260. *Quaterphenyl. Part I. Some Dihydroxy-derivatives.*

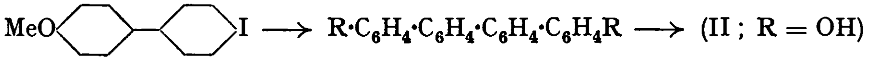
By John Harley-Mason and Frederick G. Mann.

4 : 4‴-*Dihydroxyquaterphenyl* (II; R = OH) has been synthesised through the intermediate formation of 4 : 4‴-*dimethoxyquaterphenyl* (II; R = OMe) and of 4 : 4‴-*dinitroquaterphenyl* (II; R = NO_2). It is devoid of oestrogenic properties. Although it could not be oxidised to the corresponding quinone, vigorous oxidation destroyed the terminal benzene nuclei, giving diphenyl-4 : 4′-dicarboxylic acid. Similar oxidation of the dinitro-compound (II; R = NO_2), however, ruptured the inner benzene nuclei, with the formation of 4-*nitrodiphenyl*-4′-*carboxylic acid*.

The isomeric 2 : 2‴- and 2 : 4‴-*dihydroxyquaterphenyls* have also been synthesised *via* their *dimethoxy*-derivatives, and their properties studied.

The present investigation was undertaken primarily to prepare 4 : 4‴-dihydroxyquaterphenyl * and to investigate its physiological action and its possible conversion into the corresponding quinone.

Guglialmelli and Franco (*Anal. Asoc. Quim. Argentina*, 1931, **19**, 5) prepared 4′-iodo-4-nitrodiphenyl by the simultaneous iodination and nitration of diphenyl, a method which we have improved to obtain a 30% yield of the pure product. The latter can be converted through the 4-amino- into the 4-hydroxy-compound, which on methylation gives 4′-iodo-4-methoxydiphenyl (I) (van Alphen, *Rec. Trav. chim.*, 1931, **50**, 1111). 4 : 4‴-*Dimethoxyquaterphenyl* (II; R = OMe) has been obtained by heating 4′-iodo-4-methoxydiphenyl with copper and also by converting the corresponding bromo-compound into a Grignard reagent and treating the latter with cupric chloride (cf. Krizewsky and Turner, J., 1919, **115**, 559; Bowden, J., 1931, 1111). Hey and Jackson (J., 1936, 803) state that 4′-bromo-4-methoxydiphenyl will not react with magnesium, but we find that reaction readily takes place after initiation by a small quantity of ethyl bromide. The dimethoxy-compound (II; R = OMe) was demethylated with hydrogen iodide, and the crude product purified by conversion into 4 : 4‴-*diacetoxyquaterphenyl*, which on hydrolysis gave 4 : 4‴-*dihydroxyquaterphenyl* (II; R = OH); the latter has also been characterised by conversion into 4 : 4‴-*dichloroacetoxyquaterphenyl*.



(I.) (II; R = OMe.)

Three other synthetic routes to the dihydroxy-compound (II; R = OH) were investigated. When 4′-iodo-4-nitrodiphenyl was heated with copper bronze, 4 : 4‴-*dinitroquaterphenyl* (II; R = NO_2) was obtained in a maximum yield of 20%. This yield is, however, in marked contrast with the high yield of 4 : 4′-dinitrodiphenyl similarly obtained from *p*-iodonitrobenzene, and is probably due partly to direct reduction of the nitro-group by the copper: evidence for such reduction when 2′-iodo-4-nitrodiphenyl is heated with copper has been claimed by Sako (*Bull. Chem. Soc. Japan*, 1935, **10**, 585), who, however, obtained a 53% yield of 4 : 4‴-dinitro-*o*-quaterphenyl by this method. Our attempts to prepare the dinitro-compound by direct nitration of quaterphenyl failed, the substance being either unchanged or converted into a mixture of polynitro-derivatives. Reduction of the dinitro-compound by Sako's method (*loc. cit.*) gave 4 : 4‴-*diaminoquaterphenyl* (II; R = NH_2), which, when tetrazotised and boiled with water, gave the 4 : 4‴-dihydroxy-compound. The low yield obtained makes this method inferior to the former method.

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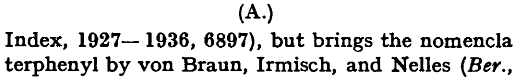
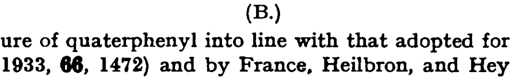
* In this paper, the *p*-quaterphenyl system has been numbered in accordance with scheme (A). This differs from scheme (B) adopted by American Chemical Abstracts (see *Chem. Abstr.*, 3rd Decennial Index, 1927—1936, 6897), but brings the nomenclature of quaterphenyl into line with that adopted for terphenyl by von Braun, Irmisch, and Nelles (*Ber.*, 1933, **66**, 1472) and by France, Heilbron, and Hey (J., 1938, 1365).



(A.)



(B.)

A third attempted synthesis was based on Bamberger's reaction (*Ber.*, 1897, **30**, 366) between *N*-nitrosoacetanilide and benzene to give diphenyl, a reaction which has been considerably extended by France, Heilbron, and Hey (J., 1938, 1364; 1939, 1283, 1288; this vol., p. 369) and Haworth and Hey (this vol., p. 361). Benzidine was therefore converted into NN'-*bisnitrosoacetylbenzidine*, and the latter treated with an excess of anisole; the only product isolated was a small quantity of diacetylbenzidine. This failure is remarkable, since Haworth and Hey (this vol., p. 366) have shown that this dinitroso-compound (no analysis or decomposition point being given) condenses with benzene to give a low yield of quaterphenyl. Furthermore, Heilbron *et al.* (*loc. cit.*) state that anisole can replace benzene in this type of reaction.

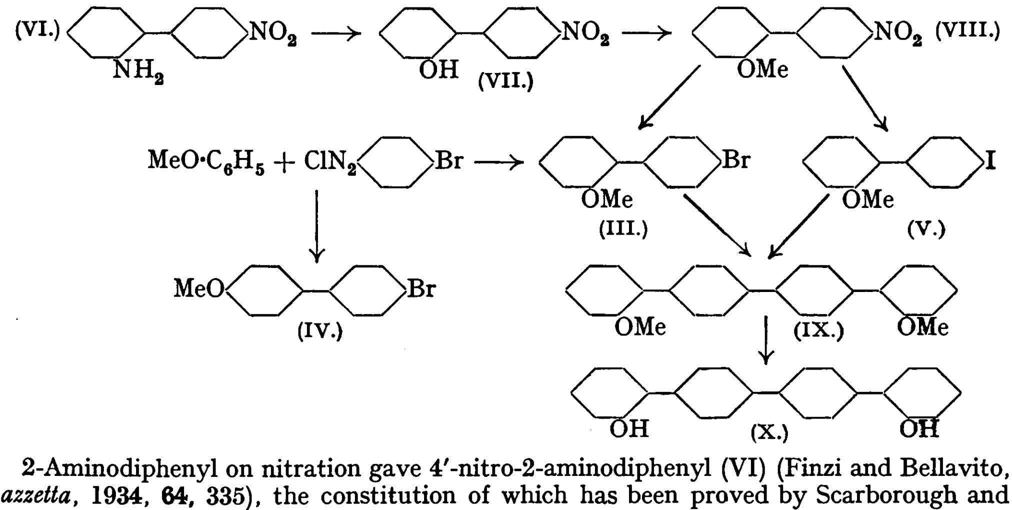
Finally, in an application of Gomberg and Bachmann's method (*J. Amer. Chem. Soc.*, 1924, **46**, 2339) for the union of aryl nuclei by the direct condensation of a diazo-compound in weakly alkaline solution with an aromatic hydrocarbon, tetrazotised benzidine was treated with an excess of anisole, but no recognisable derivative was isolated.

In view of the definite oestrogenic activity of 4 : 4'-dihydroxydiphenyl (Dodds and Lawson, *Nature*, 1936, **137**, 996), it was possible that 4 : 4'''-dihydroxyquaterphenyl would possess similar, although weaker, properties. It has been tested by Professor E. C. Dodds, who finds, however, that it is quite inactive in this respect.

Attempts to oxidise the dihydroxy-compound to the corresponding quinone, either with the usual chemical oxidising agents or with peroxidase, failed. This failure was not unexpected, in view of the experimental difficulties caused by the insolubility of the phenol, and also of the fact that, since 4 : 4'-diphenoquinone is a very unstable compound, the required quinone would probably possess extreme instability.

The application of a more vigorous oxidising agent, namely, a boiling solution of chromium trioxide in acetic acid, caused, however, a complete rupture of the two outer benzene rings in the dihydroxy-molecule, with the formation of diphenyl-4 : 4'-dicarboxylic acid in almost theoretical yield. The same oxidation occurred, but more slowly, with the dimethoxy-compound (II; R = OMe). When the dinitroquaterphenyl (II; R = NO_2) was similarly treated, rupture of the inner benzene rings occurred, with the formation of 4-*nitrodiphenyl*-4'-*carboxylic acid*.

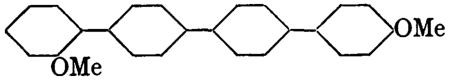
The synthesis of 2 : 2'''-dihydroxyquaterphenyl (X) was next undertaken. The interaction of anisole and *p*-bromophenyldiazotate under Gomberg and Bachmann's conditions (*loc. cit.*) gave a product from which were isolated 4'-*bromo*-2-*methoxydiphenyl* (III) and the isomeric 4-methoxy-compound (IV), previously prepared by Bell (J., 1930, 1075). *p*-Iodophenyldiazotate similarly gave 4'-*iodo*-2-*methoxydiphenyl* (V) and the isomeric 4-methoxy-compound.



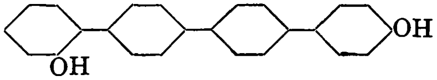
2-Aminodiphenyl on nitration gave 4'-nitro-2-aminodiphenyl (VI) (Finzi and Bellavito, *Gazzetta*, 1934, **64**, 335), the constitution of which has been proved by Scarborough and Waters (J., 1927, 89). The compound (VI) was readily converted into 4'-nitro-2-hydroxydiphenyl (VII) (Christiansen and Harris, *J. Amer. Pharm. Assoc.*, 1933, **22**, 723), which has now been characterised by the preparation of *4′-nitro-2-acetoxydiphenyl*. The hydroxy-compound on methylation gave *4′-nitro-2-methoxydiphenyl* (VIII), and the latter furnished 4′-bromo-2-methoxydiphenyl (III) and 4′-iodo-2-methoxydiphenyl (V), the constitution of which was thus confirmed.

When the iodo-compound (V) was heated with copper, or when the bromo-derivative (III) was converted into a Grignard reagent and boiled with cupric chloride, the product, after sublimation or recrystallisation, gave *2 : 2‴-dimethoxyquaterphenyl* (IX). This compound is only slightly soluble in hot alcohol, but is moderately readily soluble in boiling benzene, in which it gave a normal molecular weight. Demethylation gave *2 : 2‴-dihydroxyquaterphenyl* (X), which has been characterised by the preparation of its *diacetoxy-*, *dichloroacetoxy-*, and *di-o-nitrobenzoyl* derivatives. The compounds (IX) and (X) are more soluble in organic solvents than the isomeric 4 : 4‴-compounds (II; R = OMe) and (II; R = OH) respectively; on oxidation they also give diphenyl-4 : 4′-dicarboxylic acid.

When a mixture of equal quantities of 4′-bromo-2-methoxy- and of 4′-bromo-4-methoxydiphenyl (III and IV) was converted into a Grignard reagent and then boiled with cupric chloride, the product consisted of *2 : 4‴-dimethoxyquaterphenyl* (XI) mixed with the 2 : 2‴- and 4 : 4‴-isomerides. The 2 : 4‴-dimethoxy-compound was in most solvents less soluble than (IX) and more soluble than (II; R = OMe): it was ultimately obtained pure by fractional crystallisation, and gave a normal molecular weight in boiling benzene. Its solutions show a marked violet fluorescence. Demethylation under the usual conditions gave *2 : 4‴-dihydroxyquaterphenyl* (XII), which has also been characterised by the isolation of its *diacetoxy-*, *dichloroacetoxy-*, and *di-o-nitrobenzoyl* derivatives. Oxidation of the dimethoxy- and dihydroxy-compounds (XI and XII) gave diphenyl-4 : 4′-dicarboxylic acid.



(XI.)



(XII.)

No attempts were made to oxidise the two dihydroxy-compounds (X) and (XII) to the corresponding quinones, in view of the obvious difficulties.

EXPERIMENTAL.

4′-Iodo-4-nitrodiphenyl.—A powdered mixture of diphenyl (150 g.) and iodine (75 g.) was heated under reflux on a water-bath for 2 hours, nitric acid (360 c.c. *d* 1·4) being added during the first hour. The cold product was mixed with water, and the yellow solid collected, washed with water, and extracted with boiling alcohol (3 × 450 c.c.). The residue, after crystallisation from benzene (2 l.), gave 4′-iodo-4-nitrodiphenyl in long, pale yellow needles (92 g.), m. p. 212—214° (Guglialmelli and Franco, *loc. cit.*, give m. p. 202—206°, and Hey and Jackson, *loc. cit.*, give 210—211°).

4′-Iodo-4-methoxydiphenyl (I).—This was obtained (7 g.) by refluxing methyl iodide (8 g.), 4′-iodo-4-hydroxydiphenyl (10 g.), and sodium hydroxide (1·4 g.) in methyl alcohol (200 c.c.) for 8 hours and crystallising the yellow product from alcohol–benzene; m. p. 182—183°. The usual methyl sulphate–alkali method is unsatisfactory owing to the low solubility of the alkali salt in water.

4 : 4‴-Dimethoxyquaterphenyl (II; R = OMe).—(1) *By the copper method.* An intimate mixture of 4′-iodo-4-methoxydiphenyl (8 g.) and copper bronze (5 g.) was heated in a nitrogen atmosphere at 280° for 1 hour. The product was extracted with boiling alcohol, and the residue heated at 0·05 mm.: the *dimethoxy*-compound sublimed in colourless plates, m. p. 335—338°. A sample recrystallised from glycol monobutyl ether had m. p. 338—340° (Found: C, 85·5; H, 6·25. $C_{26}H_{22}O_2$ requires C, 85·2; H, 6·0%). The yield was considerably reduced if the copper heating was conducted in an air atmosphere. The compound was very slightly soluble in boiling xylene and glycol monobutyl ether, and moderately easily soluble in boiling nitrobenzene, the solutions having a faint blue fluorescence; it was too slightly soluble in organic solvents for molecular-weight determinations.

(2) *By the Grignard method.* A mixture of magnesium (0·9 g.), ethyl bromide (1 c.c.), and ether (10 c.c.) was brought into reaction, and immediately a solution of 4′-bromo-4-methoxy-

diphenyl (10 g.) and ethyl bromide (2 c.c.) in benzene (150 c.c.) at 30° was slowly added. The mixture was boiled with stirring for 1 hour, and anhydrous cupric chloride (7 g., dried in a current of chlorine at 250°) cautiously added. After a further 3 hours' boiling, a small quantity of water and then concentrated hydrochloric acid were added in turn, and the ether–benzene distilled off. The viscous grey residue was extracted several times with concentrated hydrochloric acid to remove cuprous chloride, and finally with boiling alcohol. The insoluble residue, a greyish-white powder, was dried and sublimed as above, giving the dimethoxy-compound in colourless plates (2·9 g.), m. p. 336—339°.

Oxidation. A mixture of the dimethoxy-compound (0·2 g.), chromium trioxide (1·4 g.; 25 mols.), and glacial acetic acid (60 c.c.) was boiled for several hours. The crude diphenyl-4 : 4'-dicarboxylic acid (0·12 g., 85% of theoretical) was identified by conversion into the methyl ester, m. p. 212—214° (Found: C, 70·8; H, 5·4. Calc. for $C_{16}H_{14}O_4$: C, 71·1; H, 5·2%). Ullmann and Meyer (*Annalen*, 1904, **332**, 73) give m. p. 214°.

4 : 4'''-*Dihydroxyquaterphenyl* (II; R = OH).—A mixture of the dimethoxy-compound (3 g.), acetic acid (20 c.c.), and hydriodic acid (10 c.c., *d* 1·7, entirely free from phosphorus compounds) was heated in a sealed tube at 180° for 4 hours. The cold product was diluted with water and the crude dihydroxy-compound was collected, dried, dissolved in boiling pyridine (100 c.c.), and after filtration boiled for a few minutes with a solution of acetic anhydride (15 c.c.) in pyridine (20 c.c.). On cooling, 4 : 4'''-*diacetoxyquaterphenyl* separated in colourless plates, m. p. 325° (decomp.) after being washed with alcohol and dried (Found: C, 79·4; H, 5·3. $C_{28}H_{22}O_4$ requires C, 79·6; H, 5·2%). A suspension of the diacetoxy-compound in alcoholic hydrochloric acid was boiled for 8 hours, giving 4 : 4'''-*dihydroxyquaterphenyl* as a microcrystalline powder, which when washed and dried had m. p. 419—422° (Found: C, 84·9; H, 5·6. $C_{24}H_{18}O_2$ requires C, 85·2; H, 5·3%). The dihydroxy-compound is soluble in pyridine, insoluble in all other organic solvents investigated and in aqueous alkali, and slightly soluble in alcoholic potash, the solution having a marked greenish-blue fluorescence.

The finely powdered dihydroxy-compound, when refluxed with an excess of chloroacetic anhydride, slowly passed into solution and then crystals of 4 : 4'''-*dichloroacetoxyquaterphenyl* rapidly separated: these were washed with alcohol, but were too sparingly soluble in organic liquids for recrystallisation. The compound decomposed at 360° without melting (Found: Cl, 14·4. $C_{28}H_{20}O_4Cl_2$ requires Cl, 14·5%). All attempts to prepare a di-*o*-nitrobenzoyl compound failed.

Attempted oxidation of the 4 : 4'''-dihydroxy-compound in pyridine solution to the corresponding quinone with lead dioxide, selenium dioxide, or chromium trioxide failed. The dihydroxy-compound was oxidised, however, by chromium trioxide in boiling acetic acid precisely as the dimethoxy-compound, except that less acetic acid (25 c.c.) was employed and the reaction was rather more rapid; the diphenyl-4 : 4'-dicarboxylic acid was again isolated as its methyl ester, m. p. 213°, unchanged by admixture with the previous sample.

4 : 4'''-*Dinitroquaterphenyl* (II; R = NO_2).—4'-Iodo-4-nitrodiphenyl (39 g.) was heated to 240°, and copper bronze (10·8 g.) then added: the mixture was stirred occasionally during 6 hours, the temperature being kept at 235—245°. Many experiments showed these to be the optimum conditions. The cold product was pulverised and extracted with boiling benzene (500 c.c.), the residue boiled with nitrobenzene (200 c.c.), and this solution filtered; on cooling, bright yellow needles of 4 : 4'''-*dinitroquaterphenyl* were deposited, and a small second crop was obtained by further extraction of the residue with nitrobenzene. Total yield, 3·2 g. These needles were sufficiently pure for reduction, but a sample was further purified by sublimation at 320°/0·01 mm., the dinitro-compound being obtained in yellow crystals, m. p. 317—320° (Found: C, 72·4; H, 4·2; N, 7·1. $C_{24}H_{16}O_4N_2$ requires C, 72·7; H, 4·0; N, 7·1%), almost insoluble in most organic solvents. Unchanged 4'-iodo-4-nitrodiphenyl was recovered from the benzene extract.

Oxidation. A mixture of the dinitro-compound (0·2 g.), chromium trioxide (1·3 g.; 22 mols.), and acetic acid (80 c.c.) was refluxed for 1 hour and cooled. The colourless crystals of 4-*nitrodiphenyl*-4'-*carboxylic acid* which separated were washed and recrystallised from acetic acid–benzene, in which they were very sparingly soluble; m. p. 338—340° (Found: C, 63·7; H, 4·0; N, 5·7. $C_{13}H_9O_4N$ requires C, 64·2; H, 3·7; N, 5·8%).

4 : 4'''-*Diaminoquaterphenyl* (II; R = NH_2).—A mixture of the finely powdered dinitro-compound (2·7 g.), stannous chloride (12 g.), and acetic acid (200 c.c.) was refluxed for 5 hours while dry hydrogen chloride was slowly passed through it. The white precipitated chlorostannate was decomposed with 20% aqueous sodium hydroxide, and the liberated diamine washed and finally sublimed at 310—320°/0·01 mm. The *diaminoquaterphenyl* was obtained in colour-

less plates, m. p. 312—315° (partial decomp.) (Found: C, 85·0; H, 5·95; N, 8·1. $C_{24}H_{20}N_2$ requires C, 85·6; H, 5·95; N, 8·3%), insoluble in most organic solvents except boiling pyridine, from which the diamine crystallised well.

When solutions of the diamine and of acetic anhydride, both in hot pyridine, were mixed, colourless plates of 4 : 4'''-*diacetamidoquaterphenyl* rapidly separated; decomp. 385° (Found: C, 79·7; H, 5·9; N, 6·9. $C_{28}H_{24}O_2N_2$ requires C, 80·0; H, 5·7; N, 6·7%).

A solution of the diamine (0·22 g.) in concentrated sulphuric acid (8 c.c.) was poured into ice-water (30 g.), sodium nitrite (0·1 g.) added, and after 3 hours' stirring at room temperature, the mixture was heated slowly and finally boiled for 20 minutes. The brown flocculent suspension was washed, dried, and sublimed at 0·01 mm. The white sublimate obtained at 320—330° was acetylated in pyridine solution, plates of 4 : 4'''-diacetoxyquaterphenyl being obtained, m. p. 325°, unchanged on admixture with an authentic sample.

NN'-*Bisnitrosoacetylbenzidine*.—A partial solution obtained by boiling powdered diacetylbenzidine (10 g.) with acetic anhydride (100 c.c.) was poured into acetic acid (150 c.c.) at 5° and stirred while nitrous fumes, generated from nitric acid and arsenious oxide and dried by passing over calcium chloride and phosphoric oxide, were passed in. After 4½ hours the solution, which had changed in colour from deep yellow to green, deposited a yellow precipitate, which was washed with ice-water and dried. The NN'-*bisnitrosoacetyl* compound (2 g.) was thus obtained in minute yellow crystals, which exploded at 84—87° (Found: N, 17·1. $C_{16}H_{14}O_4N_4$ requires N, 17·2%). A second crop (7 g.) was obtained by pouring the mother-liquor into ice-water (1000 c.c.) and stirring vigorously. Addition of phosphoric oxide (2 g.) to the original reaction mixture decreased the yield. The dinitroso-compound slowly darkened on exposure to light and developed an odour of acetic acid.

4'-*Bromo*-2-*methoxydiphenyl* (III).—A mixture of *p*-bromoaniline (215 g.) and water (100 c.c.) was heated until the amine melted, concentrated hydrochloric acid (250 c.c.) then added, and the whole rapidly cooled to 0° with stirring. A solution of sodium nitrite (90 g.) in water (200 c.c.) was slowly added with cooling and agitation, and the clear solution of the diazo-product, after addition of anisole (500 c.c.), was cooled in ice and stirred whilst 5N-sodium hydroxide (280 c.c.) was added during 1 hour. After 12 hours, the heavy brown oil which had separated was removed and distilled in steam, the flask being heated ultimately to 220°. Unchanged anisole rapidly came over, and was followed by crude 4'-bromo-2-methoxydiphenyl, which soon solidified in the chilled receiver. When, however, crystallisation started in the condenser, it indicated that the 4-methoxy-compound was beginning to distil, and a third fraction was now collected: since, however, the 4-methoxy-compound is only slightly volatile in steam even at 220°, prolonged distillation was required to obtain a good yield of this third fraction.

The intermediate fraction of the 2-methoxy-compound was recrystallised from alcohol to remove oily impurities, and then distilled under reduced pressure to remove traces of the less volatile 4-methoxy-isomeride. 4'-Bromo-2-methoxydiphenyl (64 g.) was thus obtained, b. p. 200—201°/18 mm., m. p. 63—64°: it was identified by analysis and by a mixed m. p. determination with that synthesised from 4'-nitro-2-hydroxydiphenyl (see below). The m. p. of the 2-methoxy-compound cannot be taken as a criterion of its purity, as it is unaffected by the addition of even 10% of the 4-methoxy-isomeride. Hence in the final distillation of the 2-methoxy-compound, a residue containing any 4-methoxy-compound must be left undistilled.

The third fraction was recrystallised thrice from alcohol–benzene, and pure 4'-bromo-4-methoxydiphenyl (22 g.), m. p. 144—145°, obtained. Replacement of the above steam-distillation by direct distillation under reduced pressure gave a rather smaller yield of both compounds.

4'-*Iodo*-2-*methoxydiphenyl* (V).—A mixture of *p*-iodoaniline (217 g.), concentrated hydrochloric acid (200 c.c.), and water (100 c.c.) was diazotised with sodium nitrite (72 g.) in water (200 c.c.), and the filtered diazo-solution treated with anisole (500 c.c.) and 5N-sodium hydroxide (240 c.c.) precisely as in the above preparation. Steam-distillation of the heavy oil which separated was unsatisfactory, however. The oil was therefore dried, and unchanged anisole distilled off directly: the residue was distilled under reduced pressure, and a dark brown oil came over at 180—210°/0·4 mm. and solidified. The solid, thrice recrystallised from alcohol, gave a less soluble fraction (A), m. p. 118—121°, and the mother-liquor on evaporation gave a more soluble fraction (B), m. p. 53—57°. Fraction (A), when twice recrystallised from *cyclo*hexane, gave 4'-iodo-4-methoxydiphenyl, m. p. 182—183°. *p*-Di-iodobenzene, m. p. 128—129°, was recovered from the *cyclo*hexane mother-liquor. Fraction (B) was distilled under reduced pressure. A small quantity of *p*-di-iodobenzene sublimed, and later 4'-iodo-2-methoxydiphenyl (27 g.) distilled at 140—143°/0·05 mm. and after recrystallisation from alcohol had m. p. 61—63°. Its identity was also confirmed by the synthesis given below. The occurrence of *p*-di-iodobenzene as a by-product in this reaction was unexpected and cannot at present be explained.

4′-Nitro-2-acetoxydiphenyl.—The 2-hydroxy-compound was boiled with acetic anhydride for a few minutes, and the solution poured into water. The *2-acetoxy*-compound which separated formed needles, m. p. 142—145°, when recrystallised from dilute alcohol (Found: C, 65·6; H, 4·3; N, 5·5. $C_{14}H_{11}O_4N$ requires C, 65·4; H, 4·3; N, 5·45%).

4′-Nitro-2-methoxydiphenyl (VIII).—4′-Nitro-2-hydroxydiphenyl (VII), dissolved in aqueous sodium hydroxide, was shaken with methyl sulphate (1½ mols.), and the mixture warmed at 60° for 1 hour. After cooling, the oily suspension was extracted with ether. After removal of the ether, the residue was distilled, a yellow syrup, b. p. 235—240°/30 mm., passing over and rapidly solidifying. Recrystallisation from alcohol–petrol gave the *2-methoxy*-compound in plates, m. p. 62—64° (Found: C, 68·3; H, 5·0; N, 6·1. $C_{13}H_{11}O_3N$ requires C, 68·1; H, 4·8; N, 6·1%).

4′-Amino-2-methoxydiphenyl.—A mixture of the nitro-compound (8 g.), reduced iron (7 g.), acetic acid (2 c.c.), and 70% alcohol (100 c.c.) was refluxed for 4 hours, sodium carbonate then added to precipitate the iron, and the liquid filtered. The residue was extracted with hot alcohol (100 c.c.), the alcohol added to the filtrate, and the latter distilled until an oily residue was obtained. This was dissolved in ether, dried (potassium hydroxide), filtered, and the ether removed. The residual amine solidified on standing and was then obtained as the *hydrochloride* by recrystallisation from a mixture of water (50 c.c.) and concentrated hydrochloric acid (5 c.c.) (Found: C, 66·5; H, 6·2; N, 5·9. $C_{13}H_{13}ON,HCl$ requires C, 66·3; H, 6·0; N, 6·0%).

When a mixture of the hydrochloride, sodium acetate, acetic acid, and acetic anhydride was boiled for a few minutes and then poured into water, the *acetyl* derivative separated; after crystallisation from dilute alcohol it had m. p. 147—148° (Found: C, 74·8; H, 6·3. $C_{15}H_{15}O_2N$ requires C, 74·7; H, 6·2%).

4′-Bromo-2-methoxydiphenyl (III).—A solution of 4′-amino-2-methoxydiphenyl hydrochloride (3 g.) in hot water (40 c.c.) and concentrated hydrochloric acid (4 c.c.) was quickly cooled to 20° with stirring, and the crystalline suspension diazotised by the addition of sodium nitrite (1 g.). The solution was filtered and then run slowly into a hot solution of cuprous bromide (3 g.) in concentrated hydrobromic acid (30 c.c.). The oily bromo-compound was distilled in steam at 180°. The *bromo*-compound rapidly solidified and after two recrystallisations from alcohol had m. p. 62—63° (Found: C, 59·2; H, 4·0; Br, 30·1. $C_{13}H_{11}OBr$ requires C, 59·3; H, 4·2; Br, 30·4%).

4′-Iodo-2-methoxydiphenyl (V).—The diazo-solution obtained as above was treated with potassium iodide (3 g.) dissolved in dilute sulphuric acid. The mixture was boiled, iodine removed (sodium sulphite), and the residual oil distilled in steam as before. Two recrystallisations from alcohol gave the *4′-iodo*-compound, m. p. 61—63° (Found: C, 50·0; H, 3·9. $C_{13}H_{11}OI$ requires C, 50·3; H, 3·55%).

2 : *2′′′-Dimethoxyquaterphenyl* (IX).—(1) *By the copper method.* An intimate mixture of 4′-bromo-2-methoxydiphenyl (4 g.) and copper bronze (3 g.) was heated in a nitrogen atmosphere at 280° for 1 hour. The product was extracted with boiling benzene (150 c.c.); the filtrate, when concentrated to 40 c.c. and cooled, deposited 2 : *2′′′-dimethoxyquaterphenyl* (1·5 g.), which after further recrystallisation gave colourless nodular crystals, m. p. 188—191° (Found: C, 85·4; H, 6·05; *M*, ebullioscopic in 0·94% benzene solution, 337; in 1·64% solution, 343; in 2·98% solution, 349. $C_{26}H_{22}O_2$ requires C, 85·2; H, 6·0%; *M*, 368).

(2) *By the Grignard method.* The early stages of this preparation were precisely as those of the 4 : 4′′′-isomeride, a Grignard reagent prepared from magnesium (3·6 g.), ethyl bromide (1 c.c.), and ether (20 c.c.) being treated with a solution of 4′-bromo-2-methoxydiphenyl (20 g.) in ether (100 c.c.) and later with cupric chloride (14 g.). The crude greyish-white product, however, after extraction with hydrochloric acid and then alcohol, was boiled with benzene (250 c.c.), and the solution filtered. The filtrate deposited much of the 2 : 2′′′-dimethoxyquaterphenyl on cooling, and a further crop was obtained by concentration of the mother-liquor. Recrystallisation of the united crops (5 g.) from benzene gave crystals as before, m. p. 188—191°.

2 : *2′′′-Dihydroxyquaterphenyl* (X).—Hydriodic acid (10 c.c., *d* 1·7) was added to a solution of the dimethoxy-compound (3 g.) in boiling acetic acid (100 c.c.), and the boiling continued for 3 hours. Addition of water and cooling caused the 2 : *2′′′-dihydroxy*-compound to crystallise; after two recrystallisations from 70% alcohol, it formed colourless needles, which turned pink on long exposure to light; m. p. 238—240° (Found: C, 84·3; H, 5·4. $C_{24}H_{18}O_2$ requires C, 85·2;

H, 5·3%. All the three isomeric dihydroxy-compounds tended to give low carbon values). It is easily soluble in hot alcohol, acetone, ethyl acetate, and aqueous alkalis.

The 2 : 2'''-*diacetoxy*-compound was prepared by boiling the dihydroxy-compound with excess of acetic anhydride for 15 minutes, adding alcohol, and recrystallising the precipitate from ethyl acetate; it formed colourless plates, m. p. 221—224° (Found : C, 79·1; H, 5·5. $C_{28}H_{22}O_4$ requires C, 79·6; H, 5·2%).

The 2 : 2'''-*dichloroacetoxy*-compound, similarly prepared from chloroacetic anhydride, formed needles, m. p. 166—169° (Found : C, 68·25; H, 3·9; Cl, 14·2. $C_{28}H_{20}O_4Cl_2$ requires C, 68·4; H, 4·1; Cl, 14·5%).

The 2 : 2'''-*di*-o-*nitrobenzoyl* compound was obtained by shaking a solution of the dihydroxy-compound in 10% aqueous potash with the calculated quantity of *o*-nitrobenzoyl chloride. After gentle warming, the solid product was collected, washed, dried, and thrice recrystallised from alcohol–glycol monoethyl ether, forming colourless plates, m. p. 190—192° (Found : N, 4·3. $C_{38}H_{24}O_8N_2$ requires N, 4·3%).

2 : 4'''-*Dimethoxyquaterphenyl* (XI).—A Grignard reagent was prepared as before, from magnesium (1·8 g.), ethyl bromide (1 c.c.), and ether (15 c.c.). As soon as reaction started, solutions of 4'-bromo-2-methoxydiphenyl (5 g.) in ether (25 c.c.) and of the 4-methoxy-isomeride (5 g.) in benzene (70 c.c.) were added alternately in quantities of *ca.* 5 c.c., the mixture being maintained at 30°. A vigorous reaction ensued, with ebullition of the mixture. After *ca.* 1 hour, the mixture was cooled in ice, and cupric chloride (8 g.) added as before, followed by heating on the water-bath for 2 hours with stirring. Water was added, and the residue extracted with hydrochloric acid as before. The final residue was boiled with a mixture of alcohol (100 c.c.) and benzene (50 c.c.) to extract 2 : 2'''-dimethoxyquaterphenyl and other impurities. The undissolved material was boiled with toluene (200 c.c.); the filtered liquid, on cooling, deposited some 4 : 4'''-dimethoxyquaterphenyl : this was collected, and the filtrate kept at 0° overnight. The 2 : 4'''-*dimethoxy*-compound (2·5 g.) separated in plates, m. p. 223—224° after recrystallisation from benzene (Found: C, 85·3; H, 6·4; *M*, ebullioscopic in 0·72% benzene solution, 349; in 0·78% solution, 362. $C_{26}H_{22}O_2$ requires C, 85·2; H, 6·0%; *M*, 368). The undissolved residue from the toluene extraction was almost pure 4 : 4'''-dimethoxy-compound (1·1 g.), m. p. 334—337°.

2 : 4'''-Dimethoxyquaterphenyl is almost insoluble in alcohol and acetone, sparingly soluble in benzene and acetic acid, more readily soluble in toluene, xylene, and chloroform. Its solutions have a marked violet fluorescence.

2 : 4'''-*Dihydroxyquaterphenyl* (XII).—Obtained by demethylation precisely as the 2 : 2'''-isomeride and recrystallised from alcohol–acetic acid, the 2 : 4'''-*dihydroxy*-compound was obtained as a colourless microcrystalline powder, turning pink on exposure to light, m. p. 268—270° (Found : C, 84·6; H, 5·8. $C_{24}H_{18}O_2$ requires C, 85·2; H, 5·3%). Its solubility in various organic solvents is very similar to that of the 2 : 2'''-isomeride.

The following derivatives were obtained precisely as the corresponding 2 : 2'''-derivatives : *diacetoxy*-compound, plates, m. p. 189—192° (Found : C, 78·9; H, 5·1. $C_{28}H_{22}O_4$ requires C, 79·6; H, 5·2%); *dichloroacetoxy*-compound, plates, m. p. 158—160° (Found : Cl, 14·8. $C_{28}H_{20}O_4Cl_2$ requires Cl, 14·5%); *di*-o-*nitrobenzoyl* derivative, plates, m. p. 206—208° (Found : N, 4·2. $C_{38}H_{24}O_8N_2$ requires N, 4·3%).

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