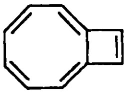
Wittig Reactions of 1,2-Dihydro-1,2-bis(triphenylphosphoranylidene)-benzocyclobutene and Benzocyclobutene-1,2-quinone. The Synthesis of Dibenzo[*a,c*]benzo[3,4]cyclobuta[1,2-*f*]cyclo-octene[1]

By **P. J. Garratt*** and **K. Peter C. Vollhardt**, Chemistry Department, University College, London W.C.1
R. H. Mitchell, University Chemical Laboratory, Lensfield Road, Cambridge

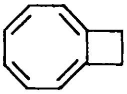
A Wittig reaction between 1,2-dihydro-1,2-bis(triphenylphosphoranylidene)benzocyclobutene (15) and biphenyl-2,2′-dicarbaldehyde (14) gave dibenzo[*a,c*]benzo[3,4]cyclobuta[1,2-*f*]cyclo-octene (3), whereas that between 2,2′-bis(triphenylphosphoranylidenemethyl)biphenyl (6) and benzocyclobutene-1,2-quinone (5) gave only acyclic products. Some reactions of (3) are described.

WHEREAS the properties of polycyclic hydrocarbons composed of fused $(4n + 2)$ π-electron rings have been well studied, particularly for six π-electron systems, little is known about the properties of hydrocarbons formed by the fusion of $4n$, or of $4n$ and $(4n + 2)$, π-electron rings. Biphenylene is the best known example of a system composed of fused $4n$ and $(4n + 2)$ π-electron rings, and its physical and chemical properties differ markedly from those of biphenyl.[2,†] Few polycyclic compounds have been prepared which contain fused $4n$ π-electron rings,[5,6] but the properties of these suggest that it is the nature of the individual $4n$ rings, and not the overall number of π-electrons, which dominates the behaviour of such systems.

Bicyclo[6,2,0]decapentaene (1), formally obtained by the fusion of cyclobutadiene and cyclo-octatetraene, is isomeric with naphthalene and azulene, has 10 π-electrons, and might on these grounds be expected to be an aromatic system. However, inspection of the three contributing resonance forms reveals that two of these contain cyclobutadiene rings, and application of the perturbational molecular orbital method[7] indicates that (1), unlike azulene and naphthalene, will have no more resonance energy than decapentaene. The concept that (1) is not an aromatic system is supported by the reported lack of success in introducing a further double bond into bicyclo[6,2,0]deca-1,3,5,7-tetraene (2).[6b] Because of this difficulty, we attempted to devise a synthesis in which the unsaturation would be introduced as part of the reaction sequence, and chose initially to try to prepare the benzo-annelated derivative, dibenzo[*a,c*]benzo[3,4]cyclobuta[1,2-*f*]cyclo-octene (3), by a double Wittig reaction. At the same time that this work was first reported,[1] Schröder and Röttele[8] described an elegant synthesis of a number of derivatives (4a—c) of (1). These compounds were extremely unstable, and this further emphasises the dissimilarity of (1) from its aromatic isomers.



(1)



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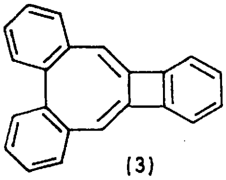

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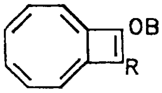

(4) a; R = H
b; R = Cl
c; R = OBu^t

The first route to (3) investigated was the reaction of benzocyclobutene-1,2-quinone (5)[9] with 2,2′-bis(triphenylphosphoranylidenemethyl)biphenyl (6).[10] The simultaneous addition of an ethereal solution of (5) and the deep red solution (in ether–benzene) of (6) [prepared by treatment of 2,2′-bis(triphenylphosphoniomethyl)biphenyl dibromide with sodamide] to vigorously stirred ether under nitrogen gave a mixture of products, which were separated by chromatography on alumina. Phenanthrene and bitolyl were the only hydrocarbons isolated, but a mixture of two isomeric monoketones (27%; ratio *ca.* 9 : 1) was also obtained (Scheme 1). The major isomer, separated by crystallisation, gave needles of (7) (m.p. 103—104°). The mass (*m*/*e* 296), n.m.r. [τ (CCl_4) 2·21 (m, 2·0H), 2·51—3·08 (m, 10·0H), 3·68 (s, 0·9H), and 8·00 (s, 3·0H)], and u.v. [$\lambda_{max.}$ (EtOH) 245 (ε 18,300), 253 (18,200), 293 (18,300), 302 (18,200), 316sh (11,600), and 366 (11,300) nm.] spectra were in accord with the gross structure assigned. The minor isomer (8) was separated by preparative t.l.c. on silica,

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† The norbiphenylene anion[3] and 2-thianorbiphenylene[4] have recently been synthesised.

[1] For a preliminary account of part of this work, see P. J. Garratt and R. H. Mitchell, *Chem. Comm.*, 1968, 719.

[2] For a general review on biphenylene and related compounds, see M. P. Cava and M. J. Mitchell, 'Cyclobutadiene and Related Compounds, Academic Press, New York, 1967.

[3] M. P. Cava, K. Narasimhan, W. Zeiger, L. J. Radonovich, and M. D. Glick, *J. Amer. Chem. Soc.*, 1969, **91**, 2378.

[4] P. J. Garratt and K. P. C. Vollhardt, *Chem. Comm.*, 1970, 109.

[5] W. Tochtermann, *Angew. Chem.*, 1963, **75**, 418.

[6] (*a*) R. Breslow, W. Horspool, H. Sugiyama, and W. Vitale, *J. Amer. Chem. Soc.*, 1966, **88**, 3677; (*b*) J. A. Elix, M. V. Sargent, and F. Sondheimer, *Chem. Comm.*, 1966, 509; *J. Amer. Chem. Soc.*, 1967, **89**, 180, 5080.

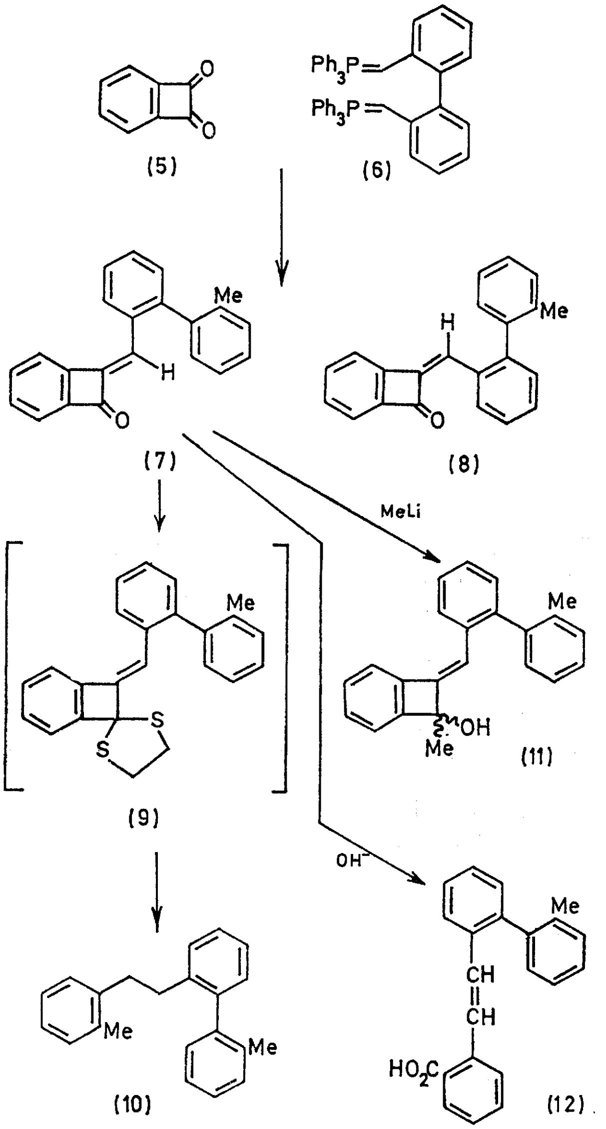
[7] M. J. S. Dewar, *Tetrahedron*, 1966, Suppl. 8, 1, 75.

[8] G. Schröder and H. Röttele, *Angew. Chem. Internat. Edn.*, 1968, **7**, 635.

[9] M. P. Cava, D. R. Napier, and R. J. Pohl, *J. Amer. Chem. Soc.*, 1963, **85**, 2076.

[10] D. M. Hall and B. Prakobsantisukh, *J. Chem. Soc.*, 1965, 6311; H. J. Bestmann, H. Haberlein, H. Wagner, and O. Kratzer, *Chem. Ber.*, 1966, **99**, 2848; E. D. Bergmann, P. Bracha, I. Agranat, and M. A. Kraus, *J. Chem. Soc.* (*C*), 1967, 328.

but was found to rearrange partially to (7), and consequently could not be obtained completely pure. The n.m.r. spectrum [τ (CCl$_4$) 1·44 (m, 0·7H), 2·52—3·06 (m, 11·5H), 3·88 (s, 0·8H), 8·00 (s, 3·1H)], and the u.v. spectrum [$\lambda_{max.}$ (EtOH) 247, 253, 278sh, 291, 277, 317, and 366 nm.] were similar to those of (7).

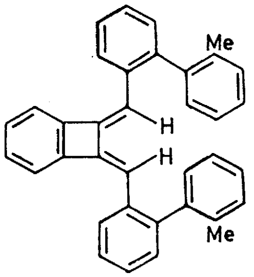


SCHEME 1

The ketones (7) and (8) were clearly geometrical isomers; similar systems had previously been examined by Blomquist and Hruby.[11] These authors found that in the n.m.r. spectra, the signal of the olefinic proton in the *trans*-isomer [*i.e.* (8)] was at lower field than the corresponding signal in the *cis*-isomer [*i.e.* (7)], which would have reversed the assignments shown. However, none of the compounds examined by Blomquist and Hruby contained a carbonyl group in the 4-membered ring. Such a group would be expected to have a greater effect on the olefinic proton of the *cis*-isomer (7) than on the corresponding proton of the *trans*-isomer (8). Attempts to transform the carbonyl group of (7) into a methylene group were unsuccessful, for Wolff–Kishner reduction gave a complex mixture of products rather than the required compound (see later), and desulphurisation of the thioacetal (9) gave the substituted 1,2-diphenylethane (10). However, treatment of (7) with methyl-lithium gave the corresponding tertiary alcohol (11). The n.m.r. spectrum of (11) showed that the olefinic proton resonance signal had moved to significantly higher field (τ 4·05) compared with that for the olefinic proton in (7). We therefore assign the *cis* stereochemistry to the major isomer (7).

Treatment of (7) with potassium hydroxide in boiling bis-(2-methoxyethyl) ether gave phenanthrene (17%) and the acid (12) (26%; m.p. 208—210°). The assigned structure (12) is based on the spectral properties and the product produced by hydrogenation of the olefinic bond (see Experimental section). The failure of the Wolff–Kishner reaction with (7) to give the corresponding methylene derivative was probably due to cleavage of the four-membered ring by base.

In an attempt to induce attack on both carbonyl groups of the quinone (5), the Wittig reaction between (5) and (6) was carried out under high dilution conditions at 120° in bis-(2-methoxyethyl) ether. The major hydrocarbon isolated was phenanthrene (28·5%), but a second hydrocarbon (0·6%; m.p. 190—191°) was obtained and assigned the structure (13) on the basis of molecular composition and spectral properties. The hydrocarbon (13) shows only one olefinic type proton in the n.m.r. spectrum, indicating that both double bonds have the same geometry, and the high-field position of the absorption (τ 4·18) suggests that (13) has the *cis,cis* stereochemistry shown. The failure to obtain cyclic products in the reaction of (5) with (6) appears to be due to the preference of the initially formed double bond to be of the *cis* orientation, unfavourable to subsequent cyclisation.



(13)

With the failure of the reaction of (5) and (6) to give the required cyclic product, the reverse reaction between biphenyl-2,2′-dicarbaldehyde (14) [12] and 1,2-dihydro-1,2-

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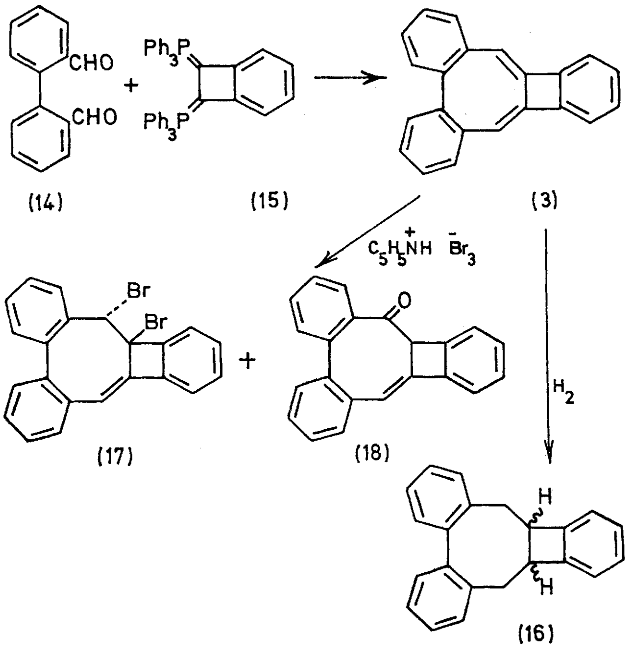
[11] A. T. Blomquist and V. J. Hruby, *J. Amer. Chem. Soc.*, 1967, **89**, 4996.

[12] P. S. Bailey and R. E. Erickson, *Org. Synth.*, 1961, **41**, 41.



SCHEME 2

bis(triphenylphosphoranylidene)benzocyclobutene (15)[11] was investigated (Scheme 2). The addition of a solution of (14) to an equimolar solution of (15) [prepared from 1,2-dihydro-1,2-bis(triphenylphosphonio)benzocyclobutene dibromide and n-butyl-lithium] in dry ether led to an immediate discharge of the deep red colour. A mixture of products was formed and these were separated by chromatography on alumina. The hydrocarbon fraction, which contained triphenylphosphine, was further fractionated by preparative layer chromatography on silica. Recrystallisation gave dibenzo[*a*,*c*]benzo[3,4]cyclobuta[1,2-*f*]cyclo-octene (3) (4%; m.p. 129—130°) as pale yellow crystals. The preparation of the bis-ylide (15) with n-butyl-lithium, rather than with sodamide in liquid ammonia as originally reported,[1] gave higher and more consistent yields of (3). The assigned structure for (3) is based on the spectral and chemical properties. The mass spectrum shows a parent peak at *m*/*e* 278·108, and the n.m.r. spectrum ([$^2H_8$]tetrahydrofuran) has absorptions at τ 2·82 (m, 9·8H), 3·06 (m, 2·1H), and 3·33 (s, 2·1H). The high-field singlet is attributed to the olefinic protons, and the position of absorption is in agreement with the finding of Blomquist and Hruby[11] for monobenzylidene derivatives of benzocyclobutene that the vinylic proton in the *trans*-derivative appears at τ *ca.* 3·50, whereas the *cis*-derivatives absorb * at τ *ca.* 3·85. The u.v. spectrum (95% EtOH) had maxima at 279 (ε 46,200) and 352 (9200) nm. For comparison the u.v. spectrum of biphenylene has maxima[13] at 250 (ε 79,000) and *ca.* 360 (6000) nm., and that of 1,2-dihydro-1,2-dimethylenebenzocyclobutene has main bands[14] at 230 (ε 66,000) and 329 (14,100) nm. Hydrogenation of (3) (5% Pd–$CaCO_3$; EtOAc) resulted in the uptake of 2 mol. of hydrogen, and gave (16), identified by spectroscopic properties.

Compound (3) when heated at 140° under nitrogen for 5 hr., was quantitatively recovered; heating at 200° for 8 hr. gave polymer with some unchanged (3). Photoirradiation gave only polymeric products. Attempts to form adducts with tetracyanoethylene (TCNE) or dimethyl acetylenedicarboxylate were unsuccessful, either (3) or polymeric materials being recovered. The behaviour of (3) towards TCNE resembles that of 1,2-dihydro-1,2-dimethylenebenzocyclobutene[14] rather than that of the bicyclo[6,2,0]decapentaene derivatives (4a—c), which gave 2 + 2 adducts.[8] When (3) was brominated with pyridinium hydrobromide perbromide in dichloromethane, a mixture of compounds was obtained which was separated by t.l.c. on silica. The major product (40%) was *trans*-9,9a-dibromo-9,9a-dihydrodibenzo[*a*,*c*]benzo[3,4]cyclobuta[1,2-*f*]cyclo-octene (17), m.p. 173—175°. The structure (17) was assigned on the basis of molecular composition and spectral properties. A second product (7%; m.p. 150—155°) was obtained which had the same molecular composition and very similar spectral properties, presumably the corresponding *cis*-isomer. A third compound obtained (31%; m.p. 199—202°) was assigned the ketonic structure (18), again on the basis of molecular composition and spectral properties.

The ready reduction of (3) with potassium in tetrahydrofuran to the dibenzo[*a*,*c*]benzo[3,4]cyclobuta[1,2-*f*]cyclo-octenyl dianion has been described elsewhere.[15]

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. N.m.r. spectra were measured for solutions in carbon tetrachloride (unless mentioned otherwise) with a Varian HA-100 spectrometer, with tetramethylsilane as internal standard. Mass spectra were determined with an A.E.I. MS-9 or MS-12 spectrometer. Alumina for chromatography was Spence grade H. Silica for t.l.c. was Merck silica gel. Light petroleum was the fraction boiling below 40°.

Wittig Reactions between Benzocyclobutene-1,2-*quinone* (5) *and* 2,2′-*Bis*(*triphenylphosphoranylidenemethyl*)*biphenyl* (6).—(a) cis- *and* trans-2-(2-o-*Tolyl*)*benzylidenebenzocyclobuten*-1-*ones*. Sodamide (1·2 g., 30 mmoles) was added to dry liquid ammonia (400 ml.; distilled over KOH) and the mixture was stirred for 10 min. 2,2′-Bis(triphenylphosphoniomethyl)biphenyl dibromide (8·6 g., 10·0 mmoles) was then added under nitrogen, and the mixture was stirred for 2 hr. A 2 : 3 mixture of benzene and ether (500 ml.) was added, and the ammonia was removed at 0° under a

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* In ref. 1 the designations *cis* and *trans* were inadvertently reversed.

[13] D. G. Farnum, E. R. Atkinson, and W. C. Lothrop, *J. Org. Chem.*, 1961, **26**, 3204.

[14] M. P. Cava, R. J. Pohl, and M. J. Mitchell, *J. Amer. Chem. Soc.*, 1963, **85**, 2080.

[15] C. S. Baxter, P. J. Garratt, and K. P. C. Vollhardt, *J. Amer. Chem. Soc.*, 1969, **91**, 7783.

nitrogen stream, and then by heating under reflux for 2 hr. The deep red solution of 2,2′-bis(triphenylphosphoranylidenemethyl)biphenyl (6) was then transferred under nitrogen to a dropping funnel, and the funnel was introduced into a three-necked flask (2 l.) fitted with a stirrer and containing dry ether (1 l.). Benzocyclobutene-1,2-quinone (5) (1·32 g., 10·0 mmoles) in dry ether–benzene (4 : 1; 500 ml.) was added to a second funnel, which was introduced into the third neck of the flask. The two solutions were added under nitrogen to the vigorously stirred ether at approximately the same rate during 90 min. The mixture was stirred for a further 14 hr., then heated under reflux for 2 hr., and evaporated under reduced pressure to *ca.* 400 ml. 2N-Hydrochloric acid (100 ml.) was then added, and the mixture was extracted with ether (1 × 300 ml.). The ethereal layer was washed with water (3 × 100 ml.), dried ($MgSO_4$), and preadsorbed on alumina (20 g.). The alumina was added to a column of alumina (150 g.) and eluted with light petroleum containing increasing amounts of ether. Bitolyl, phenanthrene, triphenylphosphine [light petroleum–ether (97 : 3)], and the mixture (820 mg., 27%) of monoketones (7) and (8) [light petroleum–ether (80 : 20)] were eluted in that order. cis-2-(2-o-*Tolylbenzylidene*)*benzocyclobuten*-1-*one* (7) was recrystallised from benzene–light petroleum and then ethanol–water to give colourless needles, m.p. 103—104° (Found: C, 89·05; H, 5·45%; M^+ 296·1206. $C_{22}H_{16}O$ requires C, 89·15; H, 5·45%; *M*, 296·1201), $\nu_{max.}$ (KBr) 1765 (C=O), 1570, 1100, 995, 975, 745, and 660 cm.$^{-1}$; for u.v. and n.m.r. spectra see Discussion section.

The combined mother liquors were reduced to small volume and subjected to preparative layer chromatography on silica [ether–light petroleum (40 : 60)] to give trans-2-(2-o-*tolylbenzylidene*)*benzocyclobuten*-1-*one* (8) (for u.v. and n.m.r. spectra see Discussion section).

(b) The bis-ylide (6) (10·0 mmoles) was prepared as in method (a) [except that the ammonia was replaced by bis-(2-methoxyethyl) ether (500 ml.)] and was added under nitrogen at the same rate as a solution of benzocyclobutene-1,2-quinone (1·32 g., 10·0 mmoles) in bis-(2-methoxyethyl) ether (500 ml.) to vigorously stirred bis-(2-methoxyethyl) ether (1 l.) at 120° during 1·5 hr. The mixture was then stirred for 18 hr. at 120°, heated under reflux for 10 min. and then worked up as in method (a). Besides phenanthrene (510 mg., 28·5%) a second hydrocarbon was isolated, identified as 1,2-*dihydro*-cis,cis-1,2-*bis*-(2-o-*tolylbenzylidene*)*benzocyclobutene* (13) (13 mg., 0·6%), m.p. 190—191° (Found: C, 93·7; H, 6·25. $C_{36}H_{28}$ requires C, 93·85; H, 6·1%), *m/e* 460, $\nu_{max.}$ (KBr) 3050, 3010, 2920, 1495, 1470, 1460, 1445, 1430, 1380, 1275, 1155, 1115, 1040, 1000, 820, 755, 735, and 725 cm.$^{-1}$, $\lambda_{max.}$ (Et_2O) 277·5 (ε 20,700) and 334·5 (14,700) nm., τ 2·1—3·3 (m, 20·2H), 4·18 (s, 1·9H), and 8·04 (s, 5·9H).

Preparation and Desulphurisation of the Thioacetal of (7). 2-*Methyl*-2′-(2-o-*tolylethyl*)*biphenyl* (10).—The monoketone (7) (100 mg., 0·338 mmole) was dissolved in ethanedithiol (1·12 g., 12 mmoles) and boron trifluoride–ether complex (3 drops) was added. The mixture was stirred at room temperature for 1 hr., methanol (5 ml.) was added, and the mixture was set aside for 16 hr. After the addition of water (10 ml.) it was extracted with ether (3 × 10 ml.), and the ethereal layer was washed with aqueous sodium hydroxide (3 × 5 ml.) and water (3 × 5 ml.), dried ($MgSO_4$), and evaporated under reduced pressure. The crude dithiol was dissolved in ethanol (50 ml.), Raney nickel (3·0 g.) was added, and the mixture was heated under reflux for 5 hr. The nickel was filtered off and washed with ethanol, and the combined ethanol layers were evaporated under reduced pressure to give a pale yellow oil. This was purified by preparative t.l.c. and identified as (10) (51 mg., 53%), *m/e* 286 and 181 (base peak), $\nu_{max.}$ (CCl_4) 3005, 2910, 2850, 1600, 1495, 1480, 1455, 1380, 1005, and 690 cm.$^{-1}$, $\lambda_{max.}$ (Et_2O) 260, 265, and 272·5 nm.

1,2-*Dihydro*-1-*methyl*-cis-2-(2-o-*tolylbenzylidene*)*benzocyclobuten*-1-*ol* (11).—Methyl-lithium (0·18 ml., 0·37 mmole) in ether was added under nitrogen to a solution of the monoketone (7) (100 mg., 0·34 mmole) in absolute ether (5 ml.). The solution was stirred for 1 hr., water was added, and the mixture was extracted with ether (5 ml.). The ethereal layer was washed with water (3 × 10 ml.) and dried (Na_2SO_4), and the products were separated by preparative t.l.c. [ether–light petroleum (30 : 70)] to give a pale yellow oil (90 mg., 0·32 mmole, 95%). Treatment of the oil with ether–light petroleum gave colourless *crystals* of (11), m.p. 107—108° (Found: C, 88·3; H, 6·35. $C_{23}H_{20}O$ requires C, 88·45; H, 6·45%), *m/e* 312, 297 ($M - CH_3$), and 279 (base peak, $M - CH_3 - H_2O$), $\nu_{max.}$ (KBr) 3300, 1450, 1370, 1125, 1010, 970, 920, 780, and 755 cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 219sh (ε 29,000), 281 (14,900), 308sh (22,600), 316 (27,000), and 329sh (18,500) nm., τ 2·22 (m, 1·0H), 2·5—3·0 (m, 11·4H), 4·05 (s, 0·7H), 7·47br (s, 1·1H), 8·00 (s, 2·9H), and 8·58 (s, 2·9H).

Reaction of cis-2-(2′-o-*Tolylbenzylidene*)*benzocyclobuten*-1-*one* (7) *with Potassium Hydroxide.* 2′-o-*Tolylstilbene*-2-*carboxylic Acid* (12).—The monoketone (7) (50 mg., 0·169 mmole) and potassium hydroxide (25 mg.) were added to bis-(2-methoxyethyl) ether (2·5 ml.) and the mixture was warmed at 80° until it turned orange and most of the base had dissolved. The mixture was then heated under reflux for 4 hr., allowed to cool, and ether was added. The ethereal layer was extracted with 0·5N-sodium hydroxide (3 × 10 ml.) and water (3 × 10 ml.), and dried ($MgSO_4$). The ether was largely removed under reduced pressure, and the remaining solution was separated by preparative t.l.c. on silica to give phenanthrene (5 mg., 17%). The basic aqueous layer was acidified with hydrochloric acid and extracted with ether (3 × 10 ml.), and the ethereal layer was washed with water (3 × 10 ml.) and dried ($MgSO_4$). Evaporation gave a yellow oil (40 mg.), which after dissolution in benzene–ether gave colourless crystals of (12) (14 mg., 26%), m.p. 208—210°, *m/e* 314, 296 ($M - H_2O$), and 281 ($M - H_2O - CH_3$), $\nu_{max.}$ (KBr) 3060, 3010, 2950, 2850, 2610, 1680 (C=O), 1475, 1425, 1270, 1005, 770, and 695 cm.$^{-1}$, $\lambda_{max.}$ (Et_2O) 287 nm.

Hydrogenation of 2′-o-*Tolylstilbene*-2-*carboxylic Acid* (12).—The acid (12) (20·0 mg.), 0·064 mmole) in ethanol (5 ml.) was hydrogenated over palladium–charcoal until no more hydrogen was absorbed (1 hr.). Removal of the catalyst and solvent left a pale yellow oil, 2-(2-o-*tolylphenethyl*)-*benzoic acid*, *m/e* 316 and 181 (base peak), $\nu_{max.}$ (CCl_4) 3050, 3000, 2900, 2830, 1700 (C=O), 1480, 1460, 1410, 1380, 1115, 1000, 725, and 690 cm.$^{-1}$, τ ($CDCl_3$) 2·4—3·2 (m, 12·1H), 6·3—7·8 (m, 3·8H), and 8·00 (s, 3·1H).

Wittig Reaction between 1,2-*Dihydro*-1,2-*bis*(*triphenylphosphoranylidene*)*benzocyclobutene* (15) *and Biphenyl*-2,2′-*dicarbaldehyde* (14). *Dibenzo*[a,c]*benzo*[3,4]*cyclobuta*[1,2-f]*cyclo-octene* (3).—1,2-Dihydro-1,2-bis(triphenylphosphonio)benzocyclobutene dibromide (23·5 g., 30 mmoles) was suspended in dry ether–benzene (3 : 1; 2 l.) under nitrogen, and 2·7M-butyl-lithium (22 ml., 60 mmoles) in hexane was added with stirring. Stirring was continued for 3 hr., then a solution of biphenyldicarbaldehyde (14) (6·3 g., 30 mmoles) in dry ether (40 ml.) was added to the dark red solution of the bis-ylide (15). The colour changed to brown; the mixture was stirred for 1 hr. at room temperature and then heated under reflux for 2 hr. The volume was reduced to *ca.* 300 ml., 2N-hydrochloric acid (100 ml.) was added, and the mixture was extracted with ether (200 ml.). The ethereal layer was washed with water (3 × 50 ml.), dried ($MgSO_4$), and evaporated under reduced pressure. The resulting dark oil was preadsorbed on alumina (35 g.) and chromatographed on an alumina column (250 g.). Elution with ether–light petroleum (6 : 94 to 10 : 90) gave a yellow oil (2·25 g.). Two separations by preparative t.l.c. on silica with ether–light petroleum (3 : 97) gave a pale yellow oil (340 mg., 4·1%) to which ether (0·5 ml.) containing a few drops of methanol was added. After 24 hr. at −30° a virtually quantitative precipitate of pale yellow crystals, m.p. 129—130°, *dibenzo*[a,c]*benzo*[3,4]*cyclobuta*[1,2-f]*cyclo-octene* (3), was obtained (Found: C, 94·55; H, 5·25. $C_{24}H_{14}$ requires C, 94·95; H, 5·05%; *M*, 278·1095), *m/e* 278·1083 (base peak), 277 (*M* − H), and 276 (*M* − 2H), $\nu_{max.}$ (KBr) 3060, 1480, 1461, 1434, 1333, 1162, 1122, 950, 880, 872, 862, 767, 762, 750, and 742 cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 263sh (ε 34,000), 279 (46,200), 341sh (8100), 352 (9200), and 366sh (7500) nm.; for n.m.r. see Discussion section.

Hydrogenation of Dibenzo[a,c]*benzo*[3,4]*cyclobuta*[1,2-f]*cyclo-octene* (3).—Compound (3) (13 mg., 0·047 mmoles) in ethyl acetate (40 ml.) was hydrogenated over 5% palladium–calcium carbonate (200 mg.) for 30 min. After filtration and evaporation, pentane (5 ml.) was added to the residue, and the pentane solution was filtered through alumina (15 g.). The solvent was removed, and the residue (13 mg.) gave colourless crystals of 9,9a,13b,14-*tetrahydrodibenzo*-[a,c]*benzo*[3,4]*cyclobuta*[1,2-f]*cyclo-octene* (16) (10 mg., 77%), m.p. 173—179° (from methanol) (Found: C, 93·4; H, 6·25. $C_{22}H_{18}$ requires C, 93·6; H, 6·4%; *M*, 282·1408), *m/e* 282·1408 (65%), 281, 267 (*M* − CH_3, base peak), and 252 (*M* − C_2H_6), $\nu_{max.}$ (KBr) 2905, 1444, 771, 754, and 750 cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 261 (ε 2680), 268 (3530), and 274 (3580) nm. τ 2·6—3·3 (m, 12H), 5·8—6·5 (m, 2H), and 6·9—7·9 (m, 4H).

Reactions of Dibenzo[a,c]*benzo*[3,4]*cyclobuta*[1,2-f]*cyclo-octene* (3) *with Dienophiles*.—(a) *Tetracyanoethylene*. To compound (3) (10 mg., 0·036 mmole) in dry benzene (0·5 ml.) was added tetracyanoethylene (4·6 mg., 0·036 mmole) in dry benzene (0·5 ml.). After 20 hr. at room temperature t.l.c. on silica revealed that only compound (3) was present. Heating the solution at 60° for 10 hr. and subsequent heating under reflux for 3 hr. afforded no change. Similar experiments with tetrahydrofuran as solvent also gave (3) unchanged. With *o*-xylene as solvent and heating to reflux, (3) disappeared, but only polymeric materials were obtained.

(b) *Dimethyl acetylenedicarboxylate*. Compound (3) (10 mg., 0·036 mmole) was added to freshly distilled dimethyl acetylenedicarboxylate, and the mixture was heated at 120—150° in a sealed tube under nitrogen. Chromatography revealed that (3) had disappeared, but only oligomers derived from dimethyl acetylenedicarboxylate could be detected (mass spectroscopy).

Bromination of Dibenzo[a,c]*benzo*[3,4]*cyclobuta*[1,2-f]*cyclo-octene* (3).—Pyridinium hydrobromide perbromide (52 mg., 0·162 mmole) and compound (3) (45 mg., 0·162 mmole) were added to dry dichloromethane (3 ml.) and the mixture was stirred under nitrogen for 20 hr. The solvent was removed and the products were separated by t.l.c. [ether–light petroleum (6 : 94)]. The chromatogram showed five bands, the first two (in order of decreasing R_F value) consisting of minor products which were not further examined. The third band yielded an orange oil, which on treatment with carbon tetrachloride–light petroleum gave pale yellow crystals (28 mg., 40%), m.p. 173—175°, of trans-9,9a-*dibromo*-9,9a-*dihydrodibenzo*[*a,c*]*benzo*[3,4]*cyclobuta*[1,2-f]-*cyclo-octene* (17) (Found: C, 60·15; H, 3·3; Br, 36·3. $C_{22}H_{14}Br_2$ requires C, 60·3; H, 3·2; Br, 36·5%), *m/e* 440, 438 (3%), 436, 359 (*M* — Br), 357 (*M* — Br), and 278 (base peak, *M* — 2Br), $\nu_{max.}$ (KBr) 1480, 1465, 1450, 900, 865, 820, 755, 710, and 685 cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 227sh (ε 33,000), 266 (14,600), and 309 (9600) nm., τ 2·16—3·30 (m, 12·1H), 3·66 (m, 1·0H), and 4·46 (m, 0·9H). The fourth band gave a pale yellow oil which on treatment with methanol–ether gave pale brown crystals (5 mg., 7%), m.p. 150—155°, of the *cis*-isomer of (17), *m/e* 440, 438 (3%), 436, 359 (*M* — Br), 357 (*M* — Br), and 278 (base peak, *M* — 2Br), $\nu_{max.}$ (KBr) 1485, 1465, 1445, 1340, 1120, 895, 850, 840, 820, 760, 750, 710, and 685 cm.$^{-1}$, $\lambda_{max.}$ (Et_2O) 243sh, 270sh, and 310 nm., τ 2·0—3·4 (m), 3·55 (m), and 4·38 (m). The fifth band gave a yellow oil, which on treatment with methanol–ether gave pale yellow crystals, m.p. 199—202° (15 mg., 31%), of *dibenzo*[a,c]*benzo*[3,4]*cyclobuta*[1,2-f]*cyclo-octen*-9(9aH)-*one* (18) (Found: C, 89·6; H, 4·6. $C_{22}H_{14}O$ requires C, 89·75; H, 4·8%), *m/e* 294 (70%) and 265 (base peak, *M* — CHO), $\nu_{max.}$ (KBr) 1705 (C=O), 1600, 1490, 1475, 1445, 1275, 785, 770, 760, and 740 cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 218sh (ε 26,500), 242 (40,500), 225sh (32,000), 305 (17,700), 311sh (16,300), and 343 (4800) nm., τ 2·1—3·2 (m, 13·1H) and 6·18 (d, 0·9H).

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