546. *Diphenylenes. Part III.*[1] *Substitution in the Nucleus.*

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A study has been made of substitution in the nucleus of diphenylene. Under carefully defined conditions it has been found possible to effect monosubstitution in the cases of acetylation, nitration, chlorination, bromination, iodination, acetoxymercuration, hydroxylation with lead tetra-acetate, and oxidative coupling, and in all these reactions a 2-substituted diphenylene results. The compounds have been orientated by direct comparison with, or by conversion into, a diphenylene of known orientation, or by reductive cleavage to give one or two diphenyls whose structures are known or now established. Dinitration and diacetylation are shown to occur in positions 2 and 6, corresponding to *meta*-substitution with respect to the first group introduced; this indicates a considerable degree of conjugation between the two benzene rings *via* the four-membered ring.

These findings are discussed in the light of theoretical predictions.

Some reactions involving substitution in diphenylene were described in Part I [2] of this series, and it was shown that acetylation under Friedel–Crafts conditions gave 2-acetyldiphenylene and a diacetyl derivative thought to be the 2 : 6-diacetyl compound. It was also shown that acetoxylation by lead tetra-acetate gave, after hydrolysis, a 1·5% yield of a hydroxydiphenylene, and that sulphonation at room temperature gave a disulphonic acid. The hydroxy-compound has since been shown [1] to be 2-hydroxydiphenylene, but the disulphonic acid has only been orientated by analogy; it is probably, the 2 : 6-disulphonic acid. The present paper describes further substitutions in diphenylene.

Acetylation.—The orientation of the acetyldiphenylene described in Part I [2] as 2-acetyldiphenylene was established by reductive cleavage of the four-membered ring with Raney nickel. This occurs in both of the possible ways, to give a mixture of 3- and 4-acetyldiphenyl, identified chromatographically as their 2 : 4-dinitrophenylhydrazones. 1-Acetyldiphenylene under these conditions would be expected to give a mixture of 2- and 3-acetyldiphenyl, but could give no 4-acetyldiphenyl.

Additional evidence concerning the structure of the acetyldiphenylene (VII) has now been obtained by converting it into the related amine (III), either directly by a Schmidt reaction with sodium azide, or by Beckmann transformation of its oxime (I) and hydrolysis of the resulting acetamido-compound [2] (II). This amine is identical with that prepared by reduction of 2-nitrodiphenylene (IV) synthesised by an unambiguous method.[1] 2-Aminodiphenylene does not undergo diazotisation in the normal manner in aqueous solution; insoluble, probably coupled products are formed.

The diacetyldiphenylene [2] which is also obtained by direct acetylation and was provisionally regarded as 2 : 6-diacetyldiphenylene (VI) was reduced by Raney nickel in alcohol to a single product in 70% yield, namely, 3 : 4′-diacetyldiphenyl, identical with a specimen synthesised by an unambiguous route.[1] The reductive cleavage of 2 : 6-diacetyldiphenylene (VI) could give only 3 : 4′-diacetyldiphenyl irrespective of which of the two central bonds was broken, and the high yield of this single product is a strong argument in support of the 2 : 6-orientation. The only other isomer which could yield 3 : 4′-diacetyldiphenyl is 1 : 7-diacetyldiphenylene and this would be expected to give, in addition, 2 : 3′-diacetyldiphenyl which is not in fact found.

The 2 : 6-orientation has been confirmed by a study of the infrared spectra of the diacetyldiphenylene, of diphenylene itself,[3] and of the following diphenylene derivatives of known orientation: 2-acetyl and its oxime, 2-acetamido, 2-amino, 2-bromo, 2-methoxy, 2-cyano, 2-carboxylic acid, 2 : 6-dinitro, and 1 : 8-dimethoxy. The spectrum of the

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[1] Part II, Baker, Barton, and McOmie, preceding paper.

[2] Part I, Baker, Boarland, and McOmie, *J.*, 1954, 1476.

[3] Wittig and Lehmann, *Chem. Ber.*, 1957, **90**, 880.

diacetyl derivative shows a strong band at 832 cm.$^{-1}$, characteristic of a 1 : 2 : 4-trisubstituted benzene. If the compound were 1 : 7-diacetyldiphenylene, strong bands at 830 ± 30 and 780 ± 30 cm.$^{-1}$ would be expected, corresponding to 1 : 2 : 4- and 1 : 2 : 3-trisubstituted benzene rings respectively, but the second band is absent. In all the compounds mentioned the benzene rings appear to contribute independently to the spectrum: a similar effect has been established for the substituted naphthalenes,[4] so that the method may be used to determine the position of substituents.

Nitration.—Diphenylene is readily attacked by nitric acid in acetic acid, but the isolation of individual substances is not easy, and alkali-soluble oxidation products are formed. Nitration with 1·5 equivalents of nitric acid in acetic anhydride at 0° gave a 23·5% yield of 2-nitrodiphenylene (IV), identical with the unambiguously synthesised material.[1] Reduction of the 2-nitrodiphenylene gave 2-aminodiphenylene (III), identical with that prepared from 2-acetyldiphenylene (VII).

Nitration with nitric–sulphuric acid mixture required the use of 72% sulphuric acid to minimise sulphonation of the diphenylene, and the reaction was again complex, giving 2-nitrodiphenylene, 2 : 6-dinitrodiphenylene (V), and a trace of a high-melting hydrocarbon which proved to be 2 : 2′-bisdiphenylenyl (XVIII) formed by an oxidative coupling. The 2 : 6-dinitrodiphenylene was identified by direct comparison with a specimen previously synthesised by an unambiguous method.[1] The hydrocarbon, which was also obtained (2·5% yield) when diphenylene was treated with nitric acid in a sulphuric–acetic acid mixture, was identical with 2 : 2′-bisdiphenylenyl prepared from 2-iododiphenylene (see below) under the conditions of the Busch coupling reaction (hydrazine hydrate, methanolic potassium hydroxide, and a palladium–calcium carbonate catalyst).[5]

Acetoxymercuration.—Diphenylene is converted into 2-acetoxymercuridiphenylene (XIII) in 79% yield (allowing for recovered diphenylene) by heating it with mercuric acetate in acetic acid.[6] The position of the acetoxymercuri-group is proved by ready conversion, by bromine in boiling chloroform, into a bromodiphenylene identical with synthetic 2-bromodiphenylene[1] (XII).

This 2-acetoxymercuridiphenylene is a readily accessible and useful intermediate for the preparation of a variety of 2-substituted diphenylenes. When treated in chloroform with hydrochloric acid and sodium chlorate it gave 2-chlorodiphenylene (XIV) in 82% yield, and when heated with iodine–potassium iodide solution it gave 2-iododiphenylene (XVII). The 2-iododiphenylene, thus readily accessible, was converted into 2-cyanodiphenylene (XVI) when heated with cuprous cyanide in pyridine, and thence by hydrolysis into diphenylene-2-carboxylic acid (XI) identical with the acid previously obtained by oxidising 2-acetyldiphenylene (VII) with sodium hypochlorite.[2] The iodo-compound was also converted into diphenylene-2-carboxylic acid though in poor yield, by passing carbon dioxide into the derived Grignard reagent; a little 2 : 2′-bisdiphenylenyl (XVIII) was also formed at the same time.

Chlorination.—Direct chlorination of diphenylene in carbon tetrachloride in presence of iodine gave complex mixtures, but rather unexpectedly 2-chlorodiphenylene (XIV) was readily obtained in good yield when diphenylene was boiled with iodine monochloride in acetic acid. Only chlorodiphenylene and no iododiphenylene was produced, even when iodine monochloride and half its weight of free iodine were used. The 2-chlorodiphenylene was identical with that prepared *via* 2-acetoxymercuridiphenylene (XIII).

Bromination.—Diphenylene reacts with bromine in carbon tetrachloride in presence of pyridine as a catalyst, to give a 49% yield of 2-bromodiphenylene (XII), identical with that previously synthesised by an unambiguous method[1] or prepared from the acetoxymercuri-compound (XIII) as described above. The bromo-compound is conveniently isolated by means of its complex with 2 : 4 : 7-trinitrofluorenone. Use of

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[4] Hawkins, Ward, and Whiffen, *Spectrochim. Acta*, 1957, **10**, 105.

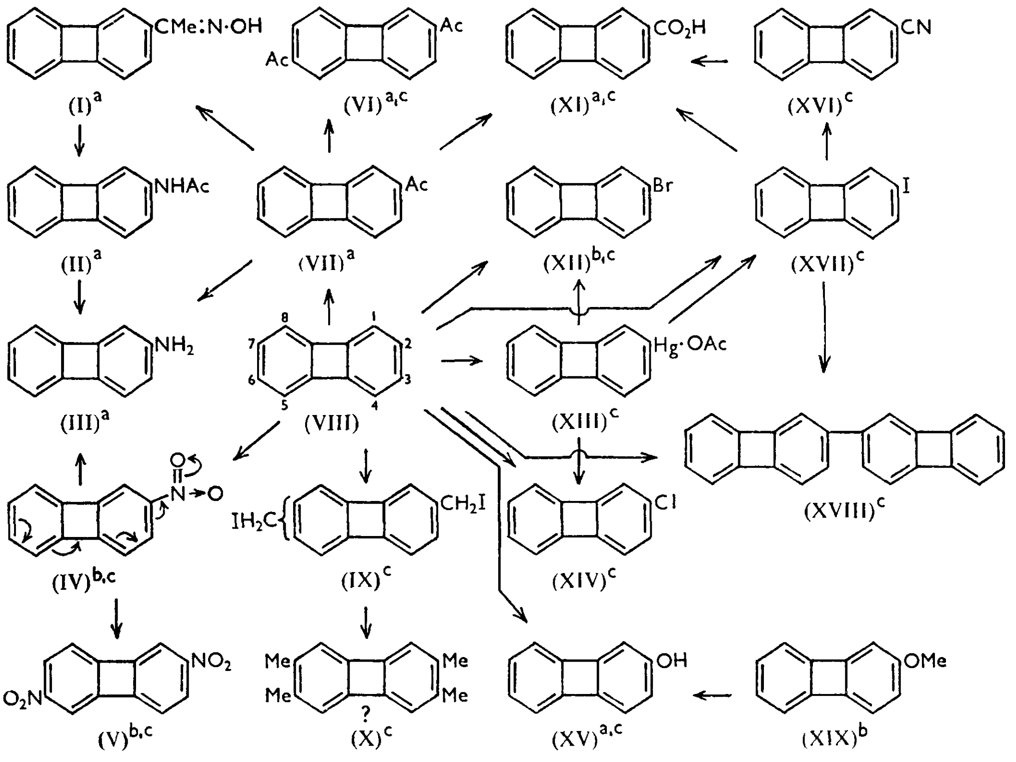
[5] Busch and Weber, *J. prakt. Chem.*, 1936, **146**, 1.

[6] Kobe *et al.*, *Ind. Eng. Chem.*, 1941, **33**, 170; 1942, **34**, 309; 1946, **38**, 247, 248.

excess of bromine led to 2-bromodiphenylene and a substance, m. p. 136—137°, probably a tetrabromo-derivative, which is being investigated further.

Iodination.—Direct iodination of diphenylene with iodine in acetic acid in presence of iodic acid gave a 5% yield of 2-iododiphenylene (XVII), but a 20% yield was obtained when sodium persulphate was used in place of the iodic acid. The product was identical with that prepared by the more convenient reaction *via* 2-acetoxymercuridiphenylene (XIII).

Iodomethylation.—Attempted chloromethylation [7] of diphenylene gave complex mixtures, but iodomethylation took place readily when diphenylene in acetic acid was treated with chlorodimethyl ether and concentrated hydriodic acid. The product was an unstable bisiodomethyl derivative, probably 2 : 6- or 2 : 7-bisiodomethyldiphenylene (IX), characterised as the dipicrate of the related bisthiuronium derivative prepared by reaction of the di-iodo-compound with thiourea.



[a] Part I, ref. 2. [b] Part II, ref. 1. [c] This paper.

An unexpected result was obtained when an attempt was made to reduce the bisiodomethyl derivative to a dimethyldiphenylene with zinc and hydrogen chloride in acetic acid. Analysis of the high-melting product and of its complex with 2 : 4 : 7-trinitrofluorenone showed that it was probably a tetramethyldiphenylene, perhaps the 2 : 3 : 6 : 7-derivative (X), which must have been formed as the result of a type of dismutation involving migration of iodomethyl groups.

The ultraviolet absorption spectra characteristics of most of the diphenylenes and of certain diphenyls described in this paper and in Part II [1] are recorded in the Table.

The spectra of diphenylene and some of its derivatives were illustrated in Part I, and

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[7] Review by Fuson and Keever, *Org. Reactions*, 1942, **1**, 63.

it was pointed out that the spectra of the other diphenylenes there described resembled in general that of the parent compound except for loss of fine structure and bathochromic shifts. This resemblance is also shown by the diphenylenes described in Part II and in this paper (see Table) except for 1-methoxy-, 1 : 8-dimethoxy-, 2-nitro-, and 2 : 6-dinitro-diphenylene, the spectra of which in 95% ethanol are shown in Figs. 1 and 2. [*Note.* In Part I, Fig. 2, the scale on the right-hand side (for 2-acetyldiphenylene) was accidentally omitted; it should have duplicated that on the right of Fig. 1.]

Ultraviolet absorption maxima in ethanol.

Diphenylene derivs.	λ (mμ)	$\log_{10} \varepsilon$	λ (mμ)	$\log_{10} \varepsilon$	λ (mμ)	$\log_{10} \varepsilon$
1-Methyl	242	4·66	326	3·31	339	3·58
	251	4·91	331	3·29	343	3·57
					358	3·75
2-Methyl	242	4·74	298	3·13	361	3·88
	250	4·93	343	3·80		
2-Methoxy	253	4·61	306	3·27	338	3·18
	275	4·22	324	3·08	356	3·17
1-Methoxy	253	4·01	345	3·02	360	3·07
					363	3·07
1 : 8-Dimethoxy	256	4·73	303	3·02	335	3·05
	265	4·97	318	3·09	350	2·82
2 : 7-Dimethoxy	245	5·03	342	4·16	360	4·25
	254	5·21				
2-Hydroxy	253	4·64	347	3·72	364	3·82
2-Nitro	232	4·19	264	4·14	348	3·32
	239	4·18	328	3·17	364	3·51
					400	3·44
2 : 6-Dinitro	258	3·88	304	3·67	365	3·34
					382	3·45
2-Bromo	245	4·59	253	4·79	344	3·61
					363	3·76
2 : 6-Diacetyl	219	3·87	286	4·34	376	3·79
	261	4·24	359	3·62		
2-Chloro	244	4·49	252	4·72	344	3·54
					363	3·66
2-Iodo	257	4·82	345	3·79	364	3·95
2-Cyano	252	5·00	334	3·56	362	4·01
	259	5·11	347	3·84	352	3·93
Tetramethyl	246	4·80	256	5·02	372	4·09
2 : 2′-Bisdiphenylenyl	247	4·25	289	4·34	372	3·90
	280	4·45	358	3·79		
Diphenyl derivs.						
3 : 4′-Diacetyl	253	4·41	277	4·50	—	—
3 : 3′-Diacetyl	236	4·81	295	3·61	—	—
4 : 4′-Diacetyl [8]	294	4·63	—	—	—	—

DISCUSSION

Because of its unusual, yet simple structure diphenylene has been the subject of many theoretical calculations, including resonance energy, strain energy, bond lengths, bond orders, and free valencies; references are given by Baker and McOmie.[9] Brown has predicted that diphenylene should undergo electrophilic and nucleophilic substitution more readily than benzene,[10] and these and other considerations by Alonzo and Domingo[11] and Alonzo and Peradejordi[12] have shown that electrophilic, nucleophilic, and homolytic reactions should all occur preferentially at position 2, in spite of the fact that the value of the free valence is greatest in position 1.

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[8] Long and Henze, *J. Amer. Chem. Soc.*, 1941, **63**, 1939.

[9] Baker and McOmie, in "Non-benzenoid Aromatic Compounds," Ed. D. Ginsburg, Interscience Publ. Inc., New York, 1958.

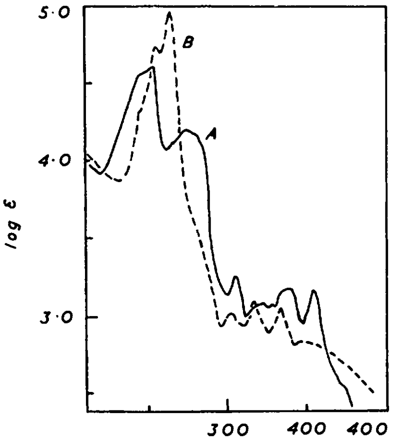
[10] Brown, *Trans. Faraday Soc.*, 1950, **46**, 146.

[11] Alonzo and Domingo, *Anales real. Soc. españ. fis. quim.*, 1955, **51**, *B*, 447.

[12] Alonzo and Peradejordi, *ibid.*, 1954, **50**, *B*, 253.

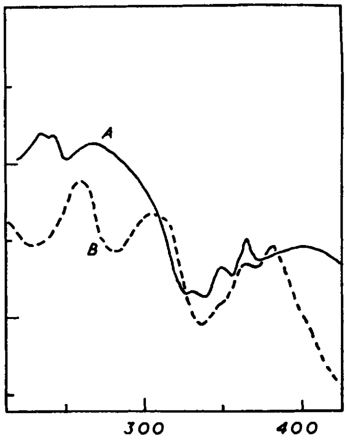
The reactions of diphenylene described in Part I of this series and in the present paper show that monosubstitution in the diphenylene nucleus usually takes place with considerable ease and in all eight cases, acetylation, nitration, chlorination, bromination, iodination, mercuration, hydroxylation with lead tetra-acetate, and oxidative coupling, substitution occurs in position 2. This does not imply that monosubstitution products are either produced in high yield or are easy to isolate. Indeed the high reactivity of the nucleus frequently leads to disubstituted derivatives, *e.g.*, a disulphonic acid (unorientated) with cold concentrated sulphuric acid,[2] or to the formation of by-products.

FIG. 1.



A, 1-Methoxydiphenylene.
B, 1 : 8-Dimethoxydiphenylene.

FIG. 2.



A, 2-Nitrodiphenylene.
B, 2 : 6-Dinitrodiphenylene.

It is necessary to consider the mechanism of these reactions when comparing the results with the theoretical predictions. The Friedel–Crafts acetylation is an electrophilic substitution,[13] though the reaction is not quite simple because its course may be influenced by changes in temperature and solvent. However, nitration, bromination catalysed by pyridine, and iodination are electrophilic reactions, so that Brown's prediction[10] and those of Alonzo and Domingo[11] are confirmed. It is probable that chlorination with iodine monochloride, and acetoxymercuration, are also electrophilic in character, although mercuric acetate in acetic acid may react by a homolytic mechanism.[14] The acetoxylation of polycyclic hydrocarbons by lead tetra-acetate is considered to be a homolytic reaction,[15] and the poor yield of 2-hydroxydiphenylene obtained by this method confirms Brown's prediction that diphenylene should be almost as unreactive as benzene towards free radicals,[16] but that substitution should occur in position 2.[10] It may be noted that diphenylene does not react with the homolytic reagent *N*-bromosuccinimide even in the presence of benzoyl peroxide.

The only two disubstitution products whose structures are known have the 2 : 6-orientation, the entry of the second group corresponding to a *meta*-position with regard to the first, as shown in formula (IV). Diacetylation and dinitration of diphenylene give 2 : 6-diacetyldiphenylene (VI) and 2 : 6-dinitrodiphenylene (V) respectively. The dinitration proceeds in only 4% yield and traces of other isomers may have been formed,

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[13] Badger, "The Structure and Reactions of the Aromatic Compounds," Cambridge Univ. Press, 1954.

[14] Ingold, "Structure and Mechanism in Organic Chemistry," Bell and Sons, Ltd., London, 1953, p. 304.

[15] Waters, " Chemistry of Free Radicals," 2nd edn., Oxford, 1948.

[16] Brown, *Trans. Faraday Soc.*, 1949, **45**, 300.

but the diacetylation proceeds in high yield and despite a careful search for other isomers none was found. Hence, the presence of a *meta*-directing substituent in one six-membered ring controls the position taken up by a second substituent which, as would be expected, enters the other benzene ring but not at random. This shows that there is a considerable degree of resonance interaction between the two benzene rings, and there must be in consequence some *cyclo*butadienoid character in the four-membered ring. This conclusion is noteworthy in view of the fact that acetylation of 4-acetyldiphenyl gives 4 : 4′-diacetyldiphenyl instead of 4 : 3′-diacetyldiphenyl which should be formed if there were effective conjugation between the two aromatic nuclei.[17] The greater conjugation between the two benzene rings in diphenylene than in diphenyl may be ascribed to the facts that diphenylene is a rigid planar molecule, whilst diphenyl is to some extent non-planar.

EXPERIMENTAL

2-*Acetyldiphenylene* (VII).—Powdered aluminium chloride (4 g.) was added in portions to a stirred solution of diphenylene (1·0 g.) and acetyl chloride (0·6 g.) in carbon disulphide (250 ml.). After being stirred for 3 hr. the mixture was kept for 8 hr., then shaken with cold, dilute hydrochloric acid, and the product, collected in carbon disulphide, was sublimed at 120—130°/12 mm., giving 2-acetyldiphenylene (0·845 g.), m. p. 132—134°. A trace of 2 : 6-diacetyldiphenylene remained undissolved in the carbon disulphide.

2-*Aminodiphenylene* (III) (for method cf. Dice and Smith [18]).—Finely powdered sodium azide (0·10 g.) was added to a mixture of 2-acetyldiphenylene (0·10 g.), trichloroacetic acid (2 g.), and tetraphosphoric acid (1 g.) at 70—80°, and after ½ hr. a further portion of sodium azide (0·10 g.) was added, and the heating continued for 6 hr. Dilution with water gave a solid which was boiled for 1 hr. with hydrochloric acid (10 ml.), water (10 ml.), and ethanol (2 ml.), then basified with sodium hydroxide, and extracted with ether. The ether yielded a solid which was sublimed at 115—120°/10 mm., giving 2-aminodiphenylene (0·037 g.; m. p. 119—120°; the pure compound has m. p. 123—124° [2]).

2 : 6-*Diacetyldiphenylene* (VI).—Powdered aluminium chloride (1·0 g.) was added in portions to a well-stirred solution of diphenylene (0·30 g.) in carbon disulphide (40 ml.) and acetyl chloride (1·0 g.). The mixture was stirred for a further 3 hr. and kept for 8 hr., then cold hydrochloric acid was added, and the solid 2 : 6-diacetyldiphenylene was collected; after one crystallisation from ethanol it formed deep yellow needles (0·30 g.), m. p. 243—245° (the pure compound has m. p. 247—248° [2]).

Reduction of 2 : 6-*Diacetyldiphenylene* (VI) *to* 3 : 4′-*Diacetyldiphenyl*.—2 : 6-Diacetyldiphenylene (0·30 g.) was refluxed for 1 hr. in ethanol (25 ml.) with Raney nickel (*ca.* 0·5 g.). The now colourless solution was filtered, the nickel washed with hot ethanol (25 ml.), the combined solutions evaporated, the residue sublimed at 130—140°/0·1 mm. (yield, 0·21 g.), and crystallised from ethanol, giving colourless needles, m. p. 100—101°. The m. p. was not depressed on admixture with authentic 3 : 4′-diacetyldiphenyl, m. p. 101—102°, described in Part II.[1]

2-*Nitrodiphenylene* (IV) *and* 2-*Aminodiphenylene* (III).—Nitric acid (0·2 ml.; *d* 1·42; 1·6 equivs.) in acetic acid (2 ml.) was added to a stirred solution of diphenylene (0·30 g.) in acetic anhydride (10 ml.) at 0°. After ¼ hr. the cooling-bath was removed, and the mixture allowed to reach room temperature (¾ hr.), poured into water, neutralised with sodium hydrogen carbonate, and steam-distilled. The distillate (1 l.) contained 2-nitrodiphenylene as deep yellow needles (0·09 g.), m. p. 105—106·5° either alone or mixed with the specimen previously prepared.[1]

2-Nitrodiphenylene (21 mg.) was boiled for ½ hr. with ethanol (0·5 ml.), concentrated hydrochloric acid (1 ml.), and stannous chloride (250 mg.), and the mixture then made alkaline with sodium hydroxide and steam-distilled. The solid was extracted into light petroleum (b. p. 40—60°), giving 2-aminodiphenylene (13 mg.; m. p. 120—121°), which after recrystallisation from the same solvent formed yellow needles, m. p. 123—124°, alone or mixed with a specimen prepared as previously described.[2, 1]

2 : 6-*Dinitrodiphenylene* (V) *and* 2 : 2′-*Bisdiphenylenyl* (XVIII).—Powdered diphenylene

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[17] Ferriss and Turner, *J.*, 1920, **117**, 1147.

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

(300 mg.) was added in portions to a stirred mixture of nitric acid (0·15 ml.; *d* 1·42; 1·2 equivs.), concentrated sulphuric acid (0·75 ml.), and water (0·25 ml.) at 0°; the mixture was then removed from the cooling-bath, and after it had reached room temperature it was diluted, neutralised, and steam-distilled. The distillate yielded a mixture of diphenylene (100 mg.) and 2-nitrodiphenylene (*ca.* 35 mg., 13·5%), the latter being removed and identified by reduction to 2-aminodiphenylene. The product not volatile in steam was sublimed at 220°/12 mm., crystallised from ethanol, giving deep yellow needles and pale yellow plates, then resublimed slowly at 170°/12 mm., and the homogeneous sublimate recrystallised from ethanol. 2 : 6-Dinitrodiphenylene was thus obtained as deep-yellow needles (12 mg., 4%) which sublimed above 260° (Found: C, 59·7; H, 2·9; N, 11·6. $C_{12}H_6O_4N_2$ requires C, 59·5; H, 2·5; N, 11·6%). The ultraviolet spectrum was identical with that of the orientated material.

The few mg. of material which did not sublime at 170°/12 mm. separated from ethanol in pale yellow leaflets, m. p. 240—242°, and proved to be 2 : 2′-bisdiphenylenyl (XVIII). This product was also obtained when diphenylene (300 mg.), suspended in a mixture of concentrated sulphuric acid (5 ml.) and acetic acid (5 ml.), was treated with nitric acid (0·2 ml.; *d* 1·42; 1·6 equivs.) in sulphuric acid (5 ml.) at 0° for ¾ hr. with stirring, and then at room temperature for 1 hr. It was isolated and crystallised as before (5 mg.) and had m. p. 242—243°. The m. p. was not depressed on admixture with a specimen prepared from 2-iododiphenylene (below).

2-*Acetoxymercuridiphenylene* (XIII).—The yellow solution obtained by heating diphenylene (300 mg.) and mercuric acetate (650 mg.) in acetic acid (10 ml.) on the water-bath for 2 hr. was diluted, and unchanged diphenylene (212 mg.) removed by rapid steam-distillation. The non-volatile material was collected at 0° and extracted with warm benzene in a Soxhlet apparatus, giving 2-*acetoxymercuridiphenylene* (187 mg.) which crystallised from benzene as a yellow powder, m. p. 176—177° (Found: C, 40·8; H, 2·7. $C_{14}H_{10}O_2Hg$ requires C, 40·9; H, 2·4%).

2-*Chlorodiphenylene* (XIV).—2-Acetoxymercuridiphenylene (180 mg.) was stirred with concentrated hydrochloric acid (50 ml.) and chloroform (25 ml.), and a saturated aqueous solution of potassium chlorate (20 mg.) was added dropwise. After ½ hr. a further portion of potassium chlorate (5 mg.) was similarly added, and stirring was continued for 4 hr. The chloroform layer was washed with aqueous sodium carbonate, and the product sublimed (crude material, 56 mg.; m. p. 56—60°), converted into the 2 : 4 : 7-trinitrofluorenone complex (scarlet needles, m. p. 133—134°), regenerated, and resublimed as in the preparation of 2-iododiphenylene. Pure 2-*chlorodiphenylene* forms very pale yellow plates, m. p. 67·5—68·5° (Found: C, 77·6; H, 3·9; Cl, 17·9. $C_{12}H_7Cl$ requires C, 77·3; H, 3·8; Cl, 19·0%).

2-*Bromodiphenylene* (XII).—2-Acetoxymercuridiphenylene (400 mg.), suspended in chloroform, was treated with bromine in chloroform (3 ml. of a solution of 1 ml. of bromine in 50 ml. of chloroform). After ¼ hr. the almost colourless solution was washed with aqueous sodium hydrogen sulphite, and the chloroform layer yielded a residue which was sublimed at 110—120°/13 mm., giving a crude product (178 mg.; m. p. 54—58°) which was purified as the 2 : 4 : 7-trinitrofluorenone complex (scarlet needles, m. p. 136—137°) and regenerated and resublimed as in the preparation of 2-iododiphenylene. The pure 2-*bromodiphenylene* formed pale yellow plates, m. p. 64—65° (Found: C, 62·1; H, 3·2; Br, 35·0. $C_{12}H_7Br$ requires C, 62·4; H, 3·0; Br, 34·6%). The m. p. was not depressed on admixture with authentic 2-bromodiphenylene synthesised as described in Part II.[1]

2-*Iododiphenylene* (XVII).—2-Acetoxymercuridiphenylene (400 mg.), suspended in a solution of iodine (1 g.) in 10% aqueous potassium iodide, was stirred for ½ hr. at 60—70°, treated with an excess of sodium hydrogen sulphite, and steam-distilled. The pale yellow solid in the distillate was extracted into light petroleum (b. p. 40—60°), giving a crude product (216 mg.; m. p. 53—56°) which was treated with the calculated quantity of 2 : 4 : 7-trinitrofluorenone in ethanol–acetic acid, and the solid was then recrystallised from ethanol, giving the deep scarlet complex, m. p. 132·5—134°. Decomposition of this complex (100 mg.) by passing its benzene solution through alumina (20 × 2 cm.), elution with the same solvent, and sublimation at 110—120°/12 mm. gave 2-*iododiphenylene* (44 mg.) as pale yellow plates, m. p. 64·5—65·5° (Found: C, 51·8; H, 2·1; I, 45·6. $C_{12}H_7I$ requires C, 51·8; H, 2·5; I, 45·7%).

2-*Cyanodiphenylene* (XVI).—2-Iododiphenylene (200 mg.) was heated under reflux for 10 hr. in an oil-bath at 140—150° with anhydrous cuprous cyanide (150 mg.) and pyridine (1 ml.), and the product extracted alternately with hot benzene and aqueous ammonia (*d* 0·880 diluted with an equal volume of water). The united benzene extracts yielded a product which was sublimed at 120—130°/11 mm. (115 mg.; m. p. 60—85°), crystallised from light petroleum (b. p. 40—60°), and resublimed, giving *2-cyanodiphenylene* as yellow plates (98 mg.), m. p. 99—100° (Found: C, 87·8; H, 4·0; N, 7·8. $C_{13}H_7N$ requires C, 88·1; H, 4·0; N, 7·9%).

Diphenylene-2-carboxylic Acid (XI).—(*a*) 2-Cyanodiphenylene (60 mg.) was boiled for 2 hr. with 20% aqueous sodium hydroxide (10 ml.) and ethanol (10 ml.); hot water (80 ml.) was then added, and the solution was filtered and acidified. The yellow solid was collected, sublimed at 150—160°/12 mm. (57 mg.; m. p. 216—218°) and crystallised from aqueous methanol, giving diphenylene-2-carboxylic acid as yellow prisms, m. p. 221—222°, alone or on admixture with a sample prepared from 2-acetyldiphenylene by treatment with sodium hypochlorite.[2]

(*b*) No reaction occurred between 2-iododiphenylene (150 mg.) and magnesium (250 mg.) in ether (2 ml.) till methyl iodide (0·5 ml.) was added in portions. After being boiled for ½ hr. the solution was poured on solid carbon dioxide, and the acidic material (5 mg.) was later isolated in the usual way. Sublimation and recrystallisation from light petroleum (b. p. 40—60°) gave the slightly impure acid, m. p. 215—218°. From the neutral product of the reaction was isolated by sublimation at 130°/12 mm. 2-iododiphenylene (106 mg.), and at 190—210°/12 mm. 2 : 2'-bisdiphenylenyl (XVIII), m. p. and mixed m. p. 240—242°.

2 : 2'-*Bisdiphenylenyl* (XVIII).—A mixture of 2-iododiphenylene (150 mg.), 1% palladium–calcium carbonate[5] (500 mg.), hydrazine hydrate (100 mg.), 5% methanolic potassium hydroxide (10 ml.), and water (1 ml.) was boiled for 1 hr. After filtration through a Soxhlet thimble the solution was brought to neutrality with concentrated hydrochloric acid, ethanol was added, the mixture was refiltered through the Soxhlet thimble, and the contents of the thimble were then extracted for 6 hr. with hot ethanol. Concentration of the extract gave a solid which was sublimed, giving at 100—120°/12 mm. diphenylene (crude 48 mg.), and at 180—200°/0·5 mm. a yellow solid (18 mg.; m. p. 210—230°) which after crystallisation from ethanol gave yellow leaflets of 2 : 2'-*bisdiphenylenyl* (12 mg.), m. p. 242·5—243·5° (Found: C, 95·5; H, 4·7. $C_{24}H_{14}$ requires C, 95·4; H, 4·6%).

Chlorination of Diphenylene.—Diphenylene (500 mg.), iodine monochloride (1 g.), and acetic acid (30 ml.) were heated (oil-bath at 120—130°) for 6 hr., and steam-distilled after addition of water and excess of sodium hydrogen sulphite. The distillate was rendered alkaline, and the solid (470 mg.; m. p. 51—56°) collected with ether and sublimed, giving a trace of diphenylene at 80°/12 mm. and 2-chlorodiphenylene at 110—120°/12 mm. Two crystallisations from aqueous methanol gave the pure compound as very pale yellow plates (355 mg.), m. p. and mixed m. p. with a specimen prepared from 2-acetoxymercuridiphenylene, 66—67°.

Bromination of Diphenylene.—A solution of bromine in carbon tetrachloride (9 ml.; made from 1 ml. of bromine and 50 ml. of carbon tetrachloride) was added to diphenylene (500 mg.), and the slow reaction was hastened by the addition of a drop of pyridine. After 10 min. a further amount of the bromine solution (5 ml.) was added, and the mixture warmed on the water-bath for 15 min. The solution was shaken with aqueous sodium hydrogen carbonate and more carbon tetrachloride, dried and distilled, giving a trace of diphenylene and then an oil, b. p. 120—130°/2 mm., which partly solidified. This crude 2-bromodiphenylene (530 mg.) was converted into the 2 : 4 : 7-trinitrofluorenone complex (890 mg.; m. p. 135—137°); the pure compound was regenerated therefrom as previously described and finally sublimed as pale yellow plates, m. p. and mixed m. p. with a specimen prepared from 2-acetoxymercuridiphenylene, 64—65°.

Iodination of Diphenylene.—(a) *Using iodine and sodium persulphate.* Diphenylene (200 mg.), iodine (300 mg.), sodium persulphate (1 g.), and acetic acid (10 ml.) were boiled for 16 hr., diluted, and steam-distilled. The distillate was extracted with ether, and the extracts, after being washed with aqueous sodium carbonate, yielded a product which was sublimed at 80°/14 mm. to remove diphenylene (127 mg.), then at 130—140°/14 mm., giving crude 2-iododiphenylene (32 mg.; m. p. 55—60°) which was purified *via* the 2 : 4 : 7-trinitrofluorenone complex and by final sublimation. The pure compound had m. p. and mixed m. p. with a specimen prepared from 2-acetoxymercuridiphenylene, 63—64°.

(b) *Using iodine and iodic acid.* A similar experiment using iodic acid instead of sodium persulphate and a reaction time of 2 hr. similarly gave unchanged diphenylene (107 mg.) and crude 2-iododiphenylene (12 mg.).

Iodomethylation of Diphenylene.—To diphenylene (100 mg.) in acetic acid (12 ml.) were added 90% chloromethyl methyl ether (4 ml.) and hydriodic acid (10 ml.; *d* 1·7); after 24 hr.

the bright yellow solid was collected, washed with acetic acid, and dried (155 mg.). This substance, probably 2 : 7- or 2 : 6-bisiodomethyldiphenylene (IX), decomposes above 86° with liberation of iodine and could not be satisfactorily crystallised. It was therefore heated with thiourea (200 mg.) in ethanol (4 ml.) for ¼ hr. and the hot solution treated with picric acid (200 mg.), giving the related *bisthiuronium dipicrate,* $C_{12}H_6(C_2H_5N_2S,C_6H_3O_7N_3)_2$ as an orange powder which was purified by digestion with boiling ethanol; it had m. p. 204—206° (decomp.) (Found: C, 43·2; H, 3·1; N, 17·7. $C_{28}H_{22}O_{14}N_{10}S_2$ requires C, 42·8; H, 2·8; N, 17·8%).

2 : 3 : 6 : 7-*Tetramethyldiphenylene* (X).—The crude bisiodomethyldiphenylene described above (390 mg.) was added to acetic acid (100 ml.) and zinc dust (0·5 g.), and the mixture was stirred and hydrogen chloride passed through at 50° for 4½ hr. with addition of more zinc dust after 1½ hr. and 3 hr. The filtered solution was diluted, and the solid collected and sublimed at 130—140°/10 mm. (57 mg.; m. p. 200—210°). The *complex* with 2 : 4 : 7-trinitrofluorenone prepared in, and crystallised from, ethanol forms deep brown needles, m. p. 171—172° (Found: C, 66·3; H, 3·7; N, 8·4. $C_{29}H_{21}O_7N_3$ requires C, 66·5; H, 4·0; N, 8·0%). The complex was decomposed by passing its solution in benzene through an alumina column and eluting this with benzene; sublimation followed by crystallisation from ethanol gave the 2 : 3 : 6 : 7-*tetramethyldiphenylene* as straw-coloured needles, m. p. 222·5—223·5° (Found: C, 92·1, 92·2; H, 7·6, 8·0. $C_{16}H_{16}$ requires C, 92·3; H, 7·7%).

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