

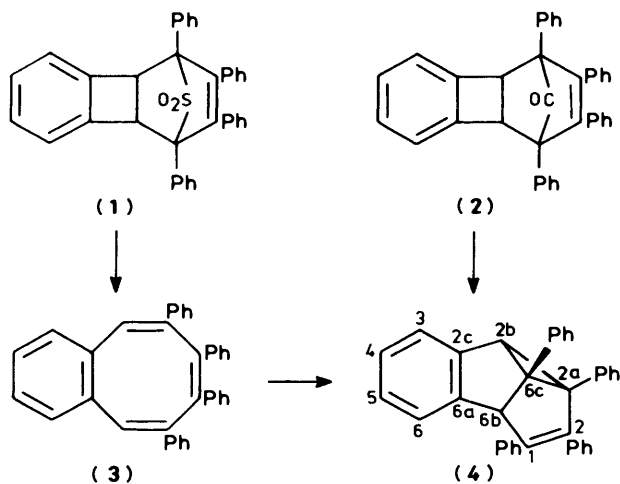
## Benzocyclo-octenes. Part 5.<sup>1</sup> Thermal Rearrangements of Benzocyclo-octenes to Benzo[*a*]cyclopropa[*c,d*]pentalenes.

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Substituted benzocyclo-octenes may undergo thermal rearrangement to 2a,2b,6b,6c-tetrahydrobenzo[*a*]cyclopropa[*c,d*]pentalenes. The ease of this reaction depends on the substituents, and is facilitated by the presence of phenyl groups in the 6- and 9- positions of the benzocyclo-octene. The mechanisms of this and secondary rearrangements are discussed.

The thermal rearrangement of cyclo-octene (cyclo-octatetraene) to 2a,2b,4a,4b-tetrahydrocyclopropa[*c,d*]pentalene (semibullvalene) is symmetry-allowed<sup>2</sup> and has been predicted to be exothermic by some 13 kcal mol<sup>-1</sup>.<sup>3</sup> Despite this, few such reactions have been reported,<sup>4,5</sup> and this isomerisation of cyclo-octene itself has only been achieved photochemically.<sup>5,6</sup> The majority of derivatives of 2a,2b,6b,6c-tetrahydrobenzo[*a*]cyclopropa[*c,d*]pentalene (benzosemibullvalene) so far reported have been prepared by the photolysis of 1,4-dihydro-1,4-ethenonaphthalenes (benzobarrelenes)<sup>7-11</sup> or of naphthalene-acetylene cycloadducts.<sup>12,13</sup> The photochemical rearrangement of 6-cyanobenzocyclo-octene to 6-cyano-2a,2b,6b,6c-tetrahydrobenzo[*a*]cyclopropa[*c,d*]pentalene has been observed,<sup>10</sup> but this appears to be an isolated example.

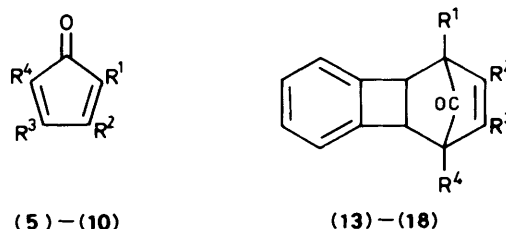


Scheme 1.

In a previous paper<sup>1</sup> we reported that a cycloaddition reaction of benzocyclobutene with 2,3,4,5-tetraphenylthiophene-1,1-dioxide gave 6,7,8,9-tetraphenylbenzocyclo-octene (3) via the presumed intermediate (1) (Scheme 1). The reaction of 2,3,4,5-tetraphenylcyclopenta-2,4-dienone, on the other hand, gave an isolable adduct (2) which underwent decarbonylation at its melting point or on heating in solvents to give the benzo[*a*]cyclopropa[*c,d*]pentalene derivative (4). Further experiments have established that compound (3) rapidly rearranges to the pentalene (4) at temperatures above 150 °C. Here, we investigate the effect on this rearrangement of the replacement of phenyl by methyl or benzyl substituents.

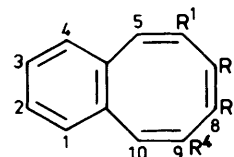
### Results and Discussion

Cyclopentadienone (5) and the so-called 'hemicyclone' (7) were prepared following literature reports<sup>14,15</sup> and the unknown cyclopentadienones (6) and (8)–(10) were synthesised by



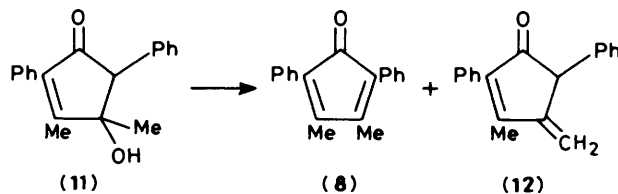
(5)–(10)

(13)–(18)



(19)–(24)

- (5),(13),(19) R<sup>1</sup> = Me; R<sup>2</sup>,R<sup>3</sup>,R<sup>4</sup> = Ph  
 (6),(14),(20) R<sup>2</sup> = Me; R<sup>1</sup>,R<sup>3</sup>,R<sup>4</sup> = Ph  
 (7),(15),(21) R<sup>1</sup>,R<sup>4</sup> = Me;R<sup>2</sup>,R<sup>3</sup> = Ph  
 (8),(16),(22) R<sup>2</sup>,R<sup>3</sup> = Me; R<sup>1</sup>,R<sup>4</sup> = Ph  
 (9),(17),(23) R<sup>1</sup> = CH<sup>2</sup>Ph; R<sup>2</sup>,R<sup>3</sup>,R<sup>4</sup> = Ph  
 (10),(18),(24) R<sup>1</sup>,R<sup>4</sup> = CH<sup>2</sup>Ph; R<sup>2</sup>,R<sup>3</sup> = Ph



Scheme 2.

analogous procedures. Isolation of the intermediate hydroxy cyclopentenones is unnecessary and, for the preparation of unsymmetrical cyclopentadienones when isomeric hydroxy cyclopentenones may form, laborious. Details of these, where isolated, are included in the Experimental section. The route to 3,4-dimethyl-2,5-diphenylcyclopenta-2,4-dienone (8) merits additional comment. Dehydration of the hydroxycyclopentenone (11), prepared from 1,3-diphenylpropan-2-one and butanedione, with sulphuric acid in acetic anhydride was unsuccessful. Azeotropic dehydration using toluene-*p*-sulphonic acid in toluene gave, in addition to the cyclone (8) (20%), the colourless methylenecyclopentenone (12) (60%) (Scheme 2). Reaction of the hydroxycyclopentenone (11) with thionyl chloride in pyridine, a method developed by Mackenzie and his co-workers,<sup>16</sup> gave compound (8) in up to 60% yield, with a negligible amount of isomer (12). In

**Table 1.** <sup>1</sup>H n.m.r. data for benzocyclobutene-cyclopenta-2,4-dienone adducts

Adduct	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	4a-H	8b-H	(5-H—8-H) and unassigned aryl substituent protons
(13)	1.59 (3 H, s)	6.53—6.58 (2 H, m, 2-, 6-H) <sup>a</sup> 7.03—7.07 (3 H, m, 3-, 4-, 5-H)	6.25—6.29 (2 H, dd, 2-, 6-H) <sup>a</sup> 6.68—6.81 (3 H, m, 3-, 4-, 5-H)	<i>b</i>	4.42 (1 H, d)	3.80 (1 H, d)	7.07—7.46 (9 H, m)
(14)	<i>b</i>	1.32 (3 H, s)	6.56—6.61 (2 H, m, 2-, 6-H) 6.93—7.00 (3 H, m, 3-, 4-, 5-H)	<i>b</i>	4.43—4.47 (2 H, dd)		7.17—7.63 (14 H, m)
(15)	1.49 (3 H, s)	6.54—6.60 (4 H, dd, 2-, 6-H) 7.00—7.05 (6 H, m, 3-, 4-, 5-H)		1.49 (3 H, s)	3.67 (3 H, s)		7.05—7.25 (4 H, m)
(16)	7.34—7.51 (5 H, m)		1.11 (6 H, s)	7.34—7.51 (5 H, m)	4.31 (2 H, s)		7.14—7.31 (4 H, m)
(17)	3.44 (2 H, dd, —CH <sub>2</sub> —)	6.54 (2 H, dd, 2-, 6-H)	6.41 (2 H, dd, 2-, 6-H)	<i>b</i>	4.37 (1 H, d)	3.86 (1 H, d)	6.68—7.42 (20 H, m)
(18)	3.29 (2 H, dd, —CH <sub>2</sub> —)	6.58 (4 H, dd, 2-, 6-H)		3.29 (2 H, dd, —CH <sub>2</sub> —)	3.65 (2 H, s)		6.70—7.24 (20 H, m)

<sup>a</sup> Off-resonance decoupling of this signal collapsed the associated ring protons to an A<sub>2</sub>B system. <sup>b</sup> Signal unresolved from aromatic multiplet.

**Table 2.** <sup>1</sup>H N.m.r. data for benzocyclo-octenes and benzo[*a*]cyclopropa[*c,d*]pentalenes

Benzocyclo-octene		Benzo[ <i>a</i> ]cyclopropa[ <i>c,d</i> ]pentalene			
		2b-H	6b-H	Others	
(19) 6-Me	: 1.98 (3 H, d)	(25) 3.52 (1 H, s)	4.14 (1 H, s)	6c-Me	: 1.21 (3 H, s);
others	: 6.50—7.62 (21 H, m)	(26) 4.27 (1 H, s) <sup>a</sup>	4.31 (1 H, s) <sup>a</sup>	1-Me	: 1.90 (3 H, s);
(20) 7-Me	: 1.72 (3 H, s)	(27) 4.08 (1 H, s)	4.71 (1 H, s)	2-Me	: 1.38 (3 H, s);
others	: 7.02—7.72 (21 H, m)	(28) 3.42 (1 H, s)	4.57 (1 H, s)	2a-Me	: 1.14 (3 H, s);
(21) 6,9-Me	: 1.96 (6 H, d)	(31) 3.88 (1 H, s)	4.24 (1 H, s)	6c-CH <sub>2</sub>	: 2.86 (2 H, dd);
5-, 10-H	: 6.42 (2 H, d)	(32) 4.27 (1 H, s) <sup>a</sup>	4.33 (1 H, s) <sup>a</sup>	1-CH <sub>2</sub>	: 3.50 (2 H, dd);
others	: 6.75—7.40 (14 H, m)	(33) 3.78 (1 H, s) <sup>a</sup>	3.80 (1 H, s) <sup>a</sup>	6c-CH <sub>2</sub>	: 2.78 (2 H, dd);
(22) 7,8-Me	: 1.66 (6 H, s)			1-CH <sub>2</sub>	: 3.37 (2 H, dd);
5-, 10-H	: 6.84 (2 H, s)				
others	: 7.15—7.52 (14 H, m)				
(23) 6-CH <sub>2</sub>	: 3.60 (2 H, m)				
5-, 10-H	: 6.58 (2 H, m)				
others	: 7.15—7.52 (24 H, m)				
(24) 6-, 9-CH <sub>2</sub>	: 3.11 (4 H, dd)				
5-, 10-H	: 6.12 (2 H, s)				
others	: 6.85—7.37 (24 H, m)				

<sup>a</sup> May be interchanged. <sup>b</sup> Signal obscured by isomers.

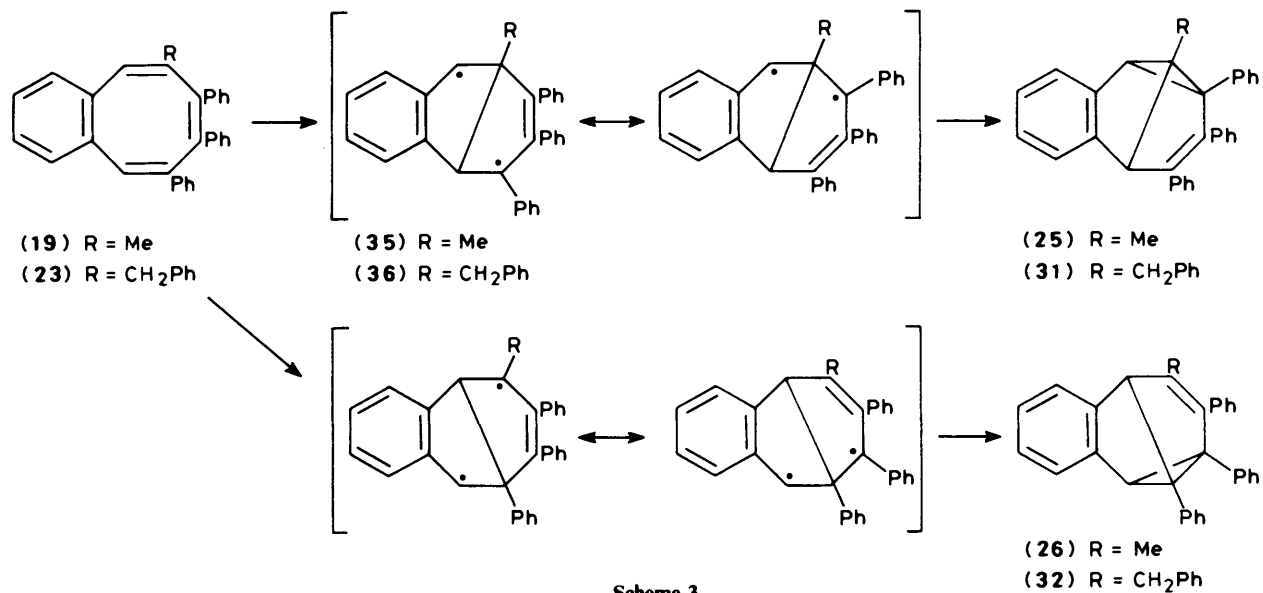
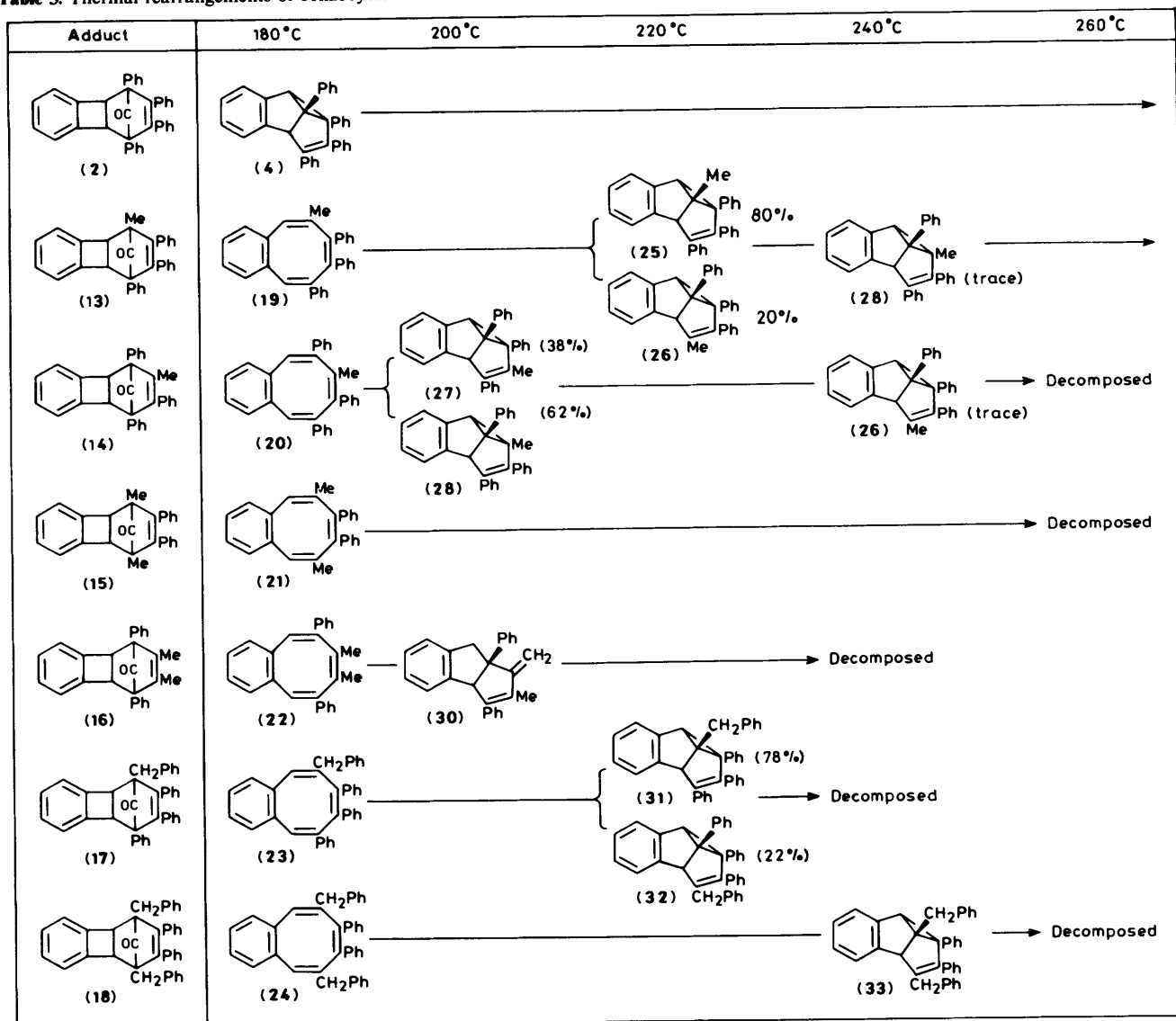
contrast to 'hemicyclone' (7), which is dimeric under normal conditions,<sup>17</sup> compound (8) is a stable red monomer. This difference must reflect the steric effect of phenyl groups relative to methyl groups when present in the 2- and 5-positions of such cyclones.

Reactions of the cyclones (5)—(10) with benzocyclobutene in tetrahydrofuran gave the colourless crystalline *endo*-adducts (13)—(18). This stereochemistry is assigned by comparison of their <sup>1</sup>H n.m.r. spectra (Table 1) with that of the *endo*-tetraphenylcyclopentadienone adduct (2).<sup>1</sup> Decarbonylation of the adducts in refluxing diglyme at 155—160 °C gave the benzocyclo-octenes (19)—(24) in essentially quantitative yields. All adducts melted with decarbonylation in the range 170—190 °C, the melt then being heated directly to effect rearrangement (Table 3). The formation of benzo[*a*]cyclopropa[*c,d*]pentalene derivatives was monitored by <sup>1</sup>H n.m.r. spectroscopy after heating at specific temperatures taken in 20 °C increments above 160 °C. The rearrangement temperatures quoted are those for greater than 50% conversion after 10 min; very slow rearrangement was usually detectable at 20 °C below this point. Where a mixture of isomers formed, yields were determined by <sup>1</sup>H n.m.r., separation of the isomers by chromatography not being possible under the conditions tried. All products could be identified unambiguously from their <sup>1</sup>H

(Table 2) and <sup>13</sup>C n.m.r. spectra. Features of the results illustrated in Table 3 are highlighted below, and are discussed in sequence. (a) Rearrangement is facilitated by phenyl substituents at positions 6 and 9, the substituents at positions 7 and 8 appearing to be less important. The methyltriphenylbenzocyclo-octene (19) required a higher rearrangement temperature than the isomer (20), and the dimethyl derivative (21) failed to rearrange below its decomposition point of ca. 260 °C. Replacement of methyl by benzyl groups does not significantly affect the rearrangement temperatures, thus relief of strain is unlikely to be the main cause of the reaction; (b) benzocyclo-octene (22) rearranges to the methylenecyclopent[*a*]indene (30), instead of to the expected benzo[*a*]cyclopropa[*c,d*]pentalene (29); and (c) a third, unpredicted, isomer forms on heating benzocyclo-octenes (19) and (20) to high temperatures.

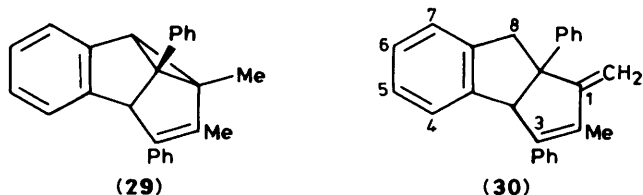
(a) *The role of the 6- and 9- substituents.* The above observations lead us to suspect that reaction occurs by a biradical pathway. The influence of the 6-substituent appears to lie in stabilising the formation of one radical centre as the C(5)—C(9) transannular bond develops, the resonance delocalisation afforded by a 6-phenyl group being substantially greater than that from hyperconjugation with a methyl or benzyl group. Cross-cyclisation thus occurs in such a way as to produce the more stable intermediate. Rearrangements of the benzocyclo-

Table 3. Thermal rearrangements of benzocyclo-octenes

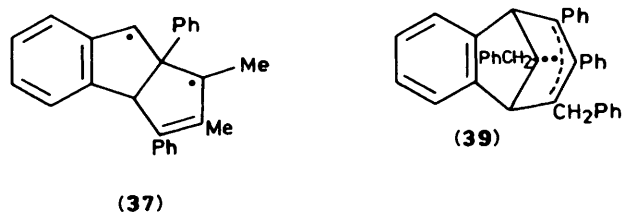


Scheme 3.

octenes (19) and (23) give the pentalenes (25), (26) and (31), (32) respectively in ratios of 4:1, the major isomers forming *via* the presumed 6-phenylallyl radicals (35) and (36) (Scheme 3). Conversely, the intermediates formed on heating compound (20) would be of comparable stability, and the observed ratio (1:1.6) of the products (27) and (28) may reflect steric constraints in the three-membered rings. The possibility of product formation by other biradical pathways<sup>18,19</sup> has not been excluded.

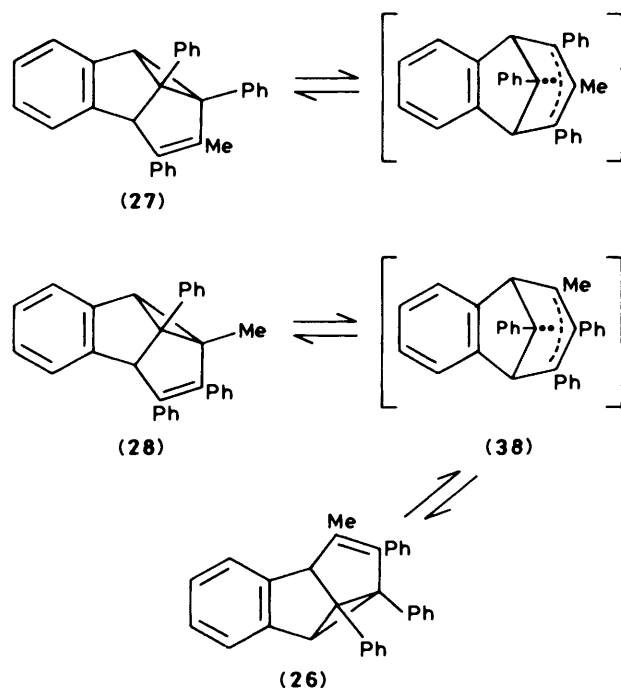


(b) *Rearrangement of compound (22)*. Thermolysis of (22) gives 1,2,8,8a-tetrahydro-2-methyl-1-methylene-3,8a-diphenylcyclopent[a]indene (30), instead of the expected benzocyclopropapentalene (29). The structure of compound (30) was established by <sup>13</sup>C n.m.r. spectroscopy, the spectrum showing resonances for only one methyl group and for two different secondary carbon atoms. The <sup>1</sup>H n.m.r. spectrum showed similar features to that of compound (12). Photosensitised and acid-catalysed rearrangements of this type have been reported,<sup>11,20,21</sup> and a related thermal rearrangement has recently been described by Greenfield and Mackenzie.<sup>22</sup> Thermolysis of compound (22) in the presence of base, using the conditions described by Criegee,<sup>20</sup> did not affect the yield of the product (30). The benzocyclopropapentalene (29) could not be detected by <sup>1</sup>H n.m.r. spectroscopy and does not appear to be an intermediate in this reaction. It seems likely that compound (30) is formed by a [1,4]-hydrogen shift; the fused five-membered rings force the biradical (37) into a conformation where hydrogen transfer from the methyl group is favourable. However, rearrangement of compound (20) gave only the benzocyclopropapentalenes (27) and (28).



(c) *Rearrangement of the benzocyclopropapentalenes (25), (26) and (27), (28)*. Prolonged heating at 240 °C of the benzocyclopropapentalenes (25) and (26) caused the slow formation of a third component (28). The mixture of the products (27) and (28) isomerised in like manner, forming a new product (26). Several examples of this type of sigmatropic shift are known. As a concerted [1,3]-suprafacial process it would be symmetry-forbidden, and a two-step migration involving formation of an intermediate [3.2.1] allyl biradical seems more likely.<sup>9,13,23</sup>

The isomerisations of compounds (27) and (28) are illustrated (Scheme 4). Note that whilst the rearrangement of compound (27) is degenerate, compound (28) can isomerise to (26) through the unsymmetrical intermediate (38). Since formation of only one new isomer is possible, this reaction confirms the structure (26) of the minor product formed on heating the benzocyclo-octene (19) and forms the basis for assignments in the <sup>1</sup>H n.m.r.



Scheme 4.

spectra of these compounds. This rearrangement has a further implication. We infer that formation of the benzocyclopropapentalenes (25) and (26) from the benzocyclo-octene (19) is essentially irreversible, an equilibrium state would be shown by formation of the fourth isomer (25) on heating compounds (27) and (28) at 240 °C, but this is not found.

The benzocyclopropapentalenes (25) and (26) rearrange in the same way, but isomer formation was not observed on heating compounds (31), (32) or (33). Isomers (31) and (32) decomposed at temperatures required to affect rearrangement in the methylbenzocyclopropapentalenes. The dibenzyl derivative (33) was stable at 240 °C, but did not isomerise below its decomposition point (*ca.* 260 °C), possibly due to the lower stability of the bridged radical (39).

## Experimental

Organic extracts were dried over sodium sulphate. <sup>1</sup>H N.m.r. spectra were obtained on a JEOL JNM FX200 spectrometer. Samples were run as solutions in CDCl<sub>3</sub> at ambient temperature and chemical shifts are recorded as p.p.m. downfield from internal tetramethylsilane. I.r. spectra were run as Nujol mulls unless otherwise stated. Mass spectra were obtained on an AEI MS902 instrument operated at 70 eV and a source temperature of 200 °C.

*3-Methyl-2,4,5-triphenylcyclopenta-2,4-dienone* (6).—1-Phenylpropane-1,2-dione<sup>24</sup> (2.9 g) was added dropwise to a stirred solution of 1,3-diphenylpropan-2-one (5.0 g) and potassium hydroxide (0.5 g) in ethanol (50 ml). After the reaction had been stirred for 3 h at room temperature, the solvent was removed under reduced pressure and the residue taken up in dichloromethane (50 ml). The extract was washed with 10% aqueous hydrochloric acid and water, then dried and evaporated; no attempt was made to isolate the isomeric hydroxycyclopentenones from this mixture. The resulting oil was dissolved in acetic anhydride (10 ml) and treated with a few drops of sulphuric acid. After 10 min the product was filtered and recrystallised from butanone-ethanol to give the title

compound (1.77 g, 30%) as purple-black crystals, m.p. 145—147 °C (Found: C, 89.4; H, 5.6.  $C_{24}H_{18}O$  requires C, 89.4; H, 5.6%);  $\nu_{\max}$ . 1 720, 1 450, 720, and 705  $cm^{-1}$ ;  $\delta_H$  7.52—7.10 (15 H, m, ArH) and 2.00 (3 H, s, 3-Me).

**3,4-Dimethyl-2,5-diphenylcyclopenta-2,4-dienone (8).**—(a) Butanedione (10 g) was added dropwise during 20 min to a stirred solution of 1,3-diphenylpropan-2-one (12 g) and 1,7-diazabicyclo[6.3.0]undec-7-ene (1 g) in ethanol (50 ml). The solution was stirred at room temperature for 12 h, then worked up as described above for compound (6). The crude mixture of hydroxycyclopentenones (13.5 g) crystallised slowly; it was usually dehydrated without further purification. Recrystallisation from aqueous isopropanol separated one isomer, m.p. 128—130 °C (Found: C, 82.1; H, 6.7.  $C_{19}H_{18}O_2$  requires C, 82.0; H, 6.5%);  $\nu_{\max}$ . 3 450, 1 690, 1 242, 1 130, and 700  $cm^{-1}$ ;  $m/z$  (%) 278 ( $M^+$ , 100) and 263 (65). This purified hydroxycyclopentenone (1 g) and toluene-*p*-sulphonic acid (50 mg) were boiled in toluene (25 ml) for 20 min, during which time the solvent volume was allowed to distil down to ca. 5 ml. The deep red solution was chromatographed on silica gel with toluene, eluting first the *title compound* (8) (0.19 g, 20%) as red crystals, m.p. 166—167 °C [from light petroleum (b.p. 80—100 °C)] (Found: C, 87.5; H, 6.4.  $C_{19}H_{16}O$  requires C, 87.7; H, 6.15%);  $\nu_{\max}$ . 1 705, 1 302, 804, and 705  $cm^{-1}$ ;  $\delta_H$  7.20 (10 H, s, ArH), and 2.21 (6 H, s, 3-, 4-Me);  $m/z$  (%) 260 ( $M^+$ , 100), 217 (20), and 116 (24), followed by 3-methyl-4-methylene-2,5-diphenylcyclopent-2-enone (12) (0.56 g, 60%), m.p. 134—136 °C (from ethanol) (Found:  $M^+$ , 260.1211.  $C_{19}H_{16}O$  requires 260.1201);  $\nu_{\max}$ . 1 695, 910, 865, and 703  $cm^{-1}$ ;  $\delta_H$  7.40—7.23 (10 H, m, ArH), 5.44 (2 H, dd, 4-H<sub>2</sub>), 4.16 (1 H, s, 5-H), and 2.38 (3 H, s, 3-Me);  $m/z$  (%) 260 ( $M^+$ , 100), 217 (33), and 115 (20).

(b) Thionyl chloride (8 ml) was added dropwise to a stirred solution of the crude hydroxycyclopentenone mixture (13.5 g), prepared as in (a), in pyridine (30 ml) at 0 °C. After 10 min the deep red solution was poured into ice-water (250 ml) and the product collected by ether extraction. The extract was washed with 10% aqueous hydrochloric acid and water, then dried and evaporated. Chromatography of the residue as in (a) gave cyclopentadienone (8) (7.5 g, 40%).

**2-Benzyl-3,4,5-triphenylcyclopenta-2,4-dienone (9).**—A solution of benzil (6 g), 1,4-diphenylbutan-2-one<sup>25</sup> (7 g), and potassium hydroxide (0.5 g) in ethanol (50 ml) was stirred at room temperature for 3 h, at which point the crystalline product was filtered. Recrystallisation from aqueous ethanol gave a hydroxycyclopentenone (2.2 g, 19%), m.p. 178—180 °C (Found: C, 86.3; H, 5.7.  $C_{30}H_{24}O_2$  requires C, 86.5; H, 5.8%);  $\nu_{\max}$ . 3 450, 1 700, and 695  $cm^{-1}$ ;  $m/z$  (%) 416 ( $M^+$ , 12), 398 ( $M^+$  - H<sub>2</sub>O, 46), 370 (60), and 325 (100). Dehydration and purification of this product as described above for compound (6) gave the *title compound* (9) (1.72 g, 17%) as brick-red crystals, m.p. 171—173 °C (Found: C, 90.6; H, 5.4.  $C_{30}H_{22}O$  requires C, 90.4; H, 5.5%);  $\nu_{\max}$ . 1 706, 765, and 702  $cm^{-1}$ ;  $\delta_H$  7.30—6.80 (20 H, m, ArH) and 3.60 (2 H, s, 2-H<sub>2</sub>);  $m/z$  (%) 398 ( $M^+$ , 100) and 370 (99).

**2,5-Dibenzyl-3,4-diphenylcyclopenta-2,4-dienone (10).**—A solution of benzil (13 g), 1,5-diphenylpentan-3-one<sup>26</sup> (13 g) and potassium hydroxide (1 g) in ethanol (100 ml) was stirred at 40 °C for 1 h, then worked up as described for compound (6). The crude hydroxycyclopentenone was usually dehydrated without further purification, but could be crystallised from [dichloromethane-light petroleum (b.p. 40—60 °C)], m.p. 89—92 °C (Found: C, 86.3; H, 6.0.  $C_{31}H_{26}O_2$  requires C, 86.5; H, 6.05%);  $\nu_{\max}$ . 3 450, 1 700, and 700  $cm^{-1}$ ;  $m/z$  (%) 430 and 339 (100). Dehydration as described for compound (6) gave a deep orange solution which was neutralised with aqueous sodium

hydrogen carbonate and the product was extracted into toluene. Chromatography over silica gel in toluene gave the *title compound* (10) (9.1 g, 34%) as a viscous, orange-red gum (Found: C, 90.3; H, 5.7.  $C_{31}H_{24}O$  requires C, 90.2; 5.8%);  $\nu_{\max}$ . 3 050, 1 720, 1 505, 1 040, and 710  $cm^{-1}$ ;  $m/z$  (%) 412 ( $M^+$ , 100), 321 (25), 293 (31), and 91 (27).

**The Cycloadducts (13), (14), and (16)—(18).**—These were prepared by the method previously described<sup>1</sup> for the adduct (2) of benzocyclobutene with 2,3,4,5-tetraphenylcyclopenta-2,4-dienone:

**1,4,4a,8b-Tetrahydro-1-methyl-2,3,4-triphenyl-1,4-methanobiphenyl-9-one (13).** Yield 82%, m.p. 174—175 °C (from chloroform-ethanol) (Found: C, 90.5; H, 5.8.  $C_{32}H_{24}O$  requires C, 90.6; H, 5.7%);  $\nu_{\max}$ . 1 765 and 702  $cm^{-1}$ ;  $m/z$  (%) 424 ( $M^+$ , 0.5) and 396 ( $M^+$  - CO, 100).

**1,4,4a,8b-Tetrahydro-2-methyl-1,3,4-triphenyl-1,4-methanobiphenyl-9-one (14).** Yield 69%, m.p. 182—183 °C [from light petroleum (b.p. 80—100 °C)] (Found: C, 90.3; H, 5.75.  $C_{32}H_{24}O$  requires C, 90.6; H, 5.7%);  $\nu_{\max}$ . 1 770, 760, and 695  $cm^{-1}$ ;  $m/z$  (%) 424 ( $M^+$ , 0.6), 396 ( $M^+$  - CO, 100), 381 (42), and 218 (30).

**1,4,4a,8b-Tetrahydro-2,3-dimethyl-1,4-diphenyl-1,4-methanobiphenyl-9-one (16).** Yield 92%, m.p. 175—177 °C [from light petroleum (b.p. 80—100 °C)] (Found: C, 89.5; H, 5.95.  $C_{27}H_{22}O$  requires C, 89.5; H, 5.95%);  $\nu_{\max}$ . 1 772, 762, 752, and 700  $cm^{-1}$ ;  $m/z$  (%) 362 ( $M^+$ , 0.2), 334 ( $M^+$  - CO, 100), and 319 (66).

**1-Benzyl-1,4,4a,8b-tetrahydro-2,3,4-triphenyl-1,4-methanobiphenyl-9-one (17).** Yield 35%, m.p. 175—177 °C [from light petroleum (b.p. 80—100 °C)] (Found: C, 90.9; H, 5.5.  $C_{38}H_{28}O$  requires C, 91.2; H, 5.6%);  $\nu_{\max}$ . 1 765, 755, and 700  $cm^{-1}$ ;  $m/z$  (%) 472 ( $M^+$  - CO, 31) and 381 (100).

**1,4-Dibenzyl-1,4,4a,8b-tetrahydro-2,3-diphenyl-1,4-methanobiphenyl-9-one (18).** Yield 36%, m.p. 185—187 °C [from light petroleum (b.p. 80—100 °C)] (Found: C, 90.85; H, 5.9.  $C_{39}H_{30}O$  requires C, 91.0; H, 5.8%);  $\nu_{\max}$ . 1 770 and 700  $cm^{-1}$ ;  $m/z$  (%) 514 ( $M^+$ , 1.8), 486 ( $M^+$  - CO, 23), 395 (100), and 304 (62).

**1,4,4a,8b-Tetrahydro-1,4-dimethyl-2,3-diphenyl-1,4-methanobiphenyl-9-one (15).**—A solution of 1,2-dibromo-1,2-dihydrobenzocyclobutene (2 g) in tetrahydrofuran (10 ml) was added dropwise to a refluxing stirred suspension of 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone dimer<sup>14</sup> (1 g) and activated zinc dust<sup>27</sup> (5 g) in tetrahydrofuran (15 ml) over a period of 15 min. The yellowish suspension was cooled, diluted with dichloromethane (100 ml), decanted from zinc residues, then washed with 10% aqueous hydrochloric acid and water. The dried solution was evaporated under reduced pressure to give a viscous gum. Chromatography on silica with ethyl acetate-light petroleum (b.p. 40—60 °C) (1:10) as the eluant gave, after a small forerun benzocyclobutene dimer,<sup>27</sup> the *title compound* (15) (0.32 g, 23%), m.p. 179—180 °C [from light petroleum (b.p. 60—80 °C)] (Found: C, 89.6; H, 6.0.  $C_{27}H_{22}O$  requires C, 89.5; H, 6.05%);  $\nu_{\max}$ . 1 770, 760, and 710  $cm^{-1}$ ;  $m/z$  (%) 362 ( $M^+$ , 1.5), 334 ( $M^+$  - CO, 100), and 319 (72).

**The Benzocyclo-octenes (19)—(24).**—These were prepared, in near to quantitative yields, by decarbonylation of the cycloadducts (13)—(18) in refluxing diglyme,\* using the method reported previously:<sup>1</sup>

**6-Methyl-7,8,9-triphenylbenzocyclo-octene (19).** Colourless oil (Found:  $M^+$ , 396.1870.  $C_{31}H_{24}$  requires  $M$ , 396.1878);  $\nu_{\max}$ . 1 610, 1 500, 1 455, 775, 760, and 702  $cm^{-1}$ ;  $m/z$  (%) 396 ( $M^+$ , 100) and 218 (30).

\* Diglyme = MeOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OMe

7-Methyl-6,8,9-triphenylbenzocyclo-octene (20). M.p. 142—143 °C (from ethanol) (Found:  $M^+$ , 396.1871.  $C_{31}H_{24}$  requires  $M$ , 396.1878);  $\nu_{\max}$ . 1 495, 1 450, 765, and 700  $cm^{-1}$ ;  $m/z$  (%) 396 ( $M^+$ , 100), 381 (42), and 218 (30).

6,9-Dimethyl-7,8-diphenylbenzocyclo-octene (21). M.p. 128—129 °C (from ethanol) (Found:  $M^+$ , 334.1722.  $C_{26}H_{22}$  requires  $M$ , 334.1721);  $\nu_{\max}$ . 1 500, 1 455, 770, and 700  $cm^{-1}$ ;  $m/z$  (%) 334 ( $M^+$ , 100) and 319 (45).

7,8-Dimethyl-6,9-diphenylbenzocyclo-octene (22). M.p. 120—122 °C (from ethanol) (Found:  $M^+$ , 334.1703.  $C_{26}H_{22}$  requires  $M$ , 334.1721);  $\nu_{\max}$ . 1 500, 1 455, 770, and 700  $cm^{-1}$ ;  $m/z$  (%) 334 ( $M^+$ , 100) and 319 (45).

6-Benzyl-7,8,9-triphenylbenzocyclo-octene (23). M.p. 148—149 °C (from ethanol) (Found: C, 93.7; H, 5.95.  $C_{37}H_{28}$  requires C, 94.1; H, 5.9%);  $\nu_{\max}$ . 1 607, 760, and 700  $cm^{-1}$ ;  $m/z$  (%) 472 ( $M^+$ , 35) and 381 (100).

6,9-Dibenzyl-7,8-diphenylbenzocyclo-octene (24). M.p. 147—148 °C (from ethanol) (Found: C, 93.8; H, 6.05.  $C_{38}H_{30}$  requires C, 93.8; H, 6.15%);  $\nu_{\max}$ . 1 495, 770, 750, and 704  $cm^{-1}$ ;  $m/z$  (%) 486 ( $M^+$ , 12), 395 (100), 304 (83), and 91 (31).

**Rearrangement of the Benzocyclo-octenes (19)–(24).**—The benzocyclo-octene (50 mg) was heated under dry nitrogen at 180 °C (silicone oilbath) for 10 min, cooled and examined by  $^1H$  n.m.r. spectroscopy. In similar experiments at 200, 220, 240, and 260 °C the cycloadducts were heated directly, decarbonylation occurring (on melting) in the range 170—190 °C. Rearrangement temperatures quoted are those for greater than 50% conversion after 10 min; very slow rearrangement was usually observed at 20 °C below this point. When a mixture of isomers formed, yields were determined by  $^1H$  n.m.r. spectroscopy upon complete rearrangement of the benzocyclo-octenes to tetrahydrobenzo[*a*]cyclopropa[*c,d*]pentalenes. Products were identified by a combination of  $^1H$  (Table 2) and  $^{13}C$  n.m.r. spectroscopy, the mass spectra being practically identical to those of the corresponding benzocyclo-octenes. Most of these compounds could not be crystallised, and were isolated as colourless oils with the following exceptions:

2a,2b,6b,6c-Tetrahydro-6c-methyl-1,2,2a-triphenylbenzo[*a*]cyclopropa[*c,d*]pentalene (25). M.p. 159—162 °C [from light petroleum (b.p. 40—60 °C)] (Found:  $M^+$ , 396.1873.  $C_{31}H_{24}$  requires  $M^+$ , 396.1878);  $\nu_{\max}$ . 1 440, 765, 750, and 685  $cm^{-1}$ ;  $m/z$  (%) 396 ( $M^+$ , 100), 381 (22), and 218 (28).

1,2,8,8a-Tetrahydro-2-methyl-1-methylene-3,8a-diphenylcyclopent[*a*]indene (30). M.p. 163—165 °C (from aqueous acetone) (Found:  $M^+$ , 334.1722.  $C_{26}H_{22}$  requires  $M$ , 334.1722);  $\nu_{\max}$ . 1 620, 1 440, 853, 754, 730, and 700  $cm^{-1}$ ;  $\delta_H$  7.48—6.54 (14 H, m, ArH), 5.07 (2 H, d, 1- $CH_2$ ), 4.79 (1 H, s, 3a-H), 3.69 (2 H,

dd, 8- $H_2$ ), and 1.87 (3 H, d, 2-Me);  $\delta_C$  130.0—123.6 (CH, ArH), 105.2 (1- $CH_2$ ), 68.7 (C-3a), 47.2 (C-8), and 11.8 (2-Me);  $m/z$  (%) 334 ( $M^+$ , 100) and 319 (21).

1,6c-Dibenzyl-2a,2b,6b,6c-tetrahydro-2,2a-diphenylbenzo[*a*]cyclopropa[*c,d*]pentalene (33). M.p. 98—100 °C (from ethanol) (Found:  $M^+$ , 486.2335.  $C_{38}H_{30}$  requires  $M$ , 486.2347);  $m/z$  (%) 486 ( $M^+$ , 15), 395 (100), 304 (78), and 91 (30).

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