Biphenylenes. Part XXV.[1] 2-Benzoylbiphenylenes and the Synthesis of Biphenylene-2-boronic and 2,6-(or 2,7-)diboronic Acid

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Nitration of 2-benzoylbiphenylene gives a mononitro-derivative, but bromination gives an inseparable mixture of mono- and di-bromo-compounds. Pure 2-benzoyl-6-bromo- and 2-benzoyl-6,7-dibromo-biphenylene have been prepared by treating sulphonated benzoylbiphenylene with bromine, and 2-benzoyl-7-bromobiphenylene has been made by benzoylation of 2-bromobiphenylene. The Baeyer–Villiger oxidation of these bromo-2-benzoylbiphenylenes has been studied. A reinvestigation of the Beckmann rearrangement of the oxime of 2-benzoylbiphenylene has shown that both possible isomeric amides are formed. The oxime of 2-benzoyl-6,7-dibromobiphenylene in the Beckmann reaction gave the anilide of 6,7-dibromobiphenylene-2-carboxylic acid.

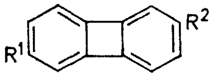
The reaction of biphenylene with boron tribromide and aluminium chloride or bromide followed by hydrolysis gave biphenylene-2-boronic acid and a diboronic acid, probably the 2,6-derivative.

THE oxidation of 2-benzoyl-[2] and 2-acetyl-biphenylenes[3] by the Baeyer–Villiger reaction has proved useful for the preparation of 2-hydroxy- and thence 2-methoxy-biphenylenes. As an extension of this work we have prepared some substituted 2-benzoylbiphenylenes and have oxidised some of them by this reaction.

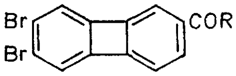
Nitration of 2-benzoylbiphenylene gave a mononitro-derivative which, by analogy with the Friedel–Crafts acetylation[3] of this compound, is assumed to be 2-benzoyl-6-nitrobiphenylene (I; $R^1 = NO_2$). For comparison, 2-*p*-nitrobenzoylbiphenylene was prepared by a Friedel–Crafts reaction. This compound exists in yellow and in orange polymorphic forms; these have been studied by Hartshorne.[4] Direct bromination of 2-benzoylbiphenylene gave an inseparable mixture of mono- and di-bromo-derivatives, but when the biphenylene was first sulphonated and then treated with bromine it gave 2-benzoyl-6-bromobiphenylene, m.p. 160° (I; $R^1 = Br$). The orientation of this compound was proved by converting it, *via* the 6-cyano-derivative, into 2-benzoylbiphenylene-6-carboxylic acid (I; $R^1 = CO_2H$), which was identical with an authentic sample made by oxidation of the furfurylidene derivative of 2-acetyl-6-benzoylbiphenylene (I; $R^1 = Ac$). Benzoylation of 2-bromobiphenylene by the Friedel–Crafts reaction would be expected to give the 2,3- or the 2,7-disubstituted biphenylene. The product, m.p. 195—197°, has an i.r. and a ^1H n.m.r. spectrum consistent with either a 2,6- or a 2,7-disubstituted biphenylene. Since the product is not the 2,6-isomer, m.p. 160°, it must be 2-benzoyl-7-bromobiphenylene. When the sulphonated 2-benzoylbiphenylene was treated with an excess of bromine it gave the 6,7-dibromo-derivative (II; R = Ph).

The Baeyer–Villiger oxidation of 2-benzoylbiphenylene to give 2-benzoyloxybiphenylene has already been recorded.[2] We now find that the use of a stronger solution of peracetic acid (18—20%) gives much more reproducible results. Oxidation of 2-benzoyl-6-bromo- and 2-benzoyl-6,7-dibromo-biphenylene gives the corresponding benzoyloxybiphenylenes. The structures of these two esters are shown by comparison of their ^1H n.m.r. spectra with those of 2-acetoxy- and 2-benzoyloxy-biphenylene, and of phenyl biphenylene-2-carboxylate. In the spectra of both Baeyer–Villiger products the complex group of peaks (τ 2·15—2·65) due to the benzoyl group is present. Attempts to oxidise 2-benzoyl-7-bromo- and 2,6-dibenzoyl-biphenylene similarly were unsuccessful. An attempt to effect the Fries rearrangement of 2-benzoyloxybiphenylene was unsuccessful, whereas 2-acetoxybiphenylene readily gives 2-acetyl-3-hydroxybiphenylene.[3] 2,6-Dibenzylbiphenylene was made from 2,6-dibenzoylbiphenylene by reduction with hydrazine and alkali: it could not be made by pyrolysis of 4-benzylphthalic anhydride.[5]

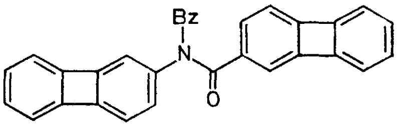
The oxime of 2-benzoyl-6,7-dibromobiphenylene (II; R = Ph) was prepared and was treated with benzenesulphonyl chloride in the expectation that the Beckmann rearrangement would yield 2-benzamido-6,7-dibromobiphenylene, by analogy with the rearrangement[2] of the oxime of 2-benzoylbiphenylene. However, hydrolysis of the rearrangement product with aqueous ethanolic hydrochloric acid gave ethyl 6,7-dibromobiphenylene-2-carboxylate (II; R = OEt). Hence the product from the Beckmann reaction must have been the anilide (II; R = NHPh) of 6,7-dibromobiphenylene-2-carboxylic acid. In view of this unexpected result the preparation



(I) R^2 = Bz
(IV) R^2 = $B(OH)_2$



(II)



(III)

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[3] J. M. Blatchly, D. V. Gardner, and J. F. W. McOmie, *J. Chem. Soc.* (*C*), 1967, 272.

[4] N. H. Hartshorne, *Proc. Roy. Micr. Soc.*, 1966, **1**, 112.

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and Beckmann rearrangement of the oxime of 2-benzoylbiphenylene were reinvestigated. Authentic samples of 2-benzamidobiphenylene, m.p. 222·5—223·5°, and of the anilide of biphenylene-2-carboxylic acid, m.p. 226—227°, were made from 2-amino- and 2-carboxy-biphenylene respectively.

Thatte [2,6] reported that 2-benzoylbiphenylene reacted with hydroxylamine hydrochloride in aqueous methanol containing sodium hydroxide to give an oxime, m.p. 160°, which on rearrangement in polyphosphoric acid gave 2-benzamidobiphenylene, m.p. 209—210°. Our attempts to repeat this preparation of the oxime failed, but when the time of reaction was increased from 30 min. to 12 hr. an inseparable mixture of oximes, m.p. 165—175°, was obtained. When this mixture was treated with polyphosphoric acid it gave an incompletely separable mixture (m.p. 193—195°) of 2-benzamidobiphenylene and the anilide of biphenylene-2-carboxylic acid. When 2-benzoylbiphenylene was treated with hydroxylamine hydrochloride in ethanol containing pyridine it gave an apparently pure oxime, as indicated by the sharp m.p. (198°). Rearrangement of this oxime by polyphosphoric acid gave 2-benzamidobiphenylene (33%) but when the rearrangement was effected by benzenesulphonyl chloride and alkali the product was a mixture, m.p. 196°, of the two possible amides, as shown by its n.m.r. spectrum. The relative areas of the NH peaks showed a ratio of *ca.* 45 : 55 of anilide to amide. Presumably the reagents used for the rearrangement caused some *cis–trans* isomerism of the oxime or its benzenesulphonate and thus led to a mixture of products. Since the two oximes of 1-benzoylnaphthalene are interconvertible by means of alkali,[7] the action of ethanolic sodium hydroxide on the mixture of oximes (m.p. 165—175°) was investigated, but no apparent change occurred.

During the Beckmann rearrangement with polyphosphoric acid a by-product, $C_{32}H_{19}NO_2$, was formed. On the basis of spectroscopic evidence (see Experimental section) this is assigned the structure (III). The same compound was formed (30%) when the mixture (m.p. 196°) of 2-benzamidobiphenylene and the anilide of biphenylene-2-carboxylic acid was heated with polyphosphoric acid.

The direct boronation of biphenylene was studied, since boronic acids can be oxidatively converted into the corresponding phenols,[8] *cf.* the synthesis of 1-hydroxybiphenylene.[9] Boronic acids are usually made by the reaction of arylmagnesium halides or aryl-lithium derivatives with alkyl borates but Gerrard and his co-workers [10] and Muetterties [11] have shown that benzene reacts with boron tribromide in the presence of aluminium chloride or aluminium powder to give phenylboron dibromide which can be hydrolysed to phenylboronic acid. The reaction of biphenylene with boron tribromide by this method was first studied by Hilpern,[12] who obtained a diboronic acid in 26% yield. The reaction is not reproducible and when repeated with either aluminium chloride or bromide a biphenylene-2-boronic acid (IV; $R^1 = H$) was always obtained except on one occasion when the diboronic acid was formed. The orientation of the monoboronic acid is shown by its i.r. spectrum and by its oxidation in very low yield to 2-hydroxybiphenylene. The structure is confirmed by the ^1H n.m.r. spectrum of a solution in dimethyl sulphoxide, which showed a broad singlet (τ *ca.* 2·4) for the hydroxy-groups, a singlet (τ 3·10) for the 1-proton, and two doublets (τ 2·86 and 3·45, *J* 6·6 c./sec.) corresponding to the 3- and 4-protons. Part of the doublet at τ 3·46 was obscured by a singlet (τ 3·42) corresponding to the 5-, 6-, 7-, and 8-protons. The ^1H n.m.r. spectrum of the diboronic acid was measured for a solution in dimethyl sulphoxide containing a little water to 'remove'

U.v. absorption maxima for solutions in 95% ethanol

Biphenylene derivative	λ(mμ)	log ε	λ(mμ)	log ε	λ(mμ)	log ε
2-Benzoyl †	260	4·74	354·5	3·82	368·5	3·98
2-*p*-nitrobenzoyl	248	4·47	348	3·64	364	3·77
	273	4·57			384	3·71
2-Benzoyl-6-bromo	221	4·16	276 *	4·58	348	3·70
	263	4·69	332	3·43	366	3·87
2-Benzoyl-6-cyano	261	4·64	344 *	3·59	353	3·83
	280	4·51			371	3·97
2-Benzoyl-6-carboxy	262	4·67	345 *	3·62	353	3·89
	281	4·49			372	4·00
2-Benzoyl-6-β-(2-furyl)-acryloyl	264	4·34	317 *	4·09	368	4·17
					386	4·20
2-Benzoyl-7-bromo	244 *	4·36	275 *	4·41	351	3·69
	260	4·59	337 *	3·40	368	3·89
2-Benzoyl-6,7-dibromo	249 *	4·47	274 *	4·67	355	3·76
	264	4·75			372	3·94
2-Benzoyloxy-6-bromo	250 *	4·91	340 *	3·55	348	3·90
	256	5·06			365	4·06
Phenyl biphenylene-2-carboxylate	219	4·48			346	3·41
	258	4·60			356	3·57
2,6-Dibenzoyl	264	4·89	353	4·25	382	4·34
	295	4·71				
2,6-Dibenzyl	250	4·82	334 *	3·63	347	3·93
	258	4·99	338 *	3·69	353 *	3·78
	269 *	3·93			366	4·11
Oxime of 2-benzoyl	256	4·31	275 *	4·20	365	3·43
	263 *	4·29				
Oxime of 2-benzoyl-6,7-dibromo	257 *	4·84			356	4·08
	261	4·89			370	4·15
2-Benzamido	230	4·33	261	4·50	351	3·87
	241	4·34			371	3·97
Anilide of biphenylene-2-carboxylic acid	238 *	4·15	256	4·63	347	3·83
	247	4·48	329	3·61	362	3·96
Anilide of 6,7-dibromo-biphenylene-2-carboxylic acid	267	4·74			358	4·15
					378	4·19
Ethyl 6,7-dibromo-biphenylene-2-carboxylate	267	4·59	354	3·62	370	3·76
					394	3·49
2-(*N*-Benzoylbiphenylene-2-carboxamido)biphenylene	244	‡	295 *		352	
	278 *		336		372	
2-Boronic acid	247	4·64	342	3·59	360	3·76
	254	4·85	346	3·59		
2,6-(or 2,7-)Diboronic acid	254	4·79			364	3·78
	260	4·90			366 *	3·66

* Shoulder or inflexion. † The log ε values reported in ref. 2 are incorrect. ‡ Qualitative spectrum.

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[9] A. J. Boulton, J. B. Chadwick, C. R. Harrison, and J. F. W. McOmie, *J. Chem. Soc.* (*C*), 1968, 328.

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[11] E. L. Muetterties, *J. Amer. Chem. Soc.*, 1960, **82**, 4163.

[12] J. W. Hilpern, Ph.D. Thesis, Bristol, 1966.

the $B(OH)_2$ protons. The spectrum showed a singlet (τ 3·03) for the 1- and 5- (or 8-) protons and two doublets (τ 2·83 and 3·40, *J* 6·8 c./sec.) corresponding to the 3-, 4-, 7-, and 8- (or 5-, and 6-) protons. Thus the compound is biphenylene-2,6-(or 2,7-)diboronic acid. The BCl_2 group is *meta*-directing, since bromination of phenylboron dichloride gives the *meta*-bromo-derivative.[13] By analogy we tentatively conclude that our diboronic acid has the 2,6-orientation [IV; $R^1 = B(OH)_2$]. Attempts to oxidise the diboronic acid with peracetic acid gave no definite products. If the corresponding dihydroxybiphenylene had been formed it might have been possible to methylate it to give either of the known 2,6- or 2,7-dimethoxybiphenylenes and thus prove the orientation of the diboronic acid. The u.v. spectra of both the mono- and the di-boronic acids (see Table) were very similar to that of biphenylene, each boronic acid group producing a bathochromic shift.

EXPERIMENTAL

2-Benzoylbiphenylene.—This was prepared by the original method [2] except that the reaction was carried out in methylene dichloride instead of carbon disulphide, and the product was purified by chromatography on a column of alumina. Elution with petroleum (b.p. 80—100°) gave biphenylene, then elution with benzene–petroleum (3 : 1) gave 2-benzoylbiphenylene (70—80%), m.p. 118—119° (lit.,[2] 116—117·5°).

2-Benzoyl-6-nitrobiphenylene.—A mixture of concentrated nitric acid (0·3 ml.) and acetic acid (3·1 ml.) was added dropwise to a stirred solution of 2-benzoylbiphenylene (280 mg.) in acetic anhydride (15 ml.) at 0°. After being kept overnight at room temperature, the mixture was diluted with water and the precipitate was collected. It gave *2-benzoyl-6-nitrobiphenylene* (50 mg., 15%) as yellow plates, m.p. 218—220° (from acetone) (Found: C, 75·6; H, 3·7. $C_{19}H_{11}NO_3$ requires C, 75·7; H, 3·7%).

*2-*p*-Nitrobenzoylbiphenylene*.—A solution of biphenylene (3·04 g.) and *p*-nitrobenzoyl chloride (4·1 g.) in carbon disulphide (50 ml.) was added dropwise to a stirred suspension of powdered aluminium chloride (2·8 g.) in carbon disulphide (50 ml.). Stirring was continued for 0·75 hr., then the mixture was boiled under reflux for 3 hr. It yielded the *biphenylene* (1·2 g., 31%), m.p. 175° [from ethanol (charcoal)] (Found: C, 75·6; H, 3·7. $C_{19}H_{11}NO_3$ requires C, 75·7; H, 3·7%), $\nu_{max.}$ 1640s cm.$^{-1}$ (C=O). The mother liquor yielded unchanged biphenylene (1·1 g.).

The ketone is dimorphic, both forms having the same m.p. It is obtained as yellow plates from a hot solution in acetic acid or ethanol and as orange prisms from warm solutions or by seeding a hot solution. When the orange form is spread on filter paper and gently warmed over a flame it changes to the yellow form, which does not revert to the orange modification when stored or when scratched (see also ref. 4).

2-Benzoyl-6-bromobiphenylene.— 2-Benzoylbiphenylene (2 g.) was dissolved in concentrated sulphuric acid (8 ml.) and, after 24 hr., the mixture was poured into water (100 ml.). The aqueous solution was stirred at 70°, and bromine (0·8 ml.) in acetic acid (2 ml.) was added dropwise during 30 min. The mixture was stirred for 3 hr. more then allowed to cool. The precipitate gave *2-benzoyl-6-bromobiphenylene* (40—50%) as glistening yellow plates, m.p. 160° [from benzene (charcoal)] (Found: C, 67·7; H, 3·3. $C_{19}H_{11}BrO$ requires C, 68·1; H, 3·3%).

2-Benzoyl-6-cyanobiphenylene.—A mixture of 2-benzoyl-6-bromobiphenylene (335 mg.) and copper(I) cyanide (1·96 g.) in dimethyl sulphoxide (15 ml.) was boiled for 2 hr. The cooled mixture was poured into a solution of ferric chloride (3 g.) in 2N-hydrochloric acid (5 ml.) and then extracted with hot benzene. The combined extracts were washed successively with 6N-hydrochloric acid, water, 10% aqueous sodium hydroxide, and water. Removal of solvent left an oil, which was triturated with pentane then dried *in vacuo*. The resulting solid (150 mg., 54%) gave *2-benzoyl-6-cyanobiphenylene* as yellow needles, m.p. 177° [from benzene (charcoal)] (Found: C, 85·2; H, 3·85; N, 4·8. $C_{20}H_{11}NO$ requires C, 85·4; H, 3·9; N, 5·0%), $\nu_{max.}$ 2200m (C≡N) and 1640s (C=O) cm.$^{-1}$.

2-Benzoylbiphenylene-6-carboxylic Acid.—(*a*) 2-Benzoyl-6-*cyanobiphenylene* (30 mg.) was boiled under reflux for 2 hr. with 10% sodium hydroxide (5 ml.) in ethanol (5 ml.). Water (10 ml.) was then added and the solution was acidified with concentrated hydrochloric acid. The product (26 mg., 81%) was collected in ether and gave *2-benzoylbiphenylene-6-carboxylic acid* as yellow needles, m.p. alone and mixed with a sample described later 279—280° (from ethanol) (Found: C, 79·6; H, 4·1. $C_{20}H_{12}O_3$ requires C, 80·0; H, 4·0%), $\nu_{max.}$ 1665s (CO_2H) and 1640s (B_3) cm.$^{-1}$.

(*b*) 2-Acetyl-6-benzoylbiphenylene [3] was condensed with furfural to give the *furfurylidene derivative* (85%) as yellow needles, m.p. 182—183° (Found: C, 82·8; H, 4·2. $C_{26}H_{16}O_3$ requires C, 83·0; H, 4·3%). The latter was oxidised by potassium permanganate in acetone at 0—5° to give 2-benzoylbiphenylene-6-carboxylic acid, m.p. 279—280°.

2-Benzoyl-7-bromobiphenylene (with Dr. P. R. CONSTANTINE).—Powdered aluminium chloride (0·95 g.) was added during 15 min. to a stirred mixture of 2-bromobiphenylene (0·64 g.) and benzoyl chloride (0·8 ml.) in methylene chloride (30 ml.). Stirring was continued for 1 hr. and the mixture was kept overnight. The product, isolated in the usual way, was recrystallised from acetone containing a little chloroform to give *2-benzoyl-7-bromobiphenylene* (0·48 g., 52%) as yellow plates, m.p. 195°, raised to 195—197° by sublimation under reduced pressure followed by recrystallisation from acetone (Found: C, 68·0; H, 3·2. $C_{19}H_{11}BrO$ requires C, 68·1; H, 3·3%).

2-Benzoyl-6,7-dibromobiphenylene.— 2-Benzoylbiphenylene (1 g.) was sulphonated as in the preparation of 2-benzoyl-6-bromobiphenylene and the sulphonic acid was poured into water (50 ml.) and stirred at 70° while bromine (0·8 ml.) in acetic acid (2·5 ml.) was added dropwise during 45 min. The mixture was stirred for a further 3 hr. then allowed to cool. The yellow solid (0·8 g.) was collected and purified by chromatography on a silica gel column (24 × 2·5 cm.) with benzene–petroleum (b.p. 60—80°) (1 : 1) as eluant. This gave the *dibromobiphenylene* (0·5 g., 31%), which formed yellow needles, m.p. 182—183° (from ethanol) (Found: C, 54·9; H, 2·65. $C_{19}H_{10}Br_2O$ requires C, 55·1; H, 2·4%), $\nu_{max.}$ 1640s cm.$^{-1}$.

2-Benzoyloxybiphenylene.—A mixture of 2-benzoylbiphenylene (2·0 g.), acetic acid (30 ml.), and 36—40% peracetic acid (30 ml.) was stirred at 35° for 48 hr. The mixture was poured into water and the precipitate gave 2-benzoyloxybiphenylene (1·3 g., 61%), m.p. 150° [from acetic acid–water (9 : 1)], $\nu_{max.}$ 1722 cm.$^{-1}$ (C=O).

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[13] K. Niedenzu and J. W. Dawson, *J. Org. Chem.*, 1961, **26**, 1671.

2-*Benzoyloxy*-6-*bromobiphenylene*.—A mixture of 2-benzoyl-6-bromobiphenylene (1 g.) in acetic acid (50 ml.) and 36—40% peracetic acid (20 ml.) containing anhydrous sodium acetate (0·33 g.) (in order to neutralise the sulphuric acid present in the commercial peracetic acid) was stirred at 40—42° for 55 hr. The cooled solution was poured into water and the yellow solid (0·78 g.) was collected. It was purified by chromatography on a column of silica gel with benzene–petroleum (b.p. 60—80°) (1 : 4) as eluant. The 2-*benzoyloxy*-6-*bromobiphenylene* (0·46 g., 44%), after two recrystallisations from ethanol, formed almost colourless needles, m.p. 168° (Found: C, 64·4; H, 3·3. $C_{19}H_{11}BrO_2$ requires C, 64·9; H, 3·1%), $\nu_{max.}$ 1720s cm.$^{-1}$.

2-*Benzoyloxy*-6,7-*dibromobiphenylene*.—Concentrated sulphuric acid (0·4 ml.), followed by 36—40% peracetic acid (20 ml.), was added to 2-benzoyl-6,7-dibromobiphenylene (180 mg.) in acetic acid (20 ml.) and the mixture was stirred at 40—42° for 52 hr. The mixture was cooled and the solid was collected and recrystallised from ethanol. The *benzoyloxybiphenylene* (45 mg., 24%) formed pale yellow needles, m.p. 181—182° (Found: C, 53·3; H, 2·2. $C_{19}H_{10}Br_2O_2$ requires C, 53·1; H, 2·3%).

Phenyl Biphenylene-2-*carboxylate* (with B. E. Ayres).—A mixture of biphenylene-2-carboxylic acid (98 mg.), phenol (47 mg.), and ' polyphosphate ester '[14] (750 mg.) in chloroform (3 ml.) was boiled under reflux for 30 min., during which time it turned dark green. The solvent was removed under reduced pressure, then ice-cold aqueous sodium hydrogen carbonate was added and the mixture was stirred for 30 min. The product was extracted into chloroform and purified by preparative t.l.c. on silica gel in benzene. The yellow band, R_F 0·6 gave *phenyl biphenylene*-2-*carboxylate* (105 mg., 77%) as yellow crystals, m.p. 167—168° (Found: C, 84·2; H, 4·35. $C_{19}H_{12}O_2$ requires C, 83·8; H, 4·4%).

2,6-*Dibenzoylbiphenylene* (with Drs. J. W. Barton and S. D. Thatte).—A solution of biphenylene (1·0 g.) and benzoyl chloride (5·5 g.) in carbon disulphide (50 ml.) was added dropwise to a suspension of powdered aluminium chloride (8·0 g.) in carbon disulphide (50 ml.). The mixture was boiled for 4 hr., and then worked up in the usual way giving 2,6-*dibenzoylbiphenylene* (1·6 g., 67%) as yellow plates, m.p. 251—253°, after two recrystallisations from chloroform (Found: C, 86·5; H, 4·4. $C_{26}H_{16}O_2$ requires C, 86·6; H, 4·5%), $\nu_{max.}$ 1643 cm.$^{-1}$ (C=O).

2,6-*Dibenzylbiphenylene*.—A mixture of 2,6-dibenzoylbiphenylene (304 mg.) and potassium hydroxide (300 mg.) in diethylene glycol (10 ml.) and 64% hydrazine (0·6 ml.) was boiled under reflux for 1 hr., then water and the excess of hydrazine were removed by distillation until the temperature of the remaining solution reached 200°. The mixture was boiled for a further 3 hr., then cooled and diluted with water. The precipitate (230 mg., 82%) was collected in benzene and then purified by chromatography on silica gel (in hexane), and gave 2,6-*dibenzylbiphenylene* as plates, m.p. 158—159° (from ethanol) (Found: C, 93·7; H, 6·25. $C_{26}H_{20}$ requires C, 93·9; H, 6·1%).

2-*Benzamidobiphenylene*.— 2-Acetamidobiphenylene[15] (233 mg.) was hydrolysed by concentrated hydrochloric acid (5 ml.) in ethanol (25 ml.) and water (5 ml.). The resulting 2-aminobiphenylene was dissolved in pyridine (20 ml.) and benzoyl chloride (0·5 ml.) and warmed on a water-bath for 85 min. The product gave 2-benzamidobiphenylene (160 mg.), m.p. 221·5—222° (from chloroform), and a second crop (68 mg.), m.p. 218—219°. An analytical sample, m.p. 222·5—223·5° (lit.,[2] 209—210°), was made by further crystallisation from ethanol (Found: C, 83·8; H, 5·2; N, 5·1. Calc. for $C_{19}H_{13}NO$: C, 84·1; H, 4·8; N, 5·2%).

Anilide of Biphenylene-2-*carboxylic Acid*.—A stirred solution of 2-formylbiphenylene[16] (250 mg.) in acetone (10 ml.) was oxidised by gradual addition of 8N-chromic oxide in sulphuric acid (Jones reagent[17]) until no further colour change occurred (*ca.* 90 min.). The solution was poured into water, and biphenylene-2-carboxylic acid, m.p. 190—192° (lit.,[15] 224°) (quantitative yield) was obtained by extraction with ether–ethyl acetate (1 : 1).

The crude acid (250 mg.) was boiled with thionyl chloride (5 ml.) for 1 hr. After removal of the excess of thionyl chloride under reduced pressure the acid chloride was added to aniline. The resulting solid was washed with 3N-hydrochloric acid and then it was purified by chromatography in benzene on silica gel. The *anilide* (125 mg., 36%) formed yellow needles, m.p. 226—227° (from ethanol) (Found: C, 83·9; H, 5·1. $C_{19}H_{13}NO$ requires C, 84·1; H, 4·8%). A 1 : 1 mixture of the anilide with 2-benzamidobiphenylene had m.p. 195—199°.

Beckmann Rearrangement of the Oxime of 2-*Benzoyl*-6,7-*dibromobiphenylene*.—The biphenylene (0·1 g.) and hydroxylamine hydrochloride (0·1 g.) in pyridine (0·1 ml.) and ethanol (12 ml.) were boiled under reflux for 3 hr. Removal of solvent followed by addition of water gave the *oxime* (0·08 g., 77%) as yellow needles, m.p. 204—205° (from ethanol) (Found: C, 53·0; H, 2·6; N, 3·2. $C_{19}H_{11}Br_2NO$ requires C, 53·1; H, 2·6; N, 3·3%).

Benzenesulphonyl chloride (2 ml.) was added dropwise (15 min.) to a stirred solution of the oxime (0·2 g.) in pyridine (5 ml.). After being stirred for 30 min. more, the mixture was boiled under reflux for 5 min., then poured into water. The product (0·1 g.) was collected in chloroform and gave the *anilide* of 6,7-*dibromobiphenylene*-2-*carboxylic acid* as yellow needles, m.p. 220—222° (from ethanol) (Found: C, 52·8; H, 2·7; N, 3·2. $C_{19}H_{11}Br_2NO$ requires C, 53·1; H, 2·6; N, 3·3%), $\nu_{max.}$ 3240m (NH) and 1640s (C=O) cm.$^{-1}$.

A solution of the anilide (0·1 g.) in ethanol (20 ml.) and concentrated hydrochloric acid (10 ml.) was boiled under reflux for 8 hr. The solution was cooled, made alkaline with 2N-sodium hydroxide, and then extracted with ether. The product, after being sublimed twice at 120°/0·5 mm. gave a few mg. of 6,7-*dibromo*-2-*ethoxycarbonylbiphenylene* as yellow plates, m.p. 113—115° (Found: C, 47·0; H, 2·7. $C_{15}H_{10}Br_2O_2$ requires C, 47·1; H, 2·6%), $\nu_{max.}$ 1700s (C=O) cm.$^{-1}$.

Oximes of 2-*Benzoylbiphenylene*.—(*a*) A mixture of 2-benzoylbiphenylene (470 mg.), hydroxylamine hydrochloride (500 mg.), and sodium hydroxide (200 mg.) in methanol (20 ml.) and water (4 ml.) was boiled under reflux for 5 hr. More sodium hydroxide (200 mg.) was added to the hot solution, which was then boiled for a further 7 hr. The mixture was poured into water and the product was collected in chloroform. The mixture of oximes (400 mg., 80%) formed yellow needles, m.p. 165—175° (from aqueous

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ethanol). The mixture could not be separated by crystallisation or by chromatography.

(*b*) Repetition of experiment (*a*) but with sodium acetate in place of sodium hydroxide gave an inseparable mixture of oximes, m.p. 166—174°.

(*c*) A mixture of 2-benzoylbiphenylene (600 mg.) and hydroxylamine hydrochloride (600 mg.) in ethanol (6 ml.) containing pyridine (0·6 ml) was heated on a steam-bath for 2 hr. The ethanol was removed under reduced pressure and water was added to the residue. The precipitate was recrystallised from benzene and gave the higher-melting *oxime* of 2-benzoylbiphenylene (90—95%) as yellow needles, m.p. 198° (Found: C, 83·9; H, 4·9; N, 5·2. $C_{19}H_{13}NO$ requires C, 84·1; H, 4·8; N, 5·2%).

Beckmann Rearrangements of the Oximes of 2-Benzoylbiphenylene.—(*a*) The mixture of oximes (m.p. 165—175°; 118 mg.) and polyphosphoric acid (2·3 g.) were heated together at 105° for 20 min. The cooled mixture was added to water and the product was collected in chloroform. The product was separated by t.l.c. into a mixture of 2-benzamidobiphenylene with the anilide of biphenylene-2-carboxylic acid [total 64 mg.; m.p. 193—195° (from cyclohexane)], and an orange gum [see (*d*)]. The cyclohexane mother liquor was evaporated to dryness, and the residue (19 mg.) was hydrolysed by boiling with concentrated hydrochloric acid (2 ml.), water (1 ml.), and ethanol (4 ml.) for 3·25 hr. The acid-soluble product was shown by t.l.c. and by u.v. spectroscopy to contain both 2-aminobiphenylene and aniline. The non-basic product was shown by t.l.c. to contain starting material and biphenylene-2-carboxylic acid.

(*b*) The oxime (m.p. 198°, 39 mg.) was stirred with polyphosphoric acid (2 g.) at 105° for 10 min. The cooled mixture was diluted with water, and then extracted with chloroform. The extract was purified by preparative t.l.c. in benzene on Kieselgel G and gave 2-benzamidobiphenylene (13 mg., 33%), m.p. and mixed m.p. 220—221°.

(*c*) A mixture of the oxime (m.p. 198°, 1·0 g.) and benzenesulphonyl chloride (1·5 ml.) in pyridine (10 ml.) was stirred for 15 min. then heated just to the boiling point and allowed to cool. Water (300 ml.) was added and the product was collected in chloroform. The material obtained (0·9 g.) formed yellow needles, m.p. 196° [from benzene (charcoal)]. It did not depress the m.p. of the product, m.p. 193—195°, obtained by method (*a*). The n.m.r. spectrum corresponded to a mixture of benzamidobiphenylene and the anilide.

(*d*) The orange gum obtained by method (*a*) gave yellow-orange clusters, m.p. 239—241° (from hexane–acetone at 0°). When these crystals were left in contact with solvent they gradually changed to a polymorphic form, obtained as dark red blades, m.p. 236—238°. Both forms of the *amide* (III) had the same u.v. spectrum (Found: *m/e* 449·1422. $C_{32}H_{19}NO_2$ requires *M*, 449·1416), $\nu_{max.}$ 1660 and 1675 cm.$^{-1}$ (C=O), *m/e* 449 (M^+, 46%), 344 (22%, ArN·CO-Ar), 270 (33%, ArN·COPh), 105 (100%, PhCO), and 77 (58%, Ph).

Reaction of Biphenylene with Boron Tribromide.—Aluminium bromide (364 mg.) was added to a solution of biphenylene (1·0 g.) in boron tribromide (*ca.* 5 ml.) and the mixture was boiled under reflux for 8 hr. The cooled solution was poured on ice and the precipitate was collected. This was extracted several times with boiling water and the combined extracts were cooled. The solid obtained gave *biphenylene-2-boronic acid* as pale yellow needles (0·2 g., 16%), m.p. 290° (decomp.) (from water) (Found: C, 73·2; H, 4·8. $C_{12}H_9BO_2$ requires C, 73·5; H, 4·6%), $\nu_{max.}$ 3400s (OH), 1340m (B–O), 735s, 845s (4 and 2 adjacent ArH), and 900w (isolated ArH) cm.$^{-1}$.

In one experiment, in which a fresh batch of aluminium bromide was used, the product was *biphenylene*-2,6(or 2,7)-*diboronic acid.* It was isolated as just described, as yellow needles, m.p. 390° (decomp.) (Found: C, 59·7; H, 4·5. $C_{12}H_{10}B_2O_4$ requires C, 60·0; H, 4·2%), $\nu_{max.}$ 1340s (B–O), 800s (2 adjacent ArH), and 888w (isolated ArH) cm.$^{-1}$.

Oxidation of Biphenylene-2-boronic Acid.—Hydrogen peroxide (30%; 12 ml.) was added gradually to a boiling solution of the boronic acid (50 mg.) in benzene (100 ml.), and boiling was continued for a further 1·25 hr. The benzene layer was taken and washed with 10% aqueous iron(II) ammonium sulphate then with water. The phenolic product was extracted from the benzene into 10% aqueous sodium hydroxide, whence acidification and collection in ether gave the crude product. It was purified by preparative t.l.c. in benzene on silica gel and gave a low yield of 2-hydroxybiphenylene, m.p. and mixed m.p. 138—139°. Its u.v. spectrum agreed with that of authentic 2-hydroxybiphenylene.[15]

N.m.r. Spectra of Biphenylenes in Deuteriochloroform.—(*a*) 2-Bromo-: τ 3·22 (1-H, dd), 3·10 (3-H, dd), 3·53 (4-H, dd), $J_{1,3}$ 1·6, $J_{1,4}$ 0·7, $J_{3,4}$ 7·5 c./sec. (*b*) 2-Benzoyl-: τ 2·15—2·65 (PhCO, m), 2·93 (1-H, dd), 2·80 (3-H, dd), 3·37 (4-H, dd), $J_{1,3}$ 1·3, $J_{1,4}$ 1·0, $J_{3,4}$ 7·2 c./sec. (*c*) 2-Benzoyl-6-bromo-: τ 2·12—2·55 (PhCO, m), 2·94 (1-H, dd), 2·74 (3-H, dd), 3·30 (4-H, dd), 3·16 (5-H, dd), 3·03 (7-H, dd), 3·35 (8-H, dd), $J_{1,3}$ 1·7, $J_{1,4}$ 0·8, $J_{3,4}$ 7·4, $J_{5,7}$ 1·2, $J_{5,8}$ 0·9, $J_{7,8}$ 7·1 c./sec. (*d*) 2-Benzoyl-7-bromo-: τ 2·28—2·72 (PhCO, m), 2·97 (1-H, dd), 2·79 (3-H, dd), 3·35 (4-H, dd), 3·46 (5-H, dd), 3·07 (6-H, dd), 3·21 (8-H, dd), $J_{1,3}$ 1·2, $J_{1,4}$ 0·8, $J_{3,4}$ 7·1, $J_{5,6}$ 7·4, $J_{5,8}$ *ca.* 0·5, $J_{6,8}$ 1·5 c./sec. (*e*) 2-Benzoyl-6,7-dibromo-: τ 2·13—2·53 (PhCO, m), 2·81 (1-H, dd), 2·64 (3-H, dd), 3·20 (4-H, dd), 2·98 (5-H or 8-H, s), 3·00 (8-H or 5-H, s), $J_{1,3}$ 1·4, $J_{1,4}$ 1·0, $J_{3,4}$ 7·6, $J_{5,8}$ 0 c./sec. (*f*) Phenyl biphenylene-2-carboxylate: τ 2·64 (1-H, dd), 2·32 (3-H, dd), 3·34 (4-H, dd), $J_{1,3}$ 1·2, $J_{1,4}$ 1·0, $J_{3,4}$ 7·0 c./sec. (*g*) 2-Acetoxy-:[3] τ *ca.* 3·6 (1-H, d), 3·70 (3-H, dd), 3·53 (4-H, d), $J_{1,3}$ 1·9, $J_{1,4}$ 0, $J_{3,4}$ 6·2 c./sec. (*h*) 2-Benzoyloxy-: τ 1·8—2·7 (PhCO·O, m), *ca.* 3·5 (1-H d), 3·57 (3-H, dd), 3·46 (4-H, d), $J_{1,3}$ 1·8, $J_{1,4}$ 0, $J_{3,4}$ 8·2 c./sec. (*i*) 2-Benzoyloxy-6-bromo-: τ 1·8—2·7 (PhCO·O, m), 3·50 (1-H, unresolved d), 3·60br (3-H, d), 3·42br (4-H, d), 3·34 (5-H, d), 3·17 (7-H, dd), 3·37 (8-H, d), $J_{1,3} < 0·5$, $J_{1,4}$ 0, $J_{3,4}$ 7·2, $J_{5,7}$ 1·5, $J_{5,8}$ 0, $J_{7,8}$ 7·2 c./sec. (*j*) 2-Benzoyloxy-6,7-dibromo-: τ 1·8—2·7 (PhCO·O, m), 3·44 (1-H, d), 3·46 (3-H, dd), 3·34 (4-H, d), 3·21 (5-H and 8-H, s), $J_{1,3}$ 2·0, $J_{1,4}$ 0, $J_{3,4}$ 7·5, $J_{5,8}$ 0 c./sec. (*k*) 2-Benzamido-: τ 0·87 (NH), 2·1—2·6 (Ph, m), 3·1—3·5 ($C_{12}H_7$, m). (*l*) Anilide of biphenylene-2-carboxylic acid: τ 0·66 (NH), 2·5—2·7 (Ph, m), 3·0—3·3 ($C_{12}H_7$, m).

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