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Sigmatropic 1,2- and 1,3-Acyl Shifts in Excited States : A Novel, General Protocol for the Synthesis of Tricyclopentanoids and Protoilludanes

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Abstract: A novel and general approach for the synthesis of linearly fused *cis:anti:cis* tricyclopentanoids and protoilludane framework having fused four, six and five membered rings from common precursors has been delineated. Photochemical sigmatropic 1,2-acyl shift (or oxa-di-π-methane rearrangement) and 1,3-acyl shift in annulated bicyclo[2.2.2]octenones are the key features of this approach. An efficient one step synthesis of epoxy ketones **15-17** *via* $\pi^4s+\pi^2s$ cycloaddition of *in situ* generated cyclohexa-2,4-dienone **11** has been reported. Further transformation of **15-17** and their congeners to a variety of chromophoric systems **22-31** has been described. The structure and stereochemistry of annulated bicyclo[2.2.2]octenones **15-31** has been established through their high field ^{1}H-NMR (300MHz), ^{13}C-NMR, decoupling experiments and cosy spectra. Photochemical behaviour of selected chromophoric systems upon triplet (^{3}T) and singlet (^{1}S) excitations has been investigated. While triplet excitation (^{3}T) of **23, 24, 26-28, 30-32** and **35** led to formation of tetracyclic systems **38-47**, the singlet excitation (^{1}S) of **23, 24, 27, 28, 29b, 31b, 36** and **55** furnished the protoilludanoids **56-63**. Interestingly, **29b** did not undergo 1,2-acyl shift upon triplet excitation, but it underwent 1,3-acyl shift upon singlet excitation to give **60**. Cleavage of cyclopropane ring in some of the tetracyclic products has also been investigated. Reductive cleavage of **38, 44, 46** and **47** to tricyclic systems **50-53** has also been reported. Copyright © 1996 Elsevier Science Ltd

Polycyclopentanoids of the hirsutane family such as coriolin **1**, hirsutic acid **2**, capnellene **3**, and the protoilludanoids (**4** and **5**) (Fig.1) are two important classes of sesquiterpenes derived from the humulene cyclization cascade.[1] While there has been a sustained interest in the chemistry of polycyclopentanoids for over two decades,[2-4] protoilludanoids have attracted attention only recently.[5,7] The interest in these two classes of natural products is partly due to novel and intricate carbocyclic network and also due to interesting biological properties exhibited by some members of both the families. For

example, coriolin 1 and hirsutic acid 2 show antitumor[8] and antibacterial[9] activities respectively, capnellenes play important role in chemical defense mechanism and prevent larval settlement and inhibit microbial growth.[10] Similarily, protoilludanes also exhibit antitumor, antibiotic and antibacterial properties[11] and also play important role in biosynthesis of other natural products including polycyclopentanoids. The unusual molecular framework, presence of an array of functional groups coupled with biological properties, have further enhanced the interest in both the classes of sesquiterpenes, especially in polycyclopentanoids. Numerous approaches have been developed for the synthesis of tricyclopentanoids. However, except for a few, the majority of methods are target specific, lack adaptability and generate triquinane frameworks after multistep sequences.

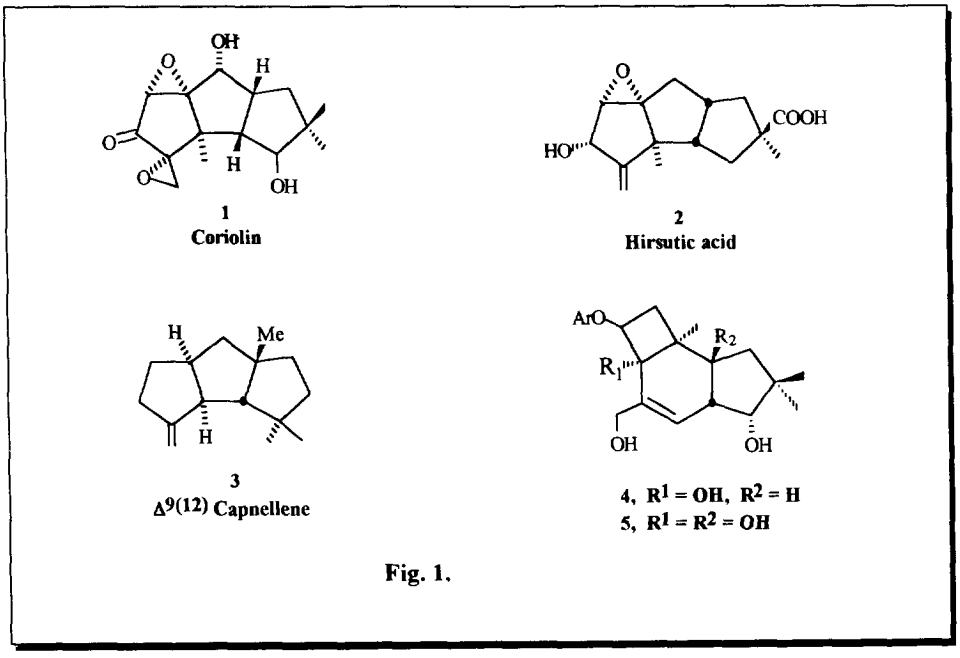
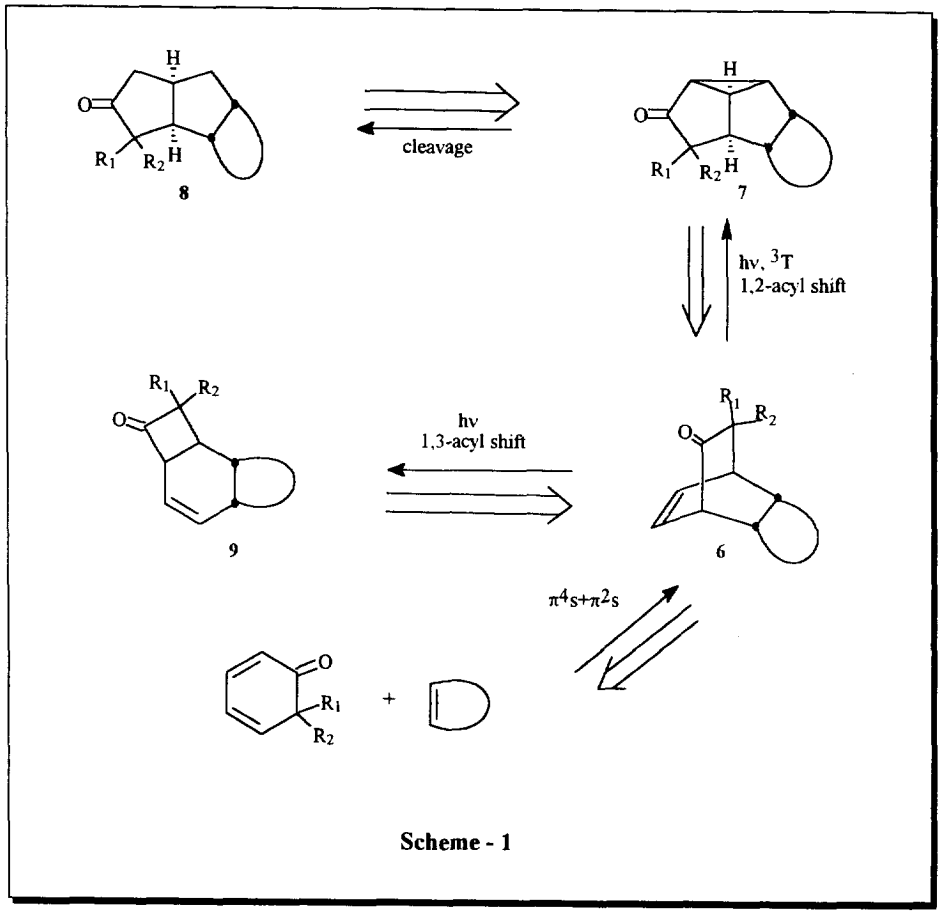


Fig. 1.

Protoilludanoids, on the other hand have received relatively less attention. Surprisingly, while there are no attempts towards synthesis of recently isolated protoilludanoids,[7] only a few routes are known[5,6] even for those members whose isolation and structure elucidation were done quite early.[11]

We therefore desired to develop new, general and efficient routes to linear *cis:anti:cis* tricyclopentanoids and protoilludanes from common precursors, employing photochemical 1,2-acyl shift or the oxa-di-π-methane rearrangement and 1,3-acyl shift,[12] as key features. We wish to report a complete account[13] on the synthesis of tricyclic systems having β,γ-unsaturated carbonyl chromophore and their photochemical reactions upon triplet (^{3}T) and singlet (^{1}S) excitations and reductive cleavage of the photoproducts leading to synthesis of linearly fused *cis:anti:cis* triquinanes and protoilludanoids.

Strategy: It was envisioned that both the *cis:anti:cis* tricyclopentanoids of type **8** and protoilludane framework **9** could be obtained from *endo* tricyclic systems **6** *via* photochemical 1,2-acyl shift (or oxa-di-π-methane rearrangement) and 1,3-acyl shift respectively, as shown in scheme-1. We further thought that the desired chromophoric systems of type **6** should be amenable through inverse demand $\pi^4s + \pi^2s$ cycloaddition of appropriate 2,4-cyclohexadienones such as **10** and dienophiles. Some of the salient features of this strategy are as follows.



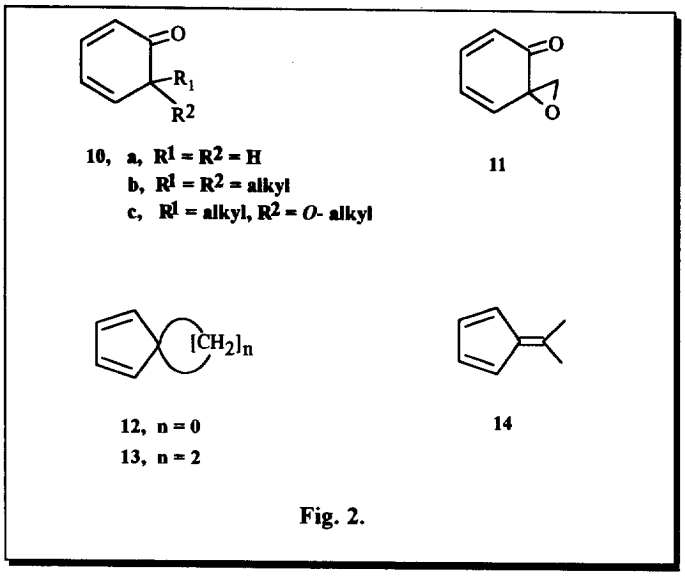
Scheme - 1

The required protoilludane and triquinane frameworks would be generated in a single stereospecific step with the desired *cis:anti:cis* geometry. Moreover, incorporation of a stereospecific and versatile $\pi^4s+\pi^2s$ cycloaddition to assemble the starting precursor provides structural and functional flexibility to the strategy.

1. Results and Discussions:

1.1. Synthesis of chromophoric systems: Salicyl alcohol as synthetic equivalent of cyclohexa-2,4-dienones.

Cyclohexa-2,4-dienones have been known[14] in the literature for a long time. However, there are only a few methods for their preparation. While there seems to be no method for the preparation of the parent cyclohexa-2,4-dienone **10a** (Fig.2), the preparation of *o*-dialkyl substituted cyclohexa-2,4-dienones of type **10b** *via* alkylation of *o*-substituted phenols proceeds in low yields.[15] Moreover, the preparation of cyclohexadienones of type **10b** by pyrolysis of epoxy fulvenes is multistep and cumbersome.[16] Oxidation of phenols and substituted benzene rings provides 2,4-cyclohexadienones as **10c** with oxygen substituents at C(6).[17] In view of the above, we designed an indirect sequence for the synthesis of chromophoric systems which is based on *in situ* generation of spiroepoxycyclohexa-2,4-dienone **11**, its interception with olefins/dienes and manipulation of the keto epoxide functionality in the resulting cycloadducts as described below. Thus, the cyclohexa-2,4-dienone **11** was generated *in situ* by periodate oxidation of salicyl alcohol in biphasic medium (CH_2Cl_2:H_2O, 1:1) following a method developed in our laboratory and subsequently intercepted with cyclopentadiene **12**, spiro[4,2]hepta-1,3-diene[18] **13** and dimethylfulvene[19] **14** which led to the formation of the adducts **15**, **16** and **17** respectively (Scheme-2). All the cycloaddtions gave single products arising from π^4s (dienone) + π^2s (diene) mode of addition wherein the cyclohexa-2,4-dienone **10** behaved as a π^4 component (diene) and the dienes **12-14** as π^2 component (dienophile).[20] Though the above cycloadditions gave single adducts in each case, the spiroepoxycyclohexadienone **11** could react with cyclopentadiene to furnish the adducts V and VI due to π^2s (dienone) + π^4s (diene) addition[20,21] and/or the adducts of type I-IV (Fig.3). It may be mentioned that the adduct **15** could also arise *via* Cope rearrangement of the compounds of type V. However, we could not isolate any adduct of type VI during the above cycloadditions. While the gross structure of adduct **15** was easily discerned from its spectral data, the distinction between its regio and stereoisomers (I-IV) was made through detailed analysis of its ^{1}H nmr and COSY spectra. Thus, ^{1}H nmr (300 MHz) spectrum of **15** exhibited signals at δ 6.4 (app. t, J=7.5Hz, 1H) and at 6.13 (app. t, J=7.5Hz, 1H) corresponding to γ and β-proton (H_{10} and H_{11}) of the β,γ-enone moiety,[22] the other two olefinic protons were observed at δ 5.73 (m of d, J=6Hz, 1H) and 5.48 (m of d, J=6Hz, 1H). The signal at δ 3.38 (d overlapped with m, total 2H) was assigned to the proton at the allylic ring junction (H_6) and bridgehead proton H_7. The complex multiplet at δ 3.05 was assigned to the proton at the other ring junction adjacent to methylene group and the signal at δ 2.63 (partly overlapped with another multiplet) was assigned to the bridgehead proton H_1. These assignments were made with the help of a COSY experiment. It was observed that the γ-proton of β,γ-enone moiety (H_{10}, δ, 6.4, dd) correlates with the signal at δ 2.63 (H_1) in addition to H_{11}, and that the resonance signal at δ 3.05 (assigned to H_2) shows cross peaks with the signals at δ 2.63 (H_1), 3.38 (H_6), and 2.05 (m of d, J=18Hz, 1H, allylic methylene group). The above



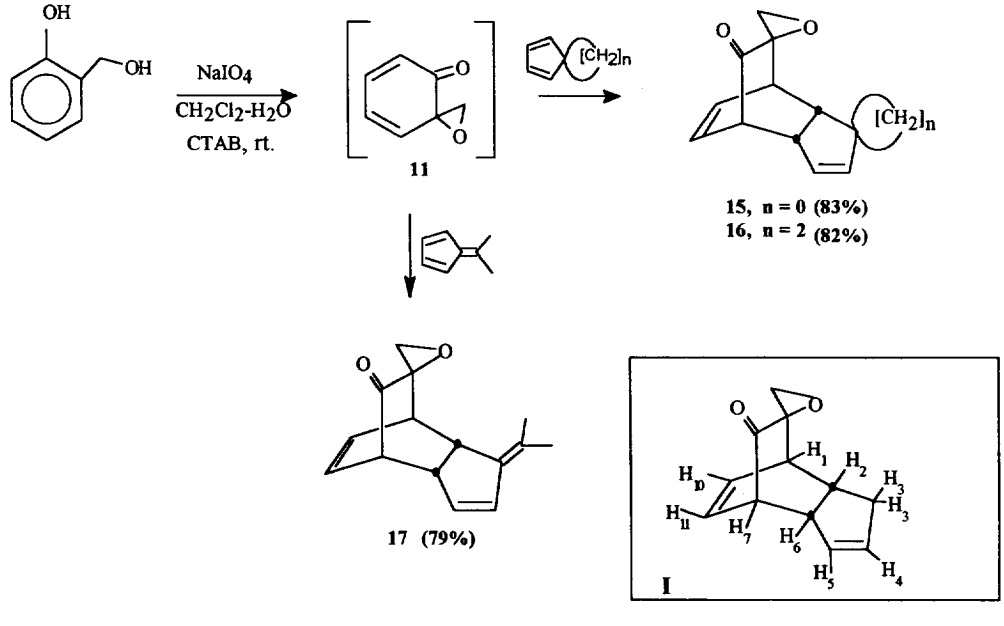
10, a, $R^1 = R^2 = H$
b, $R^1 = R^2$ = alkyl
c, R^1 = alkyl, R^2 = *O*- alkyl

11

12, n = 0
13, n = 2

14

Fig. 2.



11

15, n = 0 (83%)
16, n = 2 (82%)

17 (79%)

Scheme - 2

relationship between the protons wherein H_1 is coupled to a proton (H_2) which is further coupled to allylic methylene and H_6 clearly suggested the structure **I** (=15) for the adduct, and ruled out alternate possibilities. The *anti* orientation of the oxygen of the oxirane group was deduced on the basis of known tendency of 2,4-cyclohexadienones during their cycloaddition and through comparison of its spectral features with an authentic sample prepared by an alternate four step sequence.[23] The structures of the other adducts **16** and **17** were also deduced from their spectral and other analytical data. It may be mentioned that the present method provides a highly efficient route to a variety of tricyclic keto epoxides of type **15**.

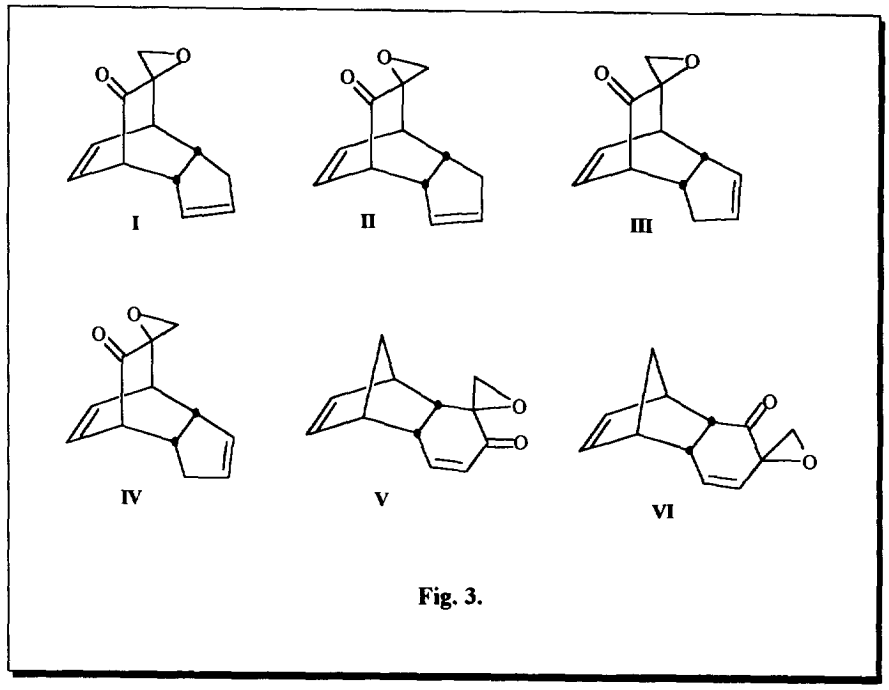


Fig. 3.

While the spiroepoxycyclohexa-2,4-dienone **11** was readily intercepted with reactive dienes, attempts to trap it with less reactive olefins such as cyclooctene and *cis:cis*-1,5-cyclooctadiene were unsuccessful and did not give the corresponding adducts. Therefore, the epoxy ketones **18** and **19** were prepared by base promoted ring closure of the readily available[24] chlorohydroxy ketones **20** and **21** (Fig.4).

1.2. Transformation of epoxy ketones 15-19.

The keto epoxide **15** was converted into monomethyl ketone **22** by reduction with zinc in dry dioxane containing ammonium chloride[25] which was alkylated with methyl iodide and allyl bromide in the presence of sodium hydride-tetrahydrofuran to give the corresponding alkylated analogoues **23** and **24** in good yields

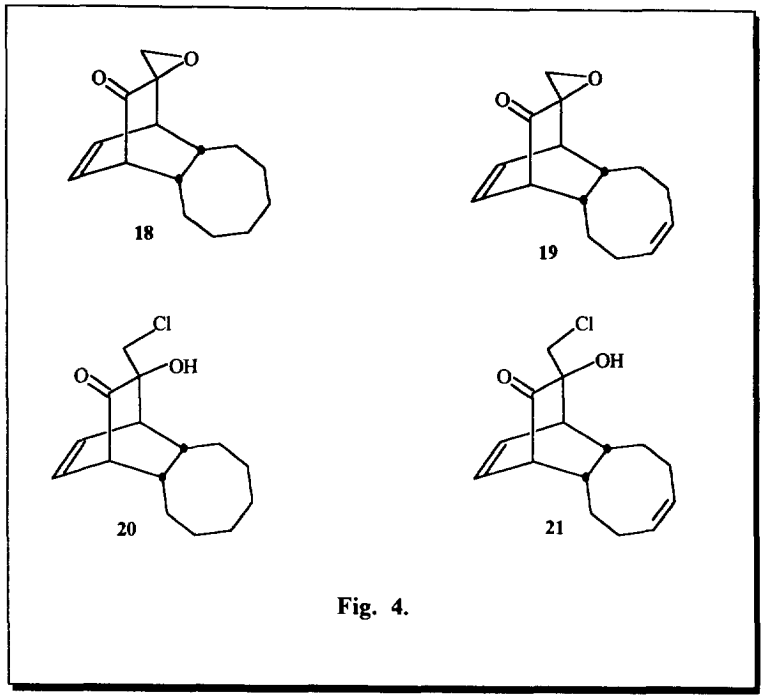
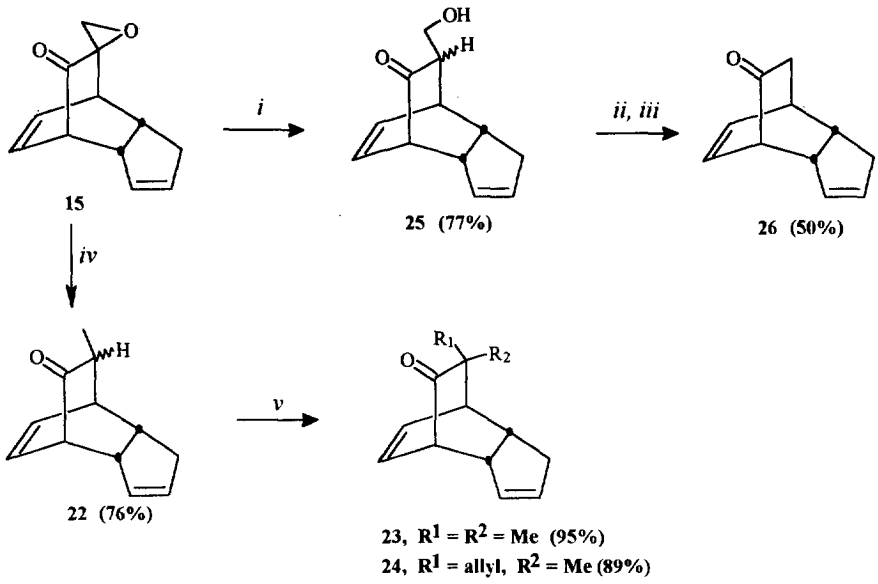


Fig. 4.

(Scheme-3). It may be mentioned that the alkylation of **22** with allyl halide proceeded stereoselectively and gave the compound **24** having allyl group *syn* to the double bond of bicyclo[2.2.2]octane moiety. Such type of stereoselectivity has also been observed by Stork and Paquette.[26]

Furthermore, the reduction of **15** with zinc in protic solvent (CH_3OH-H_2O) containing ammonium chloride gave the keto alcohol **25** as a major product which was oxidized with Jones' reagent and the resulting β-keto acid was decarboxylated to give the parent system **26** (50%) (Scheme-3). Following the above procedures the other keto epoxides **16-19** were also transformed into chromophoric systems **27-31** which are listed in Fig.5. The structures of all the compounds thus synthesized were deduced from high field ^1H nmr (300 MHz), ^{13}C nmr spectra and other analytical data. It may be mentioned that the methodology for selective manipulation of keto epoxide functionality was developed in our laboratory and the mechanism of reduction, its stereochemical features have been briefly discussed.[25] The above transformations of the keto epoxy adducts into chromophoric systems of type **23, 24** and **26** demonstrates the utility of the spiroepoxycyclohexa-2,4-dienone (and hence salicyl alcohol) as synthetic equivalent of parent as well as α,α-disubstituted cyclohexa-2,4-dienones.



Scheme - 3

Reagents/conditions : *i*, Zn, NH_4Cl, MeOH : H_2O; *ii*, Jones' reagent; *iii*, aq. $Ba(OH)_2$. THF, reflux; *iv*, Zn, NH_4Cl, dioxane, Δ; *v*, NaH, THF, Δ, MeI / allyl bromide.

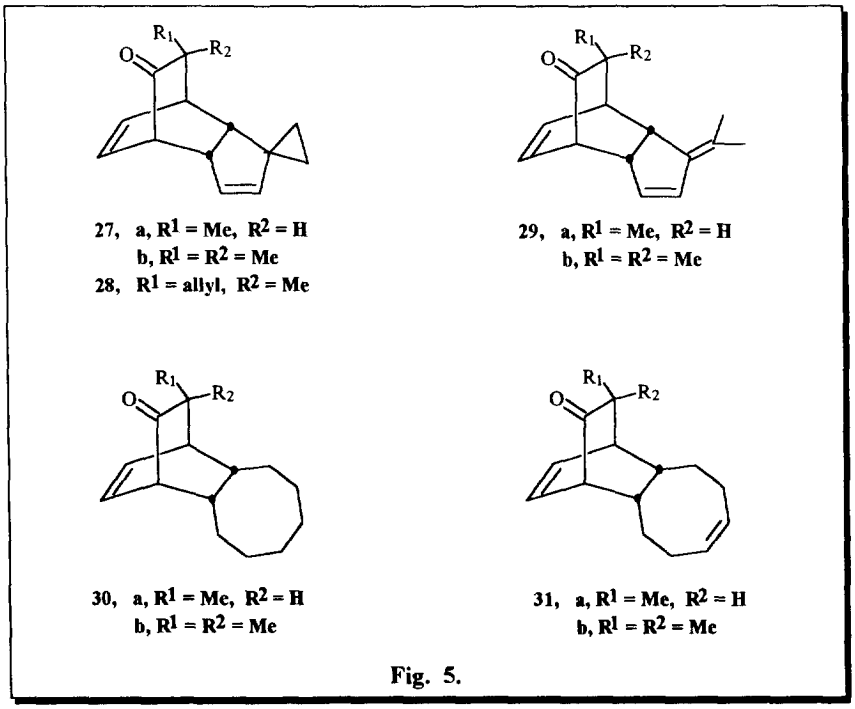


Fig. 5.

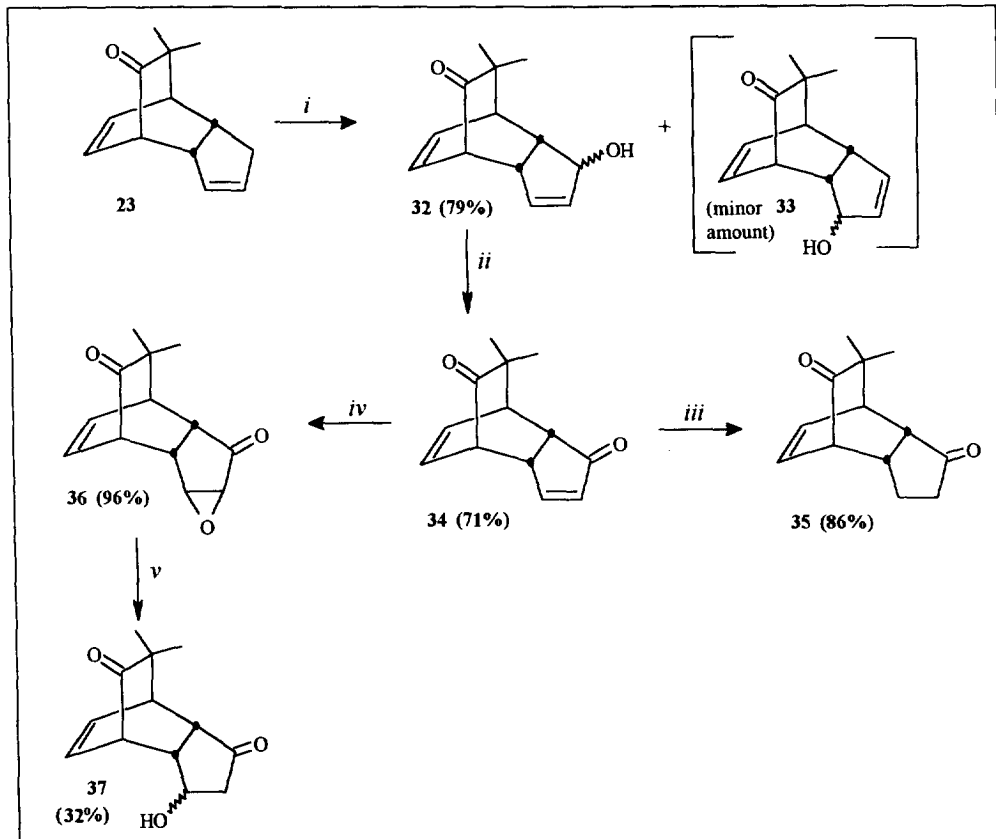
1.3. Manipulation of annulated cyclopentene ring of 23: Synthesis of functionalized chromophores

In order to extend the synthetic potential of the chromophoric system **23**, it appeared desirable to develop methods for the introduction of functional groups into the *endo* annulated five membered ring of the substrate **23**.

Thus, the ketone **23** was treated with selenium dioxide buffered with potassium dihydrogen orthophosphate in refluxing aqueous dioxane.[27] However, it furnished a regioisomeric mixture of alcohols **32** and **33** (which was evident only through inspection of the ^{13}C nmr spectrum of the product obtained from further oxidation of the alcohols). The oxidation of **23** with the same reagent at lower temperatures ~80°C furnished the desired allylic alcohol **32** in good yield (79%), along with minor amounts of rearranged product **33** (Scheme-4). Homogenity of the alcohol **32** was confirmed through its further oxidation with Jones' reagent[28] to the dienedione **34** whose structure was deduced from the following spectral data and analysis of its cosy spectrum. Thus, the ir spectrum of **34** showed two strong absorption bands at 1720 and 1700 cm^{-1} indicating the presence of both isolated and conjugated carbonyl groups.[29] Its ^1H nmr spectrum (300 MHz) displayed the following resonances. The signals at δ 7.4 (dd, J_1=6Hz, J_2=3Hz, 1H, β-proton of α,β-enone group), 6.3 (m, 2H, γ-proton of β,γ-enone group and β-proton of α,β-enone moiety), 5.82 (app. t, J=7Hz, 1H, β-proton of β,γ-enone group) clearly indicated the presence of a conjugated double bond along with the homoconjugated olefinic group. Other resonances were observed at δ 3.3 (m, 1H, methine H), 3.28 (m, 1H), 3.04 (m, 1H), 2.85 (dd, J_1=6Hz, J_2=3.5Hz, 1H, methine H), 1.15 (s, 3H, CH_3) and 1.11 (s, 3H, CH_3). Its ^{13}C nmr spectrum showed resonances at δ 214.4 and 209.6 for enone carbonyl group present in the cyclopentane ring and the carbonyl group in the bicyclo[2.2.2] framework[30] respectively. Further characteristic signals were shown at δ 162.2, 137.4, 135.2, 123.9 (olefinic carbons) 51.5, 45.3, 45.2, 42.4, 27.2, 23.3 for other methine and methyl carbons. That the structure of the above enone is indeed **34** (and hence of the alcohol **32**) and not the alternate regioisomer arising as a result of allylic rearrangement during the selenium dioxide oxidation, was confirmed through cosy analysis as described below. It was observed that the β-proton of α,β-enone moiety (δ, 7.4, dd) correlates with the signal at δ 3.3 (assigned to the proton at the allylic ring junction) and the signal at δ 3.3 showed cross peak with the signal at δ 2.85 (proton at the ring junction adjacent to the enone carbonyl group). Furthermore, the signal at δ 2.85 correlates with the signal at δ 3.04 which inturn showed correlation with both the γ-proton at δ 6.30 and β-proton at δ 5.80 of β,γ-enone moiety in the bicyclo[2.2.2] framework. The above relationship between protons clearly confirmed the formulation **34** for the enone (and hence the structure of **32**).

In this context, it may be mentioned that recent methods[31] of allylic oxidations such as SeO_2/^tBuOOH gave a complex mixture of products, and the reagents such as SeO_2/N-methylmorpholinoxide, SeO_2/Pyridine-N-oxide did not react with **23**. Furthermore, the dienedione **34** was reduced with zinc in refluxing dioxane in the presence of ammonium chloride to furnish the ene-diketone **35** in good yield (86%) (Scheme-4). The compound **35** exhibited the following spectral data. The ir spectrum of **35** showed an absorption band at 1730

cm^{-1} for both the carbonyl groups, which suggested that the conjugated double bond had been reduced. Its ^1H nmr spectrum (300 MHz) exhibited only two signals at δ 6.43 (app. t, J=6Hz, 1H) and 6.16 (app. t, J=6Hz, 1H) which clearly suggested the presence of only β,γ-unsaturated olefinic protons in **35**. Other signals were observed at δ 3.23 (d, J=6Hz, 1H), 3.00 (d, J=6Hz, 1H), 2.32 (br s, 2H), 2.30-2.06 (m, 6H), 1.76-1.6 (m, 1H) for methine and methylene protons, in addition to resonances for methyl groups at δ 1.11 (s, 3H, CH_3) and 1.06 (s, 3H, CH_3). The ^{13}C nmr spectrum of **35** also supported its structure since it displayed characteristic resonances at δ 220.60 for a cyclopentanone carbonyl and at δ 214.92 for the carbonyl group present in the ethano bridge. It also gave signals at δ 137.99 and 125.89 for only two olefinic carbons.



Scheme - 4

Reagents and conditions : *i*, SeO_2, dioxane, Δ; *ii*, Jones' reagent; *iii*, Zn, NH_4Cl, dioxane, Δ; *iv*, H_2O_2, $NaHCO_3$, EtOH; *v*, Zn, NH_4Cl, H_2O : MeOH.

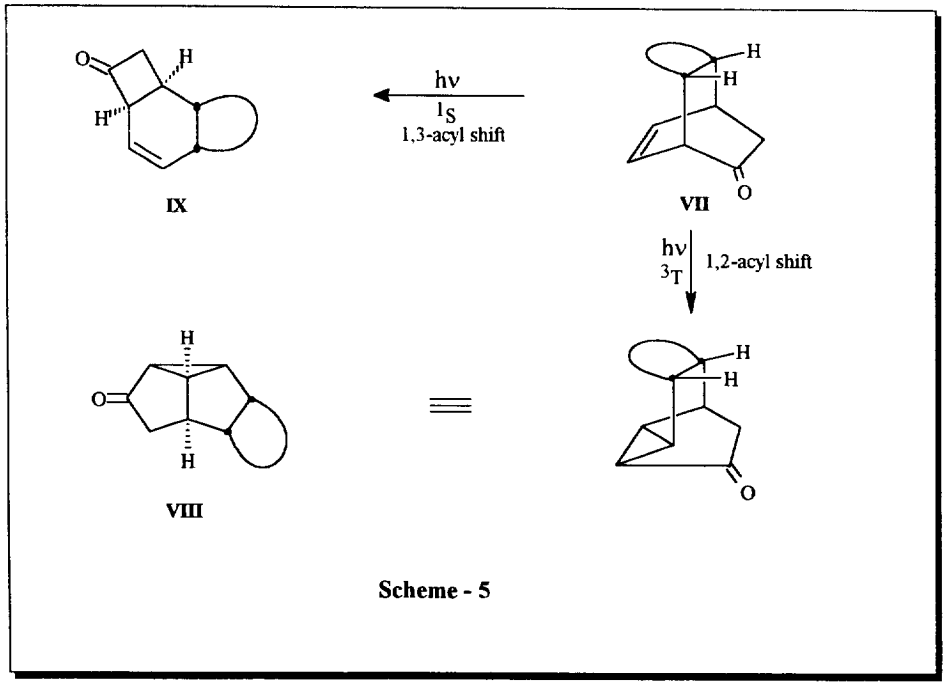
The diene-dione **34** was further converted into epoxy diketone **36** by treatment with alkaline hydrogen

peroxide in ethanol. The structure of the epoxy dione was clearly revealed from its spectral and analytical data. The oxirane ring in **36** was reduced with zinc in protic solvent (CH_3OH-H_2O) to give the hydroxy diketone **37** (Scheme-4). We have thus synthesized a number of *endo* annulated tricyclic systems having a variety of functional groups and appendages, from readily available common precursors.

2. Triplet sensitized 1,2-acyl shift (or oxa-di-π-methane rearrangement) of chromophoric systems and reductive cleavage of the photoproducts: Synthesis of triquinanes and congeners

2.1. Photochemical 1,2-acyl shift (or oxa-di-π-methane rearrangement) of 23-32 and 35.

Constrained β,γ-unsaturated ketones undergo two unique photoreactions upon electronic excitation. The triplet excitation (T_1, π-π^*) of β,γ-enones leads to a stereospecific 1,2-acyl shift with concurrent formation of cyclopropyl ketone, also known as oxa-di-π-methane rearrangement, where as the singlet excitation (S_1, n-π^*) induces a 1,3-acyl shift to give cyclobutanone derivative.[32,33] We contemplated that while the oxa-di-π-methane rearrangement of *endo* annulated tricyclic systems such as VII would provide a *cis:anti:cis* tricyclic core of polyquinane natural products, the 1,3-acyl shift would permit an efficient entry into protoilludane framework in a single stereospecific sequence (Scheme-5).



Scheme - 5

It may be mentioned that, the synthetic potential of the oxa-di-π-methane rearrangement of tricyclic systems was realized only recently.[34] Although the oxa-di-π-methane rearrangement has been employed in

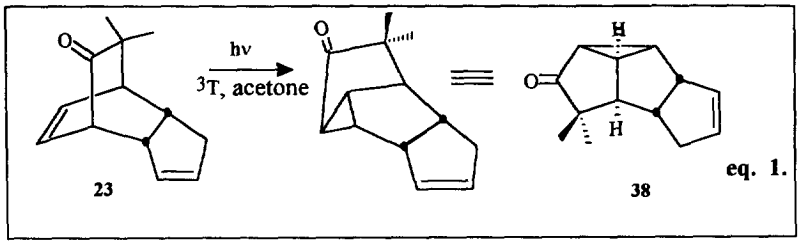
the synthesis of natural products, most of the studies were limited to simple bicyclo[2.2.2]octenones.[33] However, some examples of the use of the oxa-di-π-methane rearrangement towards synthesis of angular triquinane and triquinacene analogoues appeared[35] during our investigation.

Though the oxa-di-π-methane rearrangement and 1,3-acyl shift are characteristic reactions of the excited states, a mixture of products are obtained due to indiscriminate population of the excited states. Moreover, the photoreaction of β,γ-enones are sensitive to structure of the chromophore, functional groups and other substituents in a subtle fashion.[36] In view of the above and structural and functional complexity of the chromophoric systems, their photochemical behaviour towards sensitized irradiation was first explored. Towards this end, an acetone solution of tricycloundecadienone **23** was irradiated with a mercury vapour lamp (200 W, Hanovia) in a pyrex immersion well. Removal of the solvent followed by chromatography of the photolysate on silica gel furnished the desired photoproduct **38** in good yield (54%), along with some unchanged starting material (eq.1). The structure of the photoproduct was deduced from its spectral and analytical data. Thus, the ir spectrum of **38** showed a strong absorption band at 1730 cm^{-1} for the carbonyl group. Its ^1H nmr spectrum (300 MHz) displayed a signal at δ 5.75 (br s, 2H) corresponding to only two olefinic protons, which suggested that β,γ-unsaturated olefinic linkage in **23** had undergone the desired 1,2-acyl shift (or oxa-di-π-methane rearrangement) upon irradiation. It further showed resonances at δ 2.75 (m, 3H), 2.48 (ddd, J_1=17Hz, J_2=9Hz, J_3=1Hz, 1H), 2.35 (d, J=5Hz, 1H), 2.25 (m, 1H), 1.9 (dd, J_1=9.8Hz, J_2=5Hz, 1H), 1.67 (dd, J_1=9.8Hz, J_2=5Hz, 1H), 1.12 (s, 3H, CH_3) and 0.91 (s, 3H, CH_3). The ^{13}C nmr spectrum of the photoproduct also supported its formulation since it exhibited a resonance signal at δ 218.78 for a carbonyl carbon present in the strained five membered ring. Furthermore, it displayed only two signals at δ 133.33 and 131.89 for two olefinic carbons. Other signals were observed at δ 55.07, 53.15, 50.57, 49.87, 38.39, 35.36, 33.12, 28.64, 18.11. These spectral features clearly revealed the structure of the photoproduct as **38** and ruled out any alternate possibility. The *cis:anti:cis* stereostructure of the product followed from the *endo* stereochemistry of the starting chromophore and by comparison of its spectral features with closely related products. It is important to note the remarkable selectivity in the above photochemical reaction since products due to other competing photochemical pathways such as intramolecular $\pi^2s+\pi^2s$ cycloaddition or 1,3-acyl shift were not obtained.

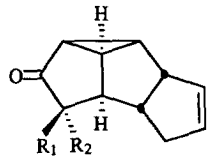
Following the above observation, other tricyclic systems **24, 26-35** were also subjected to sensitized irradiation. All the compounds except **29b** and **34** underwent 1,2-acyl shift (or the oxa-di-π-methane rearrangement) smoothly to furnish the corresponding rearranged products (**39-47**) in reasonably good yields (60%). The structures of all the photoproducts were fully consistent with their spectral data. It is worthy to note that the substrates **24** and **28** containing additional olefinic chromophore also gave the rearranged products **39** and **42** respectively, in good yields (45 and 50%). Similarily, the ene-dione **35** also underwent efficient oxa-di-π-methane rearrangement upon triplet sensitization in acetone.

Interestingly however, the chromophoric system **29b** did not undergo the desired oxa-di-π-methane

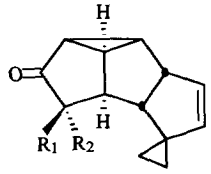
rearrangement upon triplet sensitization (eq.2). The unreactivity of **29b** upon triplet excitation (^{3}T) could be rationalised as being due to the quenching[12,32] effect of the exocyclic 1,3-diene moiety present in the annulated ring. This observation coupled with the fact that the substrate **29b** readily undergoes 1,3-acyl shift upon direct excitation (*vide infra*), further confirms the general understanding regarding reactivity *vs* excited state of β,γ-enones, that 1,2-acyl shift is a photoreaction of triplet (^{3}T, π-π^*) state.



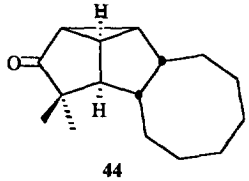
23 **38** eq. 1.



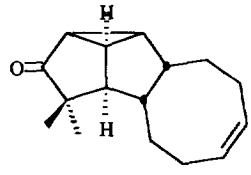
38, $R^1 = R^2 = Me$
39, $R^1 = Me$, $R^2 = allyl$
40, $R^1 = R^2 = H$



41, $R^1 = R^2 = Me$
42, $R^1 = Me$, $R^2 = allyl$



44



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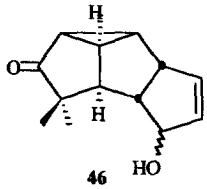

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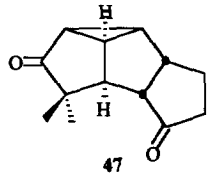
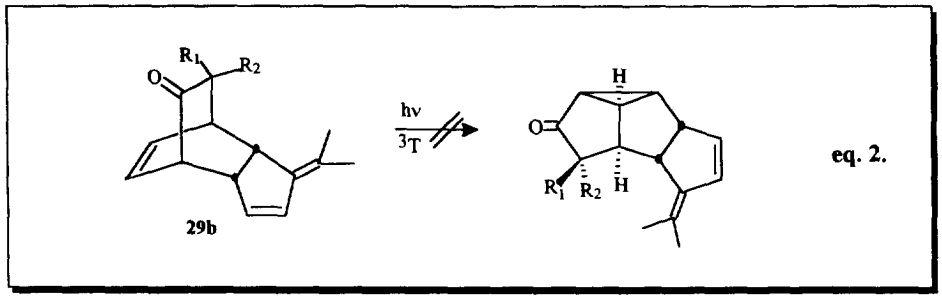


47

Fig. 6.

Moreover, the sensitized irradiation of the dienedione **34** having α,β-enone in addition to a β,γ-enone system furnished a complex mixture of products presumably due to other competing photoreactions such as intramolecular $\pi^2s+\pi^2s$ cycloaddition.



29b eq. 2.

2.2. Cleavage of cyclopropane ring of the tetracyclic photoproducts:

At this juncture it appeared desirable to develop methods for cleavage of the peripheral cyclopropane sigma bond in the products derived from the oxa-di-π-methane rearrangement in order to extend their scope (of the tetracyclic photoproducts) towards synthesis of naturally occurring tricyclopentanoids. Therefore, we briefly investigated cyclopropane ring cleavage of some representative tetracyclic polyquinanes **38**, **44**, **46** and **47**.

There are a number of methods for the cleavage of cyclopropyl conjugated ketones employing either electrophile mediated 1,4-addition or reductive opening,[37,38] the rupture of cyclopropane bond has been found to be controlled by stereoelectronic factors.[39] We first attempted the cleavage of the ketones **38** and **44** with trimethylsilyl iodide especially since it is known to affect cleavage of peripheral cyclopropane bond in simple systems.[40] Thus, the compound **38** was treated with trimethylsilyl iodide generated[41] *in situ* (trimethylsilyl chloride-sodium iodide) in acetonitrile at room temperature (30°C). Chromatography of the product mixture furnished two compounds **48** and **49** (Scheme-6) whose spectral data clearly revealed that the desired peripheral cleavage had not occurred, since both the compounds showed absorption bands at 1710 cm^{-1} characteristic of a six membered ketone. While the ^1H nmr spectrum of the above compounds lacked resonances for olefinic protons, the ^{13}C nmr spectrum of **48** and **49** showed signals at δ 211.06 and 212.09 respectively for carbonyl groups in a six membered ring. Similarly, the cleavage of **44** also gave an undesired product. The products **48** and **49** arise *via* cleavage of the cyclopropane bond followed by addition of HI presumably formed due to presence of residual moisture in the reaction medium. The details of the structure elucidation of **48** and **49** will be described in a forthcoming publication, along with other related results.

We therefore, turned our attention towards reductive cleavage of the above compounds wherein the desired peripheral cleavage was indeed observed. Several reagents have been used for the reductive cleavage[37,38] of a cyclopropane ring, we selected H_2/Pd-C as a reagent for this purpose because of convenience, simplicity and also since it is known to cleave peripheral cyclopropane sigma bonds in some

simple carbocyclic systems.[42] At the outset, however, we knew that this method of cleavage would destroy the olefinic linkages present in some tetracyclic ketones.

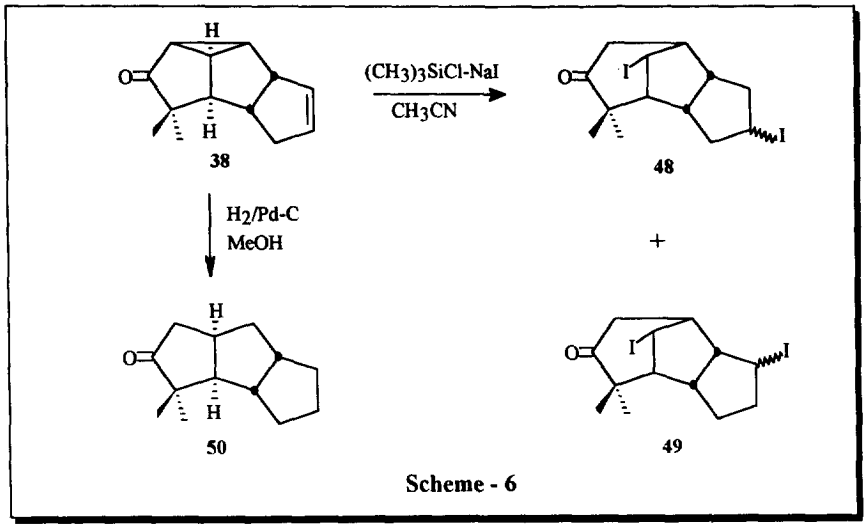
Thus, the tetracyclic ketone **38** was shaken with palladium on carbon (10%) in a hydrogen atmosphere in a parr type apparatus for about 5h. Removal of the catalyst followed by chromatography of the product gave a single desired product **50** (Scheme-6) whose structure was elucidated from its spectral and analytical data as follows. The ^{1}H nmr spectrum (300 MHz) of **50** did not show any resonance signal beyond δ 3.0 which clearly suggested that double bond had been saturated. The presence of fourteen protons of methine and methylene groups at δ 2.79 (m, 1H), 2.6 (m, 1H), 2.45 (ddd, J_1=15Hz, J_2=7Hz, J_3=1Hz, 1H) 2.14 (m, 1H), 1.9-1.8 (m, 3H), 1.7-1.5 (m, 4H), 1.5-1.3 (m, 3H) in addition to resonances at δ 1.08 and 1.04 for methyl groups, suggested that cyclopropane ring had been cleaved. The ^{13}C nmr spectrum of **50** also supported its structure since it exhibited four doublets at δ 61.4, 45.4, 43.0 and 39.3 for four methine carbons and five triplets at δ 40.9, 38.3, 33.9, 33.8 and 25.7 for five methylene carbons. That the above product is indeed a result of cleavage of peripheral cyclopropyl sigma bond leading to **50**, and the distinction between **50** and the alternate possibility **54** was made by a careful analysis of its ir spectrum and comparison of its spectral characteristics with spectral features of its precursor **38** and related compounds as briefly described below.

Thus, the ir spectrum of **50** showed a strong absorption band at 1740 cm^{-1} indicating for a carbonyl group present in a five membered ring. It may be noted that the compound **38**, the progenitor of **50** showed ir absorption band at 1730 cm^{-1} for carbonyl group due to its conjugation with cyclopropane ring. It may be also recalled that the compounds of type **54** resulting from alternate mode of cleavage (e.g.**48** & **49**) show carbonyl absorption band at ~1710 cm^{-1}, in their ir spectrum. The above spectral features clearly revealed the structure of the hydrogenated product as **50** and ruled out any other formulation.

Similarly, the reductive cleavage of **44** and **46** furnished the compounds **51** and **52** (Fig.7) as a result of desired peripheral cleavage of cyclopropyl sigma bond. The keto alcohol **52** was oxidized with Jones' reagent to the linearly fused *cis:anti:cis* tricyclic dione **53**, whose structure was also deduced by careful analysis of its ^{1}H nmr (200MHz), ^{13}C nmr (50MHz) and other spectral/analytical data. Thus, its ir spectrum showed a carbonyl absorption band at 1742 cm^{-1}, characteristic for carbonyl groups present in the five membered ring. Its ^{1}H nmr spectrum though complex, showed signals for twelve protons corresponding to methine and methylene groups, at δ 2.8-2.5 (cluster of m, 4H), 2.37 (d, overlapped with a m, J=8Hz, 1H), 2.30 (dd, J_1=15.5Hz, J_2=8Hz, 1H), 2.22-1.8 (cluster of m, 6H) and two singlets at δ 1.13 and 1.06 for methyl protons. Its ^{13}C nmr also exhibited a characteristic signal at δ 221.8 for cyclopentanone carbonyls and other signals at δ 58.9, 53.0, 50.0, 43.2, 38.2, 36.0, 34.0, 26.4, 25.3 and 19.9 for methine methylene methyl and quaternary carbons.

After having established the potential of our methodology, cycloaddition -- oxa-di-π-methane rearrangements -- reductive cleavage towards synthesis of *cis:anti:cis* tricyclopentanoids, we undertook to

study the photochemical 1,3-acyl shift of some of the tricyclic systems (**23, 24, 27, 29b, 31b, 36** and **55**) upon singlet excitation (^1S), which is presented below.



Scheme - 6

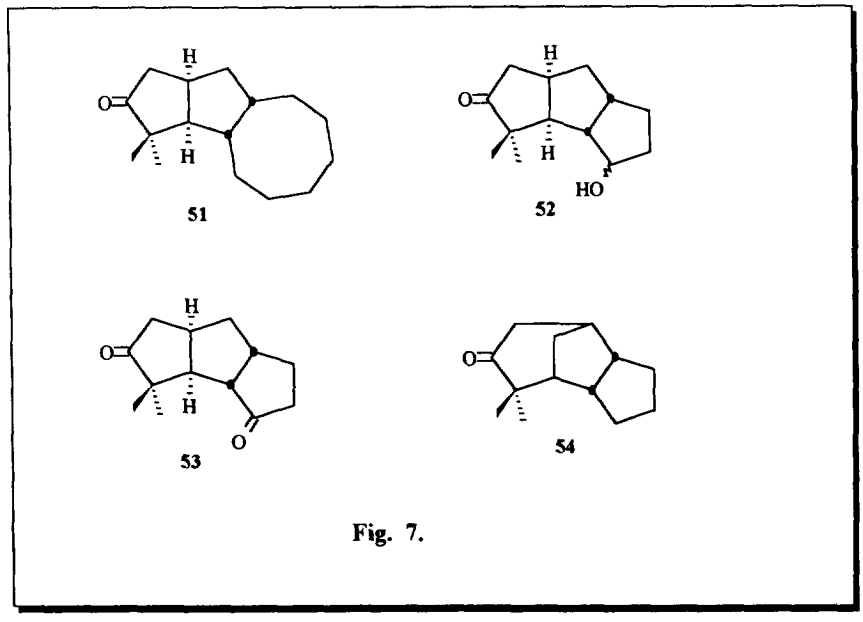
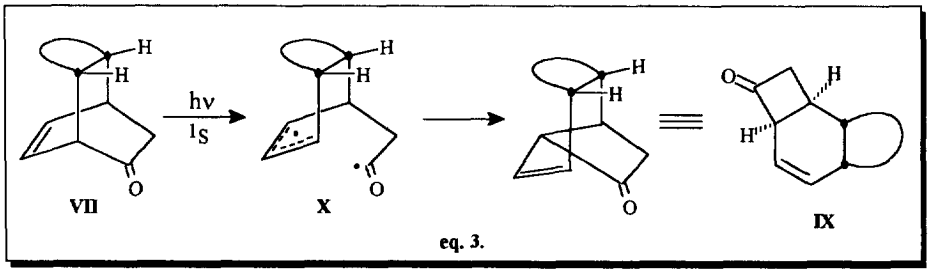


Fig. 7.

3. Studies on singlet excitation of the chromophoric systems (23, 24, 27, 29b, 31b, 36 and 55): Sigmatropic 1,3-acyl shift and a novel, general route to protoilludane framework.

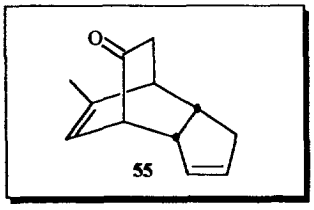
Protoilludanoids belong to a class of compounds having a tricyclic framework composed of fused four, six and five membered rings, generated in nature *via* humulene cyclisation cascade.[1] There has been a considerable interest in the chemistry of the protoilludanoids in the past[5,6] which has been further enhanced recently due to isolation of several biologically active protoilludanoids from *Armillaria Mellea*.[7] In view of the above and the correlation between the protoilludanoidal framework and the *endo* tricyclic systems of type **6** *via* a sigmatropic 1,3-acyl shift (Scheme-1) led us to explore the photoreaction of the chromophoric systems (**23, 24, 27, 29b, 31b, 36** and **55**) in their excited singlet (^{1}S) state.

As we have mentioned earlier, the 1,3-acyl shift is one of the photoreactions of β,γ-enones. However, 1,3-acyl shift in complex multichromophoric systems were neither explored nor its synthetic potential appreciated until our preliminary communication.[13] Most of the earlier studies on 1,3-acyl shift in simple bicyclic systems were conducted in conjuction with the oxa-di-π-methane rearrangements, in order to elucidate the mechanism and resolve singlet-triplet dichotomy.[12] While the dichotomy regarding reactive states *vs* nature of products in photoreaction of β,γ-enones still persists,[32-34,43] it is generally believed that 1,3-acyl shift may occur either from the excited singlet state (^{1}S) and/or from $^3T_2$ state and the reaction proceeds through initial α-cleavage to give the diradical intermediate (X) which gives the final product after ring closure (eq.3). It may be mentioned that the final product formed as a result of 1,3-acyl shift is a highly reactive substrate since it possesses a cyclobutanone homoconjugated with π bond which is known to undergo further photoreaction such as decarbonylation and other reactions during irradiation.[44]



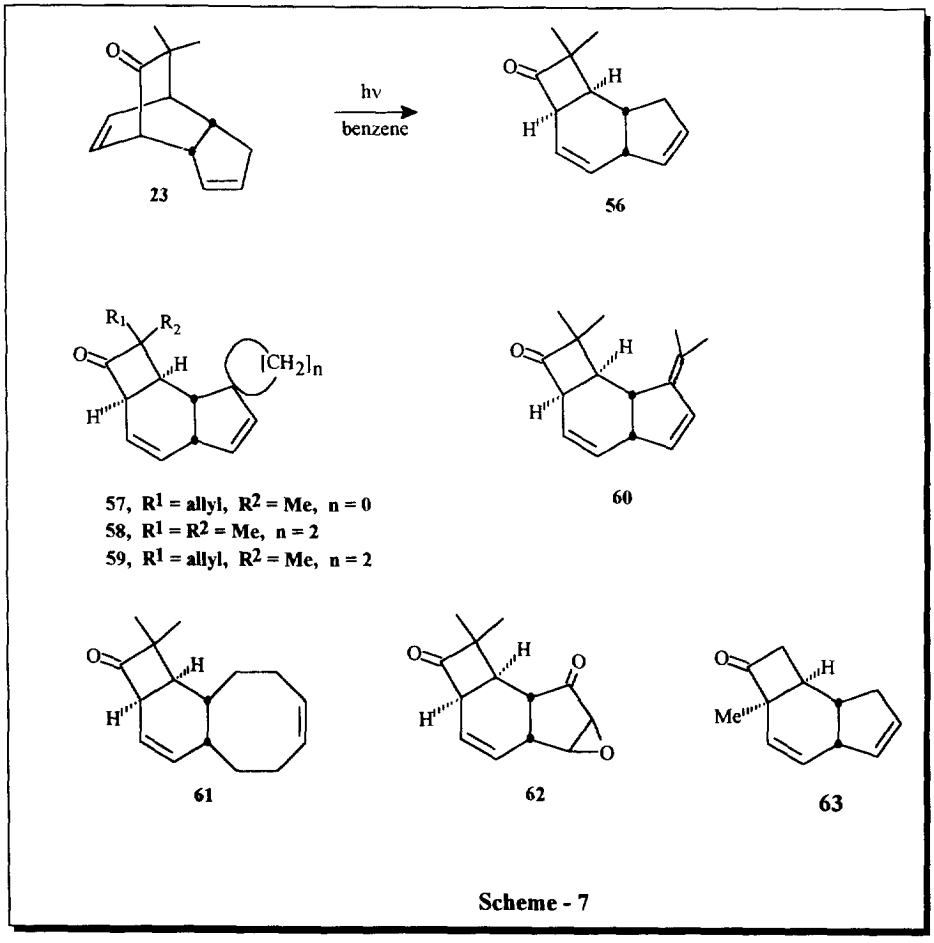
eq. 3.

In view of the above the photochemical behaviour of **23, 24, 27, 29b, 31b, 36** and **55** upon direct excitation was investigated. Synthesis of all the chromophoric system except **55** has been described in earlier section. The compound **55** was prepared from 4-methyl salicyl alcohol following the methodology described earlier.



55

Towards the above objective, we first explored the photoreaction of ketone **23** upon direct excitation. Thus, a solution of **23** in dry benzene was irradiated (200 W Hg vapour lamp, Hanovia) in a quartz immersion well. However, it gave a very complex mixture of products containing only a small amount of the desired 1,3-acyl shift product, as revealed through ir spectroscopy which showed a weak band at 1780 cm^{-1} for a cyclobutanone carbonyl group. Therefore, a solution of **23** in benzene was irradiated in a pyrex immersion well upon which a clean reaction occurred (thin layer chromatography, and ir). After 3 hours of irradiation, the solvent was removed *in vacuo* and the photolysate was carefully chromatographed on silica gel. Elution with petroleum ether-ethyl acetate (98:2) furnished the desired 1,3-acyl shift product **56** (Scheme-7) in 37% yield followed by recovery of some unchanged starting material.



Scheme - 7

The structure of the photoproduct **56** was deduced through its spectral data and comparison with the spectral features of its progenitor. The ir spectrum of **56** showed a strong absorption band at 1785 cm^{-1} characteristic of a carbonyl group in cyclobutane ring.[30] Its ^1H nmr (300 MHz) spectrum exhibited a complex multiplet at δ 5.6 for four olefinic protons indicating a major structural reorganization. It further displayed signals at δ 3.7 (m of dd, J_1=8.5Hz, J_2=4.8Hz, J_3=2Hz, 1H, H1) and 3.15 (m of d, J=8.5Hz, 1H, H4) for protons at cyclobutanone ring junction. The ^{13}C nmr spectrum of **56** showed a resonance at δ 214.77 for carbonyl carbon and signals at δ 133.26, 129.42, 128.38, 119.14 (olefinic carbons) in addition to other resonances for methine, methylene and quaternary carbons. Its mass spectrum showed a weak peak at 188 (M^+) and a prominent peak at 118. The above spectral features clearly revealed the structure **56** for the photoproduct.

Irradiation of the other chromophoric systems (**24, 27, 29b, 31b, 36 and 55**) in dry benzene also gave the corresponding protoilludanoids **57-63** (Scheme-7) respectively, in reasonably good yields (50%). It is interesting to note that the chromophoric system **29b** having exocyclic 1,3-diene moiety in its cyclopentane ring, which did not undergo any photoreaction upon triplet sensitization (*vide supra*), underwent 1,3-acyl shift in its excited singlet state (^1S) smoothly and furnished the tricyclic compound **60** upon direct irradiation. This is presumably due to the fact that excited triplet state of **29b** is quenched by another molecule of itself because of presence of diene moiety which is known to be good quencher of triplet excited state. This observation further confirms the general understanding regarding reactivity *vs* excited state of β,γ-enones that the triplet excitation leads to the oxa-di-π-methane rearrangement or 1,2-acyl shift whereas 1,3-acyl shift is observed upon singlet excitation.

It is further remarkable to note that the chromophoric system **36**, containing α,β-epoxy ketone, a highly reactive chromophore, also underwent sigmatropic 1,3-acyl shift selectively to furnish the highly functionalized system **62**. The ir spectrum of **62** also showed strong absorption bands at 1785 cm^{-1} and 1740 cm^{-1} for cyclobutanone and cyclopentanone carbonyl groups, respectively. Its ^1H nmr spectrum (300 MHz) exhibited signals at δ 5.93 (dd of d, J_1=9Hz, J_2=6Hz, J_3=2.5Hz, 1H) and 5.74 (superimposed dd of d, J_1=9Hz, J_2=2.5Hz, 1H) for two olefinic protons. It further showed signals at δ 3.89 (d, J=3Hz, 1H), 3.42 (d, J=3Hz, 1H) corresponding to protons at oxirane ring junction and at 3.7 (m of dd, J=8Hz, 1H), 3.33 (m of d, J=8Hz, 1H) for methine protons at cyclobutanone ring junction respectively. The other two protons at cyclopentanone ring junctions were observed at δ 2.93 (d, J=10Hz, 1H) and 2.82 (d with structure, J=10Hz, 1H) respectively. In addition, the methyl groups appeared at δ 1.3 (s, 3H) and 1.19 (s, 3H). Other 1,3-acyl products also exhibited similar spectral features and fully supported the structures of the photoproducts. It may be however, noted that the 1,3-acyl shift product **56-63** were extremely labile and their storage even at low temperature caused disintegration.

In summary, we have developed a novel, general and efficient protocol for protoilludanoids and linearly fused *cis:anti:cis* tricyclopentanoids from common precursors having β,γ-enone chromophores *via*

modulation of their photoreactivity through excited singlet (^{1}S) and triplet (^{3}T) state. We have also described synthesis of the desired tricyclic systems having β,γ-unsaturated carbonyl chromophore from readily available starting material. Strategic application of both the methodologies towards synthesis of natural protoilludanes and tricyclopentanoids is under way.

EXPERIMENTAL:

General remarks: IR spectra were recorded on a Perkin Elmer 681 and Nicolet FT-IR instrument Impact 400. UV spectra were recorded on Schimadzu 260 instrument. ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75 MHz) spectra were recorded on varian VXR 300s instrument. Some ^{1}H-NMR spectra (500 MHz) were taken on a Brucker instrument. All the samples were dilute solutions in $CDCl_3$ with $SiMe_4$ as internal standard. Melting points were taken on a Veego apparatus and are uncorrected. Elemental analyses were performed on a CEST 1106 instrument. All the organic extracts were dried over anhydrous sodium sulfate. Reactions were monitored with tlc and spots visualized with iodine vapour. Column chromatographic separations were done on silica gel (60-120 mesh). Petroleum ether used for column chromatography and recrystallization refers to light petroleum ether (bp 60-80°C).

9-Spiroepoxy-*endo*-tricyclo[5.2.2.0^{2,6}]undeca-4,10-dien-8-one (15):

To a mixture of salicyl alcohol (2.5g, ~20mmol), cyclopentadiene (8ml, excess) and cetyltrimethyl ammonium bromide (CTAB) (0.300g, 0.82mmol) in dichloromethane (30ml) was added an aqueous solution of sodium metaperiodate (10g, 46.75mmol) dropwise with stirring at 5°C. After stirring for 3h, the dichloromethane layer was separated and the aqueous layer was extracted with dichloromethane (4x50ml). The combined organic extract was washed with water (2x20ml), brine (2x20ml) and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel. Elution with petroleum ether-ethyl acetate (95:5) gave the adduct **15** (3.16g, 83%). IR (neat) ν_{max}: 3050, 1740 cm^{-1}. UV (MeOH) λ_{max}: 214, 305 nm. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 6.40 (app. t, J=7.5Hz, 1H, COCHRCH=C<u>H</u>-), 6.13 (app. t, J=7.5Hz, 1H, COCHRC<u>H</u>=CHR), 5.73 (m of d, J=6Hz, 1H, olefinic), 5.48 (m of d, J=6Hz, 1H, olefinic), 3.38 (d overlapped with a m, total 2H, methine H), 3.14 (d, J=6Hz, 1H, OCH<u>H</u>), 3.05 (m, 1H, methine H), 2.84 (d, J=6Hz, 1H, OCH<u>H</u>), 2.63 (m overlapped with another m, 1H), 2.6 (m, 1H, CH_2) and 2.05 (m of d, J=18Hz, 1H, CH_2 group). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 204.9 (s), 133.0 (d), 131.8 (d), 129.1 (d), 128.7 (d), 57.6 (s), 52.3 (t), 51.8 (d), 49.9 (d), 43.4 (d), 38.0 (t) and 35.7 (d). Mass (m/z): 188 (M^+).

9-Spiroepoxy-*endo*-tricyclo[5.2.2.0^{2,6}]undeca-4,10-dien-3-spirocyclopropan-8-one (16):

Oxidation of salicyl alcohol (2.5g, ~20mmol) in the presence of spiro[4,2]hepta-1,3-diene (12ml,

excess) followed by workup as described above gave a crude product, which was chromatographed on silica gel. Elution with petroleum ether-ethyl acetate (95:5) gave the adduct **16** (3.53g, 82%) as a solid, which was recrystallized from petroleum ether-ethyl acetate (92:8), mp 92°C. IR (KBr) ν_{max}: 3080, 3020, 2940, 2900, 1730 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$):δ 6.47 (app. t, J=8Hz, 1H, COCHRCH=C<u>H</u>-), 6.10 (app. t, J=8Hz, 1H, COCHRC<u>H</u>=CHR), 5.43 (dd, J_1=6Hz, J_2=2Hz, 1H, olefinic), 5.20 (m of d, J=6Hz, 1H, olefinic), 3.57 (d with str, J=8Hz, 1H, methine H), 3.45 (complex m, 1H, methine H), 3.13 (d, J=6Hz, 1H, OCH<u>H</u>), 2.8 (d, J=6Hz, overlapped with another m, total 2H, OCH<u>H</u> and methine H), 2.4 (m, 1H, methine H), 0.75 (m, 3H, cyclopropyl H) and 0.60 (m, 1H, cyclopropyl H). ^{13}C-NMR (22.5 MHz, $CDCl_3$):δ 205.2 (s), 141.4 (d), 132.6 (d), 127.7 (d), 126.5 (d), 57.1 (s), 52.7 (d), 52.7 (t), 50.6 (d), 42.9 (d), 41.6 (d), 32.6 (s), 14.8 (t) and 10.5 (t). Mass (m/z): 214 (M^+). Analysis: Found C,78.10; H,6.30% Calcd for $C_{14}H_{14}O_2$ C,78.50; H,6.54%.

9-Spiroepoxy-*endo*-tricyclo[5.2.2.$0^{2,6}$]undeca-4,10-dien-3-iso propylidine-8-one (17):

Oxidation of salicyl alcohol (2.0g, ~16mmol), with sodium metaperiodate (8.0g, excess) in the presence of dimethylfulvene (10ml, excess) as described earlier followed by workup and chromatography of the crude product on silica gel furnished the adduct **17** (2.92g, 79%). IR (nujol) ν_{max}: 1735cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 6.43 (dd, J_1=6Hz, J_2=2Hz, 1H, olefinic), 6.32 (app. t, J=7.5Hz, 1H, COCHRCH=C<u>H</u>-), 6.0 (app. t, J=7.5Hz, 1H, COCHRC<u>H</u>=CHR), 5.62 (d, J=6Hz, 1H, olefinic), 3.54-3.40 (m, 3H, methine H), 3.12 (d, J=7.5Hz, 1H, OCH<u>H</u>), 2.86 (d, J=7.5Hz, overlapped with another m, total 2H, OCH<u>H</u> and methine H), 1.78 (s, 3H, CH_3) and 1.71 (s, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 205.1 (s), 140.2 (s), 135.1 (d), 132.1 (d), 132.1 (d), 127.3 (d), 123.5 (s), 57.7 (s), 52.8 (d), 52.0 (d), 48.2 (d), 42.5 (d), 40.8 (t), 20.9 (q) and 20.8 (q). Mass (m/z): 228 (M^+).

12-Spiroepoxy-*endo*-tricyclo[8.2.2.$0^{2,9}$]tetradec-13-en-11-one (18):

To a stirred solution of the chloro alcohol **20** (2.0g, 7.5mmol) in chloroform (50ml) was added CTAB (0.05g, ~0.02mmol), and aqueous KOH (10ml, 1M) at room temperature (~30°C). After the reaction was complete (tlc), the organic layer was separated and washed with water (2x20ml), brine (2x20ml) and dried. Removal of solvent and column chromatography [(petroleum ether-ethyl acetate) (95:5)] of the residue gave the compound **18** (1.6g, 92%) as a solid, which was recrystallized from petroleum ether-ethyl acetate (90:10), mp 101-102°C. IR (nujol) ν_{max}: 1725 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 6.48 (app. t, J=7.5Hz, 1H, COCHR-CH=C<u>H</u>-), 6.25 (app. t, J=7.5Hz, 1H, COCHR-C<u>H</u>=CHR), 3.17 (m of d, J=6Hz, 1H, methine H), 3.10 (d, J=6Hz, 1H, OCH<u>H</u>), 2.82 (d, J=6Hz, 1H, OCH<u>H</u>), 2.42 (m of d, J=7Hz, 1H, methine H), 2.34 (br t, J=10Hz, 1H, methine H), 2.23 (br t, J=10Hz, 1H, methine H), 1.7-1.3 (m, 12H, methylene H). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 205.8 (s), 133.4 (d), 128.0 (d), 58.4 (d), 57.5 (s), 52.9 (t),

49.0 (t), 41.7 (d), 39.6 (d), 30.6 (t), 30.5 (t), 29.8 (t), 29.5 (t), 25.8 (t) and 25.7 (t). Mass (m/z): 232 (M^+). Analysis: Found C,77.25; H,8.35% Calcd for $C_{15}H_{20}O_2$ C,77.50; H,8.62%.

12-Spiroepoxy-*endo*-tricyclo[8.2.2.0^{2,9}]tetradeca-5,13-dien-11-one (19):

A solution of the chloro alcohol **21** (3.5g, 13mmol) in chloroform (60ml) was treated with aqueous KOH (15ml, 1M) in the presence of CTAB (0.08g, ~0.03mmol) at room temperature for 3h. The reaction mixture was worked up as described above and the product was chromatographed on silica gel. Elution with petroleum ether-ethyl acetate (95:5) gave the compound **19** (2.74g, 91%), mp 93-94°C. IR (nujol) ν_{max}: 1730 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 6.47 (app. t, J=7Hz, 1H, COCHR-CH=C<u>H</u>-), 6.23 (app. t, J=7Hz, 1H, COCHR-C<u>H</u>=CHR), 5.74 (m, 2H, olefinic), 3.17 (m, overlapped with a d, J=6Hz, total 2H, methine H and OCH<u>H</u>), 2.80 (d, J=6Hz, 1H, OC<u>H</u>H), 2.6-2.3 (m, 5H, methylene H), 2.2-1.6 (m, 6H, methylene H). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 205.5 (s), 133.7 (d), 131.6 (d), 131.1 (d), 128.4 (d), 57.4 (s), 56.8 (d), 52.9 (t), 47.5 (d), 40.7 (d), 38.9 (d), 32.8 (t), 32.4 (t), 25.8 (t) and 25.5 (t). Mass (m/z): 230 (M^+). Analysis: Found C,78.17; H,8.07% Calcd for $C_{15}H_{18}O_2$ C,78.20; H,7.80%.

9-Methyl-*endo*-tricyclo[5.2.2.0^{2,6}]undeca-4,10-dien-8-one (22):

To a suspension of zinc (8g, excess) and ammonium chloride (0.25g, excess) in dry dioxane (50ml) was added a solution of the adduct **15** (1.8g, 9.6mmol) in dioxane (10ml) all at once. The reaction mixture was then heated at 80°C for about 7h. It was then cooled and filtered to remove zinc and washed with a small amount of dioxane. The dioxane was removed *in vacuo* and the residue was diluted with water (20ml) and extracted with ether (4x20ml). The combined ether layer was washed with water (2x15ml), brine (2x15ml) and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was chromatographed. Elution with petroleum ether-ethyl acetate (97:3) gave the compound **22** (1.27g, 76%) as a *syn:anti* mixture (2.6:1). IR (neat)ν_{max}: 1725 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 6.42 and 6.3 (app. t, J=~8Hz, total 1H, COCHRCH=C<u>H</u>-), 6.02 (2xdd, overlapped, 1H, COCHR-C<u>H</u>=CH), 5.64 (m, 1H, olefinic), 5.40 (m, 1H, olefinic), 3.1 (m, 2H, methine H), 2.86 (br m, 1H, methine H), 2.7 (m, 1H, methine H), 2.54 (m of d, J_1=18Hz, 1H, methylene H), 2.10-1.98 (2xm, 2H, methine and methylene H), 1.16 and 1.10 (d, J=~6Hz, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 215, 214.3, 135.55, 133.5, 132.7, 132.5, 130.06, 130.00, 127.9, 127.1, 52.4, 52.3, 50.0, 48.8, 44.2, 43.3, 42.6, 40.1, 38.6, 38.5, 33.7, 17.0 and 13.8. Mass (m/z): 174 (M^+).

9,9-Dimethyl-*endo*-tricyclo[5.2.2.0^{2,6}]undeca-4,10-dien-8-one (23):

Sodium hydride (0.5g, 20.8mmol) was placed in a dry two necked flask, and washed with dry pentane and tetrahydrofuran (35ml) was added. A solution of the ketone **22** (1.15g, 6.6mmol) in tetrahydrofuran

(5ml) was added to the reaction mixture and it was refluxed for 1h. Methyl iodide (5ml, excess) in tetrahydrofuran (3-4ml) was added dropwise to the reaction mixture and further refluxed for 6h. It was quenched with cold water and the reaction mixture was filtered and tetrahydrofuran was removed *in vacuo*. The residue was extracted with ether (3x20ml) and washed with water (2x15ml), brine (2xl5ml) and dried over anhydrous sodium sulfate. Removal of solvent and chromatography [(petroleum ether-ethyl acetate) (97:3)] furnished the alkylated product **23** (1.16g, 95%) as a liquid. IR (neat) ν_{max}: 1725 cm^{-1}. UV (MeOH) λ_{max}: 296, 217 nm. ^{1}H-NMR (270 MHz, $CDCl_3$):δ 6.35 (app. t, J=8Hz, 1H, COCHR-CH=C<u>H</u>R), 6.05 (app. t, J=8Hz, 1H, COCHR-C<u>H</u>=CHR), 5.65 (m, 1H, olefinic), 5.45 (m, 1H, olefinic), 3.1 (br m, 2H, methine H), 2.98 (m, 1H, methine H), 2.69 (br m, 1H, methine H), 2.50 (dd, J_1=18Hz, J_2=9Hz, 1H, methylene H), 1.98 (d, J=18Hz, 1H, methylene H), 1.10 (s, 3H, CH_3) and 1.08 (s, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 215.22, 134.97, 132.11, 129.77, 126.13, 52.12, 48.35, 48.35, 43.28, 37.95, 34.83, 27.02 and 23.12. Mass (m/z): 188 (M^+).

9-Allyl-9-methyl-*endo*-tricyclo[5.2.2.0^{2,6}]undeca-4,10-dien-8-one (24):

Alkylation of the ketone **22** (1.0g, 5.7mmol) with allyl bromide (5.0ml, excess) as described earlier gave the product **24** (0.78g, 89%) after chromatography [(petroleum ether-ethyl acetate) (97:3)]. IR (neat) ν_{max}: 1720, 1650 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 6.33 (app. t, J=8Hz, 1H, COCHR-CH=C<u>H</u>-), 6.03 (app. t, J=8Hz, 1H, COCHR-C<u>H</u>=CH-), 5.8 (m, 1H, olefinic), 5.66 (m, 1H, olefinic), 5.44 (m, 1H, olefinic), 5.06 (m, 2H, olefinic), 3.13 (m, 2H), 2.9 (m, 1H, methine H), 2.78 (br m, 1H, methine H), 2.5 (dd, J_1=18Hz, J_2=10Hz, 1H, methylene H), 2.2 (dd, J_1=12Hz, J_2=8Hz, 1H, methylene H), 2.08 (dd, J_1=12Hz, J_2=8Hz, 1H, methylene H), 1.8 (m of d, J=18z, 1H, methylene H) and 1.14 (s, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 216.1 (s), 134.9 (d), 133.7 (d), 132.9 (d), 130.2 (d), 126.7 (d), 117.8 (t), 53.0 (d), 49.8 (d), 47.0 (s), 45.7 (d), 43.4 (t), 38.7 (d), 35.1 (d) and 20.6 (q). Mass (m/z): 214 (M^+).

9-Hydroxymethyl-*endo*-tricyclo[5.2.2.0^{2,6}]undeca-4,10-dien-8-one (25):

To a suspension of activated zinc (12g, excess) in CH_3OH-H_2O (7:1, 45ml) was added a solution of the epoxy ketone **15** (3.72g, 19.8mmol) in methanol (10ml), followed by ammonium chloride (0.3g, excesss) and the reaction mixture was stirred at room temperature ~30°C for about 6 hours. Usual workup and chromatography [(petroleum ether-ethyl acetate) (85:15)] furnished the compound **25** (2.77g, 77%) as a *syn:anti* mixture (3.8:1). IR (neat) ν_{max}: 3500, 1725 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 6.44 and 6.30 (app. t, J=~8Hz, 1H, COCHR-CH=C<u>H</u>-), 6.05 (m, 1H, COCHR-C<u>H</u>=CH-), 5.65 (m of d, J=~6Hz, 1H, olefinic), 5.42 (m, 1H, olefinic), 3.9 (dd, J_1=9Hz, J_2=6Hz, 1H), 3.60-3.50 (m, 2H), 3.10 (m, 3H), 2.84-2.7 (m, 1H, methine H), 2.55 (dd, J_1=17Hz, J_2=9Hz, 1H, methylene H), 2.25 (m, 1H), 2.0 (m of d, J=17Hz, 1H, methylene H). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 214.48, 231, 135.08, 133.57, 132.72, 129.60,

129.50, 127.89, 126.75, 63.51, 61.01, 52.49, 52.33, 51.82, 50.10, 49.95, 48.57, 39.66, 39.35, 39.05, 38.42, 34.13 (for each isomer). Mass (m/z): 190 (M^+).

***endo*-Tricyclo[5.2.2.$0^{2,6}$]undeca-4,10-dien-8-one (26):**

A solution of the keto alcohol **25** (1.2g, 6.3mmol) in acetone (30ml) was oxidized with freshly prepared Jones' reagent. The solvent was removed under reduced pressure and residue was extracted with ethyl acetate (4x20ml). The combined extract was washed with water (2x15ml), brine (2x20ml) and dried over anhydrous sodium sulfate. Removal of solvent gave the β-keto acid (1.1g, 85%; IR ν_{max}: 3350 cm^{-1}), which was subjected to decarboxylation as follows. The β-keto acid (0.46g, 2.5mmol) was taken in tetrahydrofuran (15ml) and aqueous barium hydroxide (20ml) was added to it and the reaction mixture was refluxed for about 12 hours. The reaction mixture was brought to room temperature and tetrahydrofuran was removed under vacuum and the aqueous medium was extracted with ether (4x20ml). The combined extract was washed with sodium bicarbonate (2x20ml), water (2x20ml), brine (2x20ml) and dried. Removal of solvent followed by chromatography [(petroleum ether-ethyl acetate) (98:2)] gave the parent system **26** (0.32g, 50%) as a colourless liquid. IR (neat) ν_{max}: 1730 cm^{-1}. UV (MeOH) λ_{max}: 208, 293 nm. ^{1}H-NMR (500 MHz, $CDCl_3$):δ 6.33 (app. t, J=7.5Hz, 1H, COCHR-CH=C<u>H</u>-), 6.03 (app. t, J=7.5Hz, 1H, COCHR-C<u>H</u>=CH-), 5.63 (m, 1H, olefinic), 5.42 (m, 1H, olefinic), 3.18 (br d, J=7.5Hz, 1H, methine H), 3.12 (d, J=7.5Hz, 1H, methine H), 3.0 (br, 1H, methine H), 2.65 (m, 1H, methine H), 2.54 (dd, J_1=16Hz, J_2=10Hz, 1H, methylene H), 2.05 (d, J=2Hz, 2H, methylene H), 1.98 (d with str, J=16Hz, 1H, allylic methylene H). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 212.8, 134.4, 132.6, 130.1, 128.2, 52.6, 49.5, 40.3, 39.9, 38.9 and 37.7. Mass (m/z): 160 (M^+).

9-Methyl-*endo*-tricyclo[5.2.2.$0^{2,6}$]undeca-4-10-dien-3-spiro cyclopropan-8-one (27a):

The epoxy ketone **16** (3g, 14mmol) was reduced with activated zinc (15g, excess) in dry dioxane (60ml) containing ammonium chloride (0.3g, excess) at ~80°C as described earlier. The reaction was worked up and the product was chromatographed [(petroleum ether-ethyl acetate) (97:3)] on silica gel to give **27a** as *syn:anti* mixture (3:1), (2.18g, 80%). IR (neat) ν_{max}: 1725 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 6.45 and 6.30 (app. t, J=7.5Hz, total 1H, olefinic), 6.0 (app. t, J=7.5Hz, 1H, olefinic), 5.38 (dd, J_1=6Hz, J_2= ~3Hz, 1H, olefinic), 5.15 (m, 1H, olefinic), 3.44 and 3.34 (d, J=9Hz, total 1H), 3.2 (m, 1H), 2.60-2.50 (m, total 2H), 2.25 and 1.9 (q, J=6Hz, total 1H), 1.08 (two sets of d, J=6Hz, total 3H, CH_3) and 0.8-0.5 (m, 4H, cyclopropyl H). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 215.1, 214.0, 141.02, 140.8, 136.14, 134.06, 127.35, 126.71, 125.93, 53.43, 53.26, 50.61, 49.41, 47.32, 43.45, 42.11, 41.94, 41.16, 40.88, 32.78, 32.60, 17.21, 15.05, 13.92, 10.97 and 1.86. Mass (m/z): 200 (M^+).

9,9-Dimethyl-*endo*-tricyclo[5.2.2.0^{2,6}]undeca-4,10-dien-3-spiro cyclopropan-8-one (27b):

To a suspension of sodium hydride (0.8g, 33.3mmol) in dry tetrahydrofuran (35ml) was added a solution of the ketone **27a** (1.6g, 8mmol) in tetrahydrofuran (6ml) and the reaction mixture was refluxed for 1h. Methyl iodide (8ml, excess) in tetrahydrofuran (3ml) was added with stirring and the refluxing was continued for 7h. The reaction mixture was cooled, water (10ml) was added to it and filtered. The filtrate was concentrated under vacuum. The residue was acidified with dilute hydrochloric acid and extracted with ether (4x20ml). The combined extract was washed with water (2x20ml), brine (2x20ml) and dried over anhydrous sodium sulfate. Removal of solvent followed by chromatography [(petroleum ether-ethyl acetate) (97:3)] of the crude product furnished the compound **27b** (1.37g, 85%) as liquid. IR (nujol) ν_{max}: 1730 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 6.40 (app. t, J=7Hz, 1H, COCHR-CH=C<u>H</u>-), 5.95 (dd, J_1=8Hz, J_2=6Hz, 1H, COCHR-C<u>H</u>=CH-), 5.39 (dd, J_1=5.5Hz, J_2=2.5Hz, 1H, olefinic), 5.17 (dd, J_1=5.5Hz, J_2=1.8Hz, 1H, olefinic), 3.41 (d, J=8.8Hz, 1H, methine H), 3.17 (d, J=3.3Hz, 1H, methine H), 2.77 (dd, J_1=9Hz, J_2=3.3Hz, 1H, methine H), 2.4 (m, 1H, methine H), 1.07 (s, 3H, CH_3) 1.05 (s, 3H, CH_3), 0.79-0.71 (m, 2H, cyclopropyl C<u>H</u>$_2$) and 0.67-0.54 (m, 2H, cyclopropyl C<u>H</u>$_2$). ^{13}C-NMR (75MHz, $CDCl_3$):δ 216.9 (s), 141.1 (d), 136.3 (d), 127.5 (d), 125.2 (d), 53.8 (d), 49.8 (d), 46.9 (d), 43.6 (s), 42.4 (d), 32.6 (S), 27.7 (q), 23.8 (q), 15.2 (t) and 11.4 (t). Mass (m/z): 214 (M^+).

9-Allyl-9-methyl-*endo*-tricyclo[5.2.2.0^{2,6}]undec-4,10-dien-3-spirocyclopropan-8-one (28):

The ketone **27a** (1.5g, 7.5mmol) was treated with sodium hydride (1.0g, excess) in tetrahydrofuran (40ml) and alkylated with allyl bromide (10ml, excess) following the procedure described earlier. The reaction mixture was worked up as described above and the resulting product was chromatographed [(petroleum ether-ethyl acetate) (97:3)] to give the allylated compound **28** (0.35g, 19%). IR (nujol) ν_{max}: 1725 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 6.39 (app. t, J=7Hz, 1H, COCHR-CH=C<u>H</u>-), 5.96 (app. t, J=7Hz, 1H, COCHR-C<u>H</u>=CH-), 5.76 (m, 1H, olefinic), 5.38 (dd, J_1=6Hz, J_2=2Hz, 1H, olefinic), 5.17 (dd, J_1=6Hz, J_2=2Hz, 1H, olefinic), 5.08 (d, J=8Hz, 1H, olefinic), 5.02 (d, J=18Hz, 1H, olefinic), 3.42 (d, J=10Hz, 1H, methine H), 3.18 (br d, J=6Hz, 1H, methine H), 2.68 (dd, J_1=10Hz, J_2=3Hz, 1H, methine H), 2.48 (m, 1H, methine H), 2.20 (dd, J_1=15Hz, J_2=8Hz, 1H, methylene H), 2.07 (dd, J_1=15Hz, J_2=8Hz, 1H, methylene H), 1.05 (s, 3H, CH_3), 0.7 (complex m, 2H, cyclopropane C<u>H</u>$_2$) and 0.55 (complex m, 2H, cyclopropane C<u>H</u>$_2$). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 215.6 (s), 141.1 (d), 135.3 (d), 133.6 (d), 127.3 (d), 125.2 (d), 117.8 (t), 53.9 (d), 50.4 (d), 46.2 (s), 43.6 (d), 43.3 (t), 42.1 (d), 32.7 (s), 20.5 (q), 15.1 (t) and 11.3 (t). Mass (m/z): 240 (M^+).

9,9-Dimethyl-*endo*-tricyclo[5.2.2.0^{2,6}]undeca-4,10-dien-3-isopropyliden-8-one (29b):

Reduction of the keto epoxide **17** (1.8g, 7.9mmol) with zinc (9g, excess) in refluxing dry dioxane

(45ml) containing ammonium chloride (0.25g, excess) as described earlier, followed by column chromatography [(petroleum ether-ethyl acetate) (97:3)] gave **29a** as a major product (*syn:anti* mixture, ^{1}H-NMR and ^{13}C-NMR) (1.7g, 69%). Alkylation of the ketone **29a** (3.8g, 1.8mmol) with methyl iodide (12ml, excess) in the presence of sodium hydride (1.65g, 68.6mmol) as described previously and column chromatography [(petroleum ether-ethyl acetate) (97:3)] of the crude product furnished the compound **29b** (3.67g, 91%). IR (nujol) ν_{max}: 1725 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 6.36 (m of d, J=6Hz, 1H, olefinic), 6.24 (app. t, J=7Hz, 1H, COCHR-CH=C<u>H</u>-), 5.85 (app. t, J=7Hz, 1H, COCHR-C<u>H</u>=CH-), 5.58 (d, J=6Hz, 1H, olefinic), 3.38 (br d, J=6Hz, 1H, methine H), 3.28 (br d, J=6Hz, 1H, methine H), 3.15 (m of d, J=6Hz, 1H, methine H), 2.96 (m, 1H, methine H), 1.82 (s, 3H, CH_3), 1.73 (s, 3H, CH_3), 1.19 (s, 3H, CH_3) and 1.07 (s, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 217 (s), 142 (s), 135.5 (d), 134.5 (d), 133 (d), 125 (d), 122 (s), 53.0 (d), 48.0 (d), 47.5 (d), 44.0 (s), 40.5 (d), 27.0 (q), 24.0 (q), 21.0 (q) and 20.8 (q). Mass (m/z): 228 (M^+).

12,12-Dimethyl-*endo*-tricyclo[8.2.2.0^{2,9}]tetradec-13-en-11-one (30b):

To a suspension of activated zinc (9g, excess) and ammonium chloride (0.25g, excess) in dry dioxane (45ml) was added a solution of the keto epoxide **18** (2g, 8.6mmol) in dioxane (8ml). The reaction mixture was heated at 80°C for about 7h. It was then cooled and filtered to remove zinc and washed with a small amount of dioxane (10ml). The dioxane was removed under vacuum and the residue was diluted with water and extracted with ether (4x20ml). The ether layer was washed with water (2x20ml), brine (2x15ml) and dried over anhydrous sodium sulfate. The solvent was removed and the residue was chromatographed. Elution with petroleum ether-ethyl acetate (97:3) gave the mono methyl ketone **30a** as a *syn:anti* mixture (3:1), (1.49g, 79%), which was recrystallized from petroleum ether-ethyl acetate (95:5) to give colourless crystals, mp 64-65°C. IR (nujol) ν_{max}: 1725 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 6.5 and 6.34 (app. t, J=7.5Hz, total 1H, olefinic), 6.14 (app. t, J=7.5Hz, 1H, olefinic), 2.94 (d, J=6Hz, 1H, methine H), 2.61 (m, 1H, methine H), 2.14-1.86 (m, 2H), 1.7-1.2 (m, 13H, methylene H), 1.14 and 1.1 (d, J=8Hz, total 3H, *anti* and *syn* CH_3). Mass (m/z): 278 (M^+). To a suspension of sodium hydride (0.6g, 22mmol) in dry tetrahydrofuran (35ml) was added a solution of the ketone **30a** (1.6g, 7.34mmol) in tetrahydrofuran (5ml) and the reaction mixture was refluxed for 1h. Methyl iodide (8ml, excess) was added to the reaction mixture, which was then refluxed for 6h, during which more methyl iodide was added. It was quenched with cold water and the reaction mixture was filtered and tetrahydrofuran was removed *in vacuo*. The residue was extracted with ether (3x20ml) and washed with water (2x20ml), brine (2x20ml) and dried over anhydrous sodium sulfate. Removal of solvent and column chromatography [(petroleum ether-ethyl acetate) (97:3)] on silica gel furnished the alkylated product **30b** (1.6g, 95%). IR (neat) ν_{max}: 1725 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 6.42 (app. t, J=7Hz, 1H, COCHR-CH=C<u>H</u>-), 6.08 (app. t, J=7Hz, 1H, COCHR-C<u>H</u>=CH-),

2.91 (br d, J=6Hz, 1H, methine H), 2.46 (m of d, J=6Hz, 1H, methine H), 2.23 (app. t, J=9Hz, 1H, methine H), 1.98 (app. t, J=9Hz, 1H, methine H), 1.66-1.2 (cluster of m, 12H, methylene H), 1.13 (s, 3H, CH_3) and 1.0 (s, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 216.5, 136.9, 125.1, 59.7, 55.1, 42.8, 40.4, 38.9, 31.1, 30.9, 30.4, 29.7, 27.0, 26.1, 25.6 and 24.1. Mass (m/z): 232 (M^+).

12,12-Dimethyl-*endo*-tricyclo[8.2.2.0^{2,9}]tetradec-5,13-dien-11-one (31b):

To a suspension of zinc (12g, excess) and ammonium chloride (0.33g, 5.58mmol) in dry dioxane (50ml) was added a solution of the keto epoxide **19** (3g, 13mmol) in dioxane (6ml) and the reaction mixture was refluxed for 5h. Workup and chromatography [(petroleum ether-ethyl acetate) (97:3)] of the resulting product on silica gel gave the compound **31a** (2.23g, 71%) as a *syn:anti* mixture (6:1). IR (neat) ν_{max} :1725 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 6.54 and 6.38 (app. t, J=8Hz, 1H, olefinic), 6.16 (app. t, J=8Hz, 1H, olefinic), 5.76 (m, 2H, olefinic), 2.93 (d, J=6Hz, 1H, methine H), 2.62 (m, 1H, methine H) 2.4 (overlapped m, 3H, methine and methylene H), 2.2-1.6 (cluster of m, 8H, methylene H), 1.15 and 1.05 (d, J= ~ 8Hz, total 3H, *anti,syn* CH_3's). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 215.21, 140.69, 137.56, 135.39, 131.48, 131.44, 129.60, 127.09, 126.28, 57.91, 48.41, 47.45, 47.22, 43.61, 43.17, 41.90, 40.96, 39.56, 36.48, 33.56, 32.91, 32.55, 31.19, 26.04, 25.90, 25.79, 17.00 and 14.18. The ketone **31a** (1.0g, 4.7mmol) was alkylated with methyl iodide (6ml, excess) in tetrahydrofuran (30ml) according to the earlier procedure to give the compound **31b** (0.97g, 90%) as a liquid. IR (neat) ν_{max}: 1720 cm^{-1}. ^{1}H-NMR (300MHz, $CDCl_3$):δ 6.42 (app. t, J=7Hz, 1H, COCHR-CH=C<u>H</u>-), 6.05 (app. t, J=7Hz, 1H, COCHR-C<u>H</u>=CH-), 5.72 (m, 2H, olefinic), 2.87 (d, J=6Hz, 1H, methine H), 2.53 (m, 1H), 2.42 (m of d, J=6Hz, 1H, methine H), 2.30 (m, 2H), 2.16 (app. t, J=10Hz, 1H), 2.10-1.6 (cluster of m, 6H, methylene H), 1.12 (s, 3H, CH_3), 1.01 (s, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 216.5, 137.8, 131.5, 131.3, 125.2, 58.6, 53.2, 42.8, 39.9, 37.9, 33.3, 33.2, 27.4, 26.4, 25.6 and 24.3. Mass (m/z): 230 (M^+).

9,9-Dimethyl-*endo*-tricyclo[5.2.2.0^{2,6}]undec-4,10-dien-3,8-dione (34):

To a stirred solution of selenium dioxide (1.01g, 9mmol) in dioxane (10ml) and water (2ml) was added potassium dihydrogen orthophosphate (0.1g, excess) and a solution of the compound **23** (0.81g, 4.3mmol) in dioxane (10ml) dropwise (5min). The reaction mixture was heated at 80°C for 6h. It was then cooled and filtered over a celite pad and washed with ether (2x20ml). The solvent was removed under reduced pressure and diluted with water (20ml) and extracted with ether (3x20ml). The combined extract was washed with water (2x20ml), brine (2x20ml) and dried over anhydrous sodium sulphate. The solvent was removed *in vacuo* and the residue was chromatographed. Elution with petroleum ether-ethyl acetate (75:25) yielded the hydroxy ketone **32** as a stereoisomeric mixture (0.69g, 78%). IR (neat) ν_{max}: 3350, 1725cm^{-1}. To a solution of the above keto alcohol **32** (1.0g, 4.9mmol) in acetone (15ml) was added freshly prepared

Jones' reagent dropwise at ~0-5°C. The solvent was removed *in vacuo* and the residue was diluted with water (15ml) and extracted with ether (4x20ml). Combined extract was washed with water (2x20ml), sodium bicarbonate (2x20ml), water (2x20ml) and brine (2x20ml). Drying and removal of solvent followed by chromatography [(petroleum ether-ethyl acetate) (80:20)] on silica gel furnished the dione **34** (0.7g, 71%) as a solid, which was recrystallized from petroleum ether-ethyl acetate mixture (80:20), mp 147-48°C. IR (nujol) ν_{max} :1720, 1700 cm^{-1}. UV (MeOH) λ_{max}: 215.4 nm. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 7.40 (dd, J_1=6Hz, J_2=3Hz, 1H, COC<u>H</u>=CH-), 6.30 (overlapped m, 2H, olefinic), 5.82 (app. t, J=7Hz, 1H, COCHR-C<u>H</u>=CH-), 3.33 (m, 1H, methine H), 3.28 (m, 1H), 3.04 (m, 1H), 2.85 (dd, J_1=6HZ, J_2=3.5Hz, 1H, methine H), 1.15 (s, 3H, CH_3) and 1.11 (s, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 214.4 (s), 209.6 (s), 162.2 (d), 137.4 (d), 135.2 (d), 123.9 (d), 51.5 (d), 45.3 (d), 45.2 (d), 42.4 (d), 27.2 (q) and 23.3 (q). Mass (m/z): 202 (M^+). Analysis: Found C,77.22; H,6.93% Calcd for $C_{13}H_{14}O_2$ C,77.20; H,6.99%.

9,9-Dimethyl-*endo*-tricyclo[5.2.2.0^{2,6}]undec-10-en-3,8-dione (35):

To a suspension of zinc (4.5g, excess) in dry dioxane (25ml) was added ammonium chloride (0.1g, excess) and a solution of the compound **34** (0.5g, 2.5mmol) in dioxane (5ml) and the reaction mixture was refluxed for 7h. The reaction mixture was filtered over a celite pad and washed with ether (2x20ml). The solvent was removed *in vacuo* and the residue was taken up in ether (30ml) and washed with water (2x20ml), brine (2x20ml) and dried. Removal of solvent followed by chromatography [(petroleum ether-ethyl acetate) (90:10)] of the residue on silica gel furnished the dione **35** (0.4g, 86%). IR (neat) ν_{max}: 1730 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 6.43 (app. t, J=~7Hz, 1H, olefinic), 6.16 (app. t, J=~7Hz, 1H, olefinic), 3.23 (d, J=6Hz, 1H, methine H), 3.00 (d, J=6Hz, 1H, methine H), 2.32 (br s, 2H), 2.30-2.06 (m, 3H), 1.76-1.6 (m, 1H), 1.11 (s, 3H, CH_3), 1.06 (s, 3H, CH_3). ^{13}C-NMR (75MHz, $CDCl_3$):δ 220.60, 214.92, 137.99, 125.89, 54.55, 48.76, 46.27, 42.81, 38.52, 35.66, 26.77, 24.72 and 24.03. Mass (m/z): 204 (M^-).

9,9-Dimethyl-*endo*-tricyclo[5.2.2.0^{2,6}]undeca-4,5-epoxy-3,8-dione (36):

To a solution of hydrogen peroxide (1.0ml, 35%) and $NaHCO_3$ (0.5g) in water-ethanol mixture (20ml) was added a solution of the enone **34** (1g, 0.5mmol) in ethanol (5ml) at room temperature (~30°C). After the reaction was complete (tlc), ethanol was removed and the residue was extracted with ethyl acetate (3x20ml). The combined extract was washed with water (2x20ml), brine (2x20ml) and dried. Removal of solvent followed by chromatography [(petroleum ether-ethyl acetate) (92:8)] of the product on silica gel gave the epoxy dione **36** (1.07g, 96%) as a solid, which was recrystallized from ethyl acetate-petroleum ether (60-80°C) (10:90), mp 135-36°C. IR (nujol) ν_{max}: 1740, 1730 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 6.37 (d of dd, J_1=J_2=7Hz, J_3=1.5Hz, 1H, COCHR-CH=C<u>H</u>-), 6.05 (app. t, J=7Hz, 1H, COCHR-C<u>H</u>=CH-), 3.67 (app. t, J=1.5Hz, 1H, O-CH<u>H</u>), 3.40 (dd, J_1=3Hz, J_2=~1Hz, 1H, O-C<u>H</u>H), 3.37 (m of d, J=6Hz, 1H, methine

H,) 3.07 (m, 2H, methine H), 2.87 (d of dd, J_1=6Hz, J_2=4Hz, J_3= ~1.5Hz, 1H, methine H), 1.1 (s, 3H, CH_3), 1.08 (s, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 213.1 (s), 208.8 (s), 137.9 (d), 124.6 (d), 59.0 (d), 57.2 (d), 50.1 (d), 45.9 (d), 44.1 (d), 43.0 (s), 38.5 (d), 26.75 (q) and 23.9 (q). Analysis: found C,71.23; H,6.57% Calcd for $C_{13}H_{14}O_3$ C,71.50; H,6.40%.

5-Hydroxy-9,9-dimethyl-*endo*-tricyclo[5.2.2.$0^{2,6}$]undec-10-en-3,8-dione (37):

To a suspension of zinc (1.0g, excess) in methanol (15ml), was added the epoxy dione **36** (0.15g, 0.7mmol), water (2ml) and ammonium chloride (0.1g, excess). The reaction mixture was stirred at 80°C for 20 hours. After which, the reaction mixture was cooled and filtered on a celite bed and the filtrate was concentrated under vacuum. The residue was extracted with ether (4x20ml) and the combined extract was washed with water (2x20ml), brine (2x15ml) and dried. Removal of solvent followed by chromatography [(petroleum ether-ethyl acetate) (70:30)] of the product on silica gel gave the keto alcohol **37** (0.04g, 32%). IR (neat) ν_{max}: 3480, 1730 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 6.43 (d of dd, J_1=J_2 =8Hz, J_3=2Hz, 1H), 6.15 (d of dd, J_1=J_2=8Hz, J_3= ~2Hz, 1H), 3.23 (br d, J=6Hz, 1H), 3.05 (d, J=6Hz, 1H), 2.9 (br m, 2H), 2.2 (m, 3H), 1.7 (m, 1H), 1.1 (s, 3H, CH_3) and 1.06 (s, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 220.6 (s), 214.9 (s), 138.0 (d), 125.9 (d), 54.58 (d), 48.7 (d), 46.3 (d), 42.8 (s), 38.5 (t), 35.6 (d), 26.8 (d), 24.7 (q) and 24.0 (q). Mass (m/z): 220 (M^+).

Sigmatropic 1,2-acyl shift (or oxa-di-π-methane rearrangement) of chromophoric systems(23,24, 26-28, 30b,31b and 35):

General procedure: A solution of the substrate in dry acetone (both as solvent and sensitizer) was irradiated by a mercury vapour lamp (200 W, Hanovia) in a pyrex immersion well under nitrogen. After ~3-4h the solvent was removed *in vacuo* and the photolysate was chromatographed on silica gel. Elution with ethyl acetate-light petroleum (60-80°C) first gave some unchanged starting material followed by the rearranged product.

6,6-Dimethyltetracyclo[6.3.0.0.^{2,4}0.^{3,7}]undec-10-en-5-one (38):

The ketone **23** (0.3g, 1.6mmol) was irradiated in acetone (300ml) under nitrogen for 3h. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel. Elution with petroleum ether-ethyl acetate (95:5) gave the title compound **38** (0.16g, 54%). IR (neat) ν_{max}: 1730 cm^{-1}. UV (MeOH) λ_{max}: 282, 216 nm. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 5.75 (br s, 2H, olefinic), 2.75 (m, 3H), 2.48 (ddd, J_1=17Hz, J_2=9Hz, J_3=1Hz, 1H), 2.35 (d, J=5Hz, 1H), 2.25 (m, 1H), 1.9 (dd, J_1=9.8Hz, J_2=5Hz, 1H, methylene H), 1.67 (dd, J_1=9.8Hz, J_2=5Hz, 1H, methylene H), 1.12 (s, 3H, CH_3) and 0.9 (s, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 218.78 (s), 133.33 (d), 131.89 (d), 55.07 (d), 53.15 (s), 50.57 (d),

49.87 (d), 38.39 (t), 35.36 (d), 33.12 (d), 32.88 (d), 28.64 (q) and 18.11 (q). Mass (m/z): 188 (M^+).

6-Allyl-6-methyltetracyclo[6.3.0.0.^{2,4}0.^{3,7}]undec-10-en-5-one (39):

Irradiation of the ketone **24** (0.6g, 2.7mmol) in acetone (300ml) under nitrogen for 4h followed by removal of solvent and column chromatography [(petroleum ether-ethyl acetate) (96:4)] of the crude product on silica gel gave the tetracyclic ketone **39** (*syn:anti* mixture) (0.25g, 45%). IR (neat) ν_{max}: 1720 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 5.74 (m overlapped with a broad s, total 3H, olefinic), 5.12 (br d, J=9Hz, 1H, olefinic), 5.07 (d, J=16Hz, 1H, olefinic), 2.84 (br d, J=6Hz, 1H, methine H), 2.72 (dd, J_1=18Hz, J_2=9Hz, 1H), 2.67 (dd, J_1=12Hz, J_2=6Hz, 1H), 2.5 (m, 2H), 2.3-2.12 (m, 3H), 1.9 (dd, J_1=10Hz, J_2= ~6Hz, 1H, methylene H), 1.7 (dd, J_1=10Hz, J_2= ~6Hz, 1H, methylene H), 0.88 and 0.81 (s, total 3H, CH_3). ^{13}C-NMR (75MHz, $CDCl_3$):δ 217.4 (s), 133.28 (d), 133.21 (d), 131.82 (d), 118.2 (t), 56.4 (s), 52.2 (d), 50.3 (d), 50.1 (d), 44.7 (t), 38.2 (d), 35.4 (t), 33.5 (d), 33.0 (d) and 15.8 (q) (signals corresponding to the major stereoisomer). Mass (m/z): 214 (M^+).

Tetracyclo[6.3.0.0.^{2,4}0^{3,7}]undec-10-en-5-one (40):

The ketone **26** (0.18g, 1.13mmol) was irradiated in acetone (300ml) under nitrogen for 3.5h as described earlier. Removal of solvent and chromatography [(petroleum ether-ethyl acetate) (95:5)] of the photolysate on silica gel furnished the rearranged product **40** (0.093g, 50%). IR (neat) ν_{max}: 1720 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 5.7 (m, 2H, olefinic), 3.10 (m, 1H, methine H), 2.80 (m, total 2H), 2.65-2.49 (m, total 3H), 2.25 (m, 1H), 1.92 (d, J=18Hz, 1H), 1.85 (dd, J_1=9.5Hz, J_2=4Hz, 1H, methylene H), 1.68 (dd, J_1=9.5Hz, J_2=6Hz, 1H, methylene H). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 215.6 (s), 133.1 (d), 131.9 (d), 57.1 (d), 50.3 (d), 49.3 (t), 42.2 (d), 38.2 (t), 35.9 (d), 35.8 (d) and 35.0 (d). Mass (m/z): 160(M^+).

6,6-Dimethyltetracyclo[6.3.0.0^{2,4}0^{3,7}]undec-10-en-9-spirocyclopropan-5-one (41):

Irradiation of the ketone **27b**(0.3g, 1.3mmol) in acetone (300ml) under nitrogen followed by removal of solvent and column chromatography [(petroleum ether-ethyl acetate) (96:4)] of the product on silica gel furnished the rearranged compound **41** (0.16g, 58%) as a solid, which was recrystallized from petroleum ether-ethyl acetate (95:5), mp 130-32°C. IR (KBr) ν_{max}: 1725 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 5.75 (dd, J_1=6Hz, J_2=3Hz, 1H, olefinic), 5.29 (d, J=6Hz, 1H, olefinic), 2.97 (dd, J_1=6Hz, J_2=3Hz, 1H, methine H), 2.68 (d, J=6Hz, 1H, methine H), 2.64 (dd, J_1=11Hz, J_2=6Hz, 1H, methine H), 1.95 (dd, J_1=11Hz, J_2= ~4.5Hz, 1H, methine H), 1.89 (d, J=4.5Hz, 1H, methine H), 1.74 (dd, J_1=11Hz, J_2=6Hz, 1H, methine H), 1.12 (s, 3H, CH_3), 0.84 (s, overlapped with a m, total 5H, CH_3 and cyclopropane C$\underline{H}_2$), 0.60 (m, 1H, cyclopropane C$\underline{H}$H) and 0.4 (m, 1H, cyclopropane C$\underline{H}$H). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 218.2 (s), 139.6 (d), 130.3 (d), 54.8 (d), 52.33 (s), 51.3 (d), 50.4 (d), 35.7 (d), 33.9 (d), 33.2 (d), 30.6 (s), 28.8 (q),

18.0 (q), 11.1 (t) and 10.9 (t). Mass (m/z): 214 (M^+). Analysis: Found C,84.43; H,8.52% Calcd for $C_{15}H_{18}O$, C,84.11; H,8.41%.

6-Allyl-6-methyltetracyclo[6.3.0.0.^{2,4}0^{3,7}]undec-10-en-9-spirocyclopropyl-5-one (42):

A solution of the ketone **28** (0.34g, 1.4mmol) in dry acetone (300ml) was irradiated under nitrogen for 3h. The solvent was removed under reduced pressure and the residue was chromatographed [(petroleum ether-ethyl acetate) (95:5)] on silica gel to give the title compound **42** (0.17g, 50%) as a solid, which was recrystallized from petroleum ether-ethyl acetate (92:8). IR (nujol) ν_{max}: 1720 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 5.7 (m, 2H, olefinic), 5.3 (d, J=6Hz, 1H, olefinic), 5.1 (m of d, J=9Hz, 1H, olefinic), 5.06 (m of d, J=15.5Hz, 1H, olefinic), 2.97 (dd, J_1=6Hz, J_2=3Hz, 1H, methine H), 2.62 [a d, (J=6Hz, 1H) overlapped with a dd, (J_1=12Hz, J_2=6Hz, 1H) total 2H, methine H], 2.18 (d, J=7Hz, 2H, methine H), 2.04 (d, J=6Hz, 1H, methine H), 1.94 (dd, J_1=~11Hz, J_2=6Hz, 1H, methine H), 1.76 (dd, J_1=11Hz, J_2=~7Hz, 1H, methine H), 0.88-0.77 (m, overlapped with a s, total 5H, CH_3 and cyclopropane C<u>H</u>$_2$), 0.58 (m, 1H, cyclopropane C<u>H</u>H) and 0.40 (m, 1H, cyclopropane C<u>H</u>H). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 217.2 (s), 139.6 (d), 133.2 (d), 130.3 (d), 118.3 (t), 55.6 (s), 54.5 (d), 50.8 (d), 48.6 (d), 45.0 (t), 36.0 (d), 34.5 (d), 33.5 (d), 30.6 (s), 15.9 (q), 11.1 (t) and 10.9 (t). Mass (m/z): 240 (M^+). Analysis: Found C,85.00; H,8.33%, Calcd for $C_{17}H_{20}O$, C,84.55; H,8.49%.

6,6-Dimethyl teracyclo[6.6.0.0.^{2,4}0.^{3,7}]tetradeca-5-one (44):

Irradiation of **30b** (1.2g, 5.2mmol) in acetone (300ml) under nitrogen for 3h followed by removal of solvent and column chromatography [(petroleum ether-ethyl acetate) (95:5)] of the residue on silica gel gave the title compound **44** (0.95g, 87%). IR (neat) ν_{max}: 1730 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 2.55 (dd, J_1=12Hz, J_2=6Hz, 1H, methine H), 2.6 (d, J=6Hz, 1H, methine H), 2.2 (dd, J_1=9Hz, J_2=6HZ, 1H, methine H), 1.86-1.68 (m, 6H), 1.64-1.4 (m, 6H), 1.3 (m, 3H), 1.06 (s, 3H, CH_3), 0.86 (s, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 218.8, 61.6, 51.4, 50.7, 46.0, 42.2, 36.6, 35.6, 31.6, 31.2, 30.2, 28.7, 27.8, 25.4, 25.0 and 16.8. Mass (m/z): 232 (M^+).

6,6-Dimethyl tetracyclo[6.6.0.0.^{2,4}0.^{3,7}]tetradec-11-en-5-one (45):

Irradiation of the ketone **31b** (0.5g, 2.2mmol) in acetone (300ml) under nitrogen for 3 hours followed by removal of solvent and column chromatography [(petroleum ether-ethyl acetate) (96:4)] of the residue on silica gel yielded the tetracyclic compound **45** (0.3g, 59%). IR (nujol) ν_{max}: 1735 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 5.56 (m, 1H, olefinic), 5.44 (m, 1H, olefinic), 2.7-2.6 (m, 2H, methine H), 2.46-2.17 (m, 3H, methine H), 2.10-1.9 (m, 5H), 1.8 (m of d, J=12Hz, 1H), 1.7 (m, 1H), 1.6 (m, 1H), 1.44 (m, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 219.0 (s), 130.6 (d), 125.9 (d), 57.5 (d), 51.0 (s), 47.8 (d), 43.9 (d), 36.6 (d),

34.5 (d), 32.4 (d), 30.1 (t), 30.1 (t), 29.4 (t), 28.7 (q), 24.6 (t) and 16.8 (q). Mass (m/z): 230 (M^+).

6,6-Dimethyltetracyclo[6.3.0.0.^{2,4}0.^{3,7}]undeca-5,9-dione (47):

Irradiation of the dione **35** (0.63g, 3.1mmol) in acetone (300ml) under nitrogen for 3h followed by removal of solvent and column chromatography [(petroleum ether-ethyl acetate) (95:5)] of the photolysate on silica gel furnished the title compound **47** (0.4g, 63%). IR (neat) ν_{max}: 2980, 1730, 1725 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 2.7 (m, 2H), 2.44 (m, 2H), 2.4-2.1 (m, 4H), 1.98 (m, 1H), 1.78 (m, 1H), 1.15 (s, 3H, CH_3), 0.91 (s, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 218.6, 216.8, 55.8, 52.6, 51.6, 48.7, 39.1, 34.6, 33.4, 31.7, 28.1, 26.4, 17.9. Mass (m/z): 204 (M^+).

Cyclopropane ring cleavage: Reaction of 38 with trimethylsilyl iodide and Formation of 4,11-diiodo-10,10-dimethyl-tricyclo[5.2.1.0^{2,6}]undecan-9-one (48 and 49):

A mixture of the tetracyclic compound **38** (0.47g, 2.5mmol), trimethylsilyl chloride (0.41g, 3.75mmol) and sodium iodide (3.75mmol) in dry acetonitrile (20ml) was stirred at room temperature (30°C) for 12h. The reaction mixture was filtered and water (20ml) was added to the filtrate and extracted with ether (3x20ml). The combined extract was washed with sodium thiosulphate (2x20ml), water (2x20ml), brine (2x20ml) and dried. Removal of solvent followed by chromatography [(petroleum ether-ethyl acetate) (95:5)] furnished the two iodo ketones **48** and **49**, which were recrystallized from petroleum ether-ethyl acetate (90:10), total yield (0.97g, 88%).

48: mp 136°C. IR (nujol) ν_{max}: 1700 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 5.08 (br s, 1H, H-C-I), 4.91 (m, 1H, H-C-I), 2.90-2.82 (m, 2H), 2.80-2.70 (m, 2H), 2.48 (m, 1H), 2.40 (d, J=2Hz, 1H), 2.30-2.18 (m, 2H), 2.02 (m, 2H), 1.24 (s, 3H, CH_3) and 1.13 (s, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 211.6 (s), 62.3 (d), 60.5 (d), 53.7 (s), 49.7 (d), 47.0 (d), 45.9 (d), 40.9 (t), 33.1 (t), 26.8, 25.9, 25.8 (q) and 23.1 (q). Mass (m/z): 444 (M^-). Analysis: Found C,35.14; H,4.22% Calcd for $C_{13}H_{18}OI_2$ C,35.14; H,4.05%.

49: mp 144°C. IR (KBr) ν_{max}: 1700 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 5.15 (s, 1H, H-C-I), 4.78 (app. t, J=4.5Hz, 1H, H-C-I), 3.2 (dd, J_1=18Hz, J_2=10Hz, 1H), 2.96-2.74 (m, 5H), 2.46 (m, 2H), 2.36 (d, J=2Hz, 1H), 2.26 (dd, J_1=18Hz, $_{J2}$=3Hz, 1H), 1.25 (s, 3H, CH_3) and 1.2 (s, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 212.0 (s), 59.4 (d), 53.9 (s), 50.0 (t), 48.2 (d), 48.0 (d), 46.4 (t), 45.5 (t), 44.9 (d), 33.0 (d), 27.4 (d), 26.1 (q) and 23.2 (q). Mass (m/z): 444 (M^+). Analysis: Found C,34.93; H,4.07% Calcd for $C_{13}H_{18}OI_2$ C,35.13; H,4.05%.

3,3-Dimethyl tricyclo[6.3.0.0^{2,6}]undecan-4-one (50):

A solution of the tetracyclic ketone **38** (0.38g, ~2mmol) in methanol (50ml) was shaken with Pd/C (10%, catalytic amount) in an atmosphere of hydrogen, in a Parr type apparatus for 4h. The catalyst was

removed by filtration and washed with methanol (10ml). Removal of methanol *in vacuo* followed by chromatography [(petroleum ether-ethyl acetate) (96:4)] of the residue furnished the tricyclic ketone **50** (0.3g, 77%). IR (neat) ν_{max}: 1740 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 2.79 (m, 1H), 2.6 (m, 1H), 2.45 (ddd, J_1=15Hz, J_2=7Hz, J_3=1Hz, 1H), 2.14 (m, 1H), 1.9-1.8 (m, 3H), 1.7-1.5 (m, 4H), 1.5-1.3 (m, 3H), 1.08 (s, 3H, CH_3) and 1.04 (s, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 61.4 (d), 50.5 (s), 45.4 (d), 43.0 (d), 40.9 (t), 39.3 (d), 38.3 (t), 33.9 (t), 33.8 (t), 26.3 (q), 25.7 (t) and 20.0 (q) (CO not observed). Mass (m/z): 192 (M^+).

3,3-Dimethyl tricyclo[6.6.0.$0^{2,6}$]tetradecan-4-one (51):

A solution of the tetracyclic ketone **44** (0.33g, 1.4mmol) in methanol (50ml) was reduced with Pd/C (10%, catalytic amount) under hydrogen atmosphere for 9h. The catalyst was removed by filtration and washed with methanol (10ml). Removal of methanol *in vacuo* and chromatography [(petroleum ether-ethyl acetate) (96:4)] of the residue on silica gel gave the tricyclic ketone **51** (0.31g, 93%). IR (neat) ν_{max}: 1740 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 2.54 (dd, J_1=12Hz, J_2=6Hz, 1H), 2.08-2.0 (m, 3H), 1.88-1.66 (m, 6H), 1.60-1.2 (m, 10H), 1.22 (s, 3H, CH_3) and 0.88 (s, 3H, CH_3). Mass (m/z): 234 (M^+).

3,3-Dimethyl tricyclo[6.3.0.$0^{2,6}$]undecan-4,11-dione (53):

A solution of the tetracyclic keto alcohol **46** (0.24g, 1.2mmol) in methanol (50ml) was shaken with Pd/C (10%, catalytic amount) in an atmosphere of hydrogen for 10h. Removal of the catalyst by filtration followed by removal of the solvent and column chromatography [(petroleum ether-ethyl acetate) (90:10)] of the residue on silica gel gave the keto alcohol **52** (0.2g, 82%) as a solid, which was recrystallized from petroleum ether-ethyl acetate (90:10), mp 67-68°C. IR (KBr) ν_{max}: 3424, 1740 cm^{-1}. To a solution of the above keto alcohol (0.2g, 0.96mmol) in acetone (15ml) was added freshly prepared Jones' reagent dropwise at room temperature (~30°C). Usual workup and chromatography [(petroleum ether-ethyl acetate) (92:8)] of the product furnished the diketone **53** (0.16g, 83%). IR (nujol) ν_{max}: 1742 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$):δ 2.8-2.5 (m, 4H), 2.37 (d, overlapped with a m, J=8Hz, 1H), 2.30 (dd, J_1=15.5Hz, J_2=8Hz, 1H), 2.2-1.8 (m, 6H), 1.13 (s, 3H, CH_3) and 1.06 (s, 3H, CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$):δ 221.8, 58.9, 53.0, 50.0, 43.2, 42.2, 38.2, 36.0, 34.0, 26.4, 25.3 and 19.9. Mass (m/z): 206 (M^+).

Sigmatropic 1,3-acyl shift of chromophoric systems(23, 24, 27, 29b, 31b, 36 and 55):

6,6-Dimethyltricyclo[6.3.0.$0^{4,7}$]undeca-2,10-dien-5-one (56):

A solution of **23** (0.3g, 1.6mmol) in benzene (300ml) was irradiated under nitrogen with a mercury vapour lamp (200 W, Hanovia) in a pyrex immersion well for 3h. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel. Elution with petroleum ether-ethyl acetate (98:2) furnished

the compound **56** (0.11g, 37%). Continued elution with the same solvent gave the unchanged starting material (0.08g). IR (neat) ν_{max}: 1785 cm^{-1}. UV (MeOH) λ_{max}: 210, 256 and 311 nm. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 5.6 (m, 4H, olefinic), 3.74 (m of dd, J_1=8.5Hz, J_2=4.8Hz, J_3=2Hz, 1H, COC<u>H</u>-R), 3.1 (m of d, J=8.5Hz, 1H), 2.65 (d of dd, J_1=J_2=J_3=8Hz, 1H, methine H), 2.50 (m of dd, J_1=16Hz, J_2=8.5Hz, 1H, C<u>H</u>H), 2.44 (d, J=8.5Hz, 1H, methine H), 2.15 (m of dd, J_1=16Hz, J_2=8.5Hz, 1H, CH<u>H</u>), 1.22 (s, 3H, CH_3) and 1.20 (s, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 214.7 (s), 133.2 (d), 129.4 (d), 128.3 (d), 119.1 (d), 60.6 (s), 53.7 (d), 42.2 (d), 38.9 (t), 37.3 (d), 33.0 (d), 24.4 (d) and 18.7 (d). Mass (m/z): 188 (M^+), 118 (M^+)-[$(CH_3)_2$-C=C=0].

6-Allyl-6-methyltricyclo[6.3.0.0^{4,7}]undeca- 2,10-dien-5-one (57):

A solution of the ketone **24** (0.25g, 1.2mmol) in dry benzene (300ml) was irradiated (200 W mercury vapour lamp, Hanovia) in a pyrex immersion well under nitrogen for 3 hours. The solvent was removed under vacuum and the residue was chromatographed on silica gel. Elution with petroleum ether-ethyl acetate (97:3) furnished the compound **57** (0.14g, 52%). IR (neat) ν_{max}: 1790 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 5.7 (m, 5H, olefinic), 5.14 (br m, 1H, olefinic), 5.10 (m of d, J=6Hz, 1H, olefinic), 3.66 (m, 1H, methine H), 3.14 (br d, J=6Hz, 1H, methine H), 2.6-2.42 (m, 3H, methine and methylene H), 2.35-2.10 (m, 3H, methine and methylene H), 1.21 (s, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 213.5 (s), 133.0 (d), 132.7 (d), 129.2 (d), 128.2 (d), 118.9 (d), 118.2 (t), 63.2 (s), 53.4 (d), 42.0 (t), 41.7 (d), 38.6 (t), 34.2 (d), 33.1 (d) and 16.4 (q). Mass (m/z): 214 (M^+), 118 (M+)-[CH_2=CH-CH_2-C(CH_3)=C=O].

6,6-Dimethyltricyclo[6.3.0.0^{4,7}]undeca-2,10-dien-9-spirocyclopropan-5-one (58):

Irradiation of the compound **27b** (0.3g, 1.4mmol) in dry benzene (300ml) in a pyrex immersion well under nitrogen as described earlier followed by chromatography [(petroleum ether-ethyl acetate) (98:2)] of the photolysate gave the compound **58** (0.16g, 55%). IR (neat) ν_{max}: 1780 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 5.76 (dd, J_1=6Hz, J_2=3Hz, 1H, olefinic), 5.7 (m, 2H, olefinic), 5.3 (dd, J_1=6Hz, J_2=1.5Hz, 1H, olefinic), 3.6 (m of dd, J_1=9Hz, J_2=4Hz, 1H, COC<u>H</u>-R), 3.31 (br d, J=9Hz, 1H, methine H), 2.70 (d, J=8.5Hz, 1H, methine H), 1.70 (d, J=8.5Hz, 1H, methine H), 1.03 (s, 3H, CH_3), 0.97 (s, 3H, CH_3), 0.82 (m, 1H, cyclopropane H), 0.58 (m, 2H, cyclopropane H), 0.4 (m, 1H, cyclopropane H). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 214.3, 136.8, 130.1, 128.5, 119.0, 60.4, 54.4, 43.1, 36.2, 33.7, 30.1, 24.4, 19.1, 10.2 and 8.1. Mass (m/z): 214 (M^+).

6-Allyl-6-methyltricyclo[6.3.0.0^{4,7}]undeca-2,10-dien-5-one (59):

Irradiation of a benzene solution of the ketone **28** (0.5g, 2.1mmol) in a pyrex immersion well under nitrogen for 3.5 hours followed by chromatography [(petroleum ether-ethyl acetate) (97:3)] of the photolysate

furnished the 1,3-acyl shift product **59** (0.24g, 48%) as a liquid. IR (neat) ν_{max}: 1785 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 5.78-5.64 (m, 4H, olefinic), 5.29 (dd, J_1=6Hz, J_2= ~1.5Hz, 1H, olefinic), 5.15-5.06 (m, 2H), 3.53 (m of d, J=8Hz, 1H, methine H), 3.30 (br d, J=8Hz, 1H, methine H), 2.65 (d, J=9Hz, 1H, methine H), 2.3-2.17 (m, 2H, methine H), 1.9 (d, J=9Hz, 1H, methine H), 1.05 (s, 3H, CH_3), 0.80 (m, 1H, cyclopropane CHH), 0.62 (m, 1H, cyclopropane CHH), 0.5 (m, 1H, cyclopropane CHH) and 0.42 (m, 1H, cyclopropane CHH). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 213.3 (s), 136.7 (d), 132.7 (d), 130.0 (d), 128.4 (d), 119.0 (d), 118.5 (t), 62.8 (s), 54.2 (d), 43.1 (d), 36.2 (d), 35.8 (d), 30.5 (d), 30.0 (s), 16.9 (q), 10.2 (t) and 8.0 (t). Mass (m/z): 144 [(M^+)-(CH_2=CH-CH_2-C(CH_3)=C=O)], 92 [(M^+)-($C_{10}H_{12}$)].

6,6-Dimethyl-9-isopropylidinetricyclo[6.3.0.0^{4,7}]undeca-2,9-dien-5-one (60):

A solution of the ketone **29b** (0.3g, 1.3mmol) in dry benzene (300ml) was irradiated (200 W mercury vapour lamp) under nitrogen for 2.5h. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel. Elution with petroleum ether-ethyl acetate (98:2) gave the 1,3-acyl shift product **60** (0.14g, 45%) followed by some unchanged starting material. IR (neat) ν_{max}: 1775 cm^{-1}. ^{1}H-NMR (300MHz, $CDCl_3$):δ 6.32 (dd, J_1=6Hz, J_2=2.5Hz, 1H, olefinic), 5.94 (d of dd, J_1=10Hz, J_2=6Hz, J_3= ~3Hz, 1H, olefinic), 5.77-5.70 (m, 2H, olefinic), 3.58 (m, 1H, methine H), 3.45 (br, 1H, methine H), 3.24 (br d, J=8Hz, 1H, methine H), 2.53 (dd, J_1=9Hz, J_2= ~2Hz, 1H, methine H), 1.80 (s, 6H, 2 x CH_3), 1.25 (s, 3H, CH_3) and 1.22 (s, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 215.4, 145.5, 135.5, 129.6, 128.8, 121.3, 119.8, 61.8, 55.1, 43.3, 39.1, 33.9, 23.7, 21.3 and 21.1. Mass (m/z): 228 (M^+).

6,6-Dimethyltricyclo[6.6.0.0^{4,7}]tetradeca-2-11-dien-5-one (61):

Irradiation of **31b** (1g, 4.4mmol) in benzene (500ml) under nitrogen for 3.5h followed by removal of solvent and chromatography [(petroleum ether-ethyl acetate) (98:2)] of the residue on silica gel furnished the rearranged product **61** (0.34g, 34%). IR (neat) ν_{max}: 1780 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 6.0 (m, 1H, olefinic), 5.7 (m, 2H, olefinic), 5.55 (m, 1H, olefinic), 4.04 (m of d, J= ~9Hz, 1H, methine H), 2.8 (br m, 1H), 2.7-2.5 (m, 2H), 2.3-2.0 (m, 4H), 1.85 (m, 1H), 1.79 (m, 1H), 1.58 (m, 2H), 1.4 (s, 3H, CH_3), 1.18 (s, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 214.2 (s), 135.7 (d), 131.5 (d), 125.1 (d), 120.1 (d), 60.6 (s), 55.3 (d), 39.9 (d), 39.4 (d), 33.1 (d), 30.3 (t), 29.7 (t), 29.5 (t), 26.5 (q), 24.8 (t) and 16.7 (q). Mass (m/z): 230 (M^+).

10,11-Epoxy-6,6-dimethyltricyclo[6.3.0.0^{4,7}]undec-2-en-5-one (62):

Irradiation of the epoxy ketone **36** (0.11g, 0.5mmol) in dry benzene (100ml) with a mercury vapour lamp (125 W) in a pyrex immmersion well under nitrogen for 2.5 hours followed by removal of solvent and chromatography [(petroleum ether-ethyl acetate) (98:2)] of the residue on silica gel gave the 1,3-acyl shift

product **62** (0.063g, 57%) as a solid, which was recrystallized from petroleum ether-ethyl acetate (95:5), mp 142-44°C. IR (nujol) ν_{max}: 1780, 1740 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 5.93 (dd of d, J_1=9Hz, J_2=6Hz, J_3=2.5Hz, 1H, olefinic), 5.74 (superimposed dd of d, J_1=9Hz, J_2=2.5Hz, 1H, olefinic), 3.89 (d, J=3Hz, 1H, COC<u>H</u>-O-), 3.7 (m of dd, J=8Hz, 1H, COC<u>H</u>(R)CH=CHR), 3.42 (d, J=3Hz, 1H, CHR-C<u>H</u>-O-), 3.33 (m of d, J=8Hz, 1H, COC(Me)-C<u>H</u>-), 2.93 (d, J=10Hz, 1H, COC<u>H</u>-R), 2.82 (d, J=10Hz, 1H, methine H), 1.3 (s, 3H, CH_3) and 1.19 (s, 3H, CH_3). Analysis: Found C,70.30; H,6.50% Calcd for $C_{13}H_{14}O_3$, C,71.56; H,6.40%.

4-Methyltricyclo[6.3.0.0^{4,7}]undeca-2,10-dien-5-one (63):

A solution of the ketone **55** (1.2g, 5.2mmol) in benzene (300ml) was irradiated (200 W Hg. vapour lamp) under nitrogen for 3h. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel. Elution with petroleum ether (60-80°C)-ethyl acetate (98:2) furnished the compound **63** (0.98g, 88%). IR (neat) ν_{max}: 1780 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$):δ 5.82 (m, 1H, olefinic), 5.69 (m, 1H, olefinic), 5.63 (dd, J_1=9Hz, J_2=3Hz, 1H, olefinic), 5.35 (br d, J=9Hz, 1H, olefinic), 3.18 (br d, J=9Hz, 1H, methine H), 2.98 (dd, J_1=9Hz, J_2=3Hz, 2H, methine H), 2.64 (dd, J_1=18Hz, J_2=10Hz, 1H, methylene H), 2.48-2.40 (m, 2H, methine H), 2.1 (m of dd, J_1=18Hz, J_2=12Hz, 1H, methylene H), 1.28 (s, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$):δ 209.0 (s), 132.2 (d), 130.2 (d), 127.9 (d), 122.9 (d), 61.3 (s), 48.3 (t), 40.31 (d), 37.0 (d), 36.7 (t), 32.7 (d) and 21.2 (q). Mass (m/z): 174 (M^+).

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