Tetrahedron Vol. 36, pp. 3021 to 3031
Pergamon Press Ltd., 1980. Printed in Great Britain

PERICYCLIC TRANSFORMATIONS OF TETRACYCLO[8,2,1,$0^{2,9}0^{3,8}$]TRIDECA-4,6,11-TRIENES, AND FORMATION OF DIHYDROSEMIBULLVALENES BY THERMAL INTRAMOLECULAR[$_{\pi}4_a + {}_{\pi}2_a$]CYCLOADDITION IN SUBSTITUTED CYCLOOCTATRIENES

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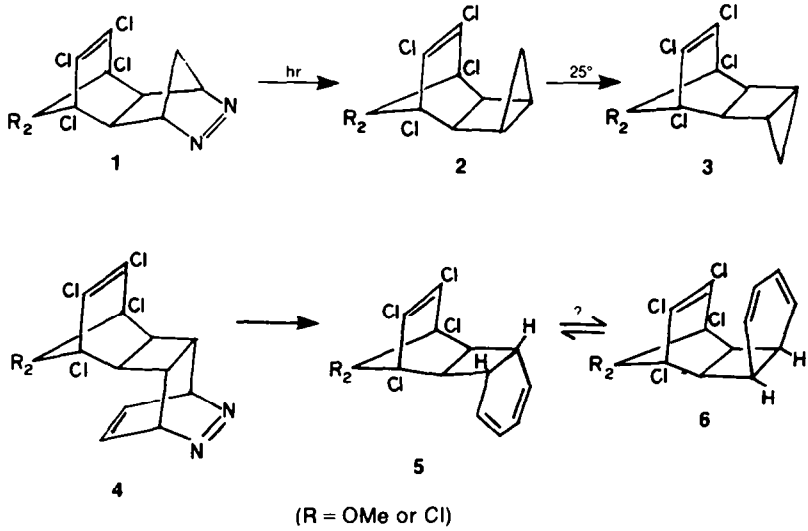
(*Received in UK* 19 *September* 1979)

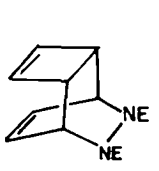
Abstract—Cyclopentadienones react with certain cyclobutene dienophiles to give the anticipated carbonyl bridge adducts; these, on relatively mild thermolysis, yield dihydrosemibullvalene derivatives by a novel *sequence* including cheletropic loss of carbon monoxide, electrocyclic ring opening of the immmediate substituted bicyclo[4,2,0]octadienes, and intramolecular [$_{\pi}4_a + {}_{\pi}2_a$]cycloaddition of the derived cyclooctatrienes. Other pericyclic reactions of compounds related to those of the title compounds are also discussed.

We earlier described[2] the synthesis of derivatives **2** and **3** of the little known[3] *syn* and *anti* isomers of tetracyclo[5,2,1,$0^{2,6}0^{3,5}$] decene. Compounds **2** and **3** are readily made by photochemical deazatation of azo compound **1** and the exceptionally facile irreversible thermal isomerisation **2** → **3** (and analogous reactions) suggested it would be of interest to explore the wider implications of these observations by investigating the synthesis and properties of homologous and related polycyclic systems having unsaturated rings fused *syn* and *anti* to the cyclobutane moiety as e.g. in the tetracyclo[8,2,1,$0^{2,9}0^{3,8}$]tridecatrienes **5** and **6**.

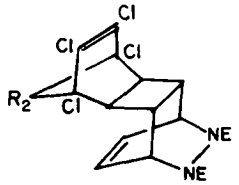
Hydrazoester **8** is (quite easily) accessible from Askanis[5] indirectly synthesised azodicarboxylate adduct **7** of cyclooctatetraene: cyclobutene dienophile **7** readily reacts with a variety of cyclopentadienones (see below) and compound **8** is stereospecifically formed by reaction with tetrachlorocyclopentadienone dimethyl acetal, the hydrogen to the proximate dichloroolefine site in stereoisomer **5** in analogy to known examples.[4] Other concerted (and non-concerted) rearrangements could be envisaged with these polycyclic compounds, e.g. photochemical cyclo-reversions, and acid catalysed rearrangements.



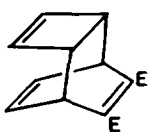
Tetracyclic trienes such as **5** and **6** could potentially exhibit at least three important classes of relatively obvious thermal pericyclic transformation: (a) electrocyclic ring-opening and closure in the bicyclo[4,2,0]octadiene component and hence isomerisation (**5**⇌**6**) *via* cyclooctatrienes; (b) irreversible intramolecular ($_{4}\pi_s + {}_{2}\pi_s$) cycloaddition in structures such as **6** giving thermally stable cage compounds; and (c) exothermic sigmatropic group transfer of allylic reaction resembling similar additions with the carbocyclic analogue **9**.[6] Heating adduct **8** with methanolic potassium hydroxide in air gives a nitrogen-free chlorohydrocarbon $C_{15}H_{14}Cl_4O_2$ assigned structure **5** on the basis of its IR (ν_{max} 1600 cm^{-1} ClC=CCl and conj. C=C), and ^{1}H NMR spectrum; the latter shows typical A_2X_2 cyclobutane multiplets[2] (τ 6.9 and 7.4) with the higher-field signal clearly coupled to the olefinic proton resonance (multiplets at τ 4.2–4.6). We previously



7: (E = CO_2Et)



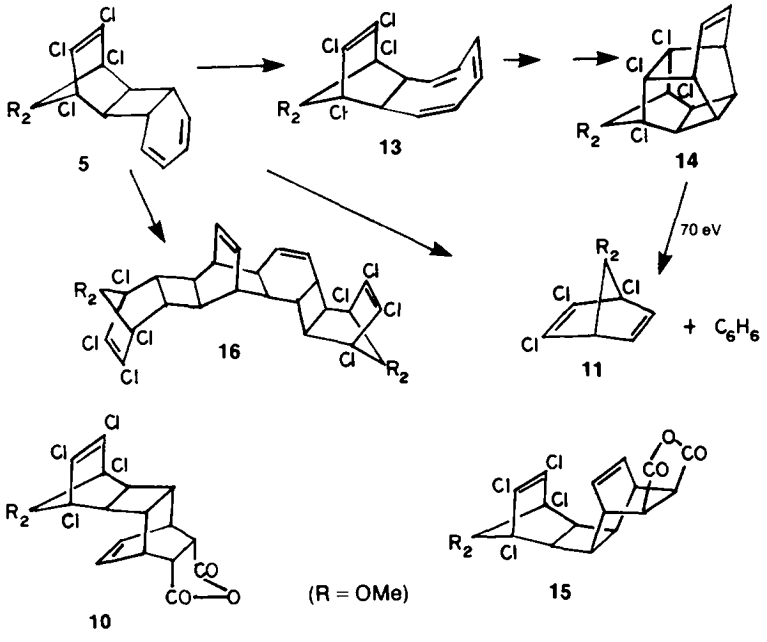
8: (R = OMe, E = CO_2Et)



9: (E = CO_2Me)

exploited the utility of measuring the principal outermost signal separation $\Delta\nu$ (Hz) in cyclobutane A_2X_2 signals as a criterion of relative stereochemistry in compounds **2** and **3** and related structures[2] where it was found that $\Delta\nu$ (*syn* isomer): $\Delta\nu$ (*anti* isomer) $\simeq 2$. The lower-field cyclobutane NMR multiplet in triene **5** shows $\Delta\nu = 4$ Hz; this *is* rather larger than the 2.5 Hz value for *endo–anti* stereoisomer **3**,[2] but it does seem very unlikely that stereomutation has accompanied such mild thermolytic deazatation from the assumed intermediate **4**. Conformational mobility in the hydrazoester system in intermediate **8** renders most of the ^{1}H NMR signals[7] broad and featureless and the cyclobutane A_2B_2 signal appears as a broad unresolved multiplet (W/2 12 Hz) at τ 7.52; evidently the $H_{AA'}$ protons in ester **8** lie in a shielding region, possibly due to the adjacent olefine, their resonance moving downfield to τ 6.7 in compound **5**

Interestingly, photolysis of triene **5** gives a mixed product containing norbornadienone acetal **11**[8] consonant with a symmetry allowed photo-cycloreversion. On the other hand, heating triene **5** gives one, or two products depending on the conditions; thermolysed in solution it gives a small amount of a dimer most likely **16**, and as major product a cage compound **14** whose structure follows from its mass spectrum (*m/e* 366, M^+) and from the appearance of only two vinylic protons (^{1}H NMR τ 3.69), whilst the OMe singlets (which coincide in triene **5** at τ 6.52) appear at τ 6.41 and 6.48—the remaining protons giving rise to an A_2X_2 system at τ 6.9 and 7.58; the former signal has $\Delta\nu$ 7.0 Hz, approximately twice the value of $\Delta\nu$ for compound **5** and its adduct **10** as expected for the *syn* fused cyclobutane necessarily resulting from intramolecular cycloaddition in intermediate triene **6**.



(similar to $H_{AA'}$ in *endo–syn* compound **2**, indicating that the cyclohexadiene ring does not shield the $H_{AA'}$ protons, unlike the cyclopropane ring in compound **3** which shields the $H_{AA'}$ protons by $\Delta\tau \sim 0.5$).

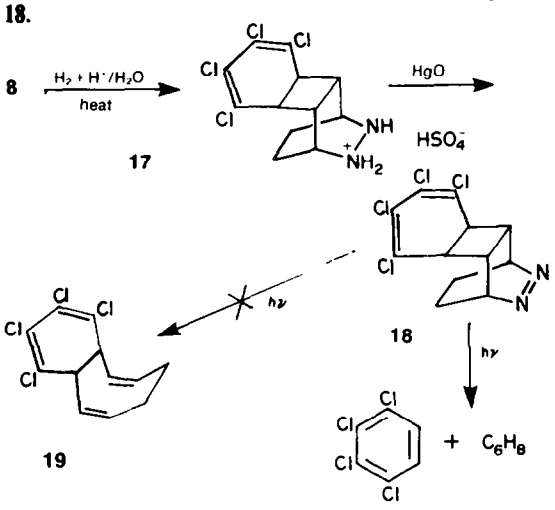
Tetracyclic triene **5** readily forms a maleic anhydride adduct **10**, an indication of the accessibility of the diene moiety, and lack of steric inhibition to adduct formation-expected however for its isomer **6**; the *anti* fused cyclobutane ^{1}H NMR multiplets are well separated in the adduct **10** with $\Delta\nu$ 3.5 Hz. No evidence for the formation of adduct **15**, and hence of diene **6** was found here.

^{13}C NMR data also accord with structure **14** for the cage compound, with 3 signals for quaternary carbon at 107.27, 82.41 and 77.71 ppm ($\rangle$C(OMe)$_2$ and two different types of $\rangle$C–Cl) and 6 rather stronger signals at 129.01, 51.84, 51.30, 48.78, 46.59 and 36.26 ppm. Thermolysis of the *neat* compound **5** however gives only the dimer **16**.

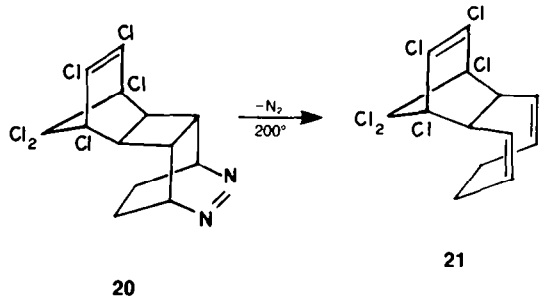
The mass spectrum of cage-compound **14** has an interesting fragment ion at *m/e* 288 ($C_9H_8Cl_4O_2^{+\cdot}$) (i.e.

11$^{+\cdot}$) and a more abundant ion at *m/e* 253 ($C_9H_8Cl_3O_2^+$) (**11**-Cl$^+$), a characteristic fragmentation in a plane through the molecule for cage structures,[9] and expected to be very favourable in the present instance where the other fragment is "benzene". The mass spectrum of the other product of thermolysis of triene **5** has *m/e* 732 ($C_{30}H_{28}Cl_8O_4^{+\cdot}$) and also consistent with structure **16** are the IR ν_{max} at 1600 cm^{-1} (ClC=CCl) and ^{1}H NMR signals at τ 4.5 (broad singlet, W/2 4 Hz) (cyclohexene (CH=CH) and a broadened triplet at τ 3.83 (bicyclooctene [*cf* adduct **10**, τ 3.55 (t), and compound **14**, 3.69 (t)] whilst the OMe signals form a narrowly separated group of four sharp singlets at τ 6.53–6.58. No plane of symmetry exists as would be the case in dimers which involved the dichloroethylene group as $_2\pi_s$ cycloaddition component.

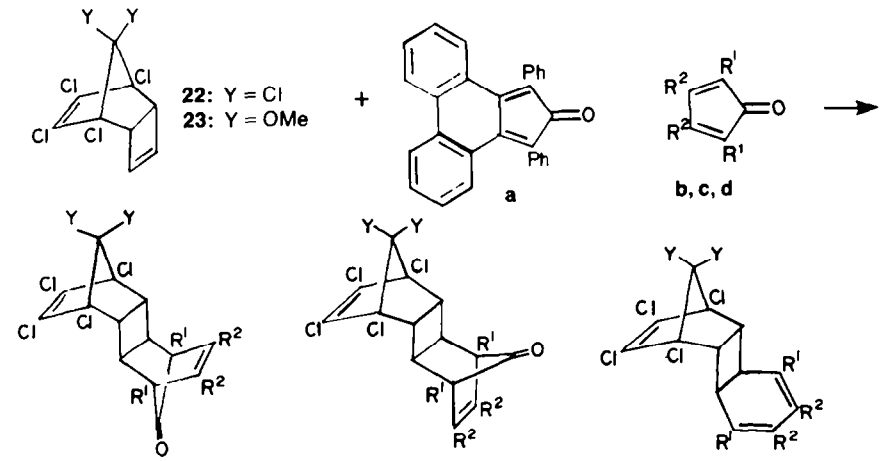
Hydrolysis of the dihydro derivative of adduct **8** with hot concentrated sulphuric acid gives the hydrazo[illegible]sulphate salt **17** whose neutralization with excess me[illegible]uric oxide results in concomitant oxidation to azo compound **18**.



Photolysis of diazatetracyclotetradecatriene **18** gives tetrachlorobenzene as the only crystalline product suggesting photochemical ($_2\pi_s + _2\pi_s$) cycloreversion as the primary step (leading to spontaneously unstable 2,3-diazabicyclo[2,2,2]octa-2,5-diene as the other product) rather than deazatation to the octadiene **19**.[10] However, base hydrolysis in air of the dihydro derivative of the hexachloro analogue of adduct **8** (R,R=Cl) gives azo compound **20** whose thermolysis at 200° results in isolation of the octatriene **21**, with no evidence for ($_2\pi_s + _2\pi_s + _2\pi_s$) intramolecular addition.



In none of these thermal reactions do any products arise which could be attributed to intramolecular hydrogen group transfer. Perhaps dimerization and intramolecular cycloaddition are much more competitive processes when steric inhibition at the cyclohexadiene system is not too severe, and in this connexion it appeared desirable to investigate compounds analogous to **5** and **6** in which the cyclohexadiene is heavily substituted. The synthesis of suitable model compounds by cycloaddition of arylated cyclopentadienones to the dienophilic butene ring system in tricyclo[4,2,1,$0^{2,5}$]nona-3,7-dienes (**22** and **23**)[6] followed by thermal or photochemical decarbonylation is readily visualised:



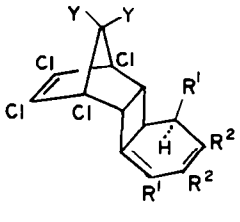
24a, b, c: Y = Cl
25a, b, c: Y = OMe
26d: Y = Cl
27d: Y = OMe
36: $R^1 = R^2 = Y$ = Cl as C(OMe)(OMe)

28a, b, c: Y = Cl
29a, b, c: Y = OMe
30d: Y = Cl
31d: Y = OMe

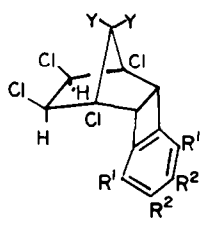
32a, b, c: Y = Cl
33a, b, c: Y = OMe
34d: Y = Cl
35d: Y = Ome
37: $R^1 = R^2$ = Cl = Y

[**a**: R^1 = Ph R^2 = o,o'-biphenylyl; **b**: $R^{1,2}$ = Ph; **c**: R^1 = *p*-MeOC$_6$H$_4$ R^2 = Ph; **d**: R^1 = Me R^2 = Ph]

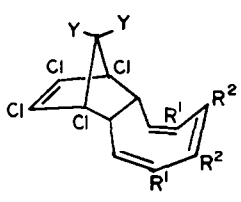
Several adducts of the general type (**24–31**) are readily made from each of the cyclobutenes (**22** and **23**) with phencyclone, tetracyclone, 3,4 - diphenyl - 2,5 - di - (p - anisyl)cyclopentadienone, 2,5 - dimethyl - 3,4 - diphenylcyclopentadienone ("hemicyclone"), acecyclone (and its 2,5-dimethyl analogue) and also with tetrachlorocyclopentadienone dimethyl acetal. The phencyclone adducts, e.g. **24a**, **25a**, **28a**, **29a**, (each R^1 = Ph, R^2–R^2 = *o,o'*-biphenylyl) are mixtures of bridge-carbonyl products derived from *exo* and *endo* diene addition in the ratio 3.5:1 and 2:1 respectively—a similar result to that in the addition of hemicyclone to compound **9**[11] (*exo*/*endo* addition ratio 6) and like all products from these additions, whether carbonyl bridge compounds or decarbonylated derivatives (**32–37**), have cyclobutane A_2X_2 ^{1}H NMR signals with $\Delta\nu$ = 3.0–3.5 Hz consistent with *anti* fused cyclobutanes. On the other hand tetrachlorocyclopentadienone dimethyl acetal gives only the *endo* diene adduct **36** with compound **22**—identical to the product of addition of hexachlorocyclopentadiene to its analogue **23**. Unlike the phencyclone adducts which are not easily decarbonylated, and decompose extensively comitant with loss of carbon monoxide, the carbonyl τ 5.7–7.0 (Table 1). Of the simple pericyclic transformation products which might be formed from the tetraphenyl diene ring compounds **32b** and **33b** ($R^{1,2}$ = Ph) e.g. arylated analogues of diene **5**, triene **13** or cage compound **14**, none satisfactorily account for the pairs of singlets and doublets in the ^{1}H NMR spectra of compounds I and II; nor can the products of thermal [1,5]-sigmatropic H shift such as structure **38** and its further sigmatropic rearrangement product. Sigmatropic group transfer to give compound **39** also seems an unlikely explanation. In some experiments, ^{1}H NMR monitoring indicates that cyclooctatriene **40b** ($R^{1,2}$ = Ph) is indeed present and may be the precursor of the unknown compound I. Consonant with this, the crude reaction products from separately heating dienophiles **22** and **23** with di-(*p*-anisyl) diphenylcyclopentadienone at 144°/18h contain respectively: carbonyl bridge adduct, 27% and 20%; tetraarylated cyclooctatrienes **40c** and **41c** (R^1 = p-$MeOC_6H_4$ R^2 = Ph), 15% and 40% and in the case of compound **22** a further component III exactly analogous to I and II in having a closely similar pair of ^{1}H NMR doublets (J = 7 Hz) and two singlets (as well as OMe and ArH signals) in the range τ 5.8–7.0 (Table 1).



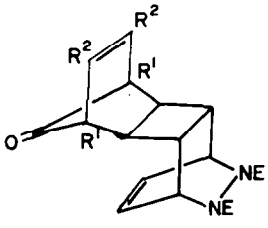
38b: Y = Cl or OMe



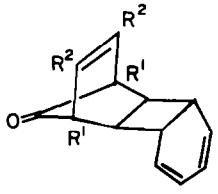
39b: Y = Cl or OMe



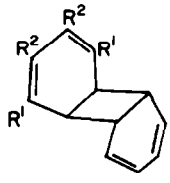
40b, c, d: Y = Cl
41b, c, d: Y = OMe



42d
43b
44a



45d
46b



47d
48b

[a R^1 = Ph R^2 = o,o'-biphenylyl; b $R^{1,2}$ = Ph; d R^1 = Me R^2 = Ph]

bridge hydrolysis product from acetal adduct **36** smoothly decarbonylates on mild thermolysis to give a rather stable tetrachlorodiene ring compound **37**;[12] again stronger heating causes extensive decomposition.

More interesting results are seen however in the thermolysis of the tetracyclone adducts **28b** and **29b** ($R^{1,2}$ = Ph) of tricyclononadienes **22** and **23**; on heating at 177–185° both compounds decarbonylate and give *not* the anticipated tetraphenyl cyclohexadienes **32** and **33b** ($R^{1,2}$ = Ph)† but monomeric products I and II which besides showing the expected ^{1}H NMR signals near τ 2.8–3.3 (Ph) [and in the case of the product from **29**—τ 6.60 and 6.67 due to $\diagdown$C(OMe)$_2$] exhibit two singlets and two doublets (J = 7 Hz) each of ^{1}H intensity in the range

Further information on the nature of compounds I–III is available from a careful study of the products of reaction of dienophile **22** with hemicyclone at 144°/18 hr. The crude product contains an adduct† **30d** (R^1 = Me, R^2 = Ph) (60%), dimethyldiphenylcyclohexadiene **34d** (R^1 = Me, R^2 = Ph) (20%) and the cyclooctatriene **40d** (Y = Cl, R^1 = Me, R^2 = Ph) (5%) from which the carbonyl-bridge and cyclohexadiene products are readily separated and characterised as *anti* fused cyclobutanes; on being separately thermolysed at 160–190° each of these compounds gives a similar product mixture. For example at 164°/24 hr the cyclohexadiene is recovered mainly unchanged (80%) but *ca* 20% cyclooctatriene tautomer is formed. At higher temperatures (190°–260°) the carbonyl-bridge (*exo*† or *endo*) adduct substantially decarbonylates (75%–100%) yielding mixtures containing **34d** cyclooctatriene **40d** and a new compound IV, analogous to compounds I–III, characterised by two ^{1}H NMR singlets and two doublets in the range τ 6.5–7.6. Singificantly *two* Me singlets appear at τ 8.2 and 9; it is

†Accelerated *endo* adduct decarbonylation may imply that single ketonic adducts isolated are products of *exo* addition (e.g. **28–31**).‡

clear (i), that compound IV is formed more slowly than the fully arylated analogues I–III,‡ and (ii), the methyl groups in compound IV are one each on saturated and vinylic carbon.

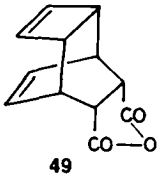
Table 1. Midfield chemical shifts τ ($CDCl_3$) in compounds I–IV

I	5.72(s)	6.23(d)	6.69(d)	6.85(s)
II	5.80(s)	6.39(d)	6.95(d)	6.93(s)
III	5.80(s)	6.25(d)	6.71(d)	6.99(s)
IV	7.06(s)	6.50(d)	7.08(d)	7.65(s)

[IV 8.2(s) (=C-Me), 9.0 (⟩C-Me)]

The addition of acecyclone (2,5-diphenyl-3,4-(1′,8′-perinaphthyl)cyclopentadienone and its analogues to dienophiles **22**, **23** occurs even under mild conditions with concomitant decarbonylation.[13] The products are unexceptional however consisting of the fused-ring cyclohexadienes **32**, **33** (R^1 = Ph and R^2,R^2 = 1′,8′-naphthyl Y = Cl or OMe) and the tautomeric cyclooctatrienes **40** and **41**, (R^1 = Ph, R^2–R^2 = 1′,8′-naphthyl) which are not appreciably isomerised by further heating.

Concurrent with these experiments we observed that Askanis' ester **7** also behaves as cyclobutene dienophile towards cyclopentadienones giving e.g. adducts **42d** (R^1 = Me, R^2 = Ph) and its analogues **43b** ($R^{1,2}$ = Ph) and **44a** (R^1 = Ph, R^2–R^2 = *o,o′*-bephenylyl).§ Alkoxide hydrolysis of esters **42d** and **43b** in air gives carbonyl-bridge compounds **45d** and **46b** with the expected IR, ^{1}H and ^{13}C NMR parameters whose thermolysis not unexpectedly[16] give *via* "benzene-dimers" **47d** and **48b** dimethyl diphenyl- and tetraphenyl-benzene respectively as the only crystalline products. Both adducts **43b** and **44a** behave quite differently however if decarbonylation is effected *first* (at 210°),[17] and the products are subsequently hydrolysed in air. In each case a nitrogen-free compound is obtained VII and VIII which is isomeric with the formally expected tetrahydrobiphenylene [e.g. **48b**], but whose ^{1}H, and especially ^{13}C, NMR spectra indicate asymmetric structures [e.g. VII, ^{1}H NMR signals at: τ 2.8–3.3 (m, 20H), 3.8–4.4 (m, 4H), 4.8 (d, 1H), 6.1 (bs, 1H), 6.98 (d, 1H) and 7.11 (br, 1H). ^{13}C, ppm downfield of TMS: 36.04, 40.77, 52.60, 57.70, 57.94 and 66.68 (six saturated C atoms, signals 1,2,3 and 6 tertiary, 4,5 quaternary) and seventeen signals resolved due to unsaturated carbon in the range 123.16–142.03 ppm]. Both compounds VII and VIII readily form (1:1) maleic anhydride adducts **50b** and **51a**, the former being identical to the product[18] of heating tetracyclone with the maleic anhydride adduct of cyclooctatetraene, **49**, (at 210°), and the spectroscopic properties of the compound are clearly *not* consistent with the expected product of decarbonylation, i.e. cyclohexadiene compound **52b**. The asymmetric nature of maleic anhydride adduct **50b** is very clearly seen in the ^{1}H NMR spectrum where *two* signals due to vinylic protons are exhibited at τ 3.81 (t, 1H) and 4.08 (t, 1H), (each being further coupled), and besides signals due to saturated centres in, and adjacent to the anhydride ring, the remaining protons appear at τ 6.04(s), 7.30(s), 6.32(m) and 7.74(m) all of equal intensity. In the ^{13}C NMR region, *ten* signals appear in the range 36.64–63.16 ppm (saturated carbon), eighteen signals in the range 125.35–142.28 ppm (unsaturated carbon) and *two* signals of equal but low intensity characteristic of carbonyl carbon appear at 171.82, 172.43 ppm.



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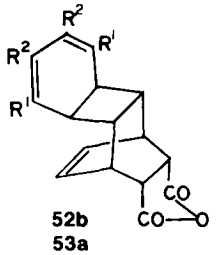


52b
53a

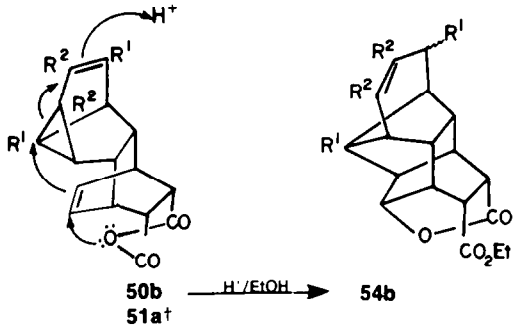
The essentially "normal" behaviour of the diazabicyclo[2,2,2]octene dicarboxylate system in the compounds **42d**, **43b**, **44a** during the sequence hydrolysis–oxidation–deazatation, giving a cyclohexadiene ring which then readily undergoes cycloaddition with maleic anhydride indicates that the source of asymmetry in the compounds VII and VIII is thermal rearrangement of the tetra-arylated bicyclo[4,2,0]octadiene system concomitant with decarbonylation, and this is confirmed by the ^{1}H NMR spectra for the hydrazodicarboxylates V and VI obtained by decarbonylation of the adducts **43b** and **44a**; [e.g. compound V: *two* signals near τ 3.6(t), 3.8(t) (=CH), *two* signals near τ 4.68(t), 5.52(m) (⟩CH-N-N-CH⟨) and separate signals near τ 6.06(bs), 7.36(bs), 6.53(m) and 7.40(m) (all 1H); in each case $\Delta\tau$ is too large to be due to conformational effects[19] in the hydrazodicarboxylate function in an otherwise symmetrical molecule[20]].

Boiling maleic anhydride adduct **50** in acidified ethanol results in slow deposition of crystals of a half-ester lactone whose X-ray crystallographic structure corresponds to the compound **54**;[21] protonation of dihydrosemibullvalene **50** with concomitant ring-closure/lactonisation as shown in the Scheme best rationalises this observation and the spectroscopic properties of compound **50** and its precursor, V. Analogous dihydrosemibullvalene structures also appear appropriate to the compounds (I–IV), (VII–VIII), and their formation can be understood as examples of hitherto unobserved thermally allowed ($_\pi4_a+_\pi2_a$) cycloaddition[22] in the cyclooctatriene ring system formed by 6π electrocyclic reversion of the relevant bicyclo[4,2,0]octadienes [e.g. (**32–35**), **52b** and **53a**] which may be inferred as common to the precursors of all the compounds I–VIII; inspection of models of these dihydrosemibullvalene compounds indicates dihedral angles of ~90° between the enivronmentally different bridgehead protons [hence each singlet, or very narrow multiplet in the case of compound VIII] and the pair of coupled ring junction protons (with ^{3}J = 7 Hz consistent with the required geometry).

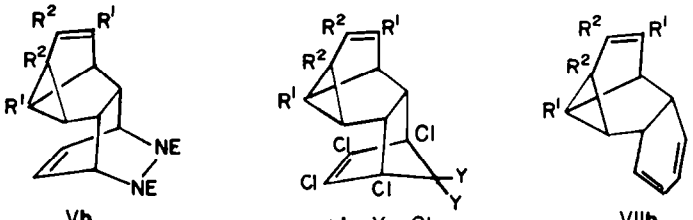
Thermal intramolecular cycloadditions of a similar type are best known in the formation of octamethylsemibullvalene from octamethylcyclooctatetraene[23] and the spontaneous cyclisation of 1,2:4,5-dibenzocyclooctatetraene to dibenzosemibullvalene[24] but there appears to be no archetype of thermal dihydrosemibullvalene formation from cyclooctatrienes.[25] Whatever the detailed mechanism of these ring closure reactions, whether by concerted electronic reorganisation[22] (Scheme 2) or by partially delocalized biradical intermediates (Scheme 3) (bis-allylic radical intermediates are implied for a number of cyclooctatetraene reactions),[26] the result once again suggests a thermal remedy for unfavourable non-bonded interactions in rather crowded

‡See I. A. Akhtar, R. J. Atkins, G. I. Fray, G. R. Geen and T. J. King, paper accompanying.

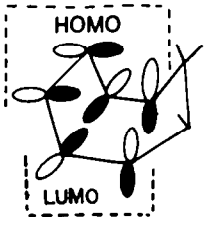
§Relative *carbonyl bridge* stereochemistry not proven.



Scheme 1.

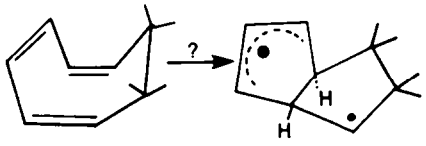


[**a**: R^1 = Ph R^2 = o,o'-biphenylyl; **b**: $R^{1,2}$ = Ph; **c**: R^1 = p $MeOC_6H_4$ R^2 = Ph; **d**: R^1 = Me R^2 = Ph]



$(_4\pi_s + _2\pi_s)$cycloaddition

Scheme 2.



Scheme 3.

structures by energy release in cyclisation from a state of relatively high potential. Further work is necessary to establish to what extent the processes leading to the compounds I–VI are reversible, and this is in hand together with a study of certain other transformations of these compounds.

EXPERIMENTAL

NMR data were obtained with Varian HA100 and Jeol PS100 spectrometers (^1H) or a Jeol JNM PS-100 FT machine (^{13}C) and refer to solns in $CDCl_3$ with TMS as internal standard. Mass spectra refer to data from a GEC-AEI MS902 double-focussing instrument; halogenated ions had the correct $^{35}Cl/^{37}Cl$ isotopic abundance ratios. IR spectra were recorded with a Perkin-Elmer 257 instrument for solutions in CCl_4 or CH_2Cl_2, and UV light absorption data were obtained for solns in EtOH or hexane using a Unicam SP800 spectrometer. Silica gel chromatography refers to preparative tlc on 0.8 mm coated plates of silica gel GF_{254} visualised under a fluoroscope, unless otherwise stated. Petroleum refers to the fraction b.p. 60–80°. M.p's are not corrected.

Addition of dimethoxytetrachlorocyclopentadiene to Askanis' ester **7**. Compound **7** prepared by R. Askanis' method[5] (7.92 g, 30 mmol) was heated at 130° with dimethoxytetrachlorocyclopentadiene (7.86 g, 30 mmol) in chlorobenzene (50 ml) 36 hr. Evaporation of the solvent gave a brown oil, which triturated with MeOH gave colourless crystals of *diethyl* 4,5,6,7 - *tetrachloro* - 15,15 - *dimethoxy* - 11,12 - *diazapentacyclo*[8,2,2,1^{4,7}0^{2,9}0^{3,8}]*pentadeca* - 5,13 - *diene* - 11,12 - *dicarboxylate* **8** (11.4 g, 70%) m.p. 193–194° ν_{max} 1680–1760 (CO_2Et) 1605 cm^{-1} (ClC=CCl) τ: 8.78 (t, J=6.5 Hz) (6H, 2-Me), 5.88(dq) (4H 2-OCH_2), 7.52(m) (4H, H-2,3 and H-8,9), 6.56(s) and 6.58(s) (each 3H 2-OCH_3), 5.13(m) (2H, H-1,10), 3.30(bd, m) (2H, H13, H14). (Found: C, 46.6; H, 4.35; Cl, 26.1. Calc. for $C_{21}H_{24}Cl_4N_2O_6$: C, 46.5; H, 4.45; Cl, 26.15%).

Hydrolysis of adduct **8** *to give anti-endo-anti-tetracyclotridecatriene* **5**. The adduct **8**, prepared as above, (10 g, 18.5 mmol) was heated with KOH (15 g, 260 mmol) in MeOH (120 ml) 12 hr under N_2. Precipitated K_2CO_3 was filtered off, and the filtrate evaporated, the residue suspended in water, extracted with CH_2Cl_2 and the extracts washed, dried (Na_2SO_4) and

†Models indicate that alternative tautomers of compound 51(a) are equally plausible.

evaporated. Column chromatography of the light-yellow oil (MFC silica gel/dichloromethane 10% in petroleum) gave a colourless solid which recrystallised from CH_2Cl_2–petroleum gave anti - endo - anti - 1,2,3,4 - *tetrachloro* - 13,13 - *dimethoxytetracyclo*[8,2,1,$0^{2,9}0^{3,8}$]*trideca* - 4,6,11 - *triene* **5** (4.7 g, 72%) m.p. 98–99° ν_{max} 1604 cm^{-1} (ClC=CCl) τ: 7.29(m) and 6.88(m) (each 2H, H-5,12 and H-6,11 A_2X_2 system), 6.53(s) (6H, 2-OMe), 4.24–4.35 and 4.47–4.62 (each m, 4H H-7,8,9,10). (Found: C, 48.8; H, 3.65. Calc. for $C_{15}H_{14}Cl_4O_2$: C, 48.9; H, 3.85%).

Photolysis of tetracyclotridecatriene **5**. The tetracyclic triene (500 mg) was irradiated (24 hr) in CH_2Cl_2 (60 ml) in a water cooled silica vessel with light from a 125W medium pressure Hg ard lamp; column chromatography of the product on silica gel gave a colourless oil (250 mg) with ν_{max} 1606 (ClC=CCl) and τ: 6.54(s), 6.56(s) (each 3H 2-OMe), 3.58(s) (=CH) (ratio OMe/=CH, 5:1). The data suggested a mixture of 1,2,3,4-tetrachloro - 7,7 - dimethoxybicyclo[2,2,1]heptadiene[8] and tetramethoxyethylene.

Thermolysis of tetracyclotridecatriene **5** *to give dimer* **16** *and cage compound* **14**. Tetracyclotriene **5** (100 mg, 2.7 mmol) was heated in a sealed tube at 180° overnight; the glassy solid obtained on cooling was recrystallised from $CHCl_3$ to give the *dimer* **16** (80 mg, 80%) m.p. 216–218° ν_{max} 1603 cm^{-1} (ClC=CCl) τ: 7.2–8.0 (complex m) (12H), 6.53, 6.55, 6.56 and 6.58 (all s, each 3H 4-OMe), 4.50 (bs W/2 4Hz) and 3.83 (t, J=4 Hz) (each 2H cyclohexene and bicyclo[2,2,2]octene CH=CH). *m/e* 732 (M^+) (Found: C, 48.75; H, 3.7. Calc. for $C_{30}H_{28}Cl_8O_4$: C, 48.9; H, 3.85%).

Tetracyclotriene **5** (200 mg, 0.54 mmol) was heated in boiling *p*-cymene (25 ml) overnight, the solvent largely removed, and the residue cooled (liq. N_2) and scratched. Crystals appeared as the sample warmed to 25°; these were filtered off and recrystallised from CH_2Cl_2–petroleum to give 1,2,7,8 - *tetrachloro* - 13,13 - *dimethoxyhexacyclo*[6,4,1,$0^{2,7}0^{3,11}0^{6,10}0^{9,12}$]*trideca* - 4 - *ene* **14** (50 mg, 25%) m.p. 170–171° ν_{max} 1600 cm^{-1} characteristic of ClC=CCl absent. τ: 6.88(m) and 7.58(cm) (each 2H cyclobutane A_2X_2 system, $\Delta\nu \sim 7$ Hz), 6.58(m) (2H C=C·CH–), 6.41 and 6.46 (both s, each 3H 2-OMe), 3.69(m) (2H bicyclo[2,2,2]octene type CH=CH). ^{13}C ppm: 36.26, 46.59, 48.78, 51.30, 51.84, 77.71 (weak $\rangle$C–Cl) 82.41 (weak $\rangle$C–Cl) 107.27 (weak $\rangle C(OMe)_2$) and 129.01. *m/e* 366 (M^+), 331 ($M-Cl^+$), 288 ($C_7H_2Cl_4(OMe)_2^+$). (Found: C, 48.6; H, 3.81. Calc. for $C_{15}H_{14}Cl_4O_2$: C, 48.9; H, 3.85%). The product residues contained dimer (16).

Maleic anhydride adduct of tetracyclotriene **5**. Compound **5**, (1.1 g, 3 mmol) was heated with maleic anhydride (490 mg, 5 mmol) in boiling benzene overnight. The crude product obtained by diluting the evaporated mixture with MeOH was recrystallised from CH_2Cl_2–petroleum to give the *adduct* **10** (1.2 g, 87%) m.p. 286–287° ν_{max} 1790 (–CO.O.CO–) 1605 cm^{-1} (ClC=CCl) τ: 7.50(m) and 7.91(m) (each 2H, cyclobutane A_2B_2 system), 6.71(m) (2H), 7.08 (t, J = 1.5 Hz) (2H), 3.55(t) (2H bicyclo[2,2,2]octene type CH=CH) (Found: C, 49.0; H, 3.35. Calc. for $C_{19}H_{16}Cl_4O_5$: C, 48.9; H, 3.45%) [*cf* Ref. 12, m.p. 289–291°].

Diethyl 4,5,6,7 - *tetrachloro* - 15,15 - *dimethoxy* - 11,12 - *diazapantacyclo*[8,2,2,$1^{4,7}0^{2,9}0^{3,8}$]*pentadec* - 5 - *ene* - 11,12 - *decarboxylate and its conversion to* 4,5,6,7 - *tetrachloro* - 11,12 - *diazatetracyclo*[8,2,2,$1^{2,9}1^{3,8}$]*tetradeca* - 4,6,11 - *triene* **18**. Adduct **8** (2.2 g, 4 mmol) in EtOAc (30 ml) containing $Pd/CaCO_3$ catalyst was treated with H_2 (uptake 120 ml/2h). The filtered product was evaporated and the residue recrystallised from CH_2Cl_2–petroleum to give the 13,14 - *dihydro derivative* of adduct **8** (2 g, 90%) m.p. 194–195° ν_{max} 1680–1750 (CO_2Et) 1602 (ClC=CCl) τ: 8.76(*t*) and 8.77(*t*) (each 3H) and 5.80–5.90(dq) (each 2H conformationally non-equivalent EtO_2C–N–N–CO_2Et), 7.69(m) and 7.00(m) (each 2H cyclobutane A_2X_2 system), 5.80–5.90(m) (2H bridgehead H-1,10 overlapping ester Et signal), 8.0(m) (4H 2-CH_2), 6.50 and 6.52 (each s, 6H 2-OMe). (Found: C, 45.95; H, 4.7. Calc. for $C_{21}H_{26}Cl_4N_2O_6$: C, 46.3; H, 4.8%).

The product from similar experiments (10 g, 18 mmol) was stirred in conc H_2SO_4 (10 ml) at 95–98° until gas evolution ceased (~ 1 hr) and the dark soln poured onto crushed ice. The crude solid product [hydrazosulphate **17**] (1 g, 2.4 mmol) was stirred with mercuric oxide (1.08 g, 5 mmol) in dry CH_2Cl_2 overnight, the grey solid filtered off and the filtrate evaporated. The colourless solid was recrystallised from CH_2Cl_2–petroleum to give *azo compound* **18** (250 mg, 33%) m.p. 205–207° (decrepitation, dec) after chromatography, ν_{max} 1618 (conj. ClC) 1515 cm^{-1} (N=N) λ_{max} 304 nm ϵ_{max} 3300 (tetrachlorocyclohexadiene system[2]) τ: 4.8(m) (2H H-1, 10), 6.54(m) and 7.57(m) (each 2H, cyclobutane A_2X_2), 8.00(d) and 8.69(d) (each 2H, J = 8 Hz 2-CH_2) *m/e* 322 (M^+) 294 ($M-N_2^+$) 259($M-N_2-Cl^+$). (Found: C, 45.35; H, 3.5; N, 8.6. Calc. for $C_{12}H_{10}Cl_4N_2$: C, 44.5 H, 3.1; N, 8.65%; M, 321.9597 requires 321.9594).

Photolysis of 4,5,6,7 - *tetrachloro* - 11,12 - *diazatetracyclo*[8,2,2,$1^{2,9}1^{3,8}$]*tetradeca* - 4,6,11 - *triene* **18**. The azo compound **18** (240 mg, 0.8 mmol) dissolved in CH_2Cl_2 (50 ml) was irradiated (5 hr) in water-cooled pyrex reactor with light from a 125W medium pressure Hg arc lamp. Evaporation of the solvent and column chromatography of the residue (silica gel, 10% CH_2Cl_2 in petroleum) gave tetrachlorobenzene (100 mg, 62%) identical to the authentic compound[27] (IR and ^1H NMR).

Diethyl 4,5,6,7,15,15 - *hexachloro* - 11,12 - *diazapentacyclo*[8,2,2,$1^{4,7}0^{2,9}0^{3,8}$]*pentadeca* - 5,13 - *diene* - 11,12 - *dicarboxylate and its conversion into azo compound* **20**. Askanis ester **7** (10 g, 37 mmol) was heated with hexachlorocyclopentadiene (10 g, 37 mmol) in boiling chlorobenzene (40 ml) *ca* 18 hr. Chlorobenzene was removed *in vacuo* and trituration of the viscous oily product with MeOH gave a colourless solid which, recrystallised from CH_2Cl_2–petroleum gave endo–exo *diethyl* 4,5,6,7,15,15 - *hexachloro* - 11,12 - *diazapentacyclo*[8,2,2,$1^{4,7}0^{2,9}0^{3,8}$]*pentadeca* - 5,13 - *diene* - 11,12 - *dicarboxylate* (14 g, 70%) m.p. 175–176° ν_{max} 1680–1760 (CO_2Et) 1608 cm^{-1} (ClC=CCl) τ: 8.78(t) (6H 2-Me), 5.84(dq) (4H 2-OCH_2–), 7.30(m) and 7.49(m) (each 2H cyclobutane A_2B_2 system), 5.10(m) (2H H-1,10), 3.33(m) (2H H-13, H-14). (Found: C, 41.55; H, 3.4. Calc. for $C_{19}H_{18}Cl_6N_2O_4$: C, 41.4; H, 3.3%). The adduct (10 g, 18 mmol), hydrogenated in ethylacetate (100 ml) over $Pd/CaCO_3$, absorbed the theoretical quantity of hydrogen; filtration and recrystallisation of the product gave a *dihydro derivative* (9.7 g, 97%) m.p. 168–169° ν_{max} 1680–1750 and 1608 cm^{-1} (CO_2Et; ClC=CCl) τ: 8.77(t) (6H 2-Me), 5.85 and 5.86 (each q, 4H 2-OCH_2), 6.80(m) and 7.60(m) (each 2H cyclobutane A_2X_2 system), 5.70–5.90(m) (2H H-1,10), 8.01(m) (4H 2-CH_2). (Found: C, 41.25; H, 3.55. Calc. for $C_{19}H_{20}Cl_6N_2O_4$: C, 41.4; H, 3.65%).

endo–exo 4,5,6,7,15,15 - *Hexachloro* - 11,12 - *diazapentacyclo*[8,2,2,$1^{4,7}0^{2,9}0^{3,8}$]*pentadeca* - 5,11 - *diene* **20**. Dihydro ester adduct, prepared as above (13 g, 23 mmol) was stirred with conc H_2SO_4 at 90–95° for 1 hr, the product poured onto crushed ice and a colourless solid filtered off. The crude hydrazo sulphate was washed several times with benzene and dried (yield 9.0 g, 80%). The hydrazosulphate (9.0 g, 18 mmol) was stirred with mercuric oxide (8.68 g, 40 mmol) in CH_2Cl_2 (120 ml) overnight at 20–25° and the mixture then filtered through celite, the filtrate decolourized with charcoal, filtered and diluted with petroleum whereupon crystals slowly separated to give endo–exo - 4,5,6,7,15,15 - *hexachloro* - 11,12 - *diazapentacyclo*[8,2,2,$1^{4,7}0^{2,9}0^{3,8}$]*pentadeca* - 5,11 - *diene* **20** (5.5 g, 80%) m.p. 198–199° ν_{max} 1610 (ClC=CCl) 1519 cm^{-1} (N=N) τ: 6.78(m) and 8.25(m) (each 2H cyclobutane A_2X_2), 8.74(d) and 8.0(d) (each 2H, 2-CH_2), 4.82(bs, W/2 8.5 Hz) (2H H-1,10). Found: C, 38.6; H, 2.45. Calc. for $C_{13}H_{10}Cl_6N_2$: C, 38.35; H, 2.45%).

cis–endo - 1,10,11,12,13,13 - *Hexachlorotricyclo*[8,2,1,$0^{2,9}$]*trideca* - 3,7,11 - *triene* **21**: Azo compound **20** from the above experiment (40 mg, 1 mmol) was heated in a small tube to 200–205° (oil bath) until gas evolution ceased. Column chromatography of the product (silica gel, petroleum) gave cis–endo - 1,10,11,12,13,13 - *hexachlorotricyclo*[8,2,1,$0^{2,9}$]*trideca* - 3,7,11 - *triene* **21**, (30 mg, 80%) m.p. 109–110° ν_{max} 1610 cm^{-1} (ClC=CCl) τ: 7.50–8.0(complex m) (4H 2-CH_2)), 6.0 (bs, W/2 6 Hz) (2H H-2,9), 4.24–4.78(cm) (4H, H-3,4 and H-7,8). (Found: C, 41.55; H, 2.85. Calc. for $C_{13}H_{10}Cl_6$: C, 41.2; H, 2.65%). Mild thermolysis of the tridecatriene **21** at 155° overnight resulted in its recovery unchanged (60%). *endo* **23** was made by the method of Warrener.[11]

Addition of phencyclone to tricyclononadiene **23**. Compound **23** (360 mg, 1.1 mol) was heated with phencyclone (420 mg,

1.1 mmol) in boiling toluene (~10 ml) 5 hr, decolorisation occurred within 2 hr and on cooling crystals separated; these were filtered off and washed with toluene and petroleum to give endo–anti–exo - 1,10,11,12 - *tetrachloro* - 13,13 - *dimethoxy* - 4,7 - - *diphenyl* - 5,6 - (o,o' - *biphenylyl*) - *pentacyclo*[8,2,1^{1,10}1^{4,7}0^{2,9}0^{3,8}]*tetradeca* - 5,11 - *dien* - 14 - *one* **29a** (550 mg, 70%) m.p. 342–344° (dec) (from *p*-cymene) ν_{max} 1790 (bridge ring CO) 1600 cm^{-1} (ClC=CCl and aromatic C=C) *m/e* 668 (M–CO$^+$), 661 (M–Cl$^+$, 633 (M–CO–Cl$^+$, 406 (cycloreversion fragment), 380 (1,4-diphenyltriphenylene). (Found: C, 68.85; H, 4.25. Calc. for $C_{40}H_{28}Cl_4O_3$: C, 68.8; H, 4.0%). Also isolated, by mother liquor evaporation the endo–anti–endo *isomer*† **25a** of the pentacyclotetradecadienone (150 mg, 20%) recrystallised benzene–MeOH m.p. 340–342° (dec) ν_{max} 1800 vs cm^{-1} (bridged ring CO) τ: 1.3(m), 2.4–3.2(m) (18H ArH), 6.5(m) (2H) and 7.25(m) (2H) (cyclobutane A_2X_2 mults. separation of principal lines 3.5 Hz), 6.62(s) (3H OMe), 7.18(s) (3H OMe), *m/e* closely similar to the carbonyl compound above 668(M–CO$^+$ 633 (M–CO–Cl$^+$ 406 (Retro–Diels–Alder fragment) 380(1,4-diphenyltriphenylene). (Found: C, 68.55; H, 4.11. Calc. for $C_{40}H_{28}Cl_4O_3$: C, 68.8; H, 4.0%).

endo-*Hexachlorotricyclo*[4,2,1,0^{2,5}]*nona*-3,7-*diene* **22** was made by an analogous method to that for compound **23**.[11]

Addition of phencyclone to tricyclononadiene **22**. Compound **22** (340 mg, 1.1 mmol) was heated with phencyclone (400 mg, 1.1 mmol) (as above) to give endo–anti–exo 1,10,11,12,13,13-*hexachloro* - 4,7 - *diphenyl* - 5,6 - (o,o' - *biphenylyl*)*pentacyclo*[8,2,1^{1,10}1^{4,7}0^{2,9}0^{3,8}]*tetradecan* - 5,11 - *dien* - 14 - *one* **28a** (350 mg, 47%) recrystallised decalin m.p. 337–338° (variable, dec) ν_{max} 1786 vs cm^{-1} (bridged-ring CO) (Found: C, 64.75; H, 3.4, average of two results. Calc. for $C_{38}H_{22}Cl_6O$: C, 64.5; H, 3.1%). Work-up of the mother liquors gave the endo–anti–endo *isomer* **24a** (190 mg, 20%) recrystallised benzene–MeOH m.p. 331–332° (dec) ν_{max} 1790 cm^{-1} *m/e* 704(M$^+$), 676(M–CO$^+$), 641(M–CO–Cl$^+$, 606(M–CO–Cl$_2^+$), 406(R–D–A fragment from M–CO$^+$), closely similar to **28a** (Found: C, 64.25; H, 3.1. Calc. for $C_{38}H_{22}Cl_6O$: C, 64.5; H, 3.1%).

Attempted decarbonylation of phencyclone adducts of compounds **22** *and* **23**. The stereoisomeric adducts, prepared as above, were heated in *p*-cymene and decalin; unchanged ketones were recovered, and these were boiled in 1,2,4-trichlorobenzene when extensive decomposition occurred.

Addition of tetracyclone to tricyclononadiene **22**. Compound **22** (280 mg, 0.9 mmol) and tetracyclone (300 mg, 0.9 mmol) were heated together and the product isolated and purified as above to give endo–anti–exo 1,10,11,12,13,13 - *hexachloro* - 4,5,6,7-*tetraphenylpentacyclo*[8,2,1^{1,10}1^{4,7}0^{2,9}0^{3,8}]*tetradecan* - 5,11 - *dien* - 14 - *one* **28b** or **24b**† (260 mg, 45%) m.p. 227–229° (dec) ν_{max} 1788 vs cm^{-1} τ: 2.75(s) and 2.77–3.4(m) (20H ArH), 7.0(bs) (4H), *m/e* 678(M-CO$^+$), 648(M–CO–Cl$^+$), 609(M–CO–Cl$_2^+$), 408(RDA fragment from 678), 382 (Ph$_4$C$_6$H$_2^{+\cdot}$). (Found: C, 64.0, H, 3.15. Calc. for $C_{38}H_{24}Cl_6O$: C, 64.3; H, 3.4%).

Thermolysis of adduct **28b** *to give dihydrosemibullvalene I*. A sample of adduct **28b** was heated in *o*-dichlorobenzene 2 hr to give 85% decarbonylated compound which recrystallised from benzene–MeOH gave endo - 1,10,11,12,13,13 - *hexachloro* - 4,5,6,7 - *tetraphenylpentacyclo*[8,2,1,0^{2,9}0^{3,7}0^{6,8}]*triadeca* - 4,11 - *diene I* m.p. 240–242° ν_{max} 1608, 1498, 1445, 700 cm^{-1} τ: 2.8(s), 2.9–3.3(m) (20H ArH), 5.7(s) (1H), 6.2(d) (1H) and 6.68(d) (1H) (J = 7.0 Hz), 6.8(s) (1H), *m/e* 678(M$^{+\cdot}$), 643(M–Cl$^+$), 609(M–Cl$_2^{+\cdot}$), 408(RDA fragment M–C$_5$Cl$_6^+$), 382(tetraphenylbenzene$^{+\cdot}$). (Found: C, 64.9; H, 3.4. Calc. for $C_{37}H_{24}Cl_6$: C, 65.2; H, 3.5%).

Addition of tetracyclone to tricyclononadiene **23**. Compound **23** (160 mg, 0.5 mmol) was heated with tetracyclone (190 mg, 0.5 mmol) in toluene (as above), the mixture was concentrated and acetone added; the pink solid product was recrystallised from benzene–MeOH to give endo–anti–exo 1,10,11,12, - *tetrachloro* - 13,13 - *dimethoxy* - 4,5,6,7 - *tetraphenylpentacyclo*[8,2,1^{1,10}1^{4,7}0^{2,9}0^{3,8}]*tetradecan* - 5,11 - *dien* - 14 - *one* **29b**† (200 mg, 57%) m.p. 242–243° (effervescence) ν_{max} 1784 (bridged-ring CO) *m/e* 670(M–CO$^{+\cdot}$), 635(M–CO–Cl$^{+\cdot}$), 408(RDA fragment from 670), 382(Ph$_4$C$_6$H$_2^{+\cdot}$). (Found: C, 68.5; H, 4.13. Calc. for $C_{40}H_{30}Cl_4O_3$: C, 68.55; H, 4.3%).

Thermolysis of adduct **29b** *to give dihydrosemibullvalene II*. The adduct (180 mg) was heated to its m.p. in a small fusion tube for 2 min. Vigorous effervescence occurred, and the cooled product was recrystallised from benzene–MeOH to give endo 1,10,11,12 - *tetrachloro* - 13,13 - *dimethoxy* - 4,5,6,7 - *tetraphenylpentacyclo*[8,2,1,0^{2,9}0^{3,7}0^{6,8}]*triadeca* - 4,11 - *diene II* (~90 mg, 55%) m.p. 188–190° ν_{max} 2950, 2840, 1603, 1495, 1445, 1190, 1130, 990, 700 cm^{-1} τ: 2.7–3.3(m) (20H), 5.8(s) (1H) 6.38(d) (1H) and 6.94(d) (1H) (J = 7.0 Hz), 6.42(s), 6.58(s), (6H 2-OMe), 6.9(s) (1H), *m/e* 670(M$^+$), 635(M–Cl$^{+\cdot}$), 408(RDA, M–C$_7$H$_6$Cl$_4$O$_2^{+\cdot}$), 382(C$_{30}$H$_{22}^{+\cdot}$). (Found: C, 69.9; H, 4.4. Calc. for $C_{39}H_{30}Cl_4O_2$: C, 69.65; H, 4.5%).

Attempted dehydrogenation of compounds I and II with bromine and 2,3-*dichloro*-5,6-*dicyanobenzoquinone*. Compounds I and II (50–200 mg) were recovered unchanged after treatment with Br_2 in boiling redistilled $CHCl_3$; or when heated with dichlorodicyanobenzoquinone in toluene in a Carius tube at 90°/96 hr.

The reaction of 2,5 - *di*(p - *methoxyphenyl*) - 3,4 - *diphenylcyclopentadienone with tricyclononadiene* **23**. Tricyclononadiene (240 mg, 0.75 mmol) and 2,5 - di(*p* - methoxyphenyl) - 3,4 - diphenylcyclopentadienone (333 mg, 0.75 mmol) were boiled in xylene (*ca* 20 ml) for 18 hr, and after vacuum evaporation and cooling 1:1 cyclohexane–MeOH (10 ml) was added; the ppt (370 mg, 64%) gave as second eluent on column chromatography (silica gel–CH_2Cl_2) the *adduct* **29c**† (80 mg, 14%) m.p. 240–242° (dec) ν_{max} 1780 vs cm^{-1} (bridge-ring CO) τ: 2.8–3.5(m) (18H ArH), 6.7(s) (6H) and 6.5, 7.8(each s, 3H) (4-OMe), 7.1(m) (2H), 7.2(m) (2H). *m/e* 730(M–CO$^{+\cdot}$), 695(M–CO–Cl$^+$), 468(RDA fragment), 442(C$_{32}$H$_{26}$O$_2$ (*p*-MeOC$_6$H$_4$)$_2$C$_6$H$_2$ (C$_6$H$_5$)$_2^{+\cdot}$) (Found: C, 66.6; H, 4.7. Calc. for $C_{42}H_{34}Cl_4O_5$: C, 66.35; H, 4.5%). Subtraction of the ^{1}H NMR spectrum from that of the crude product left signals characteristic of cyclooctatriene (41c) τ: 2.6–3.5 (18H, ArH), 4.2(m) (2H=C–H), 6.08(m) (2H C=C·CH), 6.32(s) (6H), 6.44 and 6.46 (each s, 3H) (4-OMe).

Reaction of 2,5 - *di*(p - *methoxyphenyl*) - 3,4 - *diphenylcyclopentadienone with tricyclononadiene* **22**. The cyclopentadienone (666 mg, 1.5 mmol) boiled in xylene (18h) with **22** (483 mg, 1.5 mmol) and the evaporated soln diluted with n-hexane gave a fraction A (550 mg) part of which column chromatographed on silica gel gave the *adduct* **28c**† (60 mg, 10%), m.p. 234–235° (dec) from $CHCl_3$–n-hexane, ν_{max} 1787 vs cm^{-1} (bridge-ring CO) τ: 2.8–3.4(m) (18H), 6.3(s) (6H 2-OMe), 7.05(s) (4H) coincident cyclobutane signals); *m/e* 738 (M–CO$^{+\cdot}$), 703 (M–CO–Cl$^{+\cdot}$), 468 (RDA from M$^{+\cdot}$), 442 ((*p*-MeOC$_6$H$_4$)$_2$ C$_6$H$_2$(C$_6$H$_5$)$_2^{+\cdot}$). (Found: C, 62.5; H, 3.5. Calc. for $C_{40}H_{28}Cl_6O_3$: C, 62.4; H, 3.65%). Mother liquor evaporation gave a solid B (140 mg)—substantially dihydrosemibulvalene (III), and a viscous oil C (300 mg), mainly **40c**. A similar experiment in boiling toluene (under N_2) gave adduct **28c** (60%), and from the crystallisation liquors *cyclooctatriene* **40c** (12%) m.p. 228–230° (from $CHCl_3$–MeOH) τ: 2.7–3.4(m) (18H ArH), 4.15(m) (2H =C–H), 5.88(m) (2H C=C·CH), 6.3(s) (6H 2-OMe); *m/e* 738 (M$^{+\cdot}$) 703 (M–Cl$^+$) (Found: C, 64.25; H, 3.95. Calc. for $C_{39}H_{28}Cl_6O_2$: C, 64.55; H, 3.9%).

Samples A and B of adduct **28c** (132 mg) were fused at 235° (metal bath, 2 min under N_2, CO evolved); the cooled products were dissolved in $CHCl_3$ and MeOH added. Solid precipitated from evaporated sample B was chromatographed to give one main product (65 mg); this was recrystallised (CCl_4–MeOH) and the crystals (40 mg) combined with those separated from sample A (35 mg). Recrystallisation of the combined yield gave product m.p. 231–232.5° (dec) (55 mg) which on chromatography (5% ether in CCl_4–petrol, 10 mg/20 cm × 20 cm plate) resolved into two fractions, (i) *dihydrosemibullvalene* III (36 mg, 14% m.p. 233–234° (from CCl_4 n-hexane) τ: 2.8(s) and 2.9–3.7(m) (18H ArH), 5.8(s) (1H), 6.25(d) (1H) and 6.82(d) (1H) (J = 7 Hz), 6.34 and 6.46 (each s, 3H 2-OMe), 7.0(s) (1H); *m/e* 738(M$^+$) 703(M–Cl$^{+\cdot}$) 468(RDA, M–C$_5$Cl$_6^+$); M 738.0199. Calc. for $C_{39}H_{28}Cl_6O_2$: 738.0200; and (ii) an isomer of III, (36 mg, 14%) m.p. 184–185° (CCl_4–n-hexane) τ (CCl_4) 2.8–3.7 (cm) (18H ArH), 5.85(s) (1H), 6.43(d) (1H) and 6.77(d) (1H) (J = 7 Hz), 6.24 and 6.36(s) (6H 2-OMe), 6.97(s) (1H); *m/e* identical to compound III above.

The addition of 2,5 - *dimethyl* - 3,4 - *diphenylcyclopentadienone* ("*Hemicyclone*") *to tricyclononadiene* (**22**): Hemicyclone dimer (2.0 g, 4 mmol) and **22** (2.46 g, 8.0 mmol) were boiled in xylene (40 ml; 18 hr); on cooling crystals separated and

these were filtered off to give adduct **30**†, endo–anti–exo 1,10,11,12,13,13 - *hexachloro* - 4,7 - *dimethyl* - 5,6 - *diphenylpentacyclo*[8,2,1^{1,10}1$^{4,7}0^{2,9}0^{3,8}$]*tetradecan* - 5,11 - *dien* - 14 - *one* (2.8 g, 48%) m.p. 258–259° (dec) ν_{max} 1770 vs cm^{-1} (bridge-ring CO) τ: 2.8–3.0(m) and 3.1–3.2(m) (10H ArH), 7.2(m), and 7.75(m) (each 2H) (cyclobutane A_2X_2, principal line separation 3.0 Hz in each), 8.79(s) (6H 2-Me); *m/e* 582(M$^+$) (very weak) 554(M–CO$^+$), 258($Ph_2C_6H_2Me_2^+$). (Found: C, 57.45; H, 3.5. Calc. for $C_{28}H_{20}Cl_6O$: C, 57.45; H, 3.4%). Mother liquor evaporation and recrystallisation (CCl_4–MeOH) gave **34**, endo–anti 1,10,11,12,13,13 - *hexachloro* - 4,7 - *dimethyl* - 5,6 - *diphenyltetracyclo*[8,2,1,$0^{2,9}0^{3,8}$]*triadeca* - 4,6,11 - *triene* (1.1 g, 25%) m.p. 222–223.5° (after chromatography) ν_{max} 1604, 1490, 1440 cm^{-1}. τ: 2.8–3.4(m) (10H ArH), 6.7(m) and 7.22(m) (each 2H, cyclobutane A_2X_2, principal line separation 3.5 Hz in each), 8.6(s) (6H, 2-Me); *m/e* 554(M$^+$), 519(M–Cl$^+$), 483(M–HCl$_2^+$), 258($Ph_2C_6H_2Me_2^+$) M 553.9693, $C_{27}H_{20}Cl_6$ requires 553.9696 (Found: C, 58.0; H, 3.55; Cl, 37.95 requires: C, 58.15; H, 3.6; Cl, 38.15%) ^{1}H NMR of the crude adduct indicated 5% **40**d τ: 2.8–3.5(m) (10H), 4.8(m) (2H=CH), 6.1(m) (2H C=C·CH) and 8.14(s) (6H 2-Me).

Thermolysis of carbonyl-bridge adduct **30** *and cyclohexadiene* **34**. The adduct **30** was heated in several solvents over a range of temp; ^{1}H NMR indicated formation of **34** and **40**d; heating **34** in toluene (Carius tube) at 164°/24 hr gave (by ^{1}H NMR assay) 80% unchanged **34** and 20% **40**d. In a similar experiment at 190°/24 hr, **34** gave a mixture containing starting material, **40**d and IV [5:2:4].

Two samples of **30** (each 0.5 g) were fused at 260–262° (as for **28**c); the crude product contained **34**, **40**d and IV [3:1:2]. Recrystallisation ($CHCl_3$–MeOH) and chromatography gave two main fractions (i) **34** and **40**d [3:1] (350 mg, 40%) and (ii) IV (318 mg, 33%). Fraction (ii) rechromatographed gave pure *dihydrosemibullvalene* IV, (202 mg, 19%) m.p. 210–211° (dec) (from CCl_4–MeOH) τ: 2.8–3.5(m) (10H ArH), 6.5(d) (1H), and 7.08(d) (1H) (J = 7 Hz) 7.06(s) (1H), 7.65(s) (1H), 8.2 and 9.0 (each (s) 3H, 2-Me); *m/e* 554(M$^+$), 519(M–Cl$^+$), 284(M–$C_5Cl_6^+$). (Found: C, 58.2; H, 3.7. Calc. for $C_{27}H_{20}Cl_6$: C, 58.2; H, 3.6%). ^{13}C ppm: 14.26, 14.56 (Me) 39.53, 55.61, 58.94, 64.18 (t-CH) 48.80, 51.27 (quat. C) 80.53, 82.69, 103.63 (CCl, CCl_2) 126.1–140.47 (=C, 6 weak and 5 strong freqs.).

The addition of tetracyclone to tricyclohydrazo ester **7**. Askanis' ester **7** (2.78 g, 10 mmol) and tetracyclone (3.48 g, 10 mmol) were boiled in toluene (N_2) at the b.p. 24 hr, the solvent removed *in vacuo* and the pink solid product recrystallised from aqueous acetone to give endo–exo–*diethyl* 4,5,6,7 - *tetraphenyl* - 11,12 - *diazapentacyclo*[8,2,2,1$^{4,7}0^{2,9}0^{3,8}$]*pentadeca* - 5,13 - *dien* - 15 - *one* - 11,12 - *dicarboxylate* **43**§ (5.3 g, 80% m.p. 213–214° (dec) ν_{max} 1785 and 1680–1760 cm^{-1} (CO and CO_2Et) τ: 8.71–9.04(dt) (6H 2-Me), 5.80–6.12(dq) (4H 2-OCH_2), 7.30(m) and 7.52(m) (each 2H cyclobutane A_2X_2), 4.85–4.98(m) (2H H-1,10), 2.78–3.40 (complex overlapping m) (22H, ArH and H-13,14), *m/e* 662(M$^+$), 634(M–CO$^+$). (Found: C, 78.3; H, 5.7; N, 3.95. $C_{41}H_{38}N_2O_5$: C, 77.9; H, 5.8; N, 4.2%).

Hydrolysis of tetracyclone adduct **43** *and decarbonylation of the product*. The adduct **43**, (3.31 g, 5 mmol) was boiled with a soln of KOH (1.12 g, 20 mmol) in EtOH (40 ml) for 16 hr, insoluble salts filtered off and the soln evaporated, water added and the organic product extracted with CH_2Cl_2; evaporation of the washed and dried extract and column chromatography (silica gel/CH_2Cl_2–petroleum) gave colourless crystals of endo–anti - 1,10,11,12 - *tetraphenyltetracyclo*[8,2,1,$0^{2,9}0^{3,8}$]*trideca* - 4,6,11 - *trien* - 13 - *one* **45**§ (600 mg, 25%) m.p. 212–213° (effervescence) ν_{max} 1780 cm^{-1} (bridge-ring CO) τ: 6.70(m), 7.30(m) (each 2H, cyclobutane A_2X_2) 4.22(s) (W/2 4 Hz) (4H–4,5,6,7), 2.79(m), 3.13(m), 3.33(m) (20H 4-C_6H_5), ^{13}C ppm: 30.09, 50.96 and 67.22 (saturated C) 121.65, 125.83, 126.80, 127.04, 127.47, 128.20, 129.47, 129.90, 133.17, 133.84, 142.33 (=C$\diagdown\!\!\diagup$) and 202.83(C=O). (Found: C, 91.25; H, 5.75. Calc. for $C_{37}H_{28}O$: C, 90.95; H, 5.8%).

Compound **45**, (100 mg) was heated in a small test tube until gas evolution ceased: the glassy solid product, recrystallised from CH_2Cl_2 petroleum to give 1,2,3,4 - *tetraphenyl* benzene[27] (m.p., IR and NMR comparison).

Decarbonylation of tetraphenylpentacyclodiazapentadecadienone dicarboxylate **43**. The adduct **43** (500 mg, 0.8 mmol) was heated in a small test tube (oil bath, 210°) until gas evolution ceased; the glassy solid product was recrystallised from CH_2Cl_2 petroluem to give 4,5,6,7 - *tetraphenyl* - 11,12 - *diazapentacyclo*[8,2,2,$0^{2,9}0^{3,7}0^{6,8}$]*tetradeca* - 4,13 - *dien* - 11,12 - *dicarboxylate* V (305 mg, 62%) m.p. 230–231° ν_{max} 1680–1750 (CO_2Et) 1498, 1602 cm^{-1} (conj. C=C and aryl ring) τ: 8.87(t) (6H 2-Me), 5.92 and 5.95 (each q, overlapping, 4H 2-OCH_2), 2.84–3.82(complex m) (20H 4-C_6H_5), 3.60(t), 3.80(t) (each 1H, H-13,14), 4.68(t, further coupled) and 5.52(m) (each 1H, H-1,10), 6.06(bs) and 7.36(bs) (each 1H, H-3,8), 6.53(m) and 7.40(m) (each 1H, H-9,2). (Found: C, 79.45; H, 6.2; N, 4.2. $C_{42}H_{38}N_2O_4$: C, 79.45; H, 6.05; N, 4.4%), *m/e* 634(M$^+$), 408(RDA, M–$C_{10}H_{14}N_2O_4^+$).

cis–exo - 9,10,11,12 - *Tetraphenyltetracyclo*[6,3,1,$0^{2,7}0^{9,12}$]*dodeca* - 3,5,10 - *triene* VII. The ester product from the previous experiment (3.17 g, 5 mmol) was boiled overnight in a soln of KOH (1.4 g, 25 mmol) in EtOH (55 ml). The soln was filtered and evaporated, the product suspended in water, extracted with CH_2Cl_2 and the washed and dried extracts evaporated; the product, column chromatographed on silica gel in CH_2Cl_2–petroleum gave after evaporation of fractions, crystals of cis–exo - 9,10,11,12 - *tetraphenyltetracyclo*[6,3,1,$0^{2,7}0^{9,12}$]*dodeca* - 3,5,10 - *triene* VII (1.48 g, 64%) m.p. 154–155°, ν_{max} 1498, 1602 cm^{-1} τ: 3.8–4.8 (complex m) (4H, H-3,4,5,6), 6.8–7.0(dd) (2H, H-2,7), 6.10(bs) (1H, H-1), 7.11(bs) (1H, H-8), 2.8–3.3(complex m) (20H, 4-C_6H_5), ^{13}C ppm: 36.04, 40.77, 52.60, 66.68 (saturated CH) 57.70, 57.94 (saturated quat. C); 123.16, 123.40, 125.59, 125.83, 126.14, 126.92, 127.35, 127.59, 128.20, 128.86, 128.99, 129.84, 136.39, 136.81, 137.60, 138.33, 142.03 (=C$\diagdown\!\!\diagup$, 3 pairs overlapping). (Found: C, 93.65; H, 6.15. Calc. for $C_{36}H_{28}$: C, 93.9; H, 6.1%).

Addition of maleic anhydride to tetraphenyltetracyclododecatriene VII. Compound VII (1.3 g, 3 mmol) and maleic anhydride (300 mg, 3 mmol) were heated together in boiling toluene (50 ml) overnight: the solvent was removed *in vacuo* and the product chromatographed (silica gel/20% ether in petroleum), to give *adduct* **50** (1.1 g, 66%) m.p. 264–266°, m.p., IR and ^{1}H NMR identical to the product of heating cyclooctatetraene–maleic anhydride adduct with tetracyclone in decalin,[28] ν_{max} 1786 and 1865 (–CO·O·CO–) 1498, 1602 cm^{-1} (conj. C=C and C_6H_5) τ: 3.81 and 4.08 (each t, further coupled) (each 1H, H-13,14), 6.04(s) (1H, H-3), 6.32(m) (1H, H-2), 6.8–7.1(complex m) (4H, H-1,10,11,12), 7.30(s) (1H, H-8), 7.74(d) (1H, H-9), 2.8–3.2(cm) (20H, 4-C_6H_5). ^{13}C ppm: 36.64, 37.68, 42.77, 43.62, 44.41, 45.56, 55.76, 56.24, 59.03, 63.16 (satd. C) 125.35–142.28 (18 signals, =C) 171.82 and 172.43 (2CO).

Addition of phencyclone to tricyclohydrazo ester **7**. Ester **7**, (1.6 g, 5.8 mmol) and phencyclone (2.24 g, 5.8 mmol) were heated together in boiling toluene 1 hr; on cooling crystals of *diethyl* - 4,7 - *diphenyl* - 5,6(o,o' - *biphenylyl*) - 11,12 - *diazapentacyclo*[8,2,2,1$^{4,7}0^{2,9}0^{3,8}$]*pentadeca* - 5,11,13 - *trien* - 15 - *one* - 11,12 - *dicarboxylate* **44** (R^1 = Ph R^2–R^2 = *o,o'*-biphenylyl)§ separated (3.7 g, 96%) m.p. 289–290° (dec) ν_{max} 1790, 1680–1750 cm^{-1} (bridge CO, CO_2Et) τ: 1.34–1.42(m) and 2.5–3.13(m) (20 H ArH and CH=CH), 5.10(b) (2H, H-1,10), 6.78(bs) and 7.96(bs) (4H, H-2,3,8,9), 6.00(b) and 6.44(b) (4H, 2-OCH_2), 8.84(b) (6H 2-Me). (Found: C, 77.9; H, 5.25. Calc. for $C_{43}H_{36}N_2O_5$: C, 78.15; H, 5.5%).

Decarbonylation of adduct **44**. The adduct (400 mg, 0.6 mmol) was heated at the m.p. until evolution of gases had ceased, and the product recrystallised from CH_2Cl_2–petroleum to give *diethyl* - 4,7 - *diphenyl* - 5,6 - (o,o' - *biphenylyl*) - 11,12 - *diazapentacyclo*[8,2,2,$0^{2,9}0^{3,7}0^{6,8}$]*tetradeca* - 4,13 - *dien* - 11,12 - *dicarboxylate* VI (320 mg, 80%) m.p. ~275° ν_{max} 1680–1750 cm^{-1} τ: 1.36–1.44(m) and 2.10–3.20(m) (18H ArH), 3.59(m) (2H, H-13,14), 4.77(m) and 5.25(m) (each 1H, H-1,10), 5.51(s), 7.00(m), 7.06(s), and 7.35(m) (all 1H, H-3,2,8,9), 5.9–6.2(dq) (4H, 2-OCH_2), 8.83–8.93(dt) (6H 2-Me). (Found: C, 80.15; H, 5.8. Calc. for $C_{43}H_{36}N_2O_4$: C, 79.8; H, 5.75%).

Hydrolysis and deazatation of compound VI. The product of the previous experiment (2.4 g, 3.8 mmol) was boiled in a soln containing KOH (2.9 g, 50 mmol) in EtOH (60 ml) for 48 hr. The product was isolated as for VII (above) giving cis–exo - 9,12 -

diphenyl - 10,11(o,o' - *biphenylyl*) - *tetracyclo*[6,3,1,$0^{2,7}0^{9,12}$]*dodeca* - 3,5,10 - *triene* VIII (1.3 g, 80%) m.p. 207–209° τ: 1.3–3.3(cm) (18H ArH), 4.19–4.6(cm) (4H, H-3,4,5,6), 5.51(narrow m), 6.7(d), 6.89(narrow m), 7.63–7.79(cm) (each 1H, H-1,2,8,7) ^{13}C ppm: 35.87, 41.06, 54.41, 55.09, 60.96, 61.64(saturated C) 122.89–142.07(23 signals resolved, =C). (Found: C, 94.55; H, 5.95. Calc. for $C_{36}H_{26}$: C, 94.3; H, 5.7%).

Maleic anhydride adduct of compound VIII. Heated in chlorobenzene (25 ml) 18 hr, with maleic anhydride (100 mg, 1 mmol) VIII (460 mg, 1 mmol) gave, after chromatography as above, an *adduct* (500 mg, 90%) m.p. 285–290° (Found: C, 86.05; H, 5.05. Calc. for $C_{40}H_{28}O_3$: C, 86.3; H, 5.1%).

Diethyl 4,7 - *diphenyl* - 5,6 - (*perinaphthylyl*) - 11,12 - *diazatetracyclo*[8,2,2,$0^{2,9}0^{3,8}$]*tetradeca* - 4,6,13 - *triene* - 11,12 - *dicarboxylate*. Ester **7** (3.44 g, 12 mmol) was boiled with acecyclone (4 g, 12 mmol) in chlorobenzene (40 ml) ~20 hr. The solvent was removed *in vacuo* and the residue triturated with MeOH and the solid recrystallised from CH_2Cl_2–petroleum to give *diethyl* 4,7 - *diphenyl* - 5,6 - (*perinaphthylyl*) - 11,12 - *diazatetracyclo*[8,2,2,$0^{2,9}0^{3,8}$]*tetradeca* - 4,6,13 - *trien* - 11,12 - *dicarboxylate* (5.6 g, 76%) m.p. 159–160° ν_{max} 1680–1750 cm^{-1} (CO_2Et) τ: 2.5–3.0(cm) (16H ArH), 3.49(m) (2H, H-13,14), 5.25–5.47(cm) (2H, H-1,10), 6.69–6.87(cm) and 6.89(m) (4H, H-2,3,8,9), 5.78–6.07(dq) (4H 2-OCH_2), 8.71–8.90(dt) (6H 2-Me) (Found: C, 79.0; H, 5.55. Calc. for $C_{40}H_{32}N_2O_4$: C, 79.2; H, 5.6%). Hydrolysed in an ethanolic soln of KOH the ester gave 10,13-diphenylfluoranthene (54%) m.p. 163–164° τ: 2.3–2.9(cm), *m/e* 354 ($C_{28}H_{18}^+$). (Found: C, 94.15; H, 5.35. Calc. for $C_{28}H_{18}$: C, 94.9; H, 5.1%).

Addition of 2,5 - *dimethyl* - 3,4 - *diphenylcyclopentadienone to Askanis' ester* **7**. 2,5 - Dimethyl - 3,4 - diphenylcyclopentadienone dimer[29] (2.60 g, 10 mmol) and **7** (2.78 g, 10 mmol) were boiled overnight under N_2 in toluene (50 ml). The solvent was removed *in vacuo* and the product recrystallised from CH_2Cl_2–petroleum giving *diethyl* - 4,7 - *dimethyl* - 5,6 - *diphenyl* - 11,12 - *diazapentacyclo*[8,2,2,1,$^{4,7}0^{2,9}$]*pentadeca* - 5,13 - *diene* - 15 - *one* - 11,12 - *dicarboxylate* **42**§ (4.73 g, 88%) m.p. 210°(dec) ν_{max} 1770 and 1680–1740 cm^{-1} τ: 2.8–3.6(cm) (12H 2-C_6H_5 and CH=CH), 5.0–5.2(m) (2H, H-1,10), 7.6–7.7 and 7.9–8.2 (both m, 4H, H-2,3,8,9), 8.8(s) (6H 2-Me), 5.7–6.1(bq) (4H 2-OCH_2) and 8.76(dt) (6H 2-Me), *m/e* 538(M^+), 510(M–CO^+). (Found: C, 73.65; H, 5.8. Calc. for $C_{33}H_{34}N_2O_5$: C, 73.6; H, 6.35%).

Hydrolysis of adduct **42** *with oxidative decarboxylation and deazatation to give tetracyclic ketone* **45**. The adduct (538 mg, 1 mmol) was hydrolysed with KOH (1.4 g, 25 mmol) in boiling EtOH (55 ml) during 24 hr, insoluble salts filtered off, the residue diluted with water and the organic product taken up in CH_2Cl_2; the washed and dried ($CaCl_2$) soln was evaporated *in vacuo* and the residue (355 mg) subjected to preparative tlc (1:1 CH_2Cl_2–petroleum) to give endo–anti - 1,10 - *dimethyl* - 11,12 - *diphenyltetracyclo*[8,2,1,$0^{2,9}0^{3,8}$]*tetradeca* - 4,6,11 - *triene* - 13 - *one* **45**§ (224 mg, 61%) m.p. 139–141° (from petroleum) ν_{max} 1770 cm^{-1} τ: 2.7–3.0(cm) (10H 2-C_6H_5), 4.1–4.5(cm) (4H, H-4,5,6,7), 7.3(bs) (4H, H-2,3,8,9), 8.75(s) (6H 2-Me). ^{13}C NMR ppm: 7.89, 28.76, 53.81, 56.73(saturated C), 121.04, 126.14, 127.04, 127.96, 129.23, 134.45, 142.21 (=C<) and 208.65, *m/e* 364(M^+), 336(M–CO^+), 258(M–CO–$C_6H_6^+$) (Found: C, 88.65; H, 6.55. Calc. for $C_{27}H_{24}O$: C, 88.95; H, 6.65.

Thermolysis of compound **45**. The product from the previous experiment (100 mg) was heated in hexachlorobutadiene (2 ml) at 200° until evolution of gases had ceased: the solvent was removed *in vacuo* and the residue chromatographed (1:1 CH_2Cl_2–petroleum, silica gel) to give 2',5'-dimethyl *o*-terphenyl identical to the authentic compound.[27]

Acknowledgements—W.P.L. thanks Chung Chi College, Chinese University of Hong Kong for financial assistance and leave of absence, and D.L. W.-S. and A.S.M. acknowledges the award of S.R.C. Research Studentships. We thank Dr. M. Murray for assistance with interpreting ^{13}C NMR spectra and Drs. R. W. Alder and G. I. Fray for helpful discussions. We also record our debt to Hooker Chemical Corporation (U.S.A.) and Shell Research Ltd. (U.K.) for gifts of chemicals.

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