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A NOVEL, VERSATILE SYNTHETIC APPROACH TO LINEARLY FUSED TRICYCLOPENTANOIDS *via* PHOTO-THERMAL OLEFIN METATHESIS

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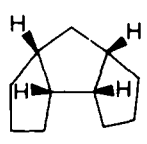
Abstract—Fifteen examples of a new, speedy and general approach to linearly fused tricyclopentanoids bearing the tricyclo[6.3.0.$0^{2,6}$]undecane (triquinane) frame of high contemporary interest is delineated. The key concept in our synthetic sequence to triquinanes is the novel photo-thermal olefin metathesis of cheap, abundantly available Diels–Alder adducts of 1,3-cyclopentadienes and p-benzoquinones. Thus, photolysis of *endo*-tricyclo[6.2.1.$0^{2,7}$]undeca-4, 9-dien-3, 6-diones (**9a–j, 13a, b**) furnished pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8, 11-diones (**10a–j, 14a, b**), which on thermal fragmentation of the cyclobutane ring gave *cis, syn, cis*-tricyclo [6.3.0.$0^{2,6}$]undeca-4, 9-dien-3, 11-diones (**11a–j, 15a, b**) in just three steps and in exceptionally good yields. A few interesting transformations of the readily available parent bis-enone **11a** which indicates its wider uses in syntheses, are described. Finally, a smooth thermal isomerisation of *cis, syn, cis*-bis-enones to *cis, anti, cis*-bis-enones is reported, which further enhances the scope and versatility of our synthetic theme.

The past decade has witnessed an upsurge of interest in the development of synthetic methodologies for the rapid and efficient acquisition of a wide variety of polycyclopentanoids (polyquinanes).[1] This high level of interest and activity has been stimulated and sustained by the unravelling of many new and challenging polycyclopentanoid carbon skeleta from plant,[2] marine[3] and fungal[4] sources on one hand and by the organic chemists quest for "exotic", symmetric, all carbon polyhedra, e.g. Woodward's triquinacene,[5] Eaton's peristylane[6] and now Paquette's dodecahedrane,[7] on the other. Among the polyquinanes, the two stereoisomeric C_{11}-triquinanes (*cis, syn, cis*-**1** and *cis, anti, cis*-**2**)[8], representing three linearly fused cyclopentane rings, have received relatively greater attention due to the fact that the *cis, anti, cis*-isomer **2** embraces the basic carbocyclic framework of biologically important sesquiterpenoids of the hirsutene family[4] e.g. coriolin **3** and marine products capnellanes, e.g. **4**. The folded form, the *cis, syn, cis*-isomer **1** can, in another arena, function as the basic building block for elaboration and evolution towards dodecahedrane and its immediate, logical precursors.[1,7] In the recent past, quite a few, new and orderly synthetic strategies have been worked out for assembling the linearly fused tricyclopentanoid frames.[10] However, many of these approaches have been target oriented endeavours and their generality remains to be firmly established.

In our quest for a simple, general method for the synthesis of tricyclo[6.3.0.$0^{2,6}$]undecane (triquinane) system, we conceived of a novel two step photo-thermal metathetic sequence,[11] (Scheme 1) that involves a photochemical $\pi_s^2 + \pi_s^2$ cycloaddition (**5**→**6**) and a regiospecific thermal fragmentation of the saturated four membered ring (**6**→**7**). The theme depicted in this scheme has many attractive and advantageous features: (i) the tricyclic system **5** can be obtained from cheap,



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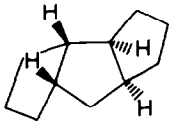

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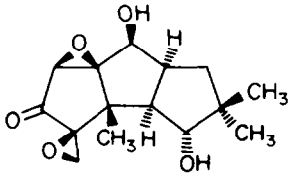

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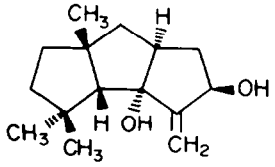

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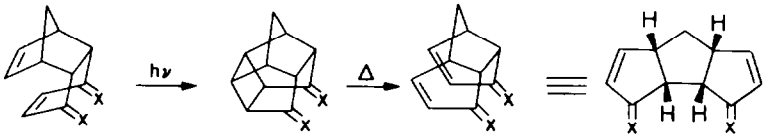
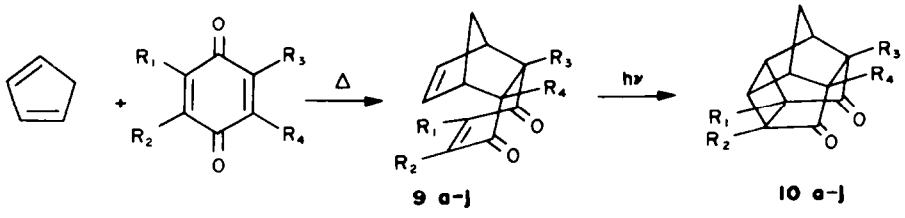


5 X = O, S, C etc. **6** **7**

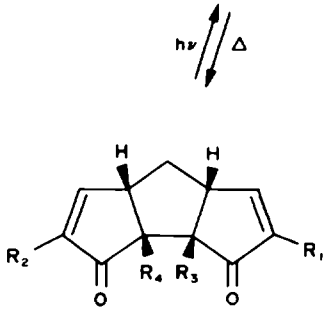
Scheme 1.

readily available starting materials, e.g. 1,3-cyclopentadiene and p-benzoquinone *via* the standard Diels-Alder reaction;[12] (ii) the thermal fragmentation of **6** furnishes stereospecifically the *cis, syn, cis*-triquinane system, adequately and appropriately functionalised; (iii) the overall three step conversion of a 1,3-cyclopentadiene and p-benzoquinone to tricyclopentanoid **7** employs, quite remarkably, only heat and light as the reagents; and (iv) the scheme has the flexibility for structural manipulations that can provide convenient entry into other tricyclic systems[13] of current interest. In this account, we delineate a general, efficient, preparative route to functionalised *cis, syn, cis*-triquinanes and describe some useful synthetic transformations of these systems. Adding to the versatility of our approach is the description of a facile thermal isomerisation of some methyl substituted *cis, syn, cis*-triquinanes to the *cis, anti, cis*-form, endowed with the requisite stereochemical pattern of hirsutene[4] and capnellane[3] group of natural products.

Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane -8, 11 - dione **10a**, readily obtainable[14] from the photolysis of cyclopentadiene-p-benzoquinone (**8a**) Diels–Alder adduct **9a**,[15] has been known[14] to be recalcitrant towards thermal activation. However, sublimation of **10a** through a quartz tube at 560° (1 torr) led to its quantitative conversion to the triquinane system **11a**, m.p. 107–8° (silky flakes from carbon tetrachloride). The bis-enone **11a** could be conveniently prepared in 5–10 g lots, required no separation manoeuvre and was obtained pure simply by direct crystallisation. Its infrared spectrum showed conjugated enone absorptions at 1720, 1590 cm^{-1} diagnostic of 2-cyclopentenone. The ultraviolet spectrum had maxima at 219 nm (ϵ = 9,800) and supported the presence of cyclopentenone chromophore (215 ± 5 nm). The ^{1}H (Fig. 1) and ^{13}C NMR spectra of **11a** further confirmed the presence of 2-cyclopentenone moiety (characteristic β-proton resonance at δ7.54 and strongly deshielded β-carbon resonance at δ165.9)[16] and established the elements of mirror plane symmetry in the molecule with five discrete proton resonances centered at δ7.54, 5.92, 3.56, 3.2, 2.1 (1:1:1:1:1) and six carbon resonances at δ207.4, 165.9, 133.5, 53.1, 50.4, 31.5 (2:2:2:2:2:1). The triquinane based bis-enone structure **11a** for the sole thermolysis product of pentacyclic dione **10a** was thus rigorously established. Although, the *cis, syn, cis*-stereochemical array for **11a** was strongly favoured on the basis of its genesis from **10a**, it could not be easily distinguished from the *cis, anti, cis*-isomer on the basis of the foregoing spectral data. A firm, unambiguous decision in favour of all *cis*-stereostructure was arrived at on the basis of facile and quantitative intramolecular $\pi_s^2 + \pi_s^2$ cycloaddition of **11a** back to **10a** on exposure to either UV lamp or more economically and conveniently to abundant sub-tropical sunlight. Subsequent chemical transformations of **11a** (*vide infra*) were fully consonant with its all-*cis*, folded geometry.



8 a $R_1 = R_2 = R_3 = R_4 = H$
b $R_1 = R_2 = CH_3$, $R_3 = R_4 = H$
c $R_1 = R_2 = Cl$, $R_3 = R_4 = H$
d $R_1 = R_4 = CH_3$, $R_2 = R_3 = H$
e $R_1 = R_4 = Cl$, $R_2 = R_3 = H$
f $R_1 = R_4 = Br$, $R_2 = R_3 = H$
g $R_1 = R_3 = Cl$, $R_2 = R_4 = OCH_3$
h $R_1 = R_4 = Cl$, $R_2 = R_3 = OCH_3$
i $R_1 = R_2 = R_3 = R_4 = Cl$
j $R_1 = R_2 = R_3 = R_4 = Br$



11 a-j

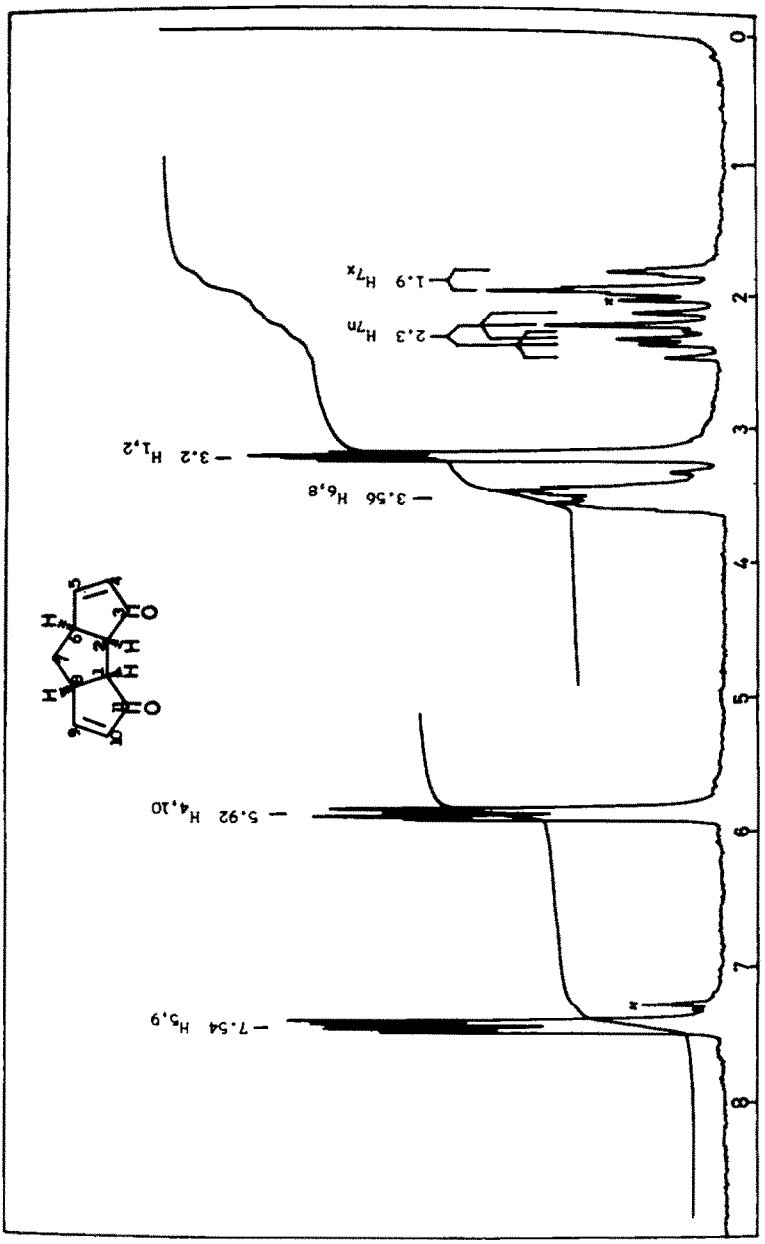
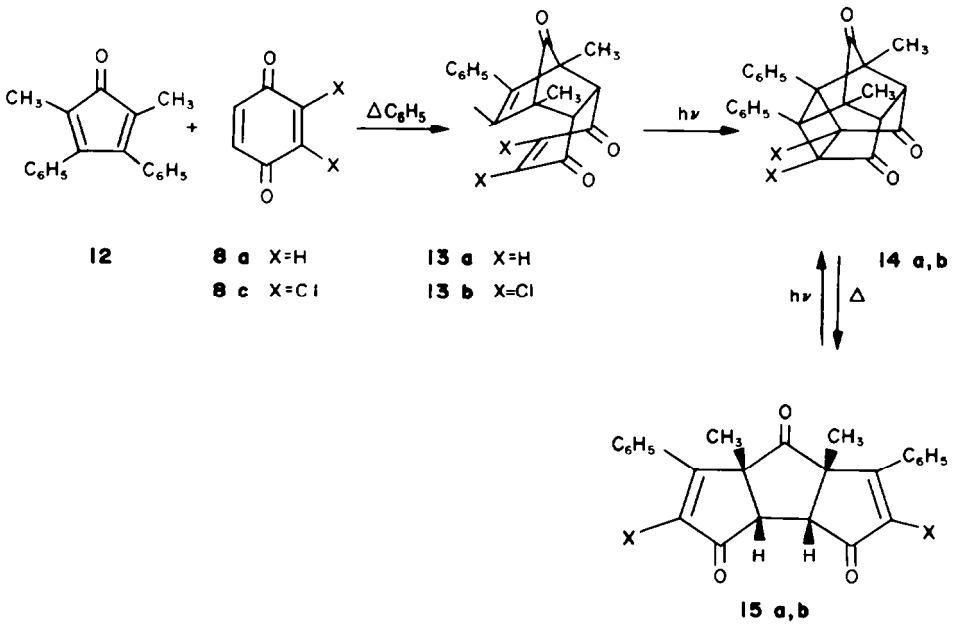


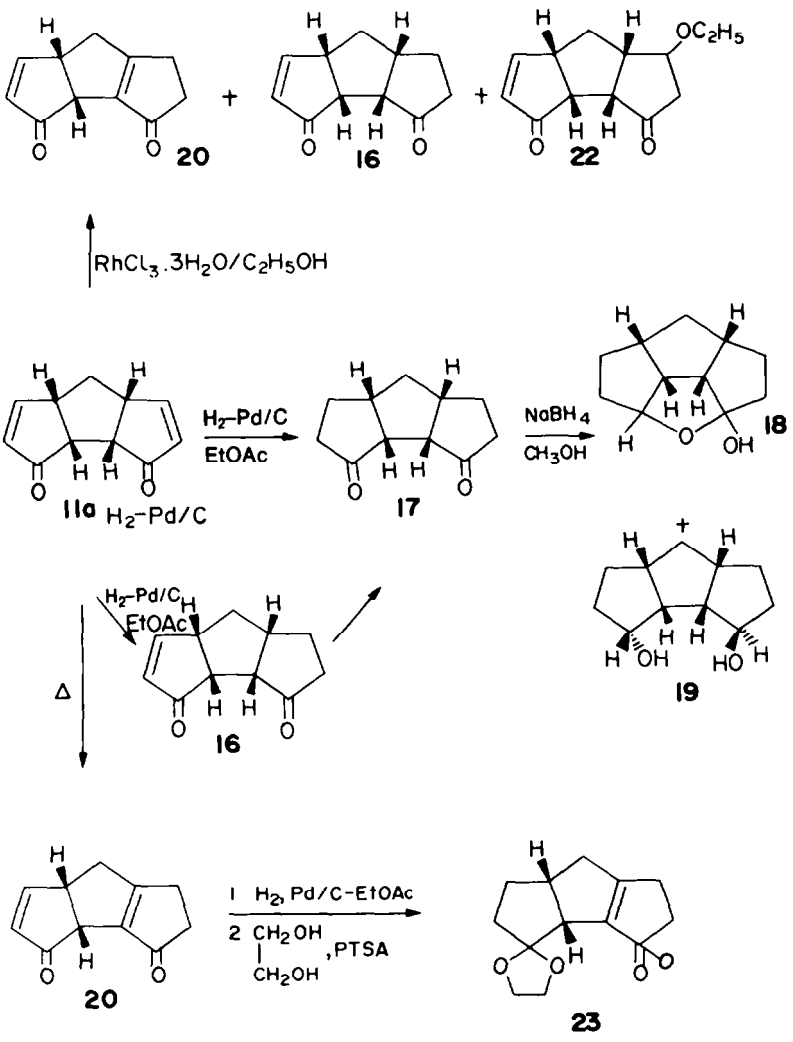
Fig. 1. ^1H NMR (100 MHz) spectrum of bis-enone **11a** in $CDCl_3$.



While the symmetrical disposition of functionality in the bis-enone **11a** proved advantageous for its exploitation in one area, efforts in another direction necessitated chemo-differentiation and relocation of the two enone moieties. Towards the latter objectives, several reactions of **11a** were studied (Scheme 2). The bis-enone **11a** could be catalytically hydrogenated either partially to **16**, m.p. 59–60° or fully to the symmetrical saturated dione **17**, m.p. 93–94°. Further reduction of **17** with methanolic sodium borohydride furnished a 5:1 mixture of hemiacetal **18** and *trans*-diol **19**. Formation of hemiacetal **18** revealed the proximity of two carbonyl groups in dione **17** but, which to some extent, proved to be an impediment in many attempted functionalisation reactions. Rhodium catalysed ($RhCl_3.3H_2O$–EtOH)[17] isomerisation of one of the disubstituted enone double bonds in **11a** to the fully substituted position and a 6:2:1 mixture of **20**, **16** and **22** was obtained in 70% yield. The structure of the new bis-enone **20**, m.p. 100–1°, emerged mainly from the ^{13}C NMR data which indicated the presence of tetrasubstituted olefinic C's of an enone moiety at δ185.1(s) and 143.8(s) and were very reminiscent of the corresponding C's in bicyclo[3.3.0]oct - 1(5) - en - 2 - one (δ187.4 and 148.9).[18] Since, the isomerised bis-enone **20** had a strategic double bond that would enable introduction of an angular methyl group (see, capnellane framework) *via* conjugate addition or could be oxidatively cleavaged to a bicyclo[6.3.0]undecane system (e.g. precapnellane,[19] fusicoccin[20] etc.) the need for a better and more efficient preparation of **20** from **11a** was felt. Towards this end, it was observed that **11a** underwent smooth thermal isomerisation (260°, DPE, 20 min) and **20** could be isolated in over 80% yield as the only product of the reaction. Partial hydrogenation and selective ketalisation of **20** led to the enone-ketal **23**, a substrate we have found valuable for the synthesis of natural products mentioned above.

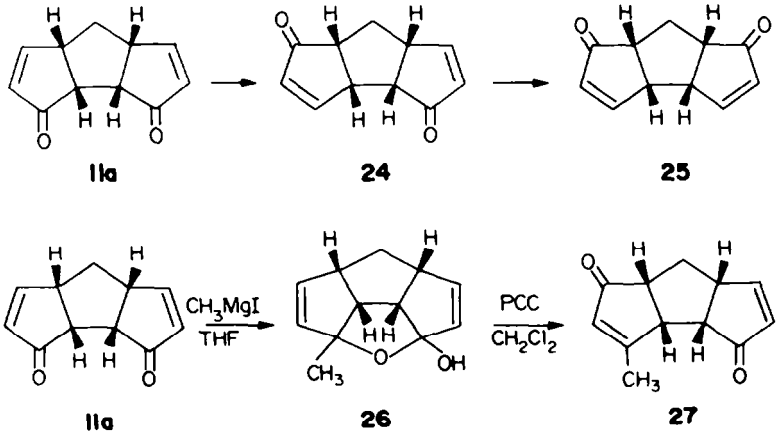
Another set of manipulations with **11a** that appeared useful and promising[21] were to transpose the enone moieties, in a sequential manner, first to the half-transposed system **24** and then to the fully transposed **25**. Several efforts at this enone transposition employing the variants of Wharton reaction[22] proved abortive. However, partial success could be readily achieved employing the alkylative enone transposition sequence.[23] Thus, reaction of **11a** with methylmagnesium iodide (1.3 molar excess) in THF and chromatography led to the isolation of crystalline hemiacetal **26**, m.p. 96–100° (chloroform–hexane). Pyridinium chlorochromate[24] oxidation of **26** resulted in the formation of half-transposed bis-enone **27**, m.p. 105–6°, in 30% yield from **11a**. The structure of **27** rests secured on its ^1H NMR spectrum which exhibited three diagnostic olefinic proton resonances at δ7.46, 5.84 and 5.7, only one of which (δ7.46) was due to the β-proton of the 2-cyclopentenone moiety. In addition, the olefinic methyl resonated downfield at δ2.24 being placed on the β-carbon of an α, β-unsaturated ketone.[25] The ^{13}C NMR resonances confirmed these assignments through characteristic[18] four olefinic carbon resonances at δ178.4(s), 168.1(d), 133.6(d), 129.6(d) with appropriate multiplicities. Like the bis-enone **11a**, the half transposed bis-enone **27** also underwent thermal isomerisation (benzyl benzoate, 300°, 30 min) to the tetrasubstituted olefinic compound **28**. Attempts at complete alkylative transposition to **29** *via* reaction with a large excess of Grignard reagent and PCC oxidation[24] led to a complex mixture from which undesired 1, 4-addition products, like **29** and **30** could be isolated and characterised. Consequently, transposition of the second enone functionality in **27** was attempted through the addition of alkylithium reagents, known for their preference for 1, 2-additions. Reaction of **27** with ethereal methyllithium resulted in initial 1, 2-addition and concomitant intramolecular Michael addition to furnish the crystalline 5-oxa-tetraquinane **31**, in 45% isolated yield. Structure of **31** was revealed through the presence of cyclopentanone absorption (1740 cm^{-1}) in the IR spectrum and the presence of two quaternary CH_3 resonances in the ^1H NMR spectrum at δ1.4 and 1.55. In a manner similar to the formation of **31**, the sodium borohydride reduction and PCC oxidation of **27** also furnished the 5-oxa-tetraquinane **32**.

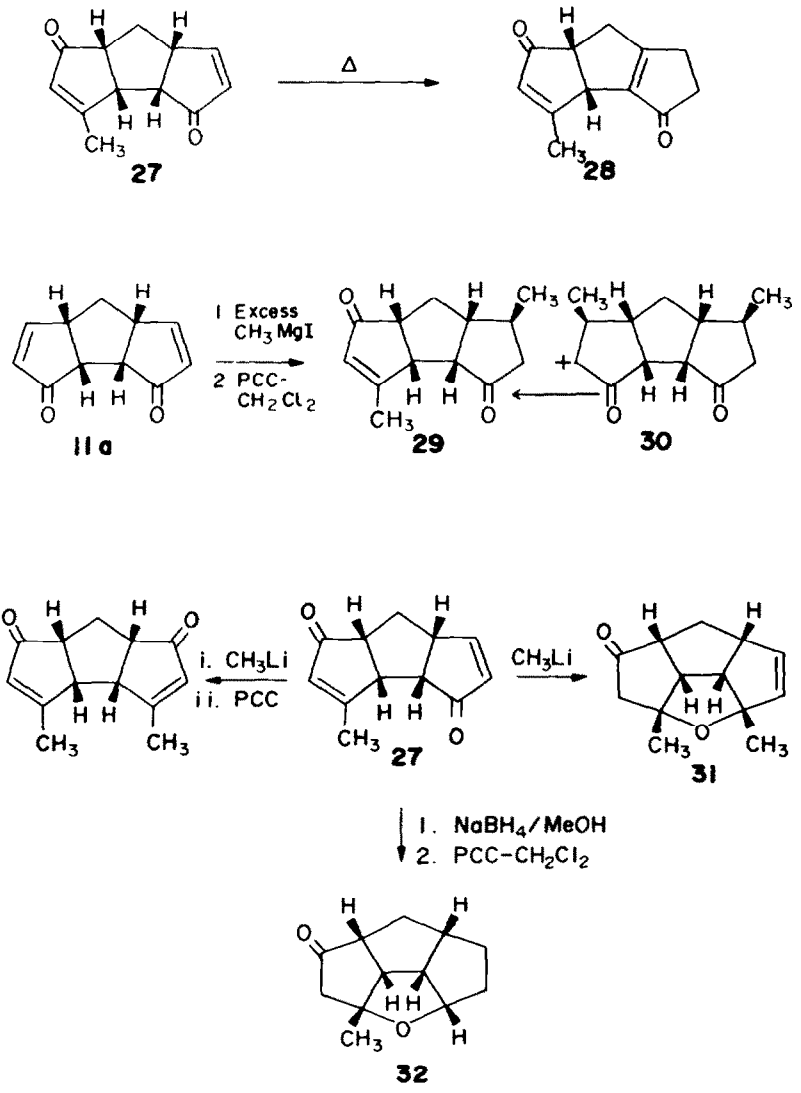
Having demonstrated some useful reactions of the parent bis-enone **11a**, attention was turned towards



Scheme 2.

establishing the generality of the key thermolysis step leading to the uncaging of pentacyclic frame to the triquinane derivatives. Eleven pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane - 8, 11 - diones (**10b-j, 14a, b**), in addition to **10a**, bearing different substituents were synthesised employing the standard methodology. The precursor Diels–Alder adducts (**9b–j**) were prepared from cyclopentadiene and appropriately substituted p-benzoquinones (**8b–j**) and were duly characterised (see Experimental). Diels–Alder adducts (**13a, b**) were prepared by the reaction of hemicyclone (**12**) with benzoquinone (**8a**) and .2, 3-dichlorobenzo-





quinone (**8c**), respectively. Irradiation of tricyclic *endo*-adducts (**9b–j, 13a, b**) using a 450 W Hanovia UV lamp in ethyl acetate or benzene yielded the pentacyclic systems (**10b–j, 14a, b**) in good yields and were spectroscopically characterised (Table 1). Some of the pentacyclic diones existed as hydrates and these were sublimed for characterisation and further use. All the pentacyclic diones (**10b–j, 14a, b**) on thermolysis either static conditions (DPE reflux) or flash conditions (pyrex tube at 450–560°/1 torr) furnished triquinane based bis-enones (**11b–j, 15a, b**) in good to excellent yields (Table 2).[26,27] Slightly lower yields were realised in some cases (entries **3e, f**, Table 2) and are attributable to the product unstability under the reaction conditions. Structures to all *cis*-bis-enones (**11b–j, 15a, b**) were assigned on the basis of UV, IR and ^{1}H NMR data (Table 3) as well as complete ^{13}C NMR analysis (Table 4). All the bis-enones (**11b–j, 15a, b**) on exposure to sunlight or UV light from a lamp underwent facile photocycloaddition to the precursor pentacyclic diones, thus reaffirming their *cis, syn, cis*-stereochemistry. Several of the bis-enones (**11b–j**) undergo reactions similar to those described for the parent **11a** and can thus provide access to many highly functionalised and useful triquinanes. However, description of all these reactions is not considered necessary here.

Further extension of the above general theme has been the synthesis of all *cis*-5-oxa-tetracyclo[7.2.1.0^{4,11}.0^{6,10}]dodecane (oxa-tetraquinane) system of potential utility and interest.[30] The oxa-tetraquinanes (**34a–c**) were obtained *via* the thermolysis of corresponding oxa-bird cage compounds (**33a–c**) as indicated in Table 2.

Structures **34a–c** were established through incisive analyses of ^{1}H and ^{13}C NMR parameters summarised in Tables (3 and 4). The precursor oxa-bird cage systems **33a–c** were most conveniently obtained from the pentacyclic dione **10a** in two steps as shown in Scheme 3. On photolysis, in presence of a sensitizer, the oxa-tetraquinanes **34a–c** cyclised back to the starting oxa-bird cage compounds **33a–c**, respectively. The structures of **34a–c** were therefore firmly established.

Speedy and efficient acquisition of some of the bis-enones **11a–j, 15a, b** and oxa-tetraquinanes **34a–c** mentioned in Tables merit special attention. For example, bis-enone **11d** with an angular methyl group has 13 of the

Table 1. Spectroscopic data for pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecea-8, 11-diones (10a–j) and 4, 8, 11-triones (14a, b)

Compound	mp(solvent)/ Time[a], Yield[b]	IR[c] cm^{-1}	^1H NMR(100 MHz)data, δ[d]	^{13}C NMR(25.0 MHz)data, δ[d]	Analytical data
10a	243-44°C (lit 245°C) (benzene-hexane), 60 min,92%	1750	$CDCl_3$:2.2-3.0(8H,m), 1.7(2H,q).	$CDCl_3$:211.9(s),54.8(d), 44.7(d),43.9(d),40.5(t), 38.9(d).	Ref. 14
10b	108°C (benzene-heptane) 30 min,98%	1750,1730	$CDCl_3$:2.76(6H,brs),1.96 (2H,m),1.02(6H,s).	$CDCl_3$:213.7(s),54.7(d), 50.1(s),44.2(d),43.4(d), 41.2(t),11.4(q).	Calcd for $C_{13}H_{14}O_2$: C,77.20; H,6.98. Found: C,77.5; H,6.99.
10c	203-5°C (sublimed) 15 min,95%	1780,1760	Acetone-d_6:2.5-3.1(6H,m), 1.5-2.1(2H,AB,J=11Hz).	DMSO-d_6[e]:202.7(s),109.9(s), 77.3(s),70.6(s),55.5(d), 51.5(d),50.0(d),48.7(d), 43.3(d),41.6(d);2 signals merged in DMSO-d_6 signals.	Calcd for $C_{11}H_8Cl_2O_2$: C,54.35; H,3.2. Found: C,54.73; H,3.52.
10d	72-73°C (benzene-hexane) 30 min,90%	1750,1740	$CDCl_3$:3.3-1.4(8H,m),1.4 (3H,s),1.12(3H,s).	$CDCl_3$:212.8(s),212.0(s), 61.4(d),57.4(s),49.2(d), 48.9(d),47.3(s),43.4(d), 43.3(d),38.7(t),34.2(d), 15.1(q),14.9(q).	Calcd for $C_{13}H_{14}O_2$: C,77.20; H,6.98. Found: C,77.15; H,6.93.
10e	179-80°C (sublimed) 20 min,92%	1760	$CDCl_3$:2.8-3.7(6H,m),2.48 (1H,d,J=11Hz),2.04(1H,d, J=11Hz).	$CDCl_3$:200.3,199.9,76.2, 64.3,62.5,51.7,49.6, 48.5,44.6,39.3,35.1.	Calcd for $C_{11}H_8Cl_2O_2$: C,54.35; H,3.2. Found: C,54.49; H,2.98.
10f	185-6°C (dichloro-methane-hexane) 15 min,94%	3500,1770	$CDCl_3$:3.04-3.7(6H,m),2.5 (1H,d,J=12Hz),2.6(1H,d,J= 12Hz).	$CDCl_3$[e]:199.6,67.7,67.2, 65.5,62.6,54.9,53.3,52.9, 52.4,51.9,50.2,49.4,45.2, 44.1,42.5,39.2,38.0,36.9.	Calcd for $C_{11}H_8Br_2O_2$: C,39.80; H,2.43. Found: C,40.3; H,2.43.
10g	liquid, 15 min,90%	3450,1760	$CDCl_3$[e]:3.64(6H,m),2.2-4.6 (5-6H,m),1.6-2.0(2H,m).		Calcd for $C_{13}H_{12}Cl_2O_4$: C,51.51; H,3.99. Found: C,51.11; H,4.20.
10h[f]	147-8°C(di-chloromethane-pet ether) 15 min,92%	3490	$CDCl_3$:3.68(6H,s),2.6-4.2 (6H,m),2.44(1H,d,J=11Hz), 1.8(1H,d,J=11Hz).	$CDCl_3$:106.1(s),96.5(s), 87.6(s),84.9(s),71.5(s), 55.2(q),54.8(q),50.7(d), 45.0(d),44.2(d),42.5(t), 42.0(d).	Calcd for $C_{13}H_{14}Cl_2O_5$: C,48.62; H,4.39. Found: C,48.25; H,4.6.
10i[f]	211-14°C (decm)(lit 215 decm)(dichloro-methane-hexane) 20 min,97%	3520,3480	$CDCl_3$:3.88(2H,s),3.12 (2H,m),2.98(2H,m),2.34 (1H,d,J=12Hz),1.82 (1H,d,J=12Hz).	$CDCl_3$[f]:107.5,87.0,74.9, 51.8,46.5,40.8.	Ref. 14
10j	238-40°C (decm) (sublimed) 10 min,95%	1780,1760	$CDCl_3$:3.98(2H,brs), 2.8-3.4(4H,m),2.56 (1H,1/2 AB,J=12Hz),1.78 (1H,1/2 AB,J=12Hz).	$CDCl_3$[f]:106.8,81.5,68.6, 54.1,49.5,41.3.	Calcd for $C_{11}H_6Br_4O_2$: C,26.94; H,1.22. Found: C,27.24; H,1.17.
14a	266-8°C(lit[42] 270°C)(benzene-hexane)3 h,90%	1755,1740	$CDCl_3$:6.6-7.4(10H,m), 3.65(2H,s),2.9(2H,s), 1.04(6H,s).	DMSO-d_6[f]:214.0,137.2,128.0, 127.2,125.8,112.1,60.6, 55.7,53.7,50.3,12.0.	Ref. 42
14b	251-2°C (sublimed) 45 min,90%	1770	Acetone-d_6:7-7.3(10H,m), 2.94(2H,s),1.18(6H,s).	DMSO-d_6[f]:209.2,135.1,129.7, 126.8,126.5,110.5,83.4, 63.7,53.9,53.0,13.5.	Calcd for $C_{25}H_{18}Cl_2O_3$: C,68.66; H,4.15. Found: C,68.4; H,4.19.

[a]Time given for the formation of pentacyclic diones and triones from its precursors during photolysis. [b]Yield obtained in the photolysis. [c]Except 10g spectra were recorded as KBr discs. 10g was recorded as a thin film. [d]All the chemical shifts are reported downfield from internal Me_4Si. [e]Mixture of diketone and hydrate. [f]Symmetrical hydrate.

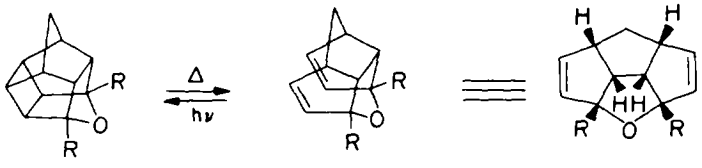
Table 2. Preparation of *cis, syn, cis*-triquinanes (**11a–j, 14a, b**) and 5-oxa-tetraquinanes (**34a–c**) through thermolyses of pentacyclic (**10a–j, 13a, b**) and hexacyclic (**33a–c**) precursors

Compound	Temp/conditions[a]	Product	mp (°C)	Yield(%)
10a	560°C/B or C	11a	107–8	96[b]
10b	450°C/B	11b	93–4	100[b]
	260°C/A, 30 min	11b	93–4	20[c]
10c	450°C/B	11c	186–7	80[b]
	220°C/A, 3 h	11c	186–7	60[c]
10d	500°C/B	11d	113	100[b]
10e	500°C/B	11e	140–1	65[c]
10f	500°C/B	11f	126–7	60[c]
10g	260°C/A, 4 min	11g	119–20	95[b]
10h	260°C/A, 10 min	11h	103	95[b]
10i	240°C/A, 30 min	11i	149–50	95[b]
10j	260°C/A, 10 min	11j	196–8(dec)	70[c]
14a	260°C/A, 3 h	15a	203–5	95[b]
14b	260°C/A, 1 h	15b	196–7	96[b]
33a	625°C(7 torr)/C	34a	119.5–120.5	95[c,d]
33b	625°C(7 torr)/C	34b	e	90[c,f]
33c	625°C(1 torr)/C	34c	144–45	82[c,g]

[a]Method A (static system in DPE), Methods B,C (flash vacuum system) are described in experimental section. [b]Product isolated through direct crystallisation. [c]Product isolated by column chromatography and yields based on recovered starting material. [d]75:25 mixture of 34a and 33a. [e]Low melting solid, solidifies on refrigeration. [f]44:56 mixture of 34b and 33b. [g]40:60 mixture of 34c and 33c.

15 carbon atoms of hirsutene framework and has been already elaborated to sesquiterpene hirsutene and antibiotic substance coriolin.[31] Real surprise entries in the Table 2 have been the formation of **15a, b** from **14a, b** without the expected and usually encountered[32] thermal decarbonylation. The prospect of ready access to triquinane bis-enones with carbonyl functionality at C_7 (e.g. **15a, b**) augurs well for further evolution towards higher quinanes employing the strategy outlined in Scheme 4. Indeed, efforts along these lines are making much headway.

Finally, we report a facile and synthetically important thermal equilibration of the methyl substituted *cis, syn, cis*-bis-enones **11b** and **11d** with the corresponding *cis, anti-cis*-systems. While the parent bis-enone **11a** thermally isomerised to the tetrasubstituted **20**, the two methyl substituted bis-enones **11b** and **11d** on thermal equilibration (benzyl benzoate, 310°, 12 min) furnished equilibrium mixtures of **11b, 36, 37** (1:2:5, GLC) and **11d, 38, 39** (14:49:37, GLC), respectively. The two equilibrium mixtures resolved nicely on tlc and were separated by column chromatography. Each of these bis-enones could be individually re-equilibrated with the other two in approximately similar ratios and thus established the intimate structural relationship between them. Structures to tetrasubstituted enones **36** and **38** were quickly assigned through routine interpretation of spectral data. The structure of *cis, anti, cis*-bis-enone **39**, m.p. 65–6° (plates, ether–pet ether) followed from its ^{13}C NMR resonances at δ211.7(s), 207(s), 165.5(d), 159.5(d), 140.2(s), 129.6(d), 57.1(d), 56.5(s), 53.5(d), 46.5(d), 34.9(t), 19.0(q), 9.7(q) and from the striking similarity of its ^1H NMR, IR and UV spectral data with the all-*cis* **11d**. Similarly, the presence of only seven carbon resonances in the ^{13}C NMR spectrum of *cis, anti, cis*-bis-enone **37**, m.p. 69–70° (white flakes, dichloromethane–pet ether) revealed the presence of requisite symmetry elements and demonstrated its close structural relationship with



33a R = H
b R = CH_3
c R = C_6H_5

34a R = H
b R = CH_3
c R = C_6H_5

Table 3. Spectroscopic data for the triquinanes (11a–j, 15a, b) and 5-oxa-tetraquinanes (34a–c)

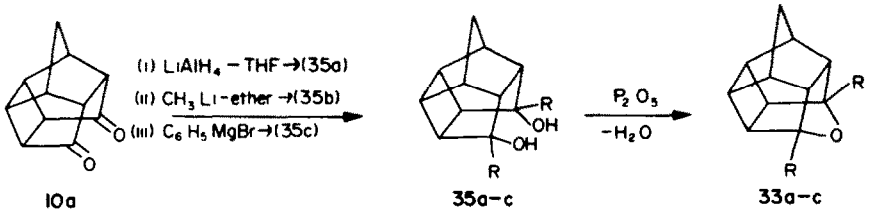
Compound	UV: $\lambda_{max}^{MeOH}(\epsilon)$	IR(KBr) cm^{-1}	^1H NMR (100 MHz) data,[a] δ	Analytical data
11a	219(9,800)	1720,1590	7.54(2H,dd,J_1=5.7Hz,J_2=2.5Hz),5.92(2H,dd,J_1=5.7Hz,J_2=2Hz),3.56(2H,m),3.2(2H,m),2.3(1H,td,J_1=14Hz,J_2=9Hz),1.90(1H,td,J_1=14Hz,J_2=1.5Hz).	Calcd for $C_{11}H_{10}O_2$:C,75.84; H,5.79. Found: C,75.54; H,5.90.
11b	231(3,000)	1710,1640	7.08(2H,brs),3.1-3.5(4H,m),2.26(1H,td,J_1=14Hz,J_2=8Hz),1.9(1H,1/2 AB,J=14Hz),1.6(6H,s with st).	Calcd for $C_{13}H_{14}O_2$:C,77.20; H,6.93. Found: C,77.53; H,6.99.
11c	235.5 (5,700)	1730,1595	7.35(2H,d,J=2.5Hz),3.16-3.7(4H,m),2.34(1H,td,J_1=14Hz,J_2=8Hz),1.9(1H,td,J_1=14Hz,J_2=2Hz).	Calcd for $C_{11}H_8Cl_2O_2$:C,54.35; H,3.32. Found: C,54.65; H,3.58.
11d	245(4,800), 218(12,300).	1720,1709, 1640,1580.	7.38(1H,brd,J=6Hz),7.1(1H,brs),5.84(1H,brd,J=6Hz),3.48(1H,brs),3.03(1H,d,J=8Hz),2.68(1H,d,J=6Hz),2.36(1H,td,J_1=14Hz,J_2=10Hz),1.93(1H,1/2 AB,J=14Hz),1.6(3H,s with st),1.4(3H,s).	Calcd for $C_{13}H_{14}O_2$:C,77.20; H,6.98. Found: C,76.99; H,7.02.
11e	230(7,800)	1720,1600, 1575.	7.40(1H,d,J=2.5Hz),7.18(1H,dd,J_1=6Hz,J_2=3Hz),5.86(1H,dd,J_1=6Hz,J_2=2Hz),3.2-4.0(3H,m),2.66(1H,td,J_1=14Hz,J_2=9Hz),2.09(1H,1/2 AB,with st J=14Hz).	Calcd for $C_{11}H_8Cl_2O_2$: C,54.35; H,3.32. Found: C,54.45; H,3.71.
11f	232(6.300)	1725,1585	7.64(1H,d,J=3Hz),7.54(1H,dd,J_1=6Hz,J_2=3Hz),6.04(1H,dd,J_1=6Hz,J_2=2Hz),3.4-4.0(3H,m),2.7(1H,m),2.02(1H,m).	Calcd for $C_{11}H_8Br_2O_2$: C,39.8; H,2.43. Found: C,39.5; H,2.43.
11g	242(3,400), 248(3,520), 254(3,630), 259(3,400).	1740,1730, 1620,1610.	7.24(1H,d,J=3Hz),6.3(1H,d,J=3Hz),3.74(3H,s),3.44(3H,s),3.2-3.9(2H,m),2.4-3.1(1H,m),1.86(1H,d,J=14Hz).	Calcd for $C_{13}H_{12}Cl_2O_4$: C,51.51; H,3.99. Found: C,51.72; H,3.95.
11h	238(3,070), 242(3,170), 249(3,070), 254(2,660), 260(2,050).	1740,1720, 1620.	7.38(1H,d,J=3Hz),5.78(1H,d,J=2Hz),3.62(3H,s),3.42(3H,s),3.3-3.8(2H,m),2.4-3.1(1H,m),1.86(1H,d with st,J=14Hz).	Calcd for $C_{13}H_{12}Cl_2O_4$: C,51.51; H,3.99. Found: C,51.24; H,3.88.
11i	244[b]	1750,1603, 1585	7.3(2H,d,J=2.5Hz),3.7(2H,dd,J=10Hz,J_2=2.5Hz),2.85(1H,td,J_1=14Hz,J_2=10Hz),2.05(1H,1/2 AB, J=14Hz).	Calcd for $C_{11}H_6Cl_4O_2$: C,42.3; H,1.92. Found: C,42.45; H,1.3.
11j	250[b]	1740,1730, 1595,1585.	7.45(2H,d,J=3Hz),3.84(2H,d with st,J=10Hz),2.84(1H,td,J_1=14Hz,J_2=10Hz),1.94(1H,td,J_1=14Hz,J_2=1.5Hz).	Calcd for $C_{11}H_6Br_4O_2$: C,26.94; H,1.22. Found: C,26.75; H,1.3.
15a	286[b]	1740,1710	7.0-7.5(10H,m),6.22(2H,s),3.2(2H,s),1.6(6H,s).	Calcd for $C_{25}H_{20}O_3$: C,81.50; H,5.47. Found: C,81.26; H,5.2.
15b	292(13,580)	1740,1734	6.9-7.5(10H,m),3.24(2H,s),1.5(6H,s).	Calcd for $C_{25}H_{18}Cl_2O_3$: C,68.66; H.4.15. Found: C,68.50; H,4.19.
34a		3100,1618, 740	5.5(4H,AB with st,J=6Hz),5.2(2H,d,J=6Hz),3.5(2H,m),3.1(2H,m),2.02(1H,dd,J_1=12Hz,J_2=8Hz),1.74(1H,d with st,J=12Hz).	Calcd for $C_{11}H_{12}O$:C,82.46; H,7.55. Found: C,80.16; H,7.45.
34b		3050,1620, 750[c]	5,43(2H,1/2 AB with st,J=5Hz),5.2(2H,1/2 AB with st,J=5Hz),2.9-3.3(4H,m),1.6-1.9(2H,m),1.37(6H,s).	Calcd for $C_{13}H_{16}O$:C,82.9; H,8.5. Found: C,82.78; H,8.73.
34c		3050,3020, 742,695.	7.0-7.6(10H,m),5.7(2H,d,J=5Hz),5.42(2H,d,J=5Hz),2.0-2.48(4H,m),1.86(2H,brs).	Calcd for $C_{23}H_{20}O$:C,88.43; H,6.45. Found: C,88.22; H,6.39.

[a] ^1H NMR spectra were recorded in $CDCl_3$(~5% solution) using Me_4Si as internal standard. [b] Extinction coefficients in these cases could not be calculated as the absorption dropped too fast on exposure to the UV lamp, perhaps due to facile intramolecular cage cyclisations. This could be readily confirmed by time scans. [c] Spectrum was recorded as a thin film.

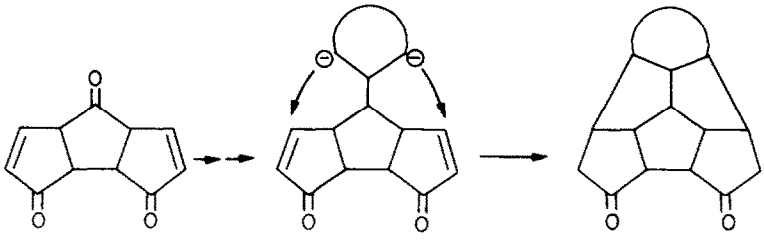
Table 4. ^{13}C NMR[a] (25.0 MHz) data for triquinanes (**11a–j, 15a, b**) and 5-oxa-tetraquinanes (**34a–c**)

Compound	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	Others
11a	53.1 (d)	53.1 (d)	207.4 (s)	133.5 (d)	165.9 (d)	50.4 (d)	31.5 (t)	50.4 (d)	165.9 (d)	133.5 (d)	207.4 (s)	-	
11b	53.4 (d)	53.4 (d)	207.3 (s)	140.4 (s)	159.6 (d)	47.7 (d)	31.2 (t)	47.7 (d)	159.6 (d)	140.4 (s)	207.3 (s)	-	9.6(q)
11c	51.9 (d)	51.9 (d)	198.4 (s)	132.2 (s)	160.9 (d)	47.5 (d)	30.6 (t)	47.5 (d)	160.9 (d)	132.2 (s)	198.4 (s)	-	
11d	59.5 (s)	60.7 (d)	208.9[b] (s)	141.2 (s)	159.7 (d)	47.2 (d)	30.9 (t)	57.5 (d)	164.1 (d)	131.5 (d)	207.6[b] (s)	-	21.6(q),10.4(q).
11e	77.6 (s)	61.6 (d)	197.3 (s)	135.2 (s)	160.7[b] (d)	45.9 (d)	30.9 (t)	60.1 (d)	158.3[b] (d)	131.0 (d)	196.0 (s)	-	
11f	68.4 (s)	61.8 (d)	197.5 (s)	125.1 (s)	158.3[b] (d)	48.0 (d)	30.9 (t)	61.2 (d)	160.7[b] (d)	130.8 (d)	196.4 (s)	-	
11g	90.5 (s)	77.9 (s)	192.1[b] (s)	133.7 (s)	152.9 (d)	56.7 (d)	31.0 (t)	48.1 (d)	127.6 (d)	154.7 (s)	194.2[b] (s)	-	54.6(q),57.0(q).
11h	78.7 (s)	90.6 (s)	193.6[b] (s)	133.0 (s)	157.9 (d)	52.0[b] (d)	30.0 (t)	53.5[b] (d)	123.0 (d)	154.8 (s)	192.4[b] (s)	-	57.2(q),54.6(q).
11i	76.7 (s)	76.7 (s)	190.2 (s)	133.7 (s)	154.2 (d)	56.7 (d)	30.4 (t)	56.7 (d)	154.2 (d)	133.7 (s)	190.2 (s)	-	
11j	69.8	69.8	c	128.3	157.4	59.2	31.0	59.2	157.4	128.3	c	-	
15a	55.7	55.7	203.9	131.7	173.9	62.6	212.6	62.6	173.9	131.7	203.9	-	130.7,128.6,128.3, 128.0,23.2.
15b	53.6 (d)	53.6 (d)	196.6 (s)	132.1 (s)	165.7 (s)	61.8 (s)	208.7 (s)	61.8 (s)	165.7 (s)	132.1 (s)	196.6 (s)	-	130.7(s),130.3(d), 128.6(d),128.1(d), 22.9(q).
34a	51.5 (d)	135.7 (d)	132.7 (d)	90.4 (d)	-	90.4 (d)	132.7 (d)	135.7 (d)	51.5 (d)	53.6 (d)	53.6 (d)	34.6 (t)	
34b	51.0 (d)	135.6 (d)	136.2 (d)	96.4 (s)	-	96.4 (s)	136.2 (d)	135.6 (d)	51.0 (d)	60.3 (d)	60.3 (d)	34.3 (t)	27.1(q)
34c	51.8 (d)	135.8 (d)	137.4 (d)	100.8 (s)	-	100.8 (s)	137.4 (d)	135.8 (d)	51.8 (d)	62.9 (d)	62.9 (d)	33.9 (t)	146.1(s),128.0(d), 126.5(d),124.9(d).

[a]Except **11c** all the spectra were recorded in $CDCl_3$. **11c** was recorded in DMSO-d_6. Chemical shifts are given in δ scale downfield from Me_4Si. Offresonance multiplicities, when recorded, given in parenthesis. [b]Assignments may be interchanged. [c]Carbonyl carbon not seen.



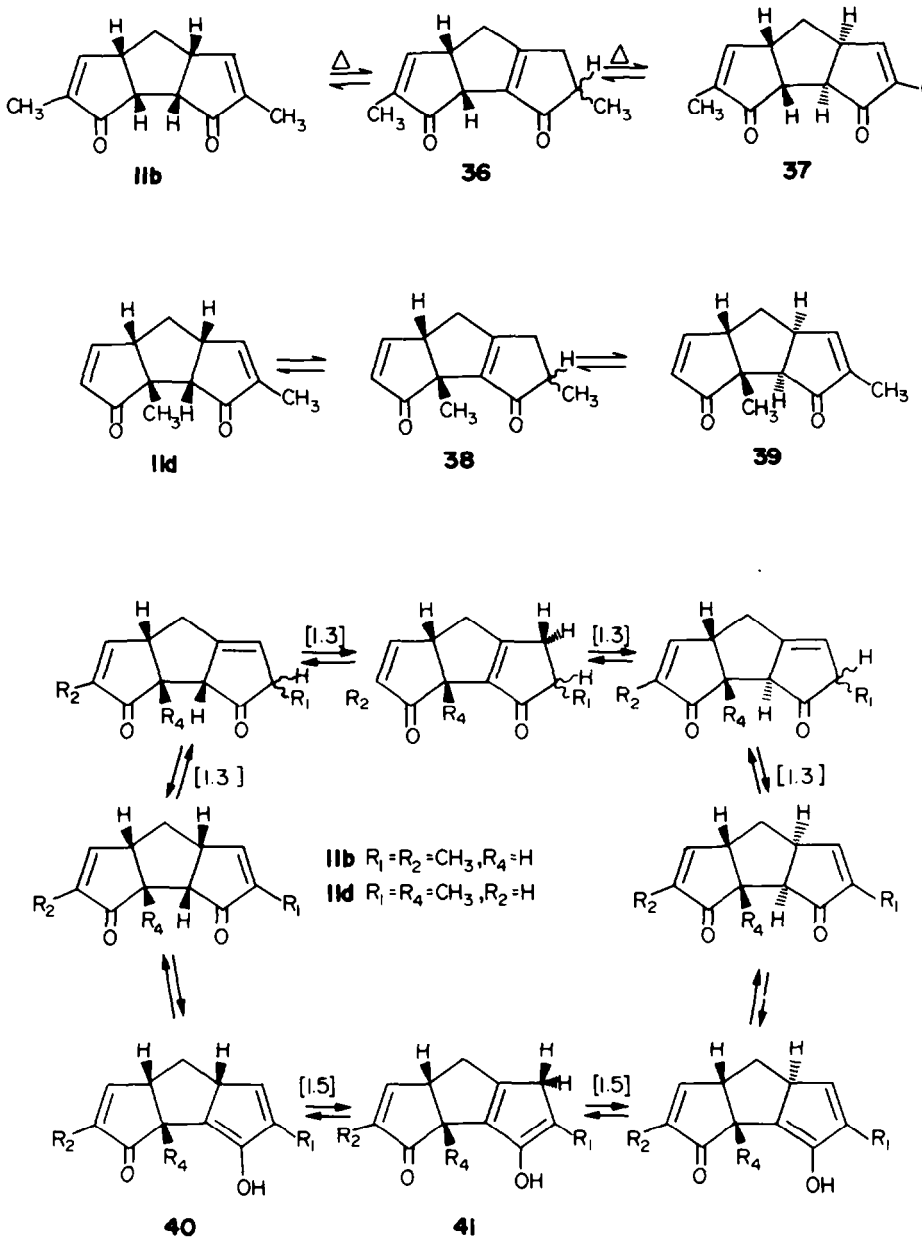
Scheme 3.



Scheme 4.

all-*cis* **11b**. As would be expected, both the *cis, anti, cis*-isomers **37** and **39** did not photocyclise intramolecularly to the precursor pentacyclic systems.

The thermal equilibration of these bis-enones can be considered either proceeding through thermal [1,5]-sigmatropic shifts in 1,3-cyclopentadiene intermediates **40** and **41** or through a series of symmetry disallowed [1,3] shifts. The concerted [1,5] shifts *a priori* should be favoured and occur even at lower temperature if sufficient concentration of the enol form **40** can be generated. However, we found that the catalytic presence of non-nucleophilic bases, e.g. K^+-t-BuO^-, NEt_3, DBU, etc., had no perceptible effect on the thermal equilibration. We, therefore, favour a series of [1,3] shifts to account for the observed equilibration (Scheme 5). In any case, the accessibility to *cis, anti, cis*-isomers



Scheme 5.

via thermal equilibration greatly enhanced the synthetic utility of our triquinane synthesis.

In conclusion, we have firmly established (15 examples) a three step photo-thermal metathetic sequence to gain access to a variety of linearly fused tricyclopentanoids, efficiently and expeditiously, employing cheap, abundantly available starting materials. We have also provided a sampling of chemical transformations that can be carried out with triquinane based bis-enones, en route to more enchanting synthetic targets.

EXPERIMENTAL

Melting points were recorded on a Buchi SMP-20 apparatus and are uncorrected. Boiling points refer to bath temperatures. UV, IR, ^{1}H NMR (100 MHz) and ^{13}C NMR (25.0 MHz) spectra were recorded on Shimadzu 200S spectrophotometer, Perkin-Elmer 297 spectrophotometer, Jeol MH-100 spectrometer and Jeol FX-100 spectrometer, respectively. ^{1}H NMR and ^{13}C NMR chemical shifts are given in δ scale using Me_4Si as internal standard. In the ^{13}C NMR spectra, *off* resonance multiplicities, when recorded, are given in parentheses. The standard abbreviations s, d, t, q and m refer to singlet, doublet, triplet, quartet and multiplet, respectively. Elemental analyses were carried out on a Hewlett-Packard 185-B CHN analyser. Glc analyses were performed on a Hewlett-Packard 5830 A analytical instrument using Apiezon-L (6' × 1/8" stainless steel) column at oven temperature in the range of 200-250°. High resolution mass measurements were carried out on an AEI MS-5076 mass-spectrometer. Hydrogenations were carried out on a Parr hydrogenation apparatus in 250 mL pressure bottles. Analytical thin layer chromatographies (tlc) were performed on (10 × 5 cm) glass plates coated (250 mμ) with Acme's silica gel G (containing 13% calcium sulfate as binder). Visualisation of the spots was achieved by exposure to iodine vapor. Acme's silica gel (100-200

mesh) was used in the column chromatography. Moisture sensitive reactions were carried out using standard syringe-septum techniques. Dry diethyl ether and tetrahydrofuran(THF) were prepared by distillation over sodium and stored over pressed sodium wire. Dichloromethane was distilled over P_2O_5. Diphenyl ether (DPE) was purified and dried through filtration from a neutral alumina column. The pet ether refers to fraction boiling between 60 and 80°. All solvent extracts were washed with brine, dried over Na_2SO_4 and concentrated on a Buchi–EL rotary evaporator. Yields of products reported here were computed on the basis of recovered starting materials.

Starting materials

All starting materials were either acquired commercially or prepared according to standard literature procedures as given below. Dicyclopentadiene (BDH or Reidel), p-benzoquinone (Loba Chemie), hemicyclone (Lancaster Syntheses) and chloranil (Fluka) were used without any purification. 2,3-Dimethyl benzoquinone,[33] 2,5-dimethyl benzoquinone,[33] dichlorodimethoxy benzoquinones,[34] 2,3 and 2,5-dichlorobenzoquinones,[35] 2,5-dibromobenzoquinone,[36] and bromanil[37] were made either according to the cited literature procedure or through minor tactical modifications of known procedures.

General procedure for the preparation of Diels–Alder adducts of 1,4-benzoquinones with 1,3-cyclopentadienes

To an approximately 20% (w/v) solution of quinone (usually 0.02–0.03 molar scale) in benzene was added either 1.2 mole equivalent of freshly cracked cyclopentadiene or commercially available hemicyclone **12**. The solution was either stirred at room temperature or refluxed (for 20–60 min) and the reaction course monitored by tlc. After the completion of the reaction the solution was concentrated and directly crystallised either from the same solvent or after dilution with pet ether. The yields were generally in the 85–95% range.

Tricyclo[6.2.1.0^{2,7}]*undeca*-4, 9-*dien*-3, 6-*dione* (**9a**)

Prepared from cyclopentadiene and benzoquinone according to the procedure of Marchand *et al.*,[38] m.p. 76° (lit 75–76°).

4,5-*Dimethyltricyclo*[6.2.1.0^{2,7}]*undeca*-4,9-*diene*-3,6-*dione* (**9b**)

Prepared from cyclopentadiene and 2,3-dimethyl benzoquinone according to the procedure of Alder *et al.*,[39] m.p. 42–44° (lit[39] 46°).

4,5-*Dichlorotricyclo*[6.2.1.0^{2,7}]*undecea*-4,9-*diene*-3,6-*dione* (**9c**)

Prepared from cyclopentadiene and 2,3-dichlorobenzoquinone according to the procedure of Rakoff *et al.*,[40] m.p. 106–108.5° (lit[40] 109–110°).

2,5-*Dimethyltricyclo*[6.2.1.0^{2,7}]*undeca*-4,9-*diene*-3,6-*dione* (**9d**)

Prepared from cyclopentadiene and 2,5-dimethyl benzoquinone according to the procedure of Alder *et al.*,[39] m.p. 64–5° (lit[39] 64°).

2,5-*Dichlorotricyclo*[6.2.1.0^{2,7}]*undecea*-4,9-*diene*-3,6-*dione* (**9e**)

Prepared from cyclopentadiene and 2,5-dichlorobenzoquinone according to the procedure of Rakoff *et al.*,[40] m.p. 112–14° (lit[40] 113–14°).

2,5-*Dibromotricyclo*[6.2.1.0^{2,7}]*undeca*-4,9-*diene*-3,6-*dione* (**9f**)

Prepared from cyclopentadiene (1g, 15 mmoles) and 2,5-dibromobenzoquinone (1.6 g, 6 mmoles) by refluxing in benzene (25 mL) for 10 min. Crystallisation from benzene yielded 1.8 g (90%) of **9f**, yellow needles, m.p. 130–1°. IR(KBr): 1780, 1680, 1580 cm^{-1}; ^{1}H NMR($CDCl_3$): δ7.3(1H, s), 6.2(2H, m), 3.5–4.0(3H, m), 2.04(1H, d with St, J = 11Hz), 1.9(1H, d with St, J = 11 Hz). (Found: C, 39.57; H, 2.32. Calc. for $C_{11}H_8Br_2O_2$: C, 39.8; H, 2.43%.)

2,4-*Dichloro*-5,7-*dimethoxytricyclo*[6.2.1.0^{2,7}]undeca-4,9-diene-3,6-dione (**9g**)

Prepared from cyclopentadiene (200 mg, 3 mmoles) and 2,6-dichloro-3,5-dimethoxy benzoquinone (**8g**, 710 mg, 3 mmoles) by refluxing in benzene (20 mL) for 15 min. Chromatography on silica gel and crystallisation from pet ether yielded, **9g**, 280 mg (97%), m.p. 94–5°. IR(KBr): 1690, 1585 cm^{-1}; ^{1}H NMR($CDCl_3$): δ5.8–6.2(2H, m), 4.06(3H, s), 3.4(3H, s), 3.2–3.6(2H, m), 2.22(1H, d, J = 10Hz), 1.92(1H, d, J = 10Hz). (Found: C, 51.55; H, 3.89. Calc. for $C_{13}H_{12}Cl_2O_4$: C, 51.51; H, 3.96%.)

2,5-*Dichloro*-4,7-*dimethoxytricyclo*[6.2.1.0^{2,7}]*undeca*-4,9-*diene*-3,6-*dione* (**9h**)

Prepared from cyclopentadiene (200 mg, 3 mmoles) and 2,5-dichloro-3,6-dimethoxybenzoquinone (**8h**, 710 mg, 3 mmoles) by refluxing in benzene (20 mL) for 30 min. Chromatography (silica gel) and crystallisation yielded 480 mg (95%), **9h**, 79–80°. IR(KBr): 1690(br), 1580 cm^{-1}; ^{1}H NMR($CDCl_3$): δ5.8–6.3(2 H, m), 4.1(3H, s), 3.38(3H, s), 3.1–3.9(2H, m), 2.28(1H, d, J = 11Hz), 1.9(1H, d, J = 11Hz). (Found: C, 51.29; H, 3.93. Calc. for $C_{13}H_{12}Cl_2O_4$: C, 51.51; H, 3.99%.)

2,4,5,7 - *Tetrachlorotricyclo*[6.2.1.0^{2,7}]*undecea* - 4,9 - *diene*-3,6 *dione* (**9i**)

Prepared from cyclopentadiene and chloranil by refluxing in benzene for 30 min and crystallisation yielded 96% of the theoretical amount, m.p. 145–46° (lit[41] 146°).

2,4,5,7 - *Tetrabromotricyclo*[6.2.1.0^{2,7}]*undeca* - 4,9 - *diene* - 3,6 - *dione* (**9j**)

Prepared from cyclopentadiene (700 mg, 10.6 mmoles) and bromanil (**8j**, 4g, 9.45 mmoles) by refluxing in benzene (40 mL) for 40 min. Crystallisation yielded **9j** (4.2 g; 90%), m.p. 164–5°. IR(KBr): 1700, 1545 cm^{-1}; ^{1}H NMR($CDCl_3$): δ6.2(2H, brs), 3.76(2H, m), 2.66 (1H, d, J = 10Hz), 2.18 (1H, d, J = 10Hz). (Found: C, 27.0; H, 1.16. Calc. for $C_{11}H_6Br_4O_2$: C, 26.94; H, 1.22%.)

1,8-*Dimethyl*-9, 10-*diphenyl*-*tricyclo*[6.2.1.0^{2,7}]*undeca*-4, 9-*diene*-3, 6, 11-*trione* (**13a**)

Prepared from hemicyclone (**12**) and benzoquinone according to the procedure of Warrener *et al.*,[42] m.p. 211–13° (lit[42] m.p. 213°).

4,5 - *Dichloro* - 1,8 - *dimethyl* - 9,10 - *diphenyl* - *tricyclo* - [6.2.1.0^{2,7}]*undeca* - 4,9 - *diene* - 3,6,11-*trione* (**13b**)

Prepared from hemicyclone (**12**, 260 mg, 1 mmole) and 2,3-dichlorobenzoquinone (177 mg, 1 mmole) by refluxing in benzene (10 mL) for 15 min. Recrystallisation from benzene yielded **13b**, 400 mg (90%), m.p. 202–3° (decom). IR(KBr): 1780, 1690 cm^{-1}, ^{1}H NMR ($CDCl_3$): δ7.2(6H, m), 6.8(4H, m), 3.48(2H, s), 1.54(6H, s). (Found: C, 68.30; H, 4.05. Calc. for $C_{25}H_{18}Cl_2O_3$: C, 68.66; H, 4.15%.)

General procedure for the preparation of pentacyclo-[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]*undeca*-8,11-*diones and* 4,8,11-*triones* (**10a–j, 14a, b**)

An ethyl acetate or benzene solution (1–1.5%, w/v) of the Diels–Alder adducts (**9a–j, 13a, b**) was carefully purged with a slow stream of dry nitrogen for 15–20 min. The solution was then irradiated with a 450 W Hanovia medium pressure mercury vapor lamp in a quartz immersion vessel using a pyrex glass filter. The reaction was monitored by tlc (generally it took 20–60 min), solvent removed under reduced pressure and the crude pentacyclic product was either directly crystallised and/or sublimed (120–160°/1 torr). Generally, high yields (greater than 90%) were obtained and the photolysed compounds were fully characterised (Table 1). In some cases where the compounds were contaminated with hydrates, complete removal of the latter required repeated sublimation.

General methods for thermolysis of pentacyclo-[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]*undeca*-8,11-*diones and* 4,8,11-*triones* (**10a–j, 14a, b**)

Method A. A solution (8–10%, w/v) of pentacyclic compounds (3–4 mmoles) in DPE was magnetically stirred and heated to 240–260° and the reaction was monitored by tlc (see Table 2). The reaction mixture was filtered through a silica gel (20 g

absorbent/g of compound) column and eluted with pet ether to remove DPE. The tricyclic compound was then collected using an appropriate solvent and crystallised. The yields and spectral properties are given in Tables 2–4.

Method B. The flash thermolysis of pentacyclic diones were carried out in a pyrex vigreux column connected to a vacuum line and provided with a collection flask and a liquid nitrogen trap. The pyrex column was heated with a nichrome coil wound around it and was insulated with asbestos padding. The column temperature was controlled by a variac and was measured by a thermocouple (Chromel-Alumel) on a Keithley digital multimeter. The column was heated and equilibrated to the requisite temperature (± 15°). The crystalline diones were slowly sublimed (100–150°/1 torr) through the pyrex column. The condensate, in most cases deposited in the delivery tube and was either directly crystallised or chromatographed (silica gel) and crystallised. The yields and spectral properties are given in Tables 2–4.

General methods of making oxa-tetraquinanes

Method C. 4-*Oxahexacyclo*[5.4.1.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.$0^{8,11}$] dodecanes (**33a–c**; usually 1g) were slowly sublimed (80–160°/1–7 torr) through a quartz tube (30 cm × 1.5 cm) packed with quartz pieces and heated (as described in Method B) to 625° (± 20°). The condensate in the receiver was carefully purified by column chromatography ($AgNO_3$ impregnated silica gel or alumina). The yields and spectral properties are given in Tables 2–4.

General procedure for photolysis of triquinanes (**11a–j, 15a, b**)

An ethyl acetate or acetone solution (10 mL) of the triquines (generally 0.1 mmole) was degassed with a slow stream of dry nitrogen in a pyrex vessel. The solution was then irradiated with sunlight, monitoring the reaction by tlc (few min to 12 hr). After

Small quantities (50 mg) of starting bis-enone **11a** was also obtained from the column.

Isomerisation of tricyclo[6.3.0.$0^{2,6}$]*undeca*-4,9-*dien*-3,11-*dione* (**11a**) *with rhodium chloride trihydrate*

A solution of bis-enone (**11a**, 530 mg, 3.05 mmoles) and $RhCl_3.3H_2O$ (37 mg, 0.15 mmole) in 10 mL of absolute ethanol was heated in a sealed corning glass tube (capacity 20 mL) to 105° (± 3°) for 20 h. The sealed tube was cooled, carefully opened and filtered through a short celite column. The glc analysis of the crude mixture showed 70% conversion to a mixture (12:2:1) of three products. The total mixture was charged on a silica gel (20 g) column and chromatographed. Elution with 10% ethyl acetate–benzene and pooling of appropriate fractions (monitored by tlc) furnished the two minor products. The first product (35 mg, 10%) was identified as tricyclo[6.3.0.$0^{2,6}$]undec-4-en-3,11-dione **16**, by comparison (IR, tlc) with the sample prepared in the previous experiment. The second minor product 20 mg (6%) was bulb to bulb distilled (160°/0.6 torr) and identified as 9-ethoxytricyclo[6.3.0.$0^{2,6}$]undec-4-en-3,11-dione **22**. IR(neat): 1745, 1705, 1585 cm^{-1}; ^1H NMR($CDCl_3$): δ7.57(1H, dd, J_1 = 6Hz, J_2 = 3Hz), 6.03(1H, dd, J_1 = 6Hz, J_2 = 2Hz), 3.78(1H, td, J_1 = 6Hz, J_2 = 5Hz), 3.43(2H, q, J = 7Hz), 1.3–3.6 (8H, m), 1.18(3H, t, J = 7Hz); ^{13}C NMR($CDCl_3$): δ213.9(s), 208.0(s), 165.8(d), 132.8(d), 78.1(d), 64.8(t), 54.2(d), 52.8(d), 52.2(d), 48.2(d), 43.9(t), 32.3(t), 15.4(q). (Found: C, 70.63; H, 7.34. Calc. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32%.)

Elution of the column with 40% ethyl acetate–benzene resulted in the isolation of starting bis-enone **11a** (150 mg). Further elution with ethyl acetate resulted in the isolation of 240 mg (70%) of tricyclo[6.3.0.$0^{2,6}$]undeca-1(8),4-dien-3,11-dione **20**, which was crystallised from carbon tetrachloride. m.p. 100–1°. UV: λ_{max}^{MeOH} 218(13,100), 242 nm(sh, 5650); IR(KBr): 1708, 1695, 1625

δ4.84(2H, brs), 4.24(2H, dd, J_1 = 16Hz, J_2 = 8Hz), 1.1–2.9(13H, m), 0.96(1H, dd, J_1 = 20 Hz, J_2 = 11Hz); ^{13}C NMR($CDCl_3$): δ76.8(d), 73.9(d), 56.4(d), 49.0(d), 45.9(d), 43.8(t), 43.4(d), 35.5(t), 35.0(t), 28.3(t), 26.8(t). (Found: 182.1306. *m/e*: Calc. for $C_{11}H_{18}O_2$: 182.1307.)

Further elution of the column with 10% ethyl acetate–benzene furnished 150mg (36%) of the lactol **18** which was crystallised from dichloromethane–hexane, m.p. 96°; IR(KBr): 3400 cm^{-1}. ^{1}H NMR($CDCl_3$): δ4.72(1H, brs), 3.96(1H, brs), 2.3–3.3(4H, m), 1.3–2.3(10H, m); ^{13}C NMR($CDCl_3$): δ118.4(s), 87.9(d), 60.9(d), 56.5(d), 47.3(d), 46.2(d), 39.7(t), 38.1(t), 34.6(t), 32.7(t), 32.3(t).

Tricyclo[6.3.0.0^{2,6}]*undeca*-1(8)-*en*-3, 11-*dione* **21**

A solution of tricyclo[6.3.0.0^{2,6}]undeca-1(8), 4-dien-3, 11-dione (**20**, 350 mg, 2 mmoles) was hydrogenated over 10% Pd–C(15 mg) catalyst at 1 atmosphere pressure for 20 min. Catalyst was removed by filtration and the filtrate concentrated. Crystallisation from carbon tetrachloride furnished the partially hydrogenated compound **21** in quantitative yield, m.p. 74–76°, UV: λ_{max}^{MeOH} 242 nm (7010); IR(KBr): 1735, 1695, 1625 cm^{-1}; ^{1}H NMR($CDCl_3$): δ3.4(2H, brs), 1.6–3.5(10 H, m); ^{13}C NMR($CDCl_3$); δ214.5(s), 201.8(s), 187.8(s), 144.0(s), 52.2(d), 44.6(d), 40.9(t), 38.7(t), 37.5(t), 28.4(t), 25.7(t). (Found: C, 74.69; H, 6.85. Calc. for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86%.)

Tricyclo[6.3.0.0^{2,6}]*undeca*-1(8)-*en*-3, 11-*dione*-3-*ethylene ketal* (**23**)

A solution of partially hydrogenated compound (**21**, 350 mg, 2 mmoles), ethanediol (0.5 mL) and toluene p-sulphonic acid (5mg) in 30 mL of benzene was refluxed with a Dean–Stark water separator for 15 min. The reaction mixture was diluted with more benzene (30 mL) and washed with aq. sodium bicarbonate. Evaporation of the solvent furnished 375 mg (85%) of the monoketal **23**, which was crystallised from pet ether, m.p. 68–9°, IR(KBr): 1690, 1640 cm^{-1}; ^{1}H NMR($CDCl_3$): δ3.6–4.2(4H, m), 2.8–3.6(3H, m), 2.2–2.8 (5H, m), 1.0–2.2(4H, m);^{13}C NMR($CDCl_3$): δ203.3(s), 186.4(s), 146.9(s), 116.9(s), 65.1(t), 64.5(t), 51.4(d), 46.1(d), 41.0(t), 39.1(t), 35.6(t), 30.6(t), 25.5(t). (Found: C, 70.67; H, 7.37. Calc. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32%.)

11-*Methyl tricyclo*[6.3.0.0^{2,6}]*undeca*-4, 10-*dien*-3, 9-*dione* (**27**)

To a magnetically stirred solution of bis-enone (**11a**, 2.0 g, 11.5 mmoles) in 25 mL of dry THF was added slowly an ethereal solution of methylmagnesium iodide [made from 365 mg (15 mmoles) of magnesium and 2 mL of methyl iodide in 30 mL of dry ether]. The reaction mixture was stirred vigorously for 20 min at room temperature and quenched by adding saturated NH_4Cl solution (30 mL). The organic layer was separated and the aqueous layer extracted with dichloromethane (2 × 50 mL). The combined organic extracts on concentration gave 3g of crude product containing ~30% lactol (**26**). An analytical sample of the lactol **26** was prepared by filtering crude lactol through a silica gel column using 5% ethyl acetate-benzene as eluent and crystallised from dichloromethane-hexane, m.p. 96–100°, IR(KBr): 3400, 1620 cm^{-1}; ^{1}H NMR($CDCl_3$): δ5.68(1H, d, J = 6Hz), 5.5(1H, d, J = 6Hz), 5.34(1H, d, J = 6Hz), 5.14(1H, d, J = 6Hz), 3.88(1H, brs), 2.7–3.3(4H, m), 1.76(2H, brs), 1.46(3H, s); ^{13}C NMR($CDCl_3$): δ139.1(d), 136.3(d), 134.7(d), 133.0(d), 119.9(s), 97.0(s), 60.2(d), 57.9(d), 51.4(d), 51.3(d), 34.3(t), 26.8(q).

The crude lactol (3g) was taken in 5 mL of dichloromethane and added to a stirring suspension of pyridinium chlorochromate (3g, 14 mmoles) in 10 mL of dichloromethane. The heterogeneous mixture was stirred vigorously for 4 hr at room temperature. The reaction mixture was filtered through a silica gel (20 g) column. Evaporation of the solvent furnished 650mg (30%) of the single transposed bis-enone **27**, which was recrystallised from dichloromethane, m.p. 105–6°, UV: λ_{max}^{MeOH} 223 nm (14,900); IR(KBr): 1700, 1618, 1585 cm^{-1}; ^{1}H NMR($CDCl_3$): δ7.46 (1H, dd, J_1 = 6Hz, J_2 = 3Hz), 5.84(1H, dd, J_1 = 6Hz, J_2 = 2Hz), 5.7(1H, brs), 3.2–3.65(2H, m), 2.7–3.2(2H, m), 1.8–2.4(2H, m), 2.24(3H, s); ^{13}C NMR($CDCl_3$): δ210.4(s), 209.1(s), 178.4(s), 168.1(d), 133.6(d), 129.6(d), 57.1(d), 52.5(d), 51.9(d), 51.3(d), 27.7(t), 20.5(q). (Found: C, 76.54; H, 6.6. Calc. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43%.)

Reaction of Tricyclo[6.3.0.0^{2,6}]*undeca*-4, 9-*dien*-3, 11-*dione* (**11a**) *with excess methylmagnesium iodide*

To a magnetically stirred solution of methylmagnesium iodide [made from 850 mg (35 mmoles) of magnesium and 4 mL of methyl iodide in 50 mL of dry ether] was slowly added a solution of bis-enone (**11a**, 1g, 5.75 mmoles) in 10 mL of dry THF. The reaction mixture was stirred for 30 min and carefully quenched with ammonium chloride solution. The whole mixture was extracted with ether (3 × 30 mL). Evaporation of the solvent furnished 1.2 g of viscous material (IR indicated the presence of a lactol). The crude lactol was taken in 5 mL of dichloromethane and added to a stirring suspension of pyridinium chlorochromate (1.5g, 7 mmoles) in 10 mL of dichloromethane. The heterogeneous reaction mixture was vigorously stirred for 4 hr at room temperature and filtered through silica gel (10g) column. Evaporation of the solvent furnished 1g of crude material which was charged on silica gel (25g) column and rechromatographed. Elution with 10% ethyl acetate–benzene and pooling of the appropriate fractions (monitored by tlc) furnished 1 minor and 1 major products. The minor product 80 mg (7%) was bulb to bulb distilled (140°/0.16 torr) and identified as 5, 9-dimethyltricyclo[6.3.0.0^{2,6}]undeca-3, 11-dione (**30**) (glc indicated only 85% purity). IR(Neat): 1745 cm^{-1}; ^{1}H NMR($CDCl_3$): δ1.0–3.2(12H, m), 1.08 (6H, d, J = 6Hz); ^{13}C NMR($CDCl_3$): δ218.2, 55.6, 51.5, 46.1, 37.2, 35.2, 21.1. The major product 760mg (65%) was bulb to bulb distilled (160°/1 torr), which was solidified on refrigeration and identified as 5, 11-dimethyl-tricyclo[6.3.0.0^{2,6}]undec-10-en-3, 9-dione **29**, UV: λ_{max}^{MeOH} 234 nm(8400): IR(Neat) 1740, 1700 and 1615 cm^{-1}; ^{1}H NMR: δ5.84(1H, brs), 3.56(1H, dd, J_1 = 11Hz, J_2 = 7Hz), 3.04(2H, m), 1.6–2.8(6H, m), 2.2(3H, s), 1.04(3H, d, J = 6Hz); ^{13}C NMR($CDCl_3$): δ218.7(s), 211.4(s), 179.5(s), 130.9(d), 55.0(d), 54.6(d), 54.0(d), 53.5(d), 46.7(t), 34.5(d), 30.6(t), 20.1(q), 19.8(q). (Found: C, 76.46; H, 7.42. Calc. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90%.)

4, 6-*Dimethyl*-5-*oxa*-*tetracyclo*[7.2.1.0^{4,11}.0^{6,10}] *dodec*-7-*en*-2-*one* (**31**)

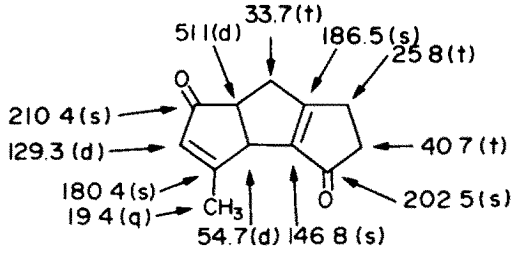
To an ice cold solution of 11-methyl tricyclo[6.3.0.0^{2,6}]undeca-4, 10- dien-3, 9-dione (**27**, 95 mg, 0.5 mmole) in 3 mL of dry THF was added ethereal methyllithium (~0.6 mmole). The ice bath was removed and the reaction mixture stirred for 30 min at room temperature. The reaction was quenched by addition of 20% HCl (2 mL), diluted with water and extracted with ether (2 × 20 mL). Concentration and filtration through silica gel (5g) column using 10% ethyl acetate-benzene as eluent furnished 46 mg (45%) of the oxa-tetraquinane **31**, which was bulb to bulb distilled (100°/1 torr) and solidified on refrigeration. IR(Neat): 3050, 1740 cm^{-1}, ^{1}H NMR($CDCl_3$): δ5.26(2H, AB, J = 6Hz), 3.1(3H, m), 1.8–2.9 (5H, m), 1.55(3H, s); ^{13}C NMR($CDCl_3$): δ220.9(s), 138.8(d), 135.9(d), 96.1(s), 85.2(s), 60.6(d), 60.1(d), 54.8(d), 53.9(t), 50.1(d), 37.5(t), 30.0(q), 25.8(q).

4-*Methyl*-5-*oxa*-*tetracyclo*[7.2.1.0^{4,11}.0^{6,10}]*dodecan*-2-*one* (**32**):

To a magnetically stirred solution of 11-methyl-tricyclo[6.3.0.0^{2,6}]undeca-4, 10-dien-3, 9-dione (**27**, 47mg, 0.25 mmole) in 5 mL of methanol was added sodium borohydride (27mg, 0.75 mmole) in small portions. The reaction mixture was stirred overnight. Methanol was removed under reduced pressure, the contents of the flask were diluted with water (10 mL) and extracted with dichloromethane (2 × 15 mL). Evaporation of the solvent furnished 48 mg of the crude alcohol. The crude alcohol was taken in 2 mL of dichloromethane and added to a stirring suspension of pyridinium chlorochromate (100 mg, 0.48 mmole) in 5 mL of dichloromethane. The heterogeneous reaction mixture was vigorously stirred for 2 hr at room temperature and filtered through a short silica gel (5g) column. Evaporation of the solvent followed by bulb to bulb distillation (120°/1 torr) furnished 40 mg (80%) of the 5-oxa-tetraquinane (**32**). IR(Neat): 1740 cm^{-1}, ^{1}H NMR($CDCl_3$): δ4.4(1H, brs), 1.2–3.4(12H, m), 1.35 (3H, s); ^{13}C NMR($CDCl_3$): δ218.5(s), 87.3(s), 84.4(d), 58.0(d), 57.5(d), 55.8(d), 52.6(t), 46.5(d), 34.7(t), 34.2(t), 30.9(t), 23.8(q). (Found: C, 75.03; H, 8.37. Calc. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%.)

11-Methyl-tricyclo[6.3.0.0^{2,6}]*undeca-2(6), 10-dien-3, 9-dione*(**28**)

A solution of 11-methyl-tricyclo[6.3.0.0^{2,6}]undeca-4, 10-dien-3, 9-dione (**27**, 15mg, 0.08 mmole) in 1 mL of benzyl benzoate was heated at 290° in a salt bath for 30 min. The reaction mixture was diluted with benzene (3 mL) and filtered through a short silica gel (5g) column. Benzyl benzoate was removed by elution with more benzene and the isomerised bis-enone **28** was collected by elution with 20% ethyl acetate-benzene as a solid compound, 12 mg (80%). It was recrystallised from dichloromethane–hexane as colourless needles, m.p. 109–10°, UV: λ_{max}^{MeOH} 223 (23,400), 240 (merged) nm, IR(CH_2Cl_2): 1700, 1640, 1630 cm^{-1}; ^{1}H NMR($CDCl_3$): δ5.8(1H, s), 3.88(1H, brs), 3.54(1H, m), 2.0–3.2 (6H, m), 2.29(3H, s).



Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]*undecane endo, endo-8, 11-diol* (**35a**)

The diol (**35a**) was prepared by the reduction of diketone (**10a**) with excess LAH according to the procedure reported by Sasaki *et al.*[43] m.p. 272–73° (lit[43] 273.5°).

8, 11-*Dimethyl pentacyclo*[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]*undecane-8, 11-diol* (**35b**)

The *endo, endo*-diol (**35b**) was prepared according to Cookson's procedure[14] by the reaction of dione **10a** with excess of methyl lithium in 75% yield, m.p. 112–13° (lit[14] 112–14°).

8,11-*Diphenyl pentacyclo*[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]*undecane-8, 11-diol* (**35c**)

To 5g (28.75 mmoles) of the diketone (**10a**) in dry ether was added PhMgBr prepared from 2.1g (90 mmoles) of Mg and 14.1 (86 mmoles) of bromobenzene. The reaction mixture was stirred at room temperature for 4 hr and quenched by careful addition of aq NH_4Cl. Exhaustive extraction with ethyl acetate (4 × 100 mL) and evaporation of solvent gave 8.0 g of the diol (**35c**) as a solid residue which was recrystallised from acetone, m.p. 273–75°. IR(KBr): 3070 (broad), 2980, 2860, 1495, 697 cm^{-1}. ^{1}H NMR($CDCl_3$) δ7.16–7.36(m), 3.34(brs), 2.4–2.9(m).

4-*Oxa-hexacyclo*[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]*dodecane* (**33a**)

1g of the diol (**35a**) was intimately mixed with P_2O_5 (~200 mg) and heated at 200° for 10 min. The black tarry residue was thoroughly extracted with dichloromethane (4 × 25 mL) and washed with aq $NaHCO_3$(2 × 20 mL). Evaporation of the solvent gave (**33a**) in 80% yield, m.p. 228–229° (lit[43] 228–230°).

3, 5 - *Dimethyl* - 4 - *oxa* - *hexacyclo*[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}] - *dodecane* (**33b**)

1g of the diol (**35b**) was intimately mixed with P_2O_5 (~200 mg) and heated at 180° for 5 min. The black residue was thoroughly extracted with dichloromethane (4 × 25 mL) and washed with aq $NaHCO_3$(2 × 20 mL). Evaporation of the solvent gave (**33b**) in 75% yield, b.p. 95–100°/5 torr. IR(Neat): 2960, 1378, 1185, 910 cm^{-1}; ^{1}H NMR($CDCl_3$): δ2.5–2.66(2H, m), 2.4(6H, m), 1.88 (1H, 1/2 AB, J = 10 Hz), 1.5(1H, 1/2 AB, J = 10Hz), 1.42(6H, s). (Found: C, 83.31; H, 8.65. Calc. for $C_{13}H_{16}O$: C, 82.94; H, 8.58%.)

3, 5-*Diphenyl-4-oxa-hexacyclo*[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]*dodecane* (**33c**)

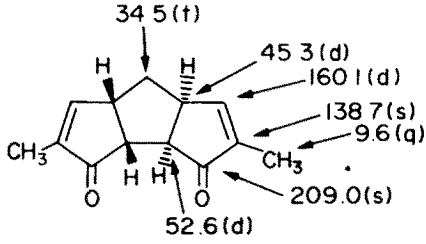
Added 2.0g of P_2O_5 to 7.0g of the diol (**35c**) in 100 mL of dichloromethane and stirred at room temperature for 45 min. The reaction mixture was diluted with water and the organic layer separated. The aqueous layer was further extracted with dichloromethane (2 × 25 mL) and the combined organic layers washed with aq $NaHCO_3$. Evaporation of the solvent furnished **33c**, 5.7g (87%) which was recrystallised from a mixture of pet ether and dichloromethane, m.p. 71–72°C. IR(KBr): 3030, 2960, 1600, 1020, 742, 695 cm^{-1}; ^{1}H NMR($CDCl_3$): δ7.12–7.6(10H, m), 2.62–3.02 (8H, m), 2.02(1H, 1/2 AB, J = 10Hz), 1.68(1H, 1/2 AB, J = 10Hz). ^{13}C NMR($CDCl_3$): δ141.5(s), 128.1(d), 126.8(d), 125.1(d), 96.9(s), 61.9(d), 51.9(d), 45.4(d), 43.6(t), 42.2(d).

General procedure for the photolysis of 5-oxa-tetracyclo[7.2.1.0^{4,11}.0^{6,10}]*dodeca-2, 7-dienes* (**34a–c**)

A solution of 5-oxa-tetraquinanes (**34a–c**) (0.15–0.25 mmole) in 120 mL of acetone was purged with a slow stream of nitrogen for 15 min. The solution was then irradiated with a 450 W medium pressure mercury arc lamp in a quartz immersion well with a pyrex filter for 2–5 hr. Removal of solvent and filtration through a short silica gel column furnished the precursor oxa-bird cage compounds (**33a–c**) in quantitative yield and were characterised by m.p., tlc and IR comparisons.

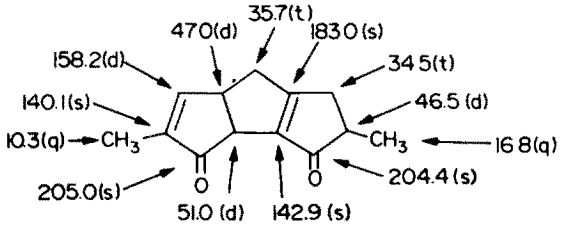
Thermal equilibration of 4,10-*dimethyl-tricyclo*[6.3.0.0^{2,6}]*undeca-4, 9-diene-3, 11-dione* (**11b**)

A benzyl benzoate solution (10 mL) of *cis, syn, cis*-triquinane (**11b**, 500mg 2.5 mmoles) was refluxed for 12 min. The mixture was diluted with dichloromethane (10 mL) and chromatographed on silica gel column (20g). Elution with dichloromethane removed benzyl benzoate. Elution with 10% EtOAc–benzene gave *cis, anti, cis*-**37**, 250 mg (50%) and was distilled at 145–150°/0.04 torr. This material solidified on refrigeration and was recrystallized from dichloromethane-pet ether to give **37** m.p. 69–70° (white flakes). IR(KBr): 1715, 1710, 1638 cm^{-1}, UV: λ_{max}^{MeOH} 228(15, 470), 234(15, 360), 276(1035), 284(1198) mm; ^{1}H NMR($CDCl_3$): δ7.02(2H, brs), 3.0(2H, brs), 2.56(2H, d, J = 6Hz), 1.54(2H, brs), 1.43(6H, s). (Found: C, 77.5; H, 6.97. Calc. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98%.)



Further careful elution with 40% ethyl acetate-benzene gave the starting bis-enone **11b** (50 mg, 10%) which was identified by IR and tlc comparison.

Continued elution with 40% EtOAc-benzene gave 50 mg (10%) of 4, 10-dimethyl tricyclo[6.3.0.0^{2,6}]undeca-1(8), 4-diene-3, 11-dione (**36**, 50mg, 10%) and was distilled at 150°/0.04 torr. Crystallisation of the distilled material from dichloromethane-pet ether gave **36** m.p. 108–9°, UV: λ_{max}^{MeOH} 224(10, 550), 241(4,570) nm; IR(KBr): 1710, 1634 cm^{-1}; ^{1}H NMR($CDCl_3$): δ7.16(1H, q, J = 1Hz), 3.86(1H, brs), 3.61(1H, brs), 1.84–3.06(5H, m), 1.77(3H, t, J = 1Hz), 1.2(3H, d, J = 8Hz). (Found: C, 77.4; H, 6.87. Calc. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98.%)



Thermal equilibration of 1, 4-*dimethyl tricyclo*[6.3.0.0^{2,6}]*undeca-4, 9-diene-3, 11-dione*(**11d**)

A benzyl benzoate (15 mL) solution of *cis, syn, cis*-bis-enone

(**11d**, 2.02g, 10 mmoles) was refluxed (317°) for 12 min. Glc analysis of the total mixture indicated 3 components in the ratio of 37:14:49. The reaction mixture was diluted with dichloromethane (20 mL) and chromatographed on silica gel (50g) column. Benzyl benzoate was removed by eluting the column with dichloromethane. Elution with 10% ethyl acetate-benzene furnished 740mg (37%) of *cis, anti, cis* compound (**39**) which was bulb to bulb distilled (150°/0.4 torr) and crystallised from ether-pet ether mixture, m.p. 65–66°; UV: λ_{max}^{MeOH} 228 nm (10, 140) nm; IR(KBr): 1710, 1640, 1585 cm^{-1}, ^1H NMR ($CDCl_3$): δ7.17(1H, q, J = 1Hz), 6.98(1H, dd, J_1 = 6Hz, J_2 = 3Hz), 6.03(1H, dd, J_1 = 6Hz, J_2 = 1Hz), 3.32(1H, brs), 3.1(1H, t, J = 6Hz), 2.82(1H, d, J = 6Hz), 1.8–2.2(2H, m), 1.75(3H, t, J = 1Hz), 1.07(3H, s); ^{13}C NMR($CDCl_3$): δ211.7(s), 207.7(s), 165.5(d), 159.5(d), 140.2(s) 129.6(d), 57.1(d), 56.5(s), 53.5(d), 46.5(d), 34.9(t), 19.0(q), 9.7(q).(Found: C, 76.91; H, 7.09. Calc. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98%.)

Further careful elution of the column with 30% ethyl acetate-benzene gave 320mg (16%) of the starting material which was characterised by IR and tlc comparisons. Finally, elution of the column with 40% ethyl acetate–benzene furnished 940mg (47%) of 2,7-dimethyltricyclo[6.3.0.$0^{2,6}$] undeca-1(8), 4-diene-3, 11-dione (**38**) as an epimeric mixture which was distilled at 150°/0.4 torr. UV: λ_{max}^{MeOH} 245(4800), 218 nm (12,300); IR(Neat): 1715, 1635, 1590 cm^{-1}, ^1H NMR($CDCl_3$): δ7.5(1H, dd, J_1 = 6Hz, J_2 = 3Hz), 6.08(1H, dd, J_1 = 6Hz, J_2 = 2Hz), 1.48–3.7 (6H, m), 1.42(3H, s), 1.18(3H, dd, J_1 = 8Hz, J_2 = 4Hz), ^{13}C NMR($CDCl_3$): δ207.9(s), 204.4(s), 182.1(s), 181.8(s), 163.6(d), 163.5(d), 145.7(s), 131.1(s), 57.6(d), 56.0(s), 46.6(d), 46.4(d), 44.7(t), 34.3(t), 18.4(q), 16.8(q), 16.4(q). (Found: C, 77.20; H, 7.06. Calc. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98%.)

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[13]For example, we have already demonstrated that the 1,3-cyclohexadiene-p-benzoquinone and 5,5-dimethoxy-tetrachloro-1,3-cyclopentadiene-1,5-cyclo-octadiene Diels–Alder adducts on two step photo-thermal metathesis provide useful entry to *cis, syn, cis*-tricyclo[7.3.0.$0^{2,6}$] dodecane and fluorenone systems, respectively. (G. Mehta, A. V. Reddy and A. Srikrishna, *Indian J. Chem.* **20B**, 698 (1981).

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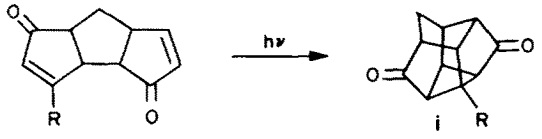
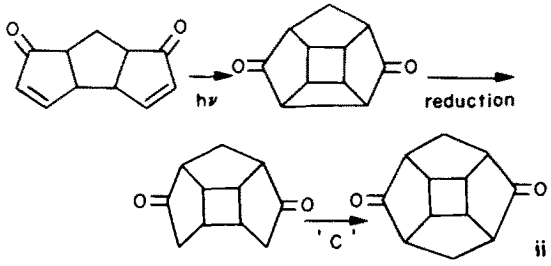
[21]The half-transposed bis-enone **24** can on photolysis provide a facile entry to the new trishomocubane system **i**. We have demonstrated this to be so and synthesised for the first time, several pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}]undecane-5, 11-diones **i** (G. Mehta and A. Srikrishna, manuscript submitted for publication.



The fully transposed bis-enone **25** is the ideal precursor, offering a short, novel route to [4]-peristylane **ii** as depicted below. Unfortunately, **25** has eluded us so far. However, we continue to strive.



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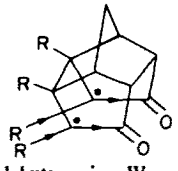
[26]We find (perusal of Table 2) that substituents on the cyclobutane ring of the pentacyclic diones (**10a–j**) have significant influence on the relative ease of thermal fragmentation. Indeed, in some cases the onset of thermal cyclobutane cleavage has been observed at much lower temperatures (150–170°) although at a very slow rate. We do not have definitive clue for this substituent mediated mellowing of thermal refractoriness but since electron donating substituents, e.g.–CH_3, –OCH_3 at C_1 and C_7 do seem to ease thermal fragmentation of the cyclobutane, a possible explanation could be in terms of Viehe's concept of capto-dative stabilisation[28] of the intermediate diradical **iii** (see arrows). However, such an explanation is untenable in the case of adducts **14a, b**, where thermal fragmentation is more likely to be initiated through the thermal cleavage of the exceptionally long (1.65 Å)[29] C_2–C_6 (Ph–C_2–C_6–



Ph) bond of the cyclobutane ring. We are currently investigating the mechanistic aspects of this reaction employing both theoretical and experimental probes.

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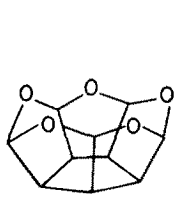
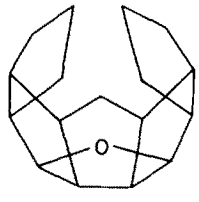
[30]Polyoxa-polyquinanes (e.g. pentaoxa-peristylane **iv**) can have interesting ion-binding and carrier properties and compounds like 5-oxa-tetraquinanes **34a–c** can serve as useful precursors to such systems. We have, for example, evolved systems like functionalised oxa-polyquinane **v** from **34a** (unpublished results with Mangalam S. Nair).





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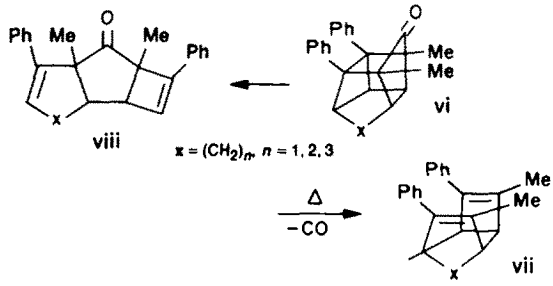

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