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REACTIONS OF CYCLO-OCTATETRAENE AND ITS DERIVATIVES—IX[1]

CYCLOPENTADIENONE ADDUCTS OF TRICYCLO[4.2.2.0^{2,5}]DECA-3,7-DIENES AND TRICYCLO[4.2.1.0^{2,5}]NONA-3,7-DIENES†

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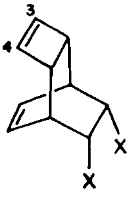
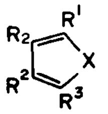
Abstract—Tetracyclo[8.2.2.0^{2,9}.0^{3,8}]tetradeca-4,6,11-trienes **5** are produced from tricyclo[4.2.2.0^{2,5}]deca-3,7-dienes **1** by reaction with cyclopentadienones **2** (or equiv) followed by thermal decarbonylation. With tetraphenylcyclopentadienone, however, the product **5e** rearranges under the conditions required for its formation to give the dihydrosemibullvalene **11**. The rearrangement evidently proceeds *via* the cyclo-octa-1,3,5-triene **14**, the ring-opening **5e** → **14** being facilitated by a phenyl-conjugation effect, uncovered in another series of experiments involving the reaction of cyclopentadienones with the tricyclo[4.2.1.0^{2,5}]nona-3,7-diene **16**. Thus the tetraphenylcyclohexa-1,3-diene **18c** undergoes ring-opening in refluxing xylene to afford the cyclo-octa-1,3,5-triene **21a**, whereas the dimethyldiphenyl-analogue **18b** resists valence isomerisation under these conditions.

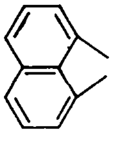
The 3,4-double bond of the tricyclo[4.2.2.0^{2,5}]deca-3,7-diene system **1** shows high dienophilic reactivity towards electron-deficient dienes.[3-6] Thus the cyclo-addition of the cyclopentadienone ketal **2a** and the cyclo-octatetraene–maleic anhydride adduct **1a** yielded the product **3a**,‡ which on hydrolysis of the ketal group, followed by thermal extrusion of carbon monoxide from the carbonyl-bridged intermediate **3b**, furnished the triene-anhydride **5a**. Our interest in this product originally centered on its possible conversion into the benzene-maleic anhydride photo-adduct **6**,[8] but we failed to accomplish the required oxidative degradation with the necessary selectivity. In an attempt to obtain the nonchlorinated analogue **5b**, compound **1a** was treated with α-pyrone **2b** in refluxing xylene. This procedure, however, resulted in the sparingly soluble dianhydride **7a**, presumably produced *via* an initial lactone-bridged adduct and the decarboxylated product **5b**, which rapidly added a second molecule of the dienophile **1a** (*cf* Ref. 9). Correspondingly, the tetrachloro-analogue **7b** was formed from **5a** by the addition of **1a**. The dianhydrides **7a** and **7b**§ were purified and characterised as the tetramethyl esters, the PMR spectra of which were consistent only with a highly symmetrical carbon skeleton.

A feature of the ¹H NMR spectra of the tetramethyl esters derived from the dianhydrides **7a** and **7b** was the presence in each of a four-proton singlet (at τ 7.32 and



1 **a**: XX = CO.O.CO
b: X = CO$_2$Me



2 **a**: R¹ = R² = R³ = Cl, X = C(OMe)$_2$
b: R¹ = R² = R³ = H, X = O.CO
c: R¹ = R³ = Me, R² = Ph, X = CO
d: R¹ = R³ = Ph, R²R² =  , X = CO
e: R¹ = R² = R³ = Ph, X = CO
f: R¹ = R² = R³ = Cl, X = CCl$_2$
g: R¹ = Me, R² = R³ = Ph, X = CO

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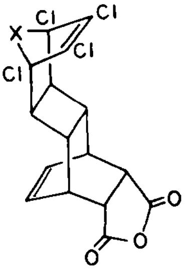
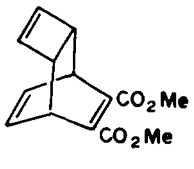
†Part of this work has been the subject of a preliminary publication.[2]

‡The stereochemistry illustrated in structure **3** is that resulting from an *endo* addition on the unhindered side of the 3,4-double bond of **1**; this addition-mode is undoubtedly shown by the diene **2a** in its reaction with the dimethyl acetylenedicarboxylate adduct **4**.[4,7]

§Stereochemistry assigned on the assumption that cycloaddition occurred on the less hindered side of the 1,3-diene system.



3 **a**: X = C(OMe)$_2$
b: X = CO



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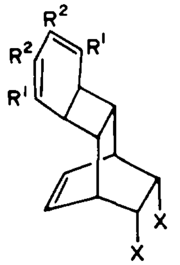
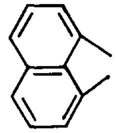


5 **a**: R^1 = R^2 = Cl, XX = CO.O.CO
b: R^1 = R^2 = H, XX = CO.O.CO
c: R^1 = Me, R^2 = Ph, X = CO$_2$Me

d: R^1 = Ph, R^{2}R^2 =  , XX = CO.O.CO

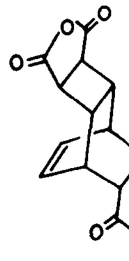
e: R^1 = R^2 = Ph, XX = CO.O.CO

7.19 respectively). By comparison with the spectrum of the dimethyl ester **1b** (which shows a two-proton singlet at τ 7.16) it may be concluded that these singlets must be due to the protons which are in the α-position with respect to an ester group. The negligible coupling of these protons with the adjacent bridgehead protons, presumably a consequence of the dihedral angles approximating to 90°, is not observed in the anhydride **1a**.

As an extension of this work we examined the reactions of the system **1** with various cyclopentadienones, using conditions (refluxing tetralin; *ca* 210°) such that thermal decarbonylation of the initial adducts ensued. The decarbonylated product from hemicyclone **2c** and the dimethyl ester **1b**† was found to possess structure **5c**, and that from acecyclone **2d** and the anhydride **1a** the analogous structure **5d**. In accord with its formulation as a cyclohexa-1,3-diene, **5c** reacted with tetracyanoethylene and with dimethyl acetylenedicarboxylate to yield the adducts **9a** and **9b** respectively.§ When an *excess* of the dimethyl ester **1b** reacted with hemicyclone **2c**, there resulted a *ca* 10:1 mixture of 1:2 adducts of m.p. 345° (dec) and 304–306° (dec), which could be formulated as **7c** and **10** respectively.§

In contrast, tetracyclone **2e** and the anhydride **1a** in refluxing tetralin did not give rise to the expected structure **5c**, but yielded an isomeric compound; the same product resulted from thermolysis of the isolated carbonyl-bridge adduct **8b** (stereochemistry unproven). In the ^{1}H NMR spectrum of this decarbonylated product the vinylic protons showed different chemical shifts, and two other protons gave rise to singlet signals at τ 6.00 and 7.27.‡ Moreover, the ^{13}C NMR spectrum indicated that the molecule contained ten saturated carbon atoms, of which two could be distinguished as *quaternary* carbons by offset proton-decoupling. Evidently, thermal decarbonylation of the initial adduct **8b** was succeeded by rearrangement of the carbon skeleton. The structure of this product remained in doubt until the following observation of a further rearrangement provided evidence for its formulation as the dihydrosemibullvalene derivative **11**.

The decarbonylated anhydride formed a dimethyl ester in refluxing methanol containing conc sulphuric acid, but prolongation of the reaction time resulted in the gradual appearance of a second product, the IR spectrum of which suggested that it was a half ester-lactone (IR ν_{max} 1768 and 1730 cm^{-1}); when ethanol was used instead of methanol, lactone-formation was much faster. An X-ray



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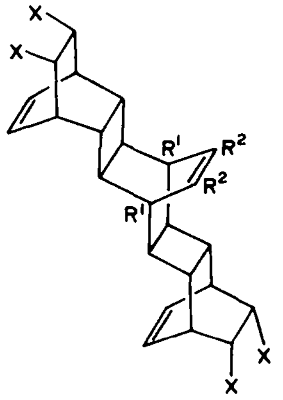
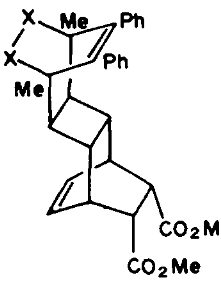
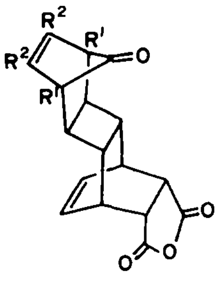


7 **a**: R^1 = R^2 = H, X = CO.O.CO
b: R^1 = R^2 = Cl, X = CO.O.CO
c: R^1 = Me, R^2 = Ph, X = CO$_2$Me





8 **a**: R^1 = Me, R^2 = Ph
b: R^1 = R^2 = Ph

9 **a**: X C(CN)$_2$ | = | X C(CN)$_2$

b: X C.CO$_2$Me | = || X C.CO$_2$Me

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†We failed to isolate a thermally decarbonylated product from hemicyclone and the anhydride **1a** [the carbonyl-bridged adduct **8a** has been prepared in refluxing toluene; *photolytic* decarbonylation was followed by fragmentation[6]].

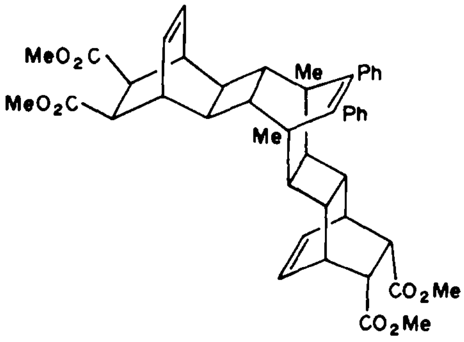
‡Products of tetracyclone-cyclobutene reactions showing similar NMR spectral characteristics have been encountered quite independently by the Bristol research groups of Drs. K. Mackenzie (see accompanying paper[10]) and J. W. Barton.

§See footnote on p. 1.

crystallographic study of the ethyl ester-lactone revealed the structure **12b**.

Details of the structure determination are given in the Experimental. Table 1 shows the fractional co-ordinates for the two independent molecules in the asymmetric unit, and Tables 2 and 3 give the bond lengths and angles.† A perspective drawing of molecule 1 is shown in Fig. 1, which also gives the crystallographic numbering.

The geometries of the two independent molecules are very similar, the largest differences being in the torsion angles between the benzene rings at C(1), C(2) and C(3). There is one anomalous bond length, that between the two C atoms of the Et group, which is clearly much too short. We have noticed this trend in other ethyl esters, particularly when the temperature factor of the methyl carbon is very high, as it is in this case.



10

A mechanism of the rearrangement terminating in structure **12** is readily visualised from the dihydrosemibullvalene **11**. Protonation of the dihydrosemibullvalene double bond (at position 4) could lead to cyclopropane ring-opening, and participation of the remaining double bond with subsequent cross-lactonisation is reminiscent of e.g. the bromo-lactonisation of **1b**, recently shown to afford a product possessing structure **13**[11] (see also Ref.

Table 1. Fractional co-ordinates ($\times 10^4$), with standard deviations in parentheses

	Molecule 1			Molecule 2		
Atom	x/a	y/b	z/c	x/a	y/b	z/c
O(1)	659(1)	8590(2)	5840(2)	4258(1)	3612(2)	9481(2)
O(2)	1099(1)	7506(2)	5529(3)	3840(1)	2686(2)	10083(2)
O(3)	884(1)	8754(3)	3457(3)	4268(1)	4060(2)	12012(2)
O(4)	241(1)	9371(2)	3702(2)	4883(1)	4544(2)	11550(2)
C(1)	1124(1)	12027(2)	7157(2)	3876(1)	6999(2)	7974(2)
C(2)	1588(1)	12251(2)	7595(3)	3420(1)	7318(2)	7692(3)
C(3)	1988(1)	11578(2)	7774(2)	2997(1)	6738(3)	7702(3)
C(4)	1816(1)	10661(3)	7418(3)	3141(1)	5822(3)	8090(3)
C(5)	1304(1)	10416(2)	7492(3)	3583(2)	5424(2)	7841(3)
C(6)	1000(1)	11101(2)	6813(3)	3974(1)	6080(3)	8357(3)
C(7)	1674(1)	10445(3)	6360(3)	3372(1)	5662(3)	9155(3)
C(8)	1148(1)	10849(2)	5934(3)	3920(1)	5967(2)	9350(3)
C(9)	1593(1)	9468(2)	6417(3)	3385(1)	4669(3)	9147(3)
C(10)	1373(1)	8992(3)	5450(3)	3662(1)	4320(3)	10100(3)
C(11)	1032(1)	9648(3)	4782(3)	4071(1)	4859(3)	10611(3)
C(12)	790(1)	10140(3)	5410(3)	4264(1)	5221(3)	9835(3)
C(13)	1208(1)	9513(3)	6961(3)	3681(2)	4560(3)	8433(3)
C(14)	727(2)	9494(2)	6173(3)	4205(2)	4495(3)	9079(3)
C(15)	1054(2)	8274(3)	5607(3)	3906(2)	3426(3)	9900(3)
C(16)	668(2)	9250(3)	3933(3)	4460(2)	4472(3)	11422(3)
C(17)	702(1)	12632(2)	7020(3)	4306(1)	7508(3)	7909(3)
C(18)	635(2)	13090(3)	7773(4)	4331(2)	7853(3)	7064(3)
C(19)	239(2)	13623(4)	7650(6)	4730(2)	8319(4)	7022(6)
C(20)	−98(2)	13717(4)	6782(6)	5116(2)	8459(4)	7800(5)
C(21)	−47(2)	13257(4)	6029(5)	5108(2)	8108(3)	8656(4)
C(22)	354(2)	12708(3)	6144(3)	4704(2)	7626(3)	8695(3)
C(23)	1739(1)	13145(2)	7951(3)	3292(1)	8220(3)	7334(3)

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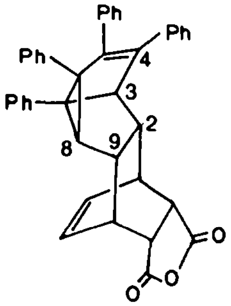
†Tables of torsion angles and of observed and calculated structure factors have been deposited in the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.

Table 1 (*Contd*)

	Molecule 1			Molecule 2		
Atom	x/a	y/b	z/c	x/a	y/b	z/c
C(24)	1994(2)	13279(3)	8888(3)	2909(2)	8367(3)	6518(3)
C(25)	2139(2)	14099(3)	9225(3)	2782(2)	9206(3)	6198(3)
C(26)	2032(2)	14816(3)	8648(3)	3019(2)	9910(3)	6679(3)
C(27)	1783(2)	14687(3)	7710(3)	3402(2)	9779(3)	7489(3)
C(28)	1645(2)	13864(3)	7374(3)	3532(2)	8946(3)	7804(3)
C(29)	2418(1)	11891(2)	7460(3)	2666(2)	7162(3)	8193(4)
C(30)	2886(2)	11879(3)	8068(3)	2163(2)	7042(4)	7824(6)
C(31)	3282(2)	12144(3)	7792(4)	1865(3)	7368(7)	8316(11)
C(32)	3210(2)	12435(3)	6889(4)	2026(5)	7801(7)	9106(10)
C(33)	2749(2)	12475(3)	6284(3)	2541(4)	7984(5)	9505(5)
C(34)	2351(2)	12207(3)	6565(3)	2858(2)	7639(4)	9018(4)
C(35)	1230(2)	10376(3)	8455(3)	3520(2)	5276(3)	6808(3)
C(36)	1541(2)	9895(4)	9157(3)	3098(2)	4875(4)	6265(3)
C(37)	1449(3)	9784(5)	10014(4)	3035(3)	4715(4)	5320(4)
C(38)	1057(3)	10167(4)	10174(4)	3400(4)	4937(5)	4933(4)
C(39)	745(2)	10660(4)	9492(4)	3808(3)	5329(5)	5459(4)
C(40)	833(2)	10764(3)	8629(3)	3875(2)	5502(4)	6409(3)
C(41)	556(2)	8333(6)	2620(5)	4609(2)	3692(5)	12838(4)
C(42)	546(7)	8800(12)	1914(12)	4685(5)	4197(12)	13603(9)



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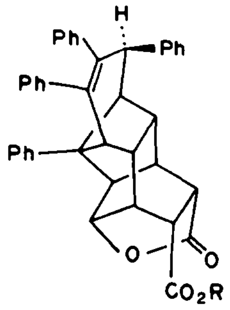
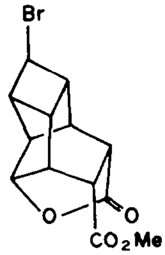


12 **a**: R = Me
b: R = Et



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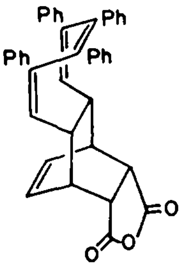

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12). Furthermore, structure **11** is consistent with the spectral evidence, and in particular explains the presence of two singlet PMR signals, which may be assigned to H-3 (low-field) and H-8 (high-field), the dihedral angles with H-2 and H-9 respectively being close to 90° (as judged from a molecular model).

The thermal rearrangement of **5e** to **11** most probably occurs *via retro*-6π electrocyclisation to the cyclo-octa-1,3,5-triene **14** (see below), which then undergoes what may be considered as a symmetry-allowed $[_{\pi}4_{a} +$

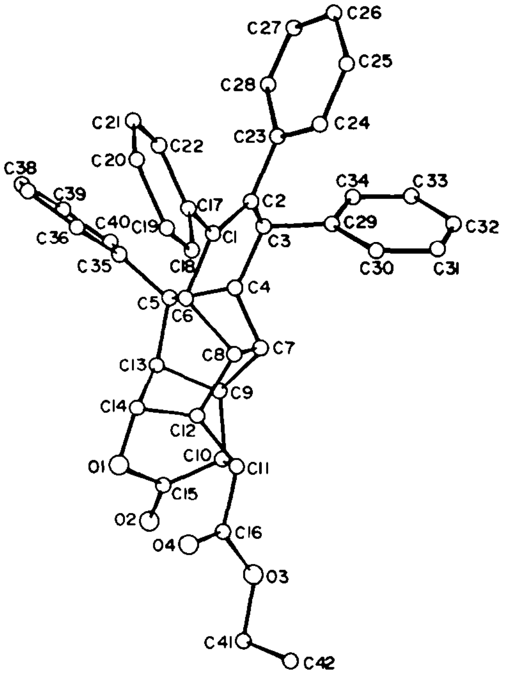


Fig. 1.

Table 2. Bond lengths in Å, with standard deviations in parentheses

	Mol.1	Mol.2		Mol.1	Mol.2
O(1) - C(14)	1.464(5)	1.470(5)	C(12) - C(14)	1.560(5)	1.556(5)
O(1) - C(15)	1.371(4)	1.372(4)	C(13) - C(14)	1.525(5)	1.530(5)
O(2) - C(15)	1.193(5)	1.196(5)	C(17) - C(18)	1.389(6)	1.389(5)
O(3) - C(16)	1.319(5)	1.332(5)	C(17) - C(22)	1.392(6)	1.382(6)
O(3) - C(41)	1.468(6)	1.440(5)	C(18) - C(19)	1.367(7)	1.371(6)
O(4) - C(16)	1.187(4)	1.194(4)	C(19) - C(20)	1.372(9)	1.360(8)
C(1) - C(2)	1.343(4)	1.343(5)	C(20) - C(21)	1.372(9)	1.392(7)
C(1) - C(6)	1.515(5)	1.515(5)	C(21) - C(22)	1.397(6)	1.394(6)
C(1) - C(17)	1.491(5)	1.492(5)	C(23) - C(24)	1.385(5)	1.394(5)
C(2) - C(3)	1.509(5)	1.511(5)	C(23) - C(28)	1.375(5)	1.384(5)
C(2) - C(23)	1.485(5)	1.487(5)	C(24) - C(25)	1.371(6)	1.381(6)
C(3) - C(4)	1.531(5)	1.528(5)	C(25) - C(26)	1.373(6)	1.360(6)
C(3) - C(29)	1.526(5)	1.514(6)	C(26) - C(27)	1.382(6)	1.383(6)
C(4) - C(5)	1.557(5)	1.554(5)	C(27) - C(28)	1.371(6)	1.374(6)
C(4) - C(7)	1.543(5)	1.546(5)	C(29) - C(30)	1.381(5)	1.398(8)
C(5) - C(6)	1.537(5)	1.531(5)	C(29) - C(34)	1.380(6)	1.396(6)
C(5) - C(13)	1.576(5)	1.571(5)	C(30) - C(31)	1.383(5)	1.379(7)
C(5) - C(35)	1.516(5)	1.513(5)	C(31) - C(32)	1.376(7)	1.310(12)
C(6) - C(8)	1.544(5)	1.546(5)	C(32) - C(33)	1.362(6)	1.450(14)
C(7) - C(8)	1.582(5)	1.584(4)	C(33) - C(34)	1.396(5)	1.427(12)
C(7) - C(9)	1.520(5)	1.528(5)	C(35) - C(36)	1.371(6)	1.383(6)
C(8) - C(12)	1.539(5)	1.543(5)	C(35) - C(40)	1.381(6)	1.375(6)
C(9) - C(10)	1.571(5)	1.558(5)	C(36) - C(37)	1.393(7)	1.403(7)
C(9) - C(13)	1.560(5)	1.562(5)	C(37) - C(38)	1.356(8)	1.376(8)
C(10)- C(11)	1.543(6)	1.533(5)	C(38) - C(39)	1.366(8)	1.342(8)
C(10)- C(15)	1.496(6)	1.494(6)	C(39) - C(40)	1.394(7)	1.398(7)
C(11)- C(12)	1.524(5)	1.532(5)	C(41) - C(42)	1.267(15)	1.341(15)
C(11)- C(16)	1.509(5)	1.500(5)			

Table 3. Bond angles in degrees, with standard deviations in parentheses

	Mol.1	Mol.2		Mol.1	Mol.2
C(14) - O(1) - C(15)	112.6(3)	112.2(3)	C(6) - C(8) - C(7)	103.4(3)	103.8(3)
C(16) - O(3) - C(41)	115.1(4)	116.1(3)	C(6) - C(8) - C(12)	107.2(3)	107.2(3)
C(2) - C(1) - C(6)	120.1(3)	120.7(4)	C(7) - C(8) - C(12)	109.9(3)	109.5(3)
C(2) - C(1) - C(17)	123.9(4)	122.8(4)	C(7) - C(9) - C(10)	115.6(3)	115.4(3)
C(6) - C(1) - C(17)	115.9(3)	116.5(3)	C(7) - C(9) - C(13)	97.5(3)	97.6(3)
C(1) - C(2) - C(3)	120.4(4)	119.8(4)	C(10)- C(9) - C(13)	110.2(3)	110.0(3)
C(1) - C(2) - C(23)	123.4(4)	124.3(4)	C(9) - C(10) - C(11)	107.1(3)	106.9(3)
C(3) - C(2) - C(23)	116.2(3)	115.9(3)	C(9) - C(10) - C(15)	107.2(3)	108.4(3)
C(2) - C(3) - C(4)	114.7(3)	114.6(3)	C(11)- C(10) - C(15)	106.2(3)	106.3(3)
C(2) - C(3) - C(29)	112.1(3)	112.3(4)	C(10)- C(11) - C(12)	104.1(3)	104.4(3)
C(4) - C(3) - C(29)	112.9(3)	110.5(3)	C(10)- C(11) - C(16)	115.1(3)	115.3(3)
C(3) - C(4) - C(5)	114.2(3)	114.7(3)	C(12)- C(11) - C(16)	112.7(3)	113.7(3)
C(3) - C(4) - C(7)	120.7(3)	121.0(3)	C(8) - C(12) - C(11)	107.6(3)	107.2(3)
C(5) - C(4) - C(7)	93.2(3)	93.3(3)	C(8) - C(12) - C(14)	106.5(3)	106.0(3)
C(4) - C(5) - C(6)	98.7(3)	98.8(3)	C(11)- C(12) - C(14)	108.0(3)	107.7(3)
C(4) - C(5) - C(13)	101.6(3)	102.5(3)	C(5) - C(13) - C(9)	104.9(3)	104.5(3)
C(4) - C(5) - C(35)	118.9(3)	116.5(3)	C(5) - C(13) - C(14)	112.7(3)	112.6(3)
C(6) - C(5) - C(13)	106.9(3)	106.9(3)	C(9) - C(13) - C(14)	102.7(3)	102.4(3)
C(6) - C(5) - C(35)	115.9(3)	117.2(3)	O(1) - C(14) - C(12)	112.7(3)	112.7(3)
C(13) - C(5) - C(35)	112.8(3)	113.1(3)	O(1) - C(14) - C(13)	106.1(3)	106.2(3)
C(1) - C(6) - C(5)	112.8(3)	113.2(3)	C(12)- C(14) - C(13)	105.8(3)	106.4(3)
C(1) - C(6) - C(8)	115.2(3)	113.8(3)	O(1) - C(15) - O(2)	119.7(4)	119.5(4)
C(5) - C(6) - C(8)	98.2(3)	98.0(3)	O(1) - C(15) - C(10)	112.0(4)	112.0(3)
C(4) - C(7) - C(8)	104.7(3)	103.9(3)	O(2) - C(15) - C(10)	128.3(4)	128.4(4)
C(4) - C(7) - C(9)	98.7(3)	98.6(3)	O(3) - C(16) - O(4)	123.4(4)	123.5(4)
C(8) - C(7) - C(9)	105.4(3)	105.5(3)	O(3) - C(16) - C(11)	111.3(4)	111.3(3)

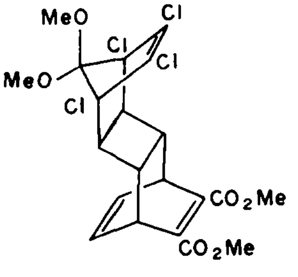
Table 3 (*Contd*)

	Mol.1	Mol.2		Mol.1	Mol.2
O(4) - C(16) - C(11)	125.3(4)	125.2(4)	C(3) - C(29) - C(30)	121.1(4)	118.8(4)
C(1) - C(17) - C(18)	120.7(4)	121.9(4)	C(3) - C(29) - C(34)	121.2(3)	120.8(6)
C(1) - C(17) - C(22)	120.5(4)	120.3(4)	C(30) - C(29) - C(34)	117.7(4)	120.4(6)
C(18) - C(17) - C(22)	118.7(4)	117.7(4)	C(29) - C(30) - C(31)	122.0(4)	118.6(7)
C(17) - C(18) - C(19)	120.5(5)	120.8(5)	C(30) - C(31) - C(32)	119.6(4)	123.6(8)
C(18) - C(19) - C(20)	120.9(6)	121.5(5)	C(31) - C(32) - C(33)	119.5(4)	120.6(7)
C(19) - C(20) - C(21)	119.9(5)	119.2(4)	C(32) - C(33) - C(34)	120.9(5)	116.8(9)
C(20) - C(21) - C(22)	119.9(6)	119.2(5)	C(29) - C(34) - C(33)	120.4(4)	119.9(8)
C(17) - C(22) - C(21)	120.0(5)	121.5(5)	C(5) - C(35) - C(36)	120.0(4)	118.7(4)
C(2) - C(23) - C(24)	120.5(3)	120.7(3)	C(5) - C(35) - C(40)	121.5(4)	121.7(4)
C(2) - C(23) - C(28)	122.3(3)	122.2(4)	C(36) - C(35) - C(40)	118.4(4)	119.5(5)
C(24) - C(23) - C(28)	117.2(4)	117.1(4)	C(35) - C(36) - C(37)	120.4(5)	119.7(5)
C(23) - C(24) - C(25)	121.1(4)	120.7(4)	C(36) - C(37) - C(38)	120.5(6)	119.4(6)
C(24) - C(25) - C(26)	121.2(4)	121.2(4)	C(37) - C(38) - C(39)	120.3(5)	120.9(6)
C(25) - C(26) - C(27)	118.1(4)	119.2(4)	C(38) - C(39) - C(40)	119.3(5)	120.5(6)
C(26) - C(27) - C(28)	120.5(4)	119.8(4)	C(35) - C(40) - C(39)	121.1(5)	120.0(5)
C(23) - C(28) - C(27)	121.9(4)	122.1(4)	O(3) - C(41) - C(42)	107.9(11)	113.4(8)

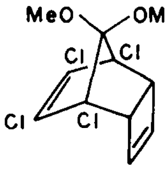
$_{\pi}2_a$]cycloaddition[13] (the possibility of a non-concerted process, involving a diradical intermediate, is discussed in the accompanying paper[10]). The only previous examples of the cyclo-octa-1,3,4-triene→dihydrosemibullvalene rearrangement known to us were photo-induced,[14] although thermal cyclo-octatetraene→semibullvalene conversions have been demonstrated.[15]

Conversion of the tetraphenyl-compound **5e** into the dihydrosemibullvalene derivative **11** occurs under conditions which fail to promote rearrangement of the closely related dimethyldiphenyl-compound **5c**. A possible reason for this substituent-group effect emerged from the results of further experiments described below.

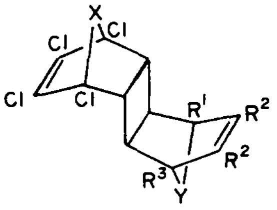
[4+2]Cycloaddition of **2a** and **4** in chloroform or toluene, followed by thermolysis of the resulting *endo* adduct **15**, leads to dimethyl phthalate and the cyclobutene **16**,[1,3,4,7,16] the stereochemistry of which has been established.[4,7,16] Further cycloaddition to **16** using **2a** gave the diketal **17a**, which was more readily obtained directly from **2a** and **4** in refluxing xylene. The illustrated *endo-anti-endo* stereochemistry of **17a**, although unproven, is strongly favoured on steric grounds. Hydrolysis of the ketal functions afforded the diketone **17b**,† which on thermal decarbonylation yielded (as expected[17]) 1,2,3,4-tetrachlorobenzene. Reaction of **15** with hexachlorocyclopentadiene **2f** in refluxing xylene gave the adduct **17d**, and hydrolysis and subsequent decarbonylation then afforded the cyclohexa-1,3-diene **18a**. This compound could be recovered after 10 min at 200° (or 8 days in refluxing xylene), and this thermal stability supports an *anti* geometry with respect to the 4-membered ring; the *syn* isomer would be expected to undergo an intramolecular [4+2]cycloaddition (*cf* Refs 10 and 18).



15



16



17 **a**: R¹ = R² = R³ = Cl, X = Y = C(OMe)₂

b: R¹ = R² = R³ = Cl, X = Y = CO

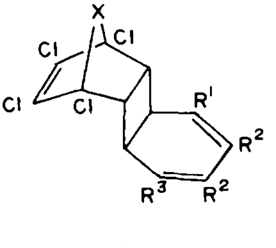
c: R¹ = R² = R³ = Cl, X = Y = C(OH)(OMe)

d: R¹ = R² = R³ = Cl, X = C(OMe)₂, Y = CCl₂

e: R¹ = R³ = Me, R² = Ph, X = C(OMe)₂, Y = CO

Treatment of **16** with hemicyclone **2c** in refluxing xylene for $2\frac{1}{4}$ hr resulted in a mixture of a carbonyl-bridged adduct, formulated as the *endo-anti-exo* compound **19a**, and the decarbonylated product **18b** (molar ratio 5.5:1 (*cf* the accompanying paper[10]). By analogy with the results obtained by Warrener *et al.*[7] in their thorough investigation of the reaction of **2c** with *cis*-3,4-dichlorocyclobutene, the initial cycloaddition probably gave a mixture of *exo* and *endo* adducts with the *exo* isomer **19a** predominating; this stereoisomer should show greater thermal stability than the *endo* compound **17e**, which should undergo more facile decarbonylation[19] with the formation of **18b**. Support for an *endo-anti-exo* structure for **19a** was obtained by the formation of an identical product from **2a** and **20**, the *exo* stereochemistry of which is proven.[7] While the adduct **19a** was apparently stable in refluxing xylene, at 240° it lost carbon monoxide to give **18b**.

In contrast with hemicyclone **2c**, tetracyclone **2e** reacted with **16** in refluxing xylene (5 hr) to yield, in addition



18 **a**: R¹ = R² = R³ = Cl, X = CCl₂

b: R¹ = R³ = Me, R² = Ph, X = C(OMe)₂

c: R¹ = R² = R³ = Ph, X = C(OMe)₂

d: R¹ = Me, R² = R³ = Ph, X = C(OMe)₂

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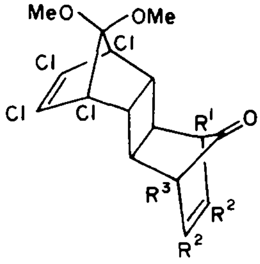
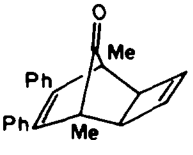
†This could not itself be crystallised; crystallisation from methanol gave the *bis*-hemiketal **17c**.



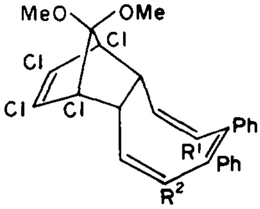
19 a: $R^1 = R^3 =$ Me, $R^2 =$ Ph
b: $R^1 = R^2 = R^3 -$ Ph
c: $R^1 =$ Me, $R^2 = R^3 =$ Ph

to the carbonyl-bridged adduct **19b**, the cyclo-octa-1,3,5-triene **21a** (molar ratio 5:4) (*cf* accompanying paper[10]). Under these conditions, therefore, the initial decarbonylation product **18c** was transformed into its valence isomer (*retro*-6π electrocyclisation). The reaction pathway also differed in another respect, in that much of the final product **21a** must have derived from the *exo* carbonyl-bridged adduct **19b**, which in a separate experiment was shown to decarbonylate slowly at *ca* 165° (refluxing mesitylene).

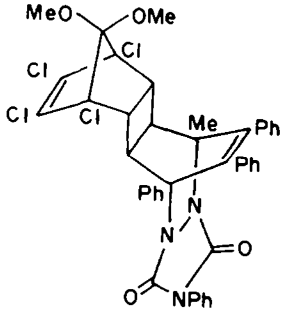
When a similar experiment was performed with 2-methyl-3,4,5-triphenylcyclopentadienone **2g**, the carbonyl-bridged adduct **19c** was accompanied by both the cyclohexa-1,3-diene **18d** and the cyclo-octa-1,3,5-triene **21b** (**18d** being characterised as the N-phenyltriazolinedione adduct **22**). The molar ratio of carbonyl-bridged adduct to decarbonylated products was 3.5:1, and that of the cyclohexa-1,3-diene to the cyclo-octa-1,3,5-triene was 3:2 (estimated from the PMR spectrum of the mixture). When the decarbonylated products **18d** and **21b** were prepared by heating **19c** at 220°/0.1 mm for a short time, their ratio was 1:4.



20



21 a: $R^1 = R^2 =$ Ph
b: $R^1 =$ Me, $R^2 =$ Ph



22

It seems clear that in this series the cyclo-octa-1,3,5-triene ring is stabilised, relative to the bicyclo[4.2.0]octa-2,4-diene system, by the presence of phenyl groups in the 2- and 5-positions. The reason for this is apparent from a study of molecular models, which show that whereas the phenyl groups in the cyclohexa-1,3-diene **18c** must be twisted out of the plane of the conjugated diene system (Fig. 2), in the cyclo-octa-1,3,5-triene **21a** the 2- and 5-phenyl groups can readily exist in planarity with the 1,2- and 5,6-double bonds respectively and can therefore attain full conjugation (Fig. 3).

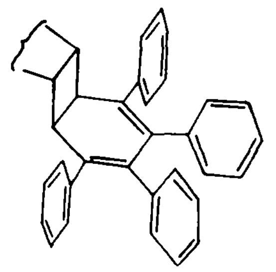


Fig. 2.

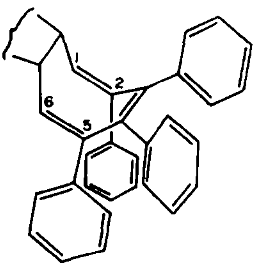


Fig. 3.

We therefore conclude that the rearrangement of the cyclohexa-1,3-diene **5e** to the dihydrosemibullvalene **11** takes place *via* the cyclo-octa-1,3,5-triene **14**, and that the valence isomerisation **5e** → **14** is facilitated by the phenyl-conjugation effect.

EXPERIMENTAL

Unless stated otherwise, light petroleum refers to the fraction of b.p. 60–80°; IR spectra were determined for Nujol mulls; ^{1}H and ^{13}C spectra were measured in $CDCl_3$ at 100 and 25.15 MHz, respectively, using Me_4Si as internal standard. The m.ps of several of the products described below were diffuse and variable.

The ketal-anhydride **3a** [With Kettlewell[3]]. The adduct **1a**[20] (12 g) and **2a**[21] (20 g) were heated in refluxing xylene (50 ml) for 6 hr. The soln was allowed to cool, and the resulting crystals were collected and recrystallised from $CHCl_3$ to give **3a** (22 g, 79%), m.p. 289–291° (dec). (Found: C, 48.7; H, 3.6; Cl, 30.5. $C_{19}H_{16}Cl_4O_5$ requires: C, 49.0; H, 3.5; Cl, 30.4%; IR ν_{max} 1848, 1767, 1610 cm^{-1}; PMR τ [$(CD_3)_2CO$] 3.45–3.6(2H), 6.5–6.6(6H), 6.7–6.85(4H), 7.35–7.45(2H) and 7.7–7.8(2H).

The tetrachloro-triene-anhydride **5a** [With Kettlewell[3]]. A mixture of the finely-ground adduct **3a** (21 g) and conc H_2SO_4 (50 ml) was heated on the steam-bath, with frequent agitation, for 20 min. The mixture was poured onto ice, and the solid was collected, washed well with water, and dried. The crude **3b** (IR ν_{max} 1850sh, 1830, 1767, 1576 cm^{-1}) was then taken up in chlorobenzene (80 ml), and the soln was heated under reflux for 2 hr. Removal of the solvent under reduced pressure, followed by recrystallisation of the residue from Me_2CO, afforded **5a** (13 g, 74%), m.p. 232–234° (dec). (Found: 49.2; H, 2.6; Cl, 36.1. $C_{16}H_{10}Cl_4O_3$ requires: C, 49.0; H, 2.6; Cl, 36.2%); IR ν_{max} 1850, 1774, 1616 cm^{-1}; UV λ_{max} (CH_3CN) 295 nm (ε 4600); PMR τ 3.55–3.75(2H), 6.5–6.75(2H), 6.85–7.0(2H), 7.25–7.5(4H).

The dianhydride **7a**. α-Pyrone[22] (1.5 g) was heated with adduct **1a** (3.0 g), in refluxing xylene (50 ml) for 2 hr. The insoluble product (2.9 g, 86%) had m.p. > 390° and showed IR ν_{max} 1855, 1830 and 1790 cm^{-1}; it did not give a correct elemental analysis, even after recrystallisation (from Ac_2O).

The tetramethyl ester (prepared with methanolic H_2SO_4) had m.p. 270–271° (from MeOH). (Found: C, 69.8; H, 6.7; OMe, 22.0. $C_{32}H_{36}O_8$ requires: C, 70.0; H, 6.6; OMe, 22.6%); IR ν_{max} 1720br cm^{-1}; PMR τ 3.45–3.8(6H), 6.50(12H, s), 7.1–7.3(4H), 7.32(4H, s), 7.45–7.65(2H), 8.15–8.3(4H), 8.4–8.55(4H).

The tetrachloro-dianhydride **7b**. A mixture of **5a** (0.39 g) and adduct **1a** (0.20 g) was kept at 160–170° (bath) under N_2 for 10 min. The crude product (IR ν_{max} 1855, 1780br, 1593 cm^{-1}) was converted (methanolic H_2SO_4) into the tetramethyl ester (0.56 g, 83%), m.p. *ca* 350° (dec) (from MeOH). (Found: C, 55.0; H, 4.6; Cl, 21.0. $C_{32}H_{32}Cl_4O_8$ requires: C, 54.7; H, 4.8; Cl, 21.3%); IR ν_{max} 1738, 1720, 1590 cm^{-1}; PMR τ 3.5–3.7(4H), 6.49(12H, s), 6.95–7.15(4H), 7.19(4H, s), 7.8–7.9(4H) and 7.9–8.05(4H).

The decarbonylated hemicyclone-adduct **5c**. The ester **1b**[20] (2.5 g), hemicyclone dimer[23] (2.5 g), and tetralin (30 ml) were heated under reflux for 4 hr. The solvent was removed under reduced pressure and the residual oil was chromatographed on alumina. Elution with Et_2O gave **5c** (0.58 g, 12%), m.p. 172–174° [from MeOH–light petroleum (b.p. 40–60°)]. (Found: C, 79.6; H, 6.5. $C_{32}H_{32}O_4$ requires: C, 80.0; H, 6.6%); IR ν_{max} 1756, 1740, 1640 cm^{-1}; UV λ_{max} (EtOH) 235, 289 nm (ε 10,800, 3600); PMR τ 2.85–3.35(10H), 3.35–3.5(2H), 6.36(6H, s), 6.85–7.15(4H; 2H s at 7.07), 7.35–7.55(4H), 8.59(6H, s).

The decarbonylated acecyclone-adduct **5d**. A mixture of **2d**[24] (2.54 g) and **1a** (1.5 g) was heated in refluxing tetralin (50 ml) for 2 hr. The soln was cooled and then poured into light petroleum (b.p. 40–60°); the resulting ppt was collected and recrystallised from C_6H_6 to give (yellow) **5d** (1.34 g, 36%), m.p. *ca* 315° (dec) (rapid heating). (Found: C, 86.1; H, 4.8. $C_{38}H_{26}O_3$ requires: C, 86.0; H, 4.9%); IR ν_{max} 1845, 1770, 1590 cm^{-1}; UV λ_{max} (EtOH) 241, 261, 368, 381 (ε 18,800, 15,200, 9000, 9000).

The dimethyl ester (prepared with methanolic H_2SO_4) had m.p. 219–221° (from MeOH) (Found: C, 83.2; H, 5.75. $C_{40}H_{32}O_4$ requires: C, 83.3; H, 5.6%); IR ν_{max} 1740, 1590 cm^{-1}; PMR τ 2.25–2.65(12H), 2.83(2H, dd, *J* 7.5 and 7.5 Hz), 3.29 (2H, d, *J* 7.5 Hz), 3.45–3.6(2H), 6.25–6.5(8H; 6H s at 6.45), 6.8–7.0(2H) and 7.1–7.35(4H).

The tetracyanoethylene-adduct **9a**. A mixture of the decarbonylated hemicyclone-adduct **5c** (100 mg) and tetracyanoethylene (28 mg) in C_6H_6 (25 ml) was heated under reflux overnight. Removal of the solvent, and recrystallisation of the residue from MeOH, gave **9a** (106 mg, 84%), m.p. 298–300° (dec). (Found: C, 74.7; H, 5.6; N, 8.95. $C_{38}H_{32}N_4O_4$ requires: C, 75.0; H, 5.3; N, 9.2%); IR ν_{max} 1743 cm^{-1}; PMR τ 2.6–3.2(10H), 3.25–3.4(2H), 6.35(6H, s), 6.8–7.05(4H; 2H s at 7.00), 7.60(4H, s), 8.60(6H, s).

The dimethyl acetylenedicarboxylate adduct **9b**. Heating the decarbonylated adduct **5c** (195 mg) and dimethyl acetylenedicarboxylate (60 mg) in C_6H_6 (40 ml) under reflux overnight, followed by removal of the solvent and recrystallisation of the residue from MeOH, furnished **9b** (198 mg, 78%), m.p. 235–236° (Found: C, 72.9; H, 6.3. $C_{38}H_{38}O_8$ requires: C, 73.3; H, 6.15%); IR ν_{max} 1720, 1603 cm^{-1}; PMR τ (CD_2Cl_2) 2.75–3.2(10H) 3.5–3.6(2H), 6.26(6H, s), 6.40(6H, s), 6.9–7.1(4H), 7.8–8.0(2H), 8.1–8.2(2H), 8.82(6H, s).

The tetramethyl esters **7c** *and* **10**. The ester **1b** (2.5 g) and hemicyclone dimer (1.3 g) were heated in refluxing tetralin (30 ml) for 24 hr, and the cooled soln was poured into light petroleum (100 ml). The resulting oily ppt slowly solidified, and recrystallisation from MeOH-light petroleum afforded **7c** (0.46 g), m.p. *ca* 345° (dec). (Found: C, 75.3; H, 6.8. $C_{46}H_{48}O_8$ requires: C, 75.8; H, 6.6%); IR ν_{max} 1758, 1732, 1710, 1598 cm^{-1}; PMR τ 2.8–3.10(10H), 3.45–3.55(4H), 6.40(12H, s), 7.0–7.2(8H), 7.7–7.9(4H), 8.4–8.5(4H), 9.16(6H, s).

The mother-liquors from the isolation of **7c** were evaporated under reduced pressure, and the residue was chromatographed on alumina. Elution with Et_2O give a further quantity of **7c** (40 mg), and elution with CH_2Cl_2 afforded a mixture of crystalline products which was extracted with warm MeOH. The MeOH-insoluble fraction proved to be **7c** (20 mg) (total yield 14%), and concentration of the methanolic extract yielded an isomer **10** (50 mg, 1.4%), m.p. 304–306° (dec). (Found: C, 75.4; H, 6.8); IR ν_{max} 1755sh, 1742, 1720, 1598 cm^{-1}; PMR τ 2.85–3.25(10H), 3.35–3.5(2H), 3.5–3.65(2H), 6.38(6H, s), 6.40(6H, s), 6.95–7.2(8H), 7.75–7.95(4H), 8.35–8.5(4H), 9.27(6H, s).

The decarbonylated tetracyclone-adduct **11a**. (a) Reaction of **2e** (18 g) with **1a** (9.5 g) in refluxing tetralin (50 ml) for 2 hr, and isolation of the product by pouring the soln into light petroleum, afforded a gum which crystallised from ether-acetone to give **11** (16 g, 61%), m.p. 271–272°. (Found: C, 86.2; H, 5.6. $C_{40}H_{30}O_3$ requires: C, 86.0; H, 5.4%); IR ν_{max} 1861, 1780, 1606 cm^{-1}; PMR τ 2.75–3.4(20H), 3.75–4.0(1H), 4.0–4.25(1H), 6.00(1H, s), 6.25–6.45(1H), 6.8–7.2(4H), 7.27(1H, s) and 7.7–7.85(1H); ^{13}C NMR δ 36.7, 37.7, 42.8, 43.7, 44.4, 45.6, 55.8, 56.2, 59.1, 63.2 (10 saturated C), 125.4, 125.8, 126.4, 126.9, 127.3, 127.7, 128.7, 129.1, 130.0, 132.0, 132.5, 135.8, 136.6, 137.5, 138.8, 142.3 (16 $=C\langle$ resolved), 171.8, 172.4 (2 C=O) ppm.

(b) Reaction of **2e** (3.8 g) and **1a** (2.0 g) in refluxing xylene (50 ml) for 15 hr yielded the adduct **8b** (4.1 g, 71%), m.p. *ca* 255° (dec) (from C_6H_6). (Found: C, 83.8; H, 5.2. $C_{41}H_{30}O_4$ requires: C, 83.95; H, 5.15%); IR ν_{max} 1859, 1780sh, 1773 cm^{-1}; PMR τ [$(CD_3)_2SO$] 2.5–3.45(22H), 6.4–6.6(2H), 6.7–6.85(2H), 7.05–7.2(2H), and 7.85–8.05(2H).

Decarbonylation of **8b** (9.4 g) in refluxing tetralin (30 ml) (2 hr) then gave a product identical with **11** (6.1 g, 68%).

The dimethyl ester of the product **11** (prepared in the usual way with methanolic H_2SO_4) decomposed at *ca* 145° with incomplete melting [from MeOH–light petroleum (b.p. 40–60°)] (Found: C, 82.9; H, 5.9. $C_{42}H_{36}O_4$ requires: C, 83.4; H, 6.0%; IR ν_{max} 1750, 1735, 1600 cm^{-1}; UV λ_{max} (EtOH) 227, 296 nm (ε 22,500, 8600); PMR τ 2.75–3.25(20H), 3.55–3.8(1H), 4.05–4.3(1H), 6.11(1H, s), 6.44(3H, s), 6.5–6.65(4H; 3H s at 6.57), 6.85–7.1(3H; 2H s at 7.07), 7.2–7.4(2H; 1H s at 7.29) and 7.65–7.8(1H).

The ester-lactones **12a** *and* **12b**. (a) A mixture of the anhydride **11** (5.4 g), MeOH (100 ml), and conc H_2SO_4 (0.1 ml) was heated under reflux for 40 hr; a crystalline product separated from the refluxing soln. The crystals were collected, washed with MeOH, and dried, giving **12a** (0.60 g, 12%), m.p. 331–333° (from EtOAc). (Found: C, 82.9; H, 5.8. $C_{41}H_{34}O_4$ requires: C, 83.4; H, 5.8%); IR ν_{max} 1768, 1730 cm^{-1}; PMR τ 2.5–3.55 (20H), 4.95–5.15 (1H), 5.80 (1H, d, *J* 6Hz), 6.27 (3H, s), 6.6–7.2(6H), 7.45–7.8(3H).

Concentration of the original methanolic soln yielded the ester **11** (0.42 g, 72%), identical with the previous sample.

(b) Similar treatment of **11** with EtOH containing conc H_2SO_4 for 5 hr afforded **12b** (72%), m.p. 332–333° (from EtOAc). (Found: C, 83.3; H, 6.2. $C_{42}H_{36}O_4$ requires: C, 83.4; H, 6.0%); IR ν_{max} 1770, 1725 cm^{-1}; PMR τ 2.4–3.5 (20H), 4.95–5.1(1H), 5.65–5.95(3H), 6.6–7.2(6H), 7.45–7.8(3H), 8.75(3H, t, *J* 7Hz).

X-ray crystallographic analysis of the ethyl ester-lactone **12b**. $C_{42}H_{36}O_4$, *M* 604.7. Monoclinic; $a = 28.787(4)$, $b = 15.323(3)$, $c = 14.925(3)$ Å, $\beta = 107.5(1)°$, $D_c = 1.28\ g \cdot cm^{-3}$, $U = 6279$ Å^3, $D_m = 1.275\ g \cdot cm^{-3}$, $Z = 8$, $F(000) = 2560$. Space group $P2_1/c$ from systematic absences. Mo-K_α radiation, $\lambda = 0.71069$ (graphite monochromator), $\mu = 0.088\ cm^{-1}$.

Measurements were made on a crystal of approximate dimensions 0.2 × 0.2 × 0.3 mm. Oscillation and Weissenberg photographs established the space group and the approximate cell dimensions. The parameters were refined by least squares on the settling angles of 23 reflections measured on a Hilger–Watt 4-circle diffractometer. Intensity measurements were made by ω-2θ scans for the range θ 1–23° (beyond this range intensities were very weak). 8895 unique reflections were counted and of these 5673 had a net count $>3\sigma(I)$ and were used in the refinement. Lorentz and polarisation but no absorption corrections were made.

The first attempt to solve the structure using MULTAN was unsuccessful, but when the phenyl atoms were entered as a partial structure during the normalisation step MULTAN revealed 83 of the expected 92 atoms. The 9 missing atoms were easily found by Fourier methods. Refinement proceeded smoothly. When the stage of anisotropic refinement of the non-H atoms was reached the number of parameters prevented full-matrix methods being used. Each molecule was then refined in separate cycles in three blocks, two blocks each including two phenyl groups and the third block the rest of the molecule. At an appropriate stage in the refinement a difference map revealed 60 of the hydrogens and it was deemed justified to include (but not refine) all the hydrogens in calculated positions. During the final stages of refinement the weighting scheme employed was $W = 1.0/(A[0] \times T[0](X) + \cdots A[3] \times T[3](X))$, in which A[I] are the coefficients of a Chebyshev series in T[I](X) where $X = F_{obs}/F_{obs(max)}$; the values of the coefficients were 84.7, 89.7, −11.0 and −19.8.

At convergence the maximum shift/standard deviation was 0.02 for positional parameters and 0.05 for thermal parameters. The conventional R was 6.83%. The Oxford CRYSTALS program package was used for all computations following the structure determination with MULTAN.

The octachloro-diketal **17a** [With Kettlewell[3]]. A mixture of the adduct **4**[20] (17 g) and **2a** (35 g) in xylene (50 ml) was heated under reflux for 24 hr. Concentration of the resulting soln yielded **17a** (35 g, 91%), m.p. 271–273° (from $CHCl_3$). (Found: C, 37.3; H, 3.0; Cl, 48.8. $C_{18}H_{16}Cl_8O_4$ requires: C, 37.3; H, 2.8; Cl, 48.9%); IR ν_{max} 1608 cm^{-1}; PMR τ 6.55(6H, s), 6.56(6H, s), 7.35(4H, s).

An identical product was obtained from the cyclobutene **16**[1] and **2a** in refluxing xylene.

The octachloro-diketone **17b**. Treatment of **17a** (10 g) with hot conc H_2SO_4 (50 ml) (see preparation of **5a**) for 5 hr gave the crude **17b** (7.8 g, 93%) (IR ν_{max} 1818 cm^{-1}).

Recrystallisation of a sample from MeOH resulted in the *bis*-hemiketal **17c**, m.p. *ca* 170° (dec). (Found: C, 34.6; H, 1.9; Cl, 51.1. $C_{16}H_{12}Cl_8O_4$ requires: C, 34.7; H, 2.2; Cl, 51.4%); IR ν_{max} 3470, 1607 cm^{-1}.

Thermolysis of the octachloro-diketone **17b**. The crude **17b** (2.5 g) was heated in refluxing xylene (100 ml) for 1 hr. Removal of the solvent and recrystallisation of the residue from light petroleum afforded 1,2,3,4-tetrachlorobenzene (2.0 g, 90%), identical with an authentic specimen.

The decachloro-ketal **17d**. A mixture of **15**[1] (20 g) and **2f** (11 g) was heated in refluxing xylene (75 ml) for 24 hr. Removal of the solvent, and crystallisation of the residue from MeOH, gave **17d** (15 g, 65%), m.p. 213.5–214.5° after recrystallisation from CH_2Cl_2. (Found: C, 32.6; H, 1.6; Cl, 59.9. $C_{16}H_{10}Cl_{10}O_2$ requires: C, 32.6; H, 1.7; Cl, 59.7%); IR ν_{max} 1601 cm^{-1}; PMR τ 6.54 (6H, apparent s), 7.1–7.2(2H), 7.2–7.4(2H).

The decachloro-triene **18**. Hydrolysis of **17d** (5.8 g) with hot conc H_2SO_4 (50 ml) (see preparation of **5a**) for 3 hr, afforded the crude ketone (4.9 g) (IR ν_{max} 1820 cm^{-1}), which was decarbonylated by heating in refluxing chlorobenzene for 30 min to yield **18a** (3.7 g, 73%), m.p. 182–183° (from MeOH). (Found: C, 30.5; H, 0.7; Cl, 68.5. $C_{13}H_4Cl_{10}$ requires: C, 30.3; H, 0.8; Cl, 68.9%); IR ν_{max} 1610, 1600 cm^{-1}; UV λ_{max} (EtOH) 285, 294, 306, 320 nm (ϵ 3390, 4780, 4550, 2500); PMR τ 6.45–6.6(2H), 6.8–7.0(2H).

Reaction of the cyclobutene **16** *with hemicyclone* **2c**. A mixture of **16**[1] (1.0 g) and hemicyclone dimer (0.80 g) was heated in refluxing xylene (25 ml) until the red colour of the cyclopentadienone was discharged ($2\frac{1}{4}$ hr). The solvent was evaporated under reduced pressure, and the residue was treated with C_6H_6–light petroleum (1:1; 30 ml). The resulting crystals were separated, washed with light petroleum, and finally recrystallised from C_6H_6–light petroleum to yield the carbonyl-bridged adduct **19a** (1.37 g, 77%), m.p. 240–241° (dec). (Found: C, 62.7; H, 4.7; Cl, 24.7. $C_{30}H_{26}Cl_4O_3$ requires: C, 62.5; H, 4.55; Cl, 24.6%); IR ν_{max} 1780, 1600 cm^{-1}; PMR τ 2.75–3.15 (10H), 6.44(3H, s), 6.46(3H, s), 7.3–7.4(2H), 7.5–7.6(2H), 8.78(6H, s).

The mother liquors were evaporated, and the oily residue was chromatographed on silica. Elution with hexane–C_6H_6 (2:1) gave the decarbonylated **18b** (0.24 g, 14%), m.p. 232–233° from hexane. (Found: C, 63.5; H, 5.0%; *M* (mass spectrum), 546 (^{35}Cl; the isotopic abundance ratio indicated the presence of 4 Cl). $C_{29}H_{26}Cl_4O_2$ requires: C, 63.5; H, 4.8%; *M*, 546 (^{35}Cl); IR ν_{max} 1605 cm^{-1}; PMR τ 2.85–3.4(10H), 6.38(3H, s), 6.41(3H, s), 6.75–6.9(2H), 7.2–7.3(2H), 8.57(6H, s).

The exo-*cyclobutene* **20**. The hemicyclone adduct of **4**[7] (2.50 g) was heated in refluxing xylene (20 ml) for 20 hr. The solvent was removed under reduced pressure, and the residue was chromatographed on silica. Elution with hexane–C_6H_6 (1:1) gave **20** (1.07 g, 69%), m.p. 135–136° (lit. 136°[7]).

Conversion of **20** *into* **19a**. Compound **20** (0.50 g) and **2a** (0.42 g) in toluene (15 ml) were heated under reflux for 24 hr. Removal of the solvent under reduced pressure, and recrystallisation of the residue from C_6H_6–hexane, then afforded **19a** (0.51 g, 56%), identical with the previous specimen.

Thermolysis of the carbonyl-bridged adduct **19a**. The adduct **19a** (0.5 g) was heated at *ca* 240° under N_2 until effervescence ceased (15 min). Recrystallisation of the residue from hexane then yielded **18b** (0.31 g, 65%), identical with the previous sample.

Reaction of the cyclobutene **16** *with tetracyclone* **2e**. An experiment similar to that described above was performed using **16** (1.00 g) and **2e** (0.90 g) in refluxing xylene (25 ml) (5 hr). Work-up as before, with minor modifications, yielded two products. (a) The adduct **19b** (0.833 g, 51%), m.p. 250–251° (dec). (Found: C, 68.5; H, 4.5; Cl, 20.4. $C_{40}H_{30}Cl_4O_3$ requires: C, 68.6; H, 4.3; Cl, 20.2%); IR ν_{max} 1790, 1605 cm^{-1}; PMR τ 2.75–3.35 (20H), 6.45 (3H, s), 6.62(3H, s), 6.9–7.05(2H), 7.1–7.2(2H). (b) Compound **21a** (0.635 g, 40%), m.p. 226–227° from hexane [Found: C, 69.4; H, 4.6%; *M* (mass spectrum), 670 (^{35}Cl; the isotopic abundance ratio indicated the presence of 4 Cl). $C_{39}H_{30}Cl_4O_2$ requires: C, 69.7; H, 4.5%; *M*, 670 (^{35}Cl)]; IR ν_{max} 1605 cm^{-1}; PMR τ 2.5–2.95 (20H), 3.9–4.0(2H), 5.9–6.0(2H), 6.35(3H, s), 6.37(3H, s).

Thermolysis of the carbonyl-bridged adduct **19b**. The adduct **19b** (0.50 g) was heated in refluxing mesitylene (10 ml) for 3 hr. The solvent was evaporated under reduced pressure, and the residue was triturated with hexane. The insoluble fraction (0.125 g) was identical with the starting material.

Concentration of the hexane soln gave **21a** (0.17 g), identical with the previous sample.

Reaction of the cyclobutene **16** *with 2-methyl-3,4,5-triphenylcyclopentadienone* **2g**. The cyclobutene **16** (1.00 g) was heated with **2g**[23] (1.00 g) in refluxing xylene (20 ml) (2 hr). Evaporation of the solvent under reduced pressure, followed by treatment of the residue with C_6H_6–light petroleum (1:4), afforded the insoluble adduct **19c** (1.18 g, 60%), m.p. 207–208° (dec) (from CCl_4–hexane) (Found: C, 65.5; H, 4.5; Cl, 22.4. $C_{35}H_{28}Cl_4O_3$ requires: C, 65.85; H, 4.4; Cl, 22.2%); IR ν_{max} 1780, 1750, 1600 cm^{-1}; PMR τ 2.6–3.4 (15H), 6.42(3H, s), 6.51(3H, s), 7.0–7.35(3H), 7.6–7.8(1H), 8.69(3H, s).

The mother liquors were evaporated, and the resulting oil was chromatographed on silica. Elution with hexane–C_6H_6 (3:2), and crystallisation of the eluted material from hexane, furnished a mixture of **18d** and **21b** (total 0.325 g, 17%); ratio 3:2 as estimated from the PMR spectrum), m.p. 205–215°; ν_{max} 1605 cm^{-1}.

A sample of the mixture (90 mg) was heated with N-phenyltriazolinedione (30 mg) in refluxing $CHCl_3$ (10 ml) for $1\frac{1}{2}$ hr, and the resulting soln was evaporated under reduced pressure. The residual gum was then subjected to preparative tlc on silica, using C_6H_6 as the mobile phase. Extraction of the separated bands with CH_2Cl_2 gave the following products. (a) Compound **21b** (25 mg), m.p. 200–201° from hexane (Found: C, 67.0; H, 4.7; Cl, 23.3%. $C_{34}H_{28}Cl_4O_2$ requires: C, 66.9; H, 4.6; Cl, 23.2%); IR ν_{max} 1605 cm^{-1}; PMR τ 2.4–3.2(15H), 4.1–4.2(1H), 4.6–4.75(1H) 6.0–6.3(2H), 6.36(3H, s), 6.39(3H, s), 8.21br (3H, s). (b) Compound **22** (35 mg), m.p. 257–259° from C_6H_6–hexane [Found: C, 63.8; H, 4.6; N, 5.0%; *M* (mass spectrum). 783 (^{35}Cl; the isotopic abundance ratio indicated the presence of 4 Cl). $C_{42}H_{33}Cl_4N_3O_4$ requires: C, 64.2; H, 4.2; N, 5.35%; *M*, 783 (^{35}Cl)]; ν_{max} 1775, 1725, 1600 cm^{-1}; PMR τ 2.4–3.4(20H), 6.37(3H, s), 6.41(3H, s), 6.7–7.1(3H), 7.35–7.45(1H), 8.23(3H, s).

Thermolysis of the carbonyl-bridged adduct **19c**. Compound **19c** (0.50 g) was heated at 220°/0.1 mm for 5 min (effervescence), and the residue was then cooled rapidly. The PMR spectrum of a sample in $CDCl_3$ indicated that the product consisted of a 1:4 mixture of **18d** and **21b**, together with some starting material; there was no change in the spectrum after the soln had been left for 72 hr at room temp.

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