

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

W. P. LAY, K. MACKENZIE*, A. S. MILLER, and D. L. WILLIAMS-SMITH
School of Chemistry, The University, Bristol BS8 ITS, England

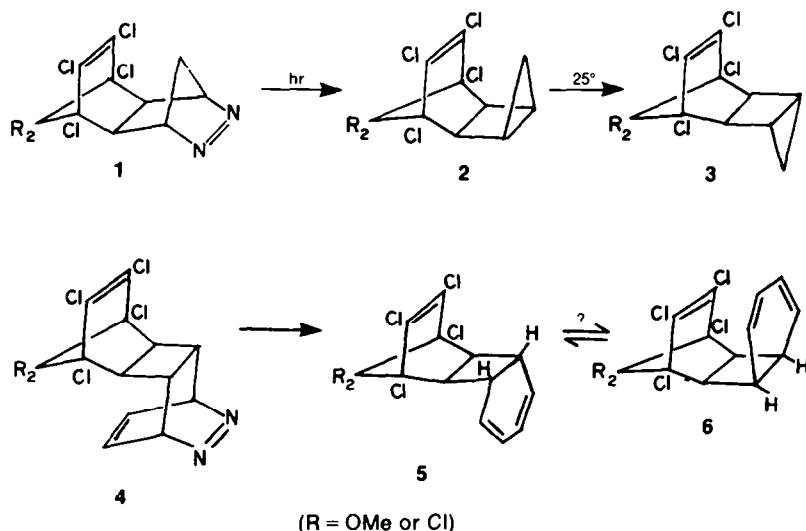
(Received in UK 19 September 1979)

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 immediate 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 described² the synthesis of derivatives **2** and **3** of the little known³ *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 deazotation of azo compound **1** and the exceptionally facile irreversible thermal isomerisation **2** $\rightarrow$ **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**.

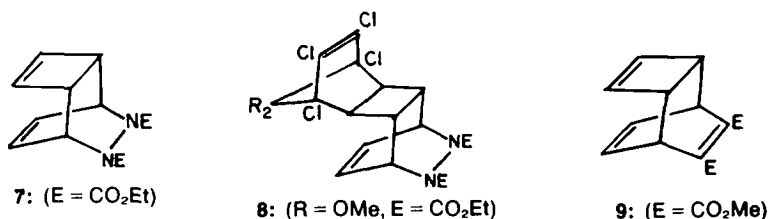
hydrogen to the proximate dichloroolefine site in stereoisomer **5** in analogy to known examples.⁴ Other concerted (and non-concerted) rearrangements could be envisaged with these polycyclic compounds, e.g. photochemical cyclo-reversions, and acid catalysed rearrangements.

Hydrazoester **8** is (quite easily) accessible from Askani⁵ 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



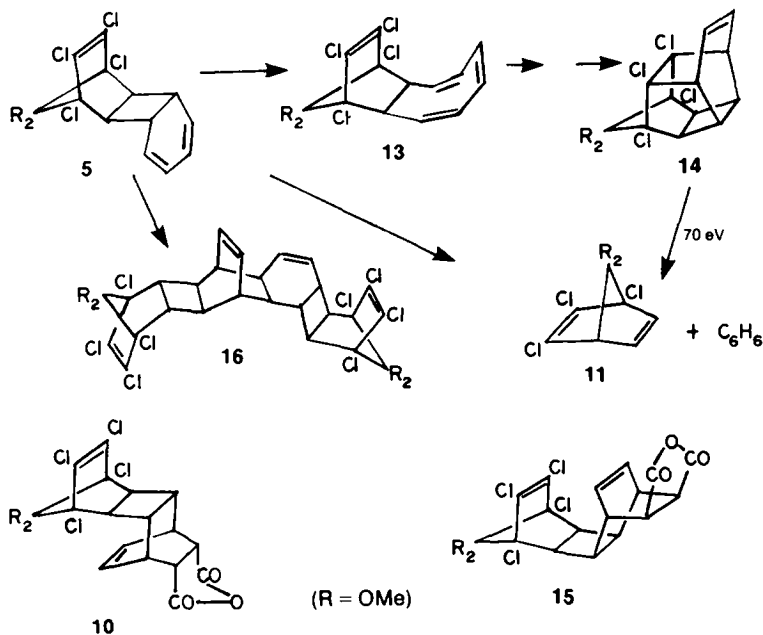
Tetracyclic trienes such as **5** and **6** could potentially exhibit at least three important classes of relatively obvious thermal pericyclic transformation: (a) electrocyclic ring-opening and closure in the bicyclo[4,2,0]octadiene component and hence isomerisation (**5** $\rightleftharpoons$ **6**) 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 ¹H NMR spectrum; the latter shows typical A_2X_2 cyclobutane multiplets² (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



exploited the utility of measuring the principal outermost signal separation $\Delta\nu$ (Hz) in cyclobutane A₂X₂ signals as a criterion of relative stereochemistry in compounds 2 and 3 and related structures² where it was found that $\Delta\nu$ (*syn* isomer): $\Delta\nu$ (*anti* isomer) = 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 deacatation from the assumed intermediate 4. Conformational mobility in the hydrazoester system in intermediate 8 renders most of the ¹H NMR signals⁷ broad and featureless and the cyclobutane A₂B₂ 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 11⁸ 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 (¹H 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 A₂X₂ 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 $\Delta\tau$ ~ 0.5).

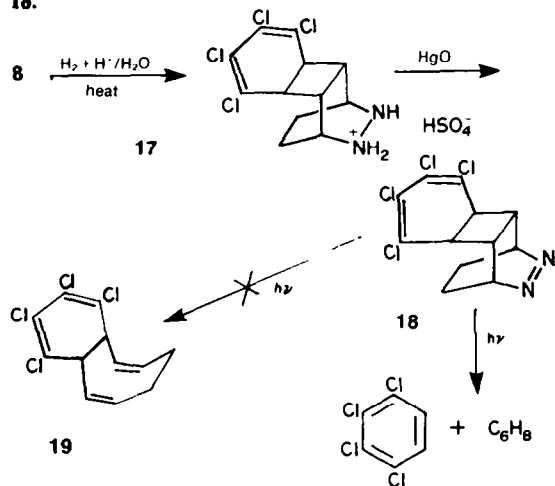
Tetracyclic triene 5 readily forms a maleic anhydride adduct 10, an indication of the accessibility of the diene moiety, and lack of steric inhibition to adduct formation—expected however for its isomer 6; the *anti* fused cyclobutane ¹H NMR multiplets are well separated in the adduct 10 with $\Delta\nu$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

¹³C 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 (>C(OMe)_2) and two different types of >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.

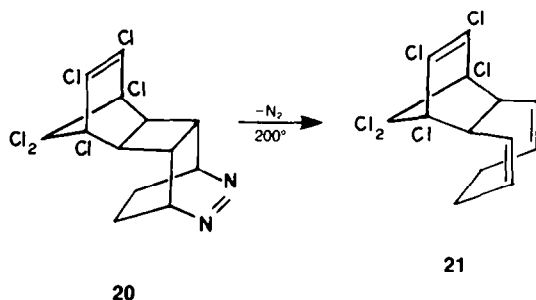
The mass spectrum of cage-compound 14 has an interesting fragment ion at *m/e* 288 (C₉H₈Cl₄O₂⁺) (i.e.

11⁺) 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 ($C_{30}H_{28}Cl_6O_4^+$) and also consistent with structure **16** are the IR ν_{max} at 1600 cm⁻¹ (C=C=Cl) and ¹H NMR signals at τ 4.5 (broad singlet, W/2 4 Hz) (cyclohexene (CH=CH) and a broadened triplet at τ 3.83 (bicyclo-octene [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.

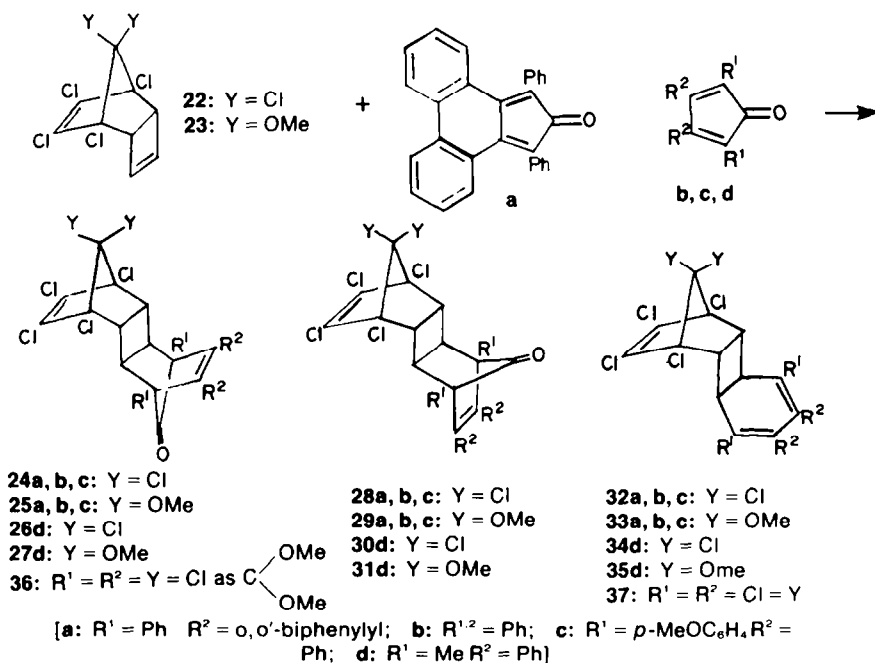
Hydrolysis of the dihydro derivative of adduct **8** with hot concentrated sulphuric acid gives the hydrazo¹ sulphate salt **17** whose neutralization with excess methylamine results in concomitant oxidation to azo compound **18**.



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 deazotation 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 ($2\pi_s + 2\pi_s$) intramolecular addition.

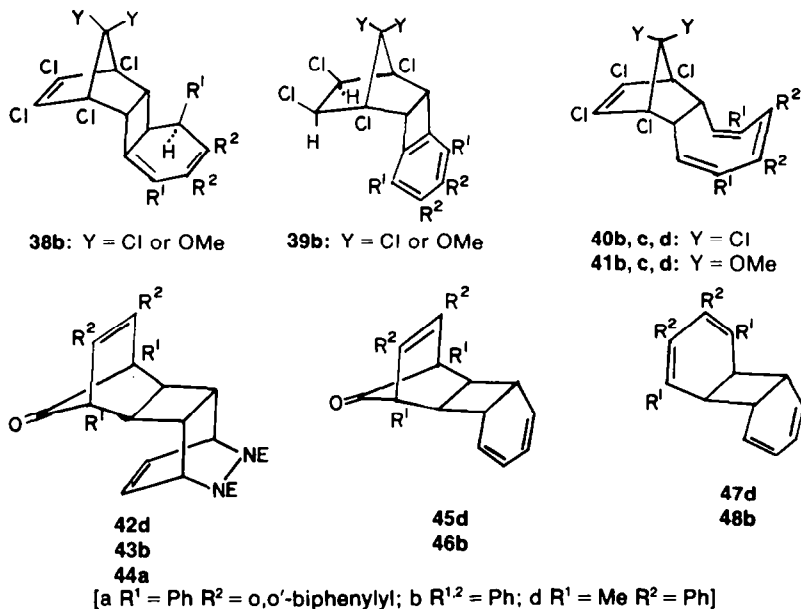


In none of these thermal reactions do any products arise which could be attributed to intramolecular hydrogen group transfer. Perhaps dimerization and intramolecular cycloaddition are much more competitive processes when steric inhibition at the cyclohexadiene system is not too severe, and in this connexion 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:



Several adducts of the general type (24–31) are readily made from each of the cyclobutenes (22 and 23) with phenyclone, tetracyclone, 3,4-diphenyl-2,5-di-(*p*-anisyl)cyclopentadienone, 2,5-dimethyl-3,4-diphenylcyclopentadienone ("hemicyclone"), accecyclone (and its 2,5-dimethyl analogue) and also with tetrachlorocyclopentadienone dimethyl acetal. The phenyclone adducts, e.g. 24a, 25a, 28a, 29a, (each $R^1 = \text{Ph}$, $R^2-R^2 = o,o'$ -biphenyl) 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 9¹¹ (*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 ^1H NMR signals with $\Delta\nu = 3.0\text{--}3.5$ 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 phenyclone 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 ($R^{1,2} = \text{Ph}$) 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 ^1H 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, ^1H NMR monitoring indicates that cyclooctatriene 40b ($R^{1,2} = \text{Ph}$) 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 ($R^1 = p\text{-MeOC}_6\text{H}_4$, $R^2 = \text{Ph}$), 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 ^1H 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).



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 ($R^{1,2} = \text{Ph}$) of tricyclononadienes 22 and 23; on heating at 177–185° both compounds decarbonylate and give *not* the anticipated tetraphenyl cyclohexadienes 32 and 33b ($R^{1,2} = \text{Ph}$)† but monomeric products I and II which besides showing the expected ^1H 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 $\text{C}(\text{OMe})_2$] exhibit two singlets and two doublets ($J = 7$ Hz) each of ^1H 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 ($R^1 = \text{Me}$, $R^2 = \text{Ph}$) (60%), dimethyldiphenylcyclohexadiene 34d ($R^1 = \text{Me}$, $R^2 = \text{Ph}$) (20%) and the cyclooctatriene 40d (Y = Cl, $R^1 = \text{Me}$, $R^2 = \text{Ph}$) (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 ^1H NMR singlets and two doublets in the range τ 6.5–7.6. Significantly *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 (CDCl₃) 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 acecycloane (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** ($R^1 = \text{Ph}$ and $R^2, R^2 = 1',8'$ -naphthyl $Y = \text{Cl}$ or OMe) and the tautomeric cyclooctatrienes **40** and **41**, ($R^1 = \text{Ph}$, $R^2-R^2 = 1',8'$ -naphthyl) which are not appreciably isomerised by further heating.

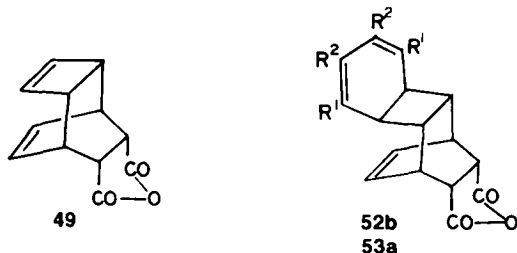
Concurrent with these experiments we observed that Askani's ester **7** also behaves as cyclobutene dienophile towards cyclopentadienones giving e.g. adducts **42d** ($R^1 = \text{Me}$, $R^2 = \text{Ph}$) and its analogues **43b** ($R^{1,2} = \text{Ph}$) and **44a** ($R^1 = \text{Ph}$, $R^2-R^2 = o,o'$ -biphenyl).§ Alkoxide hydrolysis of esters **42d** and **43b** in air gives carbonyl-bridge compounds **45d** and **46b** with the expected IR, ¹H and ¹³C NMR parameters whose thermolysis not unexpectedly¹⁶ 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 ¹H, and especially ¹³C, NMR spectra indicate asymmetric structures [e.g. VII, ¹H 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). ¹³C, 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 product¹⁸ of heating tetracycloane with the maleic anhydride adduct of cyclooctatetraene, **49**, (at

decarbonylation, i.e. cyclohexadiene compound **52b**. The asymmetric nature of maleic anhydride adduct **50b** is very clearly seen in the ¹H 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 ¹³C 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.

The essentially "normal" behaviour of the diazabicyclo[2,2,2]octene dicarboxylate system in the compounds **42d**, **43b**, **44a** during the sequence hydrolysis–oxidation–deazotation, 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 ¹H 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 effects¹⁹ in the hydrazodicarboxylate function in an otherwise symmetrical molecule²⁰].

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 ($\pi_4a + \pi_2a$) cycloaddition²² in the cyclooctatriene ring system formed by 6 π 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 $\sim 90^\circ$ between the environmentally 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 $^3J = 7$ Hz consistent with the required geometry).

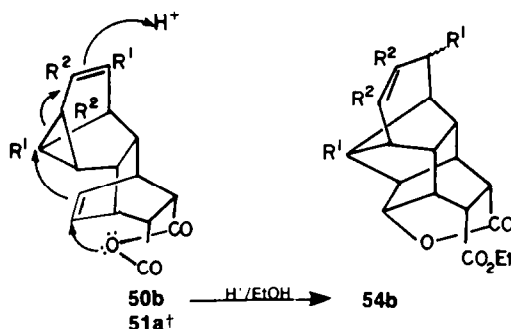
Thermal intramolecular cycloadditions of a similar type are best known in the formation of octamethyl-semibullvalene from octamethylcyclooctatetraene²³ and the spontaneous cyclisation of 1,2:4,5-dibenzocyclooctatetraene to dibenzosemibullvalene²⁴ but there appears to be no archetype of thermal dihydrosemibullvalene formation from cyclooctatrienes.²⁵ Whatever the detailed mechanism of these ring closure reactions, whether by concerted electronic reorganisation²² (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



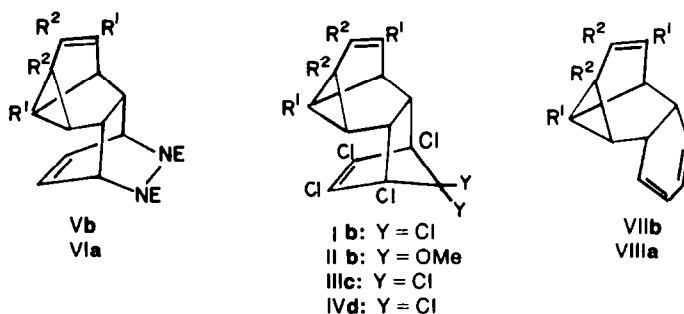
210°), and the spectroscopic properties of the compound are clearly *not* consistent with the expected product of

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

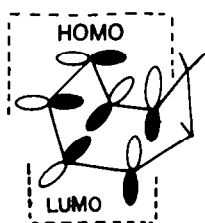
§Relative carbonyl bridge stereochemistry not proven.



Scheme 1.

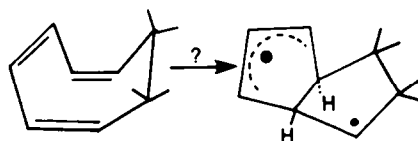


[a: R¹ = Ph R² = o,o'-biphenyl; b: R^{1,2} = Ph; c: R¹ = p MeOC₆H₄ R² = Ph; d: R¹ = Me R² = Ph]



($4\pi_s + 2\pi_a$) 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 (¹³C) and refer to solns in CDCl₃ with TMS as internal standard. Mass spectra refer to data from a GEC-AEI MS902 double-focussing instrument; halogenated ions had the correct ³⁵Cl/³⁷Cl isotopic abundance ratios. IR spectra were recorded with a Perkin-Elmer 257 instrument for solutions in CCl₄ or CH₂Cl₂, 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 GF₂₅₄.

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' method⁵ (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° $\nu_{\max}$ 1680–1760 (CO₂Et) 1605 cm⁻¹ (C=C) τ : 8.78 (t, J=6.5 Hz) (6H, 2-Me), 5.88 (dd) (4H 2-OCH₃), 7.52 (m) (4H, H-2,3 and H-8,9), 6.56 (s) and 6.58 (s) (each 3H 2-OCH₃), 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 C₂₁H₂₄Cl₄N₂O₆: C, 46.5; H, 4.45; Cl, 26.15%).

Hydrolysis of adduct 8 to give anti-endo-anti-tetracyclo-tridecatiene 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 N₂. Precipitated K₂CO₃ was filtered off, and the filtrate evaporated, the residue suspended in water, extracted with CH₂Cl₂ and the extracts washed, dried (Na₂SO₄) 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 CH₂Cl₂-petroleum gave anti-endo-anti-1,2,3,4-tetrachloro-13,13-dimethoxy-tetracyclo[8,2,1,0^{2,9},0^{3,8}]trideca-4,6,11-triene **5** (4.7 g, 72%) m.p. 98–99° $\nu_{\max}$ 1604 cm⁻¹ (C=C) τ : 7.29(m) and 6.88(m) (each 2H, H-5,12 and H-6,11 A₂X₂ 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 C₁₃H₁₄Cl₄O₂: C, 48.9; H, 3.85%).

Photolysis of tetracyclotridecatiene 5. The tetracyclic triene (500 mg) was irradiated (24 hr) in CH₂Cl₂ (60 ml) in a water cooled silica vessel with light from a 125W medium pressure Hg arc lamp; column chromatography of the product on silica gel gave a colourless oil (250 mg) with $\nu_{\max}$ 1606 (C=C) 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]heptadiene⁸ and tetramethoxyethylene.

Thermolysis of tetracyclotridecatiene 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 CHCl₃ to give the dimer **16** (80 mg, 80%) m.p. 216–218° $\nu_{\max}$ 1603 cm⁻¹ (C=C) 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 C₃₀H₂₈Cl₈O₄: 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. N₂) and scratched. Crystals appeared as the sample warmed to 25°; these were filtered off and recrystallised from CH₂Cl₂-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° $\nu_{\max}$ 1600 cm⁻¹ characteristic of C=C absent. τ : 6.88(m) and 7.58(cm) (each 2H cyclobutane A₂X₂ 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). ¹³C ppm: 36.26, 46.59, 48.78, 51.30, 51.84, 77.71 (weak

>C-Cl 82.41 (weak >C-Cl 107.27 (weak >C(OMe)_2) and 129.01. *m/e* 366 (M⁺), 331 (M-Cl⁺), 288 (C₇H₇Cl₄(OMe)₂⁺). (Found: C, 48.6; H, 3.81. Calc. for C₁₃H₁₄Cl₄O₂: 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 CH₂Cl₂-petroleum to give the adduct **10** (1.2 g, 87%) m.p. 286–287° $\nu_{\max}$ 1790 (–CO.O.CO–) 1605 cm⁻¹ (C=C) τ : 7.50(m) and 7.91(m) (each 2H, cyclobutane A₂B₂ 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 C₁₉H₁₆Cl₄O₄: 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-dicarboxylate and its conversion to 4,5,6,7-tetrachloro-11,12-diazatetracyclo[8,2,2,1^{2,9},0^{3,8}]tetradeca-4,6,11-triene 18. Adduct **8** (2.2 g, 4 mmol) in EtOAc (30 ml) containing Pd/CaCO₃ catalyst was treated with H₂ (uptake 120 ml/2h). The filtered product was evaporated and the residue recrystallised from CH₂Cl₂-petroleum to give the 13,14-dihydro derivative of adduct **8** (2 g, 90%) m.p. 194–195° $\nu_{\max}$ 1680–1750 (CO₂Et) 1602 (C=C) τ : 8.76(t) and 8.77(t) (each 3H) and 5.80–5.90(dq) (each 2H conformationally non-equivalent EtO₂C-N-N-CO₂Et), 7.69(m) and 7.00(m) (each 2H cyclobutane A₂X₂ system), 5.80–5.90(m) (2H bridgehead H-1,10 overlapping ester Et signal), 8.0(m) (4H 2-CH₂), 6.50 and 6.52 (each s, 6H 2-OMe). (Found: C, 45.95; H, 4.7. Calc. for C₂₁H₂₆Cl₄N₂O₆: C, 46.3; H, 4.8%).

The product from similar experiments (10 g, 18 mmol) was stirred in conc H₂SO₄ (10 ml) at 95–98° until gas evolution ceased (~ 1 hr) and the dark solid 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 CH₂Cl₂ overnight, the grey solid filtered off and the filtrate evaporated. The colourless solid was recrystallised from CH₂Cl₂-petroleum to give azo compound **18** (250 mg, 33%) m.p. 205–207° (decrepitation, dec) after chromatography, $\nu_{\max}$ 1618 (conj. C=C) 1515 cm⁻¹ (N=N) $\lambda_{\max}$ 304 nm $\epsilon_{\max}$ 3300 (tetrachlorocyclohexadiene system²) τ : 4.8(m) (2H H-1, 10), 6.54(m) and 7.57(m) (each 2H, cyclobutane A₂X₂), 8.00(d) and 8.69(d) (each 2H, J = 8 Hz 2-CH₂) *m/e* 322 (M⁺) 294 (M-N₂⁺) 259 (M-N₂-Cl⁺). (Found: C, 45.35; H, 3.5; N, 8.6. Calc. for C₁₂H₁₀Cl₄N₂: 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},0^{3,8}]tetradeca-4,6,11-triene 18. The azo compound **18** (240 mg, 0.8 mmol) dissolved in CH₂Cl₂ (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% CH₂Cl₂ in petroleum) gave tetrachlorobenzene (100 mg, 62%) identical to the authentic compound²⁷ (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. Askani 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 CH₂Cl₂-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° $\nu_{\max}$ 1680–1760 (CO₂Et) 1608 cm⁻¹ (C=C) τ : 8.78(t) (6H 2-Me), 5.84(dq) (4H 2-OCH₂), 7.30(m) and 7.49(m) (each 2H cyclobutane A₂B₂ 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 C₁₉H₁₈Cl₆N₂O₄: C, 41.4; H, 3.3%). The adduct (10 g, 18 mmol), hydrogenated in ethylacetate (100 ml) over Pd/CaCO₃, absorbed the theoretical quantity of hydrogen; filtration and recrystallisation of the product gave a dihydro derivative (9.7 g, 97%) m.p. 168–169° $\nu_{\max}$ 1680–1750 and 1608 cm⁻¹ (CO₂Et; C=C) τ : 8.77(t) (6H 2-Me), 5.85 and 5.86 (each q, 4H 2-OCH₂), 6.80(m) and 7.60(m) (each 2H cyclobutane A₂X₂ system), 5.70–5.90(m) (2H H-1,10), 8.01(m) (4H 2-CH₂). (Found: C, 41.25; H, 3.55. Calc. for C₁₉H₂₀Cl₆N₂O₄: 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 H₂SO₄ 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 CH₂Cl₂ (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° $\nu_{\max}$ 1610 (C=C) 1519 cm⁻¹ (N=N) τ : 6.78(m) and 8.25(m) (each 2H cyclobutane A₂X₂), 8.74(d) and 8.0(d) (each 2H, 2-CH₂), 4.82(bs, W/2 8.5 Hz) (2H H-1,10). Found: C, 38.6; H, 2.45. Calc. for C₁₃H₁₀Cl₆N₂: 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° $\nu_{\max}$ 1610 cm⁻¹ (C=C) τ : 7.50–8.0(complex m) (4H 2-CH₂), 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 C₁₃H₁₀Cl₆: C, 41.2; H, 2.65%). Mild thermolysis of the tridecatiene **21** at 155° overnight resulted in its recovery unchanged (60%). endo **23** was made by the method of Warren.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'*-biphenyl)-pentacyclo[8,2,1,1¹⁰,1⁴,0^{2,9},0^{3,8}]tetradeca-5,11-dien-14-one **29a** (550 mg, 70%) m.p. 342–344° (dec) (from *p*-cymene) $\nu_{\max}$ 1790 (bridge ring CO) 1600 cm⁻¹ (C=C) 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 C₄₀H₂₈Cl₄O₃: 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) $\nu_{\max}$ 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 A₂X₂ 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 C₄₀H₂₈Cl₄O₃: C, 68.8; H, 4.0%). endo-Hexachlorotricyclo[4,2,1,0^{2,3}]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'*-biphenyl)pentacyclo[8,2,1,1¹⁰,1⁴,0^{2,9},0^{3,8}]tetradecan-5,11-dien-14-one **28a** (350 mg, 47%) recrystallised decalin m.p. 337–338° (variable, dec) $\nu_{\max}$ 1786 vs cm⁻¹ (bridged-ring CO) (Found: C, 64.75; H, 3.4, average of two results. Calc. for C₃₈H₂₂Cl₆O: 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) $\nu_{\max}$ 1790 cm⁻¹ *m/e* 704(M⁺), 676(M-CO⁺), 641(M-CO-Cl⁺), 606(M-CO-Cl₂⁺), 406(R-D-A fragment from M-CO⁺), closely similar to **28a** (Found: C, 64.25; H, 3.1. Calc. for C₃₈H₂₂Cl₆O: 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[8,2,1,1¹⁰,1⁴,0^{2,9},0^{3,8}]tetradecan-5,11-dien-14-one **28b** or **24b**† (260 mg, 45%) m.p. 227–229° (dec) $\nu_{\max}$ 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-Cl₂⁺), 408(RDA fragment from 678), 382(Ph₂C₆H₃⁺). (Found: C, 64.0, H, 3.15. Calc. for C₃₈H₂₄Cl₆O: 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}]trideca-4,11-diene **I** m.p. 240–242° $\nu_{\max}$ 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⁺), 643(M-Cl⁺), 609(M-Cl₂⁺), 408(RDA fragment M-C₃Cl₃⁺), 382(tetraphenylbenzene⁺). (Found: C, 64.9; H, 3.4. Calc. for C₃₇H₂₄Cl₆: 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[8,2,1,1¹⁰,1⁴,0^{2,9},0^{3,8}]tetradecan-5,11-dien-14-one **29b**† (200 mg, 57%) m.p. 242–243° (effervescence) $\nu_{\max}$ 1784 (bridged-ring CO) *m/e* 670(M-CO⁺), 635(M-CO-Cl⁺), 408(RDA fragment from 670), 382(Ph₂C₆H₃⁺). (Found: C, 68.5; 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}]trideca-4,11-diene **II** (~90 mg, 55%) m.p. 188–190° $\nu_{\max}$ 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⁺), 408(RDA, M-C₇H₆Cl₄O₂⁺), 382(C₃₀H₂₂⁺). (Found: C, 69.9; H, 4.4. Calc. for C₃₉H₃₀Cl₄O₂: 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 Br₂ in boiling redistilled CHCl₃; 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-CH₂Cl₂) the adduct **29c**† (80 mg, 14%) m.p. 240–242° (dec) $\nu_{\max}$ 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⁺), 695(M-CO-Cl⁺), 468(RDA fragment), 442(C₃₂H₂₆O₂ (*p*-MeOC₆H₄)₂C₆H₃ (C₆H₅)₂⁺), (Found: C, 66.6; H, 4.7. Calc. for C₄₂H₃₄Cl₄O₅: C, 66.35; H, 4.5%). Subtraction of the ¹H 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 CHCl₃-*n*-hexane, $\nu_{\max}$ 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⁺), 703 (M-CO-Cl⁺), 468 (RDA from M⁺), 442 ((*p*-MeOC₆H₄)₂C₆H₃(C₆H₅)₂⁺). (Found: C, 62.5; H, 3.5. Calc. for C₄₀H₂₈Cl₆O₃: C, 62.4; H, 3.65%). Mother liquor evaporation gave a solid B (140 mg)—substantially dihydrosemibullvalene (III), and a viscous oil C (300 mg), mainly **40c**. A similar experiment in boiling toluene (under N₂) gave adduct **28c** (60%), and from the crystallisation liquors **cyclooctatriene 40c** (12%) m.p. 228–230° (from CHCl₃-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⁺) 703 (M-Cl⁺) (Found: C, 64.25; H, 3.95. Calc. for C₃₉H₂₈Cl₆O₂: C, 64.55; H, 3.9%).

Samples A and B of adduct **28c** (132 mg) were fused at 235° (metal bath, 2 min under N₂, CO evolved); the cooled products were dissolved in CHCl₃ and MeOH added. Solid precipitated from evaporated sample B was chromatographed to give one main product (65 mg); this was recrystallised (CCl₄-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 CCl₄-petrol, 10 mg/20 cm × 20 cm plate) resolved into two fractions, (i) **dihydrosemibullvalene III** (36 mg, 14% m.p. 233–234° from CCl₄-*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⁺) 468(RDA, M-C₃Cl₃⁺); M 738.0199. Calc. for C₃₉H₂₈Cl₆O₂: 738.0200; and (ii) an isomer of III, (36 mg, 14%) m.p. 184–185° (CCl₄-*n*-hexane) τ (CCl₄) 2.8–3.7 (cm) (18H ArH), 5.8(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 ("Hemicyclo") to tricyclononadiene (22). Hemicyclo 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 - diphenyl-pentacyclo[8,2,1,0^{2,9},3⁸]tetradecean - 5,11 - dien - 14 - one (2.8 g, 48%) m.p. 258–259° (dec) $\nu_{\max}$ 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 A₂X₂, principal line separation 3.0 Hz in each), 8.79(s) (6H 2-Me); *m/e* 582(M⁺) (very weak) 554(M-CO⁺), 258(Ph₂C₆H₂Me₂⁺). (Found: C, 57.45; H, 3.5. Calc. for C₃₈H₂₀Cl₆O: C, 57.45; H, 3.4%). Mother liquor evaporation and recrystallisation (CCl₄-MeOH) gave **34**, endo-anti 1,10,11,12,13,13 - hexachloro - 4,7 - dimethyl - 5,6 - diphenyl-tetracyclo[8,2,1,0^{2,9},3⁸]trideca - 4,6,11 - triene (1.1 g, 25%) m.p. 222–223.5° (after chromatography) $\nu_{\max}$ 1604, 1490, 1440 cm^{-1} τ : 2.8–3.4(m) (10H ArH), 6.7(m) and 7.22(m) (each 2H, cyclobutane A₂X₂, principal line separation 3.5 Hz in each), 8.6(s) (6H, 2-Me); *m/e* 554(M⁺), 519(M-Cl⁺), 483(M-HCl₂⁺), 258(Ph₂C₆H₂Me₂⁺) M 553.9693, C₂₇H₂₀Cl₄ requires 553.9696 (Found: C, 58.0; H, 3.55; Cl, 37.95 requires: C, 58.15; H, 3.6; Cl, 38.15%) ¹H NMR of the crude adduct indicated 5% **40d** τ : 2.8–3.5(m) (10H), 4.8(m) (2H=CH), 6.1(m) (2H C=C-H) 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; ¹H NMR indicated formation of **34** and **40d**; heating **34** in toluene (Carius tube) at 164°/24 hr gave (by ¹H NMR assay) 80% unchanged **34** and 20% **40d**. In a similar experiment at 190°/24 hr, **34** gave a mixture containing starting material, **40d** and IV [5:2:4].

Two samples of **30** (each 0.5 g) were fused at 260–262° (as for **28c**); the crude product contained **34**, **40d** and IV [3:1:2]. Recrystallisation (CHCl₃-MeOH) and chromatography gave two main fractions (i) **34** and **40d** [3:1] (350 mg, 40%) and (ii) IV (318 mg, 33%). Fraction (ii) rechromatographed gave pure dihydrosemitubulvalene IV, (202 mg, 19%) m.p. 210–211° (dec) (from CCl₄-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-C₂H₄Cl₂⁺). (Found: C, 58.2; H, 3.7. Calc. for C₂₇H₂₀Cl₄: C, 58.2; H, 3.6%). ¹³C 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, CCl₂) 126.1–140.47 (=C, 6 weak and 5 strong freqs.).

The addition of tetracyclone to tricyclohydrazo ester 7. Askani's ester **7** (2.78 g, 10 mmol) and tetracyclone (3.48 g, 10 mmol) were boiled in toluene (N₂) 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[8,2,2,1,0^{2,9},3^{7,6}]pentadeca - 5,13 - dien - 15 - one - 11,12 - dicarboxylate **43**[‡] (5.3 g, 80% m.p. 213–214° (dec) $\nu_{\max}$ 1785 and 1680–1760 cm^{-1} (CO and CO₂Et) τ : 8.71–9.04(dt) (6H 2-Me), 5.80–6.12(dq) (4H 2-OCH₂), 7.30(m) and 7.52(m) (each 2H cyclobutane A₂X₂), 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. C₄₁H₃₈N₂O₅: 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 CH₂Cl₂; evaporation of the washed and dried extract and column chromatography (silica gel/CH₂Cl₂-petroleum) gave colourless crystals of endo-anti - 1,10,11,12 - tetraphenyltetracyclo[8,2,1,0^{2,9},3⁸]trideca - 4,6,11 - trien - 13 - one **45**[‡] (600 mg, 25%) m.p. 212–213° (effervescence) $\nu_{\max}$ 1780 cm^{-1} (bridge-ring CO) τ : 6.70(m), 7.30(m) (each 2H, cyclobutane A₂X₂) 4.22(s) (W/2 4 Hz) (4H-4,5,6,7), 2.79(m), 3.13(m), 3.33(m) (20H 4-C₆H₅), ¹³C 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<) and 202.83(C=O). (Found: C, 91.25; H, 5.75. Calc. for C₃₇H₂₈O: 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 CH₂Cl₂ petroleum to give 1,2,3,4 - tetraphenyl benzene²⁷ (m.p., IR and NMR comparison).

Decarbonylation of tetraphenylpentacyclodiazapentadecadione 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 CH₂Cl₂ petroleum to give 4,5,6,7 - tetraphenyl - 11,12 - diazapentacyclo[8,2,2,0^{2,9},3^{7,6}]tetradecean - 4,13 - dien - 11,12 - dicarboxylate **V** (305 mg, 62%) m.p. 230–231° $\nu_{\max}$ 1680–1750 (CO₂Et) 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-OCH₂), 2.84–3.82(complex m) (20H 4-C₆H₅), 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. C₄₂H₃₈N₂O₄: C, 79.45; H, 6.05; N, 4.4%), *m/e* 634(M⁺), 408(RDA, M-C₁₀H₁₄N₂O₄⁺).

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 CH₂Cl₂ and the washed and dried extracts evaporated; the product, column chromatographed on silica gel in CH₂Cl₂-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°, $\nu_{\max}$ 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-C₆H₅), ¹³C 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<, 3 pairs overlapping). (Found: C, 93.65; H, 6.15. Calc. for C₃₈H₂₈: C, 93.9; H, 6.1%).

Addition of maleic anhydride to tetraphenyltetracyclododeca triene 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 ¹H NMR identical to the product of heating cyclooctatetraene-maleic anhydride adduct with tetracyclone in decalin,²⁸ $\nu_{\max}$ 1786 and 1865 (-CO-O-CO-) 1498, 1602 cm^{-1} (conj. C=C and C₆H₅) 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-C₆H₅), ¹³C 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 phenacyclone to tricyclohydrazo ester 7. Ester **7**, (1.6 g, 5.8 mmol) and phenacyclone (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' - biphenyl) - 11,12 - diazapentacyclo[8,2,2,1,0^{2,9},3^{7,6}]pentadeca - 5,11,13 - trien - 15 - one - 11,12 - dicarboxylate **44** (R¹ = Ph R² = R² = o,o'-biphenyl)[‡] separated (3.7 g, 96%) m.p. 289–290° (dec) $\nu_{\max}$ 1790, 1680–1750 cm^{-1} (bridge CO, CO₂Et) 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-OCH₂), 8.84(b) (6H 2-Me). (Found: C, 77.9; H, 5.25. Calc. for C₄₁H₃₈N₂O₅: 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 CH₂Cl₂-petroleum to give diethyl - 4,7 - diphenyl - 5,6 - (o,o' - biphenyl) - 11,12 - diazapentacyclo[8,2,2,0^{2,9},3^{7,6}]tetradecean - 4,13 - dien - 11,12 - dicarboxylate **VI** (320 mg, 80%) m.p. ~275° $\nu_{\max}$ 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-OCH₂), 8.83–8.93(dt) (6H 2-Me). (Found: C, 80.15; H, 5.8. Calc. for C₄₁H₃₆N₂O₄: C, 79.8; H, 5.75%).

Hydrolysis and deazotation 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' - biphenyl) - 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) ¹³C 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 C₃₆H₂₆: 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 C₄₀H₂₈O₃: C, 86.3; H, 5.1%).

Diethyl 4,7 - diphenyl - 5,6 - (perinaphthyl) - 11,12 - diaza-tetracyclo[8,2,2,0^{9,10},0^{3,8}]tetradeca - 4,6,13 - triene - 11,12 - dicarboxylate. Ester 7 (3.44 g, 12 mmol) was boiled with acetyl chloride (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 CH₂Cl₂-petroleum to give diethyl 4,7 - diphenyl - 5,6 - (perinaphthyl) - 11,12 - diaza-tetracyclo[8,2,2,0^{9,10},0^{3,8}]tetradeca - 4,6,13 - triene - 11,12 - dicarboxylate (5.6 g, 76%) m.p. 159–160° $\nu_{\max}$ 1680–1750 cm⁻¹ (CO₂Et) 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-OCH₂), 8.71–8.90(dt) (6H 2-Me) (Found: C, 79.0; H, 5.55. Calc. for C₄₀H₃₂N₂O₄: 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 (C₂₈H₁₈⁺). (Found: C, 94.15; H, 5.35. Calc. for C₂₈H₁₈: C, 94.9; H, 5.1%).

Addition of 2,5 - dimethyl - 3,4 - diphenylcyclopentadienone to Askani's ester 7. 2,5 - Dimethyl - 3,4 - diphenylcyclopentadienone dimer²⁹ (2.60 g, 10 mmol) and 7 (2.78 g, 10 mmol) were boiled overnight under N₂ in toluene (50 ml). The solvent was removed *in vacuo* and the product recrystallised from CH₂Cl₂-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) $\nu_{\max}$ 1770 and 1680–1740 cm⁻¹ τ : 2.8–3.6(cm) (12H 2-C₆H₅ 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-OCH₂) and 8.76(dt) (6H 2-Me), *m/e* 538(M⁺), 510(M-CO⁺). (Found: C, 73.65; H, 5.8. Calc. for C₃₃H₃₄N₂O₅: C, 73.6; H, 6.35%).

Hydrolysis of adduct 42 with oxidative decarboxylation and deazotation 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 CH₂Cl₂; the washed and dried (CaCl₂) soln was evaporated *in vacuo* and the residue (355 mg) subjected to preparative tlc (1:1 CH₂Cl₂-petroleum) to give endo-anti - 1,10 - dimethyl - 11,12 - diphenyl-tetracyclo[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) $\nu_{\max}$ 1770 cm⁻¹ τ : 2.7–3.0(cm) (10H 2-C₆H₅), 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). ¹³C 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-C₆H₅⁺) (Found: C, 88.65; H, 6.55. Calc. for C₂₇H₂₄O: 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 CH₂Cl₂-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 ¹³C 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.

REFERENCES

- ¹Preliminary communication in part: G. I. Fray, W. P. Lay, K. Mackenzie and A. S. Miller, *Tetrahedron Letters* 2711 (1979).
- ²W. P. Lay, K. Mackenzie and J. R. Telford, *J. Chem. Soc. (C)*, 3199 (1971); K. Mackenzie, W. P. Lay, J. R. Telford and D. L. Williams-Smith, *Chem. Comm.* 761 (1969).
- ³*cf.* E. L. Allred and J. C. Hinshaw, *J. Am. Chem. Soc.* **90**, 6685 (1968); *Chem. Comm.* 72 (1969); L. A. Paquette and L. M. Leichter, *J. Am. Chem. Soc.* **93**, 5128 (1971); *Ibid.* p. 4922.
- ⁴K. Mackenzie, *J. Chem. Soc.* 4646 (1965); K. Mackenzie, *Ibid.* (C), 1784 (1969); K. Mackenzie and C. H. M. Adams, *Ibid.* 481 (1969); *cf.* W. von E. Doering and J. W. Rosenthal, *J. Am. Chem. Soc.* **89**, 4534 (1967); B. A. Arbuzov, L. A. Shapshinsky and G. A. Prytkova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk* 2084 (1962); R. Srinivasan, *Tetrahedron Letters* 4029 (1973); D. Ginsburg, *Tetrahedron* **30**, 1494 (1974).
- ⁵R. Askani, *Chem. Ber.* **102**, 3304 (1969).
- ⁶C. M. Anderson, I. B. Bremner, I. W. McCay and R. N. Warrener, *Tetrahedron Letters* 1255 (1968); I. A. Akhtar, G. I. Fray and B. R. Kettlewell, unpublished observations.
- ⁷Two ester functions are clearly resolved in the ¹³C NMR spectrum of Askani's ester (7).
- ⁸K. Mackenzie, *J. Chem. Soc. (Supplement I)*, 5710 (1964).
- ⁹J. N. Damico, R. P. Barron and J. M. Ruth, *Organic Mass Spectrometry* **1**, 331 (1968); W. L. Dilling and M. L. Dilling, *Tetrahedron* **23**, 1225 (1967).
- ¹⁰K. Mackenzie, *Formation and Fragmentation of Cyclic Azo Compounds* Chapter 11 in *The Chemistry of the Hydrazo, Azo and Azoxy Groups* (Ed. S. Patai) Interscience, Wiley, London, New York (1975).
- ¹¹C. M. Anderson, I. W. McCay and R. N. Warrener, *Tetrahedron Letters* 2735 (1970). *cf. ibid.* 5031 (1979).
- ¹²Unpublished observations by the Bristol research group of Dr. G. I. Fray; see also accompanying paper.
- ¹³In this connexion we had earlier noted that low temperature acetylchloride-methylcyclopropene adduction resulted in steady evolution of CO on warming the product to 8–10°—among the lowest decarbonylation temp recorded.^{14,15}
- ¹⁴K. Mackenzie and S. Dent, unpublished work.
- ¹⁵*cf.* M. A. Battiste, *J. Am. Chem. Soc.* **85**, 2175 (1963); M. A. Battiste, B. Halton, R. Rehberg, C. L. Derup and M. E. Brennan, *Ibid.* **89**, 5964 (1967); M. A. Battiste, C. L. Derup, R. E. Pincock and J. Heywood-Farmer, *Ibid.* 1954; S. C. Clarke and B. L. Johnson, *Tetrahedron Letters* 617 (1967).
- ¹⁶For a discussion see J. A. Berson and R. F. Davis, *J. Am. Chem. Soc.* **94**, 3658 (1972); and G. Schröder, W. Martin and H. Röttele, *Angew. Chem. Internat. Ed.* **8**, 69 (1969); H. Röttele, W. Martin, J. F. M. Oth and G. Schröder, *Chem. Ber.* **102**, 3985 (1969); J. F. M. Oth, H. Röttele and G. Schröder, *Tetrahedron Letters* 61 (1970).
- ¹⁷Adduct 42 could not be similarly decarbonylated.
- ¹⁸Sample kindly provided by G. I. Fray.
- ¹⁹C. H. Bushweller, *Chem. Comm.* 80 (1966); J. E. Anderson and J. M. Lehn, *Tetrahedron* **24**, 137 (1968); *Ibid.* 123; J. M. Lehn and J. Wagner, *Ibid.* **25**, 677 (1969); J. Wagner, W. Wojnatoski, J. E. Anderson and J. M. Lehn, *Ibid.* **25**, 657 (1969).
- ²⁰NMR (¹³C) spectra of symmetrical cyclopentadienone adducts of Askani's ester 7 clearly exhibit twin signals for the ester alkyl groups due to this effect.
- ²¹I. A. Akhtar, R. J. Atkins, G. I. Fray, G. R. Geen and T. J. King, paper accompanying. See also A. Kondo, T. Yamane, T. Ashide, T. Sasaki and K. Kanematsu, *J. Org. Chem.* **43**, 1180 (1978).
- ²²R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry* p. 81. Verlag Chemie-Academic Press, New York (1970).
- ²³R. Criegee and R. Askani, *Angew. Chem. Int. Ed.* **7**, 537 (1968).
- ²⁴G. F. Emerson, L. Watts and R. Pettit, *J. Am. Chem. Soc.* **87**, 131 (1965); W. Mark and R. Pettit, *Ibid.* **89**, 4787 (1967).
- ²⁵Photochemical analogies are however known—see e.g. O. L. Chapman, G. W. Borden, R. W. King and B. Winkler, *J. Am. Chem. Soc.* **86**, 2660 (1964); J. Zirner and S. Winstein, *Proc. Chem. Soc.* 235 (1964); W. R. Roth and B. Peltzer, *Annalen*

- 685, 56 (1965); E. L. Allred, B. R. Beck and N. A. Mumford, *J. Am. Chem. Soc.* **99**, 2694 (1977).
- ²⁶M. Stiles and U. Burckhardt, *J. Am. Chem. Soc.* **86**, 3396 (1964); M. Jones and L. O. Schwab, *Ibid.* **90**, 6549 (1968); J. Meinwald and D. Schmidt, *Ibid.* **91**, 5877 (1969); J. Meinwald and H. Tsuruta, *Ibid.* 5877; H. E. Zimmerman, J. D. Robbins and J. Schantl, *Ibid.* 5878; W. T. Borden and A. Gold, *Ibid.* **93**, 3830 (1971).
- ²⁷K. Mackenzie, *J. Chem. Soc.* 473 (1960); cf. W. Diltthey, W. Schommer and D. Trösken, *Ber. Dtsch. Chem. Ges.* **66**, 1627 (1933).
- ²⁸Sample kindly provided by G. I. Fray, see Ref. 21.
- ²⁹F. R. Japp and A. N. Meldrum, *J. Chem. Soc.* **79**, 1024 (1901); F. W. Gray, *Ibid.* **95**, 2134 (1909).