Biphenylenes. Part XXVIII.[1] Synthesis of Some Benzo[*b*]-, Naphtho-[2,3-*b*]-, and Anthra[2,3-*b*]-derivatives of Biphenylene

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The Friedel–Crafts acylation of biphenylene with the anhydrides of succinic, phthalic, and naphthalene-2,3-dicarboxylic acids has been studied. The resulting acylbiphenylenes were then converted into benzo[*b*]-, naphtho-[2,3-*b*]-, and anthra[2,3-*b*]-biphenylene *para*-quinones [(1), (10), and (14)] and thence into other compounds including the anthracene and tetracene hydrocarbons [(11) and (13): R = H]. Acylation of biphenylene with maleic anhydride followed by attempted ring closure gave a blue Pechmann dye (8).

PREVIOUS studies on the Friedel–Crafts acylation of biphenylenes have been concerned mainly with the use of monobasic acid chlorides, *e.g.* acetyl,[2] propionyl,[3] and benzoyl[4] chloride. The only dibasic acid studied was succinic acid which was used as monoacyl chloride methyl ester and as the anhydride in the synthesis of benzo[*b*]-[5] and dibenzo[*b,h*]-[6] biphenylene, respectively. We record here the use of some dibasic acid anhydrides for the synthesis of polycyclic biphenylenequinones and thence of linear naphtho- and anthra-derivatives of biphenylene. These compounds were required as models for the possible synthesis of biphenylene-based vat dyes.

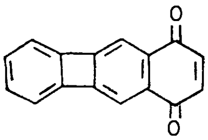
Benzo[b]*biphenylene*-6,9-*quinone* (1).—The key intermediate for the synthesis of this quinone was 8,9-dihydrobenzo[*b*]biphenylen-6(7*H*)-one (2) which had been made previously (in 27% overall yield) by treatment of biphenylene with β-methoxycarbonylpropionyl chloride under Friedel–Crafts conditions, followed by hydrolysis of the ester, reduction of the keto-acid by the Clemmensen method, and final cyclisation using polyphosphoric acid.[5] In the present work we found that the following sequence gave the tetralone (2) in an overall yield of 65%. Biphenylene was treated with succinic anhydride in nitrobenzene by the method used by Fieser[7] for the succinoylation of acenaphthene. The resulting keto-acid was reduced in higher yield by the Wolff–Kishner method than by Clemmensen reduction. The cyclisation of 2-β-carboxypropylbiphenylene to the tetralone (2) was best effected with phosphorus pentachloride and tin(IV) chloride in benzene. The tetralone (2) was dehydrogenated by heating it with sulphur at 240° to give benzo[*b*]biphenylen-6-ol, which was then oxidised to the deep red quinone (1) by treatment with potassium nitrosodisulphonate. The structure of the quinone (1) follows from its method of preparation and is confirmed by its spectroscopic properties (see Experimental section) and by the fact that reductive acetylation gives the diacetate of the corresponding hydroquinone.

In an optimistic attempt to make the same quinone or an angular isomer of it, biphenylene was treated with maleic anhydride in the presence of aluminium chloride and gave 2-β-carboxyacryloylbiphenylene (3; R = H). This acid was too sparingly soluble for its n.m.r. spectrum to be measured so it was esterified with methanol containing boron trifluoride. The minor product (5% yield) of this reaction was the ester (3; R = Me), and its n.m.r. spectrum showed it to contain a *trans*-disubstituted double bond; hydrolysis of the ester regenerated the original acid. The major product (42%) of the esterification reaction was found to be the methoxy-keto-ester (4) or (5) which had been formed by addition of methanol to the double bond as well as esterification of the carboxy-group.

When the acid (3; R = H) was treated with polyphosphoric acid it gave a polymer, whereas under the same conditions 2-cinnamoylbiphenylene (6) gave the indanone (7). When the acid (3; R = H) was heated in a melt of sodium chloride and aluminium chloride either no reaction occurred or, under more vigorous conditions, a brown infusible solid was formed. Under

[1] Part XXVII, D. V. Gardner, J. F. W. McOmie, and Miss T. P. Prabhu, *J. Chem. Soc.* (*C*), 1970, 2500.
[2] J. M. Blatchly, D. V. Gardner, and J. F. W. McOmie, *J. Chem. Soc.* (*C*), 1967, 272.
[3] J. M. Blatchly, A. J. Boulton, and J. F. W. McOmie, *J. Chem. Soc.*, 1965, 4930.
[4] J. M. Blatchly, J. F. W. McOmie, and S. D. Thatte, *J. Chem. Soc.*, 1962, 5090.
[5] W. Baker, J. W. Barton, J. F. W. McOmie, and R. J. G. Searle, *J. Chem. Soc.*, 1962, 2633.
[6] C. F. Wilcox and S. S. Talwar, *J. Chem. Soc.* (*C*), 1970, 2162.
[7] L. F. Fieser, *Org. Synth.*, Coll. Vol. III, 1955, p. 6.

similar conditions a number of substituted β-aroylacrylic acids have been isomerised to the corresponding indanones.[8] In another experiment, the acid (3;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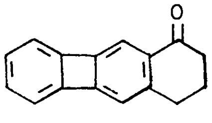
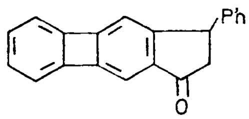

(2)

(3) Ar CO·CH=CH·CO_2R
(4) Ar CO·CH_2·CH(OMe)·CO_2Me
(5) Ar CO·CH(OMe)·CH_2·CO_2Me
(6) Ar CO·CH=CHPh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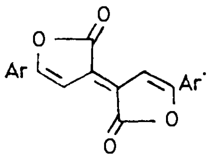
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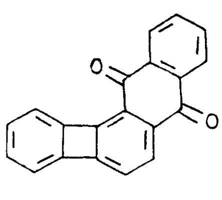
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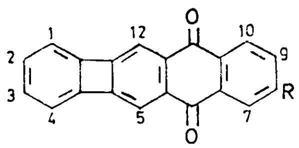
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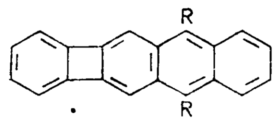
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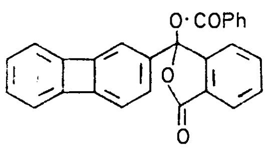
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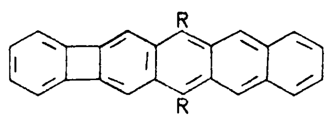
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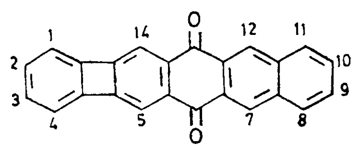
(14)

Ar = biphenylen - 2 - yl

R = H) was heated with benzoyl chloride in 1-chloronaphthalene in the hope that it might undergo thermal isomerisation about the double bond and then cyclise to give a quinone (*cf.* later). The reaction gave an intensely blue product which is thought to be the biphenylene 'Pechmann dye' (8)[9] but its dyeing properties, like those of other members of the series,[10] would not be very good since it fades slowly when exposed to u.v. light.

Benzo[3,4]*cyclobut*[1,2-b]*anthracene* (11; R = H) *and its* 6,11-*Quinone* (10; R = H).—Condensation of biphenylene with phthalic anhydride in presence of aluminium chloride gave 2-*o*-carboxybenzoylbiphenylene as shown by its i.r. spectrum and by decarboxylation to give 2-benzoylbiphenylene.[4] Cyclisation of the keto-acid was expected to give the angular polycyclic quinone (9). This prediction was based on a consideration of the Wheland-type intermediates involved in the cyclisation to give either (9) or (10). Moreover, the reaction of biphenylene with 2,2-dimethylmalonyl dichloride in the presence of aluminium chloride gives the 1,2-cyclised diacylbiphenylene.[11]

The cyclisation of *o*-benzoylbenzoic acids to anthraquinones is commonly effected by heating with concentrated sulphuric acid or with polyphosphoric acid. Under these conditions with sulphuric acid 2-*o*-carboxybenzoylbiphenylene gave only water-soluble products, presumably owing to the ease with which biphenylenes are sulphonated. With polyphosphoric acid the biphenylene gave mainly a brown, infusible, insoluble solid, but extraction of this with hot chloroform gave a red, sparingly soluble compound, $C_{40}H_{18}O_2$, whose structure is not yet known. Clar and Zander found that *o*-carboxybenzoylcoronene could be cyclised to give a naphthocoronenequinone by heating it with benzoyl chloride in 1-chloronaphthalene.[12] Under these conditions, 2-*o*-carboxybenzoylbiphenylene gave a quinone, $C_{20}H_{10}O_2$, in 57% yield. The n.m.r. spectrum of the quinone showed a two-proton singlet (H-5 and H-12) and hence the quinone must have structure (10; R = H) since the angular isomer (9) would have shown a two-proton AB quartet. Reduction of the quinone with zinc dust and propionic anhydride gave the dipropionate (11; R = O_2CEt). The quinone was reduced to benzo[3,4]cyclobut[1,2-*b*]anthracene (11; R = H) by reaction with sodium borohydride in bis-(2-methoxyethyl) ether followed by treatment with boron trifluoride.[13] The n.m.r. spectra of these two anthracenes each showed a two-proton singlet for H-5 and H-12, thereby confirming the structure of the quinone (10; R = H). Clemmensen reduction of 2-*o*-carboxybenzoylbiphenylene gave the corresponding carboxybenzyl compound, which on heating with acetic anhydride underwent cyclisation to give the linear compound, 6-acetoxybenzo[3,4]cyclobut[1,2-*b*]anthracene in very high yield.

The mechanism for the production of the quinone (10; R = H) rather than the angular isomer (9) in the cyclisation of 2-*o*-carboxybenzoylbiphenylene probably involves compound (12) as an intermediate in which the electron-withdrawing carbonyl group at position 2 of the biphenylene system has been converted into a mildly

[8] G. Baddeley, G. Holt, and S. M. Makar, *J. Chem. Soc.*, 1952, 3289.
[9] H. von Pechmann, *Ber.*, 1882, **15**, 881.
[10] E. Klingsberg, *Chem. Rev.*, 1954, **54**, 59.
[11] J. B. Chadwick and J. F. W. McOmie, unpublished work.
[12] E. Clar and M. Zander, *J. Chem. Soc.*, 1958, 1577.
[13] D. S. Bapat, B. C. Subba Rao, M. K. Unni, and K. Venkataraman, *Tetrahedron Letters*, 1960, 15.

electron-donating group, which then directs ring closure to position 3 of the biphenylene. When biphenylene was treated with 4-nitrophthalic anhydride and aluminium chloride in nitrobenzene it gave a low yield (29%) of a mixture of nitrocarboxybenzoylbiphenylenes which was not separated but was cyclised to give 8-nitrobenzo[3,4]cyclobut[1,2-*b*]anthracene-6,11-quinone (10; R = NO_2), again in rather poor yield (39%).

Benzo[3,4]*cyclobuta*[1,2-b]*tetracene* (13; R = H) *and its* 6,13-*Quinone* (14).—The Friedel-Crafts acylation of biphenylene with naphthalene-2,3-dicarboxylic anhydride gave 2-(3-carboxy-2-naphthoyl)biphenylene which, on treatment with benzoyl chloride in 1-chloronaphthalene, gave the quinone (14). The linear structure was assigned by analogy with the formation of the pentacyclic quinone (10) and it is confirmed by the n.m.r. and the i.r. spectra (see Experimental section). The quinone (14) is very sparingly soluble but the tetracene derivative (13; R = O_2CEt) (formed by reductive propionylation) and the parent hydrocarbon (13; R = H) (formed by reduction) are more so. Depending on the conditions, the reduction gave only the tetracene (90%) or a mixture of the orange tetracene (58%) and the pale yellow 6,13-dihydro-derivative (39%). The position of the extra two hydrogen atoms in the latter is shown by the n.m.r. spectrum (see Experimental section) and the u.v. spectrum, which closely resemble the sum of the appropriate spectra of 2,3-dimethylbiphenylene[14] and 2,3-dimethylnaphthalene. Tetracene itself is easily reduced and in solution it is rapidly oxidised by air to give the 5,12-epidioxy-derivative. The tetracene (13) readily undergoes oxidation and a solution of it in chloroform gave a u.v. spectrum corresponding to that of a mixture of the tetracene (13) and the quinone (14), indicating that oxidation (presumably *via* the 6,13-epidioxy-derivative) had occurred. A solution of the tetracene in deoxygenated chloroform showed the u.v. spectrum of the tetracene itself.

U.v. absorption maxima in chloroform *

Biphenylene derivative	λ/nm	log ε	λ/nm	log ε	λ/nm	log ε
(1) [a]	223	4·46	305 [b]	4·45	362	2·80
	242 [b]	4·50	314	4·47	377	2·96
	248	4·53				
(10; R = H)	253	4·30	312	4·86	367	3·67
	259	4·29	340	3·64	383	3·72
	264	4·25	363 [b]	3·62	433	3·05
	308 [b]	4·83				
(10; R = NO_2)	320	4·60	390	3·68	ca. 452	3·01
	372	3·66				
(14)	248	4·82	353	3·81	386	4·23
	260 [b]	4·45	368	4·08	409	3·73
	320	4·93				
(11; R = H)	248	5·27	298	6·14	340	5·27
	277 [b]	5·61	319	5·95	356	5·24
	286	5·91				
(13; R = H) [c]	255 [b]	0·52 [d]	308 [b]	0·60	408	0·10
	262	0·69	325 [b]	1·05	432	0·10
	280 [b]	0·25	332	1·18	460	0·06
	296 [b]	0·36				

* U.v. spectra of all other new compounds in this paper are available as Supplementary Publication No. SUP 20802 [for details of Supplementary Publications, see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20].

[a] In EtOH + 5% $CHCl_3$. [b] Shoulder or inflection. [c] Absorbance in a qualitative spectrum. [d] In deoxygenated $CHCl_3$ under N_2.

EXPERIMENTAL

2-β-*Carboxypropionylbiphenylene*.—Powdered aluminium chloride (5·5 g) was added in portions during 30 min to a stirred mixture of biphenylene (3 g) and succinic anhydride (2 g) in nitrobenzene (40 ml) at 0°. The mixture was stirred for 2 h more at 0° and then at room temperature overnight. The resulting deep red solution was again cooled to 0° and a mixture of ice (30 g) and concentrated hydrochloric acid (10 ml) was added giving a yellow, pasty precipitate. The nitrobenzene was removed by steam distillation and then the solid was filtered off and dissolved in warm aqueous 3% sodium carbonate (200 ml). This solution was steam-distilled for about 15 min to remove the last traces of nitrobenzene. The hot solution was filtered and sodium chloride (5 g) was added. The yellow sodium salt which separated on cooling was collected and dissolved in hot water (250 ml). Addition of 3N-hydrochloric acid (20 ml) gave a thick, pale-yellow precipitate of 2-β-carboxypropionylbiphenylene (4·45 g, 89%), m.p. 214—215° (lit.,[5] 215°).

When the acid was recrystallised from ethanol containing a trace of mineral acid the *ethyl ester* was formed as yellow plates, m.p. 79—80° (Found: C, 76·8; H, 5·6. $C_{18}H_{16}O_3$ requires C, 77·1; H, 5·75%), $\nu_{max.}$ 1732 (ester C=O) and 1664 cm^{-1} (aryl C=O).

2-β-*Carboxypropylbiphenylene*.— 2-β-Carboxypropionylbiphenylene (1·8 g), sodium hydroxide (0·8 g), hydrazine hydrate (1·0 ml), and diethylene glycol (30 ml) were boiled under reflux for 1 h. Solvent was removed by distillation until the solution temperature had risen to 200°. The remaining solution was boiled until nitrogen evolution ceased (*ca.* 2 h). The liquid was cooled and then added to water (500 ml). This solution was acidified with 6N-hydrochloric acid and the precipitate was dried and recrystallised from ethanol, giving the carboxypropylbiphenylene as off-white plates (1·43 g, 84%), m.p. 121—122° (lit.,[5] 118·5—119·5°). In one experiment recrystallisation of the crude product (containing traces of hydrochloric acid) from methanol gave the *methyl ester* as pale yellow crystals, m.p. 44° (Found: C, 81·3; H, 6·5. $C_{17}H_{16}O_2$ requires C, 80·9; H, 6·4%), $\nu_{max.}$ 1728 cm^{-1} (ester C=O).

8,9-*Dihydrobenzo*[b]*biphenylen*-6(7H)-*one* (2).—Phosphorus pentachloride (0·8 g) was added to a solution of 2-β-carboxypropylbiphenylene (0·8 g) in sodium-dried benzene (40 ml) at 0°. The mixture was stirred for 30 min at 0° then heated on a water-bath for 5 min. The solution was cooled in an ice-bath and stirred during the rapid addition of tin(IV) chloride (8 ml) in benzene (8 ml). The mixture was stirred at 0° for 15 min, then ice (15 g) and concentrated hydrochloric acid (25 ml) were added. Ether (3 ml) was added and the organic layer yielded a yellow solid, which gave the tetralone (2) as yellow plates (0·65 g, 88%), m.p. 135° (from aqueous methanol) (lit.,[5] 135°).

The tetralone (2) was characterised by condensing it with 2-furaldehyde to give the *furfurylidene derivative* (93%) as yellow plates, m.p. 204·5—205° (Found: C, 84·4; H, 4·6.

[14] J. W. Barton and J. A. Garside, personal communication.

$C_{21}H_{14}O_2$ requires C, 84·5; H, 4·7%), $\nu_{max.}$ 1659 (conj. C=O) and 1592 cm^{-1} (C=C).

Benzo[b]*biphenylen-6-ol*.—The tetralone (2) (300 mg) and sulphur (100 mg) were heated for 30 min in a Woods metal bath at 230—240°. The dark mass was dissolved in methylene dichloride and the solution was chromatographed on an alumina column (2 × 1 in). Elution with the same solvent gave a fraction containing unchanged tetralone and a trace of an orange compound. Elution with ethanol–methylene chloride (1 : 1) then gave an orange solution which, on evaporation and recrystallisation of the solid from aqueous ethanol gave the *hydroxy-compound* (110 mg, 37%) as buff-coloured needles, m.p. 193—194° (Found: M^+, 218·073. $C_{16}H_{10}O$ requires M, 218·073), $\nu_{max.}$ 3320 (ArOH), 873, 792, and 747 cm^{-1} (1,2,4,5-tetra-, 1,2,3-tri-, and 1,2-di-substituted benzene rings), τ ($CDCl_3$) 2·65 (OH, s), 3·06 (H-1,2,3,4,5,10, s), and 2·88—3·39 (H-7,8,9, m). An ethanolic solution of the phenol gave a blue-green colour with ethanolic iron(III) chloride.

Benzo[b]*biphenylene-6,9-quinone* (1).—A mixture of the foregoing hydroxynaphthalene (95 mg) in ethanol (40 ml) and potassium nitrosodisulphonate (400 mg) in water (30 ml) was stirred for 4 h, then water (50 ml) was added and the orange-red product was collected. Chromatography on silica gel in chloroform gave the *quinone* (60 mg, 59%) as deep red plates, m.p. 239—240° (from ethanol) (Found: C, 82·9; H, 3·5. $C_{16}H_8O_2$ requires C, 82·8; H, 3·5%), $\nu_{max.}$ 1645 (C=O) and 1600 cm^{-1} (C=C), τ ($CDCl_3$) 2·78 (H-5, H-10, s), 3·17 (H-7, H-8, s), 3·0—3·2 (H-1, 2, 3, 4, m).

Reductive acetylation of the quinone with zinc dust, acetic anhydride, and a catalytic amount of triethylamine gave 6,9-*diacetoxybenzo*[b]*biphenylene* (58%) as white flakes, m.p. 170—171° (from aqueous ethanol) (Found: C, 75·55; H, 4·05. $C_{20}H_{14}O_4$ requires C, 75·5; H, 4·4%), $\nu_{max.}$ 1725 (ester C=O), 872 and 752 (2,3-disubstituted biphenylene), and 830 cm^{-1} (2 adjacent ArH), τ ($CDCl_3$) 2·97 (H-7, H-8, s), 2·98—3·04 (H-5, H-10, H-1, 2, 3, 4, m), and 7·65 (2 × CH_3, s).

trans-2-β-*Carboxyacryloylbiphenylene* (3; R = H).—Biphenylene (3 g) was added to a stirred solution of maleic anhydride (2 g) and aluminium chloride (3 g) in 1,2-dichloroethane (40 ml). The mixture was stirred for 30 min, then cooled to 0°, and 3N-hydrochloric acid (50 ml) was added. The product was collected in methylene chloride (100 ml) and gave trans-2-β-*carboxyacryloylbiphenylene* (2·9 g, 59%) as an orange powder (from methanol), m.p. 203—204° (Found: C, 76·7; H, 4·2. $C_{16}H_{10}O_3$ requires C, 76·8; H, 4·0%), $\nu_{max.}$ 2620w (OH), 1686s (ArCO), 1638s (CO of CO_2H), 907w, 830w, and 749s cm^{-1} (2-substituted biphenylene).

Oxidation of the biphenylene with potassium permanganate gave biphenylene-2-carboxylic acid, m.p. 222·5—223·5°, identical with an authentic sample.

Esterification of 2-β-*Carboxyacryloylbiphenylene*.—The biphenylene (500 mg) and boron trifluoride–methanol complex (14% BF_3; 10 ml) were heated under reflux for 6 h, by which time most of the solid had dissolved. The products were separated by preparative t.l.c. in benzene–chloroform (1 : 1) on silica gel. The orange-yellow band, R_F 0·7, yielded trans-2-β-*methoxycarbonylacryloylbiphenylene* (3; R = Me) (29 mg, 5%) as orange needles (from methanol), m.p. 144—145° (Found: C, 76·6; H, 4·8. $C_{17}H_{12}O_3$ requires C, 77·3; H, 4·6%), $\nu_{max.}$ 1715vs (ester CO), 1654s (ArCO), 915w, 826w, and 749 cm^{-1} (2-substituted biphenylene), τ ($CDCl_3$) 2·19 ($HC\overset{t}{=}CH$, d), 3·16 ($HC\overset{t}{=}CH$, d), 2·47 (H-3, q), 2·77 (H-1, d), 6·24 (CH_3, s) ($J_{1,3}$ 1·1, $J_{3,4}$ 7·1, $J_{H,H\text{-}trans}$ 15·5 Hz). Hydrolysis of this ester with ethanolic potassium hydroxide regenerated the original acid, m.p. and mixed m.p. 144°.

The broad yellow band on the chromatogram, R_F 0·4—0·6, yielded 2-β-methoxy-β-methoxycarbonylpropionylbiphenylene (4) or its isomer (5) as yellow plates (230 mg, 39%), m.p. 104·5—105·5 (from methanol) (Found: C, 73·4; H, 5·7. Calc. for $C_{18}H_{16}O_4$: 73·0; H, 5·4%), $\nu_{max.}$ 1740s (ester CO), 1665s (ArCO), 870w, 827m, and 752s cm^{-1} (2-substituted biphenylene), τ ($CDCl_3$) 2·56 (H-3, dd), 2·84 (H-1, d), 3·10—3·38 (5 × ArH, m), 6·30 (CO_2Me, s), 6·61 (OMe, s), 5·68—7·05 (CH_2–CH, ABX system).

The Biphenylene 'Pechmann Dye' (8).—2-β-Carboxyacryloylbiphenylene (650 mg), benzoyl chloride (0·75 ml), and 1-chloronaphthalene (25 ml) were heated under reflux for 1 h. The intensely blue solution was allowed to cool, and was then diluted with methylene chloride (100 ml) and filtered through a column (3 in) of alumina; the blue fraction was collected and yielded 5,5′-*di*(*biphenylen-2-yl*)-3,3′-*bifurylidene-2,2′-dione* (140 mg, 23%) as a blue-black solid, m.p. 340° (decomp.) (Found: C, 83·2; H, 3·9%; M^+, 464. $C_{32}H_{16}O_4$ requires C, 82·75; H, 3·5%; M, 464).

2,3-*Dihydro-3-phenylcyclopenta*[b]*biphenylen-1-one* (7).—A mixture of biphenylene (1·52 g), cinnamoyl chloride (1·66 g), and aluminium chloride (2 g) in methylene chloride was stirred for 24 h. The mixture yielded 2-cinnamoylbiphenylene (2·5 g, 89%) as yellow crystals (from ethanol), m.p. and mixed m.p. 166—167°. It had previously been made by condensation of 2-acetylbiphenylene with benzaldehyde. By mistake the m.p. was given as 142—144° instead of 166—167°.[15]

A mixture of 2-cinnamoylbiphenylene (500 mg) and polyphosphoric acid (20 g) was stirred while being heated on a steam-bath for 30 min. The initial purple complex turned orange-brown during the reaction. Ice was added, and the mixture was stirred until all the viscous solution was converted into a yellow-green precipitate, which was filtered off to yield the *indanone* (7) (480 mg, 96%) as yellow needles (from aqueous ethanol), m.p. 195—195·5° (Found: M^+, 282·105. $C_{21}H_{14}O$ requires M, 282·104), $\nu_{max.}$ 1686 (ArCO), 880 and 747 cm^{-1} (2,3-disubstituted biphenylene), τ ($CDCl_3$) 2·6—3·1 (Ph, m), 3·17 (H-9, d), 3·63 (H-4, d), and 5·78, 6·93, and 7·51 ($CH{\cdot}CH_2$, AMX system) ($J_{4,9}$ 0·8, $J_{cis\text{-}2,3}$ 7·6, $J_{trans\text{-}2,3}$ 3·4, J_{gem} 18·8 Hz).

2-o-*Carboxybenzoylbiphenylene*.—Aluminium chloride (1·0 g) was added gradually to a stirred mixture of biphenylene (0·6 g) and phthalic anhydride (0·6 g) in carbon disulphide (40 ml). The mixture was stirred for 24 h then the solvent was removed by distillation. Ice (50 g) and concentrated hydrochloric acid (10 ml) were added to the purple residue and the product was collected in chloroform (2 × 100 ml). Removal of the solvent gave 2-o-*carboxybenzoylbiphenylene* (0·9 g, 75%) as yellow needles (from ethanol), m.p. 209—210° (Found: C, 79·7; H, 3·9. $C_{20}H_{12}O_3$ requires C, 79·8; H, 4·0%), $\nu_{max.}$ 2600, 2500, 1692 (CO_2H), 1644 (diaryl CO), 905, 808, 744, and 740 cm^{-1} (2-substituted biphenylene).

A small amount of the acid was heated with soda-lime. The sublimate consisted of a yellow solid identical (t.l.c.) with 2-benzoylbiphenylene.

[15] J. F. W. McOmie and S. D. Thatte, *J. Chem. Soc.*, 1962, 5298.

Reaction of 2-o-Carboxybenzoylbiphenylene with Polyphosphoric Acid.—The keto-acid (500 mg) was stirred with polyphosphoric acid (*ca.* 10 g) until the viscous pale green mixture was as homogeneous as possible. The mixture was heated on a steam-bath for 1 h, then it was cooled and ice–water was added. The brown precipitate was collected and was extracted with hot chloroform (Soxhlet). The resulting red, fluorescent solution yielded the red polycyclic quinone (110 mg, 25%), m.p. >350° (Found: C, 90·6; H, 3·45%; M^+, 530. Calc. for $C_{40}H_{18}O_2$: C, 90·5; H, 3·4%; *M*, 530), $\nu_{max.}$ 1680w, 1650m, 1620s (CO and C=C?), 880m, 770m, and 740s cm^{-1} (single, three, and four adjacent aryl H).

Benzo[3,4]*cyclobut*[1,2-b]*anthracene*-6,11-*quinone* (10; R = H).—2-*o*-Carboxybenzoylbiphenylene (1·0 g), benzoyl chloride (1 ml), and 1-chloronaphthalene (5 ml) were heated under reflux for 1·5 h. The solution, on cooling, deposited a red solid which gave the *quinone* (0·54 g, 57%) as red needles, m.p. 329—330° (from chloroform) (Found: C, 84·9; H, 3·5. $C_{20}H_{10}O_2$ requires C, 85·1; H, 3·6%), $\nu_{max.}$ 1662 (CO), 900, 750 (2,3-disubstituted biphenylene), 710 (4 adjacent aromatic H, *cf.* 710 cm^{-1} for 2-methylanthraquinone), τ ($Cl_2CH{\cdot}CHCl_2$; 100°) *ca.* 1·80 (H-7, H-10, m), *ca.* 2·29 (H-8, H-9, m), 2·53 (H-5, H-12, s), and 3·0—3·2 (H-1,2,3,4, m).

When the quinone was heated with zinc dust, propionic anhydride, and a small amount of triethylamine it gave 6,11-*bispropionyloxybenzo*[3,4]*cyclobut*[1,2-b]*anthracene* (11; R = O_2CEt) (97%) as yellow needles (from ethanol), m.p. 250—250·5° (Found: C, 79·1; H, 5·2. $C_{26}H_{20}O_4$ requires C, 78·8; H, 5·1%), $\nu_{max.}$ 1745 (ester CO), 868, and 738 cm^{-1} (2,3-disubstituted biphenylene), τ ($CDCl_3$) 2·15—2·65 (H-7,8,9,10 AA′BB′ system), 2·92br (4H, s) and 2·99 (2H, s) (H-5, H-12, and H-1,2,3,4), and 7·19 (CH_2, q) and 8·61 (CH_3, t) (*J* 7·5 Hz). The compound shows a blue fluorescence under u.v. light.

Benzo[3,4]*cyclobut*[1,2-b]*anthracene* (11; R = H).—Sodium borohydride (0·1 g) in bis-(2-methoxyethyl) ether (2 ml) was added to a stirred solution of the anthraquinone (10; R = H) (54 mg) in the same solvent (2 ml) and the mixture was warmed on a water-bath for a few seconds until the quinone dissolved. A mixture of equal volumes of boron trifluoride–ether complex and bis-(2-methoxy)ethyl ether was added dropwise until the red colour of the mixture had disappeared and a pale cream precipitate was formed. The mixture was stirred for 6 h, at 50°, and was then acidified. The solvent was removed under reduced pressure and the residue was chromatographed on a column of silica gel (28 × 2·5 cm) in chloroform. The pale yellow band gave the *anthracene* (25 mg, 52%) as lemon-yellow plates (from benzene), sublimed rapidly at 310—330° (Found: C, 94·9; H, 4·9%; M^+, 252. $C_{20}H_{12}$ requires C, 95·2; H, 4·8%; *M*, 252), $\nu_{max.}$ 905, 738, 742, and 754 cm^{-1} (single and 4 adjacent aromatic H), τ (CS_2) 2·24 (H-6, H-11, s), 2·26—2·81 (H-7,8,9,10, AA′BB′ system), and 3·07 (H-1,2,3,4,5,12, s).

2-o-*Carboxybenzylbiphenylene*.— 2-*o*-Carboxybenzoylbiphenylene (600 mg), amalgamated zinc (10 g), water (50 ml), concentrated hydrochloric acid (20 ml), acetic acid (5 ml), and toluene (40 ml) were heated under reflux for 30 h, with vigorous stirring, more hydrochloric acid (5 ml) being added every 6 h. The product was collected in ether (2 × 100 ml) and gave 2-o-*carboxybenzylbiphenylene* (280 mg, 49%) as plates (from aqueous ethanol), m.p. 192—193° (Found: C, 84·3; H, 5·1. $C_{20}H_{14}O_2$ requires C, 83·9; H, 4·9%), $\nu_{max.}$ 2620, 1685, 902, 820, 742, and 710 cm^{-1}.

6-*Acetoxybenzo*[3,4]*cyclobut*[1,2-b]*anthracene*.—A mixture of 2-*o*-carboxybenzylbiphenylene (0·1 g), acetic acid (0·6 ml), acetic anhydride (0·4 ml), and zinc chloride (0·008 g) was heated under reflux for 1 h. Water was added to the boiling solution until it became turbid, then the mixture was allowed to cool. The crude product was filtered off and chromatographed in benzene on silica gel. The pale yellow band gave a pale yellow solid (0·1 g, 92%) which showed a blue fluorescence under u.v. light. A sample of the *acetoxy-compound* crystallised from carbon disulphide had m.p. 228·5—230·5° (Found: C, 85·1; H, 4·8%; M^+, 310. $C_{22}H_{14}O_2$ requires C, 85·4; H, 4·55%; *M*, 310), $\nu_{max.}$ 1746 (ester CO), 899, 874, 858 (single ArH), 746, and 719 cm^{-1} (four adjacent ArH), τ ($CDCl_3$) 2·10 (H-11, s), 2·15—2·22 (H-7, H-10, m), 2·48—2·59 (H-8, H-9, m), 2·90br (H-5, H-12, H-1,2,3,4, s), and 7·43 (CH_3, s).

8-*Nitrobenzo*[3,4]*cyclobut*[1,2-b]*anthracene*-6,11-*quinone* (10; R = NO_2).—Aluminium chloride (4·0 g) was added in portions during 30 min to a stirred solution of biphenylene (1·5 g) and 4-nitrophthalic anhydride (1·8 g) in nitrobenzene (30 ml). The mixture was stirred overnight and then 3N-hydrochloric acid was added to decompose the aluminium complex. The mixture was steam-distilled to remove solvent and the involatile solid was collected. Recrystallisation from ethanol gave a yellow solid (0·42 g, 29%), m.p. 195—205° consisting of the isomeric nitrocarboxybenzoylbiphenylenes. This mixture (150 mg), benzoyl chloride (0·4 ml), and 1-chloronaphthalene (5 ml) were heated under reflux for 2 h. The purple crystals which separated on cooling were collected and recrystallised from chloroform giving the *nitro-quinone* (56 mg, 39%) as maroon granules, m.p. 344° (subl.) (Found: C, 73·1; H, 2·9. $C_{20}H_9NO_4$ requires C, 73·4; H, 2·8%), $\nu_{max.}$ 1658 (CO), 1534, 1300 (NO_2), 910, and 732 cm^{-1} (2,3-disubstituted biphenylene).

2-(3-*Carboxy*-2-*naphthoyl*)*biphenylene*.— Aluminium chloride (4·0 g) was added in portions during 30 min to a stirred suspension of biphenylene (1·52 g) and naphthalene-2,3-dicarboxylic anhydride (1·98 g) in ethylene dichloride (50 ml). The mixture was stirred overnight, then treated with 3N-hydrochloric acid (100 ml), and the precipitate was collected in methylene chloride. The product was chromatographed on a column of silica gel (9 × 2·5 cm). Elution with methylene chloride first removed a colourless band containing unchanged anhydride then a yellow band containing the naphthoylbiphenylene (1·0 g, 29%). A sample crystallised from methanol formed yellow needles, m.p. 230—231° (Found: C, 82·2; H, 4·2. $C_{24}H_{14}O_3$ requires C, 82·3; H, 4·0%), $\nu_{max.}$ 2650, 1675 (CO_2H), 1642 (diaryl CO), 885, 855, and 748 cm^{-1}.

When the reaction was carried out in carbon disulphide the yield was only 17%.

Benzo[3,4]*cyclobuta*[1,2-b]*tetracene*-6,13-*quinone* (14).—The preceding acid (400 mg), benzoyl chloride (0·5 ml), and 1-chloronaphthalene (5 ml) were heated under reflux for 1·5 h. The solid which separated on cooling was collected and was recrystallised from chloroform to give the *quinone* (14) (230 mg, 61%) as orange needles, m.p. 350° (subl.) (Found: C, 86·1; H, 3·8. $C_{24}H_{12}O_2$ requires C, 86·7; H, 3·6%), $\nu_{max.}$ 1666 (CO), 899, 765, 747, and 728 cm^{-1}, τ ($Cl_2CH{\cdot}CHCl_2$; 100°, 10 accumulations), 1·25 (H-7, H-12, s), 1·86—2·40 (H-8,9,10,11, m), 2·45 (H-5, H-14, s), and 3·05br (H-1,2,3,4, s).

When the quinone (50 mg) was heated with zinc powder (50 mg), propionic anhydride (*ca.* 1 ml), and triethylamine

(2 drops) on a steam-bath for 20 min it gave 6,13-*bis-propionyloxybenzo*[3,4]*cyclobuta*[1,2-b]*tetracene* (50 mg, 73%) as orange-yellow granules, m.p. 314° (decomp.) (Found: M^+, 446·150. $C_{30}H_{22}O_4$ requires M, 446·152), $\nu_{max.}$ 1740 (ester CO), 860, and 735 cm^{-1} (one single and four adjacent ArH, respectively), τ ($CDCl_3$) 2·74—2·89 (H-8,9,10,11, m) 2·97 (H-7, H-12, s), 3·05br (4H, s) and 3·13 (2H, s) (H-5, H-14 and H-1,2,3,4), and 7·20 (CH_2, q) and 8·57 (CH_3, t) (J 7·5 Hz).

Benzo[3,4]*cyclobuta*[1,2-b]*tetracene* (13; R = H).—The tetracenequinone (14) (50 mg) was reduced by sodium borohydride and boron trifluoride by the process used for the anthracenequinone (10; R = H). The mixture of products was separated by chromatography on silica gel in chloroform. The yellow band gave a solid (18 mg, 39%) which on crystallisation from benzene–n-hexane (1 : 10) gave 6,13-*dihydrobenzo*[3,4]*cyclobuta*[1,2-b]*tetracene* as pale yellow plates which sublimed rapidly at 330—360° (Found: M^+, 304·123. $C_{24}H_{16}$ requires M, 304·125), τ (CS_2) 2·45 (H-7, H-12, s), 2·30—2·78 (H-8,9,10,11, m), 3·50 (H-5, H-14, s), 3·32—3·58 (H-1,2,3,4, m), and 6·17 (6-H_2, 13-H_2, s). The silica gel containing the orange material (which stayed at the top of the column), was extruded and then stirred with chloroform. The suspension of orange solid was decanted from the gel and the solid was filtered off and washed with chloroform to give the *tetracene* (13; R = H) as an orange solid (26 mg, 58%) which sublimed rapidly at 330—360° and condensed on the cool part of the m.p. tube as a mixture of white needles, red needles, and orange plates, owing to rapid oxidation. The tetracene was too sparingly soluble to be recrystallised or for its n.m.r. spectrum to be measured (Found: M^+, 302·110. $C_{24}H_{14}$ requires M, 302·109).

When the reduction of the quinone was repeated using an excess of undiluted boron trifluoride–ether and heating the reaction mixture for 5 h at 60° it gave the tetracene (90%) as the only product.

N.m.r. Spectra of Reference Compounds.—(*a*) 2,3-Dimethylbiphenylene:[14] τ (CCl_4) 3·38—3·62 (H-5,6,7,8, AA′BB′ system), 3·66 (H-1, H-4, s), and 7·95 (2 × CH_3, s). (*b*) 2,3-Dimethylnaphthalene: τ ($CDCl_3$) 2·17—2·65 (H-5,6,7,8, AA′BB′ system), 2·38 (H-1, H-4, s), and 7·61 (2 × CH_3, s).

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