Synthesis and Rearrangement of Alkylaryl- and Aryl-substituted Dihydrosemibullvalenes by Thermolysis of 7,8-Fused Cyclo-octa-1,3,5-triene Derivatives[1]

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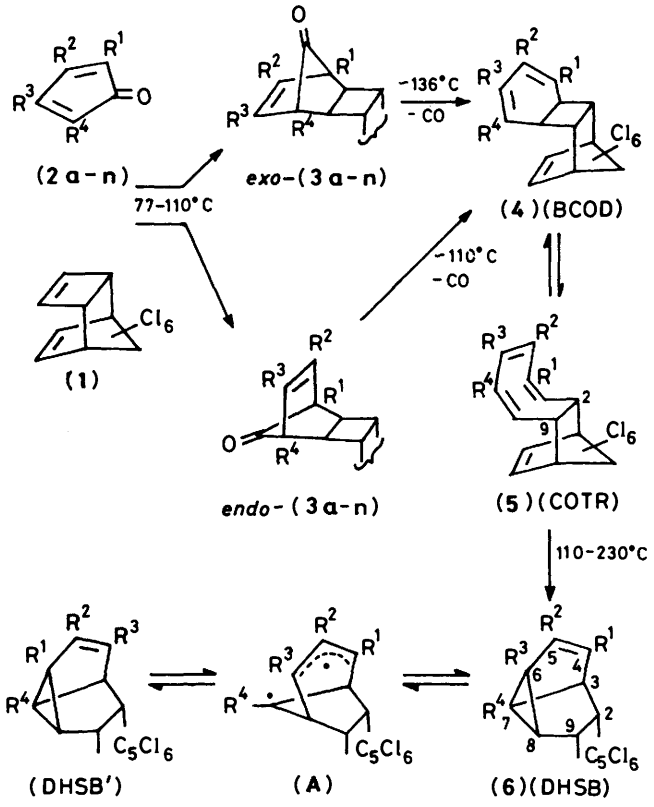
The thermal cycloaddition of a cyclobuteno-dienophile (**1**) with cyclopentadienones has been systematically investigated; the stereoisomeric adducts give convenient access by decarbonylation to a variety of tetra-aryl-, methyltriphenyl-, triphenyl-, tri-t-butyl-, and dimethyldiphenyl-cyclo-octa-1,3,5-triene derivatives as the products of electrocyclic ring-opening of the valence-tautomeric primary products of cheletropic bridge-extrusion, *viz.* bicyclo[4.2.0]octadienes. These compounds provide useful models for investigation of equilibria between the electrocyclic valence tautomers, the scope and mechanism for thermal cross-cyclisations in, for example, unsymmetrically substituted cyclo-octatrienes, and the thermal vinyl–cyclopropane (1,3-allylic shift) isomerisation and/or H-atom transfer disproportionation of the resulting arylated and alkylaryldihydrosemibullvalenes. The results best accord with diradical pathways for cyclo-octatriene–dihydrosemibullvalene conversions and subsequent rearrangements. Useful ^{13}C and ^{1}H n.m.r. structure correlations and new examples of cyclopentadienones are also reported.

Earlier papers[2a–d] have described the reaction sequence illustrated in Scheme 1 which ensues when the cyclobutene element in the tricyclononadiene (**1**) undergoes cycloaddition at 110—140 °C with the tetraphenylcyclopentadienone (**2a**). The initially formed stereoisomeric *exo*- and/or *endo*-cycloadducts (**3a**) readily extrude carbon monoxide,[3] at an appropriate reaction temperature, and similarly either the cyclo-octatriene derivative (COTR) (**5a**) or the product of an unusual intramolecular [$_{\pi}4 + _{\pi}2$] cyclisation,[4] the dihydrosemibullvalene derivative (DHSB) (**6a**), or both can readily be isolated; however, the immediate decarbonylation product, the bicyclo-octadiene derivative (BCOD) (**4a**) is elusive. In a similar reaction sequence with the bis-(*p*-methoxyphenyl)diphenylcyclopentadienone (**2b**), however, besides the *symmetrical* COTR (**5b**), and its unique cross-cyclisation product DHSB (**7**), an isomeric dihydrosemibullvalene derivative DHSB (**8**) is isolated,[2b,d] and each of the isomeric DHSBs (**7**) and (**8**), when separately heated (at *ca.* 137 °C), is cleanly converted into an approximately equimolar mixture of the two (Scheme 3).[2d] By contrast, heating the dienophile (**1**) with 2,5-dimethyl-3,4-diphenylcyclopentadienone (**2h**) (137 °C) gives both the expected decarbonylation product [the (BCOD) (**4h**)] and its electrocyclic tautomeric COTR (**5h**), but only *one* thermally stable DHSB (**9**) (Scheme 4). DHSB rearrangement (**7**) ⇌ (**8**) is most easily accommodated by reversible vinyl–cyclopropane rearrangement *via* a delocalised diradical intermediate (**A**), depending on the substituent pattern in the primary DHSB derived by cyclisation of the substituted COTR.[2d] Under the appropriate reaction conditions (heating to *ca.* 230 °C), if this interpretation is correct, a diradical analogous to (**A**) is either inacessible from the DHSB (**9**), perhaps because of its reduced stability (R^1 and R^4 being Me), or if such an intermediate is formed to a limited extent it suffers some other fate rather than collapsing into isomeric DHSBs.

Given the ready accessibility of various isomers of bis-(*p*-methoxyphenyl)diphenylcyclopentadienones,[5] some of which we had available from earlier work[6] and others which we have now unambiguously characterised (see later), we have made a systematic comparative study of the scope for dihydrosemibullvalene formation (and of subsequent rearrangements) in their thermal cycloaddition reactions with the dienophile (**1**).† For example, in the reactions of the tetraphenyl- and tetrakis-(*p*-methoxyphenyl)cyclopentadienones (**2a** and **f**) and the four isomers of bis-(*p*-methoxyphenyl)diphenylcyclopentadienone (**2b—e**) with (**1**) it was expected that the substituent MeO groups would provide useful 'labels' in ^{1}H or ^{13}C n.m.r. product analysis, complementing information derivable from the remaining characteristic[2a–d] non-aromatic proton signals, and in particular would facilitate interpretation of (i) COTR ring-closure modes in analogues (**5b—e**) where plane asymmetry, when present, allows alternative possibilities for cross-cyclisation; and (ii) the rearrangement of the resulting DHSBs [*e.g.* (**7**) ⇌ (**8**), (**10**) ⇌ (**11**) (Scheme 3)]. In connection with the isolation of *both* the dimethyldiphenyl-BCOD derivative (**4h**), and its electrocyclic tautomeric COTR (**5h**) as significant decarbonylation products of the stereoisomeric adducts (**3h**) (but not of analogous tetra-arylated BCODs in other than small amounts), and the striking absence of thermal lability in the DHSB (**9**) as compared with the tetra-arylated analogues, similar reactions of (**1**) with a variety of methyltriphenyl- and dimethyldiphenyl-cyclopentadienones (**2g—i** and **k**) also invited experiment. In particular, we have sought evidence that alkylated derivatives of the diradical intermediate (**A**) might be accessible from relevant DHSBs at higher temperatures. Finally, utilising 2,3,5-triphenyl-and 2,3,5-tri-t-butyl-cyclopentadienone (**2l** and **m**) we have examined the scope for cyclisation of the less heavily substituted COTRs (**5l** and **m**), since it is known[2b] that in the total absence of cyclo-octatriene substituents other reactions characterise the BCOD/COTR elements in analogues of (**4**) and (**5**). The results of this work together with an *X*-ray crystallographic study of the product of thermolysis of COTR (**5m**) will be reported separately.

Relative Reactivities and Products of Reaction of the Cyclopentadienones (**2**) *in Cycloaddition with the Dienophile* (**1**).—The tetracyclone (**2a**), the variously substituted methyl-

† Anderson *et al.*[7] describe a convenient synthesis of the tricyclononadiene analogues of (**1**)



a; R^{1-4} = Ph
b; $R^{1,4}$ = *p*-$MeOC_6H_4$, $R^{2,3}$ = Ph
c; $R^{1,4}$ = Ph, $R^{2,3}$ = *p*-$MeOC_6H_4$
d; $R^{1,3}$ = Ph, $R^{2,4}$ = *p*-$MeOC_6H_4$
e; $R^{1,2}$ = *p*-$MeOC_6H_4$, $R^{3,4}$ = Ph
f; $R^{1,4}$ = *p*-$MeOC_6H_4$
g; R^1 = Me, R^{2-4} = Ph
h; $R^{1,4}$ = Me, $R^{2,3}$ = Ph
i; $R^{1,3,4}$ = Ph, R^2 = Me
k; $R^{1,4}$ = Ph, $R^{2,3}$ = Me
l; $R^{1,3,4}$ = Ph, R^2 = H
m; $R^{1,2,4}$ = Bu^t, R^3 = H
n; $R^{1,4}$ = Ph, R^2R^3 = 1,8-$C_{10}H_6$

Scheme 1.

phenyl analogues (**2g**, **h**, **i**, and **k**), and the triphenyl compound (**2l**) mostly react to completion with the dienophile (**1**) (in excess) at convenient rates in boiling CCl_4 (6—70 h), facilitating relevant analysis of the mixed products as shown in Table 1. The terminally methylated cyclones (**2g** and **h**) react at least about an order of magnitude faster than the terminally phenylated compounds (**2a**, **i**, **k**, and **l**), and this is reflected in the isolation of both *exo*- and *endo*-adducts (**3g** and **h**) here, whereas for the terminally phenylated cyclones (**2a**, **i**, and **k**) reaction times to completion are sufficiently long that only the thermally more stable *exo*-adducts survive. The *exo* stereochemistry of the predominating bridge-carbonyl adduct, expected on the basis of precedent for cyclobutene–cyclone adduction,[8a] is confirmed for the *exo*-adducts (**3b**, **g**, and **k**) by observation of $^3J[^{13}C(=O), ^1H]$ n.m.r. spin-coupling to the *cis*,*endo*-ring-junction protons characteristic of *exo* but not of *endo* stereochemistry in compounds of this type.[8b] The *endo*-adducts can also be identified by their generally lower-field typical cyclobutane A_2X_2 ^1H n.m.r. multiplets,[2b,8c] and by more rapid (stereospecific cyclobutane σ-assisted[9]) decarbonylation in comparison with their *exo*-isomers (decomposition of which is very slow at 77 °C). *endo*-Adduct decarbonylation could give for example the COTRs (**5i** and **k**) directly; but more probably,[9] since traces of BCODs (**4a** and **k**) are detected, all stereoisomeric pairs of adducts give the same BCOD primarily, electrocyclic rearrangement to the relevant COTR (**5a**, **i**, or **k**) being rapid (see later). Interestingly, the triphenylcyclopentadienone (**2l**) gives only the BCOD (**4l**) and the COTR (**5l**) under these conditions, decarbonylation being unusually fast.

In boiling toluene, the tetracyclone (**2a**) and its bismethoxyphenyldiphenyl analogues (**2b**, **c**, and **e**) react *ca.* 3—3.5 times faster with the dienophile (**1**) than the least reactive cyclone used in this work, 2,3,5-tri-t-butylcyclopentadienone (**2m**). Under these conditions only the *exo*-bridge-carbonyl adducts (**3a**—**c**, **e**, and **m**) are isolated, together with *ca.* 20% of relevant COTRs (**5a**—**c** and **e**), the proportion of COTR (**5m**) rising to nearly 50% for the tri-t-butyl compounds (**3m**). [Interestingly, ^{13}C and ^1H n.m.r. spectrometry indicate restricted rotation for one of the bridgehead Bu^t groups in the *exo*-adduct (**3m**) and relief of steric occlusion could contribute to its more rapid decarbonylation.] It is significant however that both trisubstituted adducts (**3l** and **m**) are characterised by more rapid decarbonylation than any of the other compounds studied, recalling the fact that adducts of acecyclone (**2n**) are also decarbonylated exceptionally readily.[10] Electronic factors apart, these effects are suggestive of reduced substituent-group torsional interactions[11] during cheletropic bridge extrusion;[12] however, the trend towards increased *endo*-cycloaddition with less sterically demanding dienones (as reflected in increased decarbonylation product at 77 °C) implies, also, enhanced *endo*-addition with the dienone (**2l**).

For preparative-scale decarbonylations of tetra-arylated *exo*-adducts (**3**) at convenient temperatures, half-lives ($t_{\frac{1}{2}}$) are very similar, *e.g.* 18—20 h at 137 °C; but at this temperature the dimethyldiphenyl adduct *exo*-(**3h**) survives unchanged after 45 h, in striking contrast to its isomer *exo*-(**3k**) (with bridgehead phenyl rather than methyl groups), which is almost completely decarbonylated in 18 h ($t_{\frac{1}{2}}$ *ca.* 4.5 h); at 171 °C the relevant half-lives are *ca.* 4 h for the bridgehead-methylated adduct *exo*-(**3h**)

Table 1. Products of reaction of cyclopentadienones (**2**) with the dienophile (**1**) in CCl_4 and toluene at the b.p.

		Conc. (M)			% Yield			
Cyclone	Solvent	(**2**)	(**1**)	Reaction time (h)	*endo*-(**3**)	*exo*-(**3**)	BCOD (**4**)	COTR (**5**)
(**2a**)	CCl_4	0.12	0.18	54.4	*a*	87	*a*	Trace
	PhMe	0.16	0.25	19.6		77		22
(**2b**)	PhMe	0.11	0.17	27		74		21
(**2c**)	PhMe	0.07	0.10	24		78		22
(**2d**)	PhMe	0.12	0.24	22.5		68		23
(**2e**)	PhMe	0.16	0.22	24.5		75		22
(**2f**)	PhMe	0.12	0.13	45		75		20[b]
(**2g**)	CCl_4	0.12	0.18	6.5	15	84		
	PhMe	0.12	0.18	4	7[c]	81	10[c]	
(**2h**)	CCl_4	0.12	0.18	6.5	9[d]	88		
	PhMe	0.13	0.15	18		90	10	
(**2i**)	CCl_4	0.12	0.18	54.5		75		22
	PhMe	0.12	0.18	20		61		35
(**2k**)	CCl_4	0.10	0.15	66.5		71		23
	PhMe	0.07	0.09	43		44		50
(**2l**)	CCl_4	0.13	0.18	50			37[e]	
	PhMe	0.13	0.25	17			55[e]	
(**2m**)	CCl_4	0.66	0.82	73		57		11
	PhMe	0.13	0.18	70		33		48

[a] Traces of *endo*-(**3**) or BCOD (**4**) may have been present. [b] Includes *ca.* 4% dihydrosemibullvalene (**14**). [c] Estimated by n.m.r. [d] Not isolated; identified by n.m.r. [e] Combined yield based on dienone consumed.

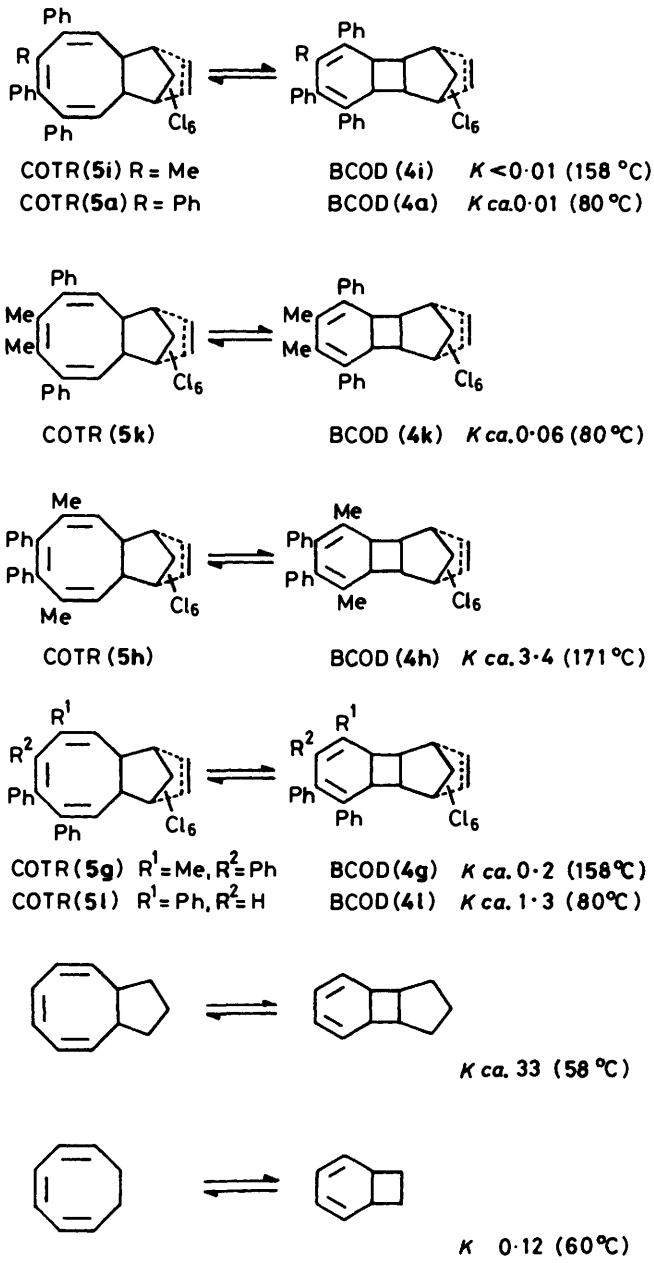
and *ca.* 0.75 h for its isomer *exo*-(**3k**). Similar contrast is seen in the decarbonylation rates for the isomeric methyltriphenyl adducts *exo*-(**3g**) and *exo*-(**3i**); after 30 h at 137 °C 35% of the adduct (**3g**) remains, but adduct (**3i**) is scarcely detectable. Under the same conditions, for comparison, the tetra-arylated adduct *exo*-(**3c**) is 80% decomposed. These results point to the effectiveness of having H or Me on the norbornenone vinylic carbon atoms in promoting decarbonylation reactivity when the bridgehead substituent is aryl. Relatively small activation differences, particularly in transition-state energies for compounds *exo*-(**3g**) and *exo*-(**3i**), are required to rationalise these effects, suggestive of stabilisation of incipient sp^2 bridgehead carbon by unsaturated (aryl) substituents.

As already indicated both *endo*- and *exo*-tetra-arylated adducts (**3**) give COTRs on decarbonylation with only traces of the immediate bicyclo-octadiene (BCOD) products (**4**), in contrast to the alkylaryl analogues where both valence tautomers are usually identifiable or isolable. In this connection it is well established[13] that cyclo-octa-1,3,5-triene (COTR) is thermodynamically preferred to its electrocyclic tautomer bicyclo[4.2.0]octa-2,4-diene (BCOD) by 1.5 kcal mol^{-1}* (see Scheme 2). In the present context we find that for the equilibrium COTR (**5h**) ⇌ BCOD (**4h**) K is *ca.* 3.4 at 171 °C, and for the slightly less substituted compounds COTR (**5l**) and BCOD (**4l**), K is *ca.* 1.3 at 80 °C; in these substituted systems the BCOD tautomer is therefore *more* stable than the COTR electrocyclomer, particularly for the less arylated compounds (by *ca.* 1.1 and 0.2 kcal mol^{-1}, respectively). These results may be usefully compared with the similar equilibrium for bicyclo-[6.3.0]undeca-2,4,6-triene (Scheme 2) [as a trimethylene-annelated cyclo-octatriene roughly similar in structural elements to the fused norborn-2-ene ring system characteristic of BCODs (**4**)], where we find K = 33 (58 °C) in favour of its more stable BCOD-type ring-closed tricyclic valence-tautomer tricyclo[5.4.0^{2,6}.0^{1,7}]undeca-8,10-diene ($\Delta G°$ *ca.* 2.3 kcal),[14] and a like preference for the bicyclic tautomer in 2,5-diphenylcyclo-octatriene.[15]

Clearly, imposition of conformational restraint on the cyclo-octatriene ring by *cis*-fusion to a saturated C_5 ring, with a necessarily eclipsed C-1/C-8 configuration, is COTR-destabilising relative to the BCOD electrocyclomer, K being an order of magnitude larger for example than for the *cis*-disubstituted but less constrained compound *cis*-7,8-dichlorocyclo-octa-1,3,5-triene[16] (that the fixed ring-fusion geometry for the bicyclic triene inhibits access to the most favoured, twist-boat conformation[17] for the cyclo-octatriene may be an important factor here). However our results show that this annelation effect is offset (and even reversed) by increasing substitution on the relevant sp^2 carbon framework (Scheme 2). If we assume the limit of detection of tetra-arylated BCOD (**4a**) is *ca.* 1% (^{1}H n.m.r.), its valence tautomer COTR (**5a**) is for example more stable by at least 3.2 kcal mol^{-1}. This relative substituent COTR-stabilising effect is most likely due to steric crowding, especially of several aryl groups, on the periphery of the cyclohexa-1,3-diene element in the BCOD tautomer, the aryl rings twisting out of the diene ring plane.[2c,15] Steric crowding may be relatively less consequential in the tub-like[18] COTR conformer; its stability can be augmented by increased conjugative interaction of methyl and phenyl groups with COTR π-bonds, especially by aryl groups at C-3 and C-6 where approximate aryl ring coplanarity with π(C-2/C-3) and π(C-6/C-7) is expected. This view is well supported by the result that in contrast to the BCOD (**4h**), the favoured of the tautomer pairs, its isomer, the BCOD (**4k**) (in which the Ph and Me groups are interchanged), is barely detectable in preparative samples of the COTR (**5k**); nevertheless on heating solutions of the COTR (**5k**) (80 °C) ^{1}H n.m.r. signals appropriate to the BCOD (**4k**) appear (*e.g.* at δ 1.76), the estimated equilibrium constant (K *ca.* 0.055) in favour of the COTR (**5k**) indicating a relative stabilisation of *ca.* 2.0 kcal mol^{-1}. Significantly also, the COTR (**5k**) includes the *cis*-but-2-ene group, rather than the more sterically demanding *cis*-stilbene element at π(C-4/C-5) in the COTR (**5h**). Similarly, whilst the COTR (**5g**) is the favoured of the isomer pairs, its tautomer the BCOD (**4g**) can be isolated and characterised (as the *N*-phenyltriazolinedione adduct)† K being *ca.* 0.2 here (158 °C) in contrast to the equilibrium position for the isomeric

* 1 kcal = 4.184 kJ.

† Akhtar *et al.*[2c] have reported the similar characterisation of a related bicyclo-octadiene derivative.



Scheme 2.

COTR (**5i**), where the BCOD (**4i**) is below the level of ^{1}H n.m.r. detection.

If the conjugative effect of substituent groups is minimised relative to steric effects as in the tri-t-butyl BCOD (**4m**) and COTR (**5m**), the latter should be strongly favoured, and we observe only the COTR (**5m**) as the product of decarbonylation of the adducts (**3m**), the equilibrium concentration of the BDOD (**4m**) again being very small.

The kinetic effect of substituents on the COTR ⇌ BCOD equilibrium may also be noted; for the COTR (**5l**) at 80 °C, k_1 is *ca.* 8.4×10^{-5} s^{-1} (k_{-1} *ca.* 6.3×10^{-5} s^{-1}); *cf.* $k_1 = 1.6 \times 10^{-5}$ s^{-1} at 20 °C for the unsubstituted COTR (Scheme 2) (k_1 is the rate coefficient of the forward and k_{-1} that of the backward reaction). The approach to equilibrium is even slower for the COTR (**5h**), requiring much higher temperature for observation of similar rates (k_1 *ca.* 7.5×10^{-4} s^{-1}, k_{-1} *ca.* 2.2×10^{-4} s^{-1} at 171 °C). The greater transition state steric demand in disrotatory electrocyclic change must be an important factor in bringing about reduced cyclisation rates for the COTRs (**5l** and **h**), although relative orbital coefficient changes at the termini of the triene system must also contribute.† Interestingly, equilibrium between the acecyclone-derived tautomeric COTR (**5n**) and BOCD (**4n**) (K = 2) is achieved in 5 d at room temperature;[21] this recalls the reduced steric effect of the 1,8-naphthylene substituent on decarbonylation rates of acecyclone adducts.[10]

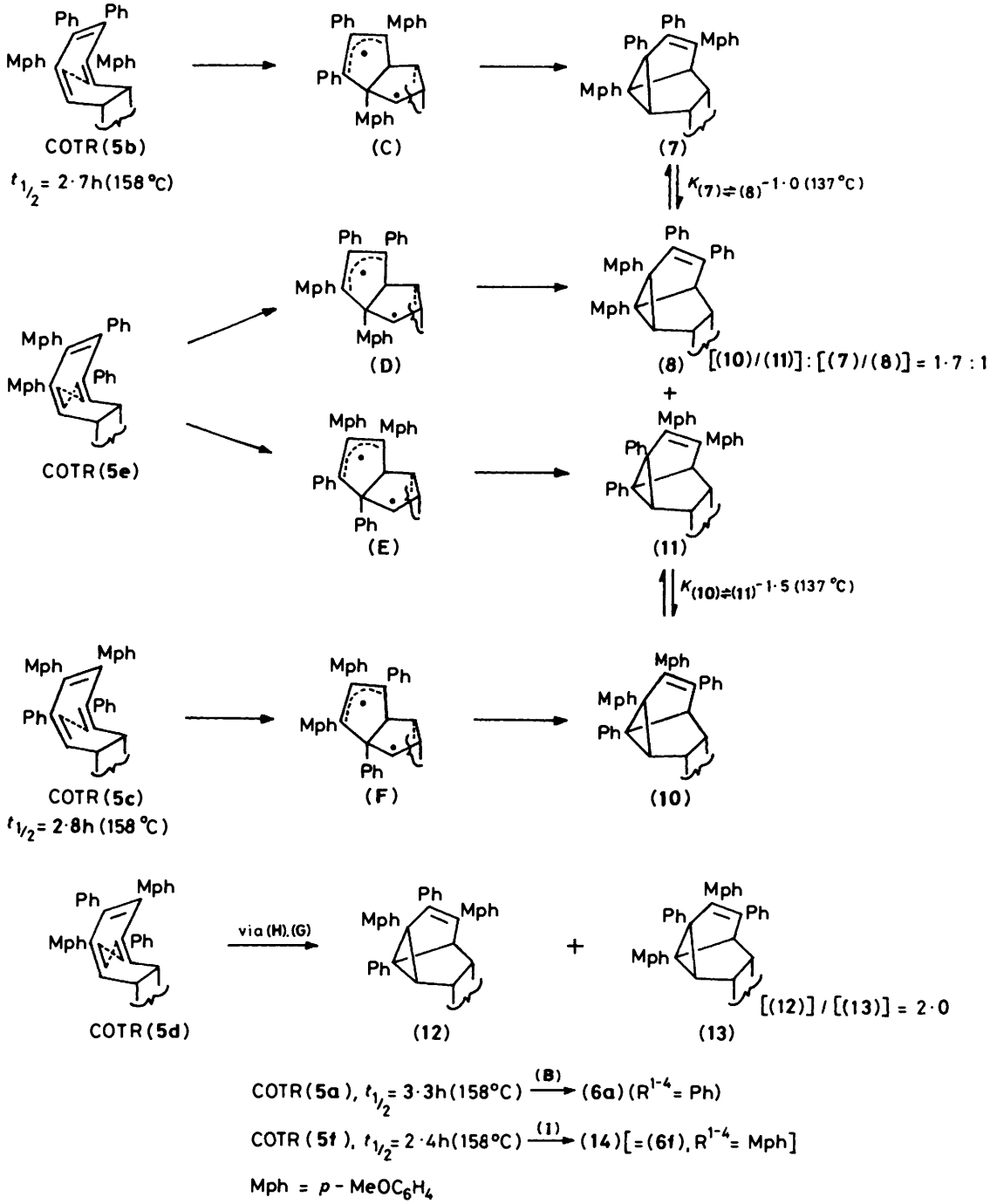
Isolation and Thermolysis of Arylated Cyclo-octatrienes (**5a**—**f**) *and their Cyclisation to Dihydrosemibullvalenes.* DHSB *Vinyl–Cyclopropane* (1,3-*Allylic*) *Rearrangements.*—Useful quantities of the various COTR derivatives (**5a**—**f**) can be made in 'one-pot' reactions between relevant cyclones (**2a**—**f**) and the dienophile (**1**), but in practice they are more conveniently isolated by thermolysis of *exo*- and/or *endo*-adducts (**3a**—**f**) in boiling 1,2-xylene (136—138 °C), the resulting mixtures of COTR (**5a**—**f**) and relevant DHSBs being easily separated (t.l.c. on silica gel–$AgNO_3$). Heating crystals of the stereoisomeric adducts (**3a**—**f**), or of the derived COTRs (**5a**—**f**), affords good yields of the relevant DHSBs and their rearrangement products (**7**)—(**14**) (Scheme 3), which are readily identified by characteristic[21] ^{1}H n.m.r. singlets for H-3 and H-8, and doublets J *ca.* 7 Hz) for H-2 and H-9.

Accordingly, heating the COTR (**5c**) (20 s at 260 °C) results in 60% conversion into a non-equilibrium mixture of approximately equal proportions of two isomers separable by t.l.c. into its components DHSBs (I), m.p. 203—204 °C, and (II), m.p. 186.5—188 °C; each isomer when separately heated (in 1,3-$C_6H_4Cl_2$ at 137 °C for 6 h) equilibrates towards the same final mixture, having a (I):(II) ratio of 1.5 ($\Delta G°$ *ca.* 0.3 kcal mol^{-1}). Under these conditions the rate of cyclisation of the COTR (**5c**) is sufficiently low that compound (II) is unambiguously detected (^{1}H n.m.r.) before its isomer (I) appears (and its concentration exceeds the equilibrium value after 6.5 h). The symmetry of the COTR (**5c**) implies that the DHSB (II) is the primary cyclisation product (**10**); compound (I) is therefore identified as its slightly more stable rearrangement isomer DHSB (**11**). Similar experiments with the symmetrical COTR (**5b**) to confirm that the DHSB (**7**) is the primary cyclisation product were inconclusive due to ^{1}H signal overlap, but there were slight indications that of the two isolated DHSBs (III) (m.p. 185 °C) actually does appear before its isomer (IV) (m.p. 234 °C), requiring that (III) is assigned structure (**7**) and (IV) structure (**8**). These structural assignments reverse those suggested earlier[2d] on the basis of limited n.m.r. evidence, but accord better with the data now available (see later).

The thermolysis experiments with the COTRs (**5b** and **c**) concurrently reveal that their cyclisations into DHSBs (**7**) [⇌(**8**)] and (**10**) [⇌(**11**)] are *irreversible* under these reaction conditions. In equilibrium conditions, whilst cycloreversion of the DHSB (**10**) potentially regenerates the symmetrical COTR (**5c**), which can equilibrate only with the DHSB (**10**), reversion of the DHSB (**11**) necessarily introduces the *unsymmetrical* COTR (**5e**); as we see later, cyclisation of the COTR (**5e**) gives besides the DHSB (**11**) the alternative ring-closure product DHSB (**8**), which is not detected as a significant product of COTR (**5c**) thermolysis.

Permuting the substituent order in the substrate COTR to an alternating sequence as in the COTR (**5d**) should in principle provide considerably more information and mechanistic insight since theoretically two alternative cross-cyclisation routes are now possible giving the DHSBs (**12**) and (**13**), and because of the

† Theoretical aspects of the cyclo-octatriene–bicyclo-octadiene conversion have received little attention; see however refs. 19 and 20 for discussion of the relevant hexatriene–cyclohexadiene conversion.



Scheme 3.

symmetry of the relevant intermediate diradicals (**A**), isomerisation of each of the DHSBs (**12**) and (**13**) should be degenerate. In addition, because neither can be converted into the other when cycloreversion to the COTR (**5d**) is unlikely, their proportions should reflect kinetic control. Consonant with this, thermolysis of the COTR (**5d**) gives only two isomeric products [(V) and (VI)], in unequal amounts, separable with difficulty and different from the DHSB/DHSB′ isomer-pairs (**7**)/(**8**) and (**10**)/(**11**). Thermolysis of the precursor of the COTR (**5d**), the *exo*-adduct (**3d**), significantly always gives a DHSB fraction rich in isomer (V) [ratio (V):(VI) = 2:1], and heating a mixture of isomer (V) containing 10% of isomer (VI) under isomerisation conditions (5 h; 136—138 °C) results in no change. These observations, in conjunction with ^1H and ^{13}C n.m.r. information, identify isomers (V) and (VI) as the expected DHSBs (**12**) and (**13**), respectively, with no easily accessible interconversion pathway. This result confirms again that DHSB cycloreversion to COTRs is unimportant, and indicates a kinetic preference (*ca.* 2 times) for cyclisation to the DHSB (**12**) rather than (**13**).

Attention is next directed to the COTR (**5e**); again alternative cyclisation modes might be expected to yield as immediate products the DHSBs (**8**) and (**11**) but here, in contrast with example COTR (**5d**), each kinetic product can rearrange

Table 2. ^{1}H N.m.r. methoxy-proton signals (δ_H; $CDCl_3$; Me_4Si) for tetrakis-*p*-methoxyphenyl- and bis-*p*-methoxyphenyldiphenyl-dihydrosemibullvalenes

Compound	*p*-MeOC$_6$H$_4$ position in DHSB[a]			
	C-6	C-5	C-7	C-4
(14)	3.60	3.67	3.72	3.79
(11) [= (I)]		3.68		3.83
(10) [= (II)]	3.62	3.69		
(7) [= (III)]			3.72	3.80
(8) [= (IV)]	3.59		3.72	
(12) [= (V)]	3.59			3.80
(13) [= (VI)]		3.68	3.73	

[a] For skeletal numbering see Scheme 1, structure (**6**).

Table 3. ^{1}H N.m.r. cyclopropane (8-H) signals (δ_H; $CDCl_3$; Me_4Si) for tetrakis-*p*-methoxyphenyl-, tetraphenyl-, and bis-*p*-methoxyphenyl-diphenyl-dihydrosemibullvalenes

Compd.	8-H	R^4 R^3 (Cyclopropane subst.)		R^2 R^1 (Vinylic subst.)	
(6)	3.22	Ph	Ph	Ph	Ph
(11) [= (I)]	3.22	Ph	Ph	Mph[a]	Mph
(10) [= (II)]	3.16	Ph	Mph[a]	Mph	Ph
(7) [= (III)]	3.13	Mph	Ph	Ph	Mph
(12) [= (V)]	3.12	Ph	Mph	Ph	Mph
(13) [= (VI)]	3.12	Mph	Ph	Mph	Ph
(8) [= (IV)]	3.08	Mph	Mph	Ph	Ph
(14)	3.03	Mph	Mph	Mph	Mph

[a] Mph = *p*-MeOC$_6$H$_4$.

towards equilibrium with its 1,3-shift isomer, respectively the DHSBs (**7**) and (**10**). Accordingly, thermolysis of the COTR (**5e**) (60 s; 250 °C) gives a crude product exhibiting at least six ^{1}H n.m.r. MeO signals in the δ 3.5—4.0 region [including two from the uncyclised COTR (**5e**)]; more significantly four sharp cyclopropane singlets in the range δ 3.07—3.19 show that essentially only four dihydrosemibullvalenes are present. Separation of this mixture into convenient amounts of its constituent DHSB/DHSB′ isomers for identification being impractiable, recourse was made to more detailed ^{1}H and ^{13}C n.m.r. analysis, and to comparison of the product mixture [freed from unchanged COTR (**5e**)] with an artificial mixture of the similar thermolysis products of the COTRs (**5b** and **c**) containing DHSB isomer-pairs (**7**)/(**8**) and (**10**)/(**11**). The artificial mixture ^{1}H signals perfectly match in chemical shift, if not in relative intensity, those of the COTR (**5e**) thermolysis product, each spectrum exhibiting four characteristic pairs of MeO singlets (Table 3) and four sharp cyclopropane (H-8) singlets (Table 4), all signals exactly coinciding in the two spectra. For the COTR (**5e**) product, equal abundances within the DHSB isomer pairs (**7**)/(**8**) and (**10**)/(**11**), with a relative composition ratio [(**10**)/(**11**)]:[(**7**)/(**8**)] *ca.* 1.7:1, is indicated by relative (H-8) signal intensities. The kinetically preferred product from the COTR (**5e**) is therefore the DHSB (**11**), which is also the thermodynamically more stable of the interconverting isomers (**10**) and (**11**). This result is entirely consistent with irreversible COTR (**5e**) cyclisation into the expected DHSBs (**8**) and (**11**), which rapidly but only partially equilibrate to their respective 1,3-shift DHSB isomers (**7**) and (**10**) under brief thermolysis conditions (Scheme 3).

^{1}H *And* ^{13}C *N.m.r. Correlations for the* DHSBs (**6**)—(**14**).—The inherent product-identification difficulties in a mixture of equilibrating tetra-arylated DHSBs [*e.g.* (**7**), (**8**), (**10**), and (**11**)] are circumvented by ^{1}H and ^{13}C structure correlations. For the isomer pairs (I)/(II), (III)/(IV), and (V)/(VI), the *p*-methoxyphenyl MeO group and cyclopropane (H-8) signals* show the largest δ_H variation between isomers, other ^{1}H signals changing very little. Comparison of these signals with those for the tetraphenyl-DHSB (**6a**) and the tetrakis-*p*-methoxyphenyl analogue (**14**) in conjunction with the chemical evidence leads to the self-consistent correlations shown in Tables 2 and 3.

Complementary structural validation is found in the ^{13}C n.m.r. spectra of DHSB analogues (Table 4), the *p*-methoxyphenyl group =^{13}C(H) nuclei giving signals well separated from those due to the Ph groups. In particular, δ_C values for the *meta*-carbon nucleus in the *p*-methoxyphenyl groups in the isomer pairs (I)—(VI) fall characteristically into two of the four narrow frequency bands found for this nucleus in the tetrakis-*p*-methoxyphenyl-DHSB (**14**), and a pattern is found resembling that of the ^{1}H MeO group resonances (Table 2). For example the DHSBs (III), (IV), and (VI) all exhibit a signal at δ *ca.* 112.8 corresponding to each having a *p*-methoxyphenyl substituent at cyclopropane C-7 in the DHSB. Similar correlations are evident for the *p*-methoxyphenyl *ortho*-carbon nuclei, which resonate in four frequency bands at lower field (δ 127.53—131.48) in accord with the π-donor effect for MeO being ineffective at this aromatic position relative to the *meta*-position. In fact the ^{13}C resonances for all =^{13}C(H) aromatic nuclei in the tetra-arylated DHSBs discussed form a completely self-consistent set in which δ_C values depend only on the relative positions of the aryl substituents on the DHSB framework. However no simple pattern can be discerned for the MeO ^{13}C nuclei.

^{13}C Resonances for the DHSB framework itself might be expected to show some systematic changes with the degree of (π-donor) methoxyphenylation, but only the protonated C-3 bridgehead ^{13}C nucleus shows any simple regular change (Table 5), its resonance moving upfield with increasing *p*-methoxyphenyl substitution, particularly at the adjacent vinylic (C-4) and cyclopropane (C-7) positions.

*Formation and Rearrangement of Dihydrosemibullvalene Derivatives from Dimethyldiphenyl-, Methyltriphenyl-, and Triphenyl-*COTRs (**5g**—i).—Only the DHSB (**9**) was originally identified[2] in the thermolysis products of the adducts (**3h**), the BCOD (**4h**), and the COTR (**5h**) (Scheme 4), and further careful analysis of minor products from similar thermolyses confirms that no isomeric DHSB intrudes; however, a bridged peroxide (**15**) was isolated, identical with the aerial photo-oxygenation product of the BOCD (**4h**) in sunlight[21] [and analogous to the bridged photoperoxide derived by direct (254 nm) or eosin-sensitised oxygenation of a related dimethyldiphenylcyclohexadiene derivative, *viz.* the decarbonylation product from cycloaddition of the cyclone (**2h**) to norbornene[24]]. A second, less abundant product isolated has been less well characterised but may be an isomeric endoperoxide. Consistent with these peroxide structures, further irradiation of their solutions and silica gel chromatography gives a mono-oxygenated compound assigned structure (**16**) on the basis of ^{1}H n.m.r., i.r., and mass spectrometry; compound (**16**) is believed to be derived from the

* The abnormally low-field ^{1}H–^{13}C n.m.r. signals for cyclopropane nuclei (H-8/C-8) in these compounds [$J(^{13}C,^1H)$ = 157 Hz][24] finds analogy in data for a benzo-annelated dihydrosemibullvalene having a single cyclopropane phenyl substituent.[22] The relative shielding of H-8 with increasing cyclopropane β-(*p*-methoxyphenyl)ation does however parallel theoretical expectation for substituent π-donor effects in cyclopropane chemistry.[23]

Table 4. ^{13}C δ values ($CDCl_3$; Me_4Si) for aromatic (=CH) nuclei of tetra-arylated dihydrosemibullvalene derivative

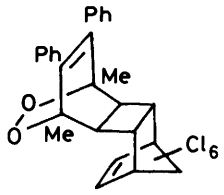
	Dihydrosemibullvalene derivative							
	(6)	(11) (I)	(10) (II)	(7) (III)	(8) (IV)	(12) (V)	(13) (VI)	(14)
7-Mph[a]				112.9	112.9		112.8	112.7
6-Mph			113.0		113.1	113.0		113.0
5-Mph		113.3	113.3				113.3	113.3
4-Mph		113.9		113.9		113.9		113.8
7-Ph	125.9	125.7	125.7			125.7		
6-Ph	126.4[b]	126.3		126.3			126.3	
7-Ph	126.4[b]	126.5	126.5			126.5		
5-Ph	126.8			126.7	126.7	126.6		
7-Ph	127.3	127.3	127.3			127.3		
7-Mph				127.6[b]	127.6[b]		127.5	127.5
4- or 6-Ph	127.5[b]	127.5	127.5	127.6[b]	127.6[b]		127.6	
5-Ph	127.9			127.9	127.9	127.9		
4-Ph	128.5		128.5		128.5		128.5	
5-Ph	128.8			128.9	128.9	128.9		
4-Ph	129.0		129.0		129.1		129.1	
5-Mph		130.1	130.0				130.0	130.0
4-Mph		130.3		130.3		130.3		130.2
6-Ph	130.4	130.5		130.5			130.5	
6-Mph			131.4		131.5	131.5		131.5
Signals expected	12	10	10	10	10	10	10	8
Signals observed	10	10	10	9	9	10	9	8

[a] MpH = *p*-$MeOC_6H_4$. [b] Two signals coincide.

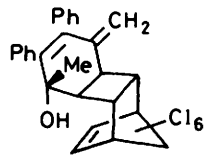
Table 5. ^{13}C N.m.r. shift data (δ_C; $CDCl_3$; Me_4Si) for bridgehead (C-3) and cyclopropyl (C-6, -7, and -8) nuclei in tetra-arylated dihydrosemibullvalene derivatives

Compound	R^1	R^4	C-3	R^2	R^3	C-6	C-7	C-8[a]
(6)	Ph	Ph	63.5	Ph	Ph	58.5	57.2	40.0
(10) [= (II)]	Ph	Ph	63.6	Mph	Mph	57.8	57.1	40.3
(13) [= (VI)]	Ph	Mph	63.6	Mph	Ph	59.6	56.7	39.8
(8) [= (IV)]	Ph	Mph	63.6	Ph	Mph	57.3	56.8	40.4
(11) [= (I)]	Mph	Ph	63.7	Mph	Ph	57.1	56.6	39.7
(12) [= (V)]	Mph	Ph	63.7	Ph	Mph	58.0	56.7	40.3
(7) [= (III)]	Mph	Mph	63.8	Ph	Ph	57.9	56.3	39.8
(14)	Mph	Mph	63.8	Mph	Mph	57.2	56.1	40.0

[a] For numbering see Scheme 1, structure (6).



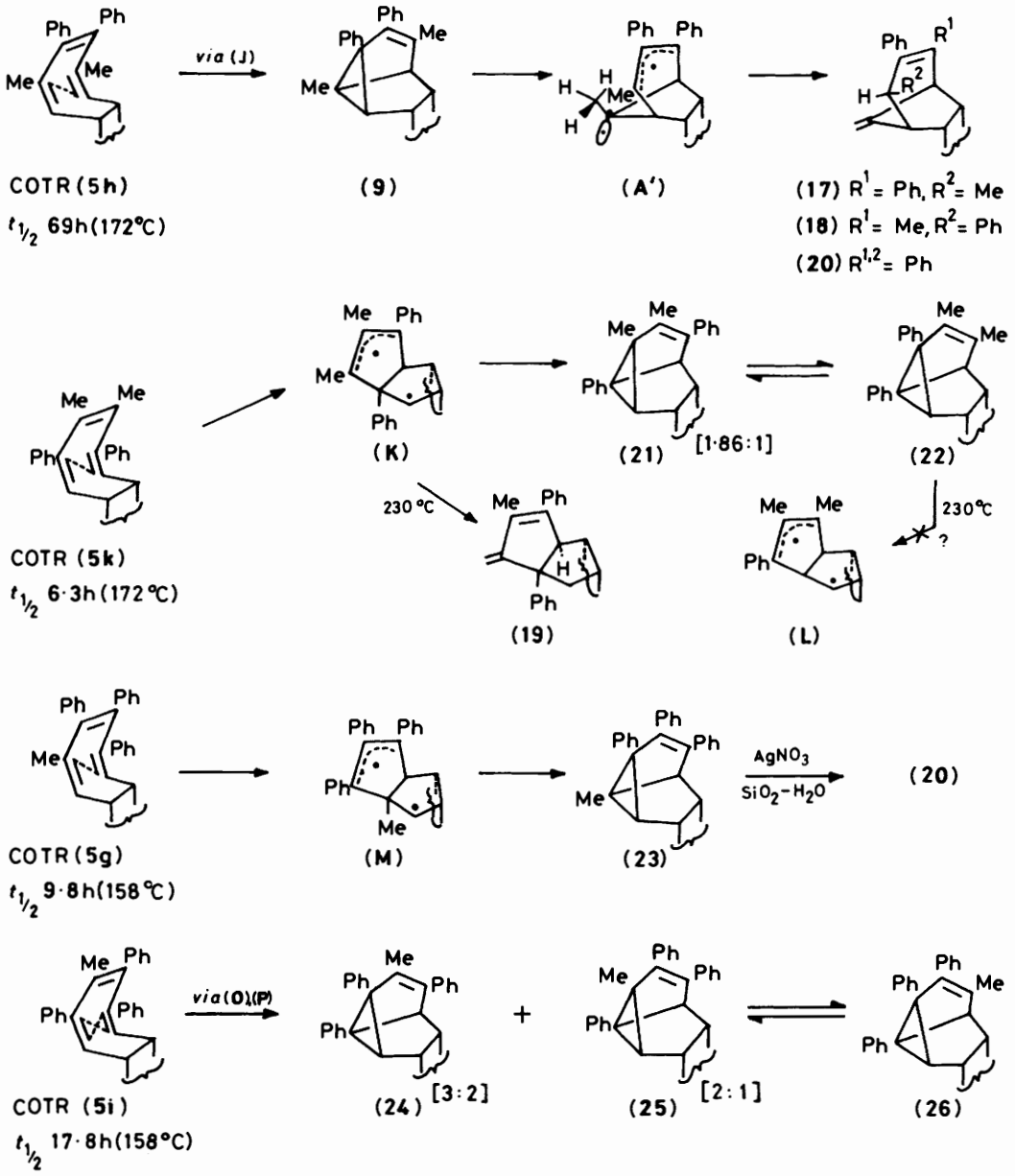
(15)



(16)

diol corresponding to reductive ring-opening of peroxide (**15**), which can be tentatively identified in the crude photolysis product but is dehydrated on silica gel.

However, heating crystals of the DHSB (**9**) (120 s; 250 °C) followed by extensive purification gives, besides unchanged (**9**), an air-sensitive gum, assigned structure (**17**). Here ^1H n.m.r. analysis indicates the presence of the DHSB (**9**) and the isomeric triene (**17**) in 1:1 ratio; a set of signals is observed of variable relative intensity in different thermolysis runs analogous to those of the triene (**17**) but with a lower-field Me singlet δ (1.72) rather than the high-field doublet (δ 0.87, *J* 7 Hz) characteristic of triene (**17**), suggestive of the prototropic tautomer (**18**) of the triene (**17**) (but which is not easily isolated). The fixed DHSB stereochemistry precludes a 1,5-homodienyl sigmatropic shift[25] in (**9**) as the source of (**17**), and cyclopropane ring-scission to a diradical (**A'**) (Scheme 4) analogous to **A** in Scheme 1 is therefore implicated; a 1,4-H shift (or even intermolecular H transfer) to the allylic radical termini accommodates the appearance of the triene (**17**) and its prototropic tautomer (**18**).[26] Such a thermal cyclopropane ring-strain dissipation pathway is not accessible in the tetra-arylated DHSBs and cannot be envisaged for either the DHSB (**21**) or the DHSB (**22**) potentially accessible from the COTR (**5k**) (Scheme 4); in fact solution thermolysis of the COTR (**5k**) (172 °C) gives the expected pair of 1,3-shift-interconverting DHSBs, (**21**) and its isomer (**22**). These are easily differentiated by the greater separation and δ values for the Me ^1H singlet resonances in the isomer (**21**) (δ 0.97 and 1.94), as compared with these signals in the isomer (**22**) (δ 1.28 and 1.76) with both Me groups vinylic; the greater cyclopropane proton (H-8) deshielding in the DHSB (**22**) (δ 2.84) than in the isomer (**21**) (δ 2.24), concomitant with two proximate Ph groups in the former, together with a similar effect at the bridgehead signal [H-6: (**21**), δ 3.88; (**22**), δ 3.52], provides adequate structural confirmation. Equilibration of either (**21**) or (**22**) (138 °C; 6 h) gives an identical mixture of isomers with composition ratio [(**21**)]:[(**22**)] 1.86:1 [isomer (**21**) being thermodynamically favoured, $\Delta G°$ *ca.* 0.5 kcal



Scheme 4.

mol^{-1}], and is fast in comparison with H-atom transfer, which is slow at 196 °C, *e.g.* for the DHSB (**9**). Briefly heating crystals of either (**21**) or (**22**) at rather higher temperatures (230 °C) gives the same product from each, containing unchanged DHSBs, (**21**) and (**22**) together with a further isomeric compound having spectroscopic properties consistent with the methylenecyclopentene structure (**19**). Compound (**19**) is rationally the H-atom transfer product derived from the diradical intermediate (**K**), the appearance of which illustrates an alternative cyclopropane bond-scission in the DHSB (**21**). No isomeric methylenecyclopentene which could arise from the DHSB (**22**) by this mechanism [*via* intermediate (**L**)] can be detected; this possibly reflects destabilising steric effects relative to the intermediate (**K**) and the relative ease of H transfer, which, if intramolecular, is confirmed by models as more favourable in the intermediate (**K**). The intermediate (**K**) is also that considered to arise directly in the cross-cyclisation of the COTR (**5k**) (see later), but both DHSBs (**21**) and (**22**) accumulate in the thermolysis product before compound (**19**) is detectable, and if diradicals such as (**K**) or (**L**) play a role in the COTR ⟶ DHSB conversions, H-atom transfer reactions must be generally slow in comparison with cyclisation in the temperature ranges employed.

Thermolysis of the methyltriphenyl COTR (**5g**) (215—230 °C) on the other hand gives *only* the DHSB (**23**) (of the two possible), and at higher temperatures the ring-scission/H-transfer product (**20**) intrudes; this behaviour is analogous to that of the DHSB (**9**). The rearrangement (**23**) ⟶ (**20**) is also catalysed by $AgNO_3$–silica gel at 25 °C; whilst it is well known that Ag^I cations catalyse rearrangements of strained-ring systems,[27] and recent reports describe Ag^I-cation-catalysed rearrangements of highly strained methyldiphenylcyclopropane compounds,[28] the low-temperature-catalysed conversion of the DHSB (**23**) is an isolated instance in the present context.

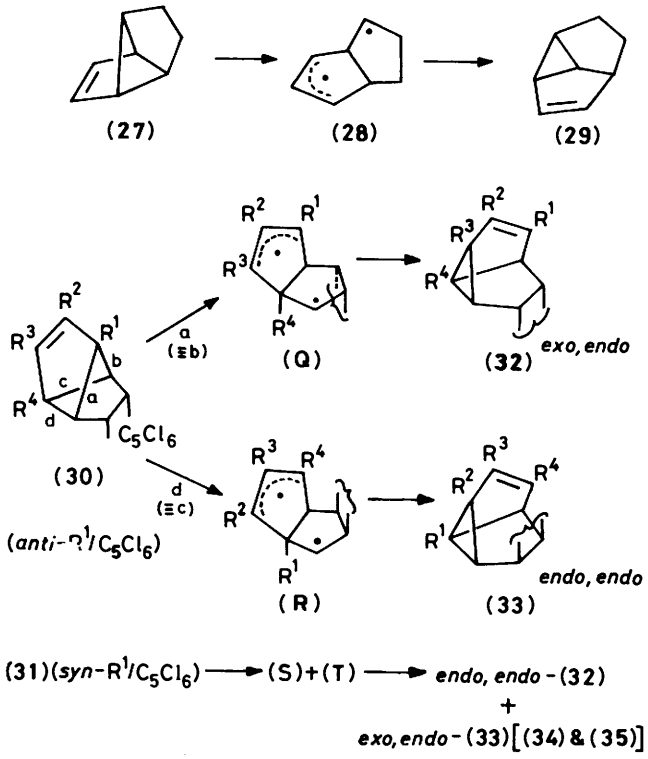
Thermolysis experiments with the isomeric methyltriphenyl COTR (**5i**) more closely model expectation in giving besides the DHSB (**24**) (the 1,3-shift rearrangement of which is degenerate), two other equilibrating isomers, the DHSBs (**25**) and (**26**), in the ratio 3:2:1, respectively. Neither of the alternative cyclisation

pathways shows kinetic preference here. [The equilibrating DHSBs (**25**) and (**26**) are also those expected, but not observed in the thermolysis of the COTR (**5g**), where only the alternative, degenerately rearranging product (**23**) is seen.] Differential Me ^{1}H chemical shifts and relative δ values for cyclopropane and bridgehead singlets again serve to distinguish the DHSBs (**25**) and (**26**) [*cf.* (**21**) and (**22**)]. The thermodynamically preferred isomer of the equilibrating pair, the DHSB (**25**) (by *ca.* 0.7 kcal mol^{-1}), is that which incorporates a stilbene element, showing some resemblance in other respects also to the more stable isomer DHSB (**21**) in the diphenyldimethyl-DHSB equilibrating pair (**21**) ⇌ (**22**), with identical Me and Ph cyclopropane substitution.

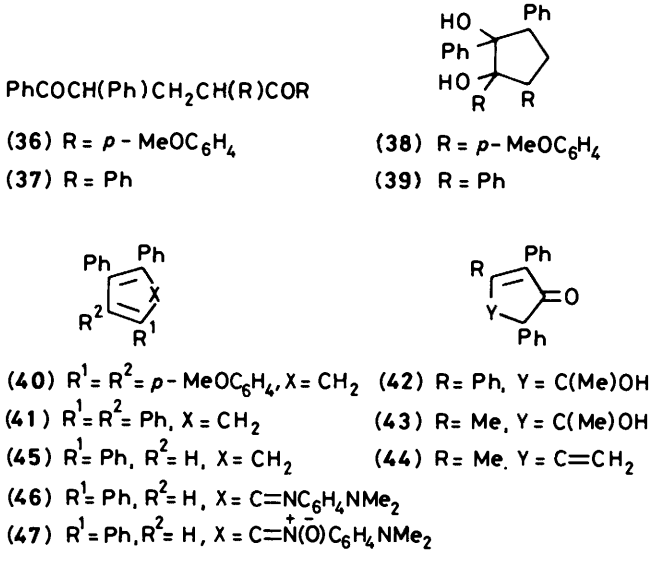
^{1}H *N.m.r. Correlations for Methyltriphenyl and Dimethyldiphenyl Dihydrosemibullvalene Derivatives.*—Unlike the methoxyphenyl-phenyl-substituted series of compounds (**6**)—(**14**), there appears to be no simple correlation (*e.g.* of Me chemical shift with substituent Me and Ph position) for the methylated DHSB series (**21**)—(**26**). However, systematic downfield shifts to higher δ_H values do occur for the cyclopropane proton (H-8) and the allylic bridgehead (H-3) signals with increased proximate phenylation, allowing deduction of a self-consistent structural correlation with spectroscopic and chemical evidence. Comparing the methyltriphenyl series (**23**)—(**26**) with the tetraphenyl compound (**6a**) gives the data in Table 6 for the increments in downfield shift (Δδ) for H-8 and H-3 as deshielding Ph groups are interchanged with Me groups at various positions. By using this information, the appropriate chemical shifts for H-8 and H-3 in the related dimethyldiphenyl compounds (**9**), (**21**), and (**22**) can be calculated and compared with the values observed (Table 6), allowing unambiguous identification of the DHSB (**9**).

COTR *Cyclisation and* DHSB *Rearrangement: Mechanistic Considerations.*—We have suggested that a possible reason for the ready thermal ring closure of the COTR derivatives (**5a**—**k**) to DHSBs resides in the concomitant relief of non-bonded steric interactions between substituents in a formal $[{}_\pi4_a + {}_\pi2_a]$ symmetry-allowed[4] intramolecular cycloaddition. It is probable that steric effects are important since 2,3,4,5-tetraphenylcyclo-octatriene is not cyclised to a dihydrosemibullvalene under comparable conditions;[29] annelation of the reacting system to give a bicyclo[2.2.1]heptene or bicyclo[2.2.2]octane ligament appears to be necessary together with extensive substitution of the cyclo-octatriene framework. (In the absence of cyclo-octatriene substituents, reactions ensue from stereoisomers of the bicyclo-octadiene tautomers in the norbornene annelated systems, *e.g.* dimerisation, and cyclohexadiene–alkene $[{}_\pi4_s + {}_\pi2_s]$ intramolecular cycloaddition to a symmetrical cage framework.[2b]) A steric component arising from the COTR substituents should be reflected in the relative cyclisation rates. In fact the half-lives for all the tetra-arylated COTRs (**5a**—**c** and **f**) are similar at 158 °C (Scheme 3), in the range 2.4—3.3 h, contrasting with the comparatively diminished cyclisation rates of the methyltriphenyl and dimethyldiphenyl compounds at this temperature (Scheme 4); for example $t_{\frac{1}{2}}$ for the methyltriphenyl compounds (**5g** and **i**) increases by factors of *ca.* 3 and *ca.* 6, respectively, in comparison with the tetraphenyl compound (**5a**), but the isomeric dimethyldiphenyl analogues (**5k** and **h**) require higher temperatures for convenient measurements ($t_{\frac{1}{2}}$ *ca.* 6.3 and *ca.* 69 h at 171 °C). The trend of these results is as expected for a correlation of ring-closure rate with steric effects in the transition state; but the kinetic ratio of 10:1 for cyclisation of dimethyldiphenyl COTRs (**5k** and **h**), and the small but systematic increase in cyclisation rate with increasing *p*-methoxyphenyl substitution in the series of COTRs (**5a**—**c** and **f**) is difficult to rationalise on this basis alone, as in the 2:1 kinetic preference for cyclisation of the COTR (**5d**) into the DHSB (**12**) rather than DHSB (**13**), and the similar kinetic partitionining (*ca.* 1.7) in favour of the DHSB (**11**) [⇌(**10**)] rather than the DHSB (**8**) [⇌(**7**)] from the COTR (**5e**). If, however, COTR cyclisations are not concerted intramolecular $[{}_\pi4_a + {}_\pi2_a]$ cycloadditions, but involve diradical intermediates, the overall reaction rates and kinetic partitioning correlate well with, for example, the degree of *p*-methoxyphenylation of the delocalised allylic elements in the tetra-arylated intermediates (**B**)—(**H**) (Schemes 3 and 4), if, as expected, *p*-methoxyphenyl groups confer greater radical stability than Ph groups when steric differences are minimised. Similarly the attenuated arylation of the intermediates (**M**), (**O**), and (**P**) for methyltriphenyl-COTR cyclisations (**5g** and **i**) could account for the relatively reduced rates, and *partially* also for the appearance of the DHSB (**23**) alone from the COTR (**5g**). This implies that closure to the intermediate (**M**) is preferred (by *ca.* 3—4 kcal mol^{-1}) over the alternative cyclisation to a diradical species where a terminal allylic Me group replaces one of three Ph groups [probably too small a structural change to account wholly for the exclusive formation of the intermediate (**M**)]. For the COTR (**5i**) the allylic element from both cyclisation modes, leading to equipartitioning between the DHSBs (**24**) and (**25**), is methyldiphenyl-substituted, the intermediates (**O**) and (**P**) being closely similar. For the dimethyldiphenyl COTRs (**5h** and **k**), in contrast, the relative cyclisation rates are the *reverse* of those expected in terms of allylic radical stabilisation, the fastest reacting *via* the intermediate (**K**) with a single terminal allylic phenyl substituent as compared with two phenyl substituents in the analogous intermediate (**J**) from the sluggish COTR (**5h**)! Significantly the COTR (**5h**) differs from *all* the other examples investigated in having both double bonds involved in the primary cross-cyclisation step substituted with Me [as opposed, for example, to each having substituent Ph groups in the COTR (**5k**)], and allylic radical stabilisation in the intermediate must be offset by some other factor affecting the initial ring closure. It is interesting too that the COTR (**5h**) is also relatively sluggish in tautomerising to the BCOD (**4h**). Rationalisation of these effects might be found in the differential π-electron populations (π-polarisation[30]) of the $MeC_\alpha{=}C_\beta H$ propene elements and $PhC_\alpha{=}C_\beta$ styrene elements present in the COTR (**5k**) (with its strongly enhanced β-electron population[31]) and a similar explanation might also account for the exclusive formation of the DHSB (**23**) from the COTR (**5g**).

The intermediacy of bicyclo[3.3.0]octa-2,6-diene-4,8-diyl in the thermal rearrangements of cyclo-octatetraene and its isomer, tricyclo[3.3.0.0^{2,6}]octa-3,7-diene, has been discussed;[32a] and the related bicyclo[3.3.0]oct-3-ene-2,6-diyl (**28**) [the proto-analogue of the intermediates (**B**)—(**P**)] could be involved in the analogous tricyclo[3.3.0.0^{2,6}]oct-7-ene–dihydrosemibullvalene conversion (**27**) ⟶ (**29**) (150 °C).[32b] (Orbital symmetry constraints preclude concerted interconversions in systems of this type.[32c]) The possibility that cyclisation of the cyclo-octatriene derivatives (**5**) could concomitantly lead to derivatives of the tricyclic system (**27**), and its consequences for DHSB-product isomerism, must therefore be considered. Because of the fixed stereochemical features imposed on the COTRs (**5**) by the *cis*-fused *endo*-hexachloronorbornene ligament, initial π–π cross-cyclisation from an appropriate twist geometry of the COTR ring can in principle lead to pairs of isomeric tricyclo-octene derivatives, *e.g.* (**30**) and (**31**), depending on the substituents R$^{1-4}$ (Scheme 5). Depending on subsequent cyclobutane bond-scission regioselectivity in production of the intermediate diradical analogues of the species (**28**), the isomer (**30**) can spawn either of two stereoisomeric intermediates (**Q**) and (**R**) [(**S**) and (**T**) from (**31**)], and finally two pairs of dihydrosemibullvalenes identical in substituent sequence but differing in stereochemistry with respect to the



Scheme 5.



norbornene ring fusion [(32)—(35)] may result. The same consequence would follow if the proposed intermediates (**B**)—(**P**)] (Schemes 3 and 4) reversibly collapsed to derivatives of the tricyclic system (**27**) before subsequent *irreversible* cyclisation to DHSB compounds. However we have found no evidence for other than the *exo*-fused series of DHSB compounds, *e.g.* for the bridge bisdechlorodimethoxy analogue of the DHSB (**6a**) the stereochemistry is confirmed by *X*-ray crystallographic data.[2d] Minor undetected products which could arise from relevant analogues of the species (**R**) and (**S**) excepted, our results best accord with cross-cyclisation from the COTR conformation depicted in (**5**) as a source of bicyclo[3.3.0]octenediyl intermediates (**B**)—(**P**) which specifically (1,3) cyclise to dihydrosemibullvalenes.

Relevant to the intermediacy of diradical intermediates (**A**) (Scheme 1), vinyl–cyclopropane 1,3-allylic isomerisations in simpler bicyclic systems (bicyclo[3.1.0]hex-2-enes)[33a] also proceed *via* allylically stabilised diradicals resulting from endocyclic cyclopropane ring-scission under conditions similar to those for isomerisation of for example, the DHSB (**7**) [⇌DHSB (**8**)]. Insofar as our results with methylated DHSBs can be taken to reflect the general behaviour of DHSB systems discussed here, the intermediate (**A**) and its analogues provide the simplest rationale for both DHSB isomerisation and disproportionation reactions; parallel observations with alkyl-aryl-substituted benzosemibullvalenes [made from, for example, cyclopentadienones (**2k** and **g**) by cycloaddition with benzocyclobutene[33b]] may be similarly rationalised, and the unsubstituted diradical analogue of (**A**) could be invoked to account for the *inferred* thermal isomerisation of the dimethylated dihydrosemibullvalene *exo*-6,*endo*-7-dimethyltricyclo-[3.3.0.0^{2,8}]oct-3-ene (at 350 °C) to its *endo*-6,*exo*-7-*dimethyl stereoisomer*.[33c]

Cyclopentadienone Synthesis.—A considerable number of aryl- and alkylaryl-cyclopentadienones (or their dissociating dimers) have been well characterised,[3c] but bis-(*p*-methoxyphenyl)diphenyl- and dimethyldiphenyl-cyclopentadienones (**2d**, **e**, and **k**) are less well known.

Condensation of *p*-methoxybenzil and 1-(*p*-methoxyphenyl)-3-phenylpropan-2-one (in $PhCH_2\overset{+}{N}Me_3\bar{O}Me$–MeOH) gives a mixture of cyclopentadienones (**2d** and **e**) (m.p. 190—198 °C; ^{1}H n.m.r. shows 4 OMe singlets at 3.74—3.75) from which, by repeated recrystallisation, the dienone (**2d**) (black, m.p. 217—218 °C) can be isolated. To identify securely the isomers (**2d** and **e**), we have made the cyclopentadienone (**2e**) by an unambiguous route following Becker's method,[34] from 1,2-diphenylprop-2-enone[35] and deoxyanisoin[36] *via* the mixture of diketones (**36**) and (**37**). Cyclisation of this product (Zn–HOAc) gives 1,5-bis-(*p*-methoxyphenyl)-2,3-diphenyl- and 1,2,3,5-tetraphenyl-cyclopentane-1,2-diols (**38**) and (**39**), which on dehydration (H^+–HOAc) give an easily separable mixture of 1,2-bis-(*p*-methoxyphenyl)-3,4-diphenyl- and 1,2,3,4-tetraphenyl-cyclopentadienes (**40**) and (**41**). Condensation of the cyclopentadiene (**40**) with *p*-nitroso-*N*,*N*-dimethylaniline followed by hydrolysis of the anil gives the bis-(*p*-methoxyphenyl)diphenylcyclopentadienone (**2e**) (dark violet, m.p. 171—172 °C). Broser *et al.*[37] have identified the condensation product of *p*-methoxybenzil and *p*-methoxyphenylpropanone (black, m.p. 212—214 °C) as the cyclopentadienone (**2e**) but this compound appears from its m.p. to be in reality impure ketone (**2d**).

Of the isomers of methyltriphenylcyclopentadienone (**2g** and **i**), only (**2g**) appears to be known;[38] however, acid-catalysed dehydration of 4-hydroxy-4-methyl-2,3,5-triphenylcyclopent-2-enone (**42**) readily gives the cyclopentadienone (**2i**). Similar strategy for the synthesis of the dimethyldiphenylcyclopentadienone (**2k**) from 4-hydroxy-3,4-dimethyl-2,5-diphenylcyclopent-2-enone (**43**) affords the methylenecyclopentenone (**44**) as the major product, and dehydration of the hydroxycyclopentenone (**43**) with $SOCl_2$–C_5H_5N gives the cyclopentadienone (**2k**) [with 33% methylenecyclopentenone (**44**)]. Unlike its dimerising isomer, the cyclopentadienone (**2h**),[39] the cyclopentadienone (**2k**) exists in the monomeric form at 20 °C.*

The 2,3,5-triphenylcyclopentadienone (**2l**) can be made by hydrolysis of the anil (**46**). However, we find, besides the purple anil (**46**) (m.p. 178—179 °C) described by Dilthey,[40] the *N*-oxide derivative (**47**) (blood-red, m.p. 177—179 °C) is formed. Acid-catalysed hydrolysis of both (**46**) and (**47**) however gives the required cyclopentadienone (**2l**) (as a dissociating colourless dimer).

* J. W. Barton and M. Shepherd (personal communication) have concurrently made the cyclopentadienone (**2k**).

Experimental

^{1}H N.m.r. data refer to solutions in $CDCl_3$ with tetramethylsilane as internal standard unless otherwise stated, and were obtained with a Varian T60, JEOL PMX60, or JNM PS100 instrument or, for ^{13}C data, with JEOL FX90Q/FX200 Fourier transform facilities. I.r. spectra were recorded for solutions in CH_2Cl_2, in 1.00 mm cells, with a Perkin-Elmer 297 machine. Electron impact mass spectra were recorded with an A.E.I. MS902 spectrometer with VG Micromass facility (70 eV); all spectra had the correct $^{35}Cl/^{37}Cl$ isotopic abundance ratios. Analytical t.l.c. was carried out on plates coated to 0.3 mm thickness with silica gel GF_{254}; for preparative-scale separations, plates of 0.5 or 0.8 mm thickness were employed (visualisation under a u.v. lamp). Petroleum refers to the fraction of b.p. 60—80 °C.

^{13}C N.m.r. and mass spectrometric data for new compounds are available as Supplementary Publication no. SUP 56635 (8 pp.).*

Cycloaddition Reactions with the Hexachlorotricyclononadiene (**1**) *and the Cyclopentadienones* (**2a**—**m**).—1,6,7,8,9,9-Hexachlor ,-*endo*-tricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene (**1**) was prepare (39% overall yield) from the cyclo-octatetraene–dimethyl acetylenedicarboxylate adduct[7] {δ_H 3.62 (s) and 6.15 (s); *m/z* 322 ($M^{+\cdot}$), 287 ([M − Cl]$^+$), and 251 ([M − HCl_2]$^+$, 100%)}.

General procedure. The cyclopentadienone (0.3—1.3 mmol) and the dienophile (**1**) (0.4—1.6 mmol) were heated in solution in the appropriate solvent (2.5—15 ml; Table 1) under N_2; boiling was continued until the intense cyclopentadienone colouration had faded. If crystallisation occurred readily after partial evaporation and dilution with methanol, the product was separated and the residue subjected to preparative t.l.c.; otherwise the whole solution was evaporated and the product similarly separated (*ca.* 1:1 CH_2Cl_2–petroleum). Products and yields are summarised in Table 1. M.p.s (recrystallisation solvent), n.m.r. (δ_H and/or δ_C), mass spectral (*m/z*), and analytical data follow for (i) arylated (or alkylarylated) derivatives of *endo,anti,endo*- and/or *endo,anti,exo*-1,10,11,12,-13,13-hexachloropentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradeca-5,11-dien-14-ones (**3**),† (ii) corresponding derivatives of *endo,anti*-1,10,11,12,13,13-hexachlorotetracyclo[8.2.1.0^{2,9}.0^{3,8}]triadeca-4,6,11-trienes ('BCOD') (**4**), and (iii) appropriate derivatives of *endo*-1,10,11,12,13,13-hexachlorotricyclo[8.2.1.0^{2,9}]triadeca-3,5,7,11-tetraenes ('COTR') (**5**). In each experiment excess of dienophile was recovered. From (**2a**) (i) *exo*-adduct (**3a**), m.p. 229—230 °C (decomp.) (lit.,[2a,b] 227—229 °C); *endo*-adduct (**3a**) identified by δ_H 3.30 and 3.52 (both 2 H, m, cyclobutane A_2X_2); (iii) *cyclo-octatriene derivative* (**5a**), m.p. 209—210 °C ($CHCl_3$–MeOH), δ_H 4.30 (2 H, m, 2- and 9-H), 6.05 (2 H, m, 3- and 8-H), and 7.08 and 7.15—7.45 (20 H, s and m, Ph); *m/z* 678 ($M^{+\cdot}$) (Found: C, 64.7, H, 3.3. $C_{37}H_{24}Cl_6$ requires C, 65.2; H, 3.55%). From (**2b**) (i) *exo*-adduct (**3b**), m.p. 232—232.5 °C (decomp.) ($CHCl_3$–hexane) (lit.,[2b] 234—235 °C), $^3J(^{13}CO,^1H)$ *ca.* 8.4 Hz; (iii) (**5b**) (identified by spectroscopic comparison[2b]). From (**2c**) (i) *exo*-adduct (**3c**), m.p. 216—217 °C (decomp.) (CH_2Cl_2–MeOH), δ_H 3.0 (4 H, s, 2-, 3-, 8-, and 9-H), 3.64 (6 H, s, 2MeO), 6.42—6.70 (8 H, m, 2C$_6H_4$OMe), and 7.32 (10 H, br, m, C_6H_5); *m/z* 738 ([M − CO]$^+$); (iii) *cyclo-octatriene derivative* (**5c**), m.p. 233—234 °C (decomp.), δ_H 3.72 (6 H, s, 2 MeO), 4.18 (2 H, m, 2- and 9-H), 6.03 (2 H, m, 3- and 8-H), and 6.61—7.46 (18 H, m, C$_6H_4$OMe and C_6H_5); *m/z* 738 ($M^{+\cdot}$) (Found: C, 62.8; H, 3.85. $C_{39}H_{28}Cl_6O_2$ requires C, 63.2; H, 3.8%). From (**2e**) (i) *exo*-adduct (**3e**), m.p. 220—220.5 °C (decomp.) (CH_2Cl_2–MeOH), δ_H 3.02 (4 H, s, 2-, 3-, 8- and 9-H), 3.66 and 3.82 (each 3 H, s, 2 MeO), and 6.44—7.40 and 7.30 (18 H, m and br s, C$_6H_4$OMe and C_6H_5); *m/z* 738 ([M − CO]$^+$); $\nu_{max.}$ 1 780vs cm^{-1} (bridge CO); (iii) *cyclo-octatriene derivative* (**5e**) (after further t.l.c.), m.p. 187—188 °C ($CHCl_3$–MeOH), δ_H 3.73 and 3.77 (each 3 H, s, 2 MeO), 4.21 (2 H, m, 2- and 9-H), 6.0 (2 H, m, 3- and 8-H), and 7.12 and 6.61—6.46 (18 H, s and br m, C_6H_5 and C$_6H_4$OMe); *m/z* 738 ($M^{+\cdot}$) (Found: $M^{+\cdot}$, 738.0230 and 740.0195. $C_{39}H_{28}{}^{35}Cl_6O_2$ requires *M*, 738.0220. $C_{39}H_{28}{}^{35}Cl_5{}^{37}ClO_2$ requires *M*, 740.0191). From (**2d**) (i) *exo*-adduct (**3d**), m.p. 220—222 °C (decomp.) (CH_2Cl_2–MeOH), δ_H 3.03 (4 H, s, 2- and 9-H), 3.64 and 3.8 (each 3 H, s, 2-MeO), and 6.46—7.40 and 7.36 (18 H, m, and br s, C$_6H_4$OMe and C_6H_5); *m/z* 738 ([M − CO]$^+$); (iii) *cyclo-octatriene derivative* (**5d**) (after further t.l.c.), m.p. 189.5—190.5 °C ($CHCl_3$–MeOH), δ_H 3.64 and 3.67 (each 3 H, s, 2 MeO), 4.11 (2 H, m, 2- and 9-H), 5.82 and 5.95 (each 1 H, m, 3- and 8-H), and 6.48—7.34 (18 H, m, C$_6H_4$OMe and C_6H_5); *m/z* 738 ($M^{+\cdot}$) (Found: $M^{+\cdot}$, 738.0195 and 740.0168. $C_{39}H_{28}{}^{35}Cl_6O_2$ requires *M*, 738.0220. $C_{39}H_{28}{}^{35}Cl_5{}^{37}ClO_2$ requires *M* 740.0191). From (**2f**) (i) *exo-adduct* (**3f**), m.p. 197.5—198.5 °C (decomp.) (CH_2Cl_2–MeOH), δ_H 2.96 (4 H, s, 2-, 3-, 8-, and 9-H), 3.63 and 3.78 (each 6 H, s, 4 MeO), and 6.44—7.30 (16 H, m, 4 C$_6H_4$OMe); *m/z* 798 ([M − CO]$^+$) (Found: C, 60.5; H, 3.8. $C_{42}H_{32}Cl_6O_5$ requires C, 60.8; H, 3.9%); (iii) *cyclo-octatriene derivative* (**5f**) (after further purification), m.p. 224—227 °C ($CHCl_3$–MeOH), δ_H 3.73 and 3.76 (each 6 H, s, 4 MeO), 4.16 (2 H, m, 2- and 9-H), 5.94 (2 H, m, 3- and 8-H), and 6.64—7.40 (16 H, m, 4 C$_6H_4$OMe) (Found: $M^{+\cdot}$, 798.0418 and 800.0381. $C_{41}H_{32}{}^{35}Cl_6O_4$ requires *M*, 798.0432. $C_{41}H_{32}{}^{35}Cl_5{}^{37}ClO_4$ requires *M*, 800.0402). From (**2h**) (i) *exo*-adduct (**3h**), m.p. 256—257 °C (decomp.) (CCl_4–EtOH) [lit.,[2b] 258—259 °C (decomp.)]; δ_H 1.20 (6 H, s, 2 Me) and 2.24 and 2.8 (each 2 H, m, 2-, 3-, 8-, and 9-H); *endo*-(**3h**), δ_H 1.30 (6 H, s, 2 Me) and 2.40 and 3.14 (each 2 H, m, 2-, 3-, 8-, and 9-H); (ii) bicyclo-octadiene derivative (**4h**), identified by comparison with the authentic compound.[2b] From (**2k**) (i) *exo*-adduct (**3k**), m.p. indefinite (slow decomp. in range 215—240 °C), δ_H 1.42 (6 H, s, 2 Me), 2.60 and 2.88 (each 2 H, m, 2-, 3-, 8-, and 9-H), and 7.1—7.5 (10 H, m, C_6H_5), $^3J(^{13}CO,^1H)$ 7.2 Hz; $\nu_{max.}$ 1 780vs cm^{-1} (CO); *m/z* 554 ([M − CO]$^+$); (iii) *cyclo-octatriene derivative* (**5k**), m.p. 249—250 °C ($CHCl_3$–MeOH), δ_H 1.88 (6 H, s, 2 Me), 3.82 (2 H, m, 2- and 9-H), 5.78 (2 H, m, 3- and 8-H), and 7.06—7.30 (10 H, m, C_6H_5); *m/z* 554 ($M^{+\cdot}$) (Found: C, 57.8; H, 3.4. $C_{27}H_{20}Cl_6$ requires C, 58.2; H, 3.6%). From (**2g**) (i) *exo*-adduct (**3g**), m.p. 222.5—223 °C (decomp.) (CH_2Cl_2–MeOH), δ_H 1.33 (3 H, s, Me), 2.31—2.43 (1 H, m, 3-H), 2.97 (3 H, m, 2-, 8-, and 9-H), and 6.6—7.2 (15 H, m, C_6H_5), $J(^{13}CO,^1H)$ 5.9 Hz; *m/z* 616 ([M − CO]$^+$) and isomeric *endo*-adduct (**3g**), m.p. 170—171 °C (decomp.) (CH_2Cl_2–MeOH), δ_H 1.45 (3 H, s, Me), 2.49—2.62 (1 H, dd, 3-H), 3.24—3.54 (3 H, m, 2-, 8-, and 9-H), and 6.6—7.3 (15 H, C_6H_5); *m/z* 616 ([M − CO]$^+$); (ii) bicyclo-octadiene derivative (**4g**) (a gum), δ_H 1.55 (3 H, s, Me), 2.85—3.04 and 3.29—3.58 (1 H and 3 H, each m, 3-H and 2-, 8-, and 9-H), and 6.4—7.3 (15 H, m, C_6H_5); (**4g**) gave an N-*phenyltriazolinedione adduct*, m.p. 247—248 °C (CH_2Cl_2–MeOH), δ_H 1.78 (3 H, s, Me), 2.5—2.8 and 2.9—3.1 (each 1 H, dd) and 3.28 (2 H, t) (cyclobutane 4 H), and 6.7—7.5 (20 H, C_6H_5); *m/z* 791 ($M^{+\cdot}$), 614 ([M − $C_8H_7N_3O_2$]$^+$), 580 ([M − $C_8H_6ClN_3O_2$]$^+$), and 320 ([$Ph_2C_6H_2Me_2$]$^+$, 100%) (Found: C, 60.7; H, 3.3; N, 5.3. $C_{40}H_{27}Cl_6N_3O_2$ requires C, 60.5; H, 3.4; N, 5.3%). From (**2i**) (i) exo-*adduct* (**3i**), m.p. 217—218 °C (decomp.) ($CHCl_3$–hexane), δ_H 1.62 (3 H, s, Me), 2.68—2.81 and 2.91—3.16 (1 H, 3 H, each m, 3-H, 2-, 8-, 9-H), and 6.85—7.52

* For details of Supplementary Publications see Instructions for Authors (*J. Chem. Soc., Perkin Trans. 2*, 1986, Issue no. 1).

† Strictly speaking conventional nomenclature requires ketones (**3**) to be stereoisomers of 1,10,11,12,14,14-hexachloropentacyclo-[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradeca-5,11-dien-13-ones (carbonyl taking precedence); to avoid confusion and simplify numbering for (**3**) and its derivatives (**4**) and (**5**) the ketonic carbon atom is designated C-14 and CCl_2 becomes C-13 throughout. Dihydrosemibullvalene derivatives (below) are aryl- and alkylaryl-substituted *endo,exo*-1,10,11,12,13,13-hexachloropentacyclo[8.2.1.0^{2,9}.0^{3,7}.0^{6,8}]triadeca-4,11-dienes.

(15 H, m, C_6H_5); *m/z* 616 ([*M* − CO]$^{+\cdot}$) (Found: C, 60.9; H, 3.2. $C_{33}H_{22}Cl_6O$ requires C, 61.2; H, 3.4%); (iii) *cyclo-octatriene derivative* (**5i**) (after extensive purification), m.p. indefinite, δ_H 2.02 (3 H, s, Me), 3.93 and 4.22 (each 1 H, dd, 2- and 9-H), 5.99 (2 H, t, 3- and 8-H), and 7.05—7.51 (15 H, m, C_6H_5); *m/z* 616 (*M*$^{+\cdot}$) (Found: *M*$^{+\cdot}$, 615.9850. $C_{32}H_{22}{}^{35}Cl_6$ requires *M*, 615.9852). From (**2l**) (ii) *bicyclo-octadiene derivative* (**4l**), m.p. 180.5—181.5 °C (CH_2Cl_2–MeOH), δ_H 3.36 and 3.59 (each 2 H, m, 2-, 3-, 8-, and 9-H), 6.65 (1 H, s, 5-H), and 6.95—7.51 (15 H, m, C_6H_5); *m/z* 602 (*M*$^{+\cdot}$) (Found: C, 61.3; H, 3.0. $C_{31}H_{20}Cl_6$ requires C, 61.6; H, 3.3%). Preparative t.l.c. of liquors on silica gel with 2% $AgNO_3$ (CH_2Cl_2–hexane, 2:1) gave more (**4l**) and (iii) *cyclo-octatriene derivative* (**5l**), m.p. 173—174 °C ($CHCl_3$–MeOH), δ_H 4.03 (2 H, t, 2- and 9-H), 6.14, 6.27, and 6.96 (each 1 H, m, m, and s, 3-, 8-, and 6-H), and 7.08—7.55 (15 H, m, C_6H_5); *m/z* 602 (*M*$^{+\cdot}$). From (**2m**) (i), exo-*adduct* (**3m**), m.p. 174.5—175.5 °C (decomp.), δ_H 1.04 and 1.37 (each 9 H, Bu^t), 1.08, 1.21, and 1.30 (each 3 H, s, 3 Me of Bu^t with restricted rotation), 2.68 (4 H, br s, 2-, 3-, 8-, and 9-H), and 6.74 (1 H, s, 6-H); *m/z* 542 ([*M* − CO]$^{+\cdot}$) (Found: C, 54.6; H, 5.8. $C_{26}H_{32}Cl_6O$ requires C, 54.5; H, 5.6%). Preparative t.l.c. of crude *exo*-adduct (**3m**) (CH_2Cl_2–hexane, 1:2) gave (iii) *cyclo-octatriene derivative* (**5m**), m.p. 161—162 °C (CH_2Cl_2–MeOH), δ_H 1.07, 1.09, and 1.21 (each 9 H, s, Bu^t), 3.64 (2 H, m, 2- and 9-H), 5.26 and 5.52 (each 1 H, m, 3- and 8-H), and 6.09 (1 H, d, *J* 0.9 Hz, 6-H?); *m/z* 544 (*M*$^{+\cdot}$ $^{35}Cl_5{}^{37}Cl$) (Found: C, 55.5; H, 6.1. $C_{25}H_{32}Cl_6$ requires C, 55.1; H, 5.9%).

Thermolysis of the Carbonyl-bridge Adducts (**3**) *and Isolation of the Cyclo-octatrienes* (**5**), *the Bicyclo-octadiene Derivatives* (**4**), *and the Dihydrosemibullvalene Derivatives* (**6a**) and (**9**)—(**14**): *General Procedure*.—The appropriate adduct (*ca.* 0.1—0.5 mmol) was heated under reflux in 1,3-dichlorobenzene, or more usually 1,2-xylene (3—6 ml), under N_2. The solvent was allowed to evaporate off and the residue separated into its components by preparative t.l.c. (silica gel with 2.5% $AgNO_3$; reaction time and eluant solvent varied as indicated). Alternatively crystals of the bridge-carbonyl compound (*ca.* 0.05 mmol) were heated at *ca.* 205 °C (360 s) or 235 °C (180 s) until gas evolution slowed, and the crude product was similarly separated into its components. M.p.s, yields, and spectroscopic and analytical data are recorded as appropriate except for n.m.r. data, which are collected in Tables 2—6 (unless useful for comparisons).

The adduct *exo*-(**3a**) (190 mg, 0.27 mmol) was heated for 2 h ($C_6H_4Cl_2$) and the products were separated (CH_2Cl_2–petroleum, 1:1) to give (**5a**) (27 mg, 15%) and (**6a**) (*ca.* 136 mg, 70%), identified by spectroscopic comparisons with authentic samples.[2b] The *exo*-adduct (**3c**) (200—300 mg samples) was heated for 16—30 h ($C_6H_4Me_2$) to give a mixture of products the composition of which varied with reaction time in each run: *e.g.* after 16 h, separation (CH_2Cl_2—CCl_4, 1:1) gave the adducts (**3c**) and (**5c**) and the dihydrosemibullvalenes (**10**) + (**11**) in the ratios 53:28:19, the proportion of the adduct (**3c**) falling and of the dihydrosemibullvalenes (**10**) + (**11**) rising with time; after 30 h, the ratio [(**3c**):(**5c**):(**10**) + (**11**)] was 20:30:50 with (**11**):(**10**) 1.5:1. Repeated chromatography of the dihydrosemibullvalene fraction (CH_2Cl_2–CCl_4, 1:4) gave, after recrystallisation ($CHCl_3$–methanol), the *isomer* (I) (**11**), m.p. 203—204.5 °C, δ_H 3.99 and 3.85 (each 1 H, d, *J* 7 Hz, 2- and 9-H) and 6.67—7.36 (18 H, m, C_6H_5 and C_6H_4OMe); *m/z* 738 (*M*$^{+\cdot}$); and the closely similar *isomer* (II) (**10**), m.p. 186.5—188 °C, δ_H 3.39 and 3.83 (each 1 H, d, *J* 7 Hz, 2- and 9-H), 6.4—7.14 (13 H, m, C_6H_4OMe and C_6H_5), and 7.26 (5 H, br s, C_6H_5); *m/z* 738 (*M*$^{+\cdot}$) (Found: *M*$^{+\cdot}$, 740.0189. $C_{39}H_{28}{}^{35}Cl_5{}^{37}Cl$ requires *M*, 740.0191).

The *exo*-adduct (**3d**), as crystals (34 mg), was heated at 230—235 °C (180 s) to give a product containing the adducts (**3d**) and (**5d**) and the dihydrosemibullvalenes (**12**) + (**13**) in ratios 1:4.5:9, from which the isomers (**12**) and (**13**) (2:1) were separated (CH_2Cl_2–CCl_4, 1:1) as a mixture, and then mutually separated and further purified (CH_2Cl_2–CCl_4, 1:4), giving the *isomer* (V) (**12**) (non-crystalline but spectroscopically pure), δ_H 3.12 (1 H, s, 8-H), 3.33 and 3.80 (each 1 H, d, *J* 7 Hz, 2-and 9-H), 3.59 and 3.80 (each 3 H, 2 MeO), 4.30 (1 H, s, 3-H), and 6.34—7.17 (18 H, C_6H_5 and C_6H_4OMe); *m/z* 738 (*M*$^{+\cdot}$) (Found: *M*$^+$, 740.0191. $C_{39}H_{28}{}^{35}Cl_5{}^{37}Cl$ requires *M*, 740.0191). The isomer (VI) (**13**) could not be completely separated from the isomer (V) (**12**); n.m.r. data refer to (**13**) admixed with *ca.* 10% of the isomer (**12**): δ_H 3.12 (1 H, s, 8-H), 3.33 and 3.80 (each 1 H, d, *J* 7 Hz), 3.68 and 3.73 (each 3 H, 2 MeO), 4.27 (1 H, s, 3-H), 6.40—7.90 (13 H, C_6H_5 and C_6H_4OMe), and 7.20 (5 H, br s, C_6H_5); *m/z* 738 (*M*$^{+\cdot}$). The *exo*-adduct (**3e**) (190 mg) was heated for 21 h (1,2-xylene) and the crude product separated (CH_2Cl_2–petroleum, 3:2), to give *exo*-(**3e**) (82 mg, 43%), (**5e**) (57 mg, 30%), and a fraction (45 mg, 24%) containing the dihydrosemibullvalenes (**7**), (**8**), (**10**), and (**11**) (^{1}H n.m.r.). A similar product mixture of dihydrosemibullvalanes (**7**), (**8**), (**10**), and (**11**) was separated (CH_2Cl_2–CCl_4, 1:1) from the unchanged cyclo-octatriene derivative (**5e**) when crystalline (**5e**) was heated at 240 °C (60 s; metal bath) [(**10**)/(**11**):(**7**)/(**8**) 1.7:1]. The dihydrosemibullvalenes (**7**) and (**8**) were made as previously described[2b,d] and an approximately equimolar mixture containing (**7**) and (**8**) with (**10**) and (**11**), prepared by thermolysis of the *exo*-adduct (**3c**), was compared (^{1}H n.m.r.) with the quaternary dihydrosemibullvalene mixture obtained from the *exo*-adduct (**3e**) [and (**5e**)]: all signals coincided, in appearance and chemical shift, with (**10**), (**11**) (**7**), and (**8**) present in ratios 1.7:1.7:1:1 in the thermolysis product from (**5e**).

The *exo*-adduct (**3f**) (85 mg) heated at 205—209 °C (360 s; metal bath); separation (CH_2Cl_2–petroleum, 3:2), gave (**5f**) (20 mg, 25%) and the *dihydrosemibullvalene* (**14**) containing traces of the adduct (**3f**), from which (**14**) was separated by further chromatography (CH_2Cl_2–hexane) as a non-crystallising spectroscopically pure gum; δ_H 3.32 (1 H, d, *J* 7 Hz, 2- or 9-H, one signal obscured by MeO signals in range 3.60—3.79; see Table 2) and 6.4—7.26 (16 H, m, C_6H_4OMe); *m/z* 798 (*M*$^{+\cdot}$) (Found: *M*$^{+\cdot}$, 798.0433. $C_{41}H_{32}{}^{35}Cl_6O_4$ requires *M*, 798.0431).

The *exo*-adduct (**3h**) (50 mg), heated ($C_6H_4Cl_2$; reflux) for 24 h, gave a crude product containing (**4h**) (58%), (**5h**) (17%), and the dihydrosemibullvalene (**9**)[2b] (25%); the *cyclo-octatriene derivative* (**5h**), separated on silica gel–$AgNO_3$ from (**4h**),[2b] had m.p. 222—224 °C ($CHCl_3$), δ_H 1.9 (6 H, s, 2 Me), 3.96 (2 H, 2- and 9-H), 5.29 (2 H, m, 3- and 8-H), and 6.9—7.2 (10 H, C_6H_5); *m/z* 554 (*M*$^{+\cdot}$) (Found: C, 58.3; H, 3.7. $C_{27}H_{20}Cl_6$ requires C, 58.2; H, 3.6%).

Equilibration of the Cyclo-octatriene Derivative (**5h**) *with the Bicyclo-octadiene Derivative* (**4h**).—The procedure described

Table 6. Variation of cyclopropane (8-H) and bridgehead (3-H) ^{1}H n.m.r. signals (δ_H; $CDCl_3$; Me_4Si) for methyltriphenyl- and dimethyl-diphenyl-dihydrosemibullvalene derivatives (**6**), (**9**) and (**21**)—(**26**)

Compd.	R^4	R^3	R^2	R^1	δ(8-H)	Δδ(8-H)	δ(3-H)	Δδ(3-H)
(**6a**)	Ph	Ph	Ph	Ph	3.22		4.35	
(**23**)	Me	Ph	Ph	Ph	2.41	−0.81	3.55	−0.80
(**25**)	Ph	Me	Ph	Ph	2.38	−0.84	4.14	−0.21
(**24**)	Ph	Ph	Me	Ph	3.05	−0.17	4.19	−0.16
(**26**)	Ph	Ph	Ph	Me	3.20	−0.02	3.75	−0.60
(**9**)	Me	Ph	Ph	Me	2.40	(2.39)[a]	2.99	(2.95)[a]
(**21**)	Ph	Me	Me	Ph	2.24	(2.21)[a]	3.88	(3.98)[a]
(**22**)	Ph	Ph	Me	Me	2.84	(3.03)[a]	3.52	(3.61)[a]
(Not seen)	Me	Me	Ph	Ph		(1.57)[a]		(3.34)[a]

[a] Predicted values in parentheses.

here is typical of equilibrium and kinetic experiments carried out in this work. This interconversion was investigated using solutions containing (**4h**) or (**5h**) (or both, in 1,2,4-$Cl_3C_6H_3$), heated for up to 18 h at 171 °C; the solutions were cooled and diluted (CCl_4), and the composition was found (^{1}H n.m.r., average of five integrations), giving the equilibrium constant for (**5h**) ⇌ (**4h**) (*K* 3.4 at 171 °C). At higher temperatures the results were non-reproducible owing to decomposition, probably of (**9**) formed from (**5h**) (see later). A similar series of experiments with the *exo*-adduct (**3h**) as *in situ* source of (**4h**) gave the same value for *K* (at 171 °C), and established $t_{\frac{1}{2}}$ for the adduct as *ca.* 4 h at this temperature. The rates of interconversion of *e.g.* (**4h**) and (**5h**) were determined by monitoring at 10 min intervals similar solutions of the pure compounds heated in ampoules for up to 45 min. Similar techniques were used to estimate from acceptably first-order ln(concn.) *vs.* time plots $t_{\frac{1}{2}}$ values for conversion of cyclo-octatriene derivatives into dihydrosemibullvalenes; data are accurate to within ±6%.

Minor Products from Thermolysis of Compounds (**3h**), (**4h**), *and* (**5h**).—Preparative t.l.c. of residual components from thermolysis of the hemicyclone-derived compounds gave the *endoperoxide* (**15**), m.p. 287—288 °C (decomp.) (CH_2Cl_2–MeOH), δ_H 1.14 (6 H, s, 2 Me), 2.50 and 3.04 (each 2 H in cyclobutane), and 6.7—7.3 (10 H, m, C_6H_5); δ_C 19.2 (CH_3), 40.6 and 49.9 (cyclobutane), 78.2 ($OCCH_3$), 80.5 (CCl), 104.1 (CCl_2), 127.3, 128.1, and 129.2 (aromatic =CH), 132.4 (=CCl), and 135.6 and 143.3 (q, aromatic and =C<); *m/z* 586 ($M^{+\cdot}$), 570 ([*M* − O]$^{+\cdot}$), 551 ([*M* − Cl]$^{+\cdot}$), 535 ([*M* − Cl − O]$^{+\cdot}$), 499 ([*M* − HCl_2 − O]$^{+\cdot}$), 316 ([*M* − C_5Cl_6]$^{+\cdot}$), 300 ([*M* − C_5Cl_6O]$^{+\cdot}$), 105 ($PhCO^+$, 100%), and 43 ($CH_3CO^{+\cdot}$) (Found: C, 55.5; H, 3.4. $C_{27}H_{20}Cl_6O_2$ requires C, 55.0; H, 3.4%). Also obtained was an unidentified colourless solid, admixed with the adduct (**3h**), δ_H 1.1 (s), 2.1 (m), and 3.7 (m) (3:1:1), and 6.8—7.2 (m, C_6H_5), possibly a stereoisomer of the endoperoxide (**15**).

Photolysis of the Bicyclo-octadiene Derivative (**4h**).—Solutions of compound (**4h**) (50—75 mg) in CCl_4 (1—1.5 ml) were exposed in air to glass-filtered sunlight for 7—10 days and the composition was monitored (^{1}H n.m.r.); the endoperoxide (**15**) appeared first, and then signals corresponding to a second component [δ 0.98, 2.44, and 3.16 (3:1:1)]; attempted isolation of this component gave, in addition to (**15**), compound (**16**), m.p. 200—202 °C (CH_2Cl_2–MeOH), δ_H 1.09 (3 H, s, Me), 1.80—2.14 (1 H, br s, OH), 2.51—2.67 and 2.85—3.21 (1 H, and 3 H, both m, cyclobutane), 4.75 (1 H, d, *J* 0.8 Hz, =CH), 5.14 (1 H, s, =CH), and 6.56—7.38 (10 H, C_6H_5); δ_C 24.7 (Me), 38.1, 47.2, 49.4, and 51.9 (cyclobutane), 70.9 (CH_3COH), 81.0 and 81.1 (CCl), 104.3 (CCl_2), and 117.4 (=CH_2), with 13 signals resolved in the range 126.8—145.4 (q, C_6H_5 and =C<); *m/z* 570 ($M^{+\cdot}$), 555 ([*M* − CH_3]$^{+\cdot}$), 552 ([*M* − H_2O]$^{+\cdot}$), 535 ([*M* − Cl]$^{+\cdot}$), 527 ([*M* − CH_3CO]$^{+\cdot}$), 517 ([*M* − Cl − H_2O]$^{+\cdot}$), 495 ([*M* − C_6H_5]$^{+\cdot}$), 256 ([*M* − $C_7H_2Cl_6$ − H_2O]$^{+\cdot}$, 100%), 105 ($PhCO^{+\cdot}$), and 43 ($CH_3CO^{+\cdot}$).

Thermolysis of the Dihydrosemibullvalene Derivative (**9**).—Samples of the dihydrosemibullvalene derivative (**9**) (30—40 mg) were heated in a fusion tube (220—230 °C; 1—3 min) and the accumulated products were separated by t.l.c. [silica gel–$AgNO_3$ (2%); CH_2Cl_2–petroleum, 1:2] to remove unchanged (**9**); further t.l.c. (silica gel; CCl_4–petroleum, 3:1) gave the rearrangement product, endo,exo-1,9,10,11,13,13-*hexachloro*-endo-6-*methyl*-12-*methylene*-4,5-*diphenyltetracyclo*-[7.2.1.$1^{3,7}$.$0^{2,8}$]*trideca*-4,10-*diene* (**17**), a yellowish gum, δ_H 0.87 (3 H, d, *J* 7 Hz, CH_3), 2.7 (1 H, d, 7-H), 3.13 (1 H, s, 3-H), 3.29 (1 H, m, 6-H), 3.40 and 3.73 (each 1 H, d, *J* 7.8 Hz, 2- and 8-H), 4.74 and 4.84 (each 1 H, s, =CH_2), and 6.84—7.18 (10 H, C_6H_5); δ_C 16.9 (Me), 45.9, 48.0, 48.3, 51.8, and 61.1 (C-2, -8, -3, -6, and -7), 80.6 and 81.2 (CCl), 100.4 (=CH_2), 126.4, 127.8, 127.9, 128.2, and 129.1 (t, C_6H_5, =CH, one signal obscure), and 138.3, 139.3, 139.7, 141.0, and 150.4 (overlapping q, C_6H_5, C-4, -5, -10, -11, and -12); *m/z* 554 ($M^{+\cdot}$, 100%), 519 ([*M* − Cl]$^{+\cdot}$), 387 ([*M* − Cl_4 − C_2H_3]$^{+\cdot}$), and 284 ([*M* − C_5Cl_6]$^{+\cdot}$) (Found: $M^{+\cdot}$, 553.9674. $C_{27}H_{20}{}^{35}Cl_6$ requires *M*, 553.9696). The isomeric compound (**18**) could not be isolated but was characterised by n.m.r.: δ_H 1.72 (3 H, s, CH_3), 2.80 (1 H, d, *J* 4 Hz, 7-H), and 4.98 and 5.10 (both, 1 H, s, =CH_2).

Preparation of the Dihydrosemibullvalene Derivatives (**21**)—(**26**).—The cyclo-octatriene (**5k**) (181 mg) was heated under reflux for 22 h (1,3-$C_6H_4Cl_2$). Evaporation, followed by t.l.c. of the residue [silica gel–$AgNO_3$ (2%); CH_2Cl_2–petroleum, 2:3)], gave two product fractions (73.5% conversion); one was the *dihydrosemibullvalene derivative* (**21**) (84 mg), m.p. 228.5—230 °C ($CHCl_3$–hexane) (50 mg recovered), δ_H 0.97 (3 H, s, Me), 1.94 (3 H, s, Me), 2.24 (1 H, s, 8-H), 3.28 and 3.44 (each 1 H, d, *J* 7 Hz, 2- and 9-H), 3.88 (1 H, s, 3-H), and 7.0—7.4 (10 H, C_6H_5); *m/z* 554 ($M^{+\cdot}$) (Found: C, 57.7; H, 3.4. $C_{27}H_{20}Cl_6$ requires C, 58.2; H, 3.6%). The second fraction, identified as the isomeric *dihydrosemibullvalene derivative* (**22**) (49 mg), had m.p. 177—178 °C ($CHCl_3$–hexane; 25 mg recovered), δ_H 1.28 (3 H, s, Me), 1.76 (3 H, s, Me), 2.84 (1 H, s, 8-H), 3.10 and 3.48 (each 1 H, d, *J* 7 Hz, 2- and 9-H), 3.52 (1 H, s, 3-H), and 6.5—7.1 (10 H, m, C_6H_5); *m/z* 554 ($M^{+\cdot}$) [Found: C, 58.3; H, 3.7%. *cf. isomer* (**21**)].

The *exo*-adduct (**3g**) (200 mg) was heated under reflux for 30 h [1,2-$C_6H_4Me_2$ (5 ml)]. Evaporation, followed by t.l.c. of the residue (silica gel; CH_2Cl_2–petroleum, 1:2) gave, in addition to recovered adduct (66 mg), two product fractions: the *cyclo-octatriene derivative* (**5g**) (44 mg, *ca.* 23%), m.p. 215—217 °C ($CHCl_3$–MeOH), δ_H 1.79 (3 H, s, Me), 4.06 (2 H, m, 2- and 9-H), 5.37 and 5.87 [each 1 H, m and d (*J* 4.6 Hz), 3- and 8-H], 6.9—7.1 (5 H, m, C_6H_5), 7.17 (5 H, br s, C_6H_5), and 7.3—7.6 (5 H, m, C_6H_5); *m/z* 616 ($M^{+\cdot}$); and the *dihydrosemibullvalene derivative* (**23**) (39 mg, *ca.* 20%), m.p. 138—140 °C ($CHCl_3$–MeOH), δ_H 1.16 (3 H, s, Me), 2.41 (1 H, s, 8-H), 3.13 and 3.72 (each 1 H, d, *J* 7 Hz, 2- and 9-H), 3.55 (1 H, s, 3-H), and 6.98, 7.10, and 7.18 (each 5 H, br s, C_6H_5); *m/z* 616 ($M^{+\cdot}$) (Found: $M^{+\cdot}$, 617.9857. $C_{32}H_{22}{}^{35}Cl_5{}^{37}Cl$ requires *M*, 617.9823). Preparative t.l.c. of compound (**23**) on silica gel–$AgNO_3$ (CH_2Cl_2–petroleum, 1:2) at 20 °C gave an *isomer* (**20**) [*cf.* compound (**17**)], m.p. 215.5—217.5 °C ($CHCl_3$–EtOH), δ_H 2.84 (1 H, d, *J* 5 Hz, 7-H), 3.22 (1 H, s, 3-H), 3.26 and 3.82 (each 1 H, d, *J* 7 Hz, 2- and 8-H), 4.75 (1 H, d, 6-H), 4.79 and 4.95 (each 1 H, s, =CH_2), 6.9 (5 H, br s, C_6H_5), and 7.0—7.2 (10 H, m, C_6H_5); δ_C 48.7, 49.0, 52.6, 58.6, and 61.0 (C-2, -8, -3, -6, and -7), 80.7 (C-1 and -9), 100.9 (=CH_2), 103.6 (C-13), 126.2, 126.4, 126.7, 127.5, 127.9, 128.1, 129.3, and 129.5 (t, C_6H_5), and 130.89, 130.91, 134.73, 139.07, 139.34, 141.61, 143.07, and 149.68 (q, C_6H_5, C-4, -5, -10, -11, and -12); *m/z* 616 ($M^{+\cdot}$), 581 ([*M* − Cl]$^{+\cdot}$), and 346 ([*M* − C_5Cl_6]$^{+\cdot}$, 100%) (Found: C, 61.7; H, 3.45. $C_{32}H_{22}Cl_6$ requires C, 62.1; H, 3.6%).

The thermolysis product from the cyclo-octatriene (**5i**) consisted of compounds (**24**) and (**25**); crystals of (**5i**) (370 mg) on fusion at 222—227 °C (5 min) followed by preparative t.l.c. (silica gel–$AgNO_3$; CH_2Cl_2–hexane, 2:3) gave three fractions: (i) a 1:1 mixture of (**5i**) and the dihydrosemibullvalene (**25**) (146 mg) (which could not be conveniently separated by t.l.c. or crystallisation), (ii) compound (**24**) (59 mg, 16%), and (iii) its isomer (**26**) (41 mg, 11%). The *dihydrosemibullvalene derivative* (**24**) had m.p. 191—192 °C (CH_2Cl_2–MeOH), δ_H 1.66 (3 H, s, Me), 3.05 (1 H, s, 8-H), 3.46 and 3.71 (each 1 H, d, *J* 7 Hz, 2- and 9-H), 4.19 (1 H, s, 3-H), and 6.8—7.6 (15 H, m, C_6H_5); *m/z* 616 ($M^{+\cdot}$) (Found: C, 61.8; H, 3.3. $C_{32}H_{22}Cl_6$ requires C, 62.1; H, 3.6%). The isomeric *dihydrosemibullvalene derivative* (**26**) had m.p. 171.5—172 °C ($CHCl_3$–MeOH), δ_H 1.98 (3 H, s, Me), 3.20 (1 H, s, 8-H), 3.23 and 3.68 (each 1 H, d, *J* 7 Hz, 2- and 9-H), 3.75 (1 H, s, 3-H), and 6.7—7.2 (15 H, m, C_6H_5); *m/z* 616 ($M^{+\cdot}$).

Crystals of compound (**26**) fused at 221—223 °C (1.5 min) gave a 2:1 mixture of dihydrosemibullvalene isomers (**25**) and (**26**) unchanged by further heating; separation of this mixture [t.l.c. on silica gel–$AgNO_3$ (2%); CH_2Cl_2–hexane, 2:3] afforded the spectroscopically pure *dihydrosemibullvalene derivative* (**25**) (which did not crystallise), δ_H 0.77 (3 H, s, Me), 2.38 (1 H, s, 8-H), 3.21 and 3.63 (each 1 H, d, *J* 7 Hz, 2- and 9-H), 4.14 (1 H, s, 3-H), and 7.0—7.4 (15 H, m, C_6H_5); *m/z* 616 ($M^{+\cdot}$) (Found: $M^{+\cdot}$, 617.9820. $C_{32}H_{22}{}^{35}Cl_5{}^{37}Cl$ requires *M*, 617.9823).

Thermolysis of the Dihydrosemibullvalene Derivatives (**21**) and (**22**).—The adduct *exo*-(**3k**) (180 mg) was fused at 265—290 °C (2 min; effervescence and discolouration) and the cooled product was then separated [silica gel–$AgNO_3$ (2%); CH_2Cl_2–hexane, 1:2], giving a homogeneous product fraction (68 mg, *ca.* 40%) consisting of a methylenecyclopentene derivative, probably endo,exo-1,10,11,12,13,13-*hexachloro*-5-*methyl*-6-*methylene*-4,endo-7-*diphenyltetracyclo*[8.2.1.$0^{2,9}$.$0^{3,7}$]*trideca*-4,11-*diene* (**19**) as a non-crystallising gum, δ_H 1.9 (3 H, s, Me), 2.1—2.7 (5 H, m, overlapping 2-, 3-, 8-, 8-, and 9-H), 4.96 and 5.19 each 1 H, s, $=CH_2$), and 7.27 and 7.34 (each 5 H, br s, C_6H_5); δ_C 11.9 (Me), 37.9 (C-8), 55.0, 60.4, and 61.1 (C-2, -3, and -9), 66.0 (C-7), 81.2 and 82.3 (C-1 and -10), 105.1 (C-13), 105.4 ($=CH_2$), 125.6, 126.4, 127.7, 128.1, 128.4, and 128.9 (t, C_6H_5), and 131.5, 132.5, 133.7, 135.3, 145.6, 146.3, and 161.2 (q, C_6H_5, C-4, -5, -6, -11, and -12); *m/z* 554 ($M^{+\cdot}$), 519 ($[M - Cl]^{+\cdot}$), 284 ($[M - C_5Cl_6]^{+\cdot}$, 100%), and 269 ($[M - C_5Cl_6 - CH_3]^{+\cdot}$) (Found: $M^{+\cdot}$, 553.9692. $C_{27}H_{20}{}^{35}Cl_6$ requires *M*, 553.9696).

Synthesis of the Cyclopentadienones (**2d**, **e**, **i**, **k**, *and* **l**).—2,4-*Bis*-(p-*methoxyphenyl*)-3,5-*diphenylcyclopenta*-2,4-*dienone* (**2d**). 1-(*p*-Methoxyphenyl)-3-phenylpropan-2-one[41] (1.8 g, 7.5 mmol) and 4-methoxybenzil[42] (1 g, 4.2 mmol) were dissolved in ethanol (10 ml), *N*-benzyltrimethylammonium methoxide (15 drops; 40% solution in MeOH) was added, and the mixture was boiled (15 min). The solution was cooled, the precipitated black gum was extracted (CH_2Cl_2), and the extracts were dried ($MgSO_4$) and evaporated. Recrystallised (ethanol–toluene), the residue gave a mixture of the cyclones (**2d** and **e**),[37] as dark violet crystals, m.p. 190—198 °C; δ_H 3.74, 3.75, 3.76, and 3.78 (all 3 H, s, OMe) and 6.6—7.3 (18 H, m, C_6H_5 and C_6H_4OMe). Similarly recrystallised several times this product gave 2,4-*bis*-(p-*methoxyphenyl*)-3,5-*diphenylcyclopenta*-2,4-dienone (**2d**) (118 mg, 5.6%), black crystals, m.p. 217—218 °C, δ_H 3.74 and 3.75 (both 3 H, s, OMe) and 6.6—7.3 (18 H, m, C_6H_5); *m/z* 444 ($M^{+\cdot}$, 100%); $\nu_{max.}$ 1 708vs (CO), 1 605ms (conjugated C=C), and 1 205ms cm^{-1} (Found: C, 83.5; H, 5.6. $C_{31}H_{24}O_3$ requires C, 83.75; H, 5.4%).

2,3-*Bis*-(p-*methoxyphenyl*)-4,5-*diphenylcyclopenta*-2,4-*dienone* (**2e**). 1,2-Diphenylprop-2-enone was made by the published procedure[34] from α-methylbenzoin;[35] the product was used either before or after purification (column chromatography; CH_2Cl_2) to remove methylbenzoin. Deoxyanisoin was prepared by reduction of anisoin (tin and conc. HCl). 1,2-Diphenylprop-2-enone (960 mg, 4.57 mmol) and deoxyanisoin (1.0 g, 3.9 mmol) were dissolved in dimethyl sulphoxide (20 ml) and *N*-benzyltrimethylammonium methoxide (as before) was added dropwise until the dark colouration persisted. The solution was set aside for 16 h (20 °C), then poured into brine (100 ml); the precipitate was filtered off and extracted (CH_2Cl_2). The extracts were washed, dried ($MgSO_4$), and evaporated to give a yellow oil which was separated [silica gel (150 g); CH_2Cl_2] into four fractions: (i) (RS,RS)-1,2,4,5-*tetraphenylpentane*-1,5-*dione* (**37**) (56 mg), m.p. 121—121.5 °C (ethanol), δ_H 2.70 (2 H, t, CH_2), 4.60 (2 H, t, 2 CHCO), and 7.34 and 7.84 (16 H, and 4 H, br s and d, C_6H_5); *m/z* [$M^{+\cdot}$ (404) absent] 300, 196, and 105 ($C_6H_5CO^{+\cdot}$, 100%); $\nu_{max.}$ 1 680vs (conjugated CO), 1 600ms, and 1 580ms cm^{-1} (Found: C, 86.3; H, 6.1. $C_{29}H_{24}O_2$ requires C, 86.1; H, 6.0%); (ii) (*RS,SR*)-1,2,4,5-tetraphenylpentane-1,5-dione (**37**) (108 mg, 7%), m.p. 148—149 °C (lit.,[43] 148 °C), δ_H 2.40 and 3.00 (each 1 H, sext, CH_2), 4.52 (2 H, t, 2 CHCO), and 7.0—7.6 and 7.9 (16 H and 4 H, each m, C_6H_5); *m/z* as for (i); (iii) (RS,SR)-1,2-*bis*-(p-*methoxyphenyl*-4,5-*diphenylpentane*-1,5-*dione* (**36**) (a slowly crystallising yellow oil; 232 mg), m.p. 112—113 °C (ethanol), δ_H 2.37 and 2.98 (each 1 H, sext, CH_2), 3.67 and 3.75 (each 3 H, s, 2 OMe), 4.41 and 4.50 (each 1 H, t, 2 CHCO), and 6.7—8.0 (18 H, m, C_6H_5 and C_6H_4OMe); *m/z* 464 ($M^{+\cdot}$); $\nu_{max.}$ 1 680vs (conjugated CO), 1 600ms (conjugated C=C), and 1 510ms cm^{-1} (Found: C, 80.1; H, 6.1. $C_{31}H_{28}O_4$ requires C, 80.15; H, 6.1%); (iv) (RS,RS)-1,2-*bis*-(p-*methoxyphenyl*)-4,5-*diphenylpentane*-1,5-*dione* (**36**) (a viscous gum; 212 mg); δ_H 2.69 (2 H, t, CH_2), 3.70 and 3.72 (each 3 H, 2 MeO), 4.47 and 4.56 (each 1 H, t, 2 CHCO), and 6.6—7.9 (18 H, m, C_6H_5 and C_6H_4OMe); *m/z* and $\nu_{max.}$ as for (iii). A mixture of the diketones (i)—(iv), similarly prepared from 1,2-diphenylprop-2-enone (4.0 g, 19 mmol) and deoxyanisoin (4 g, 14.3 mmol), was treated with zinc powder (80 g) in acetic acid (200 ml) at the b.p. (3.5 h); the mixture was cooled and poured into water (1 l), and the precipitate extracted (CH_2Cl_2); the extracts were washed, dried, and evaporated. The residual oil was taken up in acetic acid (75 ml), conc. H_2SO_4 (5 ml) was added, and the mixture was boiled (3 min), and poured into water. The product was isolated as before, and immediately chromatographed [silica gel (175 g); CH_2Cl_2] to give two fluorescent fractions: 1,2,3,4-tetraphenylcyclopentadiene (**41**) (82 mg), m.p. 180—182 °C (ethanol) (lit.,[44] 177—178 °C), δ_H 4.0 (2 H, s, CH_2) and 6.9—7.4 (20 H, m, C_6H_5); *m/z* 370 ($M^{+\cdot}$, 100%); and 1,2-bis-(*p*-methoxyphenyl)-3,4-diphenylcyclopentadiene (**40**) [a gum, oxidised by air to (**2e**)] (2.5 g), δ_H 3.66 and 3.96 (each 1 H, s, 2 CH; prototropic isomerism), 3.70 and 3.72 (each 3 H s, 2 MeO), and 6.6—7.5 (18 H, m, aryl CH); *m/z* 430 ($M^{+\cdot}$, 100%). The bis-(*p*-methoxyphenyl)diphenylcyclopentadiene (**40**) (2.5 g, 5.8 mmol) was treated at the b.p. with 4-nitroso-*N*,*N*-dimethylaniline (2.5 g, 16.7 mmol) in benzene (60 ml) containing methanol (20 ml) in the presence of *N*-benzyltrimethylammonium methoxide (2 ml, as before). The mixture was cooled after 10 min, conc. HCl (50 ml) was added, and the mixture was then heated at the b.p. for 15 min. The product was extracted with ether; the extracts were washed, dried ($MgSO_4$), and evaporated to leave a violet gum (3 g), which after chromatography [silica gel (150 g); CH_2Cl_2] gave a purple solid (2 g); this, recrystallised [toluene (4 ml) and ethanol (30 ml)], gave 2,3-*bis*-(p-*methoxyphenyl*)-4,5-*diphenylcyclopenta*-2,4-*dienone* (**2e**)* (1.59 g, 62%; 23% overall from deoxyanisoin), m.p. 170—171 °C, raised to 171—172 °C (from CH_2Cl_2–hexane), δ_H 3.76 and 3.78 (each 3 H, s, 2 MeO) and 6.6—7.3 (18 H, m, ArH); *m/z* 444 ($M^{+\cdot}$, 100%); $\nu_{max.}$ 1 710vs (CO), 1 607ms, 1 500ms, and 1 030ms cm^{-1} (Found: C, 83.4; H, 5.3. $C_{31}H_{24}O_3$ requires C, 83.75; H, 5.4%).

3,4-*Dimethyl*-2,5-*diphenylcyclopenta*-2,4-*dienone* (**2k**). 1,3-Diphenylpropan-2-one (10.7 g, 0.05 mol) in ethanol (30 ml) was stirred at 0 °C and sodium hydroxide (1.0 g) in ethanol (20 ml) was added dropwise, followed by butane-2,3-dione (4.4 g, 0.05 mol) in ethanol (25 ml). The mixture was allowed to warm to *ca.* 20 °C and after 2.5 h was poured into water. The product was extracted (CH_2Cl_2); the extracts were washed (dilute H_2SO_4, then water), dried, and evaporated, leaving a viscous red oil. Recrystallised from ethanol this gave 4-*hydroxy*-3,4-*dimethyl*-

* Heated with diphenylacetylene, the cyclone (**2e**) gave 1,2-bis-(*p*-methoxyphenyl)-3,4,5,6-tetraphenylbenzene, m.p. 302 °C (lit.,[37] 284 °C); mixed m.p. with authentic compound similarly made from the cyclone (**2c**), and having the correct elemental composition, 302—303 °C.

2,5-*diphenylcyclopent-2-enone* (**43**) (4.1 g, 30%), m.p. 152—154 °C (after further recrystallisation), δ_H 1.04 and 2.15 (each 3 H, s, 2 Me), 2.48 (1 H, br s, OH), 3.89 (1 H, s, CH), and 7.0—7.4 and 7.34 (10 H, m and s, C_6H_5); *m/z* 278 ($M^{+\cdot}$); $\nu_{max.}$ 3 600vs (sharp), 3 450vs (broad) (non-bonded and bonded OH), and 1 710 vs cm^{-1} (CO) (Found: C, 82.1; H, 6.5. $C_{19}H_{18}O_2$ requires C, 82.0; H, 6.5%). Dehydrated in acetic acid at the b.p. by addition of conc. H_2SO_4–HOAc (1:1) to a *ca.* 10% w/v solution in HOAc and isolation of the product in the usual way, the hydroxycyclopentenone (**43**) gave 2,5-*diphenyl*-3-*methyl*-4-*methylenecyclopent*-2-*enone* (**44**) (53%), m.p. 137—138 °C (CH_2Cl_2–hexane, then ethanol), δ_H 2.34 and 4.17 (3 H and 1 H, each s, Me and CH), 5.21 and 5.60 (each 1 H, d, *J* 2 Hz, =CH_2), and 7.1—7.3 and 7.38 (each 5 H, m, and s, 2 C_6H_5); *m/z* 260 ($M^{+\cdot}$, 100%); $\nu_{max.}$ 1 705vs cm^{-1} (CO) (Found: C, 87.8; H, 6.2. $C_{19}H_{16}O$ requires C, 87.7; H, 6.2%). The hydroxycyclopentenone (**43**) (2.78 g, 10 mmol) dissolved in pyridine (15 ml) was treated dropwise at 0 °C with thionyl chloride (1.19 g, 10 mmol), with swirling, and the mixture was immediately quenched in water (150 ml). Extraction (CH_2Cl_2) and work-up in th usual way gave a mixture of the cyclopentadienone (**2k**) and its isomer (**44**) (1.44:1). Recrystallisation (toluene–ethanol), and column chromatography of the mother liquors [silica gel (170 g); CH_2Cl_2] gave 3,4-*dimethyl*-2,5-*diphenylcyclopenta*-2,4-*dienone* (**2k**) (1.43 g, 55%), m.p. 167—168 °C (bronze plates from $CHCl_3$–MeOH), δ_H 2.18 (6 H, s, 2 Me) and 7.26 (10 H, s, 2 C_6H_5); *m/z* 260 ($M^{+\cdot}$, 100%); $\nu_{max.}$ 1 713vs cm^{-1} (CO) (Found: C, 87.7; H, 6.5. $C_{19}H_{16}O$ requires C, 87.7; H, 6.2%).

3-*Methyl*-2,4,5-*triphenylcyclopenta*-2,4-*dienone* (**2i**). 1-Phenylpropane-1,2-dione (made from 1-phenylpropan-2-one by oxidation with SeO_2), n_D^{20} 1.531 (lit.,[45] 1.535) (3.14 g, 21.2 mmol) and 1,3-diphenylpropan-2-one (6.3 g, 30 mmol) in ethanol (30 ml) were treated with potassium hydroxide (0.2 g) in ethanol (2 ml) and the solution was kept at *ca.* 20 °C for 24 h. It was then poured into water and the product (8.0 g, oil) isolated in the usual manner. The crude product was treated in pyridine (30 ml) with thionyl chloride (3.2 g, 27 mmol) as before, and the product was similarly isolated. Chromatography of the crude product [silica gel (440 g); CH_2Cl_2] gave a single fraction (1.3 g; red oil), recrystallisation of which (CH_2Cl_2–MeOH) gave 3-*methyl*-2,4,5-*triphenylcyclopenta*-2,4-*dienone* (**2i**) (720 mg, 10% overall), m.p. 151—152 °C (violet-black needles from CH_2Cl_2–MeOH), δ_H 2.03 (3 H, s, Me) and 7.1—7.5 (15 H, m, 3 C_6H_5); *m/z* 322 ($M^{+\cdot}$, 100%) (Found: C, 89.0; H, 5.5. $C_{24}H_{18}O$ requires C, 89.4; H, 5.6%).

2,3,5-*Triphenylcyclopenta*-2,4-*dienone* (**2l**). 1,2,5-Triphenylcyclopenta-1,3-diene[46] (1.33 g, 4.52 mmol) was treated at the b.p. with *p*-nitroso-*N*,*N*-dimethylaniline (2.5 g, 16.7 mmol) in benzene (20 ml) containing methanol (5 ml) with addition of *N*-benzyltrimethylammonium methoxide (as before) (1 ml) for 10 min. The product, isolated in the usual way, was chromatographed [Al_2O_3 (*ca.* 30 g); petroleum] giving two fractions: (i) the nitrone (**47**) (490 mg, 25%), m.p. 177—179 °C (CH_2Cl_2–MeOH), δ_H 2.8 (6 H, s, 2 Me) and 6.2 and 6.7 (2 H and 18 H, d, and m, =CH); δ_C 40.1 (Me), 110.3 (=CH), and 125.4—152.1 (25 signals resolved); *m/z* 442 ($M^{+\cdot}$); $\nu_{max.}$ 1 603vs, 1 520ms, 1 460vs, 1 368vs, 1 280vs, and 1 156vs cm^{-1}; and (ii) the anil (**46**) (740 mg, 38%), m.p. 178—179 °C (lit.,[40] 172—173 °C), δ_H 2.8 (6 H, s, 2 Me), and 6.2 and 6.5—7.5 (2 H and 18 H, d and m, =CH); δ_C 40.7 (Me), 112.0 (=CH), and 123.4—155.0 (19 signals resolved); *m/z* 426 ($M^{+\cdot}$, 100%); $\nu_{max.}$ 1 610vs, 1 513vs, 1 448vs, 1 360vs, and 1 170vs cm^{-1}. The anil (500 mg, 1.17 mmol) was treated in benzene (15 ml) containing methanol (5 ml) with conc. HCl (2 ml) at the b.p. for 10 min; the product was isolated in the usual manner giving the dimer of 2,3,5-triphenylcyclopenta-2,4-dienone (**2l**) (210 mg, 58%), m.p. 181—183 °C (decomp.) (lit.,[40] 183—184 °C) (CH_2Cl_2–MeOH), similarly made from the nitrone (**47**) (50% yield).

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