982. *Biphenylenes. Part VIII.*[1] *Synthesis and Reactions of 2-Hydroxybiphenylene and of Biphenylene-2,3-quinone.*

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2-Hydroxybiphenylene has been prepared by Baeyer–Villiger oxidation of the corresponding 2-benzoyl compound, itself made by direct substitution in biphenylene. The hydroxy-compound couples with diazonium salts in position 3, as predicted by Longuet-Higgins. Oxidation of the hydroxy-compound with potassium nitrosodisulphonate gives biphenylene-2,3-quinone (V) which is more conveniently prepared through the azophenol (III). This quinone, the first to be prepared in the biphenylene series, is remarkably stable. Under the conditions of Thiele acetylation, it behaves anomalously and yields a tetra-acetate (VI).

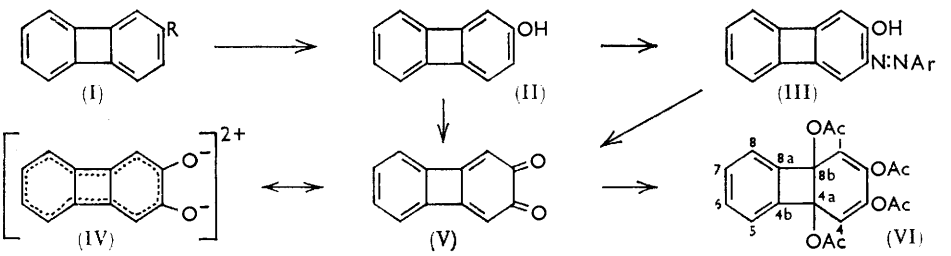
Studies of hydroxybiphenylenes and biphenylenequinones have been hampered by the inaccessibility of the hydroxy-compounds. Reaction of biphenylene with lead tetra-acetate followed by hydrolysis gives 2-hydroxybiphenylene in 1·5% yield;[2] the same compound can be made by acid hydrolysis of its methyl ether, but the latter also is difficultly accessible.[3] 2-Acetylbiphenylene did not undergo the Baeyer–Villiger reaction[2] and attempts to cleave the ether groups of 2,7-dimethoxybiphenylene have been unsuccessful.[4] We have now found that 2-benzoylbiphenylene is readily converted into 2-benzoyloxy- and thence into 2-hydroxy-biphenylene. Some reactions of this compound, including its conversion into biphenylene-2,3-quinone, are described below.

Biphenylene (I; R = H) reacted with benzoyl chloride in the presence of aluminium chloride to give 2-benzoylbiphenylene (I; R = Bz), the orientation of which was proved by conversion of the corresponding oxime into 2-benzamidobiphenylene (I; R = NHBz) by a Beckmann rearrangement. When the ketone (I; R = Bz) was treated with peracetic acid in acetic acid containing sulphuric acid (conditions critical), it gave the benzoate (I; R = OBz) which on alkaline hydrolysis yielded 2-hydroxybiphenylene (II) in *ca.* 23% overall yield from biphenylene.

The phenol (II) coupled readily with diazonium salts to give deep red azo-compounds

[1] Part VII, Blatchly, McOmie, and Watts, preceding paper.
[2] Baker, Boarland, and McOmie, *J.*, 1954, 1476.
[3] Baker, Barton, and McOmie, *J.*, 1958, 2658.
[4] Lothrop, *J. Amer. Chem. Soc.*, 1942, **64**, 1698.

(III), with the azo-group at position 3 as predicted by Longuet-Higgins in 1957.[5] This is in agreement with previous work [6] which had shown that 2-acetamidobiphenylene undergoes bromination at position 3. Bosshard and Zollinger [7] recently showed that 2-aminobiphenylene couples with benzenediazonium chloride at the same position. The azophenol (III; Ar = *p*-C_6H_4·SO_3Na) was reduced by sodium dithionite, and the resulting aminophenol was oxidised by chromium trioxide to the orange quinone (V). The same quinone



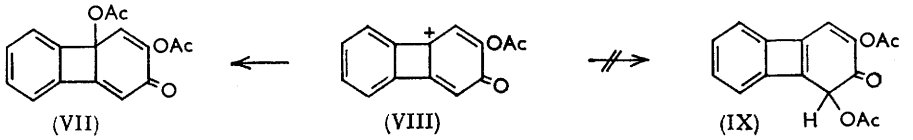
could be made, though less conveniently, by direct oxidation of 2-hydroxybiphenylene (II) with potassium nitrosodisulphonate. The quinone (V) reacted with *o*-phenylenediamine to give a quinoxaline, and with bromine to give 1,4-dibromobiphenylene-2,3-quinone. When the quinone was reduced and then methylated it gave 2,3-dimethoxybiphenylene, identical with an authentic sample.[1]

Unlike many *o*-quinones, biphenylene-2,3-quinone is very stable. This is shown by its mode of preparation in which chromic acid is used and by the fact that it shows no tendency to polymerise. It does not react with maleic anhydride, otherwise a derivative of benzocyclobutadiene might have been formed. The stability of the quinone may be attributed, in part, to the presence of the benzene ring in conjugation with the quinone ring. In the extreme polarised form (IV) the 12 carbon atoms are associated with 10 π-electrons, a number which conforms to Hückel's $(4n + 2)$ rule.[8] According to Vol'pin [9] this rule, which was derived for monocyclic systems, is applicable to fused systems provided that they contain no atoms common to more than two rings. The actual state of the molecule would, of course, be somewhere between the extreme forms (IV) and (V), and the situation would be similar to that which obtains in tropone.

When the quinone was treated with acetic anhydride in the presence of a little concentrated sulphuric acid or boron trifluoride (Thiele acetylation), it unexpectedly gave a tetra-acetoxy-compound, $C_{20}H_{18}O_8$, whereas other *o*-quinones behave normally in this reaction, *e.g.* 4,5-dimethyl-*o*-benzoquinone gives 1,2,3-triacetoxy-4,5-dimethylbenzene.[10] Attempts to hydrolyse the tetra-acetate with hydrobromic acid or with alkali in the presence of methyl sulphate (in the hope of obtaining the related tetramethoxy-compound) led to profound decomposition. The ultraviolet absorption spectrum of the tetra-acetate (see Table) shows that the compound is not a substituted biphenylene, but the spectrum is consistent with a sterically hindered biphenyl or with a derivative of benzocyclobutene (cf. Table). The infrared spectrum shows a strong band at 1760 with a high shoulder at 1772 cm.$^{-1}$, suggesting the presence of two types of carbonyl group, one of which is present as an enol acetate. Bands of medium intensity at 1670 and 845 cm.$^{-1}$ are consistent with the presence of one or more trisubstituted C=C bonds, while the absence of a band near 1625 cm.$^{-1}$ indicates that the C=C bond or bonds are not conjugated with the benzene ring. Strong bands at 1185, 1133, 1077, 1045, and 758 cm.$^{-1}$ indicate that the benzene ring is

[5] Longuet-Higgins, *Proc. Chem. Soc.*, 1957, 157.
[6] Baker, McOmie, Preston, and Rogers, *J.*, 1960, 414.
[7] Bosshard and Zollinger, *Helv. Chim. Acta*, 1961, **44**, 1985.
[8] Hückel, *Z. Phys.*, 1931, **70**, 204.
[9] Vol'pin, *Russ. Chem. Rev.*, 1960, **29**, 147.
[10] Horner and Sturm, *Annalen*, 1955, **597**, 1.

ortho-disubstituted. On the basis of the spectral evidence and consideration of the probable reaction mechanism (see below), we propose structure (VI) for the tetra-acetate. This structure is strongly supported by a study of the nuclear magnetic resonance spectrum of the compound kindly carried out by Dr. K. A. McLauchlan. The spectrum of the compound in chloroform is unusually simple and consists of an intensity 2 peak at τ 3·92 and two peaks at 7·84 and 7·99 of intensity 6. The peaks due to the phenyl protons are obscured by the solvent. The more intense peaks are due to the methyl protons in the acetoxy-groups and show that there are two non-equivalent pairs of such groups. Since the peak at 3·92 is simple and shows no coupling it must be due to two equivalent protons. These results suggest that the molecule contains a plane of symmetry. The nuclear magnetic resonance spectrum of the compound in dioxan shows a peak of intensity 4 at 2·67 due to aromatic protons and confirms the view that the benzene ring of the biphenylene-2,3-quinone has remained unattacked.



(VII) (VIII) (IX)

The formation of the tetra-acetate (VI) probably involves the attack of an acetylium ion on one of the oxygen atoms of the quinone, to give an ion (VIII) (cf. ref. 11), followed by (or synchronously with) electrophilic attack of the carbonium ion on a molecule of acetic anhyride to give a diacetate (VII). Repetition of this process then gives the tetra-acetate (VI). If the normal Thiele acetylation product (1,2,3-triacetoxybiphenylene) had been formed it would have involved an intermediate such as (IX) which is a derivative of benzocyclobutadiene. Many examples are known which indicate a marked reluctance of the 1,2-dimethylenebenzocyclobutene system to be changed into the corresponding benzocyclobutadiene.

When the tetra-acetate was first obtained it was thought to be 2,2′,4,5-tetra-acetoxybiphenyl and attempts were made to prepare this compound through the corresponding tetramethoxybiphenyl. However, when the latter had been made (see Experimental), its ultraviolet absorption spectrum was sufficiently different from that of the Thiele product to discourage further work in this direction. In an attempt to prepare 2-hydroxy-2′,4,5-trimethoxybiphenyl, the corresponding 2-aminobiphenyl was diazotised, but cyclisation occurred with concurrent demethylation to give 2,3-dimethoxydibenzofuran.

Ultraviolet absorption maxima (mμ) in 95% ethanol.

Biphenylene deriv.	λ	$\log_{10}\varepsilon$	λ	$\log_{10}\varepsilon$	λ	$\log_{10}\varepsilon$
2-Benzoyl	260	4·35	354·5	2·82	368·5	2·98
2-Benzoyloxy	244, 251	4·93, 5·14	344	3·96	362	4·06
2,3-Dimethoxy	255	4·96	362	4·09	368	4·16
2,3-Quinone	268	4·62	372	4·21		
1,4-Dibromo-2,3-quinone	222	4·21	286	4·52	389	4·17
Thiele acetyln. product	275 infl.	3·2				
Benzocyclobutene [12]	260	3·09	265·5	3·28	271·5	3·27
2,2′,4,5-Tetramethoxybiphenyl	295	3·89				
Dibenzofuran [13]	242	4·09	249·5	4·32	287	4·28
	245	4·09	281·5	4·29	298	4·06
2,3-Dimethoxydibenzofuran	220, 245	4·22, 3·88	298	3·87	310	3·88

Experimental

2-Benzoylbiphenylene (I; R = Bz) (with Dr. J. W. Barton).—A solution of biphenylene (1·52 g.) and benzoyl chloride (1·27 ml.) in carbon disulphide (25 ml.) was added dropwise to a stirred suspension of powdered aluminium chloride (1·4 g.) in carbon disulphide (25 ml.). After

[11] Mackenzie and Winter, *Trans. Faraday Soc.*, 1948, **44**, 159, 171.
[12] Cava and Napier, *J. Amer. Chem. Soc.*, 1958, **80**, 2255.
[13] Jones and Lindsey, *J.*, 1950, 1836.

being stirred for 0·5 hr. the mixture was boiled for 4 hr., then the solvent was removed. Ice-cold 2N-hydrochloric acid and methylene chloride were added to the residue, and the mixture was filtered. The organic layer yielded a solid which was recrystallised from ethanol (charcoal), giving 2-*benzoylbiphenylene* (1·5 g., 59%) as yellow plates, m. p. 115—117° raised to 116—117·5° by one more recrystallisation (Found: C, 88·85; H, 4·8. $C_{19}H_{12}O$ requires C, 89·0; H, 4·7%).

2-*Benzamidobiphenylene*.—2-Benzoylbiphenylene (0·47 g.) in methanol (10 ml.) was added to hydroxylamine hydrochloride (0·5 g.) dissolved in water (2 ml.) and 10% aqueous sodium hydroxide (2 ml.). After being boiled for 0·5 hr., the mixture was cooled and diluted with water. The precipitate was recrystallised from ethanol, giving the 2-*benzoylbiphenylene oxime* (0·43 g.) as yellow needles, m. p. 160° (Found: C, 83·9; H, 4·7; N, 4·9. $C_{19}H_{13}NO$ requires C, 84·1; H, 4·7; N, 5·0%).

The oxime (0·15 g.) was added to polyphosphoric acid (3 g.) at 110° and the mixture was stirred at this temperature for 20 min. The hot mixture was poured into water (150 ml.), and the solid was collected. It was dissolved in benzene–chloroform (1 : 1) and was purified by chromatography on alumina with benzene as eluant. 2-*Benzamidobiphenylene* (0·105 g.) formed pale yellow plates, m. p. 209—210° (Found: C, 84·2; H, 4·7; N, 4·8%). A sample of the benzamido-compound was boiled with aqueous-ethanolic hydrochloric acid and gave 2-aminobiphenylene, m. p. alone or mixed with authentic [2] material, 122·5—123·5°, and benzoic acid, m. p. and mixed m. p. 121—123°.

2-*Benzoyloxybiphenylene* (I; R = OBz).—Freshly made 15% peracetic acid (10 ml.) was added to 2-benzoylbiphenylene (0·1 g.) in acetic acid (5 ml.). To this mixture, kept below 10°, was added concentrated sulphuric acid (2·5 ml.) dropwise during 0·5 hr. The mixture was shaken from time to time to prevent supersaturation of the solution with respect to the product. The crystals which gradually separated were collected by filtration every 2—4 hr. during a total time of 12 hr. Recrystallisation from ethanol gave 2-*benzoyloxybiphenylene* (50—96 mg., 47—90%) as straw-coloured needles, m. p. 150—151° (Found: C, 83·7; H, 4·4. $C_{19}H_{12}O_2$ requires C, 83·8; H, 4·4%).

2-*Hydroxybiphenylene* (II).—A mixture of the benzoyloxy-compound (0·5 g.), ethanol (15 ml.), and sodium hydroxide (1 g., in 20 ml. of water) was heated on a water-bath for 3 hr. The ethanol was removed under reduced pressure and the alkaline solution was extracted with ether. The aqueous layer was acidified and the product collected in ether. Removal of solvent, followed by sublimation of the residue at 135—140°/12 mm., gave 2-hydroxybiphenylene (0·18 g., 50%) as yellow needles, m. p. 139—140° (Found: C, 85·7; H, 4·65. Calc. for $C_{12}H_8O$: C, 85·9; H, 4·7%). The phenol slowly darkened in air and it gave a brick-red colour with ethanolic ferric chloride (cf. ref. 2).

2-p-*Chlorophenylazo*-3-*hydroxybiphenylene* (III; Ar = *p*-C_6H_4Cl).—*p*-Chloroaniline (0·076 g.) was diazotised and added to 2-hydroxybiphenylene (0·1 g.) in 2N-sodium hydroxide (20 ml.) and ethanol (2 ml.) at 0—5°. The *azo-compound* formed deep red needles, m. p. 221—223° (decomp.), after crystallisation from ethanol (Found: C, 70·6; H, 3·6; N, 9·3. $C_{18}H_{11}ClN_2O$ requires C, 70·5; H, 3·5; N, 9·1%), $\nu_{max.}$ 740vs, 825m, and 870m cm.$^{-1}$, corresponding to 1,2-di-, 1,4-di-, and 1,2,4,5-tetra-substituted benzene rings.

2-*Hydroxy*-3-*phenylazobiphenylene* (III; Ar = Ph).—This was prepared from diazotised aniline as in the preceding experiment. After crystallisation from ethanol the red needles of the *azo-compound* had m. p. 208—210° (decomp.) (Found: C, 79·5; H, 4·5; N, 10·6. $C_{18}H_{12}N_2O$ requires C, 79·4; H, 4·4; N, 10·3%), $\nu_{max.}$ 700s, 740vs, 862m, and 880m cm.$^{-1}$, corresponding to mono-, 1,2-di-, and 1,2,4,5-tetra-substituted benzene rings.

Biphenylene-2,3-*quinone* (V).—(*a*) Potassium nitrosodisulphonate (1·5 g.) in water (100 ml.) and 0·13N-potassium dihydrogen phosphate (50 ml.) were added successively to 2-hydroxybiphenylene (0·1 g.) in methanol (20 ml.). After being kept for 2 hr. at room temperature the crystalline deposit was collected and recrystallised from ethanol, giving *biphenylene*-2,3-*quinone* (82 mg., 75%) as orange needles, m. p. 216—217° (Found: C, 78·9; H, 3·2. $C_{12}H_6O_2$ requires C, 79·1; H, 3·2%).

(*b*) A mixture of 2-benzoyloxybiphenylene (0·5 g.) in ethanol (5 ml.) and sodium hydroxide (0·4 g.) in water (10 ml.) was heated to 90° for 15 min. and then under reduced pressure to remove the ethanol. The aqueous solution was filtered and used at once for the next stage, since 2-hydroxybiphenylene is very unstable in alkaline solutions. Sulphanilic acid (0·46 g.) in water (2 ml.) containing sodium carbonate (0·17 g.) was diazotised at 5—10° in the usual

way, and after 30 min. the diazo-solution was diluted with ice–water (5 ml.) and added to the above-mentioned alkaline solution of 2-hydroxybiphenylene. After the red mixture had been kept for 30 min., sodium dithionite (0·89 g.) was added and the whole was warmed (to 80° if necessary) until the colour was discharged (*ca.* 30 min.). The mixture was cooled to 0° for 1 hr., and the buff-coloured hydroxy-amine was collected and dissolved in concentrated hydrochloric acid (0·3 ml.). Addition of dilute sulphuric acid then gave greenish-white granules of the *2-amino-3-hydroxybiphenylene sulphate dihydrate* [Found: C, 57·5; H, 4·4. $(C_{12}H_9NO)_2,H_2SO_4,2H_2O$ requires C, 57·6; H, 4·8%]. For the preparation of the quinone, the solution of the hydroxy-amine in hydrochloric acid was added dropwise to chromium trioxide (1·3 g.) in concentrated sulphuric acid (0·4 ml.) and water (5 ml.). The intermediate imino-chromate separated as an orange powder which, when the mixture was warmed to 60°, dissolved and was replaced (on cooling) by orange needles (0·115 g., 34%) of biphenylene-2,3-quinone, m. p. 216—217°.

2,3-Dimethoxybiphenylene.—Hot water (100 ml.) was added with shaking to an intimate mixture of the quinone (150 mg.) and sodium dithionite (1 g.). The greenish-yellow precipitate was at once dissolved in 2N-sodium hydroxide (20 ml.), and then ethanol (2 ml.) and sodium dithionite (50 mg.) were added. Methyl sulphate (5 ml.) was added portionwise during 15 min., the temperature being kept at 50°. After a further 30 min., the product was collected in benzene (3 × 40 ml.). Removal of the solvent under reduced pressure left a greenish-yellow residue which sublimed at 85°/12 mm., giving 2,3-dimethoxybiphenylene (42 mg., 20%) as yellow needles, m. p. 87—88°, alone or mixed with a synthetic sample.[1]

Reaction of Biphenylene-2,3-quinone with o-Phenylenediamine.—An equimolecular mixture of the quinone and *o*-phenylenediamine in acetic acid was warmed on a water-bath for 10 min. The *benzo*[3,4]*cyclobuta*[1,2-b]*phenazine* formed yellow needles, m. p. 324° after recrystallisation from acetic acid (Found: C, 84·9; H, 3·75; N, 10·9. $C_{18}H_{10}N_2$ requires C, 85·0; H, 3·9; N, 11·0%).

1,4-Dibromobiphenylene-2,3-quinone.—Bromine (88 mg.) in acetic acid (5 ml.) was added to the quinone (100 mg.) in the same solvent (10 ml.). After 1 hr., the mixture was diluted with water (50 ml.), and the product was collected in ether. After being recrystallised from ethyl acetate the *bromo-quinone* formed yellow needles, m. p. 278—279° (decomp.) (Found: C, 42·4; H, 1·3. $C_{12}H_4Br_2O_2$ requires C, 42·35; H, 1·2%). The quinone does not react when submitted to the conditions of Thiele acetylation (cf. biphenylene-2,3-quinone itself).

Thiele Acetylation of Biphenylene-2,3-quinone.—(*a*) Concentrated sulphuric acid (2 drops) was added to a warm solution of the quinone (100 mg.) in acetic anhydride (5 ml.). After being kept for 20 hr. at room temperature the mixture was diluted with water (50 ml.), and the amorphous solid was collected. After two recrystallisations from ethanol, *2,3,4a,8b-tetra-acetoxy-4a,8b-dihydrobiphenylene* (VI) (38 mg., 21%) had m. p. 143·5—144·5° (Found: C, 62·3; H, 5·1. $C_{20}H_{18}O_8$ requires C, 62·2; H, 4·9%).

(*b*) Boron trifluoride in acetic acid (2 drops of 40% solution) was added to the quinone (220 mg.) in acetic anhydride (20 ml.) at 0°. After being kept at this temperature for 12 hr. and then for 1 hr. at 12°, the mixture was diluted with water (200 ml.), and the white crystals were collected. Recrystallisation from ethanol gave the tetra-acetate (270 mg., 68%), m. p. and mixed m. p. with above material, 143·5—144·5°.

2′,4,5-Trimethoxy-2-nitrobiphenyl.—Copper bronze (12·0 g.) was added gradually to a stirred mixture of *o*-iodoanisole (17·6 g.) and 4-bromo-5-nitroveratrole (15·4 g.) while the temperature was kept at 190—205°. After 2 hr. more at 190° the mixture was cooled and the product extracted into chloroform. Removal of the solvent gave a brown oil which was boiled with methanol (80 ml.) and filtered while hot to remove 4,5,4′,5′-tetramethoxy-2,2′-dinitrobiphenyl (1·2 g.; m. p. 219—220°). On cooling, the filtrate yielded yellow needles of *2′,4,5-trimethoxy-2-nitrobiphenyl* (8·5 g., 50%), m. p. 126—128° raised to 127—128° by one recrystallisation from methanol (Found: C, 61·9; H, 5·1. $C_{15}H_{15}NO_5$ requires C, 62·3; H, 5·2%).

2-Methoxy-5-o-methoxyphenylbenzo-1,4-quinone.—The above nitrobiphenyl (5·78 g.) in boiling ethanol (40 ml.) was reduced by gradual addition of stannous chloride dihydrate (14·0 g.) in concentrated hydrochloric acid (30 ml.) during 20 min. An excess of aqueous sodium hydroxide was added and the mixture was extracted with ether. Removal of the solvent gave the amine which was at once dissolved in concentrated hydrochloric acid (4 ml.) and water (200 ml.). The solution was filtered and then oxidised by chromium trioxide (8·2 g.) in water (300 ml.) at 6—9°. The imino-chromate separated as a dark green solid and was collected.

It was then stirred with water (100 ml.) containing concentrated sulphuric acid (6 ml.). The suspension was warmed to 60° for a few minutes, then cooled to 0°, and after 30 min. the solid was collected and recrystallised from methanol. The filtrate at 0° was extracted with chloroform and yielded 0·2 g. more of the *quinone* (total yield 0·9 g., 18%). It formed orange plates, m. p. 143° (Found: C, 68·5; H, 4·9. $C_{14}H_{12}O_4$ requires C, 68·8; H, 4·95%).

2,4,5,2′-*Tetramethoxybiphenyl*.—The preceding quinone (488 mg.) in water (5 ml.) and methanol (5 ml.) was reduced by sodium dithionite (400 mg.). Methyl sulphate (0·5 ml.) and potassium hydroxide (300 mg.) in water (0·5 ml.) were added at 60° and the methylation was completed by the addition of more methyl sulphate (0·2 ml.) and potassium hydroxide (150 mg.) in water (0·25 ml.). After being made strongly alkaline, the mixture was boiled for a few minutes and then cooled. The product was collected in ether, then sublimed under reduced pressure, and finally recrystallised from methanol (90%), giving the *tetramethoxybiphenyl* (100 mg., 18%) as granules, m. p. 82—83° (Found: C, 70·4; H, 6·7. $C_{16}H_{18}O_4$ requires C, 70·1; H, 6·5%).

2,3-*Dimethoxydibenzofuran*.—2′,4,5-Trimethoxy-2-nitrobiphenyl (1·0 g.) was reduced as above and the amine was dissolved in concentrated sulphuric acid (0·55 ml.) and water (10 ml.). Sodium nitrite (0·27 g.) in water (5 ml.) was added at 5—10°. The mixture was run dropwise into a boiling solution of cupric sulphate (saturated at 30°) (20 ml.). The resulting mixture was cooled and the solid was collected and recrystallised from benzene–light petroleum (b. p. 60—80°) (charcoal). The crystals (100 mg.) were purified by sublimation, giving 2,3-*dimethoxydibenzofuran* as white plates, m. p. 114° (Found: C, 73·4; H, 5·3. $C_{14}H_{12}O_3$ requires C, 73·7; H, 5·3%). The compound was insoluble in aqueous alkali and its ultraviolet spectrum was similar to that of dibenzofuran.

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