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Pericyclic Reaction of Cyclohexa-2,4-dienones with Cyclohexa-1,3-diene and Cycloheptatriene: The Role of Cyclohexadienones as π^4 and π^2 Component, Cope Rearrangement and Photoreaction of the Adducts

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Abstract: Pericyclic reaction of cyclohexa-2,4-dienones **8a-c** with cycohexa-1,3-diene **2b** and cycloheptatriene **5** has been reported. Cyclohexadienones react with **2b** and **5** to give cycloadducts **9a-c,10a-c** and **13a-c,15b,c** respectively. Cope rearrangement of the adducts **10a-c** and **15b,c** to **9a-c** and **13b,c**, respectively has been described. It has been shown that cyclohexa 2-4-dienones behave as 4π component (diene) and they react in a primary inverse demand fashion via π^{4s} (dienone) + π^{2s} (diene/triene) mode.

There has been a resurgence of interest in the pericyclic reactions of conjugated polyenes such as cycloheptatriene, fulvene and tropone due to their potential for rapid creation of complex carbocyclic systems.[1,2] Cyclohexa-2,4-dienones are emerging as valuable intermediates in organic synthesis,[3-6] because of their rich and diverse chemical behaviour. Pericyclic reactions of cyclohexa-2,4-dienones offer a highly potential and versatile synthetic methodology for efficient synthesis of various types of complex polycyclic systems and precursors to a variety of natural products.[4] However, there has been a mechanistic dichotomy regarding the formation of adducts and the role of cyclohex-2,4-adienones during their cycloaddition with conjugated polyenes since cyclohexadienones may enter into multiple modes of addition.[7] For example, the addition of cyclohexa-2,4-dienone (dienone) of type **1** with a cyclic 1,3-diene (diene) such as **2** may give two types of aducts, **3** and/or **4** as a result of π^{4s}(diene) + π^{2s}(dienone) and/or π^{2s}(diene) + π^{4s}(dienone) addition respectively(Fig-1). Similarly the cyclohexa-2,4-dienones may add to a conjugated triene **5** in three different pericyclic modes,[7] Viz. π^{4s}(dienone) + π^{2s}(triene), π^{4s}(dienone) + π^{2s}(triene) and π^{4s} (dienone) + π^{6s}(triene) addition respectively.

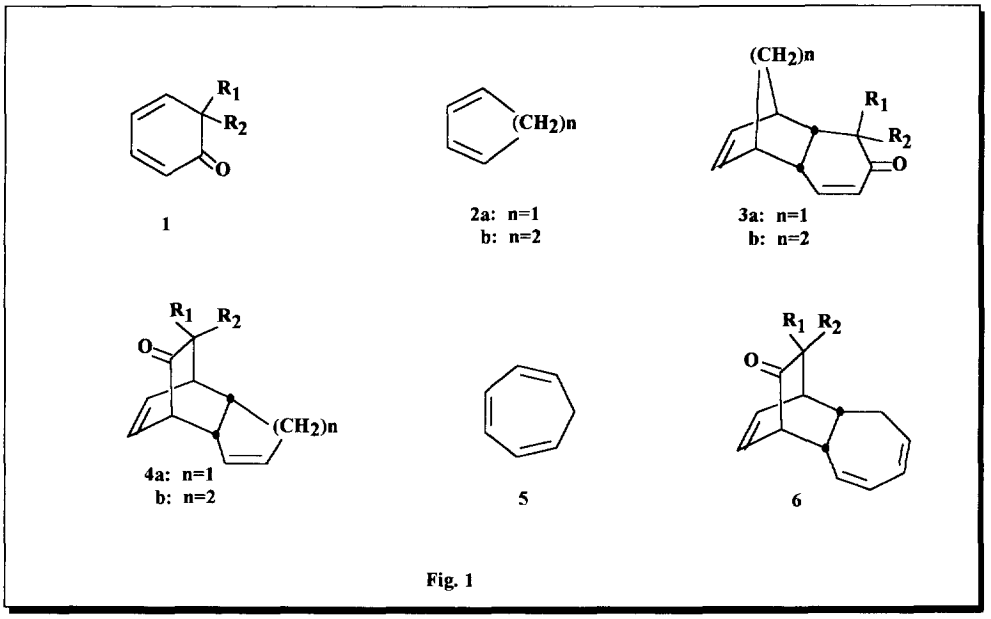


Fig. 1

In this context, it may noted that the addition of cyclopentadiene (**2a**) with some cyclohexadienones of type **1** exclusively gives the adduct of type **4a**.[4,5] It has been suggested[5] that the adducts of type **4a** do not arise via a primary inverse demand cycloaddition in which the cyclohexadienones behave as a 4π partner (diene) but, that the adducts **4a** are obtained through Cope rearrangement of **3a** which are initially formed as a result of π^{2s} (cyclohexadienone) + π^{4s}(cyclopentatiene) addition. However, the Cope rearrangement of 3a to **4a** has not been demonstrated. Moreover attempts to isolate the adducts of type 3 have proved to be futile.[5] Only recently a few adducts of type **3a** were isolated and found to rearrange to **4a** in chloroform solution at room temperature.[6]

In order to obtain a deeper insight in to afore mentioned dichotomy, develop a route towards tricyclic systems such as **4b** and **6** and explore their synthetic potential, we examined pericyclic reactions of cyclohexa-1,3-diene (**2b**) and cycloheptatriene **5** with a variety of cyclohexa-2,4-dienones.

We wish to report herein cycloaddition of **8a-c** with cyclohexa-1,3-diene leading to the formation of the adducts **9a-c** and **10a-c** via both modes of addition viz. π^{2s}(dienone) + π^{4s}(diene) and π^{4s}(dienone) + π^{2s}(diene), respectively. We also report on the

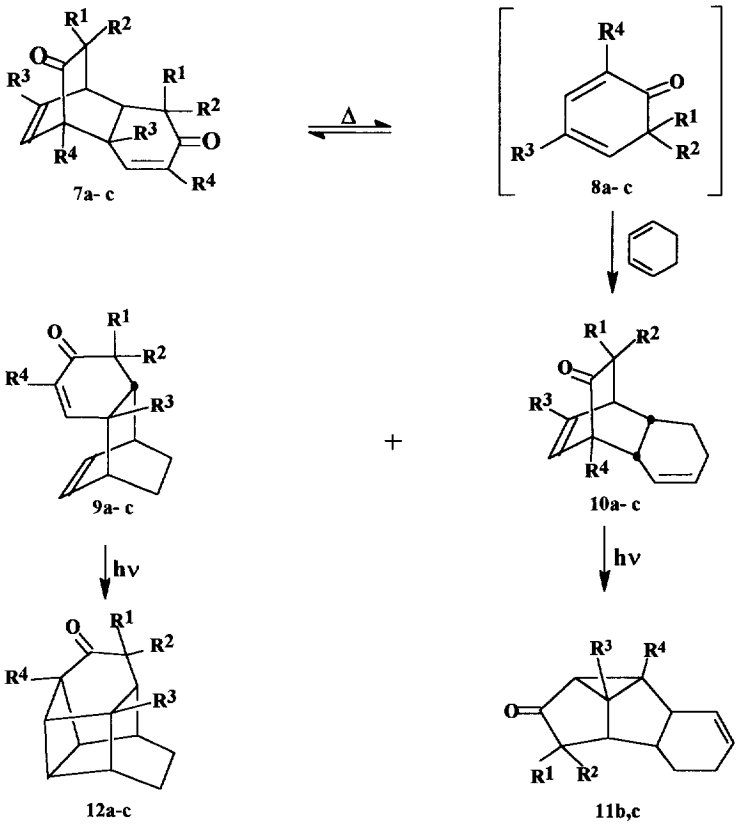
periselective reaction of cycloheptatriene with cyclohexa-2,4-dienones leading to the adducts of type **13** and **14** (Scheme 2) and their thermal and photochemical transformation.[8] We have provided for the first time, a direct evidence for a primary inverse demand π^{4s}(dienone) + π^{2s}(diene) cycloaddition via studies on Cope rearrangement of the cycloadducts.

Results and Discussions:

Generation of cyclohexa-2,4-dienone **2a** by pyrolysis[4a] of the readily available dioldimer **1a** at 160^0 C and subsequent trapping with cycxlohexa-1,3-diene, *in situ*, gave a mixture of two adducts **9a** and **10a** **(Scheme-1)** which were separated by a careful column chromatography of the crude product over silicagel. The structure of the adducts were deduced by spectral analysis and photochemical transformations as follows.

The adduct **9a** showed an absorption band at 1695 cm^{-1} in its infra-red spectrum indicating the presence of an α,β-unsaturated carbonyl group. The ^1H NMR (300 MHz, $CDCl_3$) of **9a** displayed resonances at δ 6.6 (dd, J_1=10Hz, J_2=6Hz, 1H) and 6.04 (J_1=10Hz, J_2=2Hz, 1H) characteristic of protons attached to β and α carbons of an α,β-enone, respectively. It also showed signals at δ 6.10 (dd, J_1=J_2=7Hz, 1H) and 5.86(dd, J_1=J_2=7Hz, 1H) for the olefinic protons present in the bicyclo[2.2.2]octane frame work.[10] Furthermore, the bridgehead protons at C_1 and C_8 gave signals at 3.0 (m, 1H) and 2.75 (m, 1H), the protons at ring junctions at C_7 and C_2 showed resonances at 2.94 (complex m of d, 1H) and 2.38 (dd, J_1=8Hz, J_2=2.5Hz, 1H), respectively. These assignments were made with the help of the cosy experiment. The ^{13}C NMR also corroborated with the proposed structure **9a** since it showed signals at δ 198.04 for carbon of a conjugated carbonyl group, in addition to resonances at δ 150.86, 125.77 for β and α carbons of α,β-enone and at δ 133.40, 132.91 for the other olefinic carbons.[11] The *endo* stereo structure of the adduct **9a** was proved through its facile intramolecular π^{2s} + π^{2s} photocycloaddition to give a novel cage molecule **12** (80%) which showed a carbonyl absorption band at 1720 cm^{-1} in its IR spectrum. The structure of the cage product **12** was also supported from its ^1H and ^{13}C NMR spectra. The orientation of chloromethyl group in the adduct **9a** is based on the known tendency of cyclohexadienones during cycloaddition,[4,9] transformation of **9a** to the keto epoxide **9d** and comparison of their spectral features with analogous adducts.

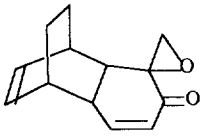
The structure of the other adduct, **10a** was also revealed from its spectral data which showed a carbonyl absorption band at 1735 cm^{-1} in its infra-red spectrum. The ^1H NMR of **10a** gave signals at δ 6.45 (dd, J_1=J_2=8Hz, 1H, H_{11}) and 6.15(dd, J_1=J_2=8Hz, 1H, H_{12}) characteristic of a



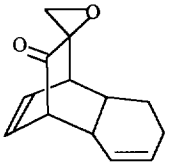
a. $R^1 = CH_2Cl$, $R^2 = OH$, $R^3 = R^4 = H$

b. $R^1 = R^3 = R^4 = CH_3$, $R^2 = OH$

c. $R^1 = R^4 = CH_3$, $R^3 = H$, $R^2 = OH$



9d



10d

Scheme 1

β,γ-enone moiety in bicyclo[2.2.2]octane framework. Other characteristic resonances were observed at δ 5.94(complex m, 1H, H5), 5.45(d with structure, J=10Hz, 1H, H6) and 3.6(AB system, J=11Hz, 2H, CH_2Cl) for olefinic protons in the cyclohexene ring and chloromethyl group, respectively. The ^{13}C NMR of the adduct also supported its formulation as **10a** since it showed signals at δ 209.68 for carbonyl carbon and 135.53, 130.64, 127.75, 127.55 for the four olefinic carbons, respectively. The *syn* orientation of chloromethyl group is deduced via its conversion to the keto epoxide **10d** and comparison of its spectral features (^1H, ^{13}C NMR), with analogous compounds.

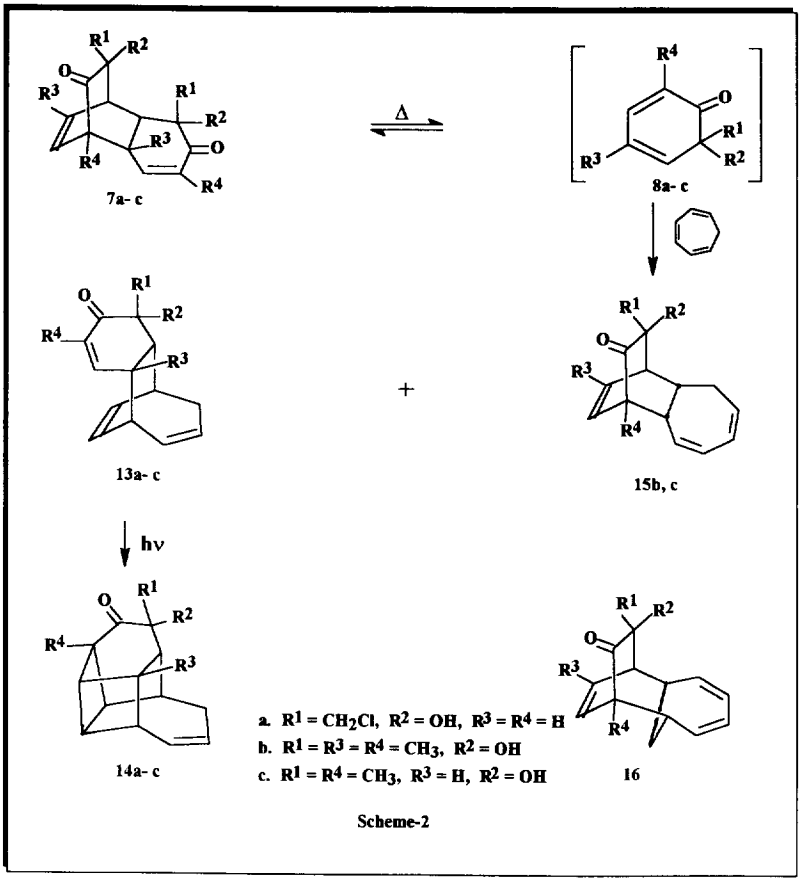
Similarly the cycloaddition of other cyclohexa-2,4-dienones **8b,c** with cyclohexadiene also furnished the adducts **9b,c** and **10b,c,** respectively whose structures were clearly revealed through their spectral data and other chemical and photochemical transformations. Here again, the enones **9b,c** were quantitatively converted into their cage isomers **12b,c**, respectively upon irradiation (125w Hg vapour lamp, Applied Photophysics) in acetone which confirmed the *endo* stereo structure for the adducts. The presence of β,γ-enone moiety in **10b-c** was readily proved through the sensitized irradiation of the adducts **10b-c** which furnished tetracyclic compounds **11b,c,** respectively (Scheme-1) via oxa-di-π-methane rearrangement, a characteristic photochemical reaction of β,γ-enones[4,12] (Scheme-1).

The formation of the adducts **9** and **10** from both the pericyclic modes of cyclohexa-2,4-dienone was indeed remarkable especially since cyclohexadienones are known to react with cyclopentadiene to give exclusively a single adduct.

b) Pericyclic reaction of cyclohexa-2,4-dienones (8a-c) with cycloheptatriene:

The reaction of cycloheptatriene (CHT) with cyclohexadienone (dienone) **8a** furnished the aduct **13a** as the exclusive product in excellent yield (82.5%)(Scheme 2). The structure of the adduct was deduced from spectral and analytical data as follows.

The IR spectrum of **13a** showed absorption band at 1690 cm^{-1} characteristic of a conjugated ketone. Its ^1H NMR spectrum (300 MHz, $CDCl_3$) displayed resonances at δ 5.63 (dd, J_1=10Hz, J_2=3H, 1H) and 6.15 (dd with long range couplings, J_1=10Hz, J_2=3H, 1H) corresponding to protons at β and α carbon atoms of α,β-enone. It also showed signals at δ 6.02 (dd, $J_1=J_2$=8Hz, 1H, H_{12}/H_{13}), 5.92 (dd, $J_1=J_2$=8Hz, 1H, H_{13}/H_{12}) and 5.48(t of d, J_1=12Hz, J_2=4Hz, 1H) for H_{12}-H_{13}, and H_9,H_{10}, respectively. Other resonances appeared at δ 3.7(AB, J=12Hz, 2H), 3.44(d of dd, J_1=9Hz,



Scheme-2

J_2=3Hz, 1H) and 2.92(d, J=8Hz, 1H) for CH_2Cl, H_2, and H_7, respectively. The signals for other protons were observed at 2.78(m, 2H) and 2.2(m, 2H). The above assignments were made with the help of cosy experiment. The structure **13a** of the adduct was also supported by its ^{13}C NMR spectrum which showed signals at δ 197.38 for a enone carbonyl and at 152.5, 134.1, 130.4, 129.5, 127.2 and 126.4 for six olefinic carbons in addition to other signals. The *endo* structure of **13a** was confirmed through its facile $\pi^{2s} + \pi^{2s}$ ring closure to cage compound **14a** upon irradiation in acetone. The cage molecule **14a** showed a carbonyl absorption band at 1720 cm^{-1} in its IR spectrum, and displayed signals for only two olefinic protons in its ^1H NMR spectrum.

It was indeed surprising that no adducts coresponding to alternate symmetry allowed modes such as π^{6s}(CHT) + π^{4s}(dienone) and π^{2s}(CHT) + π^{4s} (dienone) were obtained, especially since cyclohexa-2-4-dienones are well known to react as 4π addend during their cycloaddition with dienes. We therefore investigated the reaction of other cyclohexa-2,4-dienones **8b-c** with cycloheptatriene.

Interestingly, the cycloaddition of **8b** and **8c** with cycloheptatriene furnished two products each **13b**, **15b** and **13c** and **15c**, respectively, the adducts **13b** and **15c** being the minor products (Scheme 2). Here again no product corresponding to π^{6s}(CHT) + π^{4s} (diene) mode of addition was obtained. While the structures of the adducts **13b** and **13c** were easily deduced by comparison of their spectral features with that of the enone **13a** and their photoconversion to cage products **14b**, **14c**, respectively, the structure of the minor adducts **15b** and **15c** were determined through detailed analysis of ^{1}H NMR spectra and cosy analysis. Thus, the minor adduct **15c** showed absorption bands at 3480, and 1720 cm^{-1} in its IR spectrum. The ^{1}H NMR of **15c** gave signals at δ 6.35(dd, J_1=J_2=7Hz, 1H) corresponding to γ-proton of the β,γ-enone moiety and 5.9(cluster of multiplets, 4H) and 5.75(br m, 1H). Further, it gave a signal at 3.50(m of d, J=10Hz, 1H), 3.00(m of d, J=7Hz, 1H) for protons at allylic ring junction and allylic bridgehead, respectively. The proton at the other ring junction adjacent to methylene was observed at δ 2.6(complex m, 1H) in addition to signals due to methylene, hydroxyl and methyl protons. The above assignments were made with the help of cosy analysis. The signal at δ 3.5 assigned to allylic ring junction showed cross peaks with the signals at δ 2.6 and 3.00. Similarly, the signal at δ 3.00 assigned to allylic bridgehead proton showed cross peaks with the resonance signals at δ 6.35 and 3.50, and the signal at δ 2.6 showed connectivity with the signals at δ 2.15 (methylene) and 3.50. These relationships between protons clearly suggested structure **15c** for the minor adduct and ruled out the alternate possibility **16**. The adduct **15b** also showed similar spectral features. Furthermore, the structure **15b** and **c** were further confirmed through their Cope rearrangement.

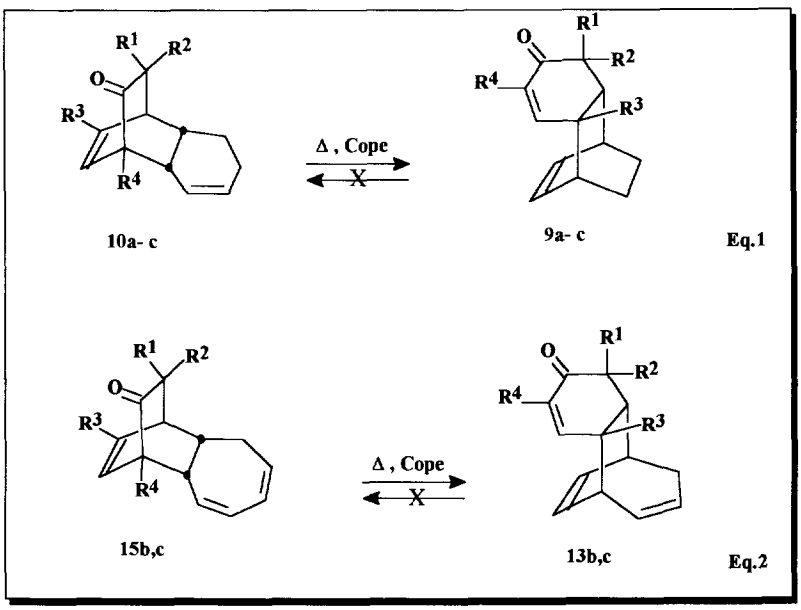
Cope rearrangement of the adducts:

It was remarkable to observe the formation of adducts coresponding to both pericyclic modes, viz. π^{2s}(dienone) + π^{4s}(CHD) and π^{4s} (dienone) + π^{2s}(CHD) of addition during cycloaddition of cyclohexa-2,4-dienones **8a-c** with cyclohexadiene(CHD). Moreover, the periselective reaction of cyclohexadienones **8a-c** with cycloheptatriene also appeared to be surprising. The role of cyclohexadienones as 2π component (dienophile) in the above cycloadditions appeared to be highly unusual. Formation of both types of adducts **9a-c**, **10a-c** and **13a-c**, **15b,c** during above cycloadditions, however, provided excellent opportunity to ascertain the role of cyclohexa-2,4-dienones and the origin of the adducts as to whether these are obtained as a result of primary cycloaddition or one is an artefact of the other. In view of the above, Cope rearrangement of

cycloadducts was studied especially since we realized that both types of adducts **9a-c**, **10a-c**, and **13a-c**, **15b,c** are interconvertible through a symmetry allowed thermal 3,3-sigmatropic shift.

It was indeed surprising to observe that while the enone **9a** failed to undergo the Cope rearrangement to **10a** even after prolonged thermal activation at 160^0 C, the adduct **10a** smoothly rearranged to the enone **9a** (IR, NMR). Similarly, the adducts **10b,c** were also found to undergo Cope rearrangement to **9b,c,** respectively upon further heating, and the enones **9b,c** were inert to thermal activation (eq.1).

The adducts **13a-c** and **15b,c** obtained during cycloaddition of **8a-c** with cycloheptatriene(CHT) also behaved in an analogous fashion towards Cope rearrangement. Thus the enones **13a-c**, formal products of π^{2s}(dienone) + π^{4s}(CHT) modes of addition did not undergo the Cope rearrangement while the adducts **15b** and **15c** rearranged to **13b** and **13c** **(IR, NMR)**, respectively, upon further heating (eq.2). The above results on Cope rearrangement clearly suggest the role of cyclohexa-2,4-dienones **8** as 4π partners (diene) in the above pericyclic reaction and the formation of adducts **10a-c** and **15b,c** via a primary inverse demand π^{4s}(dienone) + π^{2s} (CHD/CHT) cycloaddition between the respective addends. Further experiments on the above cycloaddition suggested that the adducts of type **9** and **13** are formed at later stages of the reaction and probably arise via Cope rearrangement of **10** and **15**, respectively. However, the possibility of a competitive π^{2s}(dienone) + π^{4s} (diene/triene) cannot be ruled out.



While the thermal transformations of the adducts **10** to **9** and **15** to **13** are in accordance[13] with the general tendency of 1,5-dienes towards Cope rearrangement in which the position of equilibrium is governed by substitution pattern,[14] ring strain[15] and conjugation,[16] the above behaviour of adducts towards Cope rearrangement and the modes of pericyclic addition of cyclohexa-2,4-dienones are in contrast with the suggestion and observation made in context with reaction of cyclohexadienones with cyclopentadiene (vide supra).

In summary, we have deduced the mode of cycloaddition of cyclohexa-2,4-dienones with cyclohexa-1,3-diene and cycloheptatriene for the first time. The adducts corresponding to the two modes of addition were isolated and their Cope rearrangement studied. We have proved that cyclohexa-2,4-dienones behave as 4π component (diene) during their pericyclic reaction with cyclohexa-1,3-diene and cycloheptatriene.

Experimental:

General remarks: IR spectra were recorded on a Perkin-Elmer 681 instrument. UV spectra were recorded on Schimadzu 260 instrument. ^{1}H NMR spectra were recorded on 300 MHz, Varian VXR 300S instrument and on 90 MHz, Jeol FX 90Q instrument. ^{13}C NMR spectra were recorded on 75 MHz, Varian VXR 300S instrument. All the samples were dilute solutions in $CDCl_3$ with $SiMe_4$ as internal standard. Melting points were recorded on a Veego apparatus and are uncorrected. Elemental analysis were performed on a CEST 1106 instrument. All organic extracts were dried over anhydrous Na_2SO_4. Reactions were monitored with tlc and the spots visualized with iodine vapour. Chromatographic separations were done on silicagel.

Pericyclic reaction of cyclohexa-1,3-diene with cyclohexadienone 8a : formation of 3-hydroxy-3-chloromethyl *endo* tricyclo[6.2.2.0^{2,7}]dodec-5,9-dien-4-one (9a) and 10-Hydroxy-10-chloromethyl *endo* tricyclo[6.2.2.0^{2,7}]dodec-5,11-diene-9-one (10a).

A solution of the dimer **8a**(2.5g, 7.87mmol) and cyclohexadiene (8.4g, 10ml excess) in o-dichlorobenzene(5ml) was heated at 160^{0}C for 4 hours. The reaction mixture was chromatographed on silicagel. Elution with petroleum ether (60-80^0) gave first the unreacted cyclohexadiene and o-dichlorobenzene. Continued elution with pet ether-ethyl acetate(98:2) first gave the enone **9a**(1.17g, 29.7%) as a solid.

mp. 89^{0}C; IR (nujol) ν_{max} : 3420, 1695 cm^{-1}. ^{1}H NMR(300 MHz, $CDCl_3$): δ 6.6(dd, J_1=10Hz, J_2=6Hz, 1H), 6.10(dd, J_1=J_2=7Hz, 1H), 6.04(dd, J_1=10Hz, J_2=2Hz, 1H), 5.86(dd, J_1=J_2=7Hz, 1H), 4.25(s, 1H, OH), 3.6(AB system, J=10Hz, 2H, CH_2Cl), 3.0(br dd, J_1=6Hz, J_2=2.5Hz, 1H, methine H), 2.94 (complex m, 1H, bridgehead H), 2.73(m, 1H, bridgehead H), 2.40 (dd,

J_1=8Hz, J_2=2.5Hz, 1H), 1.8-1.4(m, 3H) and 1.25(m, 1H); ^{13}C NMR(75MHz, $CDCl_3$): δ 198.04 (CO), 150.86, 133.40, 132.91, 125.77 (olefinic carbons), 53.52, 46.11, 41.82, 35.81, 29.76, 26.27 and 23.82. Mass (m/z) : 238.5 (M^+).

Further elution with the same solvent furnished the ketone **10a** (1.33 g, 35.3%) as a liquid.

IR(neat) ν_{max} : 3450, 1735 cm^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$): δ 6.45 (dd, J_1=J_2=8Hz, 1H), 6.15(dd, J_1=J_2=8HZ, 1H), 5.92(complex m, 1H), 5.45(d with structure, J=10Hz, 1H), 3.6(AB system, J=11 Hz, 2H, CH_2Cl), 3.2(d with structure, J=6Hz, 2H, methine H), 2.9-2.8(m, 2H), 2.78-2.70(m, 1H), 2.0-1.8(m, 2H, CH_2), 1.7(m, 1H) and 1.2(m, 1H); ^{13}C NMR(75MHz,$CDCl_3$): δ 209.68(CO), 135.53, 130.64, 127.75, 127.55 (olefinic carbons), 74.03, 53.57, 50.98, 46.53, 36.50, 31.78, 25.94 and 23.27; Mass (m/z): 238.5 (M^+).

3-Hydroxy-3,5,7-trimethyl *endo* tricyclo[6.2.2.$0^{2,7}$]dodeca-5,9-dien-4-one (9b) and 10-Hydroxy-8,10,11-trimethyl *endo* tricyclo[6.2.2.$0^{2,7}$] dodeca-5,11-dien-9-one (10b).

Pyrolysis of the dimer **8b**(0.7g, 2.3 mmol) and cyclohexadiene (3ml, excess) in o-dichlorobenzene (3ml) at 140^{0}C for 4h followed by careful chromatography furnished the enone **9b**(0.135g, 12.73%) as a liquid and the ketone **10b**(0.66g, 61.3%).

9b: IR(neat) ν_{max} : 3480, 1690 cm^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$): δ 5.95(m overlapped with a br s, total 3H, olefinic protons), 3.98(br s, 1H, OH), 3.0(br m, 1H, methine H), 2.22(m, 1H, methine H), 1.98(complex m, 1H, methylene H), 1.91(br s, 1H, methine H), 1.74(d, J=1.5 Hz, olefinic CH_3), 1.48(m, 1H, methylene H), 1.38(s, 3H, CH_3), 1.32(s, 3H, CH_3), 1.28-1.16(m, 2H, methylene H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 203.61(CO), 150.14, 135.83, 131.17, 130.36(olefinic carbons), 73.77, 56.69, 42.31, 41.39, 32.20, 31.21, 26.19, 25.34, 19.48, 15.56; Mass(m/z): 232 (M^+).

10b : mp. 140^0 C, IR(KBr) ν_{max} : 3450, 1715 cm^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$) : δ 5.96(complex m of d, J=10Hz, 1H, olefinic H), 5.65(br d, J=10Hz, 1H, olefinic H), 5.3(br s, 1H, β-H of β,γ-enone moiety), 2.86(s, 1H, OH), 2.80(complex m, 1H), 2.47(br t, J=3Hz, 1H, methine H), 2.25(br d, J=8Hz, 1H, methine H), 1.98-1.86(multiplet merged with d, (J=1Hz) total 5H, olefinic CH_3 and methylene H), 1.66(m, 1H, methylene H), 1.26(s, 3H, CH_3), 1.24(s, 3H, CH_3) and 1.18(m, 1H, methylene H); ^{13}C NMR(75 MHz, $CDCl_3$): δ 214.80(CO), 144.50, 130.83, 125.19, 123.62(olefinic carbons), 72.13, 54.74, 51.35, 39.33, 32.78, 25.85, 24.86, 23.51, 23.35 and 15.20. Mass(m/z): 232 (M^+).

3-Hydroxy-3,5-dimethyl *endo* tricyclo[6.2.2.$0^{2,7}$]dodeca-5,9-dien-4-one (9c)

and 10-Hydroxy-8,10-dimethyl *endo* tricyclo[6.2.2.$0^{2,7}$] dodeca-5,11-dien-9-one (10c).

The dimer **8c**(0.6g, 2.17 mmol) was heated with cyclohexadiene(2.0 ml, excess) in o-dichlorobenzene at 140^{0}C for 2h. Chromatography of the product mixture on silicagel furnished the enone **9c**(0.28g, 30%) after elution with petroleumether(60-80^0)-ethyl acetate(98:2). Further elution with pet.ether-ethyl acetate(95:5) gave the ketone **10c**(0.56g, 59.3%) as a solid which was recrystallized from pet.ether: ethyl acetate.

9c: IR (neat) ν_{max} : 3490, 1690 cm^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$): δ 6.22(d with long range coupling, J=6Hz, 1H, βH of α,β-enone moiety), 6.04(superimposed dd with structure, J_1=J_2=8H, 1H, olefinic H), 5.79(superimposed dd with structure, J_1=J_2=8H, 1H, olefinic H), 4.04(br s, 1H, OH), 2.96(m, 1H, methine H), 2.86(complex m, 1H, methine H), 2.66(m, 1H, methine H), 2.32(d with long range coupling, J=9Hz, 1H, ring junction H), 1.75 (superimposed dd, J_1=J_2=1.5 Hz (allylic and long range coupling), 3H, olefinic CH_3), 1.65(complex m, 1H, methylene H), 1.53(complex m, 1H), 1.4 (m, 1H, methylene H), 1.28(s, 3H, CH_3), 1.19(complex m, 1H, methylene H). ^{13}C NMR(75 MHz, $CDCl_3$): δ 202.98(CO), 144.93, 133.02, 132.66, 132.28 (olefinic carbons), 73.84, 48.99, 40.88, 36.21, 31.34, 29.80, 26.47, 23.56 and 15.49. Mass(m/z): 218 (M^+).

10c : mp. 114-115^{0}C, IR (nujol) ν_{max} : 3500, 1725 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.36(dd, J_1=J_2=7.8Hz, 1H, γ H of β,γ-enone moiety), 5.95(complex m, 1H, olefinic H), 5.72(d with structure J=7.8Hz, 1H, βH of β,γ-enone moiety), 5.67(br d with structure, J=10Hz, 1H, olefinic H), 2.89(complex m, 1H), 2.82(m, 2H), 2.3(br d, J=9.4Hz, 1H), 1.9(complex multiplet, 2H, methylene H), 1.3(m merged with a s, total 4H, CH_3 and methylene H) and 1.29(s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 215.22(CO), 135.71, 131.85, 131.02, 125.19 (olefinic carbons), 72.58, 52.14, 49.84, 40.68, 33.03, 26.39, 26.33, 23.32 and 15.27; Mass(m/z): 218 (M^+).

Preparation of 3-spiroepoxy *endo* tricyclo[6.2.2.$0^{2,7}$]dodeca-5,9-dien-4-one (9d) :

To a solution of the adduct **9a**(1.16g, 4.88mmol) in chloroform (10ml) containing cetyltrimethylammonium bromide (CTAB) (0.05g) as a phase transfer catalyst, was added an aqueous solution of potassium hydroxide (1M, 10ml). The reaction mixture was stirred at room temperature (30^{0}C) for 4h after which the organic phase was separated and the aqueous layer extracted with chloroform (3x15ml). The combined organic extract was washed with brine and dried over anhydrous sodium sulfate. Removal of the solvent followed by chromatography gave the epoxy ketone **9d**(0.91g,92%). mp.: 98^{0}C; IR (nujol) ν_{max} : 1685 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.67(dd, J_1=10Hz, J_2=4.3Hz, 1H, βH of α,β-enone), 6.33(superimposed dd,

$J_1=J_2=7Hz$, 1H, olefinic H), 6.03 (dd, $J_1=10Hz$, $J_2=2Hz$, 1H, α-H of α,β-enone), 6.01 (superimposed dd with structure, J=7Hz, 1H, olefinic H), 3.06(m of d, J=5Hz, 1H,methine H), 2.83(part of AB system, J=6.5Hz, overlapped with a multiplet, 2H, CH_2O and methine H), 2.74 (part of AB system, J=6.5Hz, overlapped with a multiplet, 2H, CH_2O and methine H), 2.16(dd, $J_1=9Hz$, $J_2=2$ Hz, 1H, methine H), 1.7(m, 1H), 1.57-1.44(complex m, 2H, methylene H), 1.3(m, 1H, methylene H). Mass (m/z) : 202 (M^+).

Preparation of 10-spiroepoxy *endo* tricyclo[6.2.2.$0^{2,7}$] dodeca-5,11-dien-9-one (10d):

To a solution of the adduct **10a** (1.3g, 5.45mmol) in chloroform (15ml) containing cetyltrimethylammonium bromide (CTAB) (0.05g) as a phase transfer catalyst, was added an aqueous solution of potassium hydroxide (1M, 10ml). The reaction mixture was stirred at room temperature (30^0C) for 4h after which the organic phase was separated and the aqueous layer extracted with chloroform (3x15ml). The combined organic extract was washed with brine and dried over anhydrous sodium sulfate. Removal of the solvent followed by chromatography gave the epoxy ketone **10d**(0.88g, 80.3%).

mp. 85^0C; IR (KBr) ν_{max} : 1720 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) : δ 6.48(m of superimposed dd, $J_1=J_2=8Hz$, 1H, γ H of β,γ-enone moiety), 6.18(m of superimposed dd, $J_1=J_2=8HZ$, 1H, βH of β,γ-enone moiety), 5.95(complex m, 1H, olefinic H), 5.55(d with structure, J=10Hz, 1H, olefinic H), 3.28(t of d, $J_1=6Hz$, $J_2=2H$, 1H, methine H), 3.13 (part of AB system, J=6Hz, 1H, CH_2O), 2.88 (part of AB system, J=6Hz, 1H, CH_2O), 2.80-2.66(complex m, 2H), 2.54(t of d, $J_1=6Hz$, $J_2=2Hz$, 1H, methine H), 2.0-1.86(m, 2H), 1.76(complex m, 1H, methylene H), 1.38-1.26(complex m, 1H, methylene H). ^{13}C NMR (75MHz, $CDCl_3$): δ 205.47(CO), 134.45, 130.53, 127.97, 127.80 (olefinic carbons), 57.83, 53.80, 52.87, 45.14, 35.83, 34.77, 25.89, and 22.93; Mass (m/z): 202(M^+).

6-hydroxy-2,3,6-trimethyl tetracyclo[6.3.0.$0^{2,4}$, $0^{3,7}$]dodec-11-ene-5-one (11b):

A solution of the adduct **10b** (0.2g, 0.86mmol) in acetone was irradiated(125 W, Hg vapour lamp) in a pyrex immersion well for 4h. Removal of solvent followed by chromatography of the residue on silicagel gave the product **11b** (o.11g 55%).

mp. 145^0C. IR (KBr) ν_{max} : 3450, 1715 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 5.87(m of d, J=10 Hz, 1H, olefinic H), 5.63(m of d, J=10Hz, 1H, olefinic H), 2.50(br s, 1H, OH), 2.3-2.2(m, 2H), 2.1(s, 1H), 1.98(m, 2H), 1.62(br s, 1H), 1.55 (m, 1H), 1.44 (s, 3H, CH_3), 1.40(m, 1H), 1.30(s, 3H, CH_3), 1.18(s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 215.75(CO), 128.87, 126.10

(olefinic carbons), 80.25, 76.41, 60.50, 45.03, 43.98, 42.31, 42.22, 27.36, 25.08, 24.30, 16.70, 15.32; Mass(m/z): 232(M^+).

6-Hydroxy-2,6-dimethyl tetracyclo[6.3.0.$0^{2,4}$.$0^{3,7}$]dodec-11-ene-5-one : (11c).

The compound **11c** was prepared from **9c** following the above procedure (yield 50%).

mp 128-29^{0}C; IR(KBr) ν_{max} : 3450, 1720 cm^{-1}; ^{1}H NMR(300 MHz,$CDCl_3$): δ 5.86(m of d, J=9Hz, 1H, olefinic H), 5.62(dd of d, J_1=9Hz, J_2=5Hz, J_3=2Hz, 1H, olefinic H), 2.4-2.3(m, 3H), 2.2 (br s, 1H, OH), 2.0-1.9(m, 3H), 1.6-1.4(m, 2H), 1.3(s, 3H, CH_3), 1.2(s, 3H, CH_3). ^{13}C NMR(75 MHz, $CDCl_3$): δ 216(CO), 129.08, 125.95(olefinic carbons), 80.7, 54.25, 43.75, 42.31, 40.74, 40.31, 38.26, 27.18, 25.18, 24.21, 19.96; Mass(m/z): 218 (M^+).

Preparation of 7-hydroxy-7-chloromethyl pentacyclo[6.4.0.$0^{2,5}$.$0^{3,12}$.$0^{4,9}$] dodecan-6-one (12 a):

A solution of the enone **9a**(0.12 g, 0.50mmol) in acetone was irradiated(125 W, Hg vapour lamp, APP) under nitrogen in a pyrex immersion well for about 5h(tlc). Removal of solvent under vacuum followed by chromatography of the photolysate on silicagel furnished the cage compound **12a** as a solid (0.93 g, 76.86%) which was recrystallized from petroleum ether.

mp.88^{0}C; IR (KBr) ν_{max} : 3468, 1716 cm^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$): δ 3.58(part of AB system, J=12 Hz, 1H, CH_2Cl), 3.44(part of AB system, J=12 Hz, 1H, CH_2Cl), 3.40(s, 1H, OH), 3.15(dd, J_1=7.5 Hz, J_2=4.5 Hz, 1H), 2.96(m, 1H), 2.84-2.7(m, 3H), 2.65 (m, 1H), 2.56(br d, J=4.5 Hz, 1H), 2.28(dd, J_1=J_2=5Hz, 1H), 1.9(m, 1H), 1.6-1.4(m, 3H). ^{13}C NMR(75 MHz, $CDCl_3$): δ 213.87 (CO), 76.25, 47.72, 47.55, 42.13, 41.51, 36.53, 34.45, 34.11, 32.54, 27.12, 21.45 and 16.60; Mass(m/z): 238.5(M^+).

7-Hydroxy-1,5,7-trimethyl pentacyclo[6.4.0.$0^{2,5}$.$0^{3,12}$.$0^{4,9}$]dodecan-6-one (12b):

Irradiation of **9b** (0.89g, 0.38 mmol) as described above gave **12b** (0.064g, 71.9%) after chromatography.

mp. 120^0 C; IR (KBr) ν_{max} : 3432, 1705 cm^{-1}; ^{1}H NMR (200MHz,$CDCl_3$): δ 3.1(m, 1H), 2.8(br s, 1H, OH), 2.4(m, 1H), 2.2(m, 1H), 2.1(m, 1H), 2.0 (m, 1H), 1.75(m, 1H), 1.55-1.40(m, 3H), 1.3(s, 3H, CH_3), 1.25(s, 3H, CH_3) and 1.20(s, 3H, CH_3).

7-Hydroxy-5,7-dimethyl pentacyclo[6.4.0.$0^{2,5}$.$0^{3,12}$.$0^{4,9}$]dodecan-6-one (12c):

Irradiation of **9c**(0.4g, 0.183 mmol) furnished the cage product **12c**

(0.30g, 75.75%).
mp. 80-82^0 C; IR(KBr) ν_{max} : 3470, 1706 cm^{-1}; ^{1}H NMR(200 MHz,$CDCl_3$): δ 3.05(m, 1H), 2.95(s, 1H, OH), 2.75(m, 1H), 2.55(m, 2H), 2.25(br m, 2H), 1.8(m, 1H), 1.5(m, 2H), 1.20(s, 3H, CH_3), 1.15(s, 3H, CH_3); Analysis: found C,77.43, H,8.24% Calcd. for $C_{14}H_{18}O_2$ C,77.06, H,8.26%.

Pericyclic reaction of cycloheptatriene 5 with cyclohexadienone 8a: formation of 3-Hydroxy-3-chloromethyl *endo* triecyclo[6.3.2.0^{2,7}] tridec-5,9,12-triene-4-one(13a)

The dimer **7a**(2.2g, 10mmol) and cycloheptatriene(10ml, excess) in o-dichlorobenzene was heated at 160^0 C for 16h. The reaction mixture was chromatographed on silicagel. Elution with petroleum ether first gave unreacted cycloheptatriene and solvent. Further elution with petroleum ether-ethylacetate(95:5) furnished the adduct **13a** as a sole product (3.47g, 82.5%). It was recrystallized from pet.ether-ethylacetate (95:5). mp. 111^{0}C; IR(KBr) ν_{max} : 3480, 1690 cm^{-1}; UV λ_{max} : 318, 233nm; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.53(dd, J_1=10Hz, J_2=3Hz, 1H, proton at β-carbon of α,β-enone), 6.15(dd with long range couplings, J_1=10Hz, J_2=3Hz, 1H, proton at α-carbon of α,β-enone), 6.02(dd, J_1=J_2=8Hz, 1H, H_{13}/H_{12}), 5.92(dd, J_1=J_2=8Hz, 1H, H_{12}/H_{13}), 5.85(m of dd, J_1=12 Hz, J_2=9Hz, J_3=3H, 1H, H_9), 5.48(t of d, J_1=12Hz, J_2=4Hz, 1H, H_{10}, olefinic H adjcent to methylene), 4.2(s, 1H, OH), 3.7(AB system, J=2Hz,2H, CH_2Cl), 3.44(d of dd, J_1=8Hz, J_2=3Hz, 1H, proton at allylic ring junction), 2.92(d, J=8Hz, 1H, ring junction H), 2.78(m, 2H), 2.2(m, 2H). ^{13} C NMR (75MHz, $CDCl_3$): δ 197.38(enone CO), 152.5, 134.1, 130.4, 129.5, 127.2, 126.4(olefinic carbons), 77.1 (CH_2Cl), 52.8, 46.4, 45.3, 38.3, 35.5, and 28.6. Mass(m/z): 250.5 (M^+). Analysis: found C,67.18, H,5.89%; Calcd. for $C_{13}H_{15}O_2Cl$ C,67.06, H,5.98%

3-Hydroxy-3,5,7-triemethyl *endo* tricyclo[6.3.2.0^{2,7}]tridec-5,9,12-triene-4-one(13b) and 11-hydroxy-9,11,12-trimethyl *endo* tricyclo[7.2.2.0^{2,8}] tridec-4,6,12-trien-10-one (15b):

The dimer **7b**(1.65 g, 5.5 mmol) and cycloheptatriene (8 ml, excess) were heated at 150^{0}C for 4h, and the reaction mixture was carefully chromatographed on silicagel. Elution with petroleum ether :ethylacetate (98:2) first gave the enone **13b**(0.38 g, 14.4%) as a liquid. Further elution with the same solvent furnished the ketone **15b**(1.32 g, 49.8%). **13b:** IR (neat) ν_{max} : 3480, 1690 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) : δ 6.05(dd, J_1=J_2=8Hz, 1H, olefinic H), 5.9(br s, 1H, olefinic H), 5.8(dd, J_1=J_2=8Hz, 1H, olefinic H), 5.75(t of dd, J_1=J_2=8.5Hz, J_3=3Hz, 1H, olefinic H), 5.46(t of d, J_1=11Hz, J_2=3.5Hz, 1H), 2.92(m, 1H), 2.33(s, 1H), 2.31(d, J=8Hz, 1H), 2.18(m, 2H), 1.75(s, 3H, CH_3), 1.45(s, 6H,

$2xCH_3$).

15b: mp. 123^{0}C; IR(KBr) ν_{max} : 3450, 1720 cm^{-1}; ^{1}H, NMR(500 MHz, $CDCl_3$): δ 6.0(m, 1H, olefinic H), 5.9-5.8(m, 3H, olefinic H), 5.44(br s, 1H, βH of β,γ-enone moiety), 3.45(d, J=10Hz, 1H, ring junction H), 2.68(t, J=2Hz, 1H, methine H), 2.6(d of t, J_1=10 Hz, J_2=3Hz, 1H, ring junction H), 2.5(br s, 1H, OH), 2.18-2.05(m, 2H), 1.92(d, J=1.5Hz, 3H, CH_3), 1.25(s, 3H, CH_3) and 1.15(s, 3H, CH_3); Analysis found C,78.43, H,8.22% Calcd. for $C_{16}H_{12}O_2$, C,78.68, H,8.19%.

3-Hydroxy-3,5-dimethyl *endo* tricyclo[6.3.2.$O^{2,7}$] tridec-5,9,12-trien-4 one (13c) and 11 Hydroxy-11,12-dimethyl *endo* tricyclo[7.2.2.$O^{2,8}$] tridec-4,6,12-trien-10-one (15c).

Reaction of the dimer **7c**(2.0 g, 6.9 mmol) with cycloheptatriene (10 ml, excess) in o-dichlorobenzene at 140^{0}C for 3h, followed by chromatography first gave the enone **13c** as a liquid(1.99 g, 59.64 %). Further elution of the column with petroleum ether: ethylacetate(95:5) furnished the ketone **15c** as a solid (0.61 g, 18.3%).

13c: IR (neat) ν_{max} : 3460, 1690 cm^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$): δ 6.15(m, 1H, olefinic H), 5.95(d of dd, J_1=J_2=8Hz, J_3=1.5Hz, 1H), 5.88(dd, J_1=J_2=8Hz, 1H), 5.82(m, 1H), 5.45 (t of d, J_1=10Hz, J_2=3.5Hz, 1H), 4.0(br s, 1H, OH), 3.38(complex m, 1H), 2.81(d, J=8Hz, 1H), 2.7(m, 2H), 2.17(m, 2H), 1.8(dd, J_1=2.5 Hz, J_2=1.25Hz, 3H, olefinic CH_3), 1.2(s, 3H, CH_3). ^{13}C NMR(75 MHz, $CDCl_3$): δ 202.5(CO), 147.3, 134.2, 132.9, 130.7, 129.4, 127.5, 74.5, 49.6, 44.6, 38.9, 35.8, 29.7, 28.4, 15.4; Analysis: found C,78.4, H,8.0% Calcd. for $C_{15}H_{18}O_2$, C,78.26, H,7.82 %.

15c: IR (KBr) ν_{max} :1720 cm^{-1}; ^{1}H NMR(270 MHz, $CDCl_3$): δ 6.35(superimposed dd, J_1=J_2=8Hz, 1H, γ-H of β,γ-enone moiety), 6.0-5.75(cluster of m, 5H, olefinic H), 3.5(d with structure, J=9Hz, 1H, allylic ring junction H), 3.00(m of d, J=8Hz, 1H, bridgehead H), 2.6(complex m, 1H, ring junction proton adjacent to methylene), 2.3(br s, 1H, OH) and 2.1(m, 2H, methylene H); Mass(m/z): 230 (M^+).

Preparation of 7-Hydroxy-7-chloromethyl pentacyclo [6.5.0.$O^{2,5}$.$O^{3,13}$.$O^{4,9}$] tridecan-6-one 14a :

A solution of the enone **13a**(1.0 g, 4 mmol) in acetone was irradiated (125 W, Hg vapour lamp) in a pyrex immersion well for about 5h(tlc). Removal of the solvent in vacuo followed by chromatography of the residue on silicagel furnished the cage molecule **14a** (0.90 g, 90%).

mp. 141^{0}C; IR (KBr) ν_{max} : 3480, 1720 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 5.8(m of d, J=12Hz, 1H, olefinic H), 5.55(m of dd, J=12Hz, 1H, olefinic H), 3.6(part of AB system, J= 12Hz, 1H, CH_2Cl), 3.42(part of AB system, J=12Hz, 1H, CH_2Cl), 3.40(m, 1H), 3.2(m, 1H), 3.13(s, 1H, OH), 3.05(m, 2H,

CH), 2.85 (m, 3H, CH), 2.65(dt of part of AB system, J_1=18 Hz, J_2=6Hz, J_3=2Hz, 1H, CH_2), 2.5(q of the part of AB system, J_1=18Hz, J_2=3Hz, 1H, CH_2) and 2.30(m, 1H, CH); ^{13}C NMR(75 MHz, $CDCl_3$): δ 214.3(CO), 132.4, 127.0(olefinic carbons), 78.85, 47.47, 46.7, 46.2, 44.6, 42.8, 42.37, 38.65, 37.8, 35.4 and 32.2. Analysis: found C,67.3, H,6.4% Calcd. for $C_{14}H_{15}O_2Cl$, C,67.06, H,5.98%.

Preparation of 7-Hydroxy-1,5,7-trimethyl pentacyclo [6.5.0.$0^{2,5}$.$0^{3,13}$.$0^{4,9}$] tridecan-6-one 14b :

Irradiation of the enone **13b** (0.60 g, 2.2 mmol) in acetone as described above furnished **14b**(0.5 g, 83%).
mp. 120^{0}C, IR (KBr) ν_{max} : 3480, 1710 cm^{-1}; ^1H NMR (300MHz, $CDCl_3$): δ 5.6(complex m, 2H, olefinic H), 3.5(dd, J_1=15Hz, J_2=10Hz, 1H), 2.82(s, 1H, OH), 2.6(m, 1H), 2.45(complex m, 2H), 2.3(complex m, 4H), 1.2(s, 3H, CH_3) and 1.0(s, 6H, 2xCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 219.22(CO), 132.21, 125.97(olefinic carbons), 50.9, 48.7, 47.41, 44.81, 44.0, 36.23, 35.71, 27.25, 25.43 and 15.29.

Preparation of 7-Hydroxy-5,7-dimethyl pentacyclo[6.5.0.$0^{2,5}$.$0^{3,13}$.$0^{4,9}$] tridecan-6-one 14c :

Irradiation of **13c**(1.43g, 6.22 mmol) as described earlier gave the cage ketone **14c** (1.2 g, 84.5%).
mp. 110^{0}C. IR (KBr) ν_{max} : 3500, 1720 cm^{-1}; ^1H NMR(90 MHz, $CDCl_3$) : δ 5.5(m, 2H, olefinic H), 3.45(m, 1H, methine H), 3.2-2.7(br, 4H, methine H), 2.6-2.3(m, 5H, methine, methylene and OH), 1.22(s, 3H, CH_3) and 1.20 (s, 3H, CH_3). ^{13}C NMR (75MHz, $CDCl_3$): δ 218.8(CO), 132.3, 127.2 (olefinic carbons), 51.98, 47.27, 46.1, 45.6, 43.3, 37.8, 36.2, 35.6, 22.2 and 15.1; Analysis : found C,78.4; H,8.0%, Calcd.for $C_{15}H_{18}O_2$, C,78.26; H,7.82 %.

Cope rearrangement of the adducts 10a-c and 15b-c to 9a-c and 13b-c :
General procedure:

The adducts (**10a-c** and **15b-c**) were heated in o-dichlorobenzene at 140-160^{0}C and the reaction was monitored with tlc and infra-red spectroscopy. After a few hours (3h) the reaction was terminated and carefully chromatographed over silicagel to first give the corresponding enones(**9a-c**, **13b-c**) respectively which were found identical in all respects (tlc, IR, NMR) to the previously obtained enones **9a-c** and **13b-c** respectively. Continued elution furnished the unconverted ketones. Under similar conditions the enones **9a-c** and **13b-c** were found inert and did not undergo Cope rearrangements.

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