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Biphenylenes. Part XXVII.[1] Synthesis of Compounds derived from 2-Acetylbiphenylene

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Mild reduction, followed by dehydration, of 2-acetylbiphenylene gave 2-vinylbiphenylene. Treatment of 2-acetylbiphenylene with phosphorus pentachloride gave 2-chloroacetyl- and *cis*-dichlorovinyl-biphenylene; some transformations of these compounds are described. Friedel–Crafts acetylation of 2-methylbiphenylene gave mainly the 3-acetyl and 3,7-diacetyl derivatives. Friedel–Crafts acylation of biphenylene with ethoxalyl chloride could be made to give either the 2-glyoxylic ester or a mixture of the mono ester and the 2,6-diglyoxylic ester. Appropriate reduction of biphenylene-2-glyoxylic acid gave the acetic acid and the α-hydroxyacetic acid.

With sulphuric acid 2-acetylbiphenylene gave the 6-sulphonic acid which with bromine gave 6-bromo-2-tribromoacetylbiphenylene. Condensation of 2-acetyl- and 2,6-diacetyl-biphenylene with furfural gave the corresponding furfurylidene derivatives, some reactions of which are described. Some heterocyclic compounds derived from 2-acetylbiphenylene have been prepared.

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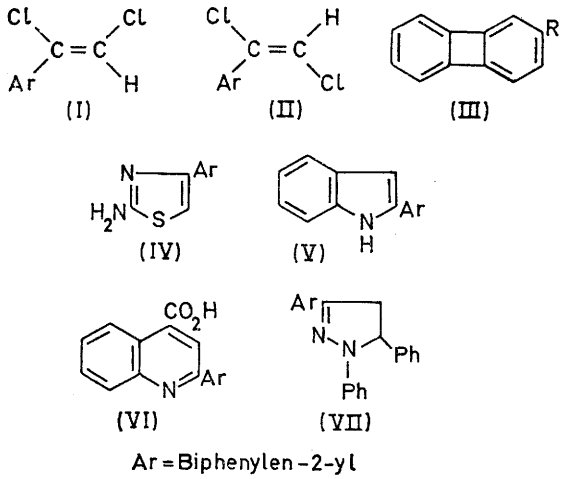
2-ACETYLBIPHENYLENE can be prepared in 66% yield by the Friedel–Crafts acetylation of biphenylene.[2] This readily available compound has been used as the starting material for the preparation of many mono- and di-substituted biphenylenes, some of which are described below.

2-Acetylbiphenylene reacted readily with sodium borohydride in ethanol to give 2-(1-hydroxyethyl)-biphenylene in 90% yield, but attempts to dehydrate this alcohol, either with dilute sulphuric acid or with formic acid, gave unidentified mixtures of products. However, with phosphoryl chloride in pyridine as dehydrating agent,[3] 2-vinylbiphenylene (23% yield) was obtained as a lemon-yellow solid, m.p. 67—69°, which, when kept for a few months decomposed to a dark-brown oil.

When 2-acetylbiphenylene was treated with phosphorus pentachloride in methylene chloride,[4] either at 40 or 0°, two major products were isolated. The first was a yellow solid, $C_{14}H_9ClO$, m.p. 107—108°, with $\nu_{max.}$ (ArCO) at 1675 cm.$^{-1}$. The ^{1}H n.m.r. spectrum showed seven aromatic protons and a singlet (τ 5·59) which integrated for two protons. This compound is, therefore, 2-chloroacetylbiphenylene and, when reduced with sodium borohydride, it gave a high yield of 2-(2-chloro-1-hydroxyethyl)biphenylene. The second product was a pale-yellow solid, m.p. 125—126°, $C_{14}H_8Cl_2$. Spectroscopic evidence showed that this product is one of the two geometric isomers [(I) or (II)] of 2-(1,2-dichlorovinyl)biphenylene. Chemical evidence strongly suggests that the two chlorine atoms have the *cis*-configuration as in (I). Thus reaction of the dichloro-olefin with zinc powder[5] in acid-free ethanol gave 2-vinylbiphenylene and not 2-ethynylbiphenylene. If the two chlorine atoms possessed the *trans*-configuration, as in (II), then the acetylene would have been expected as the major product. Also, treatment[5] of the dichloro-olefin with potassium hydroxide in ethanol readily gave 2-chloroethynylbiphenylene, thus indicating that the hydrogen and chlorine atoms in the original olefin were *trans* to one another (*i.e.* the two chlorine atoms were *cis* to one another). The formation of 2-chloroacetylbiphenylene and 2-(*cis*-1,2-dichlorovinyl)biphenylene may be rationalised by assuming that the first step of the reaction involves chlorination of the methyl group of 2-acetylbiphenylene. Subsequent attack by phosphorus pentachloride at the carbonyl group, followed by elimination of hydrogen chloride and phosphoryl chloride in the normal manner, could lead to the dichloro-olefin obtained.



Ar = Biphenylen-2-yl

In an attempt to prepare a 2,3-disubstituted biphenylene which might be oxidised easily to give biphenylene-2,3-dicarboxylic acid, 2-(*cis*-1,2-dichlorovinyl)biphenylene was formylated with dichloromethyl methyl ether.[6] The monoformylated product, m.p. 100—115° was obtained in very low yield. It was probably a mixture of isomers resulting from substitution at positions 6 and 7 of the biphenylene nucleus. The i.r. spectrum of the product did not show absorption bands corresponding to a 2,3-disubstituted biphenylene.

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Friedel–Crafts acetylation of 2-methylbiphenylene [7] gave mainly 2-acetyl- and 2,6-diacetyl-3-methylbiphenylene, together with small amounts of other mono- and di-acetylated products (*cf.* the acetylation of 2-ethylbiphenylene [8]). The low yield of 2-acetyl-3-methylbiphenylene discouraged attempts to oxidise it to the 2,3-dicarboxylic acid.

U.v. absorption maxima in 95% ethanol

Biphenylene derivative	λ (mμ)	$\log_{10}\varepsilon$	λ (mμ)	$\log_{10}\varepsilon$	λ (mμ)	$\log_{10}\varepsilon$
2-(1-Hydroxyethyl)	238	4·45	340	3·75	348	3·55
	242 *	4·75	343	3·69	359	3·93
	251	5·01				
2-Vinyl	231	4·29	270	4·72	374	3·98
	245 *	4·35	356	3·95	396	3·35
	262	4·82				
2-Chloroacetyl	231	4·16	335 *	3·31	348	3·58
	239	4·21	345 *	3·55	363	3·78
	265	4·58				
2-(*cis*-1,2-Dichlorovinyl)	221	3·99	268	4·56	367	3·83
	242	4·27	351	3·75		
2-Chloroethynyl	236	3·70	265	4·85	352	3·86
	246	4·33	340	3·59	368	4·05
	257	4·73	349	3·86		
2-Acetyl-3-methyl	257	4·72	347	3·64	364	3·82
Mixture of 2-acetyl-6- and 2-acetyl-7-methyl	232	q	268 †	q	352	q
	242	q	341	q	369	q
2,6-Diacetyl-3-methyl	222	4·15	284	4·54	378	4·07
	262	4·60	359	3·89		
-2-Glyoxylic acid	242	4·17	330	3·46	366	3·78
	268	4·53	348	3·57		
-2-Glyoxylic acid, ethyl ester	234	4·23	278	4·49	366	3·75
	240	4·23	330	3·49	391	3·67
	271 *	4·46	348	3·61		
-2-Glyoxylic acid oxime	258	4·51	332	3·16	344	3·47
			340	3·44	360	3·61
2-Carboxymethyl-	243	4·33	332	3·46	344	3·75
	251	4·58	340	3·78	359	3·95
	327	3·44				
-2-(α-Hydroxyacetic) acid	253	4·77	330	3·44	344	3·74
	257 *	4·69	340	3·72	358	3·91
2,6-Diglyoxylic acid, diethyl ester	265	5·42	349 *	4·73	384	5·04
	299	5·47	367	4·97		
2-Acetyl-6-sulphonic acid trihydrate	213	4·08	350	3·71	366	4·86
	268	4·69				
2-β-(2-Furyl)acryloyl-	242	4·43	275	4·25	366	4·24
	264	4·32	346	4·33	380 *	4·13
2-(7-Carboxy-4-oxohexanoyl)-	220	4·13	263	4·70	348	3·74
	232 *	4·19	339 *	3·57	363	3·90
	241 *	4·30				
Compound (IV)	253	4·51	358	3·68	374	3·68
	283 *	3·90				
Phenylhydrazone of 2-acetyl-	252	4·67	282	4·17	347	4·17
	273 *	4·17	340 *	4·17	382	4·25
Compound (V)	249	4·43	310	4·28	382	4·14
	258	4·47	366	4·11		
Compound (VI)	238	4·33	323 *	3·76	370	4·04
	273	4·72	356	3·89	380 *	3·99
Compound (VII)	239 *	4·21	256	4·48	396	3·11

* Denotes a shoulder or an inflexion. † Denotes the strongest absorptions in a qualitative spectrum.

The oxidation of 2-acetylbiphenylene with potassium permanganate to give biphenylene-2-glyoxylic acid has already been described,[9] however it is more conveniently prepared by treating biphenylene with ethoxalyl chloride under Friedel–Crafts reaction conditions, followed by hydrolysis of the ester. By appropriate treatment the glyoxylic acid has been converted into the corresponding oxime, the acetic acid (III; R = CH_2CO_2H), also the hydroxyacetic acid [III; R = $CH(OH)\cdot CO_2H$] and its methyl ester [III; R = $CH(OH)\cdot CO_2Me$]. When the glyoxylic ester (III; R = $CO\cdot CO_2Et$) was treated with ethoxalyl chloride it gave diethyl biphenylene-2,6-diglyoxylate, which was also obtained by treatment of biphenylene with an excess of ethoxalyl chloride. The orientation of the diester is assumed by analogy with other Friedel–Crafts diacylations [10] and from the fact that the diester does not fluoresce under u.v. light: all the known 2,7-diacylbiphenylenes fluoresce brightly under u.v. light whereas the 2,6-diacyl compounds do not.[8]

Sulphonation of 2-acetylbiphenylene gave a mono-acid which is assumed to be the 6-sulphonic acid. When this was treated with bromine side-chain bromination, as well as replacement of the sulphonic acid group, occurred and the tetrabromo-product is thought to be 6-bromo-2-tribromoacetylbiphenylene (the ^1H n.m.r. spectrum showed no aliphatic protons). Condensation of 2-acetyl- and 2,6-diacetyl-biphenylene with furfural gave the mono- and di-furfurylidene compounds respectively. Oxidation of the mono-furfurylidene compound gave biphenylene-2-carboxylic acid while hydrolysis [11] gave the keto-acid (III; R = $COCH_2\cdot CH_2\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H$).

2-Acetylbiphenylene was treated with thiourea and iodine in dioxan to give 2-(2-aminothiazol-4-yl)biphenylene (IV) (method of Dodson and King [12]). Application of the Fischer indole synthesis [13] and the Pfitzinger quinoline synthesis [14] to 2-acetylbiphenylene gave the corresponding biphenylenylindole (V) and quinoline (VI) respectively. Treatment of 2-cinnamoylbiphenylene with phenylhydrazine gave the pyrazolinyl derivative (VII) *cf.* ref. 15.

EXPERIMENTAL

2-(1-*Hydroxyethyl*)*biphenylene*.—Sodium borohydride was added in portions to a stirred solution of 2-acetylbiphenylene (1·0 g.) in ethanol (150 ml.) until the solution was almost colourless (*ca.* 1 hr.). The excess of sodium borohydride was decomposed by the addition of dilute hydrochloric acid after which most of the ethanol was removed under reduced pressure. The remaining solution was diluted with water and the resulting precipitate was collected. Recrystallisation from cyclohexane gave 2-(1-*hydroxyethyl*)*biphenylene* (0·9 g., 90%) as an off-white solid, m.p. 115—116° (Found: C, 85·6; H, 6·1. $C_{14}H_{12}O$ requires C, 85·7; H, 6·2%), τ ($CDCl_3$) 3·3—3·7 (m, ArH), 5·52 (q, C**H**OH), 7·92 (s, OH), and 8·64 (d, Me), $J_{H,Me}$ 6·0 c./sec.

2-*Vinylbiphenylene*.—A solution of 2-(1-hydroxyethyl)-

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biphenylene (118 mg.) and phosphoryl chloride (0·1 ml.) in dry pyridine (2 ml.) was boiled under reflux for 2 hr., then cooled, diluted with water, and extracted with carbon tetrachloride. The organic layer yielded a yellow solid which was sublimed at 40°/0·5 mm. to give 2-*vinylbiphenylene* (25 mg., 23%) as lemon-yellow needles, m.p. 67—69° (Found: C, 94·4; H, 5·7. $C_{14}H_{10}$ requires C, 94·3; H, 5·7%), τ (CCl_4) 3·25—3·50 (m, ArH), 3·5 (dd, C**H**=CH_2), 4·48 (dd, HC$\overset{t}{=}$CH), and 4·93 (dd, HC$\overset{c}{=}$CH), $J_{H,H\ cis}$ 10·8, $J_{H,H\ trans}$ 18·0, $J_{H,H\ gem}$ 1·1 c./sec.

When the above experiment was repeated on ten times the scale, the yield dropped to 10%.

Reaction of 2-Acetylbiphenylene with Phosphorus Pentachloride.—A stirred solution of 2-acetylbiphenylene (1·0 g.) and phosphorus pentachloride (3·0 g., 2·8 equiv.) in dry methylene chloride (30 ml.) was boiled under reflux for 4 hr. and then cooled. Water was added to destroy the soluble red complex and the organic layer was removed. The aqueous layer was extracted once with chloroform and the combined organic extracts were dried ($MgSO_4$). Removal of the solvent gave a dark-brown oil which was chromatographed on silica. Elution with hexane yielded a mixture of two pale-yellow compounds (461 mg.) from which it was possible to isolate 2-(cis-1,2-*dichlorovinyl*)*biphenylene*, the major component, by crystallisation from ethanol as lemon-yellow needles, m.p. 125—126° (Found: C, 67·7; H, 3·0. $C_{14}H_8Cl_2$ requires C, 68·0; H, 3·2%). The isotope pattern associated with the molecular ion at *m/e* 246 corresponded to the presence of two chlorine atoms. τ ($CDCl_3$) 3·25 (m, 1-H, 5-H, 6-H, 7-H, and 8-H), 3·07 (dd, 3-H), 3·39 (dd, 4-H), and 3·39 (s, =CHCl), $J_{1,3}$ 1·5, $J_{1,4}$ 0·9 $J_{3,4}$ 7·3, c./sec. The minor component was found to be unstable in most solvents, decomposing principally to give the above dichloro-olefin, and could not be identified. Final elution of the column with hexane–benzene (4 : 1) gave 2-*chloroacetylbiphenylene* (708 mg., 60%) which separated from cyclohexane as long yellow needles, m.p. 107—108° (Found: C, 73·3; H, 3·8. $C_{14}H_9ClO$ requires C, 73·2; H, 3·9%), τ ($CDCl_3$) 2·64 (dd, 3-H), 3·23 (m, 5-H, 6-H, 7-H, 8-H), 2·94 (dd, 1-H), 3·37 (dd, 4-H), and 5·59 (s, CH_2), $J_{1,3}$ 1·4, $J_{1,4}$ 0·9, $J_{3,4}$ 7·4 c./sec.

2-(2-*Chloro*-1-*hydroxyethyl*)*biphenylene.*—Sodium borohydride was added to 2-chloroacetylbiphenylene (321 mg.) in ethanol (30 ml.) until the yellow solution became colourless, the reduction being extremely rapid. The solution was stirred for 10 min. after which the excess sodium borohydride was decomposed by addition of dilute hydrochloric acid. After removal of most of the solvent under reduced pressure the residue was diluted with water. Two extractions with ether gave an oil which was chromatographed on silica-gel in hexane–benzene (3 : 2) to give the product (302 mg., 93%) as an off-white solid. 2-(2-*Chloro*-1-*hydroxyethyl*)*biphenylene* formed needles, m.p. 75—76° (from hexane–ether) (Found: C, 73·0; H, 5·0. $C_{14}H_{11}ClO$ requires C, 72·9; H, 4·8%).

Reaction of 2-(cis-1,2-*dichlorovinyl*)*biphenylene with Zinc Powder.*—The biphenylene (100 mg.) and zinc powder (1 g.) in acid-free ethanol (6 ml.) were stirred and boiled under reflux for 6 hr. The solution was cooled and filtered after which the solvent was removed under reduced pressure, leaving a lemon-yellow solid which rapidly turned dark green. The solid, on sublimation at 60°/0·4 mm., gave a small amount of 2-vinylbiphenylene, m.p. 66—68°, which was identified by its i.r. and u.v. spectra.

No reaction occurred when acetone was used in place of ethanol as the solvent.

Reaction of 2-(cis-1,2-*dichlorovinyl*)*biphenylene with Potassium Hydroxide.*—A mixture of the biphenylene (100 mg.) and potassium hydroxide (100 mg.) in ethanol (6 ml.) and water (1 ml.) was boiled under reflux for 5·5 hr. The cooled mixture was diluted with water and then extracted with chloroform. The organic layer yielded a yellow oil which was subjected to t.l.c. on silica-gel with hexane as eluant. The yellow band of highest R_F value was extracted with chloroform. Removal of the solvent left a solid which, after sublimation at 60°/0·4 mm., gave 2-*chloroethynylbiphenylene* (20 mg., 23%) as yellow crystals, m.p. 101—102·5° (Found: C, 80·1; H, 3·0. $C_{14}H_7Cl$ requires C, 79·8; H, 3·3%).

Acetylation of 2-*Methylbiphenylene.*—Aluminium chloride (0·5 g.) was added, in portions, to a stirred solution of 2-methylbiphenylene [7] (167 mg.) and acetyl chloride (113 mg.) in carbon disulphide (15 ml.). After 11·5 hr., the product was isolated and subjected to t.l.c. in benzene to give three major products (listed in order of decreasing R_F value): (1) 2-*acetyl*-3-*methylbiphenylene* (51 mg., 25%) which, after sublimation at 80°/0·4 mm., was obtained as pale yellow needles, m.p. 83·5—84·5° (Found: C, 86·2; H, 5·6. $C_{15}H_{12}O$ requires C, 86·5; H, 5·8%), τ ($CDCl_3$) 3·11 (s, 1-H), 3·46 (s, 4-H), 3·24 (m, 5-H, 6-H, 7-H, and 8-H), 7·53 (s, CH_3), and 7·63 (s, CH_3). (2) A mixture of 2-acetyl-6-methyl- and 2-acetyl-7-methyl-biphenylene (15 mg., 7%) which, after sublimation at 80°/0·4 mm., was obtained as pale yellow needles, m.p. 83—88° (Found: C, 87·0; H, 5·7%). (3) 2,6-Diacetyl-3-methylbiphenylene (84 mg., 33%) containing a trace of the fluorescent 2,7-diacetyl-3-methylbiphenylene. Recrystallisation of the mixture of isomers from ethanol gave 2,6-*diacetyl*-3-*methylbiphenylene* as a pale-yellow powder, m.p. 161—162·5° (Found: C, 81·3; H, 5·4. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6%), τ ($CDCl_3$) 3·00 (s, 1-H), 3·35 (s, 4-H), 2·73 (t, 5-H), 2·46 (dd, 7-H), 3·23 (dd, 8-H), 7·50 (s, 2 × CH_3), and 7·61 (s, CH_3), $J_{5,7}$ 1·5, $J_{7,8}$ 7·4 c./sec.

Biphenylene-2-glyoxylic acid (With Dr. B. E. Ayres).—Aluminium chloride (4·5 g.) was added in portions to a stirred mixture of biphenylene (1·5 g., 0·01 mole) and ethoxalyl chloride (2·4 g., 0·018 mole) in carbon disulphide (30 ml.). After being stirred at room temperature overnight, the mixture was treated with cold 3N-hydrochloric acid after which it was extracted with methylene chloride (70 ml.). The organic extract yielded an oil which soldified when kept. It was chromatographed in benzene on silica-gel and gave *ethyl biphenylene-2-glyoxylate* (1·8 g., 72%) as orange plates, m.p. 68—69° (from methanol) (Found: C, 76·3; H, 4·7. $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·8%), $\nu_{max.}$ 1672 (ArCO), 1712 (CO_2Et), 750, 832, and 905 $cm.^{-1}$ (2-substituted biphenylene).

Potassium hydroxide (250 mg.) in ethanol (5 ml.) was added to a warm solution of the ethyl ester (250 mg.) in the same solvent (5 ml.). Hydrolysis occurred rapidly and the precipitated potassium salt was filtered off. It was dissolved in water and acidified with dilute hydrochloric acid. The orange precipitate was *biphenylene-2-glyoxylic acid* (200 mg., 90%), m.p. 165—166° (from methanol) (Found: C, 74·7; H, 3·6. $C_{14}H_8O_3$ requires C, 75·0; H, 3·6%) (the acid, when made previously, had not been obtained pure [9]), $\nu_{max.}$ 1728 (ArCO), 1633 (CO_2H), 750, 852, and 897 $cm.^{-1}$ 2) substituted biphenylene).

Diethyl biphenylene-2,6-diglyoxylate (With Dr. B. E.

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AYRES).—(*a*) Powdered aluminium chloride (6 g.) was added during 30 min. to a stirred solution of ethyl biphenylene-2-glyoxylate (500 mg., 0·002 mole) and ethoxalyl chloride (2·4 g., 0·018 mole) in methylene chloride (25 ml.). The stirring was continued for a further 2 hr. after which the mixture was cooled to 0° and acidified with ice-cold 3N-hydrochloric acid (50 ml.). The organic layer was evaporated and the residue was chromatographed in benzene on silica-gel. The orange band, R_F 0·2 was eluted and gave the *diethyl ester* (340 mg., 49%) as orange granules, m.p. 100—101° (from ethanol) (Found: C, 68·6; H, 4·5. $C_{20}H_{16}O_6$ requires C, 68·2; H, 4·6%), $\nu_{max.}$ 1665 (ArCO), 1715 (CO_2Et), 848, 900 cm.$^{-1}$ (ArH; 2,6- or 2,7-disubstituted biphenylene).

(*b*) Biphenylene (300 mg., 0·002 mole) and ethoxalyl chloride (1·8 g., 0·012 mole) in dry methylene chloride (15 ml.) were treated with dry powdered aluminium chloride (3 g.) in portions during 30 min. The reaction mixture was stirred at room temperature for 2 hr. after which time ice-cold 3N-hydrochloric acid was added. The brown organic layer was washed with water, dried, and evaporated to a small volume. The product, purified by t.l.c. in benzene on silica-gel, gave diethyl biphenylene-2,6-diglyoxylate (175 mg., 25%) as orange granules (from ethanol), m.p. 99—101°, and ethyl 2-biphenylenylglyoxylate (50 mg., 10%) as yellow crystals (from methanol), m.p. 68—69°.

Reaction of Biphenylene-2-glyoxylic acid with Hydroxylamine (With Dr. P. R. CONSTANTINE).—A mixture of hydroxylamine hydrochloride (600 mg.), sodium acetate hydrate (600 mg.), and the glyoxylic acid (600 mg.) in ethanol (30 ml.) and water (4 ml.) was boiled for 3 hr. The mixture was cooled, diluted with water, and the products were collected in chloroform. The mixture of products was separated by chromatography in benzene on a column of silica gel and gave 2-cyanobiphenylene (200 mg., 42%), m.p. 100° (lit.,[2] m.p. 99—100°) and the *oxime* of *biphenylene-2-glyoxylic acid* (200 mg., 31%) as yellow needles, m.p. 223—225° (Found: C, 69·8; H, 4·2. $C_{14}H_9NO_3$ requires C, 70·3; H, 3·8%).

Reduction of the oxime with zinc dust gave a nitrogen-containing product but the desired biphenylenylglycine could not be obtained analytically pure.

Biphenylene-2-acetic Acid (With Dr. P. R. CONSTANTINE).—A mixture of biphenylene-2-glyoxylic acid (600 mg.) and hydriodic acid (4 ml., 55% aqueous solution) in acetic acid (5 ml.) was boiled under reflux for 3 hr. When worked-up the mixture gave *biphenylene-2-acetic acid* (450 mg., 80%) as needles, m.p. 175—176° (sublimes) (from aqueous methanol) (Found: C, 80·3; H, 5·0. $C_{14}H_{10}O_2$ requires C, 80·0; H, 4·8%), $\nu_{max.}$ 1680 cm.$^{-1}$ (C=O), τ ($CDCl_3$) 3·20—3·45 (m, ArH), 0·42 (s, OH), and 6·58 (s, CH_2).

Biphenylene-2-α-hydroxyacetic Acid and Methyl Ester (With Dr. P. R. CONSTANTINE).—Sodium borohydride (50 mg.) in water (3 ml.) and 2N-sodium hydroxide (0·5 ml.) was added in portions to a stirred solution of biphenylene-2-glyoxylic acid (600 mg.) in methanol (30 ml.) at 15°. The mixture was maintained below 25° by external cooling for 20 min. after which it was acidified with dilute hydrochloric acid. The resulting precipitate was collected and gave the α-hydroxyacetic acid (545 mg., 90%) as pale yellow needles, m.p. 215—220° (from benzene). A small portion of the acid was treated with diazomethane and gave the *methyl ester* as yellow needles, m.p. 114—114·5° (from aqueous methanol) (Found: C, 74·7; H, 4·9. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0).

2-Acetylbiphenylene-6-sulphonic Acid (With Dr. J. W. HILPERN).—2-Acetylbiphenylene (500 mg.) was dissolved in concentrated sulphuric acid (20 ml.) and the solution was kept at room temperature for 48 hr. It was then poured into water (100 ml.) and neutralised by addition of calcium hydroxide. The solution was filtered, and the solid was well washed with water. Sodium carbonate was added to the combined filtrate and washings until no more calcium carbonate was precipitated. The aqueous solution was filtered and concentrated to 50 ml.; a yellow solid (970 mg.) separated from the cool solution. This was purified *via* its *S*-benzylthiouronium salt and gave the *sulphonic acid trihydrate* (*ca.* 65% yield), m.p. 130° (from water) [Found (in material dried at room temperature): C, 51·4; H, 4·9. $C_{14}H_{10}O_4S,3H_2O$ requires C, 51·2; H, 4·9%. Found (in material dried in high vacuum): C, 57·2; H, 4·3. $C_{14}H_{20}O_4S,H_2O$ requires C, 57·5; H, 4·1%].

2-Bromo-6-tribromoacetylbiphenylene.— 2-Acetylbiphenylene (0·5 g.) was dissolved in concentrated sulphuric acid (20 ml.). After 24 hr., the solution was poured into water (100 ml.) and bromine (0·8 ml.) in acetic acid (2·0 ml.) was added dropwise during 30 min. to the stirred solution at 70°. After being stirred for a further 3·5 hr. the solution was cooled and the yellow precipitate (0·25 g.) was filtered off. The crude product was chromatographed on a column (22 × 2·5 cm.) of silica-gel. Elution with benzene–light petroleum (b.p. 60—80°) (1 : 9) gave a few mg. of yellow solid which was discarded; elution with benzene–light petroleum (b.p. 60—80°) (1 : 4) then gave the *bromobiphenylene* (120 mg., 9%) as bright yellow needles, m.p. 200—201° (from ethanol) (Found: C, 33·3; H, 1·1. $C_{14}H_6Br_4O$ requires C, 33·0; H, 1·2%), $\nu_{max.}$ 1675 (C=O), 840, and 870 cm.$^{-1}$ (2,6- or 2,7-disubstituted biphenylene), τ (C_5D_5N) 2·3—3·0 (complex multiplets, ArH).

2-β-(2-Furyl)acryloylbiphenylene.—Furfuraldehyde (195 mg.) in ethanol (5·0 ml.) was added dropwise during 15 min., to a stirred mixture of 2-acetylbiphenylene (390 mg.) and sodium hydroxide (1·1 g.) in ethanol (40 ml.). The mixture was stirred for 3 more hr. after which the precipitate was collected. The *product* (0·5 g., 92%) formed golden-yellow plates, m.p. 175° (from ethanol) (Found: C, 84·0; H, 4·3. $C_{19}H_{12}O_2$ requires C, 83·8; H, 4·4), $\nu_{max.}$ 1640 cm.$^{-1}$ (C=O).

A sample of the compound was oxidised by potassium permanganate in acetone and gave biphenylene-2-carboxylic acid, m.p. 224° (lit.,[16] 223—224°) (31%).

2-(7-Carboxy-4-oxohexanoyl)biphenylene.—A solution of 2-β-(2-furyl)acryloylbiphenylene (109 mg.) in ethanol (4·0 ml.) and concentrated hydrochloric acid (1·0 ml.) was boiled under reflux for 18 hr. The ethanol was removed under reduced pressure and to the residue was added concentrated hydrochloric acid (2·0 ml.), glacial acetic acid (2·0 ml.), and water (4·0 ml.). This mixture was then boiled under reflux for 2 hr. after which time the aqueous solution was quickly pipetted out, leaving behind a dark brown oil. The aqueous solution was cooled and the dioxo acid, which separated as yellow needles, was collected; the mother liquors were boiled with the brown oil again for 1 to 2 hr. in order to extract further acid. This procedure was repeated and the successive crops of the diketo-acid were collected and recrystallised from ethyl acetate to give

[16] W. Baker, M. P. V. Boarland, and J. F. W. McOmie, *J. Chem. Soc.*, 1954, 1476.

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2-(7-*carboxy*-4-*oxohexanoyl*)*biphenylene* (50 mg., 41%) as yellow needles, m.p. 182° (Found: C, 74·4; H, 5·3. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%), $\nu_{max.}$ 1655, 1685 cm.$^{-1}$ (C=O groups).

2,6-Bis[β-(2-*furyl*)*acryloyl*]*biphenylene*.—Condensation of 2,6-diacetylbiphenylene with furfuraldehyde, by the method used above for 2-acetylbiphenylene, gave the bis-*derivative* (91%) as yellow plates, m.p. 260—261° (decomp.) (from ethanol) (Found: C, 79·7; H, 4·25. $C_{26}H_{16}O_4$ requires C, 79·6; H, 4·1%). Attempts to oxidise the compound to biphenylene-2,6-dicarboxylic acid were unsuccessful.

2-(2-*Aminothiazol*-4-*yl*)*biphenylene* (IV).—A mixture of 2-acetylbiphenylene (485 mg.), iodine (630 mg.), and thiourea (380 mg.) in dioxan (5 ml.) was heated on a steam-bath for 72 hr. The cooled mixture was diluted with water and then filtered. The solid was extracted several times with boiling water, and the extracts were filtered. The combined filtrates were cooled and were made alkaline by the addition of concentrated aqueous ammonia. The resulting precipitate gave the *thiazole* (0·30 g., 48%) as yellow needles, m.p. 187—188° (from benzene) (Found: C, 71·9; H, 4·2; N, 11·3. $C_{15}H_{10}N_2S$ requires C, 72·0; H, 4·0; N, 11·2%).

2-*Indol*-2-*ylbiphenylene* (V).—Phenylhydrazine (0·4 ml.) and acetic acid (2 drops) were added to 2-acetylbiphenylene (485 mg.) in ethanol (10 ml.). The mixture was heated on a steam-bath for 20 min. and then cooled to 0°. The solid was collected and gave the *phenylhydrazone* of 2-acetylbiphenylene as yellow needles (0·64 g., 90%), m.p. 166° (from ethanol) (Found: C, 84·7; H, 5·4; N, 9·6. $C_{20}H_{16}N_2$ requires C, 84·5; H, 5·6; N, 9·85%).

The phenylhydrazone (0·5 g.) was added in portions to stirred polyphosphoric acid (*ca.* 5 g.) preheated to 70°. The rate of addition was adjusted so as to keep the temperature between 100 and 110°. The mixture was heated at the same temperature for a further 15 min. after which it was cooled rapidly to 60° and diluted with water. The product was collected in chloroform and then purified by chromatography on silica gel. Elution with benzene–light petroleum (b.p. 60—80°) (1 : 9) removed most of the impurity: elution of the yellow band with a 1 : 4 mixture of solvents then gave the *indole* (0·1 g., 21%) as needles, m.p. 240° (from benzene) (Found: C, 89·7; H, 5·1; N, 5·1. $C_{20}H_{13}N$ requires C, 89·9; H, 4·9; N, 5·2%).

2-(4-*Carboxyquinolin*-2-*yl*)*biphenylene* (VI).—A mixture of 2-acetylbiphenylene (582 mg.) in ethanol (10 ml.) and isatin (462 mg.) in 30% aqueous potassium hydroxide (5·0 ml.) was boiled under reflux for 14 hr. The mixture was cooled, diluted with water (400 ml.) and then acidified with acetic acid. The orange precipitate could not be crystallised. It gave the quinoline (0·75 g., 77%) as a yellow amorphous powder, m.p. 304—305° (decomp.) (from ethyl acetate) (Found: C, 81·3; H, 4·0; N, 4·2. $C_{22}H_{13}NO_2$ requires C, 81·7; H, 4·0; N, 4·3%).

2-(2,3-*Diphenylpyrazolin*-5-*yl*)*biphenylene* (VII).—2-Cinnamoylbiphenylene (282 mg.) [9] and phenylhydrazine (216 mg.) in acetic acid (15 ml.) were boiled under reflux for 14 hr. The mixture was cooled and the *pyrazoline* (260 mg., 70%) separated as bright yellow crystals, m.p. 192—194° (from ethanol) (Found: C, 86·9; H, 5·3; N, 7·4. $C_{27}H_{20}N_2$ requires C, 87·1; H, 5·4; N, 7·5%). The ^{1}H n.m.r. spectrum in $CDCl_3$ shows a 12-line AMX pattern for the three nonaromatic protons (CH–CH_2–) and thus confirms the pyrazoline structure. As expected, the compound shows an intense yellowish green fluorescence in ethanol, *cf.* ref. 15.

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