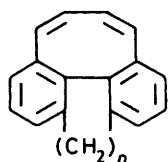


Biphenylenes. Part 33.¹ Synthesis of Bisbenzo[3,4]cyclobuta[1,2-*b*; 1',2'-*h*]- and Bisbenzo[3,4]cyclobuta[1,2-*c*; 1',2'-*g*]-phenanthrene, and Attempts to Prepare Planar Derivatives of Cyclo-octatetraene

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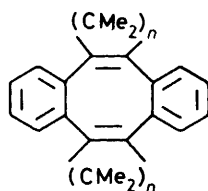
The title compounds have been synthesized but neither the second of them nor 1,1'-bisbiphenylenyl could be dehydrocyclised to give biphenyleno-annulated derivatives of cyclo-octatetraene. 2-Styrylbiphenylene undergoes photodimerisation and not cyclisation. Lithiation of 2-hydroxymethylbiphenylene gives the 1-lithio derivative from which a series of 1,2-disubstituted biphenylenes has been made. The ¹H n.m.r. spectra of 1,1'-bisbiphenylenyl and its 2,2'-diformyl derivative, also of bisbenzo[3,4]cyclobuta[1,2-*c*; 1',2'-*g*]phenanthrene are discussed.

According to Hückel's $(4n + 2)$ π -electron rule a planar [8] annulene should be antiaromatic and would be expected to sustain a paramagnetic ring current. The simplest [8] annulene, cyclo-octatetraene (COT), is non-planar and its properties are similar to those of an open-chain polyene. However, a few derivatives of COT have been made, e.g. compounds (1),² (2),³ (3),⁴ and (4),⁵ in which the 8-membered ring is forced to be planar and these compounds show evidence of a paramagnetic ring current. The biphenylene ring system contains a rigid group of four carbon atoms (1, 8, 8a, and 8b) and if two biphenylene molecules could be joined at the 1,1'- and 8,8'-positions they would give a rigid, planar polycyclic system (5) which formally



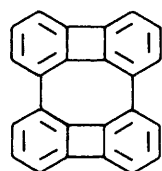
(1) $n = 0$

(2) $n = 1$

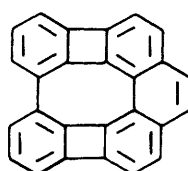


(3) $n = 0$

(4) $n = 1$



(5)



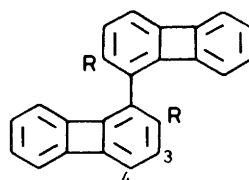
(6)

contains a planar COT as well as two cyclobutadiene systems. Moreover, the periphery of compound (5) can be regarded as a [20] annulene and hence compound (5) would be expected to show a very large paramagnetic ring current. We record here the synthesis of many new biphenylenes, including the title compounds, which were made during attempts to prepare compound (5) and its benzo derivative (6).

Attempts to Synthesize the COT Derivative (5).—Treatment of 1-lithiobiphenylene with cobalt(II) chloride gave 1,1'-bisbiphenylenyl (7) in 31% yield. Similar treatment of 2-lithio-

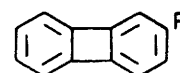
biphenylene gave 2,2'-bisbiphenylenyl (9) (74%) which had previously been obtained in low yields by other reactions.⁶ Many attempts were made to dehydrocyclise 1,1'-bisbiphenylenyl (7) to the COT derivative (5). These included heating of compound (7) with aluminium chloride,⁷ with a mixture of aluminium chloride and tin(IV) chloride,⁸ or with 10% palladium-on-charcoal,⁹ also irradiation with u.v. light in the absence and in the presence of iodine.¹⁰

The mass spectrum of the biaryl (7) showed the relative abundances of M^+ , $(M - 1)^+$, and $(M - 2)^+$ peaks to be 100, 12, and 33% respectively. The relatively high abundance of the $(M - 2)^+$ peak suggests that dehydrocyclisation of the biaryl (7), to give the molecular ion of the desired compound (5), had occurred in the mass spectrometer.¹¹ However, there are two probable reasons why compound (7) does not cyclise under either thermal or photochemical conditions. First, compound (7)



(7) $R = H$

(8) $R = CHO$



(9) $R = \text{Biphenylen-2-yl}$

(10) $R = CH_2Br$

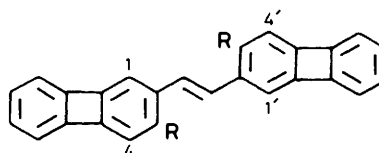
(11) $R = CH_2P^+Ph_3Br^-$

(12) $R = Me$

(13) $R = \text{Biphenylen-2-yl}(CH_2CH_2)-$

(14) $R = CH(OH)CH_2Ph$

(15) $R = E-CH=CHPh$



(16) $R = H$

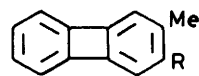
(17) $R = Me$

probably exists mainly in a transoid configuration as shown and, second, the sum of the free-valence indices (ΣFr^*) at C-8 and C-8' (0.904) is less than unity whereas photocyclisation normally occurs only when the sum is greater than unity.^{11,12}

Synthesis of Bisbenzo[3,4]cyclobuta[1,2-*b*; 1',2'-*h*]phenanthrene (20).—*E*-1,2-Diarylethenes readily undergo photoisomerisation into the *Z*-isomers which usually undergo photocyclisation and dehydrogenation to give phenanthrenes.^{10,12} Application of this reaction to *E*-1,2-bisbiphenyl-ene-2-yl-ethene (16) might give compounds (18), (20), or (less likely) a compound in which a bond had been formed between C-1 and C-3'. In the desired compound (18) C-1 and C-14 are held close together and are thus favourably situated for the formation of the C-1 to C-14 bond to give the COT derivative (6).

The *E*-ethene (16) was made from 2-bromomethylbiphenyl-ene (10) *via* the Wittig reagent (11). A solution of the ethene (16) in benzene was irradiated for 75 h and gave a mixture of 2-formylbiphenylene and a lemon-yellow solid (28% yield) the elemental analysis and spectral properties of which showed it to be bisbenzo[3,4]cyclobuta[1,2-*b*; 1',2'-*h*]phenanthrene (20). In particular, its ¹H n.m.r. spectrum showed only three absorptions: δ 6.92 (br s, 1-, 2-, 3-, 4-, 5-H), 7.32 (s, 6-H), and 7.60 (br s, 13-H). These values agree well with those estimated for compound (20) from the n.m.r. spectra of benzo[*b*]biphenylene¹³ and phenanthrene, but do not agree with those expected for compound (18). More recently we synthesized compound (18) unambiguously (see below) and it is different from the product (20) obtained by photocyclisation of ethene (16). The finding that photocyclisation occurred at C-3 and C-3' of compound (16) rather than at the desired C-1 and C-1' positions is in agreement with the calculated sums of free-valence indices, namely $\Sigma F_{3,3} = 1.0473$, $\Sigma F_{1,3} = 0.9998$, and $\Sigma F_{1,1} = 0.9524$.

The photocyclisation of 1,2-diarylethenes proceeds *via* a 4a,4b-*trans*-dihydrophenanthrene which is readily dehydrogenated, for example, by air or iodine. If the ethene (16) underwent cyclisation at C-1, C-1' the dihydrophenanthrene intermediate would have structure (19) in which a double-bond has been localised in each of the 4-membered rings. This is known to be highly unfavourable. In contrast, the dihydro precursor (21) of compound (20) has two double-bonds fixed



(22) R = Br

(23) R = CO₂Et

(24) R = CH₂OH

(25) R = CH₂Br

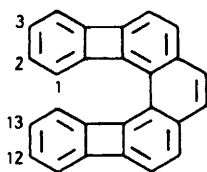
(26) R = CH₂P⁺Ph₃Br⁻

the C-3, C-3' positions of the ethene (16) we prepared the dimethyl analogue (17). Its synthesis involved the conversion of 2-methylbiphenylene (12) (made by a new method) *via* compounds (22), (23), (24), and (25) into compound (26) which then underwent a Wittig reaction with 2-formyl-3-methylbiphenylene to give the dimethyl compounds (17). A solution of the latter in benzene, containing a small amount of iodine, was irradiated with u.v. light for 94 h. The final mixture and aliquots (taken at 3.5 and 22 h) were examined by t.l.c. and by i.r. spectroscopy. These techniques showed that very little change had occurred apart from oxidation to give small amounts of 2-formyl-3-methylbiphenylene. In another experiment, a solution of the ethene (17) and the stoichiometric amount of diphenyl diselenide in benzene was flushed with nitrogen then irradiated for 19 h (*cf.* ref. 14) but no photocyclised product could be detected.

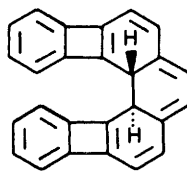
In an attempted synthesis of compound (18) or (20) by a non-photochemical method, we prepared 1,2-bisbiphenyl-ene-2-yl-ethane (13) by reaction of the bromide (10) with phenyl-lithium. However, when the ethane (13) was treated with aluminium chloride in carbon disulphide it gave a very complex mixture, which could not be purified, whereas under the same conditions bibenzyl gives phenanthrene in 21% yield.¹⁵

Preparation and Photoreaction of 2-Styrylbiphenylene (15).—We studied the photoreaction of 2-styrylbiphenylene to see if it would behave like the diarylethane (16). The synthesis of the styryl compound was achieved *via* the secondary alcohol (14) which, on dehydration with hot formic acid, gave *E*-2-styrylbiphenylene (15) (53%) and a dimer (or mixture of dimers), C₄₀H₂₈, m.p. 130–135 °C (32% yield). Irradiation of the styryl compound gave an inseparable mixture of dimers (20% yield), m.p. 101–150 °C, the ¹H n.m.r. spectrum of which was similar to that of the dimer, m.p. 130–135 °C. This failure of the styryl compound to undergo photodehydrocyclisation to give benzo[3,4]cyclobuta[1,2-*b*]- (or much less likely) benzo[3,4]cyclobuta[1,2-*c*]-biphenylene is surprising since the sum of the free-valence indices for these cyclisations are $\Sigma F_{3,ortho} = 1.02576$ and $\Sigma F_{1,ortho} = 0.95074$ respectively. Evidently the styryl compound (15) behaves like *E*-stilbene which, on irradiation, gives a mixture of two stereoisomers of 1,2,3,4-tetraphenylcyclobutane.¹⁶

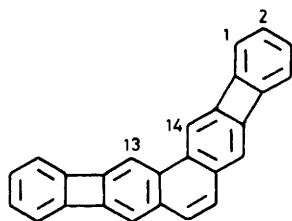
Synthesis of Bisbenzo[3,4]cyclobuta[1,2-*c*; 1',2'-*g*]phenanthrene (18).—The attempted dehydrocyclisation of the biaryl (7) might have failed partly because the biaryl exists mainly in the *transoid* form. We therefore wished to prepare an analogue of biaryl (7) in which the carbon atoms C-2 and C-2' are joined *via* a two-carbon chain thus ensuring that the carbon atoms C-8 and C-8' are rigidly held in close proximity. In this approach, the problem lay in the synthesis of 1,2-disubstituted biphenylenes, very few of which had previously been prepared. For example, attempts to formylate 1-iodobiphenylene using dichloromethyl methyl ether and tin(IV) chloride gave intractable mixtures, although the method works well with



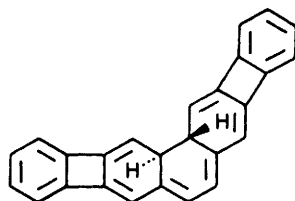
(18)



(19)



(20)

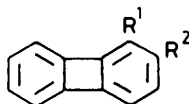


(21)

exo to each of the 4-membered rings. Bond arrangements similar to those of precursors (19) and (21) are present in the Wheland-type of intermediates involved in electrophilic α - and β -substitution respectively of biphenylene. It is well established that β -substitution of biphenylenes occurs readily whereas α -substitution very rarely takes place.

In an attempt to prevent photocyclisation from occurring at

biphenylene itself.¹⁷ The problem was solved by making use of the observations that lithiation of biphenylene occurs preferentially at C-1,¹⁸ and that benzyl alcohols can be specifically lithiated *ortho* to the CH₂OH group.¹⁹ In this way, 2-hydroxymethylbiphenylene was converted into the 1-lithio derivative (27) and thence, by treatment with 1-chloro-2-iodoethane,²⁰ into 2-hydroxymethyl-1-iodobiphenylene (28) in 58% yield. When iodine or di-iodomethane were used as iodinating agents the yield of iodo alcohol (28) was only 35%. Incidentally, 1-chloro-2-iodoethane can be prepared easily, although in modest yield (19%), by boiling a large excess of 1,2-dichloroethane with sodium iodide and acetone. The iodo alcohol (28) was oxidised to the corresponding aldehyde (29) (82%) which, on being heated with copper powder, gave the dialdehyde (8) (52% yield). As an alternative to the Ullmann reaction, the aldehyde (29) was converted into the cyclohexylimine (30) and then treated successively with butyl-lithium and



- (27) $R^1 = \text{Li}$; $R^2 = \text{CH}_2\text{Oli}$
 (28) $R^1 = \text{I}$; $R^2 = \text{CH}_2\text{OH}$
 (29) $R^1 = \text{I}$; $R^2 = \text{CHO}$
 (30) $R^1 = \text{I}$; $R^2 = \text{CH}=\text{NC}_6\text{H}_{11}$

the copper(I) iodide-triethyl phosphite complex (Ziegler's biaryl synthesis²¹). However, this method gave a lower yield (28%) of the dialdehyde (8) and is much less convenient than the conventional Ullmann method. The dialdehyde (8) was converted directly into bisbenzo[3,4]cyclobuta[1,2-*c*; 1',2'-*g*]phenanthrene (18) (68%) by heating it with hydrazine (Bacon's method²²).

The phenanthrene (18) forms bright yellow crystals and solutions of it are fluorescent in daylight. Its mass spectrum shows the molecular ion (M^+ 326) as base peak and an ($M - 2$)⁺ peak with a relative intensity of 46%. This suggested that dehydrocyclisation might be effected fairly easily to give the desired COT derivative (6). However, all our attempts to effect cyclisation failed. For example, no reaction occurred when compound (18) was heated with iodine in dichloromethane, with sodium tetrachloroaluminate at 150 °C,²³ or with titanium tetrachloride at 140 °C. When compound (18) was heated with sulphur or with 10% palladium-on-charcoal at 300 °C decomposition occurred. Irradiation of compound (18) with u.v., in the presence of iodine, gave a low yield of an unidentified solid (M^+ 488). Flash vacuum thermolysis (600 °C/0.04 mmHg) of compound (18) gave back the starting material. Probably the main reason for the failure of compound (18) to undergo dehydrocyclisation is that the reaction would involve a high-energy intermediate similar to structure (19).

Discussion of N.m.r. Spectra.—The ¹H n.m.r. spectra of most of the biphenylenes described in this paper are straightforward but the spectra of compounds (8) and (18) show special features. For comparison, the n.m.r. spectrum of the biaryl (7) was determined using computer-assisted calculations. Protons 2-H, 3-H, and 4-H form an ABX system with δ values of 6.90, 6.83, and 6.59 respectively. From the n.m.r. standpoint, the substituent at position-1 scarcely affects the unsubstituted 6-membered ring the protons of which give rise to a symmetrical AA'BB' system centred on δ 6.71 similar to that of biphenylene

which is centred on δ 6.66.²⁴ The chemical shifts in the ABX system are consistent with those in biphenyl where the protons 2-H, 3-H, and 4-H have δ values of 7.59, 7.41, and 7.32 respectively, compared with benzene δ 7.35.²⁵ In compound (8) the protons 3-H and 3'-H appear as doublets at low field (δ 7.42) as expected. However, two of the other protons give rise to a multiplet at highfield (δ ca. 6.35) and we propose that these are 8-H and 8'-H which are situated within the shielding zones of the carbonyl groups attached at C-2' and C-2 respectively. The biaryl (8) may be regarded as a 2,2',6,6'-tetrasubstituted biphenyl and hence the two halves will almost certainly be non-coplanar, but will exist (in solution) mainly in a transoid, rather than cisoid, conformation to minimise repulsion between the two carbonyl groups. In this way 8-H would be situated near to the carbonyl at C-2' (and similarly for 8'-H) and this would thus account for the shielding of these two protons. In compound (18) the protons in the phenanthrene moiety give rise to an AB quartet and a singlet. The δ values of these protons are smaller than those of the corresponding protons in phenanthrene itself because of the shielding effect of the 4-membered rings. Six of the remaining protons form a multiplet centred at ca. δ 6.5 and two form a multiplet centred at ca. δ 6.36. We attribute this upfield multiplet to protons 1-H and 14-H. At first sight the protons 1-H and 14-H might be expected to be strongly deshielded just like the corresponding protons in pentahelicene (dibenzo[*c,g*]phenanthrene) which appear at δ 8.48,²⁶ the deshielding being the result of the severe, mutual steric compression of 1-H and 14-H (the van der Waals effect²⁷). Compound (18) is almost certainly non-planar, like pentahelicene, but since the strain is spread over more carbon atoms in the former than in the latter compound, the steric compression of 1-H and 14-H will be less severe and, consequently, the deshielding will be less. In addition, in compound (18) each of the protons 1-H and 18-H is nearly equidistant from the centres of both 4-membered rings and hence each proton will experience the shielding effect of two paramagnetic ring currents. The net effect of the lessened deshielding (compared with pentahelicene) and the increased shielding (compared with biphenylene) results in the observed small upfield shift.

Experimental

Unless otherwise stated the following conditions apply. I.r. spectra were measured in Nujol mulls. ¹H N.m.r. spectra were recorded on a Varian HA-100 or a Jeol JNM-PS-100 as solutions in CDCl₃ with SiMe₄ as internal standard. Merck Kieselgel G and Kieselgel G₂₅₄ were used for t.l.c.; silica gel M.F.C. (Hopkin and Williams) or aluminium oxide (Brockmann activity II) for column chromatography; and Merck Kieselgel 60 (Art 9385) for flash chromatography. Petroleum refers to light petroleum (b.p. 60–80 °C). Irradiations were carried out using a Hanovia 100-W medium-pressure mercury-vapour lamp surrounded by a water-cooled quartz jacket. The jacketed lamp was placed in the solutions which were stirred with a magnetic stirrer and were open to the atmosphere.

1,1'-Bisbiphenylenyl (7).—This experiment was performed under nitrogen. An ethereal solution (41 ml) of 1.3M-butyl-lithium (prepared by Gilman's method²⁸) was added to biphenylene (2 g) in dry tetrahydrofuran (60 ml), and the solution was kept at room temperature, in the dark, for 72 h. The resulting deep blue solution was added dropwise (15 min) to a stirred mixture of bromobenzene (9.8 g), and anhydrous cobalt(II) chloride (860 mg) in ether cooled in an ice-bath. The mixture was then poured into ice-water (300 g) containing acetic acid (10 ml). The ether layer was separated and the aqueous layer extracted with dichloromethane. The organic

extracts were evaporated and the residue chromatographed on a column of alumina (with hexane as eluant), thereby giving biphenylene (57 mg) and 1,1'-bisbiphenylenyl (7) (610 mg, 31%) as pale yellow needles (from hexane), m.p. 162–163 °C (Found: C, 95.8; H, 4.6%; M^+ , 302; $C_{24}H_{14}$ requires C, 95.3; H, 4.7%; M , 302); λ_{\max} . (EtOH) 243, 256sh, 288, 369, and 385sh nm (log ϵ 4.82, 4.50, 4.51, 4.10, and 4.08); δ (200 MHz; computer-derived values) 6.59 (4-H), 6.71 (A,A',B,B', 5-, 6-, 7-, 8-H), 6.83 (3-H), and 6.90 (2-H), $J_{2,3}$ 8.5, $J_{3,4}$ 6.8, and $J_{2,4}$ 0.6 Hz.

2,2'-Bisbiphenylenyl (9).—2-Lithiobiphenylene was prepared by adding an ethereal solution (6.9 ml) of 1.31M-butyl-lithium to a solution of 2-iodobiphenylene⁶ (2.5 g) in ether (25 ml). This was treated with bromobenzene and cobalt(II) chloride as in the preparation of 1,1'-bisbiphenylenyl and gave crude 2,2'-bisbiphenylenyl (9) (1.0 g, 74%), m.p. 210–230 °C. After recrystallisation from ethanol it formed yellow leaflets, m.p. 246–248 °C (lit.,⁶ 243–244 °C) (Found: C, 95.3; H, 4.7%).

2-Bromomethylbiphenylene (10).—Freshly distilled phosphorus tribromide (0.2 ml) was added dropwise to a cooled and stirred solution of 2-hydroxymethylbiphenylene¹⁷ (100 mg) in benzene (ca. 2 ml). The mixture was kept overnight at room temperature, then chromatographed on a short column of silica gel with benzene as eluant. The first band to be eluted was evaporated and gave 2-bromomethylbiphenylene (10) (110 mg, 82%) as yellow plates (from $CHCl_3$ -n-hexane, 1:5), m.p. 108–109 °C (Found: C, 64.1; H, 3.7; M^+ , 244, 246. $C_{13}H_9Br$ requires C, 63.7; H, 3.7%; M , 244, 246).

Biphenylen-2-ylmethyltriphenylphosphonium Bromide (11).—A mixture of 2-bromomethylbiphenylene (0.13 g) and triphenylphosphine (0.145 g) in benzene (5 ml) was refluxed for 2 h. After being cooled, the salt (0.17 g, 62%) was collected, washed with ether, and then recrystallised from methanol-ether (1:5) to give the phosphonium bromide (11) as yellow prisms, m.p. 268–270 °C (Found: C, 70.9; H, 5.3. $C_{31}H_{24}BrP \cdot CH_3OH$ requires C, 71.2; H, 5.2%).

E-1,2-Bisbiphenylen-2-yloethene (16).—The phosphonium bromide (11) (300 mg) and dry toluene (10 ml) were put into a 2-necked 25-ml flask, provided with a condenser and a dropping funnel, which had been flushed out with nitrogen. Butyl-lithium (50 mg) in ether was added dropwise with stirring, the temperature being kept at 15–20 °C. When the addition was complete, the mixture was stirred for 30 min more then heated to 110 °C while sulphur (25 mg) in warm toluene (2 ml) was added dropwise during 2 h. The solvent was then removed under reduced pressure and the residue chromatographed on silica gel in benzene. The yellow band, after being eluted, yielded a solid, which on recrystallisation from CH_2Cl_2 -n-hexane (1:7) gave the E-ethene (16) (80 mg, 82%) as yellow needles, m.p. 287–287.5 °C (Found: C, 95.1; H, 4.9%; M^+ 328; $C_{26}H_{16}$ requires C, 95.1; H, 4.9%; M , 328); λ_{\max} . ($CHCl_3$) 248, 255sh, 292sh, 302, 314, 360sh, 388sh, 407, 418, and 444 nm (log ϵ 4.51, 4.45, 4.43, 4.67, 4.76, 4.10, 4.35, 4.45, 4.45, and 4.23); δ 6.56–6.89 (8 H, m). Solutions of the ethene were strongly fluorescent under u.v. light.

The same ethene was obtained (74%) by reaction of the phosphonium bromide (11) with 2-formylbiphenylene in the presence of lithium methoxide (cf. ref. 29).

Photo-dehydrocyclisation of the Ethene (16).—The ethene (16) (200 mg) in benzene (1 l) was placed in the flask of a Hanovia 1-l Photochemical Reactor, and the temperature of the solution was kept below 30 °C by external cooling. The progress of the reaction was followed by removing 1-ml aliquots of solution every 4 h and examining their u.v. spectra in $CHCl_3$ after

removing the benzene. The peaks at 407 and 417 nm gradually disappeared and another peak developed at 364 nm.

After completion of the reaction (75 h) the solvent was removed under reduced pressure and the residue was chromatographed on silica gel with benzene as eluant. The yellow band (strongly fluorescent under u.v. light) yielded bisbenzo[3,4]cyclobuta[1,2-b; 1',2'-h]phenanthrene (20) (56 mg, 28%) as a lemon-yellow solid, m.p. 305–307 °C (from $CHCl_3$) (Found: C, 95.6; H, 4.2%; M^+ , 326.109; $C_{26}H_{24}$ requires C, 95.7; H, 4.3%; M 326.109); λ_{\max} . 253, 270, 301sh, 310, 325, 345, 365, 391, 410, and 433 nm (relative absorbance 0.99, 0.60, 1.00, 1.22, 1.37, 0.50, 1.10, 0.17, 0.07, and 0.04). Further elution of the column gave a brown oil which, on sublimation at 60 °C and 0.01 Torr, gave 2-formylbiphenylene (15 mg).

2-Methylbiphenylene (12).—Biphenylene (4.57 g) and *N*-bromosuccinimide (5.40 g) were stirred in *N,N*-dimethylformamide (75 ml) for 2.5 h (Mitchell's method of bromination³⁰). The mixture was poured into water (200 ml) and the product (6.47 g, 93%) was collected and dried in air. It was sublimed at 90 °C and 0.05 Torr and gave 2-bromobiphenylene, m.p. 59–62 °C (lit.,⁶ 64–65 °C). Sublimed 2-bromobiphenylene (4.62 g) in dry ether (200 ml) was treated at –10 °C, under nitrogen, with butyl-lithium (1.4M in hexane; 16 ml). The orange solution was stirred for 10 min then methyl iodide (6.5 ml) was added and the mixture allowed to warm to room temperature (ca. 1 h). Water was added and the ethereal layer was separated. The aqueous layer was extracted with ether and the united ethereal extracts yielded a yellow oil which crystallised. It was sublimed at 60 °C and 0.05 Torr and gave 2-methylbiphenylene (2.67 g, 80%) as pale yellow crystals, m.p. 42–44 °C (lit.,³¹ 45–46 °C).

2-Bromo-3-methylbiphenylene (22).—2-Methylbiphenylene (2.49 g) and *N*-bromosuccinimide (2.67 g) in *N,N*-dimethylformamide (20 ml) were stirred for 18 h. The mixture was poured into water and the solid (3.32 g, 90%) was collected. It was recrystallised twice from methanol and gave 2-bromo-3-methylbiphenylene (22) as crystals, m.p. 138–139 °C (Found: C, 63.8; H, 3.8. $C_{13}H_9Br$ requires C, 63.7; H, 3.7%; δ 2.20 (s, CH_3), 6.52 (s, 4-H), 6.57–6.72 (m, 5-, 6-, 7-, and 8-H, and 6.76 (s, 1-H).

2-Ethoxycarbonyl-3-methylbiphenylene (23).—Butyl-lithium (1.2M in hexane; 1 ml) was added to a solution of 2-bromo-3-methylbiphenylene (245 mg) in dry ether (25 ml) at –10 °C under nitrogen. After 5 min ethyl chloroformate (0.3 ml) was added to the orange solution. The mixture was kept for 15 min then water was added. The product was collected in ether which, on evaporation, gave a yellow oil. This was chromatographed on a column of silica gel (with CH_2Cl_2 as eluant) and gave 2-ethoxycarbonyl-3-methylbiphenylene (23) (130 mg, 55%) as yellow crystals, m.p. 95 °C (after softening above 86 °C) after being sublimed at 90 °C and 0.05 Torr (Found: C, 80.1; H, 5.9; M^+ , 238. $C_{16}H_{14}O_2$ requires C, 80.6; H, 5.9%; M , 238); ν_{\max} . 1 710 cm^{-1} ; δ 1.35 (t, CH_3), 2.45 (s, Ar- CH_3), 4.29 (q, CH_2), 6.52 (s, 4-H), 6.63–6.90 (m, 5-, 6-, 7-, 8-H), and 7.10 (s, 1-H).

2-Hydroxymethyl-3-methylbiphenylene (24).—(a) 2-Formyl-3-methylbiphenylene¹⁷ (582 mg) in tetrahydrofuran (10 ml) was added all at once to a solution of sodium borohydride (170 mg) in ethanol (10 ml). After 20 min the mixture was evaporated to dryness then partitioned between water and CH_2Cl_2 . The organic phase, on evaporation, gave 2-hydroxymethyl-3-methylbiphenylene (24) (579 mg, 98%) as pale yellow crystals (from CCl_4), m.p. 146–148 °C (Found: C, 86.2; H, 6.0; M^+ , 196.088 9. $C_{14}H_{12}O$ requires C, 85.7; H, 6.2%; M , 196.088 7); δ

1.53 (OH, removed by D₂O), 2.18 (s, CH₃), 4.50 (s, CH₂), and 6.5—6.8 (m, 6ArH).

(b) A solution of the ester (**23**) (1.0 g) in dry ether (50 ml) was added dropwise to a slurry of lithium aluminium hydride (0.5 g) in dry ether (100 ml) during 30 min. The mixture was boiled under reflux for 1 h and then allowed to cool; 1M-hydrochloric acid was then added and the product collected in ether. Evaporation of the ether gave a solid which was purified by chromatography on a silica-gel column (with CH₂Cl₂ as eluant) and gave 2-hydroxymethyl-3-methylbiphenylene (0.603 g, 73%).

2-Bromomethyl-3-methylbiphenylene (25).—Phosphorus tribromide (380 mg) in heptane (20 ml) was added during 5 min to a solution of the alcohol (**24**) (560 mg) in dry ether (20 ml). After the mixture had been refluxed for 5 min more phosphorus tribromide (5 drops) was added and refluxing was continued for a further 5 min. The mixture was poured into saturated brine (20 ml), shaken, and then the layers were separated. The organic layer yielded yellow crystals (715 mg, 97%). A sample purified by sublimation under reduced pressure gave the bromomethyl compound (**25**) as yellow prisms, m.p. 125 °C (after softening at ca. 118 °C) (Found: C, 64.9; H, 4.1. C₁₄H₁₁Br requires C, 64.9; H, 4.3%).

3-Methylbiphenylen-2-ylmethyltriphenylphosphonium Bromide (26).—A mixture of the bromide (**25**) (715 mg), triphenylphosphine (868 mg), and acetonitrile (40 ml) was boiled under reflux for 10 min. The solvent was removed and the residue washed with pentane (3 × 50 ml) to remove the excess of PPh₃. The solid was dried for 3 h at 130 °C and 0.05 Torr to remove traces of water. The pale yellow solid consisted of the phosphonium bromide (**26**) (1.376 g, 96%) (from ethyl acetate-methanol), m.p. 274—276 °C (Found: C, 73.4; H, 4.9. C₃₂H₂₆BrP requires C, 73.7; H, 5.0%).

E-1,2-Bis(3-methylbiphenylen-2-yl)ethene (17).—Lithium methoxide (0.63M in methanol; 1.5 ml) was added to a boiling solution of 2-formyl-3-methylbiphenylene¹⁷ (97 mg) and the phosphonium salt (**26**) (287 mg) in dry methanol (20 ml) during 15 min to give extensive precipitation. The mixture was boiled for a further 15 min after which the solvent was removed and the residue chromatographed on a column of silica gel (with toluene as eluant). The large, yellow band gave the ethene (**17**) as yellow crystals (163 mg, 92%) (from toluene-heptane), m.p. 285—286 °C, which fluoresce in daylight (Found: C, 94.7; H, 5.7%; M⁺, 356. C₂₈H₂₀ requires C, 94.3; H, 5.7%; M, 356). The ethene sometimes crystallises as orange needles (polymorphic form), m.p. 285—286 °C; λ_{max}(CH₂Cl₂) 242, 306, 317, 414sh, 429, and 455 nm (log ε 5.02, 4.87, 4.91, 4.67, 4.68, and 4.48); δ 2.12 (s, CH₃), 6.38 (s, —CH=CH—), 6.42 (s, 4-H), 6.47 (s, 1-H), and 6.52—6.75 (m, 5-, 6-, 7-, 8-H).

1,2-Bisbiphenylen-2-ylethane (13).—Phenyl-lithium (84 mg) in dry ether was introduced, by means of a syringe, into a solution of 2-bromomethylbiphenylene (**10**) (500 mg) in dry ether (under nitrogen) as fast as refluxing allowed. Ice and water were added and the ethereal layer collected. Removal of the solvent gave the ethane (**13**) (300 mg, 89%) as pale yellow plates (from CHCl₃-n-hexane), m.p. 212—214 °C (Found: C, 94.3; H, 5.7. C₂₆H₁₈ requires C, 94.5; H, 5.5%; δ 2.57 (s, CH₂) and 6.42—6.67 (m, ArH).

1-Biphenylen-2-yl-2-phenylethanol (14).—Benzylmagnesium bromide (1.0 g) in dry ether (3 ml) was added dropwise to a stirred solution of 2-formylbiphenylene¹⁷ (0.7 g) in dry ether during 20 min. The mixture was then refluxed for 30 min, cooled in ice, and added to dilute hydrochloric acid. The product was collected in ether and was purified by chromatography on three

thick-layer silica-gel plates (20 × 20 cm) with n-hexane as eluant. The phenylethanol (**14**) was obtained as crystals (0.57 g, 54%) (from CCl₄), m.p. 125—126 °C (Found: C, 87.9; H, 6.1. C₂₀H₁₆O requires C, 88.2; H, 5.9%).

E-2-Styrylbiphenylene (15).—A solution of the phenylethanol (**14**) (100 mg) in 98% formic acid (10 ml) was boiled under reflux for 1 h, after which it was cooled and extracted with ether. The solvent was removed and the residue chromatographed on a column of alumina (with benzene as eluant). The first band to be eluted yielded E-2-styrylbiphenylene (**15**) (50 mg, 53%) as yellow needles (from benzene), m.p. 171—172 °C (Found: C, 94.6; H, 5.7. C₂₀H₁₄ requires C, 94.45; H, 5.55%; λ_{max}(EtOH) 230sh, 244, 280sh, 289sh, 300, 311, 382, 396sh, and 408sh (log ε 4.18, 4.36, 4.30, 4.46, 4.58, 4.50, 4.17, 4.10, and 3.79); δ 6.4—6.8 (m, 7-H) and 7.0—7.3 (m, 7-H). The second band to be eluted yielded a dimer (30 mg, 32%), m.p. 130—135 °C (softening from 105 °C); m/z 508 (M⁺).

1-Chloro-2-iodoethane.—Sodium iodide (30 g) was placed in a Soxhlet thimble and extracted with the condensate from the vapours of a boiling mixture of 1,2-dichloroethane (500 ml) and acetone (200 ml) during 2 h. The acetone was distilled from the mixture which was then washed with aqueous Na₂S₂O₅, dried (MgSO₄), and fractionally distilled to give 1-chloro-2-iodoethane (7.14 g, 19%), b.p. 137—139 °C (lit.,³² 140 °C).

2-Hydroxymethyl-1-iodobiphenylene (28).—2-Hydroxymethylbiphenylene¹⁷ (1.82 g, 10 mmol) in dry ether (200 ml) was treated with n-butyl-lithium (1.4M in hexane; 15 ml, 21 mmol). The mixture was refluxed for 1 h, cooled in an ice-bath, and 1-chloro-2-iodoethane (2.30 g, 12.5 mmol) was added. The mixture was boiled for 30 min, cooled, and water added. The ether layer was evaporated and the residue purified by chromatography on a short column of alumina (with CH₂Cl₂ as eluant) thereby giving a pale yellow solid (1.99 g), which was shown by the ¹H n.m.r. spectrum of its oxidation product (**29**) to be 90% by weight of the iodobiphenylene (**28**) (hence the yield was 58%). A sample of the product was purified by flash chromatography on Kieselgel 60 (with CH₂Cl₂ as eluant) and gave 2-hydroxymethyl-1-iodobiphenylene (**28**) as crystals (from CCl₄), m.p. 136—138 °C (Found: C, 50.4; H, 3.0. C₁₃H₉IO requires C, 50.7; H, 2.9%; δ 1.88 (br s, OH), 4.45 (s, CH₂), 6.53 (d, 4-H), and 6.62—6.90 (m, 3-, 5-, 6-, 7-, 8-H).

2-Formyl-1-iodobiphenylene (29).—A solution of potassium dichromate (100 mg) in water (2 ml) and concentrated sulphuric acid (0.2 ml) was added, during 2 min, to a solution of 2-hydroxymethyl-1-iodobiphenylene (**28**) (305 mg) in acetone (30 ml). After being stirred for 5 min the solution was decanted from green chromium(III) residues, evaporated nearly to dryness, and then extracted with dichloromethane. This extract yielded an oil which was chromatographed on a column of alumina (with toluene as eluant) and gave 2-formyl-1-iodobiphenylene (**29**) as yellow crystals (248 mg, 82%), m.p. 96—99 °C (after being sublimed at 80 °C and 0.05 Torr) (Found: C, 51.3; H, 2.3. C₁₃H₇IO requires C, 51.0; H, 2.3%; ν_{max} 1 680 cm⁻¹; δ 6.57 (d, 4-H), 6.67—6.95 (m, 5-, 6-, 7-, 8-H), 7.25 (d, 3-H), and 9.72 (s, CHO).

2-Cyclohexyliminomethyl-1-iodobiphenylene (30).—A mixture of the iodo-aldehyde (**29**) (647 mg), cyclohexylamine (220 mg), and benzene (50 ml) was refluxed for 2 h, water being removed by means of a Dean-Stark trap. Evaporation of the benzene left an orange oil (782 mg, 96%) which crystallised with time. Recrystallisation of the solid from toluene-hexane gave the imino compound (**30**) as fluffy, yellow needles, m.p. 127—130 °C (Found: C, 58.9; H, 4.7; N, 3.7. C₁₉H₁₈IN requires C,

58.9; H, 4.7; N, 3.6%); δ 1.10—2.40 (m, C₆H₁₁), 3.27 (m, CH—N), 6.59 (d, 4-H), 6.68—6.93 (m, 5-, 6-, 7-, 8-H), 7.39 (d, 3-H), and 8.28 (s, CH=N).

2,2'-Diformyl-1,1'-bisbiphenylenyl (8).—[The purification of 2-hydroxymethyl-1-iodobiphenylene is inefficient so the crude product was oxidised to the iodo-aldehyde (29) and 2-formylbiphenylene (composition estimated each time from the ¹H n.m.r. spectra) which was used in the Ullmann reaction]. A mixture of the iodo-aldehyde (29) (84% molar in iodo-aldehyde, 800 mg) was heated in a test-tube at 150 °C and freshly precipitated copper (dried under high vacuum, 900 mg) was added and the mixture was stirred with a glass rod. The mixture was kept at 150 °C for 1 h, then at 165 °C for 30 min, 175 °C for 30 min, and finally heated at 190 °C for 15 min. At this stage t.l.c. of an aliquot portion showed that no iodo-aldehyde remained. The cooled mixture was extracted with dichloromethane which, on evaporation, gave a sticky, yellow froth (521 mg). This was purified by chromatography on a column of alumina (with toluene as eluant). The first band eluted contained 2-formylbiphenylene. Elution of the next band with dichloromethane gave 2,2'-diformyl-1,1'-bisbiphenylenyl (8) (219 mg, 52%) as a yellow frothy solid, m.p. 170—173 °C (Found: *M*⁺ 358.0984. C₂₆H₁₄O₂ requires *M*, 358.0994); ν_{\max} 1 680, 1 210, 840, and 745 cm⁻¹; λ_{\max} (EtOH) 250, 279, and 372 (log ϵ 4.78, 4.76, and 4.03); δ 6.30—6.41 (m, 8-H), 6.61—6.82 (m, 4-, 5-, 6-, 7-H), 7.42 (d, 3-H), and 9.66 (s, CHO).

Bisbenzo[3,4]cyclobuta[1,2-c; 1',2'-g]phenanthrene (18).—A solution of hydrazine hydrate (3 mg) in acetic acid (1.2 ml) was added dropwise to a refluxing solution of the dialdehyde (8) (16 mg) in acetic acid (1 ml) during 30 min. After being refluxed for 1.5 h the mixture was poured into 1M-sodium hydroxide and then extracted with dichloromethane. Removal of the solvent gave a sticky solid which, after being chromatographed on a short column of alumina (with toluene as eluant), gave the phenanthrene (18) (10 mg, 68%) as bright yellow crystals (from hexane), m.p. 176—179 °C (Found: C, 95.7; H, 4.1. C₂₆H₁₄ requires C, 95.7; H, 4.3%); ν_{\max} 1 415, 835, and 730 cm⁻¹; λ_{\max} (CH₂Cl₂) 236sh, 248, 285sh, 292, 316sh, 334, 372, 414sh, 431, and 447sh (log ϵ 4.83, 4.90, 4.68, 4.71, 4.09, 4.06, 4.12, 3.87, 3.92, and 3.87); δ 6.30—6.43 (m, 1-H), 6.46—6.66 (m, 2-, 3-, 4-H), 6.75 (d, 5-H), 6.91 (s, 7-H), and 7.01 (d, 6-H), *J*_{5,6} 7.5 Hz.

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