Aromatics to Triquinanes. Synthesis and Photoreaction of Tricyclo[5.2.2.0^{2,6}]undecanes Having an α-Methoxy *β,γ*-Unsaturated Carbonyl Chromophore: A Novel, Efficient, and General Route to Linearly Fused *Cis*:*Anti*:*Cis* Tricyclopentanoids

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A novel, general, and stereoselective route for rapid creation of functionalized, linearly fused *cis*:*anti*:*cis* triquinanes from aromatic precursors has been presented. Cycloaddition of 2-methoxyspiro[cyclohexa-2,4-diene-6-2′-oxacyclopropan]one with various dienophiles and the photochemical reaction of appropriately designed tricyclic systems, having an α-methoxy *β,γ*-enone chromophore upon triplet (^{3}T) sensitization, are the key elements of our approach. A new and efficient methodology for the synthesis of *endo*-annulated bicyclo[2.2.2]octenones having an α-methoxy *β,γ*-enone chromophore (**23**−**36**) from *o*-vanillyl alcohol has been reported. The 2-methoxyspiro[cyclohexa-2,4-diene-6-2′-oxacyclopropan]one was generated by oxidation of *o*-vanillyl alcohol and trapped with cyclopentadiene (**17**), spiroheptadiene (**18**), and dimethylfulvene (**19**) to give the adducts **20**−**22**, which were elaborated to a variety of chromophoric systems **23**−**36**. The structure and stereochemistry of the tricyclic chromophoric systems (**20**−**36**) has been established through their high-field (300 MHz) ^{1}H NMR, ^{13}C NMR, and COSY spectra. Triplet-sensitized photochemical reaction of the chromophoric systems (**23**, **28**−**35**) has been investigated. The triplet excitation of **28**−**34** led directly to the formation of functionalized triquinanes (**43**-**48**) in a single, stereoselective step. Interestingly, the irradiation of **23** furnished a novel tetracyclic product **40**, whereas the irradiation of the substrate **35**, having an additional α,*β*-enone chromophore, gave a highly unusual pentacyclic product **55** as a result of participation of the OCH_3 group in the photoreaction.

There has been worldwide interest in the chemistry of polycyclopentanoids during the past two decades.[1−5] This has been mainly due to the occurrence and isolation of a large number of natural products with fused cyclopentane rings in their frameworks and also because many of the natural products exhibit interesting biological properties.[6] Among the various polycyclopentanoids, the linearly fused tricyclopentanoids bearing the *cis*:*anti*:*cis* tricyclo[6.3.0.0^{2,6}]undecane moiety **1** as the core ring systems are the most common. Coriolin (**2**), hirsutene

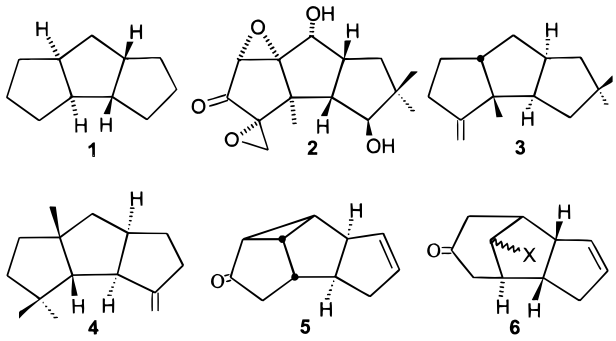

Figure 1.

(**3**), and capnellene (**4**) (Figure 1) are some examples that possess the triquinane framework.[1] The presence of a linearly fused *cis*:*anti*:*cis* framework, **1**, in a large number of natural products has initiated a flurry of activity in the design and development of synthetic routes to polycyclopentanoids, and a number of approaches have been

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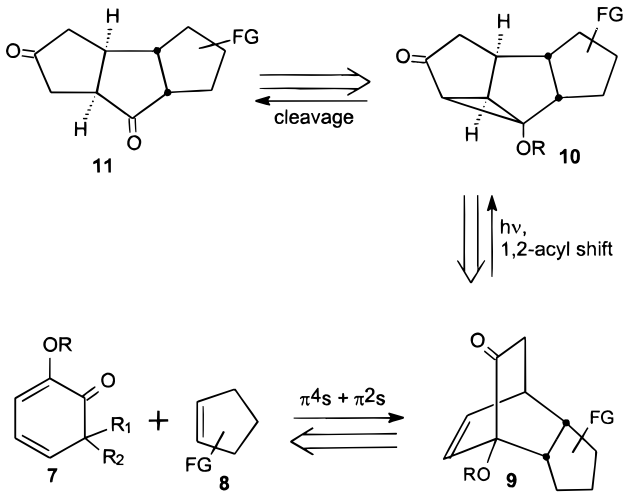
Scheme 1



developed.[1−5] However, except for a few,[5] most of the methods are target oriented, lack adaptability, and generate triquinane framework after a long multistep sequence. The search for methods that rapidly and efficiently generate polycyclopentanoids is continuing.[1,2]

Some time ago,[7] we initiated an exploratory project to develop a general route to polyquinanes employing the photochemical oxadi-π-methane rearrangement as the key feature of our strategy. In this context, we recently reported a unified approach for the synthesis of linearly fused triquinanes *via* the tetracyclic intermediate **5** through regioselective cleavage of the cyclopropane σ bond. However, the electrophile-assisted cleavage of the cyclopropane ring led to the formation of product **6** (Figure 1) due to an undesired mode of cleavage.[7]

Strategy

In order to circumvent the aforementioned problem of regioselective cleavage of the peripheral σ bond, we contemplated that the functionalized triquinanes of type **11** could be readily obtained from the tetracyclic intermediate **10** *via* a regioselective cleavage of the alkoxycyclopropane ring. We further recognized that the intermediate **10** is related to the tricyclic system **9** by a photochemical reaction known as oxadi-π-methane rearrangement or [1,2]-acyl shift.[8] The tricyclic system **9** was thought to be assembled through $\pi^{4s} + \pi^{2s}$ cycloaddition[9] between cyclohexa-2,4-dienones such as **7** and an appropriate dienophile (Scheme 1). Some of the salient features of this strategy are as follows. The required triquinane framework would be obtained in a single stereoselective sequence with the desired *cis*:*anti*:*cis* geometry. It would also furnish the triquinane framework having carbonyl groups for further manipulation. Some triquinane natural products bear the oxygen functionalities at the same positions, e.g. coriolin, hirsutic acid, etc. Furthermore, the incorporation of a stereospecific and versatile $\pi^{4s} + \pi^{2s}$ cycloaddition to assemble the desired chromophoric system would further provide structural flexibility to the strategy. Depending upon the nature of the desired triquinane system, the starting precursor could be appropriately designed by changing the dienone and the dienophile.

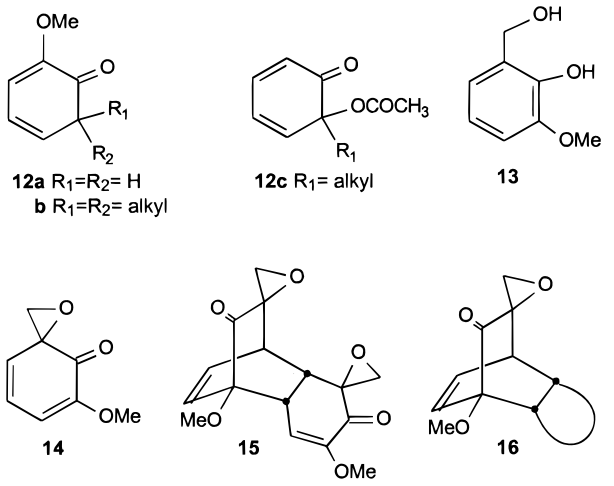


Figure 2.

However, it was clear at the outset that the success of the above strategy would highly depend upon the accessibility of the tricyclic systems of type **9** having an α-methoxy β,γ-enone chromophore and the feasibility of the key photochemical reaction, especially since the chromophoric systems of type **9** were unknown in the literature when this project was initiated.

We wish to report herein a comprehensive account[10] on the synthesis of tricyclo[5.2.2.$0^{2,6}$]undecanes having an α-methoxy β,γ-enone chromophore and their triplet (^{3}T)-sensitized photoreactions, which led to the development of a novel, general, stereoselective, and efficient route to linearly fused *cis*:*anti*:*cis* tricyclopentanoids, along the lines discussed above.

Results and Discussion

$\pi^{4s} + \pi^{2s}$ Cycloaddition of 2-Methoxyspiro[cyclohexa-2,4-diene-6-2′-oxacyclopropan]ones and Synthesis of the Chromophoric Systems. The synthesis of the desired chromophoric systems of type **9** by Diels−Alder reaction of 2-methoxycyclohexa-2,4-dienones of type **12a,b** (Figure 2), though conceptually simple, appeared to be a difficult task in practice because of a lack of methods for preparation of 2-alkoxycyclohexa-2,4-dienones. Cyclohexa-2,4-dienones have been known in the literature for a long time.[11a] However, there are only a few methods for their preparation. Oxidation of phenols with lead tetraacetate[11b,c] is occasionally employed for this purpose; however, it produces 6-acetoxycyclohexa-2,4-dienones of type **12c**. Other oxidizing agents such as thallium trinitrate[12] give mainly *o*-quinones upon treatment with alkoxyphenols. Other methods for the

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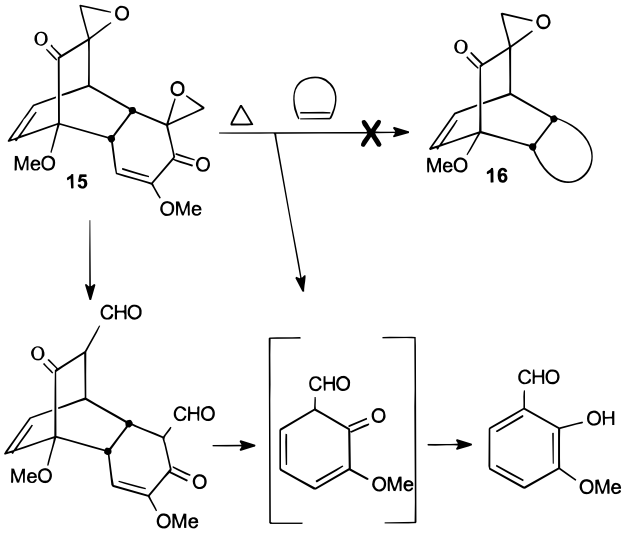
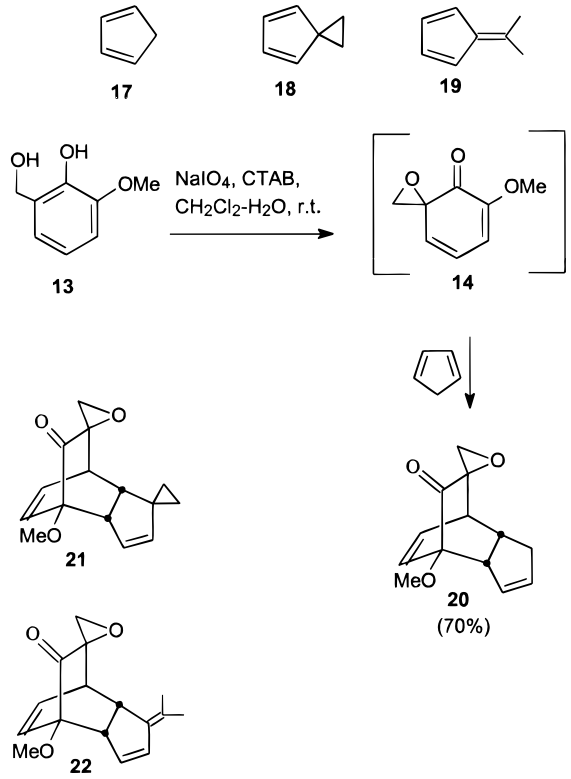
Scheme 2



Scheme 3



preparation of cyclohexa-2,4-dienones such as O-alkylation of phenols[13] and the method developed by Schultz[14] and co-workers also appeared to be unsuitable for our purpose.

In view of the above, we thought to explore an indirect sequence to the chromophoric system of type **9** *via* the interception of the highly reactive 2-methoxyspiro[cyclohexa-2,4-diene-6-2′-oxacyclopropan]one **14** with olefins/dienes and subsequent manipulation of the resulting adducts of type **16** (Figure 2). It may be mentioned that the spiro[cyclohexa-2,4-diene-6-2′-oxacyclopropan]one **14** has a fleeting existence during the oxidation of *o*-vanillyl alcohol and instantaneously dimerizes to the bisepoxy dione **15** (Figure 2).[15] Initially, we considered that the retro Diels−Alder reaction of the dimer **15** may generate the cyclohexa-2,4-dienone **14**, which upon interception with suitable diene/olefin may lead to the adducts of type **16**, having the α-methoxy β,γ-enone chromophore. However, pyrolysis of the dimer **15** in the presence of a variety of olefins and dienes under various conditions did not give any product of type **16**, instead *o*-vanillin was obtained (Scheme 2). The formation of *o*-vanillin could be presumably due to thermal rearrangement of the oxirane moiety to the aldehyde followed by retro Diels−Alder and aromatization.[16] In order to avoid the above problem, efforts were made to open the oxirane ring with various electrophiles. However, all the attempts were futile and led to a complex mixture of products apparently due to the presence of the sensitive enol−ether moiety.

At this juncture, we decided to devise a new phase-transfer method for *in situ* generation of the spiro[cyclohexa-2,4-diene-6-2′-oxacyclopropan]one **14** and its interception during the oxidation of *o*-vanillyl alcohol itself. Indeed, the biphasic oxidation of *o*-vanillyl alcohol **13**, with sodium metaperiodate in the presence of cyclopentadiene and cetyltrimethylammonium bromide (CTAB) as a phase-transfer catalyst, furnished the desired adduct **20** in very good yield (70%) (Scheme 3). Similar oxidation of *o*-vanillyl alcohol in the presence of spiro[4.2]hepta-1,3-diene[17] (**18**) and dimethylfulvene[18] (**19**) also gave the adducts **21** and **22,** respectively.

It is remarkable to note that all the cycloadditions occurred in a highly regio- and stereospecific manner to give single *endo* adducts in each case, during which the cyclohexadienone **14** behaved as a diene (π^4 component) and the dienes **17**−**19** as dienophiles (π^2 component). In principle, the aforementioned cycloadditions could give a number of products as a result of various modes of addition.[19] The structure and *endo* stereochemistry of the adducts **20**−**22** were deduced through detailed analysis of high-field ^{1}H NMR, ^{13}C NMR, and COSY spectra.[20,21]

Transformation of the *β*-Keto Epoxide Group in the Adducts 20 and 21. The presence of an α,β-epoxy ketone group and the double bond in the annulated five-membered ring in the adducts **20** and **21** provided a unique opportunity for further synthetic manipulation

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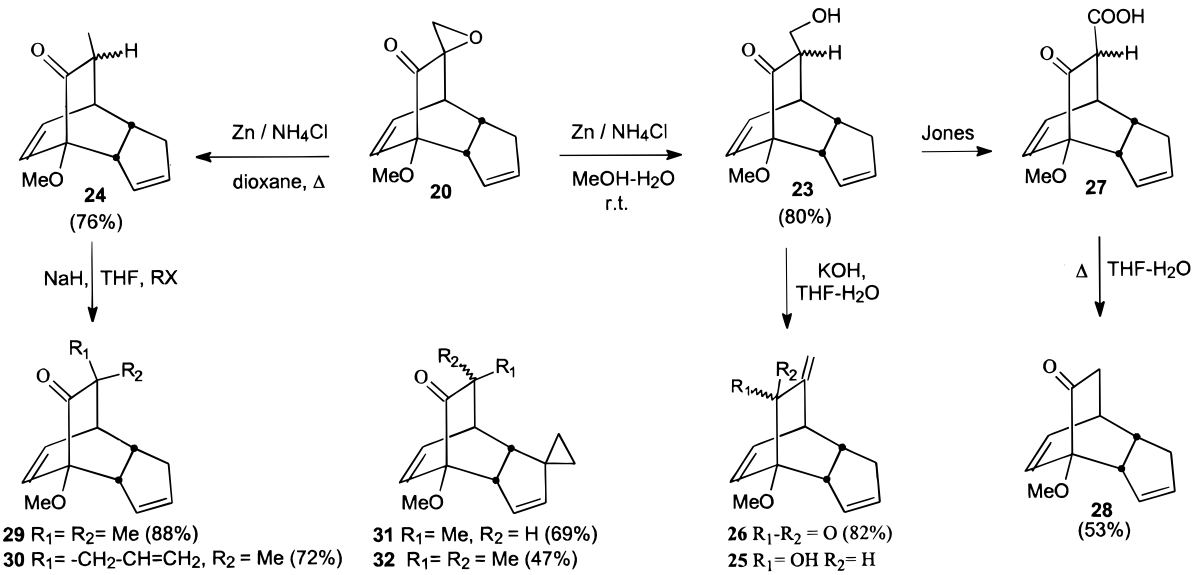
Scheme 4

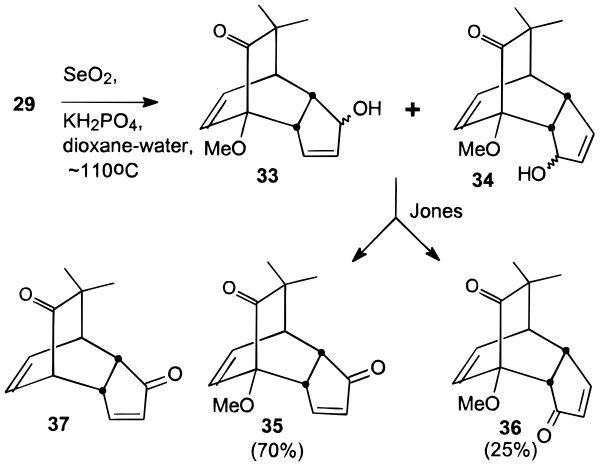


in order to create annulated bicyclo[2.2.2]octenones having a variety of functional groups and appendages, in addition to an α-methoxy β,γ-unsaturated carbonyl chromophore.

Treatment of the epoxy ketone **20** with activated zinc[22] in methanol containing ammonium chloride gave a mixture of products **23**, **24**, and **25**. It was soon discovered that the keto alcohol **23** and the monomethyl ketone **24** can be prepared selectively[7a,23] by the reduction of **20** with zinc in appropriate solvents. Thus, the reduction of **20** with zinc in protic solvent (CH_3OH-H_2O) containing ammonium chloride gave the keto alcohol **23** in major amounts (80%) as a *syn*:*anti* (1:3) mixture as revealed through its high-field (300 MHz) ^{1}H NMR spectrum, while the reduction of **20** in aprotic solvent (dry dioxane) gave the monomethyl ketone **24** in major amounts (76%), also as a *syn*:*anti* (1:13) mixture (Scheme 4), along with minor amounts of **25**.

The keto alcohol **23** was converted into the enone **26** by treatment with KOH in THF. The alcohol **23** was further transformed into the parent tricyclic system **28** *via* its oxidation[24,25] to the β-keto acid **27** and then subsequent decarboxylation. The monomethyl ketone **24** was alkylated[26] with methyl iodide and allyl bromide in the presence of sodium hydride in THF to give the compounds **29** and **30**, respectively. It is interesting to note that alkylation of **24** with allyl bromide proceeded stereoselectively to give compound **30** having the allyl group *syn* to the double bond of the bicyclo[2.2.2]octenone framework. This type of stereoselective alkylation has also been observed by Stork[27a] and Paquette.[27b] The structures of all the compounds **23**−**30** were deduced from the detailed analysis of their high-field ^{1}H NMR and ^{13}C NMR spectra and other analytical data. Following the above procedure, the adduct **21** was also transformed into the tricyclic systems **31** and **32** (Scheme 4), whose structures were fully consistent with their spectral and analytical data.

Scheme 5



Functionalization of the Cyclopentene Ring of 29: Synthesis of Functionalized Chromophoric Systems. In order to demonstrate the scope of the aforementioned tricyclic systems toward funtionalized *cis*:*anti*:*cis* triquinanes, it was desired to functionalize the annulated cyclopentene ring of the substrate **29**. Thus, the compound **29** was oxidized with SeO_2[28] in dioxane−water at ∼100 °C, which gave a regioisomeric mixture of allylic alcohols **33** and **34** containing **33** as a major isomer (Scheme 5). The mixture of alcohols was further oxidized with Jones' reagent,[24] and the resulting product was chromatographed to give the less polar enone **35** (mp 121−122 °C) as the major product (70%) followed by the more polar enone **36** (25%). The structures of the enones **35** and **36** were elucidated on the basis of their spectral and physical characteristics and comparision with analogous compound **37**.[29]

Thus, we have developed a novel and efficient route to a variety of *endo*-annulated tricyclo[5.2.2.0^{2,6}]undecane

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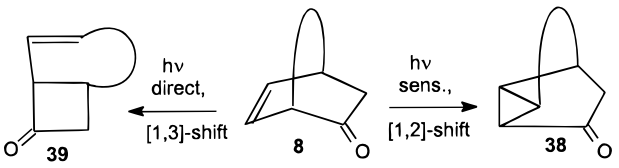
Scheme 6



systems having an α-methoxy β,γ-enone carbonyl chromophore *via* $\pi^{4s} + \pi^{2s}$ cycloaddition of spiro[cyclohexa-2,4-diene-6-2′-oxacyclopropan]ones and manipulation of the resulting adducts. The work presented in this section clearly demonstrates that *o*-vanillyl alcohol is synthetically equivalent to 2-methoxyspiro[cyclohexa-2,4-dien-6,2′-oxacyclopropan]one, 2-methoxy-6,6-disubstituted cyclohexa-2,4-dienone, and 2-methoxycyclohexa-2,4-dienone, which are otherwise not accessible.

After having developed the facile route to the desired tricyclic chromophoric systems (**23**−**36**) having an α-methoxy β,γ-enone group, we set out to explore their photochemical behavior upon triplet sensitization. The efforts made and the results obtained are presented in the following sections.

Photochemical Reaction of the Tricyclic Systems (23, 28−35) upon Triplet Sensitization. Oxadi-π-methane Rearrangement and Cleavage of the Alkoxycyclopropane Ring in Tandem: A Novel, Efficient, and Stereoselective Route to Functionalized *Cis*:*Anti*:*Cis* Tricyclopentanoids. β,γ-Unsaturated ketones undergo two major types of photoreactions upon electronic excitation. It has been observed that the sensitized irradiation of β,γ-unsaturated enones constrained in rigid bicyclic framework causes a [1,2]-shift of acyl group leading to a cyclopropyl ketone of type **38** as shown in Scheme 6. This photochemical reorganization is commonly known as oxadi-π-methane rearrangement[8] because of its similarity to the well-known "di-π-methane" or "Zimmerman rearrangement".[30] The direct irradiation of these enones, however, is known to follow a different course, namely, the [1,3]-acyl shift[8,31] leading to cyclobutanones of type **39**. Although these two kinds of photoreactions are characteristic of their excited states, i.e., [1,3]-acyl shift from singlet and oxadi-π-methane rearrangement from triplet states, respectively, a mixture of products may be obtained due to indiscriminate population of either of the excited states during irradiation. The reaction mechanism of oxadi-π-methane rearrangement and [1,3]-acyl shift have been studied in great detail, and a correlation between excited state spin multiplicity and electronic configuration with reaction type has been established.[30b,32]

We realized that the oxadi-π-methane rearrangement of a tricyclic system having a β,γ-unsaturated carbonyl chromophore as in **9** would directly provide a novel entry into a variety of tetracyclic frameworks **10** depending upon the nature of the ring annulated onto the bicyclic framework.[7,33] It is interesting to note that the stereochemistry at the ring junctions in the rearranged product would depend upon the orientation of the annulated ring. If it is "*endo*" it would produce directly in a single step the *cis*:*anti*:*cis* triquinane framework. We were specifically interested in oxadi-π-methane rearrangement of the annulated chromophoric system of type **9** having an alkoxy group at the bridgehead so that the peripheral cyclopropane σ bond in the resulting photoproduct **10** (Scheme 1) could be selectively and easily cleaved due to assistance from the alkoxy group present on the cyclopropane ring.

It may be mentioned that though photochemical reactions of β,γ-enones have been studied, most of the earlier studies have been made on simple bicyclic systems and were focused on elucidation of mechanism and resolving the singlet−triplet dichotomy.[8,30] The synthetic potential of the photochemical oxadi-π-methane (ODPM) rearrangement was not realized until very recently.[7,33,34] Although Demuth and co-workers have employed ODPM rearrangement toward synthesis of natural products, most of their studies were limited to simple bicyclo[2.2.2]octenones leading to diquinane systems.[34] During our investigations, however, we have found examples of oxadi-π-methane rearrangement toward angular and propellane-type polyquinane.[35]

Though the range of the oxa-di-π-methane rearrangement appears to be wide, it is quite sensitive to the nature of both functional groups and the substituents.[36] Considering the structural and functional complexity of the above chromophoric systems, many photochemical reactions such as intramolecular cycloaddition,[37] [1,3]-acyl shift, and oxadi-π-methane rearrangement might be expected. Keeping in mind the structural dependence on the photoreactivity of β,γ-enones and the structural, functional complexity of our tricyclic chromophoric systems, we set out to explore the behavior of **23** and **28**−**35** upon triplet sensitization.

Thus, a solution of the ketone **29** in acetone was irradiated with a mercury vapor lamp (200 W, Hanovia) in a Pyrex immersion well for ∼3 h under nitrogen. Interestingly, the removal of solvent in *vacuo* and chromatography of the residue on silica gel furnished a crystalline photoproduct **44** (mp 56 °C) in good yield (55%), instead of the expected compound **51** (Scheme 7). The structure of the photoproduct **44** was deduced from its ^{1}H NMR, ^{13}C NMR, and COSY spectra. The *cis*:*anti*:*cis* stereostructure of the photoproduct was followed from *endo* stereochemistry of its precursor, from the spectral data, and by comparison of the spectral features with closely related compounds.

Similarly irradiation of the other chromophoric systems **28**−**32** in acetone (both sensitizer and solvent) gave the

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(31) (a) Sato, H.; Furutachi, N.; Nakanishi, K. *J. Am. Chem. Soc.* **1972**, *94*, 2150−2152. (b) Furutachi, N.; Nakadaira, Y.; Nakanishi, K. *Ibid*. **1969**, *91*, 1028−1030. (c) Givens, R. S.; Oettle, W. F.; Coffin, R. L.; Carlson, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 3957−3962.

(32) (a) Houk, K. N.; Northington, D. J.; Duke, R. E., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 6233−6235. (b) Mirbach, M. J.; Henne, A.; Schaffner, K. *J. Am. Chem. Soc.* **1978**, *100*, 7127−7128. (c) Dauben, W. G.; Lodder, G.; Robins, J. D. *J. Am. Chem. Soc.* **1976**, *98*, 3030−3031. (d) Henne, A.; Siew, N. P. Y.; Schaffner, K. *J. Am. Chem. Soc.* **1979**, *101*, 3671−3673. (e) Schuster, D. I.; Calcaterra, G. T. *J. Am. Chem. Soc.* **1981**, *103*, 2460−2461.

(33) (a) Singh, V. K.; Deota, P. T.; Raju, B. N. S. *Synth. Commun.* **1987**, *17*, 115−124. (b) Singh, V. K.; Raju, B. N. S.; Deota, P. T. *Indian J. Chem.* **1987**, *26B*, 301−304. (c) Singh, V. K.; Raju, B. N. S. *Synth. Commun.* **1988**, *18*, 1513−1524.

(34) Demuth, M.; Schaffner, K. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 820−836.

(35) (a) Demuth, M.; Hisken, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 973−975. (b) Mehta, G.; Subrahmanyam, D.; Subbarao, G. S. R.; Pramod, K. *Indian J. Chem.* **1985**, *24B*, 797−798. (c) Schultz, A. G., Lavieri, F. P., Snead, T. E. *J. Org. Chem.* **1985**, *50*, 3086−3091.

(36) Demuth, M. In *Organic Photochemistry*; Padwa, A., Ed.; Marcell Dekker, Inc.: New York, 1991; Vol. 11, pp 37−97.

(37) Engel, P. S.; Schexnayder, M. A. *J. Am. Chem. Soc.* **1972**, *94*, 4357−4358.

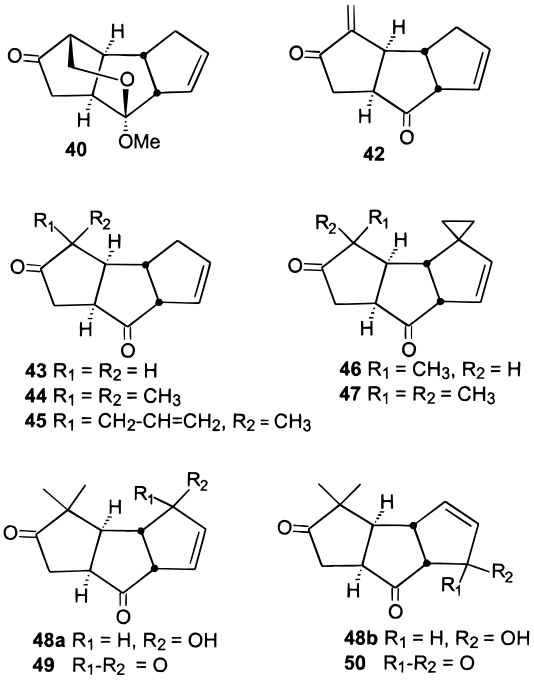


Figure 3.

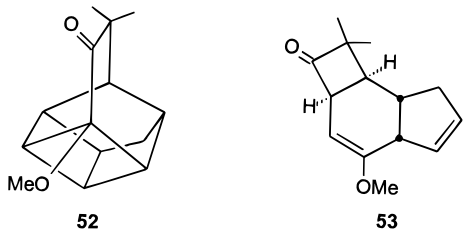
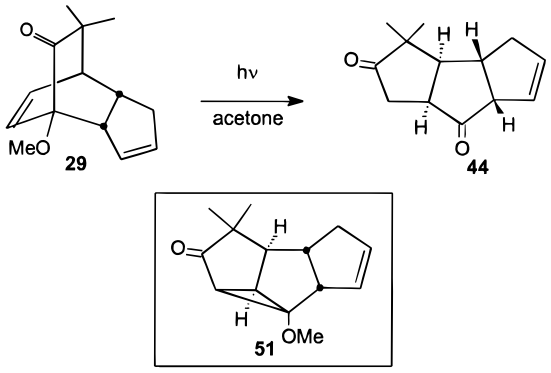


Figure 4.

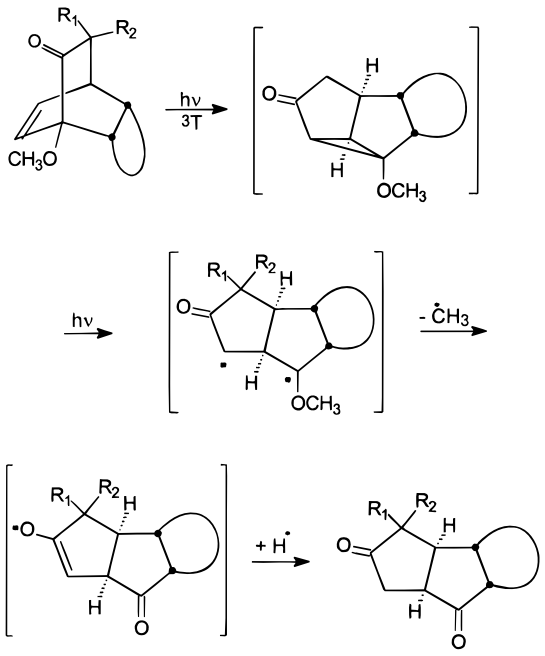
Scheme 7



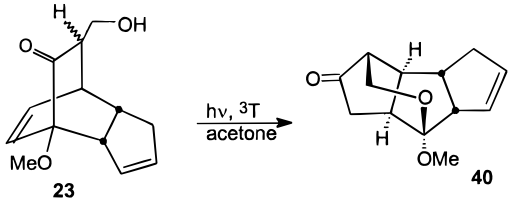
corresponding photoproducts **43**−**47**, respectively, in good yields (Figure 3). The structures of all the photoproducts were clearly revealed from their spectral and analytical data. It was indeed surprising to note that no products of type **51** from the usual oxadi-π-methane rearrangement were obtained in the above photoreactions. It was also remarkable to note the selectivity during the above photoreactions since products such as **52** and **53** from intramolecular $\pi^{2s} + \pi^{2s}$ cycloaddition and [1,3]-acyl shifts, respectively, were not observed (Figure 4).

It appears that the above photochemical transformation proceeds through an initial [1,2]-acyl shift or oxadi-π-methane rearrangement to give the tetracyclic intermediate of type **51**, which upon photochemical cleavage of the peripheral cyclopropane σ bond and loss of methyl

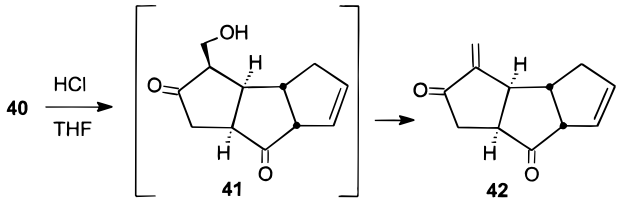
Scheme 8



Scheme 9



Scheme 10



radical followed by hydrogen abstraction finally gives the product[38] (Scheme 8). However, we have not been able to isolate the initial [1,2]-acyl shift product of type **51**. The above mechanism is also supported from the observation that triplet-sensitized irradiation of the keto alcohol **23** in acetone under nitrogen furnished a novel tetracyclic compound **40** (Scheme 9). The compound **40** is apparently formed through interaction of the primary alcoholic function with diradical intermediate obtained after the cleavage of peripheral cyclopropane σ bond. The structure of compound **40** was deduced from its spectral data (Experimental Section) and chemical transformation as described below.

We considered that if the above formulation (**40**) is correct, its acidic hydrolysis should give either **41** and/or the enone **42**. Indeed, the treatment of the compound **40** with HCl in THF gave the dienone **42** (Scheme 10) in good yield, whose structure was easily discerned from its spectral data. The presence of two carbonyl carbons, four olefinic carbons, four methine, and two methylene car-

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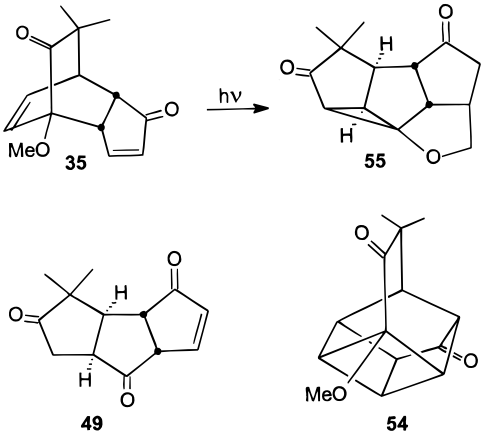
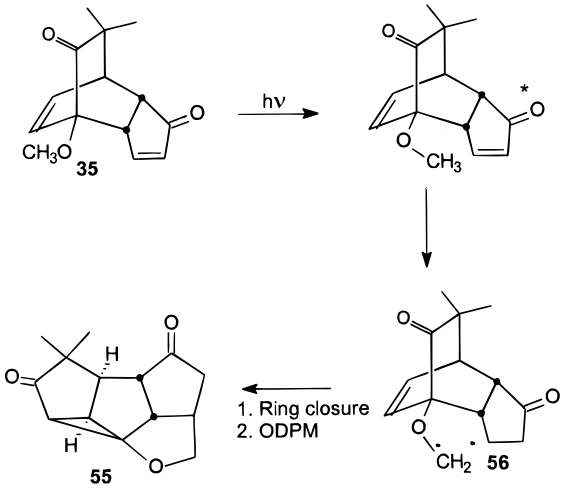
Scheme 11



Scheme 12



bons in the molecular framework of the dienone clearly confirmed its formulation as **42**. The dienone **42** is obviously generated through elimination of the β-hydroxyl group of the hydroxymethyl moiety in **42**, which is initially formed *via* acidic hydrolysis of the tetracyclic product **41** (Scheme 10).

The above photoreaction of the tricyclic systems having an α-methoxy β,γ-enone chromophore proved to be even more fruitful and advantageous than we initially envisaged, especially since it directly gave the linearly fused triquinanes *via* cleavage of the peripheral cyclopropane σ bond in the resulting tetracyclic [1,2]-acyl shift product. It may be mentioned that, while the photoreaction of complex systems having α-methoxy β,γ-enone chromophore were not recorded prior to our own preliminary report, except for an isolated instance where a similar cleavage was observed in a simple bicyclic system.[38] It may be further mentioned that such a cleavage of cyclopropane ring is usually not observed during the photoreaction of β,γ-enones.

In order to further explore the potential of the aforementioned photoreaction toward synthesis of linearly fused triquinanes having functional groups in all the three cyclopentane rings, we examined the photoreaction of the chromophoric systems **33**−**35** under triplet sensitization. The sensitized irradiation of the regioisomeric mixture of keto alcohols **33** and **34** in acetone gave the expected photoproduct, which was oxidized with Jones reagent to give the enetriones **49** and **50** (Figure 3), which were separated by careful chromatography. However, the photoreaction of the dienedione **35** in acetone took a highly novel pathway as described below. Irradiation of a solution of the dienedione **35** in acetone with a mercury vapor lamp (125 W, APP) for ∼3 h followed by removal of solvent in *vacuo* and chromatography of the residue gave a crystalline product to which the structure **55** was tentatively assigned on the basis of a detailed analysis of its ^{1}H NMR (300 MHz), ^{13}C NMR, and mass spectra (Scheme 11). It is indeed remarkable that neither the usual oxadi-π-methane product **49** nor the more probable cage product **54** was obtained in the above photoreaction.

Though the mechanism of the above photoreaction is not clear, the formation of **55** may be explained by the mechanism shown in Scheme 12. Irradiation of the compound **35** in acetone may selectively excite the α,β-enone moiety. Presumably, the abstraction of a hydrogen radical from the methoxy group by the α-carbon of excited the α,β-enone moiety leads to the formation of the diradicaloid **56**. The ring closure of **56** followed by the oxadi-π-methane rearrangement gives the final pentacyclic compound **55**. In the absence of any data regarding competitive sensitization of β,γ-enone and α,β-enone moieties, it is premature to dwell further on the mechanism of the above photoreaction. To the best of our knowledge, a reaction of this type has not been reported in the literature.

In conclusion, a novel, general, and stereoselective route for rapid creation of functionalized, linearly fused *cis*:*anti*:*cis* triquinanes from readily available aromatic precursors has been reported. In this context, a novel and efficient methodology for the synthesis of the desired *endo*-annulated bicyclo[2.2.2]octenones having an α-methoxy β,γ-enone group *via in situ* generation of highly reactive 2-methoxyspiro[cyclohexa-2,4-diene-6-2′-oxacyclopropan]ones and its subsequent interception with cyclic dienes has been developed. We have also demonstrated the synthetic equivalence between various substituted and unsubstituted 2-methoxycyclohexa-2,4-dienones with *o*-vanillyl alcohol. The structure and photochemical reactivity of various substrates have also been investigated. While the photoreaction could tolerate a number of functional groups/appendages, the presence of an additional α,β-enone moiety in the substrate led to the formation of a highly unusual pentacyclic product (**35** → **55**). The photoreaction of a chromophoric system having a hydroxymethyl group at the α′-carbon in addition to an α-methoxy β,γ-enone group, interestingly, gave a tetracyclic photoproduct (**23** → **40**). Application of this methodology toward synthesis of coriolin is underway.

Experimental Section

1-Methoxyspiro[*endo*-tricyclo[5.2.2.0^{2,6}]undeca-3,10-diene-8-2′-oxacyclopropan]-9-one (20). To a mixture of *o*-vanillyl alcohol (2.5 g, 16.2 mmol), cyclopentadiene (8 mL, excess), and cetyltrimethylammonium bromide (CTAB) (0.3 g, 0.8 mmol) in dichloromethane (30 mL) was added an aqueous solution of sodium metaperiodate (10 g, 46.8 mmol) dropwise with stirring at ∼5 °C. After the reaction mixture was stirred for 8 h, the dichloromethane layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic extract was washed with water and brine and dried. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel. Elution with petroleum ether first gave the unreacted cyclopentadiene dimers. Continued elution with petroleum ether−ethyl acetate (95:5) gave the adduct **20** (2.5 g, 70%): mp 86−88 °C; UV (MeOH) λ_{max} 317 (w), 217 (s) nm; IR (Nujol) ν_{max} 1737 cm^{-1};

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.36 (dd, J_1 = 8.5 Hz, J_2 = ~7 Hz, 1H, γ-proton of β,γ-enone moiety), 6.18 (d with structure, J = 8.5 Hz, 1H, β-proton of β,γ-enone moiety), 5.8 (m of d, J = 6 Hz, 1H, olefinic H), 5.62 (m of d, J = 6 Hz, 1H, olefinic H), 3.59 (s, 3H, OCH_3), 3.44 (m of d, J = 9 Hz, 1H, methine H), 3.15 (part of an AB system, J_{ab} = 7 Hz, 1H, OCH_2), 3.12−3.06 (m, 1H, methine H), 2.86 (part of an AB system, J_{ab} = 7 Hz, 1H, OCH_2), 2.7−2.61 (m of dd, J_1 = 15 Hz, J_2 = 8 Hz, 1H, methylene H), 2.59 (m, partly overlapped with other signal, 1H, methine H), 2.02 (m of d, J = 15 Hz, 1H, methylene H); ^{13}C NMR (75MHz, $CDCl_3$) δ 204.38 (s, CO), 134.35 (d), 131.12 (d), 129.8 (d), 127.75 (d), 87.60 (s), 57.70 (s), 53.6 (q, OCH_3), 53.1 (t, OCH_2), 52.80 (d), 42.98 (d), 38.9 (t), 37.25 (d); MS (*m/e*) 218 (M^+), 152 (base peak). Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.55; H, 6.42. Found: C, 71.75; H, 6.86.

1-Methoxyspiro[*endo*-tricyclo[5.2.2.0^{2,6}]undeca-3,10-diene-5-spirocyclopropane-8-2′-oxacyclopropan]-9-one (21). Oxidation of *o*-vanillyl alcohol (1 g, 6.4 mmol), with sodium metaperiodate (5.0 g, 23.4 mmol) in the presence of spiro-[4.2]hepta-1,3-diene (5 mL, excess) in dichloromethane containing CTAB (0.15 g, 0.4 mmol) followed by workup as described above gave the product, which was chromatographed over silica gel. Elution with petroleum ether−ethyl acetate (95:5) gave the compound **21** (0.73 g, 46%) as a solid that was recrystallized with petroleum ether−ethyl acetate mixture (95:3): mp 138 °C; UV (MeOH) λ_{max} 317 (w), 215 (s) nm; IR (Nujol) ν_{max} 1737 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.40 (dd, J_1 = 8 Hz, J_2 = 7 Hz, 1H, γ-proton of β,γ-enone moiety), 6.14 (d with structure, J = 8 Hz, 1H, β-proton of β,γ-enone group), 5.54 (d with structure, J = 7 Hz, 1H, olefinic H), 5.30 (d with structure, J = 7 Hz, 1H, olefinic H), 3.75 (d with structure, J = 9 Hz, 1H, methine H), 3.60 (s, 3H, OCH_3), 3.15 (part of an AB system, J_{AB} = ~7 Hz, 1H, OC*H*H), 2.85 (m overlapped with another signal, 1H, methine H), 2.80 (part of an AB system, J_{ab} = ~7 Hz, 1H, OCH*H*), 2.35 (complex m, 1H, methine H) and 0.80−0.55 (m, 4H, cyclopropyl CH_2s); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 204.7 (CO), 142.6, 130.4, 129.8, 125.1 (olefinic carbons), 88.2, 57.2, 53.8 (two carbons), 53.1, 44.1, 41.0, 33.2, 15.2, 10.46 for quaternary methine and methylene carbons; MS *m/e* 152 (M^+ − C_7H_8, base peak). Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.77; H, 6.55. Found: C, 73.98; H, 6.87.

5-Isopropylidene-1-methoxyspiro[*endo*-tricyclo-[5.2.2.0^{2,6}]undeca-3,10-diene-8-2′-oxacyclopropan]-9-one (22). Oxidation of *o*-vanillyl alcohol (1.0 g, 6.4 mmol) with sodium metaperiodate (5.0 g, 23.4 mmol) in the presence of dimethyl fulvene (4 mL, excess) and CTAB (0.15 g, 0.4 mmol) in dichloromethane as described earlier, followed by workup and chromatography of the crude product over silica gel, furnished the adduct **22** (0.9 g, 54%): mp 131 °C; IR (Nujol) ν_{max} 1740 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.49 (dd, J_1 = 6 Hz, J_2 = 2 Hz, 1H, olefinic proton of the five-membered ring), 6.28 (dd, J_1 = 8 Hz, J_2 = 6 Hz, 1H, γ-proton of the β,γ-enone moiety), 6.06 (d with structure, J = 8 Hz, 1H, β-H of the β,γ-enone group), 5.78 (d with structure, J = 6 Hz, 1H, olefinic proton of the five membered ring), 3.61 (s, 3H, OCH_3), 3.55 (m, 2H, methine H), 3.15 (part of an AB system, J_{ab} = ~7 Hz, 1H, OCH*H*), 2.87 (part of an AB system, J_{ab} = ~7 Hz, 1H, OC*H*H), 2.80 (m of d, J = ~7 Hz, 1H, methine H), 1.77 (s, 3H, CH_3), 1.75 (s, 3H, CH_3); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 204.6 (CO), 140.4, 136.2, 130.6, 130.0, 129.6, 123.7 (olefinic carbons), 87.7, 57.8, 53.8, 53.1, 51.52, 42.0, 41.9, 21.2, 20.9; MS *m/e* 258 (M^+).

1-Methoxy-8-(hydroxymethyl)-*endo*-tricyclo-[5.2.2.0^{2,6}]undeca-3,10-dien-9-one (23). To a suspension of activated zinc (8 g, excess) in CH_3OH-H_2O (4:1, 50 mL) was added a solution of the epoxy ketone **20** (2.5 g, 11.46 mmol) in methanol, followed by ammonium chloride (0.25 g), and the reaction mixture was stirred at room temperature (~30 °C) for about 8 h. It was filtered to remove zinc and washed with a small amount of methanol. The methanol was removed *in vacuo*, and the residue was diluted with water and extracted with ethyl acetate. The ethyl acetate layer was washed with water and brine and dried. The solvent was removed, and the residue was chromatographed. Elution with petroleum ether−ethyl acetate (80:20) furnished the compound **23** (2.0 g, 80%) as a *syn*:*anti* (1:3) mixture: UV (MeOH) λ_{max} 304 (w), 220 (s) nm; IR (neat) ν_{max} 3440, 1720 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.42 (dd, J_1 = 9 Hz, J_2 = 6 Hz, 1H, γ-proton of the β,γ-enone moiety), 6.15 (br d, J = 9 Hz, 1H, β-proton of the β,γ-enone group), 5.78−5.71 (complex m, 1H, olefinic H), 5.62−5.57 (complex m, 1H, olefinic H), 3.91 (dd, J_1 = 10 Hz, J_2 = 6 Hz, 1H, CH_2-O), 3.74−3.62 (m, 1H, CH_2-O), 3.54 (s, 3H, OCH_3), 3.11 (m of d, J = 9 Hz, 1H, methine H), 3.06−3.00 (complex m, 1H, methine H), 2.93−2.76 (complex m, 1H, methine H), 2.57 (m of dd, J_1 = 18 Hz, J_2 = 9 Hz, 1H, CH_2 of cyclopentene ring), 2.32 (d of t, J_1 = 6 Hz, J_2 = 3 Hz, 1H, OCH_2-CH), 1.98 (m of d, J = 18 Hz, 1H, CH_2 of cyclopentene ring) (one OH not shown) (major isomer); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.28 (*C*0), 134.18 (d), 133.65 (d), 129.14 (d), 128.26 (d) (olefinic carbons), 87.76 (quaternary C, *C*-OCH_3), 62.07 (t, O*C*H$_2$), 53.95 (two carbons), 50.28 (d), 39.43 (d), 39.06, 36.33 for 13 carbons of the major isomer; MS *m/e* 220 (M^+).

1-Methoxy-8-methyl-*endo*-tricyclo[5.2.2.0^{2,6}]undeca-3,10-dien-9-one (24). To a suspension of zinc (8 g, excess) and ammonium chloride (2.5 g, excess) in dry dioxane (50 mL) was added the adduct **20** (2.5 g, 11.5 mmol). The reaction mixture was refluxed for about 4 h. It was filtered to remove zinc and washed with small amount of dioxane. The dioxane was removed in *vacuo*, and the residue was diluted with water and extracted with ethyl acetate. The ethyl acetate layer was washed with water and brine and dried. The solvent was removed, and the residue was chromatographed. Elution with petroleum ether−ethyl acetate (97:3) first gave the compound **24** (1.27 g, 76%) as a *syn*:*anti* (1:13) mixture. Continued elution with petroleum ether−ethyl acetate (90:10) gave the trienol **25** (0.12 g, 5%). Further elution with petroleum ether−ethyl acetate (80:20) gave the β-keto alcohol **23** (0.4 g, 16%).

Data for compound **24**: UV (MeOH) λ_{max} 302 (s), 209 (s) nm; IR (Nujol) ν_{max} 1728 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.38 (dd, J_1 = 9 Hz, J_2 = 6 Hz, 1H, γ-proton of the β,γ-enone moiety), 6.12 (d with str, J = 9 Hz, 1H, β-proton of the β,γ-enone group), 5.76−5.72 (d with str, J = 6 Hz, 1H, olefinic H), 5.62−5.58 (m, 1H, olefinic H), 3.55 (s, 3H, OCH_3), 3.11−3.06 (m of d, J = 9 Hz, 1H, methine H), 2.96−2.88 (m, 1H, methine H), 2.85−2.75 (br m, 1H, methine H), 2.64−2.54 (m of dd, J_1 = 15 Hz, J_2 = 9 Hz, 1H, methylene H), 2.2−2.1 (q with str, J = 9 Hz, 1H, CH_3C*H*), 2.49 (m of d, J = 15 Hz, 1H, methylene H), 1.16 (d, J = 9 Hz, 3H, CH_3) for the major isomer; ^{13}C NMR (50 MHz, $CDCl_3$) δ 213.04 (*C*O), 133.75, 128.97 (two carbons), 128.15, (olefinic carbons), 87.16 (*C*-OMe), 53.43, 53.19, 42.54 (*C*H), 42.21 (*C*H), 39.02 (*C*H$_2$), 35.10 (*C*H), 13.78 (*C*H$_3$); MS *m/e* 204 (M^+).

Data for 1-methoxy-9-hydroxy-*endo*-tricyclo[5.2.2.0^{2,6}]undeca-3,8(12)10-triene (**25**): UV (MeOH) λ_{max} 212 (s) nm; IR (neat) ν_{max} 1720 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.20−6.10 (m, 2H, olefinic H), 5.7−5.64 (m, 2H, olefinic H), 5.07−5.05 (m, 2H, olefinic H), 4.28 (t, 1H, HOC*H*), 3.46 (s, 3H, OCH_3), 3.32 (m of d, J = 12 Hz, 1H, methine H), 3.13−3.10 (complex m, 1H, methine H), 2.67−2.55 (m, 1H, methine H), 2.50 (dd with str, J_1 = 15 Hz, J_2 = 12 Hz, 1H, methylene H), 2.1 (br, 1H, OH), 1.88 (m of d, J = 15 Hz, 1H, methylene H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.24 (*C*=CH_2), 132.66, 131.53, 130.41, 129.59, 108.54 (t, C=*C*H$_2$), 83.93 (quaternary carbon, *C*OCH$_3$), 69.32 (d, *C*HOH), 51.57 (q, OCH_3), 49.14 (d), 45.27 (d), 41.19 (d), 38.57 (t, CH_2); MS *m/e* 204 (M^+).

1-Methoxy-*endo*-tricyclo[5.2.2.0^{2,6}]undeca-3,8(12),10-trien-9-one (26). To a solution of β-keto alcohol **23** (0.2 g, 0.9 mmol) in THF−water (4:1, 20 mL) was added potassium hydroxide (0.4 g) and the mixture refluxed for 1 h. THF was removed in *vacuo*, and water (10 mL) was added to the residue and extracted with ethyl acetate. The combined extract was washed with water and brine and dried. Removal of the solvent under vacuum and column chromatography [(petroleum ether−ethyl acetate) (95:5)] gave the title compound **26** (0.15 g, 82%); IR (neat) ν_{max} 1710, 1625 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.27 (m, 1H, γ-H of β,γ-enone group), 6.11 (br d, J = ~9 Hz, 1H, β-proton of β,γ-enone group), 5.81 (s, 1H, *H*CH=C), 5.73−5.72 (m, 1H, olefinic H), 5.62−5.61 (m, 1H, olefinic H), 5.19 (s, 1H, HC*H*=C), 3.61 (s, 3H, OCH_3), 3.49−3.46 (m, 1H, methine H), 3.25 (br d, J = 9 Hz, 1H, methine H), 2.76−2.73 (m, 1H, methine H), 2.57 (br dd, J_1 = 17 Hz, J_2 = ~10 Hz, 1H, methylene H of cyclopentene ring), 2.01 (br d,

J = 17 Hz, 1H, methylene H of cyclopentene ring); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.15 (s, enone carbonyl), 141.51 (s), 134.02 (d), 130.96 (d), 130.18 (d), 128.47 (d), 115.44 (t) (olefinic carbons), 87.39 (s), 53.78 (q), 52.15 (d), 44.45 (d), 41.03 (d), 39.03 (d); MS *m/e* 202 (M^+).

1-Methoxy-*endo*-tricyclo[5.2.2.0^{2,6}]undeca-3,10-dien-9-one (28). To a solution of the β-keto alcohol **23** (1.25 g, 5.6 mmol) in acetone (30 mL) was added freshly prepared Jones' reagent dropwise until the orange color persisted (monitored by TLC also). After the reaction was completed (1 h, TLC), the solvent was removed, and water was added to the residue and extracted with ethyl acetate. The combined extract was washed with water and saturated sodium bicarbonate solution. The aqueous layer was acidified with cold 1:1 HCl. The acidified solution was extracted with ethyl acetate. The combined ethyl acetate extract was washed with water and brine and dried. Removal of the solvent gave the β-keto acid, which was subjected to decarboxylation as follows. The β-keto acid thus obtained was taken in THF−water (4:1, 20 mL) and was refluxed for about 2 h. THF was removed under vacuum, and the aqueous medium was extracted with ethyl acetate. The combined extract was washed with sodium bicarbonate, water, and brine and dried. Removal of the solvent followed by chromatography [(petroleum ether−ethyl acetate) (95:5)] of the residue gave the parent system **28** (0.57 g, 53%) as a colorless liquid: IR (neat) ν_{max} 1730 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.33 (dd, J_1 = 9 Hz, J_2 = 7 Hz, 1H, γ-H of β,γ-enone moiety), 6.10 (d with str, J = 9 Hz, 1H, β-H of β,γ-enone group), 5.74 (m of d, J = 6 Hz, 1H, olefinic H), 5.60 (m of d, J = 6 Hz, 1H, olefinic H), 3.57 (s, 3H, OCH_3), 3.26 (m of d, J = 9 Hz, 1H, methine H), 2.96 (br m, 1H, methine H), 2.82−2.73 (complex m, 1H, methine H), 2.6 (dd with str, J_1 = 18 Hz, J_2 = 12 Hz, 1H, allylic methylene), 2.15 (d, J = 3 Hz, 2H, methylene protons α to carbonyl), 1.98 (m of d, J = 18 Hz, 1H, allylic methylene); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.62 (CO), 133.83, 132.82, 129.58, 128.45 (olefinic carbons), 87.52 (quaternary carbon at the bridgehead), 53.70 (OCH_3), 52.48 (methine carbon), 41.21 (methylene carbon), 40.22 (methine carbon), 39.58 (methine carbon), 36.70 (methylene carbon) for a total of 12 carbons; (assignments were made with the help of ^{13}C NMR spectra recorded in APT mode) MS *m/e* 190 (M^+).

1-Methoxy-8,8-dimethyl-*endo*-tricyclo[5.2.2.0^{2,6}]undeca-3,10-dien-9-one (29). Sodium hydride (0.4 g of 60% w/w suspension, excess) was placed in a dry two-necked flask and washed with dry pentane, and THF (5 mL) was added. A solution of the ketone **24** (2.0 g, 9.8 mmol) in THF (5 mL) was added to the reaction mixture, and it was refluxed for 0.5 h. The reaction mixture was brought down to room temperature, and methyl iodide (2.5 mL, excess) in THF (3−4 mL) was added dropwise to the reaction mixture, which was then stirred for 6−7 h. It was quenched with cold water, and THF was removed in *vacuo*. Water was added to the residue and extracted with ethyl acetate. The combined extract was washed with water and brine and dried. Removal of solvent and chromatography [(petroleum ether−ethyl acetate) (95:5)] furnished the alkylated product **29** (1.87 g, 88%) as a liquid: UV (MeOH) λ_{max} 299 (w), 215 (s) nm; IR (neat) ν_{max} 1726 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.28 (dd, J_1 = 9 Hz, J_2 = 7 Hz, 1H, γ-proton of the β,γ-enone moiety), 6.02 (d with long range couplings, J = 9 Hz, 1H, β-proton of the β,γ-enone moiety), 5.72 (m of d, J = 6 Hz, 1H, olefinic H), 5.60 (m of d, J = 6 Hz, 1H, olefinic H), 3.56 (s, 3H, OCH_3), 3.16 (m of d, J = ∼9 Hz, 1H), 3.00 (complex m, 1H, methine H), 2.62 (m, 1H, methine H), 2.53 (dd with fine structure, J_1 = 17 Hz, J_2 = 9 Hz, 1H, methylene protons of cyclopentene ring), 1.96 (m of d, J = 17 Hz, 1H, methylene protons of cyclopentene ring), 1.12 (s, 3H, CH_3), 1.05 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.74 (s, CO), 134.09 (d), 133.90 (d), 128.70 (d), 128.23 (d) (olefinic carbons), 87.27 (s, *C*OMe), 53.60 (q), 51.90 (d), 48.08 (d), 44.10 (s), 39.29 (t), 36.68 (d), 27.65 (q), 23.95 (q); MS *m/e* 218 (M^+).

1-Methoxy-8-allyl-8-methyl-*endo*-tricyclo-[5.2.2.0^{2,6}]undeca-3,10-dien-9-one (30). The ketone **24** (1.0 g, 4.9 mmol) was treated with sodium hydride (0.2 g, excess) in THF (20 mL) and alkylated with allyl bromide following the procedure described earlier. Workup and chromatography [(petroleum ether−ethyl acetate) (97:3)] of the crude product gave the allylated compound **30** (0.89 g, 72%); UV (MeOH) λ_{max} 301 (w), 209 (s) nm; IR (neat) ν_{max} 1725 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.29 (dd, J_1 = 9 Hz, J_2 = ∼7 Hz, 1H, γ-proton of the β,γ-enone moiety), 6.04 (d with long range couplings, J = 9 Hz, 1H, β-proton of the β,γ-enone group), 5.86−5.70 (complex m, 2H, olefinic H), 5.62 (m, 1H, olefinic H), 5.12−5.00 (m, 2H, olefinic H), 3.56 (s, 3H, OCH_3), 3.18 (d with str, J = ∼9.5 Hz, 1H, methine H), 3.00−2.90 (complex m, 1H, methine H), 2.72 (m, 1H, methine H), 2.56 (d with str, J_1 = 18 Hz, J_2 = ∼9.5 Hz, 1H, allylic methylene of cyclopentene ring), 2.21 (d of the part of an AB system, J_1 = ∼13 Hz, J_2 = 6 Hz, 1H, methylene of the allylic chain), 2.07 (d of the part of an AB system, J_1 = ∼13 Hz, J_2 = 8 Hz, 1H, methylene H of the allylic chain), 1.97 (m of d, J = 18 Hz, 1H, methylene of the cyclopentene ring), 1.14 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.73 (s, CO), 134.13 (d), 133.29 (d), 133.04 (d), 128.53 (d), 128.28 (d), 118.16 (t) (six olefinic carbons), 87.37 (s), 53.60 (q), 52.56 (d), 46.88 (s), 44.76 (d), 43.28 (t), 39.37 (t), 36.34 (d), 20.72 (q); MS *m/e* 244 (M^+).

1-Methoxy-8-methylspiro[*endo*-tricyclo-[5.2.2.0^{2,6}]undeca-3,10-diene-5-1′-cyclopropan]-9-one (31). To a suspension of zinc (3 g, excess) and ammonium chloride (1.0 g, excess) in dry dioxane (40 mL) was added the adduct **21** (1.0 g, 4.0 mmol). The reaction mixture was refluxed for about 4 h. It was 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 and extracted with ethyl acetate. The ethyl acetate layer was washed with water and brine and dried. The solvent was removed, and the residue was chromatographed. Elution with petroleum ether−ethyl acetate (97:3) gave the compound **31** (0.65 g, 69%): UV (MeOH) λ_{max} 213 (s), 308 (w) nm; IR (KBr) ν_{max} 1720 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.43 (dd, J_1 = ∼9 Hz, J_2 = 6 Hz, 1H, γ-proton of β,γ-enone moiety), 6.05 (d, J = ∼9 Hz, 1H, β-proton of the β,γ-enone group), 5.52 (br d, J = 6 Hz, 1H, olefinic H), 5.23 (br d, J = 6 Hz, 1H, olefinic H), 3.56 (s, 3H, OCH_3), 3.34 (br d, J = 9 Hz, 1H, methine H), 2.67 (m of d, J = 9 Hz, 1H, methine H), 2.57−2.50 (br m, 1H, methine H), 2.11 (d of q, J_1 = 7 Hz, J_2 = 3 Hz, 1H, CH_3-C-H), 1.07 (d, J = 7 Hz, 3H, CH_3), 0.85−0.72 (complex m, 2H, methylene of cyclopropane), 0.7−0.51 (complex m, 2H, methylene of cyclopropane); MS *m/e* 230 (M^+).

1-Methoxy-8,8-dimethylspiro[*endo*-tricyclo-[5.2.2.0^{2,6}]undeca-3,10-diene-5-1′-cyclopropan]-9-one (32). The ketone **31** (1.0 g, 4.3 mmol) was treated with sodium hydride (0.2 g, excess) in THF (20 mL) and alkylated with methyl iodide following the procedure described earlier. Workup and chromatography [(petroleum ether−ethyl acetate) (95:5)] of the crude product gave the methylated compound **32** (0.50 g, 47%): UV (MeOH) λ_{max} 301 (w), 212 (s) nm; IR (neat) ν_{max} 1721 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.34 (dd, J_1 = ∼9 Hz, J_2 = 6 Hz, 1H, γ-proton of β,γ-enone group), 5.98 (d with str, J = ∼9 Hz, 1H, β-proton of the β,γ-enone moiety), 5.56 (dd, J_1 = 6 Hz, J_2 = 2 Hz, 1H, olefinic H), 5.23 (dd, J_1 = 6 Hz, J_2 = 2 Hz, 1H, olefinic H), 3.58 (s, 3H, OCH_3), 3.46 (d with str, J = 9 Hz, 1H, methine H), 2.81 (dd, J_1 = 9 Hz, J_2 = 3 Hz, 1H, methine H), 2.33 (br m, 1H, methine H), 1.08 (s, 6H, two CH_3), 0.88−0.53 (m, 4H, cyclopropane CH_2s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.66 (CO), 142.17 (d), 134.33 (d), 126.65 (d), 125.83 (d) (for olefinic carbons), 87.94 (s, *C*-OMe), 53.68 (OCH_3), 52.53 (d), 45.93 (d), 43.64 (quaternary carbon of cyclopropane ring), 43.37 (d), 33.05 (s, $C(CH_3)_2$), 27.70 (q), 23.93 (q) (methyl carbons), 15.21 (t), 11.00 (t) (methylene carbons of cyclopropane ring); MS *m/e* 244 (M^+), 152 ($M^+ - 92$), 92 (base peak).

1-Methoxy-*endo*-tricyclo[5.2.2.0^{2,6}]undeca-3,10-diene-5,9-dione (35) and 1-Methoxy-*endo*-tricyclo[5.2.2.0^{2,6}]-undeca-4,10-diene-3,9-dione (36). To a stirred solution of selenium dioxide (0.8 g, 7.2 mmol) in dioxane (16 mL) and water (4 mL) were added potassium dihydrogenorthophosphate and the compound **29** (1.5 g, 6.8 mmol). The reaction mixture was heated at ∼100 °C for 6 h. It was filtered over a Celite pad and washed with ethyl acetate. The solvent was removed under reduced pressure, and the residue was diluted with water (25 mL) and extracted with ethyl acetate. The combined extract was washed with water and brine and dried.

The solvent was removed in *vacuo*, and the residue was chromatographed. Elution with petroleum ether−ethyl acetate (70:30) yielded an inseparable mixture of hydroxyketones (**33** and **34**) as a stereoisomeric mixture.

To a solution of the above mixture of the keto alcohols (1.6 g, 6.83 mmol) in acetone (25 mL) was added freshly prepared Jones' reagent dropwise at ∼0−5 °C. After the reaction (TLC), the solvent was removed in *vacuo*, and the residue was diluted with water and extracted with ethyl acetate. Combined extract was washed with water and brine and dried. The solvent was removed, and the residue was chromatographed on silica gel. Elution with petroleum ether−ethyl acetate (90:10) furnished the dienedione **35** (1.1 g, 70%) as a solid, which was recrystallized with petroleum ether−ethyl acetate mixture (80:20). Continued elution with petroleum ether−ethyl acetate (70:30) gave the other, more polar diene dione **36** (0.4 g, 25%).

Data of compound 35: mp 121−122 °C; UV (MeOH) λ_{max} 212 (s) nm; IR (Nujol) ν_{max} 1725, 1700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (dd, $J_1 = 6$ Hz, $J_2 = \sim 2.5$ Hz, 1H, β-proton of α,β-enone group), 6.33 (dd, $J_1 = 6$ Hz, $J_2 = \sim 1.5$ Hz, 1H, α-proton of α,β-enone moiety), 6.23 (dd, $J_1 = 9$ Hz, $J_2 = 7.5$ Hz, 1H), 5.85 (d with str, $J = 9$ Hz, 1H), 3.6 (s, 3H, OCH_3), 3.36 (m of d, $J = \sim 6$ Hz, 1H, methine H), 3.03 (complex m, 1H, methine H), 2.90 (dd, $J_1 = 6$ Hz, $J_2 = 3.5$ Hz, 1H, methine H), 1.17 (s, 3H, CH_3), 1.12 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 212.46 (CO), 208.73 (CO), 161.38, 137.86, 132.99, 125.55 (olefinic carbons), 86.73 (quaternary carbon at the bridgehead), 53.58 (OCH_3), 45.80 (*C*H), 45.33 (*C*H), 44.21 (*C*H), 42.64 (quaternary center α to CO), 26.92 (CH_3), 23.23 (CH_3) (assignments were made with ^{13}C NMR recorded in "dept" mode); MS *m/e* 232 (M^+). Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.41; H, 6.89. Found: C, 72.18; H, 6.63.

Data of compound 36: mp 114 °C; UV (MeOH) λ_{max} 313 (w), 225 (s) nm; IR (Nujol) ν_{max} 1725, 1700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (dd, $J_1 = 6$ Hz, $J_2 = \sim 3$ Hz, 1H), 6.28 (dd, $J_1 = 6$ Hz, $J_2 = \sim 2$ Hz, 1H), 6.12 (dd, $J_1 = \sim 9$ Hz, $J_2 = \sim 7$ Hz, 1H), 5.9 (d with str, $J = 9$ Hz, 1H), 3.71 (s, 3H, OCH_3), 3.65 (m, 1H, methine H), 2.92 (dd, $J_1 = 6$ Hz, $J_2 = \sim 1.5$ Hz, 1H, methine H), 2.78 (complex m, 1H, methine H), 1.22 (s, 3H, CH_3), 1.15 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.61 (CO), 204.90 (enone CO), 164.50, 138.21, 132.75, 127.55 (olefinic carbons), 86.57 (*C*OMe), 53.91 (OCH_3), 45.49, 44.59, 43.99, 40.70, 28.21, 23.71 for other methine, methylene, and methyl carbons; MS *m/e* 232 (M^+).

Photoreaction of Chromophoric Systems (23, 28−35): General Procedure. A solution (0.1%) of the substrate in dry acetone (both as solvent and sensitizer) was irradiated by a mercury vapor lamp (200 W, Hanovia) in a Pyrex immersion well under nitrogen. After ∼3 h of irradiation, 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.

1-Methoxy-2-oxatetracyclo[6.5.0.0^{4,8}.0^{9,13}]tridec-11-en-6-one (40). Irradiation of the β-keto alcohol **23** (0.3 g, 1.3 mmol) in acetone under nitrogen for 3 h followed by removal of solvent and column chromatography [(petroleum ether−ethyl acetate) (90:10)] of the residue furnished the rearranged product **40** (0.2 g, 67%) as a solid, which was recrystallized from petroleum ether−ethyl acetate mixture (95:5): mp 100−102 °C; UV (MeOH) λ_{max} 297 (w), 206 (s) nm; IR (KBr) ν_{max} 1738 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (dd of d, $J_1 = 6$ Hz, $J_2 = 4.5$ Hz, $J_3 = 3$ Hz, 1H, olefinic H), 5.60 (dd of d, $J_1 = 6$ Hz, $J_2 = 4.5$ Hz, $J_3 = 3$ Hz, 1H, olefinic H), 3.95 (d of part of an AB system, $J_1 = 10$ Hz, $J_2 = 3$ Hz, 1H, OCH_2), 3.90 (m of the part of an AB system, $J_{AB} = 10$ Hz, 1H, OCH_2), 3.44 (s, 3H, OCH_3), 3.36 (m, 1H), 2.96−2.78 (overlapped m, 2H), 2.60 (dd, $J_1 = 8$ Hz, $J_2 = \sim 5$ Hz, 1H), 2.45−2.35 (m, 2H), 2.30 (m of d, $J = 15$ Hz, 1H), 2.20 (d with str, $J = 6$ Hz, 1H), 2.10 (complex m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 218.51 (s, CO), 133.42 (d), 128.64 (d) (olefinic carbons), 108.54 (s, CH_2-O-*C*-OCH_3), 63.93 (t, OCH_2), 56.42 (d), 51.34 (q, OCH_3), 50.77 (d, *C*H), 49.42 (d, *C*H), 42.77 (d, *C*H), 41.65 (t, *C*H_2), 37.54 (d, *C*H), 36.13 (t, *C*H_2) for a total of 13 carbons; MS *m/e* 220 (M^+). Anal. Calculated for $C_{13}H_{16}O_3$: C, 70.90, H, 7.27. Found: C, 70.78, H, 7.31.

Tricyclo[6.3.0.0^{2,6}]undeca-3(12),9-diene-4,7-dione (42). To a solution of compound **40** (0.1 mg, 0.4 mmol) in methanol−water (4:1, 10 mL) was added HCl (25%, 1 mL) and the mixture stirred at ambient temperature. After the completion of the reaction (TLC), methanol was removed under vacuum and the aqueous layer extracted with dichloromethane. The combined organic layer was washed with water and brine and dried. Removal of dichloromethane and column chromatography [(petroleum ether−ethyl acetate) (95:5)] gave the enedione **42** (0.57 g, 67%): UV (MeOH) λ_{max} 300 (w), 260 (s) nm; IR (CCl_4) ν_{max} 1740, 1700, 1640 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.13 (d, $J = 3$ Hz, 1H, exocyclic olefinic H), 5.92 (m of d, $J = 6$ Hz, 1H, olefinic H), 5.62 (m of d, $J = 6$ Hz, 1H, olefinic H), 5.52 (d, $J = 3$ Hz, 1H, exocyclic olefinic H), 3.43 (complex m, 1H), 3.24 (m of d, $J = 9$ Hz, 1H), 3.10−2.94 (overlapped m, total 3H), 2.68−2.50 (cluster of m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 217 (isolated CO), 204 (enone CO), 147.30, 133.54, 127.36, 119.23 (olefinic carbons), 60.07, 48.94, 44.89, 43.33, 40.78 (methylene C), 37.92 (methylene C). This compound was found to be quite labile and disintegrates even upon storage at low temperatures.

Tricyclo[6.3.0.0^{2,6}]undec-9-ene-4,7-dione (43). The ketone **28** (0.07 g, 0.36 mmol) was irradiated in acetone (150 mL) under nitrogen for 3.5 h as described above. Removal of the solvent and chromatography [(petroleum ether−ethyl acetate) (90:10)] of the photolysate over silica gel furnished the rearranged product **43** (0.03 g, 50%); IR (neat) ν_{max} 1739 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.90 (complex m, 1H, olefinic H), 5.63 (complex m, 1H, olefinic H), 3.54 (complex m, 1H), 3.40 (m, 1H), 2.98−2.80 (overlapped multiplets, total of 3H), 2.72 (d of dd, $J_1 = 16$ Hz, $J_2 = 6$ Hz, $J_3 = 3$ Hz, 1H), 2.66−2.34 (overlapped m, 3H), 1.94 (dd, $J_1 = 18$ Hz, $J_2 = 6$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 216.99 (CO), 216.40 (CO), 134.12, 127.51 (olefinic C), 59.89, 47.51, 44.58, 44.01, 42.28, 40.88, 38.37; MS *m/e* 176 (M^+).

3,3-Dimethyltricyclo[6.3.0.0^{2,6}]undec-9-ene-4,7-dione (44). Irradiation of the ketone **29** (0.2 g, 0.91 mmol) in acetone (300 mL) under nitrogen followed by removal of the solvent and column chromatography [(petroleum ether−ethyl acetate) (85:15)] of the crude product over silica gel furnished the rearranged compound **44** (0.103 g, 55%) as a solid, which was recrystallized from petroleum ether−ethyl acetate mixture (95:5): mp 56 °C; IR (film) ν_{max} 1735 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 (complex m, 1H, olefinic H), 5.61 (complex m, 1H, olefinic H), 3.47 (m of d, $J = \sim 7.5$ Hz, 1H), 2.95 (superimposed ddd, $J_1 = 10$ Hz, $J_2 = 8$ Hz, 1H, ring junction proton), 2.85 (m of dd, $J_1 = \sim 15$ Hz, $J_2 = \sim 7$ Hz, 1H, proton of the allylic methylene group), 2.70 (complex m, 1H, ring junction proton), 2.55 (dd, $J_1 = \sim 17$ Hz, $J_2 = 10$ Hz, 1H, ring junction proton), 2.35 (dd, partly overlapped with another signal, $J_1 = \sim 17$ Hz, $J_2 = 10$ Hz, 1H, methylene H), 2.30 (d with str, $J = 15$ Hz, 1H, methylene H), 2.28 (m, overrlapped with the signal at δ 2.30, 1H), 1.07 (s, 3H, CH_3), 0.97 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 219.44 (s, CO), 217.02 (CO), 132.90 (d), 127.45 (d) (olefinic carbons), 60.93 (d), 55.59 (d), 49.12 (s), 44.91 (d), 41.31 (t), 38.24 (d), 35.83 (t), 24.81 (q), 19.32 (q); MS *m/e* 204 (M^+). Anal. Calcd for $C_{13}H_{16}O_2$; C, 76.47; H, 7.84. Found C: 75.91; H, 7.7.

3-Methyl-3-(3-propenyl)tricyclo[6.3.0.0^{2,6}]undec-9-ene-4,7-dione (45). A solution of the ketone **30** (0.2 g, 0.8 mmol) in acetone (300 mL) was irradiated under nitrogen for 4 h. Removal of solvent followed by column chromatography [(petroleum ether−ethyl acetate) (85:15)] of the residue over silica gel gave the tricyclic ketone **45** (0.09 g, 50%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.86 (m, 1H, olefinic H), 5.71 (t of dd, $J_1 = \sim 16.5$ Hz, $J_2 = 10$ Hz, 1H, allylic H), 5.62 (m, 1H, olefinic H), 5.16−5.05 (cluster of m, 2H, olefinic H), 3.51−3.46 (m, 1H, methine H), 3.01−2.70 (complex multiplets, 3H), 2.58−2.39 (multiplets, 3H), 2.31 (complex m of d, $J = 17$ Hz, 1H), 2.18−2.14 (m, 2H, CH_2), 0.96 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 218.90 (s, CO), 216.96 (s, CO), 133.08 (d), 132.95 (d, H*C*=CH_2), 127.50 (d), 118.99 (t, HC=*C*H_2), 60.90 (d, CH), 52.63 (d, CH), 52.22 (s, quaternary C), 44.62 (d, CH), 42.03 (t, CH_2), 41.32 (t, CH_2), 38.10 (d, CH), 36.07 (t, CH_2), 17.50 (q, CH_3); MS *m/e* 230 (M^+).

3-Methylspiro[tricyclo[6.3.0.0^{2,6}]undec-9-ene-11-1′-cy-

clopropane]-4,7-dione (46). Irradiation of **31** (0.1 g, 0.43 mmol) in acetone (300 mL) under nitrogen for 3 h followed by removal of solvent and column chromatography [(petroleum ether−ethyl acetate) (85:15)] of the residue gave the title compound **46** (0.045 g, 48%): UV (MeOH) λ_{max} 303 (w), 209 (s) nm; IR (neat) ν_{max} 1740 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.56 (dd, $J_1 = \sim 5$ Hz, $J_2 = \sim 3$ Hz, 1H), 5.42 (dd, $J_1 = \sim 5$ Hz, $J_2 = \sim 2$ Hz, 1H), 3.71 (d with str, $J = 8$ Hz, 1H, methine H), 3.07 (ddd, $J_1 > 10$ Hz, $J_2 = \sim 10$ Hz, $J_3 = 2$ Hz, 1H, methine H), 2.70 (d with str, $J = 19.5$ Hz, 1H, methylene H), 2.60 (d, $J = 8$ Hz, 1H, methine H), 2.34 (dd, $J_1 = 19.5$ Hz, $J_2 = 10$ Hz, 1H, methylene H), 2.22 (dd, $J_1 = 10$ Hz, $J_2 = \sim 8.5$ Hz, 1H, methine H), 1.63 (q with str, $J = \sim 6.5$ Hz, 1H, *H*C-CH_3), 1.07 (d, $J = \sim 6.5$ Hz, 3H, CH_3), 0.98−0.85 (m, 2H, CH_2), 0.82−0.71 (m, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 216.99 (s, CO), 216.84 (s, CO), 141.81 (d), 124.62 (d) (olefinic carbons), 59.40 (d), 48.94 (d), 48.53 (d), 46.79 (d), 44.38 (d), 36.78 (t, CH_2), 34.28 (s, quaternary C of cyclopropane ring), 15.00 (t, *C*H_2 of cyclopropane ring), 11.86 (q, CH_3), 9.8 (t, *C*H_2 of cyclopropane ring); MS *m/e* 216 (M^+).

3,3-Dimethylspiro[tricyclo[6.3.0.0^{2,6}]undec-9-ene-11-1′-cyclopropane]-4,7-dione (47). Irradiation of the ketone **32** (0.15 g, 0.61 mmol) in acetone under nitrogen for 3 h followed by column chromatography [(petroleum ether−ethyl acetate) (85:15)] yielded the tricyclic compound **47** (0.068 g, 48%): IR (neat) ν_{max} 1734 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.50 (dd, $J_1 = \sim 5$ Hz, $J_2 = \sim 3$ Hz, 1H, olefinic H), 5.35 (dd, $J_1 = \sim 5$ Hz, $J_2 = \sim 3$ Hz, 1H, olefinic H), 3.6 (br d, $J = 7.5$ Hz, 1H), 3.00 (ddd, $J_1 = J_2 = 10$ Hz, $J_3 = \sim 4$ Hz, 1H), 2.61 (dd, $J_1 = \sim 19.5$ Hz, $J_2 = 4$ Hz, 1H, methylene H α to carbonyl), 2.48 (br d, $J = 8$ Hz, 1H), 2.41−2.33 (cluster of multiplets, 2H), 0.97 (s, 3H, CH_3), 0.93−0.70 (complex m, overlapped with another signal, 4H, cyclopropane H), 0.70 (s, 3H, CH_3); MS *m/e* 230 (M^+).

3,3-Dimethyltricyclo[6.3.0.0^{2,6}]undec-10-ene-4,7,9-trione (49) and 11,11-Dimethyltricyclo[6.3.0.0^{2,6}]undec-5-ene-3,7,10-trione (50). A solution of the regioisomeric hydroxy ketones **33** and **34** (0.1 g, 0.42 mmol) in acetone (150 mL) was irradiated under nitrogen. After the reaction (TLC, 3 h), the solvent was removed under reduced pressure, and the residue was chromatographed [(petroleum ether−ethyl acetate) (80:20)] over silica gel to give a regioisomeric mixture of the tricyclic ketoalcohols (0.5 g). The mixture of the ketoalcohols was taken in acetone (10 mL), and Jones' reagent was added dropwise at ∼5 °C until the color of the reagent persisted (monitored also by TLC). Usual workup and removal of solvent gave the crude product, which was chromatographed on silica gel. Elution with petroleum ether−ethyl acetate (80:20) first gave compound **49** (0.03 g, 60%). Continued elution with petroleum ether−ethyl acetate (75:25) furnished the trione **50** (0.015 g, 30%).

Data of compound 49: UV (MeOH) λ_{max} 299 (w), 239 (s) nm; IR (Nujol) ν_{max} 1745 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (br m, 1H, β-proton of α,β-enone group), 6.36 (br m, 1H, α-proton of α,β-enone moiety), 3.68−3.64 (br m, 1H), 3.00−2.90 (multiplets, 2H), 2.78−2.70 (multiplets, 2H), 2.41 (dd, $J_1 = \sim 20$ Hz, $J_2 = 11$ Hz, 1H), 1.18 (s, 3H, CH_3), 0.82 (s, 3H, CH_3); MS *m/e* 218 (M^+).

Data of compound 50: UV (MeOH) λ_{max} 233 (s) nm; IR (neat) ν_{max} 1739, 1707 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (br m, 1H, β-proton of α,β-enone group), 6.26 (br d, 1H, α-proton of α,β-enone moiety), 3.59 (br m, 1H), 3.33 (d, $J = \sim 5$ Hz, 1H), 2.93 (m, 1H), 2.82 (d, $J = \sim 20$ Hz, 1H, methylene H α to carbonyl), 2.65 (d, $J = 9$ Hz, 1H), 2.41 (dd, $J_1 = \sim 20$ Hz, 1H, methylene H α to carbonyl), 1.18 (s, 3H, CH_3), 0.83 (s, 3H, CH_3); MS *m/e* 218 (M^+).

9,9-Dimethyl-2-oxatetracyclo[5.5.1.0^{8,12}.0^{4,13}]trideca-6,10-dione (55). Irradiation of a solution of the ketone **35** (0.15 g, 0.64 mmol) in acetone (300 mL) under nitrogen for 3 h followed by removal of the solvent and column chromatography [(petroleum ether−ethyl acetate) (85:15)] of the residue yielded the pentacyclic compound **55** (0.06 g, 40%): mp 94−95 °C; IR (film) ν_{max} 1730 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.02 (d of part of an AB system, $J_{AB} = 12$ Hz, $J_2 = 6$ Hz, 1H, OCH_2), 3.92 (part of an AB system, $J_{AB} = 12$ Hz, 1H, OCH_2), 2.72−2.66 (overlapped m, 2H), 2.58−2.46 (complex m, total 3H), 2.38−2.32 (m, 2H), 1.94 (dd with str, $J_1 = \sim 12$ Hz, $J_2 = 6$ Hz, 1H), 1.01 (s, 3H, CH_3), 0.89 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 223.06 (CO), 214.87 (CO), 72.70 (OCH_2), 59.75 (methine C), 51.43 (quaternary), 50.22 (methine C), 48.21 (methine C), 42.19 (two carbons, methine carbons), 30.78 (methine C), 26.76 (CH_3), 24.64 (methylene C), 17.28 (CH_3), (one quaternary carbon not shown); MS *m/e* 232 (M^+).

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Supporting Information Available: Copies of ^{1}H NMR spectra including some expanded spectra and ^{13}C NMR spectra (52 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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