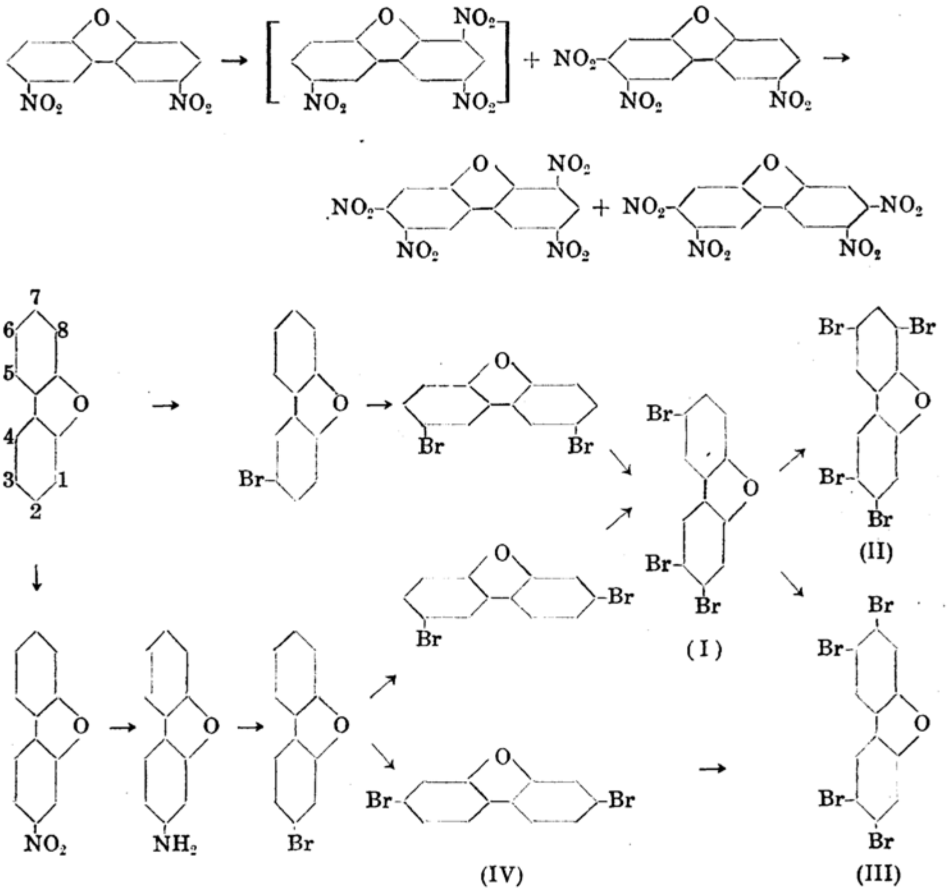
The present author obtained recently one tribromo- and two tetrabromo-biphenylene oxides, by isolating them from the bromination products of 3,6-dibromobiphenylene oxide. He inferred, from his experiment on the nitration of 3,6-dinitrobiphenylene oxide, that each of these newly obtained compounds might be respectively 2,3,6-tri- and 1,3,6,7- and 2,3,6,7-tetra-bromo compounds (I, II and III), because in that experiment 3,6-dinitrobiphenylene oxide gave mainly the 2,3,6-trinitro-compound (together with the 1,3,6-trinitro-compound by the bye) which converted into 1,3,6,7- and 2,3,6,7-tetranitrobiphenylene oxides. In order to confirm this inferrence, the bromination of biphenylene oxide and its bromo derivatives was again examined systematically, and in that experiment a new dibromobiphenylene oxide was also obtained. Its result may be described here in order.

First, biphenylene oxide and 2-bromobiphenylene oxide were brominated and it was found that the former substance gives mainly the 3-bromo- and 3,6-dibromo-derivatives; none of the 2-bromo- and 2,6-dibromo derivatives being obtained so much as can be isolated from the reaction mixture, while the latter, mainly 2,6-dibromobiphenylene oxide and, along with it, a new dibromobiphenylene oxide melting at 199–200° (corr.). Now, in general, negative atoms or negative groups replace the hydrogen atoms of biphenylene oxide more freely at the positions 3(6) and 2(7) than at 1(8) and 4(5), and in the case of bromination, especially, the substitution takes place most freely at the position 3(6), as is shown by the above-mentioned experimental results. The tendency of the substitution of hydrogen atoms of biphenylene oxide by bromine, therefore, can be represented in the order of positions 3(6) > 2(7) > 1(8), 4(5)– and probably 1(8) > 4(5)–, and, as a consequence, the by-product obtained from 2-bromobiphenylene oxide should be 2,7-dibromobiphenylene oxide.

Next, 3,6-dibromobiphenylene oxide was brominated and a tribromo- and a tetrabromo-compounds were obtained this time. This tribromo-compound, which melts at 202–203° (corr.), is proved to be 2,3,6-tribromobiphenylene oxide, because it is identical with the corresponding compound which was obtained from 2,6-dibromobiphenylene oxide. The last compound gave on bromination two tetrabromo compounds besides the 2,3,6-tribromo-compound. The tetrabromo compounds isolated in these experiments are identical with the corresponding compounds which can be obtained from 2,3,6-tribromobiphenylene oxide.

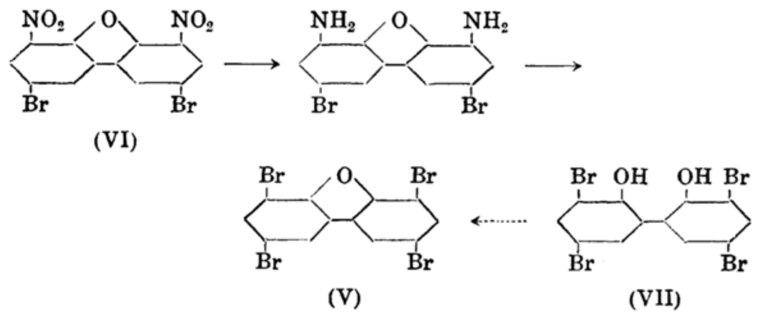
When 2,3,6-tribromobiphenylene oxide was brominated, it converted into two tetrabromo-compounds, one of which, melting at 306–307° (corr.), is the main product, while the other meltitng at 248–249° (corr.), a by-product. Judging from this experimental result and the above-mentioned tendency of the substitution by bromine, it is rather reasonable to conclude that the higher melting one is 2,3,6,7-tetrabromobiphenylene oxide, and the lower, 1,3,6,7-tetrabromobiphenylene oxide. Further support for this conclusion can be found in the result of bromination of the 2,7-dibromo-compound mentioned above, because this compound converts into a tetrabromo-compound which is identical with the higher melting tetrabromobiphenylene oxide.

In summary, the processes of the reactions, which were utilized to establish the constitutions of the new bromo derivatives of biphenylene oxide, therefore, may be represented by the following schemes:

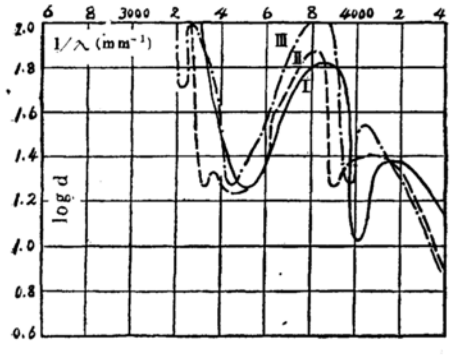


For the purpose of comparing with one another the possible isomers of the tetrabromobiphenylene oxides which would be found in the bromination products of 3,6-dibromobiphenylene oxide, 1,3,6,8-tetrabromobiphenylene oxide (V) was prepared from 3,6-dibromo-1,8-dinitrobiphenylene oxide (VI) which will be described in Part VII. The process of the reactions in that case is represented by the real-lined arrows in the scheme shown below. It was tried in vain, however, to prepare the same tetrabromo compound from 3,3′,5,5′-tetrabromo-2,2′-dihydroxydiphenyl (VII) by heating it in a sealed tube, for 5 hours at about 195–200°, in the presence of hydrobromic acid and a small quantity of red phosphorus, or by melting its acetyl derivative in mixing with dry carbonate of sodium or of barium.

The physical properties and the absorption curves of biphenylene oxide and its bromo-derivatives were compared as in Table 1 and Figs. 1–4, which will be utilized for the benefit of isolation and identification of these compounds.

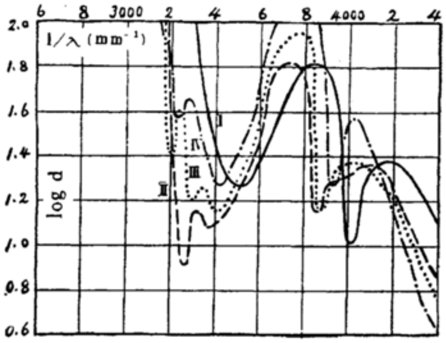


Comparison of the absorption curves of biphenylene oxide and its bromo derivatives.



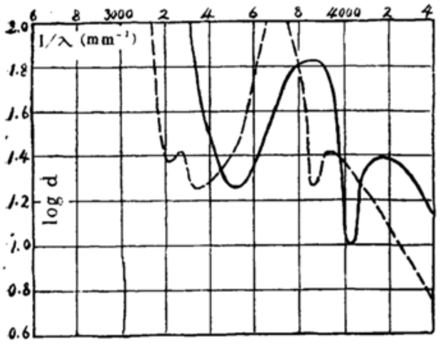
I (——) Biphenylene oxide.
II (---) 2-Bromobiphenylene oxide.
III (-·-) 3-Bromobiphenylene oxide.

Fig. 1. Monobromobiphenylene oxides, M/10000 alcoholic solutions.



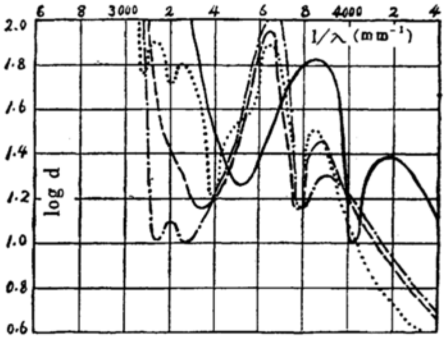
I (——) Biphenylene oxide.
II (---) 2,7-Dibromobiphenylene oxide.
III (····) 2,6-Dibromobiphenylene oxide.
IV (-·-) 3,6-Dibromobiphenylene oxide.

Fig. 2. Dibromobiphenylene oxides, M/10000 alcoholic solutions.



I (——) Biphenylene oxide.
II (---) 2,3,6-Tribromobiphenylene oxide.

Fig. 3. Tribromobiphenylene oxide, M/10000 alcoholic solution.



I (——) Biphenylene oxide.
II (---) 1,3,6,7-Tetrabromobiphenylene oxide.
III (····) 1,3,6,8-Tetrabromo- ,, ,, .
IV (-·-) 2,3,6,7-Tetrabromo- ,, ,, .

Fig. 4. Tetrabromobiphenylene oxides, M/10000 alcoholic solutions.

Table 1. Comparison of the physical properties of biphenylene oxide and its bromo derivatives.

Compound	M. p. (corr.)	Crystalline form (crystallizing solvent)	Solubility (e: easily soluble, e-m: less easily soluble, m: moderately soluble, d-m: less difficultly soluble, d: difficultly soluble; e > e-m > m > d-m > d.)										
			Ligroin	Ether	Carbon tetra-chloride	Chloro-form	Benzene	Ethyl acetate	Methanol	Ethanol	Acetone	Acetic acid	Toluene
Biphenylene oxide	86–87°	Colorless thin blades (ethanol)	e	e	e	e	e	e	e	e	e	e	e
2-Bromo-biphenylene oxide	121–122°	Colorless hexagonal plates (ethanol)	e	e	e	e	e	e	m	m	e	e	e
3-Bromo-biphenylene oxide	109–110°	Colorless thin blades (ethanol)	m	e	e	e	e	e	m	m	e	e	e
2,6-Dibromo-biphenylene oxide	178–179°	Colorless needles (acetone)	d	e-m	e	e	e	e	d	d	e-m	m	e
2,7-Dibromo-biphenylene oxide	199–200°	Colorless needles (acetone)	d	e-m	e	e	e	e	d	d	e-m	m	e
3,6-Dibromo-biphenylene oxide	199–200°	Colorless rectangular plates (acetic acid)	d	m	e	e	e-m	e	d	d	e	m	e-m
2,3,6-Tribromo-biphenylene oxide	202–203°	Colorless needles (acetone)	d	d	m	m	e-m	m	d	d	d-m	d	e-m
1,3,6,8-Tetrabromo-biphenylene oxide	237–238°	Pale yellow small needles (carbon tetrachloride)	d	d	e-m	e-m	e-m	e-m	d	d	d-m	d-m	e-m
1,3,6,7-Tetrabromo-biphenylene oxide	248–249°	Colorless needles (toluene)	d	d	m	m	m	d-m	d	d	d-m	d-m	m
2,3,6,7-Tetrabromo-biphenylene oxide	306–307°	Colorless large needles (toluene)	d	d	d	d	d-m	d	d	d	d	d	m

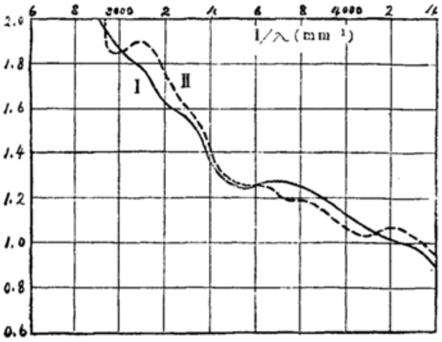
From the comparison of these absorption curves in Figs. 1–4, it may be found that the introduction of bromine into biphenylene oxide shifts always bathochromically the absorption bands of the parent compound, and in many cases gives rise to some new characteristic absorption bands. With regard to the strength of absorption, however, the effect exerted by bromine depends on the position of bromine introduced and the order of the absorption bands of biphenylene oxide.

The introduction of a bromine atom into the position 2 of biphenylene oxide (Fig. 1, Curve II) exerts an effect somewhat hyperchromically on the first less refrangible band of the parent compound, but hypochromically on the second more refrangible one, and moreover gives rise to a small characteristic band at $1/\lambda$ (mm^{-1}) 4330, whereas the introduction of a bromine atom into the position 3 (Fig. 1, Curve III) exerts no effect upon the strength of absorption in the first band of the parent compound, but it shows a hypochromic effect on the second one and moreover gives rise to a selective absorption band at 3220.

Among the absorption spectra of the dibromobiphenylene oxides compared in Fig. 2, those of 2,7- and 3,6-dibromobiphenylene oxides (Curves II and IV) have each three bands which are similar to a series of bands of 2- and 3-bromobiphenylene oxides respectively except for the strength of absorption, this being increased—especially so in the case of the 2,7-dibromo-compound—owing to the symmetrical constitutions of these two dibromo compounds; on the contrary, that of the unsymmetrical 2,6-dibromobiphenylene oxide (Curve III) has four bands, of which the bands located at $1/\lambda$ 4420 and 4890 correspond to the two characteristic bands of biphenylen oxide, and those at 3220 and 3300 are the characteristic bands of the bromine atoms introduced. These latter two bands are to be attributed to the presence of bromine at the positions 6 and 2 respectively. Therefore, so far as it goes at least, the additivity of the characteristic absorption bands may be detected in this case.

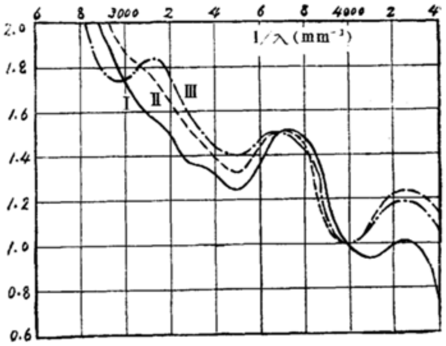
As will be seen from the curves in Figs. 3 and 4, however, the characteristic bands of the bromine atoms in a polybromobiphenylene oxide are not always developed separately, but rather partly or perfectly overlap one another in many cases, the curve of the polybromo-compound being often simpler than those of the lower bromo-compounds. In the 2,3,6-tribromo- and 2,3,6,7-tetrabromo-compounds (Fig. 3, Curve II and Fig. 4, Curve II), for example, though the characteristic band of the bromine atom at the position 2 or 7 can be found, the same at 3 and 6 can not be perceived in their curves, and in the 1,3,6,7-tetrabromo-compound (Fig. 4, Curve III) even none of them comes out in its curve. 1,3,6,8-Tetrabromobiphenylene oxide, however, gives a special curve (Fig. 4, Curve IV), and it possesses two characteristic bands at $1/\lambda$ 3100 and 3220 besides those at 3400 and 3780 which characterize the parent compound. As the band at 3220 of the former two corresponds to the characteristic band of the bromine atom at the position 3 or 6, the band at 3100 must be attributed to the same atom at 1 or 8.

A support for this view may be found in the comparisons between the absorption spectra of 1,3,6-trinitro- and 8-bromo-1,3,6-trinitro-biphenylene oxides (Fig. 5, Curves I and II) on the one hand and also among those of 1,6-dinitro-, 3-bromo-1,6-dinitro- and 3,8-dibromo-1,6-dinitro-bipheny-



I 1,3,6-Trinitro-biphenylene oxide.
II 8-Bromo-1,3,6-trinitro- „ „ .

Fig. 5. M/10000 alcoholic solutions.



I 1,6-Dinitro-biphenylene oxide.
II 3-Bromo-1,6-dinitro- „ „ .
III 3,8-Dibromo-1,6-dinitro- „ „ .

Fig. 6. M/10000 alcoholic solutions.

lene oxides (Fig. 6, Curves I, II, and III) on the other hand, because the compounds alone that have bromine at the position 8 give a distinct selective absorption band respectively in the neighbourhood of 1/λ 3000.

Experimental.

(1) *1,3,6- and 2,3,6-Trinitrobiphenylene oxides from 3,6-Dinitrobiphenylene oxide.* 3,6-Dinitrobiphenylene oxide (5.16 g.) was dissolved in fuming nitric acid (d 1.52; 20 c.c.) at room temperature and after being kept for 10 minutes at this temperature the reaction mixture was poured into water, when the reaction product separated as yellow precipitates. The trinitrobiphenylene oxides thus obtained (Yield almost theoretical) were extracted with a mixture of acetone and alcohol, and the residue was recrystallized from a small quantity of acetone, colourless rectangular plates melting at 311–312° (corr.) (Yield 0.28 g., 4.6% of the theoretical. Found: N, 13.92. Calc. for $C_{12}H_5O(NO_2)_3$: N, 13.87%). The acetone-alcoholic extract was evaporated and the crystals separated on cooling were recrystallized from acetic acid, colourless needles melting at 236–237° (corr.) (Yield 3.61 g., 60% of the theoretical. Found: N,12.82. Calc. for $C_{12}H_5O(NO_2)_3$: N, 13.87%). No depression of the melting point was observed each time when the former trinitro-compound was mixed with 1,3,6-trinitrobiphenylene oxide(4) obtained from 1,6-dinitrobiphenylene oxide, and the latter one, with 2,3,6-trinitrobiphenylene oxide(5) obtained from 2,6-dinitrobiphenylene oxide.

(2) *1,3,6,7- and 2,3,6,7-Tetranitrobiphenylene oxides from 2,3,6-trinitrobiphenylene oxide.* 2,3,6-Trinitrobiphenylene oxide (3.01 g.) was heated for one hour with fuming nitric acid (d 1.52; 15 c.c.) on the water bath and the reaction mixture was poured into water, giving pale yellow precipitates. The reaction product was recrystallized from acetic acid, colourless rectangular plates melting at 285–286° (corr.) (Yield 1.83 g., 53% of the theoretical. Found: N, 16.23. Calc. for $C_{12}H_4O(NO_2)_4$: N, 16.10%). The mother-liquor was concentrated and then diluted with water precipitating the other component of the nitration product. The precipitates were extracted with much alcohol to remove the contaminated sparingly soluble component and the extract was evaporated to dryness and then recrystallized repeatedly from benzene, colourless needles melting at 249–250° (corr.) (Yield 0.35 g., 10% of the theoretical. Found: N, 15.98. Calc. for $C_{12}H_4O(NO_2)_4$: N, 16.10%). No depression was observed

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(4) S. Yamashiro, *J. Chem. Soc. Japan*, **59** (1938), 449.
(5) S. Yamashiro, *ibid.*, **59** (1938), 450.

in the mixed melting points of these nitration products when the higher melting one was mixed with 2,3,6,7-tetranitrobiphenylene oxide obtained from 2,3,7-trinitrobiphenylene oxide, and the lower melting one, with 1,3,6,7-tetranitrobiphenylene oxide obtaind from 1,3,6-trinitrobiphenylene oxide.

(3) *3-Bomo- and 3,6-dibromobiphenylene oxides from biphenylene oxide.* In the hope of obtaining the theoretical quantity of dibromobiphenylene oxides, biphenylene oxide (84 g.) was heated for 60 hours with bromine (160 g.) in boiling carbon tetrachloride (500 c.c.), but the bromination was incomplete. After the remaining bromine and the solvent had been distilled off, the reaction product (144.6 g.) was washed with hot water and recrystallized from acetic acid, colourless rectangular plates, m.p. 199–200° (corr.) (Yield 41 g. Found: Br, 49.12. Calc. for $C_{12}H_6OBr_2$: Br, 49.03%). The more soluble part was recovered from the mother-liquor and extracted with much hot alcohol to remove the sparingly soluble (in alcohol) dibromo-compound. The monobromo-compound was obtained on concentrating the alcoholic extract and recrystallized from the same solvent, colourless plates, m.p. 109–110° (corr.) (Yield 15 g. Found: Br, 32.31. Calc. for $C_{12}H_7OBr$: Br, 32.36%). Judging from the literature on the bromo derivatives of biphenylene oxide, this monobromo-compound must be 3-bromobiphenylene oxide and the dibromo-compound obtained above, 3,6-dibromobiphenylene oxide. The alcoholic mother-liquor was evaporated to dryness and the residue was extracted with cold ligroin, 3-bromobiphenylene oxide being almost removed. The ligroin extract was again evaporated to dryness and the residue was recrystallized from alcohol in the hope of isolating 2-bromobiphenylene oxide, but in vain.

(4) *2,6- and 2,7-Dibromobiphenylene oxides from 2-bromobiphenylene oxide.* 2-Bromobiphenylene oxide was prepared from 2-aminobiphenylene oxide by means of the Sandmeyer's diazo-reaction described by E. Noelting and his co-workers⁽⁶⁾ and purified by sublimation and recrystallization from alcohol, colourless hexagonal plates, m.p. 121–122° (corr.) (Yield 56%). 2-Hydroxybiphenylene oxide described by K. Tatematsu and B. Kubota⁽⁷⁾, m.p. 139–139.5° (corr.), was also obtained as a by-product, yield 5%.

2-Bromobiphenylene oxdie (15 g.) was heated for 48 hours with bromine (10 g.) in boiling carbon tetrachloride (50 c.c.) and after addition of acetic acid (50 c.c.), heating was continued until the colour of bromine disappeared. When the solvents were almost recovered by distilation from the reaction mixture, the residue was diluted with water. The reaction product thus separated (Yield 21.5 g.) was repeatedly extracted with hot alcohol and the residue was recrystallized from a small quantity of acetone, colourless needles, m.p. 178–179° (corr.) (Yield 9.2 g., 46.5%. Found: Br, 49.20. Calc. for $C_{12}H_6OBr_2$: Br, 49.03%). The crystals separated on cooling from the alcoholic extracts were repeatedly recrystalliezd from a mixture of acetone and alcohol, colourless needles, m.p. 199–200° (corr.) (Yield 0.4 g., 2.2%. Found: Br, 49.15. Calc. for $C_{12}H_6OBr_2$: Br, 49.03%). It was found very difficult to gather more crop of the last crystals, owing to the resemblance between the solubilities of those isomers. Judging from the literature on the dibromobiphenylene oxides (2,3-dibromo compound, m.p. 150–150.5°⁽¹⁾ and 2,6-dibromo compound, m.p. 176°⁽²⁾ and also from the orientation of bromine which has been mentioned in the introductory part of this paper, the lower melting isomer of those reaction products must be 2,6-dibromobiphenylene oxide, and the higher melting one, 2,7-dibrobiphenylene oxide.

(5) *2,3,6-Tribromo- and 2,3,6,7-tetrabromo-biphenylene oxides from 3,6-dibromobiphenylene oxide.* 3,6-Dibromobiphenylene oxide (16.3 g.) was heated for 12 hours with a large excess of bromine (30 g.) in boiling acetic acid (500 c.c.), when the colour of bromine disappeared. The reaction mixture was concentrated, diluted with water, and the reaction product thus separated was filtered and dried (Yield 22 g.). After extraction with carbon tetrachloride, the sparingly soluble part of the reaction product was recrystallized fom toluene, large colourless needles, m.p. 306–307° (corr.) (Yield 4 g. Found: Br, 66.15. Calc. for $C_{12}H_4OBr_4$: Br, 66.05%). The carbon tetrachloride extract was evaporated to dryness, the residue was fractionally extracted

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(6) E. Noelting, A. Braun and G. Thesmar, *Ber.* **34** (1901), 2253.
(7) K. Tatematsu and B. Kubota, this Bulletin, **9** (1934), 452.

with acetone, and the fraction melting at 193–198° (uncorr.) was recrystallized from acetone, colourless needles, m.p. 202–203° (corr.) (Yield 8.6 g. Found: Br, 59.34. Calc. for $C_{12}H_5OBr_3$: Br, 59.20%). Both of those bromination products gave no depression of their melting points when the tribromo compound was mixed with the corresponding compound obtained from 2,6-dibromobiphenylene oxide, and the tetrabromo-compound, with the corresponding compound obtained from 2,7-dibromobiphenylene oxide. Those products, therefore, were evidently identified respectively as 2,3,6-tribromobiphenylene oxide and 2,3,6,7-tetrabromobiphenylene oxide.

(6) *2,3,6,7-Tetrabromobiphenylene oxide from 2,7-dibromobiphenylene oxide.* 2,7-Dibromobiphenylene oxide (0.2 g.) was heated for 4 hours with a large excess of bromine (2 g.) in boiling glacial acetic acid (40 c.c.), when the colour of bromine disappeared. The crystals separated on cooling from the reaction mixture were recrystallized from toluene, colourless needles, m.p. 306–307° (corr.) (Yield 0.21 g., 71%). The good yield of this 2,3,6,7-tetrabromo-compound from 2,7-dibromobiphenylene oxide owes to the fact that the most favourable positions 3 and 6 for the introduction of bromine remains free in the last compound.

(7) *2,3,6-Tribromo- and 1,3,6,7- and 2,3,6,7-tetrabromo-biphenylene oxides from 2,6-dibromobiphenylene oxide.* 2,6-Dibromobiphenylene oxide (3.26 g.) was heated for 12 hours with bromine (6 g.) in boiling glacial acetic acid (100 c.c.), when the colour of bromine disappeared. After distillation of the solvent, the reaction mixture was diluted with water to the precipitation of a white crystalline mass, which was filtered, dried (Yield 4.4 g.) and then extracted with hot benzene. From the sparingly soluble residue, 2,3,6,7-tetrabromobiphenylene oxide was isolated by recrystallization from toluene in large colourless needles, m.p. 306–307° (corr.) (Yield 1.6 g.). The benzene extract was evaporated to dryness and fractionated into 10 parts by means of the fractional extraction of the residue with acetone. Of these fractions the part melting at 238–240° (uncorr.) was recrystallized from toluene, colourless needles, m.p. 248–249° (corr.) (Yield 0.3 g. Found: Br, 66.08. Calc. for $C_{12}H_4OBr_4$: Br, 66.05%) and the part melting at 196–198° (uncorr.) was recrystallized from acetone to the isolation of 2,3,6-tribromobiphenylene oxide, colourless needles, m.p. 202–203° (corr.) (Yield 0.8 g.). The lower melting tetrabromo-compound obtained here was identical with the corresponding compound which was obtained as a by-product from 2,3,6-tribromobiphenylene oxide and consequently concluded to be 1,3,6,7-tetrabromobiphenylene oxide.

(8) *1,3,6,7- and 2,3,6,7-Tetrabromobiphenylene oxides from 2,3,6-tribromobiphenylene oxide.* 2,3,6-Tribromobiphenylene oxide (1 g.) was heated for 12 hours with a large excess of bromine in boiling acetic acid (200 c.c.), the solvent was distilled off and the residue was then diluted with water. The reaction product thus separated was filtered, dried, and after extraction with benzene, recrystallized from toluene, colourless needles of 2,3,6,7-tetrabromobiphenylene oxide, m.p. 306–307° (corr.) (Yield 0.6 g.). The benzene extract was evaporated to dryness, the residue was repeatedly extracted with ligroin, and the sparingly soluble part was recrystallized from toluene, colourless needles of 1,3,6,7-tetrabromobiphenylene oxide, m.p. 248–249° (corr.) (Yield 0.06 g.). 2,3,6-Tribromobiphenylene oxide was recovered from the ligroin extract.

(9) *1,3,6,8-Tetrabromobiphenylene oxide from 3,6-dibromo-1,8-dinitrobiphenylene oxide.* (i) 1,8-Diamino-3,6-dibromobiphenylene oxide. 3,6-Dibromo-1,8-dinitrobiphenyoxide (2.08 g.) was heated with stannous chloride (10 g.) and concentrated hydrochloric acid (10 c.c.) in boiling acetone (300 c.c.), when the colourless needle crystals of 1,8-diamino-3,6-dibromobiphenylene oxide dihydrochloride separated; which were filtered on cooling and washed successively with hydrochloric acid, water and then with acetone. The filtrate was distilled to the recovery of acetone, dilute hydrochloric acid was added and the second crop of the dihydrochloride thus separated was treated as before (Yield 2.07 g., 97%). The dihydrochloride was converted into the free base by treating it with an excess of sodium acetate solution, and was recrystallized from chloroform, small colourless needles which take blue colour on standing in the wet air, m.p. 276.5–277.5° (corr.) (Found: N, 7.94. Calc. for $C_{12}H_4OBr_2(NH_2)_2$: N, 7.87%). 1,8-Diamino-3,6-dibromobiphenylene oxide is soluble easily in acetone and ethyl acetate, moderately in benzene and chloroform, but difficultly in alcohol, ether, ligroin, and carbon tetrachloride. The dihydrobromide of this base was obtained by

treating the base with hydrobromic acid in acetone solution, colourless needles (Found: Br, 61.58. Calc. for $C_{12}H_4OBr_2(NH_2)_2$ 2HBr: Br, 61.77%).

(ii) 1,8-Biacetamino-3,6-dibromobiphenylene oxide, 1,8-Diamino-3,6-dibromobiphenylene oxide (0.178 g.) was heated with a mixture of glacial acetic acid (2 g.) and acetic anhydride (0.1 g.), and diluted with water, when a white crystalline mass separated. The reaction product (Yield 0.222 g.) was recrystallized from alcohol, small colourless needles, m.p. 358–360° (corr.) (Found: N, 6.42. Calc. for $C_{12}H_4OBr_2(NHCOCH_3)_2$: N, 6.36%). It is soluble fairly in acetone, alcohol, and acetic acid, but sparingly in the other ordinary organic solvents.

(iii) 1,3,6,8-Tetrabromobiphenylene oxide. Finely powdered 1,8-diamino-3,6-dibromobiphenylene oxide (1.39 g.) was suspended in 10% hydrobromic acid, and was diazotized with sodium nitrite (0.46 g.) under ice cooling, when the base changed slowly into the yellow diazo-compound. Cuprous bromide, on the other hand, was prepared by heating a mixture of crystalline copper sulphate (1.8 g.), copper bronze (0.7 g.), potassium bromide (3 g.), concentrated sulphuric acid (0.8 g.) and water (12 c.c.) until the blue colour of the cupric salt disappeared. After being washed with cold air-free water, cuprous bromide was added to the above-mentioned ice-cold suspension of the diazo-compound. This mixture was allowed to stand overnight under cooling and then gradually heated on the water bath to complete the decomposition of the diazo-compound, when the brown solid separated out. The reaction product was filtered, washed well with hot water, dried and extracted with benzene. The extracted was evaporated to dryness and, after being extracted again with acetone to the removal of the easily soluble impurity, the residue was recrystallized from carbon tetrachloride, pale yellow small needles, m.p. 237–238° (corr.) (Yield 0.51 g. Found: Br, 65.01 Calc. for $C_{12}H_4OBr_4$: Br, 65.05%).

Summary.

For the purpose of confirming the constitution of the polybromo-compounds obtained directly from biphenylene oxide by bromination, the following experiments were performed by the present author:

(1) Verification of the formation of 2,3,6-trinitro- and 1,3,6,7- and 2,3,6,7-tetranitro-biphenylene oxides from 3,6-dinitrobiphenylene oxide and of the formation of 2,3,6-tribromo- and 1,3,6,7- and 2,3,6,7-tetra-bromo-biphenylene oxides from 3,6-dibromobiphenylen oxide.

(2) Isolation of 2,7-dibromobiphenylene oxide from the bromination products of 2-bromobiphenylene oxide, and preparation of 1,3,6,8,-tetra-bromobiphenylene oxide from 3,6-dibromo-1,8-dinitrobiphenylene oxide.

(3) Comparative studies on the characteristics and the absorption spectra of biphenylene oxide and its bromoderivatives.

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