545. *Diphenylenes. Part II.* Syntheses of Substituted Diphenylenes and of Related Diphenyls.*

By Wilson Baker, J. W. Barton, and J. F. W. McOmie.

Unambiguous syntheses of a number of methyl-, methoxy-, nitro-, bromo-, and acetyl-diphenylenes and -diphenyls are described. These compounds were required in order to orientate products, obtained by direct substitution into the diphenylene nucleus, which are described in the following paper. The diphenylenes were all synthesised from the appropriate 2 : 2′-di-iododiphenyls, *e.g.*, (IV), by treatment with cuprous oxide.

Further studies on the chemistry of diphenylene, and in particular investigation of the course of substitution in the nucleus, are described in this and the following paper. Three methods have been used for the orientation of substituents introduced directly into diphenylene: (1) comparison with substituted diphenylenes of known orientation synthesised from appropriately substituted 2 : 2′-di-iododiphenyls; (2) reduction of the substituted diphenylene with Raney nickel in alcohol whereby the four-membered ring is opened, giving substituted diphenyls whose orientation is established by comparison with diphenyls of known orientation synthesised by more direct methods; (3) conversion of an already orientated derivative into a substance prepared by direct substitution into the nucleus, or *vice versa*.

This paper describes the synthesis of a number of mono- and di-substituted diphenylenes and of a few diphenyl derivatives, most of which were required in order to establish the orientation of products, described in the following paper, obtained as the result of direct substitution in the diphenylene nucleus.

Apart from some minor modifications and one exception (2-bromodiphenylene) the diphenylenes have been prepared by the following general method, illustrated by the synthesis of 1-methyldiphenylene. An Ullmann reaction between one molecule each of *o*-iodonitrobenzene and 2-iodo-3-nitrotoluene gave 2-methyl-6 : 2′-dinitrodiphenyl (I) accompanied by some 2 : 2′-dimethyl-6 : 6′-dinitrodiphenyl. A 1-substituted diphenylene ultimately results from an *o*-iodonitrobenzene carrying a substituent in the *ortho*-position to either the iodine atom or the nitro-group, and a 2-substituted diphenylene results from the use of an *o*-iodonitrobenzene with a substituent in the *para*-position either to the

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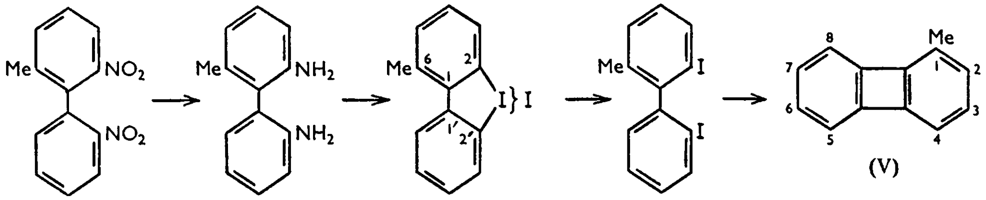
* The paper entitled " Preparation and Reactions of Diphenylene " by W. Baker, M. P. V. Boarland, and J. F. W. McOmie [1] is to be regarded as Part I of this series.

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

iodine atom or to the nitro-group; in each case the more accessible starting material was chosen. Reduction of the dinitrodiphenyl (I) to the diamine (II) followed by tetrazotisation and treatment with potassium iodide gave a mixture of 6-methyldiphenylene-2 : 2′-iodonium iodide (III) and the isomeric 2 : 2′-di-iodo-6-methyldiphenyl (IV). These two di-iodo-, and similarly related, compounds may be separated by taking advantage of the much smaller solubility in organic solvents of the ionised compound. In practice, however, this is not necessary because in the final step in the synthesis, involving rapid heating at 350° with cuprous oxide, the iodonium iodide (III) is first converted into the di-iodo-compound (IV) from which the iodine atoms are lost to give 1-methyldiphenylene (V).



(I) (II) (III) (IV) (V)

This method of cyclisation to a diphenylene, originally due to Lothrop,[2] with the improvements described by Baker, Boarland, and McOmie,[1] remains the most practical for their preparation. Other methods by which the diphenylene nucleus has been prepared are discussed in a forthcoming comprehensive article by Baker and McOmie.[3]

1-*Methyldiphenylene* (V).—This was prepared as described. It is a liquid at room temperature and was characterised as its picrate and as its complex with 2 : 4 : 7-trinitrofluorenone. It may be recalled that 1-methylnaphthalene, unlike 2-methylnaphthalene, is also a liquid at room temperature.

2-*Methyldiphenylene.*—This solid was prepared from *o*-iodonitrobenzene and 4-iodo-3-nitrotoluene, as in the case of its isomeride. It was purified by regeneration from its picrate, and was characterised as its complex with 2 : 4 : 7-trinitrofluorenone.

1-*Methoxydiphenylene.*—The starting point for this synthesis was 2-iodo-3-nitroanisole, m. p. 102·5—103·5°, which was prepared by methylation of 2-iodo-3-nitrophenol, itself obtained from *m*-nitrophenol by acetoxymercuration followed by treatment with iodine.[4] The substance, m. p. 122—123°, obtained from *m*-nitrophenol by direct iodination and methylation [5,6] has been shown [7] not to be 2-iodo-3-nitroanisole. A mixed Ullmann reaction between *o*-iodonitrobenzene and 2-iodo-3-nitroanisole gave the two symmetrical coupling products and a 12% yield of 2-methoxy-6 : 2′-dinitrodiphenyl. The usual sequence of reactions *via* the diamine and the two di-iodo-compounds then gave 1-methoxydiphenylene, the yield in the final stage being 25%, after isolation as the 2 : 4 : 7-trinitrofluorenone complex.

2-*Methoxy- and* 2-*Hydroxy-diphenylene.*—The crossed Ullmann reaction between *o*-iodonitrobenzene and 4-iodo-3-nitroanisole gave a difficultly separable mixture of the three coupling products. The 4-methoxy-2 : 2′-dinitrodiphenyl was converted as in the previous cases into the related iodonium iodide, but the cyclisation to 2-methoxydiphenylene occurred in only 8% yield. An attempt to demethylate 2-methoxydiphenylene with hydrobromic and acetic acid led only to extensive decomposition, but 2-hydroxydiphenylene was obtained by heating the ether for five minutes with pyridine hydrochloride.

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[2] Lothrop, *J. Amer. Chem. Soc.*, 1941, **63**, 1187; 1942, **64**, 1698.

[3] Baker and McOmie, Chapter on " Cyclobutadiene and Related Compounds " in " Non-benzenoid Aromatic Compounds," Ed. D. Ginsburg, Interscience Publ. Inc., New York, 1958.

[4] Wawzonek and Wang, *J. Org. Chem.*, 1951, **16**, 1271.

[5] Schlieper, *Ber.*, 1893, **26**, 2465.

[6] Datta and Prasad, *J. Amer. Chem. Soc.*, 1917, **39**, 441.

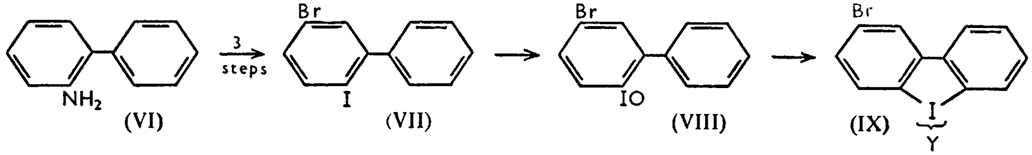
[7] Brenans and Larivaille, *Compt. rend.*, 1935, **201**, 81.

1 : 8-*Dimethoxydiphenylene.*—2 : 2′-Dimethoxy-6 : 6′-dinitrodiphenyl, obtained as a by-product in the synthesis of 1-methoxydiphenylene, was converted *via* the related diamino- and di-iodo-compounds into 1 : 8-dimethoxydiphenylene. 2 : 7-Dimethoxydiphenylene has been similarly prepared by Lothrop.[2]

2-*Nitrodiphenylene.*—Wasylewsky, Brown, and Sandin[8] converted diphenylene-2 : 2′-iodonium iodide into the nitrate, which in concentrated sulphuric acid passed into 4-nitrodiphenylene-2 : 2′-iodonium sulphate which could then be converted into the nitrate. This nitrate has now been converted by potassium iodide into 4-nitrodiphenylene-2 : 2′-iodonium iodide, which when heated with cuprous oxide gave 2-nitrodiphenylene in 20% yield.

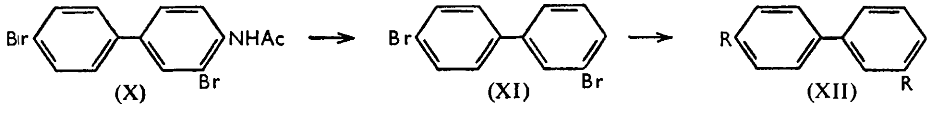
2 : 6-*Dinitrophenylene.*—The essential intermediate for this synthesis, 2 : 2′-diamino-4 : 5′-dinitrodiphenyl, was prepared by modification of the method due to Sako,[9] namely, nitration of 2 : 2′-disuccinimidodiphenyl, separation of the desired 4 : 5′- from the 4 : 4′- and 5 : 5′-dinitro-derivatives, and hydrolysis with ethanolic hydrochloric acid. Subsequent conversion into 2 : 6-dinitrodiphenylene was carried out in the usual way, but the yield in the final step was not above 1%.

2-*Bromodiphenylene.*—The 5-bromodiphenylene-2 : 2′-iodonium iodide (IX; Y = I) required for this synthesis was prepared from the commercially available 2-aminodiphenyl (VI), which was brominated directly to 2-amino-5-bromodiphenyl, then diazotised and treated with potassium iodide giving 5-bromo-2-iododiphenyl (VII). Oxidation of this with peracetic acid gave 5-bromo-2-iodosodiphenyl (VIII). It was shown by Beringer *et al.*[10] that iodosobenzenes condense with aromatic compounds in presence of sulphuric acid to give diaryliodonium salts, and Collette, McGreer, Crawford, Chubb, and Sandin[11] have applied this reaction to 2-iodosodiphenyl, thereby converting it in very high yield into a diphenylene-2 : 2′-iodonium salt. Taking advantage of this reaction 5-bromo-2-iodosodiphenyl (VIII) has been converted in high yield into 5-bromodiphenylene-2 : 2′-iodonium hydrogen sulphate (IX; Y = HSO_4), which without isolation gave the related iodide when treated with concentrated aqueous potassium iodide. Final heating with cuprous oxide gave 2-bromodiphenylene in 10% yield, accompanied rather unexpectedly by diphenylene itself in 12% yield.



(VI) (VII) (VIII) (IX)

3 : 4′-*Diacetyldiphenyl* (XII; R = Ac).—This substance was required for the orientation of the diacetyldiphenylene obtained by Friedel–Crafts acetylation of the hydrocarbon. 4-Acetamidodiphenyl was brominated in acetic acid–sodium acetate, to give



(X) (XI) (XII)

4-acetamido-3 : 4′-dibromodiphenyl[12] (X), and hydrolysis with ethanolic sulphuric acid and treatment with sodium nitrite without isolation of the free amine led to deamination with production of 3 : 4′-dibromodiphenyl (XI). Reaction of 3 : 4′-dibromodiphenyl with

[8] Wasylewsky, Brown, and Sandin, *J. Amer. Chem. Soc.*, 1950, **72**, 1038.

[9] Sako, *Mem. Coll. Eng. Kyushu*, 1932, **6**, 307, 327; see *Brit. Chem. Abs.*, 1932, *A*, 508, or *Chem. Abs.*, 1932, **26**, 3245, 3248.

[10] Beringer, Drexler, Gindler, and Lumpkin, *J. Amer. Chem. Soc.*, 1953. **75**, 2705.

[11] Collette, McGreer, Crawford, Chubb, and Sandin, *ibid.*, 1956, **78**, 3819.

[12] Case and Sloviter, *ibid.*, 1937, **59**, 2381.

cuprous cyanide in pyridine gave a 67% yield of 3 : 4′-dicyanodiphenyl (XII; R = CN), which was converted by treatment with an excess of methylmagnesium iodide into 3 : 4′-diacetyldiphenyl (XII; R = Ac).

The ultraviolet absorption spectra of some of the compounds described in this paper are recorded in Part III.

EXPERIMENTAL

2-*Methyl*-6 : 2′-*dinitrodiphenyl* (I).—2-Amino-3-nitrotoluene [13] was converted into 2-iodo-3-nitrotoluene,[14] and to a stirred mixture of this iodo-compound (15 g.), *o*-iodonitrobenzene (14·5 g.), and nitrobenzene (30 ml.) in an oil-bath at 190—200° was added copper bronze (15 g.) during ¼ hr. After a further ½ hour's heating benzene was added, the mixture was filtered and steam-distilled, and the non-volatile oil was collected into ether and distilled, mainly at 175—180°/0·3 mm. The product crystallised on slow evaporation at room temperature of its solution in methanol. Two further recrystallisations gave 2-*methyl*-6 : 2′-*dinitrodiphenyl* as pale yellow needles (3·8 g.), m. p. 70—71° (Found: C, 60·8; H, 4·0; N, 10·7. $C_{13}H_{10}O_4N_2$ requires C, 60·5; H, 3·9; N, 10·9%). The mother-liquor yielded 2 : 2′-dimethyl-6 : 6′-dinitrodiphenyl, m. p. 106—107° (lit.,[2] m. p. 107—108°).

2 : 2′-*Diamino*-6-*methyldiphenyl* (II).—The preceding dinitro-compound (4 g.) in ethanol (75 ml.) was reduced by hydrogen at 3 atm. in presence of platinum oxide (0·1 g.) (4 hr.). The filtered, and then concentrated solution was diluted with water, and the solid recrystallised from 50% ethanol, giving 2 : 2′-*diamino*-6-*methyldiphenyl* (2·8 g.) as a hemihydrate, m. p. 61—62° (Found: C, 75·4; H, 6·8; N, 13·7. $C_{13}H_{14}N_2,\frac{1}{2}H_2O$ requires C, 75·4; H, 7·2; N, 13·5%). In a desiccator the substance loses water and liquefies.

2 : 2′-*Di-iodo*-6-*methyldiphenyl* (IV) *and* 6-*Methyldiphenylene*-2 : 2′-*iodonium Iodide* (III).—The preceding diamine (2·8 g.) in concentrated hydrochloric acid (15 ml.) and water (15 ml.) was tetrazotised at 0° by slow addition of sodium nitrite (2·1 g.) in water (10 ml.), and a concentrated aqueous solution of potassium iodide (9 g.) was then added. After 1 hr. the mixture was warmed on the water-bath and treated with excess of sodium hydrogen sulphite, and the solid was collected, washed, and warmed with methanol (100 ml.), leaving a brown residue (1·1 g.) of crude 6-methyldiphenylene-2 : 2′-iodonium iodide. The methanolic extract deposited 2 : 2′-di-iodo-6-methyldiphenyl which after several crystallisations was obtained as an orange-brown solid (1·5 g.), m. p. 96—97° (Found: C, 37·3; H, 2·3. $C_{13}H_{10}O_2$ requires C, 37·2; H, 2·4%).

1-*Methyldiphenylene* (V).—When either of the above di-iodo-derivatives (1·3 g.) was finely powdered with cuprous oxide (20 g.) and rapidly heated in a metal-bath at 350° for 5 min. as previously described [1] a yellow oil was obtained. This was distilled in steam, and the oil was collected into ether and treated with ethanolic picric acid, giving the scarlet *picrate* (0·5 g.) of 1-methyldiphenylene, which after recrystallisation from ethanol had m. p. 91—92° (Found: C, 57·8; H, 3·7; N, 10·8. $C_{13}H_{10},C_6H_3O_7N_3$ requires C, 57·8; H, 4·0; N, 10·6%). 1-*Methyldiphenylene*, regenerated from the picrate by passage of its solution in benzene through an alumina column, forms a yellow oil (Found: C, 93·8; H, 5·9. $C_{13}H_{10}$ requires C, 94·0; H, 6·0%). The 2 : 4 : 7-*trinitrofluorenone complex* separates from ethanol–ethyl acetate in deep scarlet needles, m. p. 162—163·5° (Found: C, 64·6; H, 3·3; N, 8·9. $C_{13}H_{10},C_{13}H_5O_7N_3$ requires C, 64·8; H, 3·1; N, 8·7%).

4-*Methyl*-2 : 2′-*dinitrodiphenyl*.—*o*-Iodonitrobenzene (14·5 g.) and 4-iodo-3-nitrotoluene (15 g.) (prepared from the corresponding amines by Wheeler and Liddle's method [14]) in nitrobenzene (30 ml.) were stirred at 170—180°, and copper bronze (15 g.) added during ¼ hr. After being heated for a further ¼ hr. the mixture was cooled, filtered after the addition of benzene, and steam-distilled, and the residue which solidified was crystallised from ethanol, giving 4-*methyl*-2 : 2′-*dinitrodiphenyl* as pale yellow needles, m. p. 93—95° (7·3 g., 54%). Sublimation at 150—160°/2 mm. and recrystallisation gave material of m. p. 94—95° (Found: C, 60·7; H, 3·7; N, 10·6. $C_{13}H_{10}O_4N_2$ requires C, 60·5; H, 3·9; N, 10·6%).

2 : 2′-*Diamino*-4-*methyldiphenyl*.—The preceding dinitro-compound (7 g.) was hydrogenated at 110°/6—7 atm. for 2 hr. in ethanol (75 ml.) in presence of Raney nickel (1 g.); heating was

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[13] Cohen, *J.*, 1891, **79**, 1127.

[14] Wheeler and Liddle, *Amer. Chem. J.*, 1909, **42**, 451.

then stopped and reduction continued for 2 hr. The filtered solution was distilled, giving 2 : 2′-*diamino*-4-*methyldiphenyl*, b. p. 160—164°/0·8 mm. (3·1 g., 59%) (Found: C, 78·6; H, 7·1; N, 14·6. $C_{13}H_{14}N_2$ requires C, 78·8; H, 7·1; N, 14·2%).

4-*Methyldiphenylene*-2 : 2′-*iodonium Iodide and* 2 : 2′-*Di-iodo*-4-*methyldiphenyl*.—The preceding diamine (2·8 g.) was tetrazotised and treated with potassium iodide as described in the case of its isomer, and the crude, washed product was extracted with methanol (100 ml.) in a Soxhlet apparatus. There remained in the thimble the iodonium iodide as a cream-coloured powder, m. p. 201—202° (decomp.) (2·1 g.). The product from the extract was sublimed at 100—110°/1 mm. and crystallised twice from methanol, giving 2 : 2′-*di-iodo*-4-*methyldiphenyl* as prisms, m. p. 85—86° (0·8 g.) (Found: C, 36·7; H, 2·2. $C_{14}H_{10}I_2$ requires C, 37·2; H, 2·4%).

2-*Methyldiphenylene*.—After either of the above di-iodo-compounds had been heated at 350—370° with 10 times the weight of dry cuprous oxide as described previously,[1] the product, a resinous solid, was steam-distilled, giving a yellow solid in low yield. Crystallisation from saturated ethanolic picric acid gave a picrate as crimson needles, m. p. 86—87° after recrystallisation. The *hydrocarbon* was regenerated by passing the picrate in ethanol through alumina and after sublimation at 60—80°/10 mm. and crystallisation from methanol formed pale straw-coloured needles, m. p. 45—46° (Found: C, 93·7; H, 6·0. $C_{13}H_{10}$ requires C, 94·0; H, 6·0%). The 2 : 4 : 7-*trinitrofluorenone complex* prepared in and crystallised from acetic acid formed deep purple needles, m. p. 150—151° (Found: C, 64·7; H, 3·2; N, 8·9. $C_{26}H_{15}O_7N_3$ requires C, 64·8; H, 3·1; N, 8·7%).

2-*Iodo*-3-*nitroanisole*.—2-Iodo-3-nitrophenol[4] (35 g.) was methylated in 10% aqueous sodium hydroxide (50 ml.) at 60° by shaking it with methyl sulphate (35 ml.) and more alkali (50 ml.) in alternate portions; finally the mixture was refluxed for 2 hr. with 20% aqueous sodium hydroxide (50 ml.), cooled, and the washed solid crystallised from carbon tetrachloride, giving bright yellow plates, m. p. 97—100° (22·5 g.). After several crystallisations the m. p. was 102·5—103·5° (Found: C, 30·0; H, 2·4; N, 5·3; I, 45·3. $C_7H_6O_3NI$ requires C, 30·1; H, 2·2; N, 5·0; I, 45·5%).

2-*Methoxy*-6 : 2′-*dinitrodiphenyl*.—*o*-Iodonitrobenzene (23 g.) and 2-iodo-3-nitroanisole (21·5 g.) were stirred and heated in nitrobenzene (40 ml.) at 190—200° for 50 min., copper bronze (25 g.) being added during the first 20 min. The mixture was diluted with benzene, filtered, and steam-distilled, the residue was dissolved in hot acetone (charcoal), then concentrated, and warm methanol was added. On cooling, 2 : 2′-dimethoxy-6 : 6′-dinitrodiphenyl (3·8 g.) separated. The product from the mother-liquor was fractionally crystallised from methanol, giving 2-*methoxy*-6 : 2′-*dinitrodiphenyl* (2·6 g., 12%), m. p. 152—154·5°, and crude 2 : 2′-dinitrodiphenyl (2·3 g.). After further crystallisation from methanol and sublimation under reduced pressure the pure 2-methoxy-6 : 2′-dinitrodiphenyl had m. p. 157—158° (Found: C, 56·9; H, 3·7; N, 10·2. $C_{13}H_{10}O_5N_2$ requires C, 57·0; H, 3·7; N, 10·2%).

A closely similar reaction using *o*-bromonitrobenzene and 2-chloro-3-nitroanisole but without solvent gave a 10% yield of 2-methoxy-6 : 2′-dinitrodiphenyl.

2 : 2′-*Diamino*-6-*methoxydiphenyl*.—The preceding dinitro-compound (4·9 g.), granulated tin (20 g.), concentrated hydrochloric acid (40 ml.), and acetic acid (10 ml.) were heated on a water-bath until a clear solution was obtained. After dilution with water (100 ml.) and passage of hydrogen sulphide, the filtered solution was made alkaline with sodium hydroxide and extracted with ether. The extract yielded 2 : 2′-*diamino*-6-*methoxydiphenyl*, needles (from ethanol), m. p. 98—99° (3·1 g.) (Found: C, 72·7; H, 6·6; N, 12·9. $C_{13}H_{14}ON_2$ requires C, 72·9; H, 6·6; N, 13·1%).

6-*Methoxydiphenylene*-2 : 2′-*iodonium Iodide and* 2 : 2′-*Di-iodo*-6-*methoxydiphenyl*.—The 2 : 2′-diamino-6-methoxydiphenyl (2·6 g.) was converted by the procedure described in the case of 2 : 2′-diamino-6-methyldiphenyl (II) into a mixture of 6-methoxydiphenylene-2 : 2′-iodonium iodide, a light grey powder, m. p. 209—210° (decomp.) (1·1 g.), and 2 : 2′-*di-iodo*-6-*methoxydiphenyl* which separated from methanol (charcoal) in golden-yellow needles, m. p. 138·5—139·5° (1·2 g.) (Found: C, 36·1; H, 2·2; OMe, 7·3. $C_{12}H_7I_2 \cdot OMe$ requires C, 35·8; H, 2·3; OMe, 7·1%).

1-*Methoxydiphenylene*.—A mixture of the preceding di-iodo-compound (0·6 g.), the iodonium iodide (0·9 g.), and cuprous oxide (25 g.) was heated as in the previous diphenylene preparations, and the product steam-distilled, extracted with ether, and treated with 2 : 4 : 7-trinitrofluorenone (0·35 g.) in acetic acid–ethanol. The *complex* (0·43 g.) after recrystallisation formed deep maroon needles, m. p. 157·5—159° (Found: C, 62·5; H, 3·2; N, 8·3. $C_{26}H_{15}O_8N_3$ requires

C, 62·8; H, 3·0; N, 8·5%). Dissociation was effected by passing its benzene solution through alumina, and the product was twice distilled at *ca.* 150°/16 mm. on to a cold-finger condenser, giving 1-*methoxydiphenylene* as pale-yellow needles, m. p. 41—42° (Found: C, 85·4; H, 5·6. $C_{13}H_{10}O$ requires C, 85·7; H, 5·5%).

4-*Methoxy*-2 : 2′-*dinitrodiphenyl*.—*o*-Iodonitrobenzene (100 g.) and 4-iodo-3-nitroanisole (112 g.) in nitrobenzene (200 ml.) were stirred at 190—200° during slow addition of copper bronze (100 g.) and for ½ hr. after. The cooled mixture was diluted with benzene, filtered, and steam-distilled to remove the solvents, and the non-volatile product crystallised from methanol (charcoal). Two crops (total 13 g.) of crude 4 : 4′-dimethoxy-2 : 2′-dinitrodiphenyl, m. p. 122—126°, were obtained, and slow evaporation at room temperature cause the deposition of successive crops of crude 4-*methoxy*-2 : 2′-*dinitrodiphenyl* which was recrystallised from methanol, giving material of m. p. 92—100° (42 g.). Repeated crystallisation from methanol finally gave flat, bright-yellow needles, m. p. 108—109°, which slowly darkened on exposure to light (Found: C, 57·0; H, 3·8; N, 10·1; OMe, 11·7. $C_{12}H_7O_4N_2$·OMe requires C, 57·0; H, 3·7; N, 10·2; OMe, 11·3%).

2-*Methoxydiphenylene*.—The preceding crude dinitro-compound (12·5 g.) was reduced in the manner described for its isomer, giving 2 : 2′-diamino-4-methoxydiphenyl, b. p. 180—185°/0·5 mm. (5·8 g.). Conversion of the diamine (5·5 g.) into 4-methoxydiphenylene-2 : 2′-iodonium iodide (orange-brown powder; 5·1 g.) was carried out as in the case of the preparation of the 6-methyl compound (II); the related 2 : 2′-di-iodo-4-methoxydiphenyl could not be extracted by means of methanol. When the iodonium iodide (14 g.) was heated with cuprous oxide (120 g.), and the product isolated as usual by steam-distillation, crystallisation from light petroleum (b. p. 40—60°) and sublimation at 100—110°/10 mm. gave 2-*methoxydiphenylene* (0·48 g.) as thick lemon-yellow needles, m. p. 69—70° (Found: C, 85·6; H, 5·3. $C_{13}H_{10}O$ requires C, 85·7; H, 5·5%). The 2 : 4 : 7-*trinitrofluorenone complex* prepared in and crystallised from ethanol forms deep purple needles, m. p. 140—141° (Found: C, 63·0; H, 3·1; N, 8·4. $C_{26}H_{15}O_8N_3$ requires C, 62·8; H, 3·0; N, 8·5%).

2-*Hydroxydiphenylene*.—2-Methoxydiphenylene (50 mg.) and pyridine hydrochloride (500 mg.) were placed in an oil-bath at 230° for 5 min., the flask was rapidly cooled, and the dark contents were washed out with 10% aqueous sodium hydroxide. The filtered solution was acidified, and the solid was sublimed twice at 130—140°/14 mm., giving 2-*hydroxydiphenylene* as pale yellow needles (14 mg.), m. p. 140—141° (Found: C, 86·0; H, 4·7. $C_{12}H_8O$ requires C, 85·7; H, 4·8%). The m. p. was not depressed on admixture with the hydroxydiphenylene, m. p. 139—140°, prepared by oxidising diphenylene with lead tetra-acetate.[1]

2 : 2′-*Diamino*-6 : 6′-*dimethoxydiphenyl*.—2 : 2′-Dimethoxy-6 : 6′-dinitrodiphenyl (see preparation of 2-methoxy-6 : 2′-dinitrodiphenyl) (7·5 g.) was reduced with tin and hydrochloric acid in the same manner as the monomethoxy-compounds, giving 2 : 2′-*diamino*-6 : 6′-*dimethoxydiphenyl* (4·7 g.) which separated from dilute ethanol in hexagonal prisms, m. p. 90—91° (Found: C, 63·8; H, 6·8; N, 10·5. $C_{14}H_{16}O_2N_2,H_2O$ requires C, 64·2; H, 6·9; N, 10·7%).

6 : 6′-*Dimethoxydiphenylene*-2 : 2′-*iodonium Iodide and* 2 : 2′-*Di-iodo*-6 : 6′-*dimethoxydiphenyl*.—The preceding diamine (3·3 g.) was tetrazotised and then treated with potassium iodide, and the products were isolated as in the previous cases, giving the iodonium iodide as an orange-brown powder [0·6 g.; m. p. 168° (decomp.)], insoluble in cold ethanol, and 2 : 2′-*di-iodo*-6 : 6′-*dimethoxydiphenyl* as pale orange needles (2·4 g.), m. p. 182—184° (from methanol; charcoal) [Found: C, 36·4; H, 2·7; OMe, 13·0. $C_{12}H_6I_2(OMe)_2$ requires C, 36·1; H, 2·6; OMe, 13·3%].

1 : 8-*Dimethoxydiphenylene*.—Rapid distillation of the foregoing two iodo-compounds with cuprous oxide as in the previous diphenylene preparations, and prolonged steam-distillation gave 1 : 8-*dimethoxydiphenylene* which crystallised from methanol in bright yellow tablets, m. p. 107—108° (Found in material sublimed at 130°/12 mm.: C, 79·0; H, 5·7. $C_{14}H_{12}O_2$ requires C, 79·3; H, 5·7%). This m. p. is the same as that of 2 : 7-dimethoxydiphenylene,[2] but a mixed m. p. shows a depression.

4-*Nitrodiphenylene*-2 : 2′-*iodonium Iodide*.—Diphenylene-2 : 2′-iodonium iodide was converted into 4-nitrodiphenylene-2 : 2′-iodonium nitrate according to the method of Wasylewski, Brown, and Sandin;[8] the crude nitrate (4·5 g.) was supended in boiling water (1 l.), a saturated solution of potassium iodide (10 g.) was added, and the mixture was stirred at 100° for 1 hr. The *iodonium iodide* was collected, digested with boiling water, and dried (2·5 g.); it formed a dull yellow powder, m. p. 197—199° (Found: N, 2·9. $C_{12}H_7O_2NI_2$ requires N, 3·1%).

2-*Nitrodiphenylene*.—Distillation of the preceding iodonium iodide with cuprous oxide in the usual manner gave a partly solid product which was sublimed at 120°/10 mm. and then crystallised from ethanol, giving material (0·18 g.), m. p. 102—104°. Pure 2-*nitrodiphenylene*, prepared by steam-distillation and crystallisation from light petroleum (b. p. 40—60°), formed yellow needles, m. p. 107—108° (Found: C, 72·9; H, 3·7; N, 7·0. $C_{12}H_7O_2N$ requires C, 73·1; H, 3·6; N, 7·1%).

2 : 2′-*Diamino*-4 : 5′-*dinitrodiphenyl*.—2 : 2′-Disuccinimidodiphenyl (20 g.) [15, 9] was nitrated according to Sako's directions [9] and the washed, dried product was extracted with hot methanol (1 l.) in a Soxhlet apparatus for 6 hr., leaving 4 : 4′-dinitro-2 : 2′-disuccinimidodiphenyl as a white powder, m. p. 295—304°; the cooled, seeded filtrate yielded a small amount of the same compound (total 4·7 g.). The filtrate was concentrated to 200 ml., the solid collected, and the process repeated till no further solid was obtained. By repeated crystallisation of the whole material from methanol containing 5% of acetic acid there was obtained 4 : 5′-dinitro-2 : 2′-disuccinimidodiphenyl as yellow prisms (9·5 g.), m. p. 270—272° (lit., m. p. 271—272°), and 5 : 5′-dinitro-2 : 2′-disuccinimidodiphenyl as a yellow powder (1·1 g.), m. p. 315—317°. The 4 : 5′-dinitro-compound (16 g.) was hydrolysed by boiling it for 5 hr. with concentrated hydrochloric acid (150 ml.), ethanol (150 ml.), and water (75 ml.), the mixture was poured on ice, and the 2 : 2′-diamino-4 : 5′-dinitrodiphenyl collected, washed and dried whereupon it darkened (7·2 g.; m. p. 170—172°) (lit., dimorphic, yellow form, m. p. 143—144°, orange form, m. p. 179—180°.

4 : 5′-*Dinitrodiphenylene*-2 : 2′-*iodonium Iodide and* 2 : 2-*Di-iodo*-4 : 5′-*dinitrodiphenyl*.—The preceding diamine (1·8 g.) was tetrazotised at 0° in concentrated hydrochloric acid (20 ml.) and water (5 ml.) by slow addition of sodium nitrite (0·97 g.), and the solution then added to a stirred solution of potassium iodide (10 g.) in water (20 ml.), heated gently for ½ hr., and set aside with an excess of sodium hydrogen sulphite. The solid was collected, washed, and boiled with ethanol, leaving the insoluble 4 : 5′-*dinitrodiphenylene*-2 : 2′-*iodonium iodide* as a yellow-brown powder [1·6 g.; m. p. 171—172° (decomp.)]. The ethanol extract yielded a product which was successively sublimed (temp. raised to 180°/0·3 mm.), chromatographed in benzene on alumina, and eluted with the same solvent (leaving bright yellow material on the column), and crystallised from ethanol, giving 2 : 2′-*di-iodo*-4 : 5′-*dinitrodiphenyl* as pale yellow, flat prisms (0·8 g.; m. p. 167—168°) (Found: C, 28·7; H, 1·3; N, 5·3. $C_{12}H_6O_4N_2I_2$ requires C, 29·0; H, 1·2; N, 5·45%).

2 : 6-*Dinitrodiphenylene*.—The crude 4 : 5′-dinitrodiphenylene-2 : 2′-iodonium iodide (1·5 g.) was heated with cuprous oxide (25 g.) at 350° in the usual manner, and the sublimate was crystallised three times from ethanol (charcoal), giving 2 : 6-dinitrodiphenylene as deep yellow needles (3 mg.) which sublimed without melting above 260°. A similar experiment using 2 : 2′-di-iodo-4 : 5′-dinitrodiphenyl (0·5 g.) gave almost the same yield of the dinitrodiphenylene. There was insufficient material for analysis, but the characteristic ultraviolet spectrum was identical with that of the dinitro-compound prepared by the nitration of diphenylene as described in the following paper.

5-*Bromo*-2-*iododiphenyl* (VII).—2-Amino-5-bromodiphenyl hydrobromide was prepared in 97% yield by the direct bromination in carbon tetrachloride of commercial 2-aminodiphenyl (VI) according to the directions of Scarborough and Waters [16] who also established the position of the bromine atom. This hydrobromide (13·2 g.) in water (200 ml.) containing concentrated sulphuric acid (4·2 g.) was diazotised at 0—2°, and a strong solution of potassium iodide (24 g.) added below 5°; the mixture was kept overnight, then warmed to 40°. Free iodine was removed by the addition of sodium thiosulphate, the product extracted with ether, and the organic layer washed with aqueous sodium carbonate and water, dried, and distilled, giving 5-*bromo*-2-*iododiphenyl* as a pale yellow oil (11·5 g.), b. p. 180°/15 mm. (Found: C, 40·5; H, 2·4. $C_{12}H_8BrI$ requires C, 40·2; H, 2·2%).

5-*Bromo*-2-*iodosodiphenyl* (VIII) *and* 5-*Bromodiphenylene*-2 : 2′-*iodonium Iodide* (IX; Y = I).—5-Bromo-2-iododiphenyl (VII) (6 g.) in acetic anhydride (25 ml.) was added at 0° to a solution of peracetic acid (30 ml.) (made by slowly adding 30% hydrogen peroxide to 4 times its volume of acetic anhydride at 0°, and keeping the whole at room temperature overnight). The mixture was kept at room temperature for 18 hr. The solution, which then contained the iodoso-compound (VIII), was treated at 0° with concentrated sulphuric acid (6·5 ml.), and after 6 hr. water (120 ml.) was added, and the mixture shaken and extracted with benzene. The aqueous

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[15] Dice and Smith, *J. Org. Chem.*, 1949, **14**, 179.

[16] Scarborough and Waters, *J.*, 1927, 89.

layer was treated with aqueous sodium hydrogen sulphite until no iodine was liberated on addition of potassium iodide, and a concentrated solution of potassium iodide was then added till no further precipitation of the iodonium iodide (IX; Y = I) occurred. This product was collected, washed well with water in which it is almost insoluble, and dried at 60° (yield about 2 g.) (decomp. above 250°).

2-*Bromodiphenylene*.—The foregoing iodonium iodide (4 g.) was heated at 360° for 20 min. in the usual way with cuprous oxide (40 g.). The distillate, collected by dissolving it in hot methanol, was heated at 70—80°/12 mm. for 3 hr., giving a sublimate of pale yellow needles (0·15 g.), m. p. and mixed m. p. with diphenylene 110—111°. The remaining product (0·28 g.) was converted in ethanol–acetic acid (1 : 2) into the 2 : 4 : 7-trinitrofluorenone complex, m. p. 135—136°. Regeneration of the 2-bromodiphenylene by passage through alumina in benzene, recovery, and sublimation at 115—125°/13 mm. gave cream-coloured plates (0·20 g.), m. p. 64—65°, undepressed when mixed with a specimen prepared by either of the methods described in Part III (for analyses see Part III).

3 : 4′-*Dicyanodiphenyl* (XII; R = CN).—4-Acetamido-3 : 4′-dibromodiphenyl[12] (X) (10 g.) was refluxed for 24 hr. with ethanol (100 ml.) containing concentrated sulphuric acid (10 ml.). Diluted sulphuric acid (50 ml.; 50% v/v) was added and to the boiling mixture a concentrated aqueous solution of sodium nitrite (8 g.) was dropped in during 1 hr. After being boiled for a further ½ hr. the solution was extracted with ether, and the crude 3 : 4′-dibromodiphenyl (XI) distilled as an amber-coloured oil (5·6 g.; b. p. 135—140°/1 mm.). This dibromo-compound (5·6 g.) was next heated under reflux (bath-temp. 180—190°) for 20 hr. with pyridine (10 ml.) and anhydrous cuprous cyanide (3·6 g.), and the solid, cooled product was shaken alternately several times with a mixture of equal volumes of concentrated aqueous ammonia and water, and with benzene. The benzene extracts were washed with dilute aqueous ammonia, then with 4N-hydrochloric acid, and yielded 3 : 4′-*dicyanodiphenyl* which separated from benzene–light petroleum (b. p. 60—80°) as a cream-coloured powder, m. p. 129—131° (Found: C, 82·2; H, 4·2; N, 13·5. $C_{14}H_8N_2$ requires C, 82·4; H, 3·9; N, 13·7%).

3 : 4′-*Diacetyldiphenyl* (XII; R = Ac).—3 : 4′-Dicyanodiphenyl (1 g.) in benzene (25 ml.) was added to the Grignard reagent prepared from methyl iodide (2·8 g.) and magnesium (0·5 g.) in ether (20 ml.), the ether distilled away, and the benzene solution boiled under reflux for 1 hr. Next day the mixture was heated with dilute hydrochloric acid for 1 hr. The benzene layer and extract yielded a product which was sublimed at 130—140°/0·1 mm., and then crystallised from ethanol. The 3 : 4′-*diacetyldiphenyl* (0·4 g.) formed colourless needles, m. p. 101—102° (Found: C, 80·5; H, 5·6. $C_{16}H_{14}O_2$ requires C, 80·7; H, 5·9%).

3 : 3′-*Diacetyldiphenyl*.—3-Nitroacetophenone[17] was reduced to 3-aminoacetophenone[18] and then converted into 3-iodoacetophenone.[19] The iodo-compound (2 g.) was heated with copper bronze (2 g.) (oil-bath at 240—260°) for ½ hr. and the product extracted with boiling ethyl acetate, giving a crude solid which was sublimed at 140—150°/1 mm. and recrystallised from ethyl acetate. 3 : 3′-Diacetyldiphenyl was obtained as colourless needles (350 mg.), m. p. 121—122°. Simpson *et al.*[20] prepared this compound as a by-product in the conversion of 3-aminoacetophenone into 3-chloroacetophenone by the diazonium reaction and described it as pale brown prisms, m. p. 123—124°.

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[17] *Org. Synth.*, Coll. Vol. II, 1943, p. 434.
[18] Morgan and Moss, *J. Soc. Chem. Ind.*, 1923, **42**, 461.
[19] Evans, Morgan, and Watson, *J.*, 1935, 1167.
[20] Simpson, Atkinson, Schofield, and Stephenson, *J.*, 1945, 646.