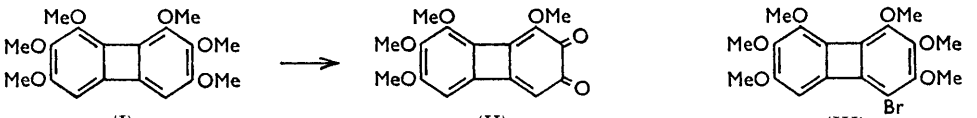
205. *Biphenylenes. Part XI.*[1] *Some Reactions of* 1,2,3,6,7,8-*Hexamethoxybiphenylene.*

By Wilson Baker, N. J. McLean, and J. F. W. McOmie.

1,2,3,6,7,8-Hexamethoxybiphenylene underwent oxidative demethylation when treated with nitric acid, giving 1,6,7,8-tetramethoxybiphenylene-2,3-quinone. Reaction of bromine with the hexamethoxybiphenylene was complex, giving this same quinone, its 4-bromo-derivative, 4-bromo-1,2,3,6,7,8-hexamethoxybiphenylene, and 2,2′-dibromo-3,4,5,3′,4′,5′-hexamethoxybiphenyl. Demethylation of the hexamethoxybiphenylene with methylmagnesium iodide gave the 2,7-dihydroxy-compound, and this was oxidised to the extended quinone 1,3,6,8-tetramethoxybiphenylene-2,7-quinone. Hydrogenolysis of the hexamethoxybiphenylene gave both possible hexamethoxybiphenyls.

Of the known methoxylated biphenylenes, one of the most readily accessible is 1,2,3,6,7,8-hexamethoxybiphenylene (I) whose preparation was described in Part X.[1] This biphenylene was expected to be very reactive owing to the presence of the six methoxyl groups, yet its reactions should be simplified by its possession of only two identical unsubstituted aromatic positions. The presence of the methoxyl groups also held out the possibility of the preparation of extended quinones and of degradative attack on one of the benzene nuclei leading to derivatives of benzocyclobutene.

In Part X [1] it was recorded that during the preparation of 1,2,3,6,7,8-hexamethoxybiphenylene (I) by heating 2,2′-di-iodo-3,4,5,3′,4′,5′-hexamethoxybiphenyl with cuprous oxide a small quantity (3%) of a stable red quinone was produced which proved to be 1,6,7,8-tetramethoxybiphenylene-2,3-quinone (II), a reaction involving cyclisation, demethylation, and oxidation. This quinone is formed almost quantitatively by treatment of (I) with nitric acid, which first gives a black intermediate complex. The formation of an *o*-quinone by simple oxidative demethylation with nitric acid is noteworthy; there are many examples of the production of *p*-benzoquinones by this method, though few *o*-quinones have been so prepared; examples of the latter type are bruciquinone [2] and one of the quinones yielded by melicopicine.[3] Reduction and methylation of the quinone



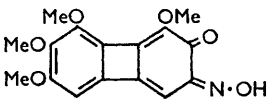
(I) (II) (III)

(II) regenerates the hexamethoxybiphenylene (I), and reductive acetylation gives 2,3-diacetoxy-1,6,7,8-tetramethoxybiphenylene. That (II) is an *o*-quinone is established by its reaction with *o*-phenylenediamine to yield a quinoxaline, and the choice between the 1,2- and the 2,3-quinone is decided in favour of the latter by the close similarity of the ultraviolet spectrum of (II) to that of 6,7-dimethoxybiphenylene-2,3-quinone,[4] making allowance for the additional methoxyl groups in (II). Moreover, the 1,2-quinone would be a derivative of benzocyclobutadiene, and all such substances are known to undergo immediate dimerisation,[5] in contrast with which the quinone (II) and the other two biphenylene-2,3-quinones are extremely stable. Thus compound (II) does not undergo Thiele acetylation, and it does not react with either maleic anhydride or *N*-phenylmaleimide under Diels–Alder conditions.

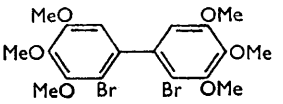
[1] Part X, Baker, McLean, and McOmie, *J.*, 1963, 922.
[2] Leuchs, Seeger, and Jaegers, *Ber.*, 1938, **71**, 2023.
[3] Crow, *Australian J. Sci. Res.*, 1949, **2***A*, 264.
[4] Baker, McOmie, and Watts, unpublished work.
[5] *E.g.*, Cava and Muth, *J. Org. Chem.*, 1962, **27**, 1561.

Bromination of the quinone (II) gave a monobromo-derivative which most probably is 4-bromo-1,6,7,8-tetramethoxybiphenylene-2,3-quinone, since the halogen is readily hydrolysed by alkali. When it was reduced and methylated it gave 4-bromo-1,2,3,6,7,8-hexamethoxybiphenylene (III). This bromo-derivative (III) was also obtained as one of the products of the direct bromination of (I) (see below), thus affording the first example of direct substitution at position 1 of a biphenylene.

The quinone (II) readily yields a mono-oxime which may be either the 2- or the 3-hydroxyimino-compound; the activity of the carbonyl group in position 3 may be expected to be diminished by the electromeric effect of the methoxyl group in position 1 with which it is conjugated, but at the same time it is not subject to the same deactivating steric effect as is the carbonyl group in position 2. In view of the fact that 2-methoxy-6-methyl-*p*-benzoquinone yields the 4- rather than the 1-mono-oxime,[6] it appears that the steric factor may be more important that the electromeric, and we therefore tentatively regard the mono-oxime of the quinone (II) as the 3-oxime (IV).



(IV)



(V)

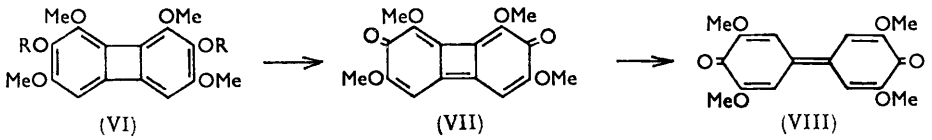
The bromination of 1,2,3,6,7,8-hexamethoxybiphenylene proved unexpectedly complex. With one equivalent of bromine in acetic acid an almost black precipitate was immediately formed and this slowly decomposed in a few hours to give an orange complex mixture. Chromatography yielded six substances which are as follows, in the order of their elution [the yields in parentheses refer, unless otherwise stated, to pure compounds, and are calculated on the amount of starting material (I) consumed]: 4-bromo-1,2,3,6,7,8-hexamethoxybiphenylene (III) (4%, crude), unchanged 1,2,3,6,7,8-hexamethoxybiphenylene (I), 2,2′-dibromo-3,4,5,3′,4′,5′-hexamethoxybiphenyl (V) (6%), 4-bromo-1,6,7,8-tetramethoxybiphenylene-2,3-quinone (15%), 1,6,7,8-tetramethoxybiphenylene-2,3-quinone (II) (29%), and a colourless substance (11%) showing a strong peak in the infrared spectrum, at 1760 cm.$^{-1}$, typical of an ester group, which may be 2-acetoxy-2′-bromo-4,5,6,4′,5′,6′-hexamethoxy- or 2-acetoxy-2′-bromo-3,4,5,3′,4′,5′-hexamethoxy-biphenyl formed by cleavage of one of the bridge bonds.

The 2,2′-dibromo-3,4,5,3′,4′,5′-hexamethoxybiphenyl (V) arises by brominolysis of one of the central bonds of the biphenylene structure, a reaction exactly analogous to the conversion of biphenylenes into biphenyls by reductive cleavage with Raney nickel. In almost all cases of such cleavage of substituted biphenylenes so far examined, both possible isomeric biphenyls, arising by breakage of one or other of the central bonds, have been isolated, and there is evidence that (V) is accompanied by about twice the amount of the isomeric 2,2′-dibromo-4,5,6,4′,5′,6′-hexamethoxybiphenyl, but this compound is not known and we were unable to obtain our material in the crystalline state. An earlier case of the brominolysis of a biphenylene to a 2,2′-dibromobiphenyl was afforded by 2-acetamido-3-bromobiphenylene, which gave 3-acetamido-4,6,2′-tribromobiphenyl.[7] The rather surprising formation of the two quinones, (II) and its 4-bromo-derivative, as the major products of the reaction, involves oxidative demethylation by bromine in acetic acid at room temperature for which we know of no analogy. An authentic specimen of 2,2′-dibromo-3,4,5,3′,4′,5′-hexamethoxybiphenyl (V), required for comparison with that prepared by the action of bromine upon 1,2,3,6,7,8-hexamethoxybiphenylene (I) (above), was prepared either by dibromination of 3,4,5,3′,4′,5′-hexamethoxybiphenyl or by methylation of 2,2′-dibromo-4,4′-dihydroxy-3,5,3′,5′-tetramethoxybiphenyl.

It has not been found possible to demethylate 1,2,3,6,7,8-hexamethoxybiphenylene

[6] McOmie and White, *J.*, 1955, 2619.
[7] Baker, McOmie, Preston, and Rogers, *J.*, 1960, 414.

(I) satisfactorily with any of the usual reagents, *e.g.*, hydrobromic acid, hydriodic acid, or aluminium chloride, because of the immediate formation of insoluble black stable addition products. Grignard reagents at elevated temperatures are, however, capable of cleaving phenol ethers,[8] and in the case of pyrogallol trimethyl ether selective demethylation occurs with production of 2,6-dimethoxyphenol in high yield.[9] Application of this method to the hexamethoxybiphenylene, by boiling it in toluene with methylmagnesium iodide, readily gave 2,7-dihydroxy-1,3,6,8-tetramethoxybiphenylene (VI; R = H), best isolated as its diacetyl derivative (VI; R = Ac). This diacetyl derivative, when hydrolysed and methylated, regenerated 1,2,3,6,7,8-hexamethoxybiphenylene (I). The free dihydroxy-compound (VI; R = H) is slowly oxidised by air in aqueous ethanolic solution, yielding the intensely mauve extended quinone 1,3,6,8-tetramethoxybiphenylene-2,7-quinone (VII).



(VI) (VII) (VIII)

The structures assigned to the dihydric phenol (VI; R = H), its diacetyl derivative (VI; R = Ac), and the extended quinone (VII) were confirmed by the following experiment. The quinone (VII) was boiled with Raney nickel in ethanol, thus bringing about reduction to the dihydric phenol (VII; R = H) and cleavage, in both possible ways, of the four-membered ring to give a mixture containing 4,4′-dihydroxy-3,5,3′,5′-tetramethoxybiphenyl and 3,3′-dihydroxy-2,4,2′,4′-tetramethoxybiphenyl. Without separation the product was then oxidised with chromium trioxide in acetic acid–water, and the very sparingly soluble and characteristic 3,5,3′,5′-tetramethoxybiphenoquinone (coerulignone) (VIII) was isolated in 26% yield. Clearly therefore the compounds (VI) and the quinone (VII) all possess two units derived from 2-hydroxy-1,3-dimethoxybenzene. The 2,7-quinone (VII) is the first example of an extended quinone of the biphenylene series, of which two other types are theoretically possible, namely, the 1,6- and the 1,8-quinones.

An attempt to synthesise 2,7-diacetoxy-1,3,6,8-tetramethoxybiphenylene (VI; R = Ac) by heating 4,4′-diacetoxy-2,2′-di-iodo-3,5,3′,5′-tetramethoxybiphenyl with cuprous oxide was unsuccessful, giving a black tar; this result is probably caused by the instability of the acetoxyl groups under the vigorous reaction conditions. The necessary 4,4′-diacetoxy-2,2′-di-iodo-3,5,3′,5′-tetramethoxybiphenyl was prepared from the readily accessible 3,5,3′,5′-tetramethoxybiphenoquinone (VIII) by successive reduction, acetylation, and iodination.

Reductive cleavage of 1,2,3,6,7,8-hexamethoxybiphenylene (I) with Raney nickel in ethanol occurred in both possible ways to give a mixture of almost equal quantities of 2,3,4,2′,3′,4′- and 3,4,5,3′,4′,5′-hexamethoxybiphenyl.

Experimental

1,6,7,8-*Tetramethoxybiphenylene*-2,3-*quinone* (II).—1,2,3,6,7,8-Hexamethoxybiphenylene (I) (100 mg.) was added (10 min.) in portions to stirred 5N-nitric acid (2 ml.) at 0°, the black complex initially formed at the crystal surfaces being converted into an orange solid. Stirring was continued for ½ hr. at 0°, water (3 ml.) was added, and the solid was collected, washed, and dried, giving the quinone (II) as red needles (from ethanol) (87 mg., 96%), m. p. 214—215° (Found: C, 63·2; H, 4·8. Calc. for $C_{16}H_{14}O_6$: C, 63·6; H, 4·7%), $\lambda_{max.}$ (in EtOH) 264, 306, 423 mμ (log ε 4·23, 4·36, 4·02), identical (mixed m. p., and ultraviolet and infrared spectra)

[8] Grignard, *Compt. rend.*, 1910, **151**, 322.
[9] Hurd and Winburg, *J. Amer. Chem. Soc.*, 1942, **64**, 2086.

with the quinone obtained as a by-product from the reaction between 2,2′-di-iodo-3,4,5,3′,4′,5′-hexamethoxybiphenyl and cuprous oxide at 340°.[1]

The quinoxaline derivative was obtained by boiling the quinone (II) (45 mg.) in ethanol (10 ml.) with *o*-phenylenediamine (16 mg.) for 3 hr., and then adding water; the product separated from ethanol as orange needles (52 mg.), m. p. 186—187° (Found: C, 70·7; H, 4·7; N, 6·8. $C_{22}H_{18}N_2O_4$ requires C, 70·6; H, 4·8; N, 7·5%), $\lambda_{max.}$ (in EtOH) 238, 294, 310, 357, 365, 370, 440 (infl.), 453 mμ (log ε 4·31, 4·76, 4·72, 5·00, 5·01, 5·02, 5·31, 5·34). The ethanolic solution shows a vivid yellow-green fluorescence in ultraviolet light.

Reduction and Methylation of 1,6,7,8-*Tetramethoxybiphenylene*-2,3-*quinone* (II).—The quinone (31 mg.) in ethanol (5 ml.) was reduced with aqueous sodium dithionite (2 ml.; 10%), and the dihydroxy-derivative was isolated as a yellow oil (28 mg.) by addition of water and extraction with ether. Methylation with methyl sulphate and aqueous sodium hydroxide (15%) in methanol, in presence of sodium dithionite and in an atmosphere of nitrogen, gave (from cyclohexane) 1,2,3,6,7,8-hexamethoxybiphenylene (I) (21 mg.), m. p. and mixed m. p. 91—91·5°.

The crude dihydroxy-compound (above) is best isolated as its diacetyl derivative. The quinone (II) (108 mg.) was heated for 2½ hr. with acetic anhydride (2 ml.) and zinc dust (80 mg.) with the further addition of zinc dust (50 mg.) after the first ½ hr. The 2,3-*diacetoxy*-1,6,7,8-*tetramethoxybiphenylene* was isolated by dilution of the mixture with water and extraction with ether; it formed yellow plates (from cyclohexane) (103 mg.), m. p. 130—131° (Found: C, 61·5; H, 5·3. $C_{20}H_{20}O_8$ requires C, 61·9; H, 5·2%), $\lambda_{max.}$ (in EtOH) 269, 346, 365 mμ (log ε 4·70, 4·59, 4·57).

4-*Bromo*-1,6,7,8-*tetramethoxybiphenylene*-2,3-*quinone*.—The quinone (II) (131 mg.) in acetic acid (20 ml.) was treated with bromine (77 mg.) in acetic acid (2 ml.). After ½ hr. water was added and the collected and washed precipitate was crystallised several times from ethanol, yielding the *product* (134 mg.) as brown leaflets, m. p. 205—206° (Found: C, 49·8; H, 3·5. $C_{16}H_{13}BrO_6$ requires C, 50·4; H, 3·4%), $\lambda_{max.}$ (in EtOH) 289, 318, 436 mμ (log ε 4·26, 4·31, 4·04). When the bromoquinone was boiled for a few minutes with ethanolic potassium hydroxide the bromine was liberated as the anion.

4-*Bromo*-1,2,3,6,7,8-*hexamethoxybiphenylene* (III).—The preceding quinone (53·5 mg.) in ethanol (2 ml.) was reduced and methylated as in the case of the quinone (II), except that, because of its sparing solubility, a 65% aqueous solution of sodium dithionite was used for the reduction, and acetone in place of methanol during the methylation. After being crystallised several times from ethanol, the *product* (III) was obtained as yellow plates (38 mg.), m. p. 128—129° (Found: C, 52·2; H, 5·1; OMe, 44·5. $C_{18}H_{19}BrO_6$ requires C, 52·6; H, 4·7; 6 OMe, 45·3%), $\lambda_{max.}$ (in EtOH) 286, 350, 368, 382 mμ (log ε 4·64, 4·23, 4·26, 4·31).

Mono-oxime (*probably* IV) *of* 1,6,7,8-*Tetramethoxybiphenylene*-2,3-*quinone* (II).—The quinone (II) (310 mg., 1 mol.) was added to a solution of hydroxylamine hydrochloride (72 mg., 1 mol.) and anhydrous sodium acetate (80 mg.) in water (0·5 ml.) and ethanol (10 ml.) at 80°, and the mixture was boiled with the addition of enough ethanol (*ca.* 30 ml.) to cause complete solution of the quinone. After 4 hr. the mixture was concentrated (to *ca.* 20 ml.), and on standing it yielded the *mono-oxime* which formed fine, golden-yellow needles (from ethanol) (289 mg.), m. p. 220—221° (Found: C, 60·55; H, 4·7; N, 4·0. $C_{16}H_{15}NO_6$ requires C, 60·4; H, 4·8; N, 4·4%), $\lambda_{max.}$ (in EtOH) 235, 301, 419 mμ (log ε 4·09, 4·42, 4·07).

Bromination of 1,2,3,6,7,8-*Hexamethoxybiphenylene* (I).—A solution of bromine (240 mg., 1 equiv.) in acetic acid (9 ml.) was added dropwise at room temperature to a stirred solution of the biphenylene (I) (500 mg., 1 equiv.) in acetic acid (10 ml.). A dark blue precipitate appeared immediately, and stirring was continued for 4 hr. with the addition of more acetic acid (15 ml.) after the first ½ hr. During this time the blue complex decomposed to give an orange solution which was poured into water and extracted with benzene (8 × 10 ml.). The extracts were washed repeatedly with water, dried ($MgSO_4$), concentrated (to *ca.* 30 ml.) under reduced pressure, and passed through a silica gel column (1·5 × 24 cm.). Elution gave five fractions. Fraction 1 (benzene, 100 ml.) yielded a gum (23 mg.) which gave orange needles of 4-bromo-1,2,3,6,7,8-hexamethoxybiphenylene (III), m. p. and mixed m. p. 128—129° (from ethanol) (Found: C, 52·5; H, 4·3. Calc. for $C_{18}H_{19}BrO_6$: C, 52·6; H, 4·7%); the infrared and ultraviolet spectra of the two specimens were identical. Fraction 2 (benzene, 100 ml.) gave unchanged 1,2,3,6,7,8-hexamethoxybiphenylene (I) (58 mg.) (m. p. and mixed m. p.). Fraction 3 (benzene, 200 ml.) yielded a fawn resin (110 mg.) which gave colourless material, m. p. 141—162° (from ethanol); this was fractionally crystallised, first from methanol, then from acetic

acid, and finally from methanol, giving needles (36 mg.) of 2,2′-dibromo-3,4,5,3′,4′,5′-hexamethoxybiphenyl (V), m. p. and mixed m. p. 162—163° (see below; the infrared and ultraviolet spectra of the two samples were identical). The other component of this fraction could not be obtained pure, but it was almost certainly the isomeric dibromobiphenyl, since the analysis of the mixture was almost identical with that of the purified isomer. Fraction 4 (3 : 1 benzene–chloroform, 450 ml.) gave a dark red solid (240 mg.). Careful crystallisation from ethanol yielded first 4-bromo-1,6,7,8-tetramethoxybiphenylene-2,3-quinone (74 mg.), m. p. and mixed m. p. (see below) 205—206°; this was followed by the more soluble 1,6,7,8-tetramethoxybiphenylene-2,3-quinone (II) (118 mg.), red needles, m. p. and mixed m. p. 214—215°. Fraction 5 (chloroform, 200 ml.), yielded a pale oil (126 mg.); crystallisation from methanol (charcoal) gave a *substance* as colourless plates (72 mg.), m. p. 141—142° (decomp.) (Found: C, 50·5; H, 4·6. $C_{20}H_{23}BrO_8$ requires C, 50·95; H, 4·9%).

2,2′-*Dibromo*-3,4,5,3′,4′,5′-*hexamethoxybiphenyl* (V).—(a) *From* 3,4,5,3′,4′,5′-*hexamethoxybiphenyl*. The hexamethoxybiphenyl [1] (0·1 g.) in acetic acid (2 ml.) was treated slowly with a solution of bromine (0·105 g.) in acetic acid (2 ml.), and air was then passed until the solution became colourless. Addition of water (8 ml.) gave a solid which was collected and washed giving the *product* (V) as plates (from acetic acid) (0·13 g.), m. p. 162—163° (Found: C, 44·0; H, 3·9; Br, 36·1. $C_{18}H_{20}Br_2O_6$ requires C, 43·9; H, 4·1; Br, 36·6%).

(b) *From* 2,2′-*dibromo*-4,4′-*dihydroxy*-3,5,3′,5′-*tetramethoxybiphenyl*. This hydroxybiphenyl (0·01 g.), prepared according to Levine,[10] in methanol (1 ml.) was treated, with stirring, at 25—30° with 40% aqueous sodium hydroxide (1 ml.) and methyl sulphate (0·8 ml.) in alternate portions in presence of sodium dithionite (0·01 g.). Stirring was continued for a further 3 hr., water (10 ml.) was added, and the solid was collected, washed, and crystallised from methanol, giving the product (V) as needles, m. p. and mixed m. p. 162—163°.

When heated with cuprous oxide at 350° the dibromo-compound (V) gave a low yield of 1,2,3,6,7,8-hexamethoxybiphenylene (I),[1] m. p. and mixed m. p. 90—91·5°. The infrared spectra of the two specimens were identical.

2,7-*Diacetoxy*-1,3,6,8-*tetramethoxybiphenylene* (VI; R = Ac).—1,2,3,6,7,8-Hexamethoxybiphenylene (I) (330 mg.) in toluene (5 ml.) was added to a solution of methylmagnesium iodide, prepared from methyl iodide (1·17 g.) and magnesium (0·2 g.) in ether (3·5 ml.), a yellow precipitate being formed. After removal of the ether, the mixture was boiled for 1 hr., the solid becoming bright red; the mixture was poured into dilute hydrochloric acid and extracted several times with ether, the extracts were shaken with aqueous sodium hydrogen carbonate (5%), the alkaline layer was acidified, and the orange oil (130 mg.), isolated by extraction with ether, was at once boiled with acetic anhydride and anhydrous sodium acetate. The isolated acetyl derivative was chromatographed in benzene solution on silica, giving the *product* (VII; R = Ac) as lemon-yellow plates (from ethanol) (176 mg.), m. p. 142—143° (Found: C, 61·6; H, 5·3. $C_{20}H_{20}O_8$ requires C, 61·9; H, 5·2%), $\lambda_{max.}$ (in EtOH) 271, 345, 364 mμ (log ε 4·59, 4·36, 4·71).

Simultaneous hydrolysis and methylation of this compound (58 mg.) with methyl sulphate and aqueous methanolic sodium hydroxide regenerated 1,2,3,6,7,8-hexamethoxybiphenylene (I) (34 mg.), m. p. and mixed m. p. 90—91°.

1,3,6,8-*Tetramethoxybiphenylene*-2,7-*quinone* (VII).—2,7-Diacetoxy-1,3,6,8-tetramethoxybiphenylene (VI; R = Ac) (112 mg.) was warmed in ethanolic potassium hydroxide (10 ml.; 10%) for 1½ hr. and the solution was carefully neutralised with 1·2N-hydrochloric acid. A slow current of air was passed through the solution for 1½ days, water being added from time to time to keep the volume constant. The dark precipitate which slowly formed was washed with water and methanol, giving the *product* (VII) (21 mg.) as deep mauve needles (from acetic acid), m. p. 265—266° (Found: C, 63·6; H, 5·0. $C_{16}H_{14}O_6$ requires C, 63·6; H, 4·7%), $\lambda_{max.}$ 258, 298, 401 mμ (log ε 4·17, 4·32, 4·15). The intense colour of this quinone in alcoholic solution is discharged by aqueous sodium dithionite. The quinone dissolves in concentrated sulphuric acid to give a brick-red colour, unlike 3,5,3′,5′-tetramethoxybiphenoquinone which under these conditions gives an intensely coloured cornflower-blue solution.

Reductive cleavage of this quinone (VII) (102 mg.) was effected by boiling its alcoholic solution for 1 hr. in nitrogen with W-2 Raney nickel (0·4 g.). The dark residue from filtration and evaporation in nitrogen was oxidised by stirring for 2 hr. with acetic acid (8 ml.) and a

[10] Levine, *J. Amer. Chem. Soc.*, 1926, **48**, 796.

solution of chromium trioxide (80 mg.) in water (1 ml.), the solids being washed with water and with much acetone, thus leaving a purple solid (27 mg.), identified as 3,5,3′,5′-tetramethoxybiphenoquinone (IX) by comparison of its infrared and ultraviolet spectra with those of authentic material (the m. p. depends on rate of heating and is not a satisfactory criterion of identity).

3-*Iodo*-2,6-*dimethoxyphenyl Acetate*.—2-Acetoxy-1,3-dimethoxybenzene [11] (2·0 g.) in acetic acid (30 ml.) was treated with iodine (1·0 g.), and to the resulting solution at 100° was added, dropwise with stirring, a solution of iodic acid (0·36 g.) in water (3·0 ml.). After 10 hr., the cooled solution was poured into water (100 ml.) and decolourised with a little sodium pyrosulphite. The precipitated *product* separated from light petroleum (b. p. 60—80°) as needles (2·8 g.), m. p. 71·5—72° (Found: C, 37·2; H, 3·6; I, 39·6. $C_{10}H_{11}IO_4$ requires C, 37·2; H, 3·4; I, 39·4%).

3-*Iodo*-2,6-*dimethoxyphenol*.—The preceding acetate (3·2 g.), 20% aqueous sodium hydroxide (20 ml.), and ethanol (20 ml.) were heated on a water-bath for 4 hr., and the mixture was then acidified and extracted with ether, giving a yellow oil which was distilled at 130°/0·2 mm. and crystallised from di-isopropyl ether. The *product* was obtained as stout prisms (2·1 g.), m. p. 56—57° (Found: C, 34·2; H, 3·0; I, 42·7. $C_8H_9IO_3$ requires C, 34·3; H, 3·2; I, 43·3%). This substance did not undergo oxidative coupling to give a biphenoquinone, and was recovered after treatment in acetic acid with either chromic acid or ferric chloride (conditions which oxidise 2,6-dimethoxyphenol to 3,5,3′,5′-tetramethoxybiphenoquinone). The position of the iodine atom was shown by the fact that methylation with dimethyl sulphate and alkali gave 4-iodopyrogallol trimethyl ether, m. p. and mixed m. p. 41—42°; the two specimens gave identical infrared spectra.

4,4′-*Diacetoxy*-2,2′-*di-iodo*-3,5,3′,5′-*tetramethoxybiphenyl*.—A solution of sodium dithionite (30·1 g.) in water (60 ml.) was added to a stirred suspension of 3,5,3′,5′-tetramethoxybiphenoquinone (coerulignone [12]) (26·8 g.) in ethanol (250 ml.), and stirring was continued for a further 3 hr. Next day, water (500 ml.) was added and the 4,4′-dihydroxy-3,5,3′,5′-tetramethoxybiphenyl (25·8 g.) was collected. The dihydroxybiphenyl (5 g.) was heated on the steam-bath for 2 hr. with acetic anhydride (30 ml.) and anhydrous sodium acetate (1·5 g.). After shaking with water (150 ml.), the solid was collected, washed, and dried, giving the diacetoxy-compound as needles (from ethanol) (6·2 g.), m. p. 239—240°. A solution of this substance (3·7 g.) and iodine (2·0 g.) in acetic acid (60 ml.) at 100° was stirred during and after the dropwise addition of iodic acid (0·72 g.) in water (2 ml.) (total time 16 hr.). After addition of water and a little sodium pyrosulphite, the product was collected, washed, and dried, giving 4,4′-diacetoxy-2,2′-di-iodo-3,5,3′,5′-tetramethoxybiphenyl (4·2 g.) as plates (from benzene), m. p. 223—225° (Found: C, 37·2; H, 3·5; I, 39·6. $C_{20}H_{20}I_2O_8$ requires C, 37·4; H, 3·1; I, 39·4%).

Reductive Cleavage of 1,2,3,6,7,8-*Hexamethoxybiphenylene* (I).—The biphenylene (I) (112 mg.) in ethanol was boiled with W-2 Raney mickel (0·5 g.) for 2 hr. and the mixture then filtered; the residue (110 mg.) from evaporation was fractionally crystallised from light petroleum (b. p. 60—80°), giving almost equal amounts of 2,3,4,2′,3′,4′-hexamethoxybiphenyl, m. p. and mixed m. p. 123—124°, and 3,4,5,3′,4′,5′-hexamethoxybiphenyl, m. p. and mixed m. p. 126—127°.

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[11] Graebe and Hess, *Annalen*, 1905, **340**, 237.
[12] Hofmann, *Ber.*, 1878, **11**, 335.