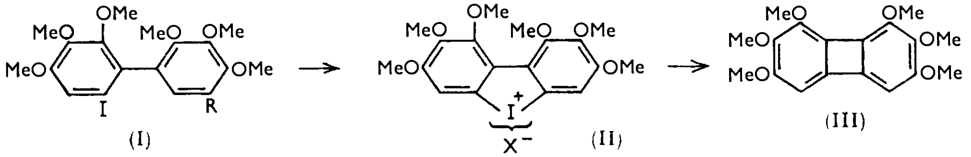
170. *Biphenylenes. Part X.*[1] *Tetra-, Hexa-, and Octa-methoxybiphenylenes.*

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

The following methoxybiphenylenes have been prepared: 1,2,7,8-tetramethoxy-4,5-dimethyl-, 1,2,3,6,7,8-hexamethoxy-, 1,2,4,5,7,8-hexamethoxy-, and octamethoxy-biphenylene.

In continuation of the work described in Part V[2] four new polymethoxybiphenylenes have been prepared by methods already employed in similar cases. The chemical behaviour of these compounds will be described in a later paper.

1,2,3,6,7,8-*Hexamethoxybiphenylene* (III).—*Method* (a). The required precursor of this biphenylene was 6,6′-di-iodo-2,3,4,2′,3′,4′-hexamethoxybiphenyl. Di-iodination of 2,3,4,2′,3′,4′-hexamethoxybiphenyl, either with iodine and iodic acid or with iodine monochloride, gave a single di-iodo-derivative, but this failed to yield a biphenylene when heated with cuprous oxide; later observations proved that the substance was 5,6′-di-iodo-2,3,4,2′,3′,4′-hexamethoxybiphenyl (I; R = I). Monoiodination of the hexamethoxybiphenyl readily yielded a single compound, 6-iodo-2,3,4,2′,3′,4′-hexamethoxybiphenyl (I; R = H), the orientation of the iodine atom being proved by the subsequent indirect conversion of the substance into the 6,6′-di-iodo-compound and thence into the hexamethoxybiphenylene (III) as described below. The direct entry of the second iodine atom into position 5 of the monoiodo-compound is clearly controlled by the steric effect of the iodine atom already present.



The monoiodo-compound (I; R = H) was oxidised with peracetic acid to 6-iodoso-2,3,4,2′,3′,4′-hexamethoxybiphenyl which, without isolation, was cyclised by sulphuric acid to 2,3,4,2′,3′,4′-hexamethoxybiphenylene-6,6′-iodonium hydrogen sulphate (II; X = HSO_4), then converted into the related 6,6′-iodonium iodide (II; X = I), which was isomerised by heat to give 6,6′-di-iodo-2,3,4,2′,3′,4′-hexamethoxybiphenyl. This general method for the preparation of 6,6′-di-iodobiphenyls is based on the work of Collette, McGreer, Crawford, Chubb, and Sandin[3] (for a previous application in this series see Baker, Barton, and McOmie[4]). Finally distillation of the di-iodo-compound with cuprous oxide gave 1,2,3,6,7,8-hexamethoxybiphenylene (III).

Method (b). 5-Nitropyrogallol trimethyl ether was reduced with hydrazine hydrate and palladium, and the resulting amine was converted into 5-iodopyrogallol trimethyl ether from which 3,4,5,3′,4′,5′-hexamethoxybiphenyl was prepared by an Ullmann reaction.[5] A more convenient preparation of 3,4,5,3′,4′,5′-hexamethoxybiphenyl started from 2,6-dimethoxyphenol, itself prepared by partial demethylation of pyrogallol trimethyl ether[6] by heating it with methylmagnesium iodide.[7] Oxidation of 2,6-dimethoxyphenol with chromic acid gave an 80% yield of 3,5,3′,5′-tetramethoxybiphenoquinone (coerulignone)[8] from which 3,4,5,3′,4′,5′-hexamethoxybiphenyl was obtained by reduction and

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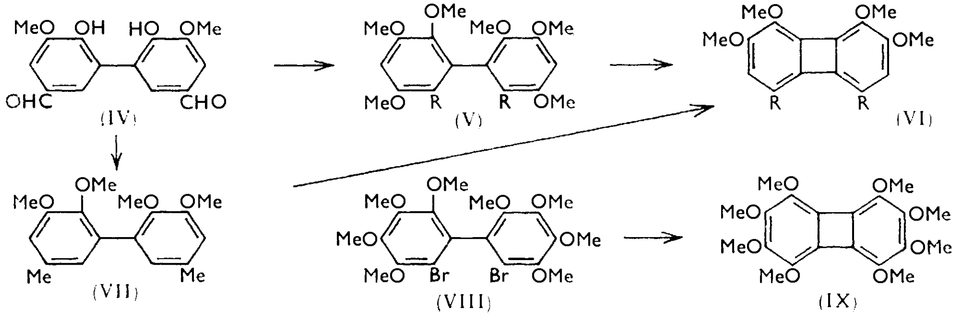
[1] Part IX, McOmie and Thatte, *J.*, 1962, 5298.
[2] Baker, Barton, McOmie, Penneck, and Watts, *J.*, 1961, 3986.
[3] Collette, McGreer, Crawford, Chubb, and Sandin, *J. Amer. Chem. Soc.*, 1956, **78**, 3819.
[4] Baker, Barton, and McOmie, *J.*, 1958, 2658.
[5] Graebe and Suter, *Annalen*, 1905, **340**, 222.
[6] Baker, *J.*, 1941, 662.
[7] Hurd and Winburg, *J. Amer. Chem. Soc.*, 1942, **64**, 2086.
[8] Hofman, *Ber.*, 1878, **11**, 335.

methylation. Iodination of the hexamethoxybiphenyl with iodine and iodic acid gave 2,2′-di-iodo-3,4,5,3′,4′,5′-hexamethoxybiphenyl which was then heated with cuprous oxide. Four compounds were isolated: (*a*) unchanged di-iodo-compound, (*b*) 1,2,3,6,7,8-hexamethoxybiphenylene (III), identical with that previously prepared from the isomeric di-iodo-compound, (*c*) 3,4,5,3′,4′,5′-hexamethoxybiphenyl, and (*d*) 1,6,7,8-hexamethoxybiphenylene-2,3-quinone (the structure of this compound and another synthesis of it will be discussed in a later paper [9]).

1,2,4,5,7,8-*Hexamethoxybiphenylene* (VI; R = OMe).—2,4,5,2′,4′,5′-Hexamethoxybiphenyl, obtainable directly in quantitative yield from 1,2,4-trimethoxybenzene by reaction with iodine monochloride in acetic acid,[10] appeared to offer an easy route to 1,2,4,5,7,8-hexamethoxybiphenylene, but many attempts either to iodinate or to brominate 2,4,5,2′,4′,5′-hexamethoxybiphenyl resulted in the immediate formation of black complexes from which no simple halogenated derivatives could be obtained. Attention was therefore directed to the preparation of 2,3,5,2′,3′,5′-hexamethoxybiphenyl (V; R = H). Oxidation [10] of vanillin with aqueous sodium persulphate yielded 5,5′-diformyl-2,2′-dihydroxy-3,3′-dimethoxybiphenyl (dehydrodivanillin) (IV), oxidation of which with alkaline hydrogen peroxide under the conditions of the Dakin reaction and methylation of the resulting 2,5,2′,5′-tetrahydroxy-3,3′-dimethoxybiphenyl gave 2,3,5,2′,3′,5′-hexamethoxybiphenyl (V; R = H). Di-iodination of this ether (V; R = H) with iodine and iodic acid gave a high yield of 2,2′-di-iodo-3,5,6,3′,5′,6′-hexamethoxybiphenyl (V; R = I) whose structure was established by its successful conversion into 1,2,4,5,7,8-hexamethoxybiphenylene (VI; R = OMe) when heated with cuprous oxide.



Octamethoxybiphenylene (IX).—1,2,3,4-Tetramethoxybenzene was monoiodinated, and converted into 2,3,4,5,2′,3′,4′,5′-octamethoxybiphenyl by heating it with copper. Attempts to effect either mono- or di-iodination of this highly substituted biphenyl by all the usual methods were unsuccessful; it was either unaltered or converted into tarry material. This effect is attributed to steric hindrance, a view which is supported by the fact that dibromination occurred at room temperature, giving 2,2′-dibromo-3,4,5,6,3′,4′,5′,6′-octamethoxybiphenyl (VIII) as an uncharacterised oil which gave a 5% yield of octamethoxybiphenylene (IX) when heated with cuprous oxide. This low yield of the biphenylene is not unexpected, since, *e.g.*, 2,2′-dibromobiphenyl gives a much lower yield of biphenylene than does the 2,2′-di-iodo-derivative,[11] and in the present case steric effects may also be expected to hinder ring closure.

1,2,7,8-*Tetramethoxy*-4,5-*dimethylbiphenylene* (VI; R = Me).—The dialdehyde (IV) was methylated, then reduced by the Wolff–Kishner method to 2,3,2′,3′-tetramethoxy-5,5′-dimethylbiphenyl (VII), and iodinated giving the 2,2′-di-iodo-5,6,5′,6′-tetramethoxy-3,3′-dimethylbiphenyl. Distillation of the di-iodo-compound with cuprous oxide gave

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[9] Baker, McLean, and McOmie, unpublished work.
[10] Erdtman, *Proc. Roy. Soc.*, 1934, *A*, **143**, 177.
[11] Lothrop, *J. Amer. Chem. Soc.*, 1941, **63**, 1187.

1,2,7,8-tetramethoxy-4,5-dimethylbiphenylene (VI; R = Me), thus establishing the positions of the iodine atoms in the di-iodobiphenyl.

EXPERIMENTAL

5,6'-*Di-iodo*-2,3,4,2',3',4'-*hexamethoxybiphenyl* (I; R = I).—Pyrogallol trimethyl ether [6] was iodinated [12] with iodine and mercuric oxide, and the resulting 4-iodopyrogallol trimethyl ether was treated with copper bronze to give 2,3,4,2',3',4'-hexamethoxybiphenyl.[5]

(*a*) To the hexamethoxybiphenyl (1·0 g., 1 mol.) in acetic acid (30 ml.) at 105° was added iodine (0·68 g.) and then a solution of iodic acid (0·25 g.) in water (2 ml.) (2·3 equiv. of iodine available) was added during ¼ hr. with stirring at 100—105° which was continued for 3 hr. The cooled mixture was poured into water (100 ml.) containing sodium metabisulphite (1 g.), and the washed product crystallised from methanol, giving 5,6'-*di-iodo*-2,3,4,2',3',4'-*hexamethoxybiphenyl* as needles (1·41 g., 70%), m. p. 115·5—116° (Found: C, 36·6; H, 3·5; I, 42·7. $C_{18}H_{20}I_2O_6$ requires C, 36·9; H, 3·4; I, 43·3%).

(*b*) To the hexamethoxybiphenyl (0·85 g.) in acetic acid (15 ml.) at room temperature was added dropwise with stirring iodine monochloride (0·89 g., 2·2 equiv.) in acetic acid (10 ml.); the mixture was then stirred for 3 hr. at 90°, decolorised by the addition of sodium metabisulphite (1 g.), and poured into water. The dried solid, dissolved in benzene, was passed through a column of silica (4 × 1 cm.), recovered, and finally recrystallised from methanol, giving needles (65%), m. p. 115—116°, identical (mixed m. p., ultraviolet and infrared spectra) with those described in (*a*) (above).

6-*Iodo*-2,3,4,2',3',4'-*hexamethoxybiphenyl* (I; R = H). Iodination of 2,3,4,2',3',4'-hexamethoxybiphenyl (5·0 g.) in acetic acid (150 ml.) at 100° by the addition of iodine (1·71 g.) and a solution of iodic acid (0·63 g.) in water (5 ml.) was carried out, and the product isolated after 12 hr. at 50°, as in the previous section (*a*). Sublimation at 110°/2 mm. and crystallisation from cyclohexane gave 6-*iodo*-2,3,4,2',3',4'-*hexamethoxybiphenyl* as prisms (6·2 g., 81%), m. p. 142—143° (Found: C, 47·3; H, 4·7; I, 27·1. $C_{18}H_{21}IO_6$ requires C, 47·5; H, 4·6; I, 27·6%).

6,6'-*Di-iodo*-2,3,4,2',3',4'-*hexamethoxybiphenyl*.—(*a*) 2,3,4,2',3',4'-*Hexamethoxybiphenylene*-6,6'-*iodonium hydrogen sulphate* (II; X = HSO_4). A solution of peracetic acid was prepared by adding 30% hydrogen peroxide to four times its volume of distilled acetic anhydride at 0°, with occasional shaking at 0° during 5 hr., and the then homogeneous solution was kept overnight at room temperature. This solution (1·5 ml.) was then added to 6-iodo-2,3,4,2',3',4'-hexamethoxybiphenyl (0·5 g.) in acetic anhydride (1 ml.), and after 12 hr. water (0·06 g.) was added. After a further 3 hr. the mixture was cooled to 10—15°, treated with concentrated sulphuric acid (0·3 ml.), and after 8 hr. diluted with water (10 ml.). The precipitate of the iodonium hydrogen sulphate was collected and washed with water and then ethanol (yield 0·14 g., 22%).

(*b*) 2,3,4,2',3',4'-*Hexamethoxybiphenylene*-6,6'-*iodonium iodide* (II; X = I). The preceding iodonium hydrogen sulphate (0·1 g.) in boiling water (16 ml.) was treated with aqueous potassium iodide till no further precipitate was formed, and, after cooling, the solid iodonium iodide was collected, washed, and dried (yield 0·1 g., 90%).

(*c*) 6,6'-*Di-iodo*-2,3,4,2',3',4'-*hexamethoxybiphenyl*. The preceding iodonium iodide (0·1 g.) was dried at 150°/1 hr., then sublimed at 120°/0·2 mm., and crystallised from methanol, giving 6,6'-*di-iodo*-2,3,4,2',3',4'-*hexamethoxybiphenyl* as needles (0·09 g.), m. p. 170—171° (Found: C, 37·1; H, 3·65; I, 42·9. $C_{18}H_{20}I_2O_6$ requires C, 36·9; H, 3·4; I, 43·3%).

1,2,3,6,7,8-*Hexamethoxybiphenylene* (III).—The preceding di-iodo-compound (80 mg.) was intimately mixed with cuprous oxide (1 g.) and heated for ½ hr. at 350°. A benzene solution of the condensed yellow oil, and a hot benzene extract of the residual solid, were united, concentrated (10 ml.), and purified by passage through a column of silica (10 × 1 cm.) and elution with benzene. The fraction containing the fast-moving, yellow band yielded a solid which was crystallised from cyclohexane, yielding 1,2,3,6,7,8-hexamethoxybiphenylene (8 mg., 18%), m. p. 90—91°, identical (mixed m. p., ultraviolet and infrared spectra) with material prepared by the more convenient route described below.

5-*Aminopyrogallol Trimethyl Ether*.—5-Nitropyrogallol trimethyl ether [13] (10 g.), suspended

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[12] Baker, Kirby, and Montgomery, *J.*, 1932, 2876.

[13] Hughes, Neill, and Ritchie, *Austral. J. Sci. Res.*, 1950, **3**, *A*, 497.

in ethanol (30 ml.) and 64% hydrazine hydrate (8 ml.), was treated in portions with palladium black (0·4 g.). Vigorous reaction with rise of temperature to 60° set in, and after 2 hr. the mixture was warmed on a water-bath for ½ hr., filtered hot, and left overnight. The 5-aminopyrogallol trimethyl ether was collected and crystallised twice from ethanol in an atmosphere of nitrogen, giving colourless needles (7·2 g., 88%), m. p. 112—113°. Hughes, Neill, and Ritchie [13] reduced the nitro-compound with ferrous sulphate and iron, obtaining 5-aminopyrogallol trimethyl ether in 83% yield, with m. p. 114°.

2,2′-*Di-iodo*-3,4,5,3′,4′,5′-*hexamethoxybiphenyl*.—The preceding amine was converted into 5-iodopyrogallol trimethyl ether [5] and thence by an Ullmann reaction into 3,4,5,3′,4′,5′-hexamethoxybiphenyl.[5] The latter (1·0 g.) in acetic acid (10 ml.) was iodinated with iodine and iodic acid as in the case of the isomeric 2,3,4,2′,3′,4′-hexamethoxybiphenyl. The product was crystallised first from glacial acetic acid and then from ethanol, giving 2,2′-*di-iodo*-3,4,5,3′,4′,5′-*hexamethoxybiphenyl* as needles (1·8 g.; 80%), m. p. 166—167° (Found: C, 36·8; H, 3·4%).

Reaction of 2,2′-*Di-iodo*-3,4,5,3′,4′,5′-*hexamethoxybiphenyl with Cuprous Oxide: Isolation of* 1,2,3,6,7,8-*Hexamethoxybiphenylene* (III), 3,4,5,3′,4′,5′-*Hexamethoxybiphenyl, and* 1,6,7,8-*Hexamethoxybiphenylene*-2,3-*quinone*. The di-iodo-compound (20 g.) was intimately ground with cuprous oxide (200 g.), and heated in eleven separate portions (20 g. each) at 340° (metal-bath) for ¼ hr. till nothing further distilled into the upper receiver; the pressure was then reduced to 20 mm. and heating continued for 20 min. An ethanolic solution of the distilled material, combined with a hot benzene extract of the residue, yielded a gum (4·9 g.), which in a small amount of benzene was adsorbed on a silica gel column (20 × 4 cm.) and eluted with (1) light petroleum, b. p. 60—80° (500 ml.), (2) cyclohexane (1500 ml.), (3) benzene (500 ml.), and (4) benzene–chloroform (50% v/v) (500 ml.). Eluate (1) (1·27 g.) yielded unchanged 2,2′-di-iodo-3,4,5,3′,4′,5′-hexamethoxybiphenyl, m. p. 166—167°. The yellow eluate (2) (2·62 g.) yielded 1,2,3,6,7,8-*hexamethoxybiphenylene* (III) which separated from cyclohexane as thick, yellow needles (2·60 g., 22%), m. p. 91—91·5° [Found: C, 64·8; H, 6·1; OMe, 59·0. $C_{12}H_2(OMe)_6$ requires C, 65·1; H, 6·0; OMe, 59·3%], $\lambda_{max.}$ (in EtOH) 270, 346, 365 mμ (log ε 4·50, 4·19, 4·22 respectively); the *picrate*, prepared from alcoholic solution, separated in black needles, m. p. 128—129° (Found: C, 50·8; H, 3·8; N, 6·7. $C_{24}H_{23}N_3O_{13}$ requires C, 51·2; H, 3·8; N, 7·1%). Eluate (3) (0·61 g.) was crystallised several times from methanol (charcoal), giving 3,4,5,3′,4′,5′-hexamethoxybiphenyl as needles, m. p. and mixed m. p. 126—127°. The red eluate (4) (0·09 g.) was crystallised twice from ethanol, giving red needles (80 mg.), m. p. 213—214° (Found: C, 63·4; H, 4·6. $C_{16}H_{14}O_6$ requires C, 63·6; H, 4·6%). This substance was later shown to be identical (mixed m. p., ultraviolet and infrared spectra) with authentic 1,6,7,8-*hexamethoxybiphenylene*-2,3-*quinone*.[9]

2,3,5,2′,3′,5′-*Hexamethoxybiphenyl* (V; R = H).—Vanillin was oxidised by sodium persulphate to 5,5′-diformyl-2,2′-dihydroxy-3,3′-dimethoxybiphenyl in 80% (crude) yield.[10] This biphenyl (6·0 g.) in 10% aqueous sodium hydroxide (20 ml.) was then oxidised in an atmosphere of nitrogen by the addition of 3% aqueous hydrogen peroxide (50 ml.). The mixture darkened with rise of temperature to 65°, and after ½ hr. it was acidified with hydrochloric acid, filtered to remove starting material, and extracted with ether. The extracts, concentrated under reduced pressure in nitrogen, left crude 2,5,2′,5′-tetrahydroxy-3,3′-dimethoxybiphenyl as a brown oil (3·1 g.); this was directly methylated in acetone (15 ml.) and methyl sulphate (10 ml.) by addition with stirring of 10% aqueous potassium hydroxide (100 ml.) and a little sodium dithionite, first at 15° and finally on the steam-bath. Addition of water and crystallisation from ethanol gave 2,3,5,2′,3′,5′-hexamethoxybiphenyl as prisms (2·9 g.), m. p. 119—120° (lit.,[14] 119—120°).

2,2′-*Di-iodo*-3,5,6,3′,5′,6′-*hexamethoxybiphenyl* (V; R = I).—To the preceding compound (0·51 g.) and iodine (0·34 g.) in acetic acid (15 ml.) at 60° was added iodic acid (0·12 g.) in water (1 ml.) with stirring. After 1 hr. the mixture was kept overnight at 40°, poured into water (50 ml.), and decolorised by sodium metabisulphite, and the solid was collected and crystallised from ethanol, giving 2,2′-*di-iodo*-3,5,6,3′,5′,6′-*hexamethoxybiphenyl* as needles (0·66 g., 70%), m. p. 298—300° (Found: C, 36·5; H, 3·5. $C_{18}H_{20}I_2O_6$ requires C, 36·9; H, 3·4%).

1,2,4,5,7,8-*Hexamethoxybiphenylene* (VI; R = OMe).—The preceding di-iodo-compound (V; R = I) (0·5 g.) and cuprous oxide (5·0 g.) were heated at 330° for 20 min. and at 350°/20 mm. till no further product condensed. The condensate was treated with cyclohexane and

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[14] Erdtman, *Proc. Roy. Soc.*, 1934, *A*, **143**, 191.

filtered from unchanged di-iodo-compound, and the solution passed through a silica column (10 × 1 cm.). The material in the yellow band crystallised from cyclohexane, giving yellow plates (0·082 g., 30%) of 1,2,4,5,7,8-*hexamethoxybiphenylene* (VI: R = OMe), m. p. 119—119·5° [Found: C, 65·05; H, 6·2; OMe, 58·6. $C_{12}H_2(OMe)_6$ requires C, 65·1; H, 6·0; OMe, 59·3%], $\lambda_{max.}$ (in EtOH) 272, 309, 336 mμ (log ε 4·74, 3·35, 3·19, respectively). The *picrate* prepared in, and recrystallised from ethanol, formed black needles, m. p. 145—146° (Found: C, 51·1; H, 3·5; N, 6·8. $C_{24}H_{23}N_3O_{13}$ requires C, 51·2; H, 3·9; N, 7·1%).

2,3,4,5,2′,3′,4′,5′-*Octamethoxybiphenyl.*—2-Hydroxy-3,4-dimethoxyacetophenone [6] was oxidised by alkaline hydrogen peroxide to 3,4-dimethoxycatechol [15] in 59% yield and this was then treated with an excess of methyl sulphate and potassium hydroxide in dilute ethanol in presence of sodium metabisulphite, giving, after sublimation at 80°/0·3 mm. and crystallisation from light petroleum (b. p. 60—80°), 1,2,3,4-tetramethoxybenzene, m. p. 89—90°, in 81% yield. The tetramethoxybenzene was iodinated in presence of hydrogen peroxide, giving 1-iodo-2,3,4,5-tetramethoxybenzene [13] (b. p. 141°/0·4 mm., 79%). The iodo-compound was treated with an equal weight of copper bronze at 220°/1 hr., passed through a silica column in benzene solution, and crystallised from aqueous methanol, giving 2,3,4,5,2′,3′,4′,5′-*octamethoxybiphenyl* as needles (69%), m. p. 141—142° (Found: C, 60·4; H, 6·95. $C_{20}H_{26}O_8$ requires C, 60·9; H, 6·6%).

Octamethoxybiphenylene (IX).—The 2,3,4,5,2′,3′,4′,5′-octamethoxybiphenyl (4 g.) in carbon tetrachloride was stirred during the slow addition of bromine (5·1 g., 3·1 mol.) in the same solvent, and a slow current of air was passed to remove the hydrogen bromide. After 5 hr. the solution was washed with aqueous sodium metabisulphite, dried and evaporated, leaving crude 2,2′-dibromo-3,4,5,6,3′,4′,5′,6′-octamethoxybiphenyl (VIII) as a viscous oil (4·2 g.). This material and cuprous oxide (40 g.) were heated in the usual way at 310° for 20 min., then at 350°/25 mm. for 10 min. Purification of the yellow distillate in benzene on a column of silica (20 × 1 cm.) and elution with benzene yielded a solid which was crystallised from cyclohexane, giving *octamethoxybiphenylene* (IX) as yellow needles (0·18 g., 4%), m. p. 138—139° (Found: C, 62·2; H, 6·2. $C_{20}H_{24}O_8$ requires C, 61·9; H, 6·2%), $\lambda_{max.}$ (in EtOH) 268, 310, 351, 376 mμ (log ε 4·68, 4·12, 3·98, 4·07, respectively). The *picrate*, prepared in and crystallised from ethanol, formed black needles, m. p. 168—169° (Found: C, 49·7; H, 4·2. $C_{26}H_{27}N_3O_{15}$ requires C, 50·2; H, 4·35%).

2,3,2′,3′-*Tetramethoxy*-5,5′-*dimethylbiphenyl* (VII).—The dialdehyde (IV) was converted into the tetramethoxy-derivative by treatment with an excess of methyl sulphate and potassium hydroxide in aqueous acetone (yield 72%; m. p. 137—138°; lit.,[16] m. p. 137°). This ether (3·3 g.) and potassium hydroxide (1 g.) were refluxed in diethylene glycol (40 ml.) and 64% hydrazine hydrate (1·1 g.) for 1 hr., then distilled until the temperature of the mixture reached 210°, and refluxed again at this temperature for 2 hr. Addition of water and extraction with ether gave 2,3,2′,3′-tetramethoxy-5,5′-dimethylbiphenyl (VII) which separated from cyclohexane in cubes (0·5 g.), m. p. 116—117°. During this reaction a considerable amount of demethylation occurred, and acidification of the remaining alkaline liquor, extraction with ether, and remethylation gave a further quantity (1·1 g.) of the biphenyl (VII). This substance was made in two different ways by Richtzenhain [17] and was described as an oil.

2,2′-*Di-iodo*-5,6,5′,6′-*tetramethoxy*-3,3′-*dimethylbiphenyl.*—Iodic acid (0·07 g.) in water (1 ml.) was added to a stirred solution of 2,3,2′,3′-tetramethoxy-5,5′-dimethylbiphenyl (0·20 g.) and iodine (0·13 g.) in acetic acid (10 ml.) at 100°. After 1 hr. iodine (0·13 g.) was added and stirring continued for 12 hr. at 70°. Addition of water (50 ml.) and sodium metabisulphite (0·3 g.) precipitated 2,2′-*di-iodo*-5,6,5′,6′-*tetramethoxy*-3,3′-*dimethylbiphenyl* which separated from ethanol in plates (0·26 g., 69%), m. p. 161—162° (Found: C, 38·8; H, 3·5. $C_{18}H_{20}I_2O_4$ requires C, 39·0; H, 3·6%).

1,2,7,8-*Tetramethoxy*-4,5-*dimethylbiphenylene* (VI; R = Me).—The preceding di-iodo-compound (0·20 g.) was heated with cuprous oxide (2·5 g.) in the usual manner. A solution of the yellow product in cyclohexane was purified by passage through a silica column, and elution with and crystallisation from the same solvent gave 1,2,7,8-tetramethoxy-4,5-dimethylbiphenylene as yellow needles (0·03 g., 27%), m. p. 129—132°. Recrystallisation from cyclohexane and sublimation at 110—120°/0·1 mm. gave 1,2,7,8-*tetramethoxy*-4,5-*dimethylbiphenylene*

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[15] Baker, *J.*, 1934, 1683.

[16] Elbs and Lerch, *J. prakt. Chem.*, 1916, **93**, 1.

[17] Richtzenhain, *Chem. Ber.*, 1949, **82**, 447.

(VI; R = Me), m. p. 132—133° (Found: C, 70·8; H, 6·7. $C_{18}H_{20}O_4$ requires C, 71·0; H, 6·8%), $\lambda_{max.}$ (in EtOH) 251, 257, 280, 316, 340 mμ (log ε 4·41, 4·27, 3·21, 3·07, 3·11, respectively).

We thank the Department of Scientific and Industrial Research for a Studentship awarded to N. J. McL.

THE UNIVERSITY, BRISTOL. [*Received, July* 24*th*, 1962.]