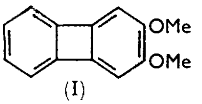
981. *Biphenylenes. Part VII.*[1] *Synthesis of 2,3-Dimethoxybiphenylene.*

By J. M. Blatchly, J. F. W. McOmie, and (in part) M. L. Watts.

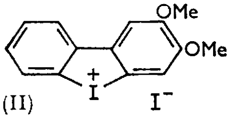
2,3-Dimethoxybiphenylene has been synthesised from 4-hydroxybiphenyl. Better yields of the biphenylene are obtained by two other routes starting from veratrole. Several biphenyls and quaterphenyls related to the present work are described.

2,3-Dimethoxybiphenylene (I) was required in order to confirm the structure of a biphenylene-*o*-quinone prepared from 2-hydroxybiphenylene.[2] The present paper describes the synthesis of this dimethoxy-compound from 4,5-dimethoxy-2,2′-biphenylyleneiodonium iodide (II), itself made by three independent routes. The first route to the iodonium iodide was unambiguous but the yields were low. The other two routes were developed therefore and they both gave satisfactory yields.

(*a*) 4-Hydroxybiphenyl was treated with iodine chloride, thereby giving 4-hydroxy-3-iodobiphenyl,[3] which was conveniently hydrolysed to 3,4-dihydroxybiphenyl by boiling aqueous sodium hydroxide. Previously the dihydroxy-compound had been made by heating 3-bromo-[4] or 3-chloro-4-hydroxybiphenyl[5] with alkali in an autoclave. Methylation of the dihydroxybiphenyl then gave 3,4-dimethoxybiphenyl (III; R = H) which on reaction with iodine and iodic acid gave 2-iodo-4,5-dimethoxybiphenyl (III; R = I).



(I)



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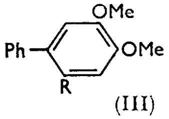
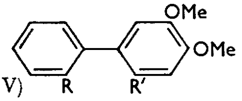


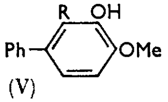
(III)

The latter was converted into the iodonium iodide (II) by the procedure of Collette *et al.*[6] When this iodonium iodide was heated with cuprous oxide it yielded 2,3-dimethoxybiphenylene (I). It was necessary to prove the orientation of the intermediate iodo-compound (III; R = I) since if iodination of 3,4-dimethoxybiphenyl had occurred at position 2 it would have resulted in 1,2-dimethoxybiphenylene. Nitration of 3,4-dimethoxybiphenyl gave 2-nitro- and 2,4′-dinitro-4,5-dimethoxybiphenyl, the structures of which were proved by comparison with the products from appropriate crossed Ullmann reactions. Reduction of the mononitro-compound followed by diazotisation and treatment with potassium iodide gave 2-iodo-4,5-dimethoxybiphenyl which was identical with the product from the direct iodination of 3,4-dimethoxybiphenyl.

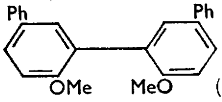
(*b*) 4,5-Dimethoxy-2,2′-dinitrobiphenyl (IV; R = R′ = NO$_2$), made both by a crossed Ullmann reaction and by nitration of 3,4-dimethoxy-2′-nitrobiphenyl (IV; R = NO$_2$, R′ = H), was converted by reduction and tetrazotisation into a mixture of 2,2′-di-iodo-4,5-dimethoxybiphenyl (IV; R = R′ = I) and the iodonium iodide (II).

(IV)





(V)



(VI)

(*c*) 3,4-Dimethoxy-2′-nitrobiphenyl (IV; R = NO$_2$, R′ = H) was treated with iodine and iodic acid, to give the corresponding iodo-compound (IV; R = NO$_2$, R′ = I). The

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[1] Part VI, Baker, Barton, McOmie, and Searle, *J.*, 1962, 2633.

[2] Blatchly, McOmie, and Thatte, following paper.

[3] Colbert, Houghton, Schmidt, and Abernethy, *J. Amer. Chem. Soc.*, 1944, **66**, 122.

[4] Allen and van Allan, *J. Org. Chem.*, 1949, **14**, 798.

[5] Harvey, U.S.P. 1,952,755; *Chem. Abs.*, 1934, **28**, 3426.

[6] Collette, McGreer, Crawford, Chubb, and Sandin, *J. Amer. Chem. Soc.*, 1956, **78**, 3819.

position of the iodine atom was confirmed by the conversion of the iodo-compound into the previously prepared iodonium iodide (II) by reduction followed by diazotisation. An attempt to convert 2'-amino-3,4-dimethoxybiphenyl into the corresponding 2'-iodo-compound by the Sandmeyer reaction gave only 2,3-dimethoxybenzo[*c*]cinnoline.

In connexion with the orientation of 2-iodo-4,5-dimethoxybiphenyl, 3-acetyl-4-methoxybiphenyl was oxidised by the Baeyer–Villiger method to 3-acetoxy-4-methoxybiphenyl, which on hydrolysis gave the corresponding hydroxy-compound (V; R = H). When this compound was treated with iodine chloride a chloro-derivative was obtained, in contrast to the similar iodination of 4-hydroxybiphenyl by this reagent. The chloro-compound is probably 2-chloro-3-hydroxy-4-methoxybiphenyl (V; R = Cl) since on methylation it gives a chloro-3,4-dimethoxybiphenyl which is not identical with 2-chloro-4,5-dimethoxybiphenyl (III; R = Cl) obtained by reduction and diazotisation of the corresponding 2-nitrobiphenyl (III; R = NO_2). 3-Iodo-4-methoxybiphenyl has been converted by the Ullmann reaction into 2,2'-dimethoxy-5,5'-diphenylbiphenyl (VI) and thence into 2,2'-dihydroxy and a dinitro-compound, probably 2,2'-dimethoxy-3,3'-dinitro-5,5'-diphenylbiphenyl.

EXPERIMENTAL

3,4-*Dimethoxybiphenyl* (III; R = H).—A mixture of copper bronze (10 g.), 4-hydroxy-3-iodobiphenyl[3] (29·6 g.), and 20% aqueous sodium hydroxide (270 ml.) was boiled under reflux for 4·5 hr. The cooled product was filtered rapidly and the residue was washed with boiling water (200 ml.). The deep red filtrate and washings were acidified with hydrochloric acid, and the resulting precipitate was collected and then extracted with methanol (100 ml.). Dilution of the methanol gave 3,4-dihydroxybiphenyl (13·7 g., 73%), m. p. 139·5—140·5° (lit.,[4] m. p. 139—140°). With dimethyl sulphate and aqueous potassium hydroxide it gave 3,4-*dimethoxybiphenyl* (53% overall yield from the iodobiphenyl), m. p. 60—62°. A sample recrystallised from methanol as needles, m. p. 67—68° (lit.,[7] 70°), b. p. 319—320°/752 mm. (Found: C, 78·6; H, 6·8. $C_{14}H_{14}O_2$: requires C, 78·5; H, 6·5%). This compound was recorded by Harris and Christiansen[7] but they gave no experimental details.

2-*Iodo*-4,5-*dimethoxybiphenyl* (III; R = I).—(*a*) 3,4-Dimethoxybiphenyl (4·4 g.) and iodine (2·5 g.) in acetic acid (50 ml.) were boiled under reflux while iodic acid (0·94 g.) in water (5 ml.) was added during 15 min. After being boiled for a further 5 hr., the solution was cooled and ice-cold aqueous sodium hydrogen sulphite was added to it until the colour of iodine had disappeared. The brown solid obtained by cooling the mixture to 0° was collected and recrystallised three times from methanol, thereby giving 2-*iodo*-4,5-*dimethoxybiphenyl* (3·66 g., 53%), m. p. 109° (Found: C, 49·2; H, 4·1. $C_{14}H_{13}IO_2$ requires C, 49·4; H, 3·8%).

Using twice the amounts of iodine and iodic acid gave a mixture of the monoiodo-compound and a small amount of (probably) 2,4'-*di-iodo*-4,5-*dimethoxybiphenyl*, plates, m. p. 135—136° (from benzene) (Found: C, 35·9; H, 2·5. $C_{14}H_{12}I_2O_2$ requires C, 36·1; H, 2·5%), $\nu_{max.}$ 804vs and 885m $cm.^{-1}$ (two adjacent aromatic CH and isolated aromatic CH, respectively). An attempt to prepare this di-iodo-compound from 2,4'-dinitro-4,5-dimethoxybiphenyl by reduction and diazotisation was unsuccessful.

(*b*) Stannous chloride dihydrate (3·5 g.) in concentrated hydrochloric acid (7 ml.) was added to a suspension of 4,5-dimethoxy-2-nitrobiphenyl (1·26 g.) in warm ethanol (15 ml.). After being boiled under reflux for 10 min., the mixture was cooled and made strongly alkaline by the addition of 10% aqueous sodium hydroxide. The liberated amine was extracted into ether (2 × 40 ml.) and, after evaporation of the solvent, concentrated hydrochloric acid (4 ml.) was added. The resulting solution of the amine hydrochloride was cooled to 5° and sodium nitrite (0·4 g.) in water (3 ml.) was added during 5 min. After 15 min., potassium iodide (2 g.) in water (2 ml.) was added and the mixture was set aside for 15 min. before being heated to 40° for a further 15 min. The resulting black tar was shaken with aqueous sodium hydrogen sulphite and then with water. It recrystallised from methanol (charcoal), giving 2-iodo-4,5-dimethoxybiphenyl (0·1 g.), m. p. 107—108° [mixed m. p. with the iodo-compound made as in (*a*) 108—109°].

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[7] Harris and Christiansen, *J. Amer. Pharmaceut. Assoc.* (*Sci. Edn.*), 1934, **23**, 530; *Chem. Abs.*, 1935, **29**, 2527.

4,5-Dimethoxy-2,2′-biphenylyleneiodonium Iodide (II) *and 2,2′-Di-iodo-4,5-dimethoxybiphenyl* (IV; R = R′ = I).—(*a*) Peracetic acid was made by mixing acetic anhydride (100 ml.) and 30% hydrogen peroxide (25 ml.) and keeping the mixture for 24 hr. with occasional shaking. A mixture of 2-iodo-4,5-dimethoxybiphenyl (1·0 g.) and acetic anhydride (2 ml.) was warmed just enough to dissolve the solid, then peracetic acid (5 ml.) was added, with shaking to keep the precipitate finely divided. After the mixture had been kept for 2 days at 22°, water (0·2 ml.) was added, and next day the solution was filtered to remove starting material. The filtrate was kept at 10—15° during addition of concentrated sulphuric acid (0·6 ml.) in acetic anhydride (2 ml.). After being kept for 12 hr. the mixture was diluted with water (20 ml.) and the tarry precipitate was collected and washed with ethanol, leaving the iodonium hydrogen sulphate as a yellow powder. This was dissolved in boiling water (5 ml.), and potassium iodide solution was added, thereby giving the iodonium iodide (150 mg., 15%) as a yellow precipitate. The preparation was not always reproducible.

(*b*) *4,5-Dimethoxy-2,2′-dinitrobiphenyl* (0·61 g.) was reduced in the usual way by stannous chloride dihydrate (3·5 g.) in concentrated hydrochloric acid (7·0 ml.) and ethanol (10 ml.) to the corresponding diamine, which was then extracted with ether. After removal of the ether the diamine was dissolved in 17% aqueous hydrochloric acid (10 ml.) and tetrazotised below 0° by sodium nitrite (0·3 g.) in water (2 ml.). After being kept for 10 min. the orange solution was poured into a solution of potassium iodide (3·0 g.) in water (5 ml.) at 0°, and the resultant mixture was set aside. Next day it was heated for 15 min. on a water-bath and treated with aqueous sodium hydrogen sulphite before being cooled and then filtered. The solid was extracted with methanol, giving *2,2′-di-iodo-4,5-dimethoxybiphenyl* (120 mg.) as granules, m. p. 140° (Found: C, 36·2; H, 2·3. $C_{14}H_{12}I_2O_2$ requires C, 36·1; H, 2·5%). The methanol-insoluble material consisted of 4,5-dimethoxy-2,2′-biphenylyleneiodonium iodide and it was obtained as a brown powder (240 mg.) after thorough washing with benzene and chloroform. The total yield of iodo-compounds was 40%.

(*c*) Unpurified 2′-amino-2-iodo-4,5-dimethoxybiphenyl made by reduction of the corresponding 2′-nitro-compound (1·68 g., for details see below) was suspended in 17% hydrochloric acid (50 ml.), and the mixture was kept below 0° during slow addition of sodium nitrite (0·33 g.) in water (5 ml.). After being kept at 0° for 10 min., the solution was filtered and added to 30% potassium iodide (50 ml.) at 0°. The mixture was allowed to warm to room temperature, then it was heated on a water-bath for 10 min. before addition of sodium hydrogen sulphite solution. The pale buff iodonium iodide (1·25 g., 62%) was collected and washed with water and methanol. It could not be purified owing to its sparing solubility. A well-washed sample was analysed (Found: C, 38·2; H, 2·6. Calc. for $C_{14}H_{12}I_2O_2$: C, 36·1; H, 2·5%). The compounds made by all three methods showed almost identical infrared spectra.

2,3-Dimethoxybiphenylene (with M. L. Watts).—The iodonium iodide (180 mg.) was heated with cuprous oxide (1·8 g.) at 330—360° in the usual way,[8] giving a sublimate (11 mg.) which on resublimation gave *2,3-dimethoxybiphenylene* (5 mg.) as yellow needles, m. p. 87—88° (Found: C, 79·5; H, 5·8. $C_{14}H_{12}O_2$ requires C, 79·35; H, 5·75%).

4,5-Dimethoxy-2-nitrobiphenyl (III; R = NO_2).—(*a*) Copper bronze (6·4 g.) was added during 30 min. to a stirred mixture of 4-bromo-5-nitroveratrole (8·24 g.) and iodobenzene (8·0 g.) at 195—200°. After being kept at this temperature for 2 hr. the mixture was cooled and extracted with chloroform (2 × 25 ml.). The solvent was removed and the residue was boiled with methanol (100 ml.) and filtered. The filtrate yielded 4,5-dimethoxy-2-nitrobiphenyl (3·1 g., 38%) as pale yellow needles, m. p. and mixed m. p. 113—114°. The material insoluble in methanol consisted of 4,4′,5,5′-tetramethoxy-2,2′-dinitrobiphenyl (1·2 g.), m. p. 215—217°.

(*b*) Concentrated nitric acid (1·38 g.) in acetic acid (5 ml.) was added during 5 min. to a stirred solution of 3,4-dimethoxybiphenyl (3·9 g.) in acetic acid (15 ml.). The mixture was stirred for 15 min. more at room temperature and then for 2 hr. at 50°. Ice-cold water (250 ml.) was added to the cooled mixture, and the yellow solid was collected after 2 hr. at 0°. The solid recrystallised from methanol, giving *4,5-dimethoxy-2-nitrobiphenyl* (3·55 g., 75%), m. p. 109—110° raised to 114° by one further recrystallisation from methanol (Found: C, 64·9; H, 5·3; N, 5·1. $C_{14}H_{13}NO_4$ requires C, 64·9; H, 5·0; N, 5·4%).

4,5-Dimethoxy-2,4′-dinitrobiphenyl.—(*a*) 4,5-Dimethoxy-2-nitrobiphenyl (0·7 g.) and 23%

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[8] Baker, Boarland, and McOmie, *J.*, 1954, 1476.

nitric acid (40 ml.) were boiled under reflux for 5 hr. The solid which separated on cooling was collected and recrystallised twice from acetone, giving the dinitro-compound as a yellow powder (0·12 g.), m. p. and mixed m. p. (see below) 202°.

(*b*) A mixture of *p*-iodonitrobenzene (4·76 g.) and 4-bromo-5-nitroveratrole (4·0 g.) was heated to 190° and copper bronze (3·1 g.) was added gradually to keep the temperature of the exothermic reaction at 190—200°. Heating at this temperature was continued for 2 more hours. After being cooled the mixture was extracted with chloroform, and the product obtained was recrystallised (charcoal) from acetone, giving 4,5-*dimethoxy*-2,4'-*dinitrobiphenyl* (2·5 g., 54%) as yellow needles, m. p. 202° (Found: C, 55·8; H, 4·0. $C_{14}H_{12}N_2O_6$ requires C, 55·3; H, 4·1%).

4,5-*Dimethoxy*-2,2'-*dinitrobiphenyl* (IV; R = R' = NO_2).—(*a*) (With M. L. WATTS.) Concentrated nitric acid (200 mg.) in acetic acid (0·5 ml.) was added dropwise to 3,4-dimethoxy-2'-nitrobiphenyl (500 mg.) in acetic acid (5 ml.). Next day the mixture was poured into water (100 ml.), and the product collected. Recrystallisation of it from benzene–light petroleum (b. p. 80—100°) gave the 4,5-*dimethoxy*-2,2'-*dinitrobiphenyl* (550 mg., 93%) as yellow plates, m. p. 150—151° (Found: C, 55·0; H, 3·9%).

(*b*) Copper bronze (6·2 g.) was added gradually to a hot mixture of *o*-bromonitrobenzene (7·7 g.) and 4-bromo-5-nitroveratrole (8·0 g.), at 190—200°. After a total of 2 hr. at this temperature, the mixture was cooled and extracted with chloroform. The mixture of biphenyls was then fractionally crystallised from methanol, giving first 4,4',5,5'-tetramethoxy-2,2'-dinitrobiphenyl (1·3 g.), m. p. 219°, then the required dimethoxybiphenyl (1·9 g., 21%), m. p. 147°. A sample was recrystallised from methanol, with seed crystals from preparation (*a*), m. p. rising to 150—151°. The infrared spectra of pure samples from methods (*a*) and (*b*) were identical.

3,4-*Dimethoxy*-2'-*nitrobiphenyl* (IV; R = NO_2, R' = H) (with M. L. WATTS). 4-Bromoveratrole (20·6 g.), *o*-chloronitrobenzene (15·0 g.), and copper bronze (18 g.) were heated together at 190—200° for 10 hr., the temperature finally being raised to 240° for 1 hr. The cooled mixture was extracted as usual with chloroform, and the organic products were recrystallised from methanol, giving the *nitrobiphenyl* (6·0 g., 25%) as yellow granules, m. p. 98° (Found: C, 64·9; H, 5·2; N, 5·1. $C_{14}H_{13}NO_4$ requires C, 64·9; H, 5·05; N, 5·4%).

2-*Iodo*-4,5-*dimethoxy*-2'-*nitrobiphenyl* (IV; R = NO_2, R' = I).—Iodic acid (0·34 g.) in water (2 ml.) was added dropwise to a mixture of 3,4-dimethoxy-2'-nitrobiphenyl (1·8 g.) and iodine (0·84 g.) in acetic acid (30 ml.), and the whole was boiled under reflux for 4 hr. The cooled mixture was poured into aqueous sodium hydrogen sulphite, and the resulting precipitate was collected. Recrystallisation from ethanol gave the *iodo-compound* (2·4 g., 90%) as yellow granules, m. p. 132—133° (Found: C, 43·75; H, 3·2. $C_{14}H_{12}INO_4$ requires C, 43·6; H, 3·1%).

2'-*Amino*-2-*iodo*-4,5-*dimethoxybiphenyl* (IV; R = NH_2, R' = I).—The preceding nitro-compound (1·0 g.) and ethanol (8 ml.) were boiled under reflux while a solution of stannous chloride dihydrate (1·9 g.) in concentrated hydrochloric acid (4·5 ml.) was added down the condenser. After 5 min. the mixture became colourless and was poured into 10% aqueous sodium hydroxide, and the resulting solid was collected and recrystallised from ethanol–benzene, giving the *amine* (0·7 g., 76%), m. p. 191° (Found: C, 47·7; H, 3·9. $C_{14}H_{14}INO_2$ requires C, 47·3; H, 3·9%). The amine is stable in air.

2,3-*Dimethoxybenzo*[c]*cinnoline* (with M. L. WATTS).—(*a*) Sodium nitrite (0·07 g.) in water (2 ml.) at 0° was added to a stirred solution of 2'-amino-3,4-dimethoxybiphenyl (0·21 g.) in concentrated hydrochloric acid (15 ml.) also at 0°. After 10 min. the clear solution was poured into ice-cold 20% potassium iodide (20 ml.). The mixture was diluted with water (100 ml.) containing sodium sulphite (0·5 g.), and the solid was collected. It was purified by chromatography in benzene on a column of silica gel. Recrystallisation from benzene–light petroleum (b. p. 80—100°) gave the *cinnoline* (0·164 g.) as pale yellow needles, m. p. 200—201° (Found: C, 69·5; H, 5·0; N, 11·75. $C_{14}H_{12}N_2O_2$ requires C, 70·0; H, 5·0; N, 11·7%).

(*b*) W-2 Raney nickel (1 g.) was added cautiously to a mixture of 4,5-dimethoxy-2,2'-dinitrobiphenyl (0·5 g.), ethanol (50 ml.), and 100% hydrazine hydrate (10 ml.) at a rate sufficient to maintain the vigorous reaction. When the addition was complete (*ca.* 30 min.) more Raney nickel (0·5 g.) was added and the mixture was boiled until the smell of hydrazine had disappeared (*ca.* 15 min.). The colourless solution was filtered and the solvent removed, leaving an oil which was warmed in acetic anhydride (5 ml.) and concentrated sulphuric acid (1 drop) on the water-bath for 1 hr. The mixture was diluted with water (100 ml.) and neutralised with aqueous sodium carbonate, and the resulting solid was collected and recrystallised as in (*a*), giving the cinnoline (0·26 g.), m. p. and mixed m. p. 200—201°.

3-*Acetoxy*-4-*methoxybiphenyl*.—3-Acetyl-4-methoxybiphenyl [9] (3·0 g.) was dissolved in acetic acid (8 ml.) by warming and was then cooled without allowing crystallisation to occur. Concentrated sulphuric acid (0·15 ml.) was added; an intense colour developed which was destroyed by addition of 15% peracetic acid (14 ml.). After being kept for 80 hr. the mixture was diluted with water, and the product recrystallised from ethanol and then light petroleum (b. p. 60—80°), giving the *acetoxy-compound* (0·6 g.) as plates, m. p. 99° (Found: C, 74·6; H, 6·2. $C_{15}H_{14}O_3$ requires C, 74·4; H, 5·8%). Concentration of the mother-liquors gave more (1·0 g.) of the acetoxy-compound which was discoloured but pure enough for the next step (hydrolysis).

3-*Hydroxy*-4-*methoxybiphenyl* (V; R = H).—3-Acetoxy-4-methoxybiphenyl (1·0 g., unpurified material) was boiled with a 10% solution of potassium hydroxide in aqueous ethanol (1 : 1) for 1 hr. Dilution of the mixture gave an oil which solidified at 0°. After being filtered, the solution was acidified with hydrochloric acid, and the 3-*hydroxy*-4-*methoxybiphenyl* was collected. It had m. p. 118° after being recrystallised from benzene–light petroleum (b. p. 60—80°) (Found: C, 78·0; H, 6·3. $C_{13}H_{12}O_2$ requires C, 78·0; H, 6·0%). A sample of the phenol was methylated and yielded 3,4-dimethoxybiphenyl, m. p. and mixed m. p. 69°. The *benzoate* of the phenol was made by warming it with benzoyl chloride. It formed plates, m. p. 98—99°, from ethanol (Found: C, 79·0; H, 5·5. $C_{20}H_{16}O_3$ requires C, 78·9; H, 5·3%). The benzoate could not be obtained by the Baeyer–Villiger reaction of the known 3-benzoyl-4-methoxybiphenyl.[10]

2-*Chloro*-3,4-*dimethoxybiphenyl*.—3-Hydroxy-4-methoxybiphenyl (1·67 g.) and iodine chloride (1·36 g., 1·0 equiv.) in acetic acid (20 ml.) were heated at 100° for 2 hr. and then at 50° for 24 hr. The cooled mixture was added to aqueous sodium hydrogen sulphite, and the white solid was collected and recrystallised from aqueous ethanol, giving 2-chloro-3-hydroxy-4-methoxybiphenyl (0·6 g.) as feathery clusters, m. p. 123°. This was treated with dimethyl sulphate and alkali, yielding 2-*chloro*-3,4-*dimethoxybiphenyl* as white granules (from ethanol), m. p. 118° (Found: C, 67·1; H, 5·3. $C_{14}H_{13}ClO_2$ requires C, 67·6; H, 5·2%). A mixed m. p. with 2-chloro-4,5-dimethoxybiphenyl (m. p. 108°) was 94—100°. The infrared spectra of the hydroxy-compound showed bands at 701, 770, and 805 cm.$^{-1}$, and the dimethoxy-compound at 708, 775, and 802 cm.$^{-1}$. These bands indicate that both compounds contained 5 and 2 adjacent aromatic CH groups and confirm their structures.

2-*Chloro*-4,5-*dimethoxybiphenyl* (III; R = Cl).—2-Nitro-4,5-dimethoxybiphenyl (1·28 g.) in ethanol (10 ml.) was reduced by stannous chloride dihydrate (3·5 g.) in concentrated hydrochloric acid (4 ml.). The amine, extracted in the usual way, was dissolved in concentrated hydrochloric acid (4 ml.) and water (2 ml.). Sodium nitrite (0·4 g.) in water (3 ml.) was added dropwise at 5—10°. 15 Min. later a freshly made solution of cuprous chloride (1·2 g.) in concentrated hydrochloric acid (1·9 ml.) was added at 0° and the mixture was allowed to warm to 20° After 12 hr. at room temperature the mixture was filtered and the solid was extracted with methanol. The methanol solution was diluted with water, and the solid obtained was purified by sublimation, followed by crystallisation from methanol. The 2-*chloro*-4,5-*dimethoxybiphenyl* (80 mg.) formed prisms, m. p. 108° (Found: C, 67·3; H, 5·7. $C_{14}H_{13}O_2Cl$ requires C, 67·6; H, 5·2%).

2,2′-*Dimethoxy*-5,5′-*diphenylbiphenyl* (VI).—4-Hydroxy-3-iodobiphenyl was treated with dimethyl sulphate and aqueous sodium hydroxide, giving 3-*iodo*-4-*methoxybiphenyl* as needles, m. p. 85—86°, after crystallisation from ethanol–benzene (Found: C, 50·5; H, 3·6. $C_{13}H_{11}IO$ requires C, 50·3; H, 3·55%).

A mixture of 3-iodo-4-methoxybiphenyl (5 g.) and copper bronze (5 g.) was heated to 260° and kept at this temperature for 15 min. after the initial exothermic reaction had subsided. The benzene-soluble product was recrystallised from benzene–methanol, giving 2,2′-*dimethoxy*-5,5′-*diphenylbiphenyl* (4′,6″-*dimethoxy*-1,1′:3′:1″:3″,1‴-*quaterphenyl*) (1·7 g., 59%), m. p. 179° (Found: C, 85·4; H, 6·4. $C_{26}H_{22}O_2$ requires C, 85·25; H, 6·0%).

2,2′-*Dimethoxy*-3,3′-*dinitro*-5,5′-*diphenylbiphenyl* (4′,6″-*Dimethoxy*-5,5″-*dinitro* 1,1′:3′:1″:3″:1‴-*quaterphenyl*).—The above diphenylbiphenyl (100 mg.) was boiled under reflux with concentrated nitric acid (10 ml.) in acetic acid (10 ml.) for 2 hr. After cooling and

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[9] Cheetham and Hey, *J.*, 1937, 770.

[10] Hey and Jackson, *J.*, 1936, 802.

dilution of the mixture with water, the yellow *dinitro-compound*, m. p. >250°, was collected. Its solubility was too small to permit recrystallisation. A well-washed sample was analysed (Found: C, 68·2; H, 4·55. $C_{26}H_{20}N_2O_6$ requires C, 68·4; H, 4·4%). The nitro-groups are probably in the denoted positions.

2,2'-Dihydroxy-5,5'-diphenylbiphenyl (*4',6''-Dihydroxy-1,1':3',1'':3'':1'''-quaterphenyl*).—A mixture of 2,2'-dimethoxy-5,5'-diphenylbiphenyl (3·0 g.), acetic acid (10 ml.), and 50% hydrogen bromide in acetic acid (20 ml.) was boiled under reflux for 3 hr. The cooled mixture was diluted with water and the product collected by filtration. Two recrystallisations from aqueous acetic acid gave the *dihydroxy-compound* (1·1 g.) as feathery crystals, m. p. 182° (Found: C, 85·1; H, 5·3. $C_{24}H_{18}O_2$ requires C, 85·2; H, 5·4%).

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