JOC*Article*

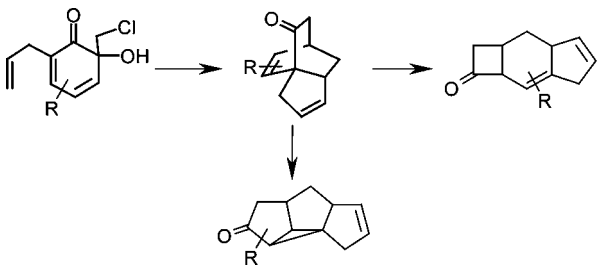
Cycloaddition of Cyclohexa-2,4-dienones, Ring-Closing Metathesis, and Photochemical Reactions: A Common Stereoselective Approach to Duprezianane, Polyquinane and Sterpurane Frameworks

Vishwakarma Singh,*[,†] G. D. Praveena,[†] Kapil Karki,[†] and Shaikh M. Mobin[‡]

Department of Chemistry and National Single X-ray Diffraction Facility, Indian Institute of Technology, Bombay, Mumbai 400 076, India

vks@chem.iitb.ac.in

Received November 23, 2006



A novel approach to three different types of carbocyclic frameworks belonging to duprezianane, sterpuranes, and polyquinanes from simple aromatic precursors has been presented. Cycloaddition of appropriately appended cyclohexa-2,4-dienones with acyclic dienes gave bridged bicyclic octanes suitably disposed with olefinic chains, which upon ring-closing metathesis led to functionalized tricyclo[5.2.2.0^{1,5}]-undecanes related to dupreziananes. Photochemical sigmatropic 1,2- and 1,3-acyl shifts in tricyclo[5.2.2.0^{1,5}] undecanes upon triplet and singlet excitation provided stereoselective routes to sterpurane and polyquinane frameworks.

Introduction

Creation of structural, functional, and stereochemical complexity in efficient fashion from simple precursors is one of the most desired aspects of development of new synthetic methodology.[1] Tandem reactions,[2,3] multicomponent reactions[4] and reactive species from aromatics[5] have been employed to achieve these objectives. β-Duprezianane, sterpuranes, and polyquinanes are important classes of sesquiterpenoids, of which the last two are formed via a common biogenetic pathway involving a humulene cyclization cascade.[6a] Among these, polyquinane natural products have stimulated intense interest for the past 2 decades[6b−d] that is continuing unabated.[7,8] This

[†] Department of Chemistry.

[‡] National Single X-ray Diffraction Facility.

(1) (a) Chanon, M.; Barone, R.; Baralotto, C.; Julliard, M.; Hendrickson, J. B. *Synthesis* **1998**, 1559−1583. (b) Corey, E. J.; Cheng, X.-M. *The Logic of Chemical Synthesis*; John Wiley & Sons: New York 1989.

(2) (a) Tietze, L. F. *Chem. Rev.* **1996**, *96*, 115−136. (b) Hudlicky, T. *Chem. Rev.* **1996**, *96*, 3−30. (c) Winkler, J. D. *Chem. Rev.* **1996**, *96*, 167−176. (d) Malacria, M. *Chem. Rev.* **1996**, *96*, 289−306. (e) Sheehan, S. M.; Lalic, G.; Chen, J. S.; Shair, M. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 2714−2715.

(3) (a) De Boeck, B.; Harrington-Frost, N. M.; Pattenden, G. *Org. Biomol. Chem.* **2005**, *3*, 340−347. (b) Curran, D. P. *Aldrichimica Acta* **2000**, *33*, 104−110. (c) Nicolaou, K. C.; Sugita, K.; Baran, P. S.; Zhaong, Y-L. *J. Am. Chem. Soc.* **2002**, *124*, 2221−2232.

(4) (a) Ugi, I. *Pure Appl. Chem.* **2001**, *73*, 187−91. (b) Bertozzi, F.; Gundersen, B. V.; Gustafsson, M.; Olsson, R. *Org. Lett.* **2003**, *5*, 1551−54. (c) Mironov, M. A.; Mokrushin, V. S.; Maltsev, S. S. *Synlett* **2003**, *7*, 943−946.

(5) (a) Magdziak, D.; Meek, S. J.; Pettus, T. R. R. *Chem. Rev.* **2004**, *104*, 1383−1430 and references therein. (b) Liao, C. C.; and Peddinti, R. K. *Acc. Chem. Res.* **2002**, *35*, 856−866. (c) Drutu, I.; Njardarson, J. T.; Wood, J. L. *Org. Lett.* **2002**, *4*, 493−496. (d) Quideau, S.; Lebon, M.; Lamidey, A.-M. *Org. Lett.* **2002**, *4*, 3975−3978. (e) Bonnarme, V.; Mondon, M.; Gesson, J.-P.; Cousson, A. *J. Chem. Soc., Chem. Commun.* **1999**, 1143−1144.; (f) Carlini, R.; Higgs, K.; Rodrigo, R.; Taylor, N. *J. Chem. Soc., Chem. Commun.* **1998**, 65−66.

(6) (a) Ayer, W. A.; Browne, L. M. *Tetrahedron* **1981**, *37*, 2197−2248. (b) Mehta, G.; Srikrishna, A. *Chem. Rev.* **1997**, *97*, 671−719. (c) Little, R. D. *Chem. Rev.* **1996**, *96*, 93−114. (d) Paquette, L. A.; Doherty, A. M. *Polyquinane Chemistry*; Springer-Verlag: Berlin, 1987.

(7) (a) Wu, Y. T.; Vidovic, D.; Magull, J.; De, Meijere, A. *Eur. J. Org. Chem.* **2005**, *8*, 1625−1636. (b) Tripp, J. C.; Schiesser, C. H.; Curran, D. P. *J. Am. Chem. Soc.* **2005**, *127*, 5518−5527. (c) Banwell, M. G.; Edward, A. J.; Harfoot, G. J.; Jolliffe, K. A. *Tetrahedron* **2004**, *60*, 535−547. (d) Davis, C. E.; Duffy, B. C.; Coates, R. M. *J. Org. Chem.* **2003**, *68*, 6935−6943. (e) Dhimane, A.; Aissa, C.; Malacria, M. *Angew. Chem. Int. Ed.* **2002**, *41*, 3284−3287. (f) Srikrishna, A.; Dethe, D. H. *Org. Lett.* **2003**, *5*, 2295−2298. (g) Mehta, G.; Murthy, A. S. K. *Tetrahedron Lett.* **2003**, *44*, 5243−5246. (h) Wang, J.-C.; Krische, M. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 5855−5857. (i) Banwell, M. G.; Edward, A. J.; Harfoot, G. J.; Jolliffe, K. A. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2439−2441. (j) Paquette, L. A.; Feng, G. *J. Am. Chem. Soc.* **2002**, *124*, 9199−9203.

10.1021/jo062416m CCC: $37.00
Published on Web 02/21/2007

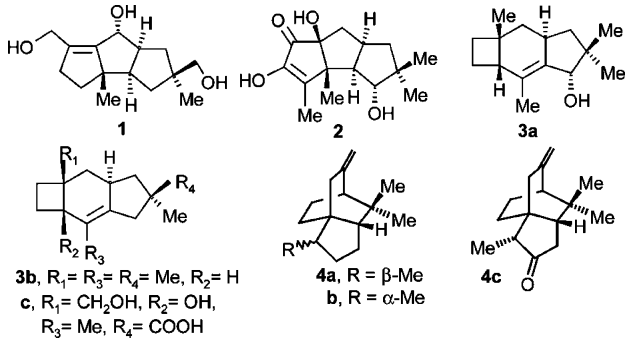
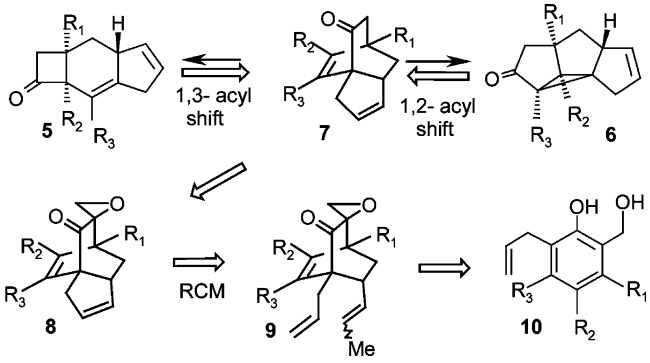


FIGURE 1. Structures of polyqinane natural products, sterpuranes, and duprezianes.

is presumably due to continuing isolation of new polyquinane natural products from various sources and their interesting biological properties.[9] For example, dichotimol **1**[9a] and connatusin A **2** and congeners,[9c] recently isolated from the mycelial cultures of *Dichomitus squalens* and the fungus *Lentinus connatus*, respectively, exhibited nematicidal and cytotoxic activities.

Sterpuranes, though not as abundant as polyquinanes, are a unique class of sesquiterpenoids. The earlier members such as **3b**,**c** (Figure 1) were isolated from *Stereum perpureum*[10] and are known to be responsible for silver leaf disease in plants. Subsequently, many other sterpuranes were also isolated from various sources.[11] Recently, the hydroxysterpurene **3a** was isolated from *Gloeophyllum*, a fungus causing brown rot of colonized wood.[11a] Despite their structural and stereochemical complexity, sterpuranes have elicited only modest interest, and there are only a few methods for their synthesis.[12,13] Recently, highly elegant routes to sterpurene employing quasi-Favorskii reaction[12a] and iron−carbene complexes[12c] have been reported. However, except for a few, most of the methods generate the tricyclic ring system in iterative fashion and employ a π2s + π2s cycloaddition for the creation of the four-membered ring.

SCHEME 1



β-Duprezianane **4a**, its epimer **4b**, and its functionalized analogue **4c** are a rare class of sesquiterpenes, isolated from the essential oil of *Juniperus thurefera L.* that contain an unusual tricyclo[5.2.2.0^{1,5}]undecane framework in their molecular architecture.[14a] Tricyclic systems having annulated bicyclo[2.2.2]-octane framework are also present in other natural products such as lacinanes,[14b] khusiol,[14c] and ermolactones.[14d]

In continuation of our interest[15] we considered the development of a common route to sterpurane, polyquinane, and duprezianane frameworks and wish to report herein a stereoselective approach to all the three types of carbocyclic frameworks from *o*-hydroxymethyl phenols.

Our strategy for the synthesis of functionalized duprezianane, sterpurane, and triquinane frameworks is outlined in Scheme 1. The cornerstone of our plan is the recognition of a structural and stereochemical relationship between the tricyclic network **7** belonging to duprezianane and those of sterpuranes and triquinanes. It was considered that the tricyclic system of type **7** may be obtained from the bridged bicyclic system **9** via ring-closing metathesis to **8** followed by functional group manipulation. The precursor **9** was thought to be accessible via oxidation of the phenol **10** into the corresponding cyclohexa-2,4-dienone and interception with acyclic-1,3-dienes. Further, it was envisioned that a sigmatropic 1,3-acyl shift in tricyclic compounds such as **7** upon singlet (^{1}S) excitation would generate the sterpurane framework **5** in a fashion so as to create all three rings of sterpuranes in correct relative orientation and place the double bond in the desired position, in a single stereoselective step. On the other hand, it was also considered that a triplet sensitized 1,2-acyl shift or oxa-di-π-methane rearrangement[16] in **7** would give the tricyclic compound **6** containing a triquinane framework.

There are several noteworthy features in the aforementioned strategy. For example, one of the olefinic tethers required in the precursor **9** is derived from the aromatic compound **10**, while

(8) (a) Harrowven, D. C.; Lucas, M. C.; Howes, P. D. *Tetrahedron* **2001**, *57*, 9157−9162. (b) Ader, T. A.; Champey, C. A.; Kuznetsova, L. V.; Li, T.; Lim, Y. H.; Rucando, D.; Sieburth, S. M. *Org. Lett.* **2001**, *3*, 2165−2167. (c) Rawal, V. H.; Reddy, J. *Org. Lett.* **2000**, *2*, 2711−2712. (d) Harrowven, D. C.; Lucas, M. C.; Howes, P. D. *Tetrahedron Lett.* **2000**, *41*, 8985−8987. (e) Dvorak, C. A.; Dufour, C.; Iwasa, S.; Rawal, V. H. *J. Org. Chem.* **1998**, *63*, 5302−5303.

(9) (a) Huang, Z.; Dan, Y.; Huang, Y.; Lidong, L.; Li, T.; Ye, W.; Wei, X. *J. Nat. Prod.* **2004**, *67*, 2121−2123. (b) Shim, S. H.; Swenson, D. C.; Gloer, J. B.; Dowd, P. F.; Wicklow, D. T. *Org. Lett.* **2006**, *8*, 1225−28. (c) Rukachaisirikul, V.; Tansakul, C.; Saithong, S.; Pakawatchai, C.; Isaka, M.; Suvannakad, R. *J. Nat. Prod.* **2005**, *68*, 1674−1676. (d) Winner, M.; Gimenez, A.; Schmidt, H.; Sontag, B.; Steffan, B.; Steglich, W. *Angew. Chem., Int. Ed. Engl.* **2004**, *43*, 1883−1886. (e) Hellwig, V.; Dasenbrock, J.; Steglich, W.; Leonhardt, K, Anke, T. *Eur. J. Org. Chem.* **1998**, 73−79.

(10) (a) Ayer, W. A.; Saeedi-Ghomi, M. H.; Engen, D. V.; Tagle, B.; Clardy, J. *Tetrahedron* **1981**, *37*, 379−385. (b) Ayer, W. A.; Saeedi-Ghomi, M. H. *Can. J. Chem.* **1981**, *59*, 2536−2538. (c) Ayer, W. A.; Saeedi-Ghomi, M. H. *Tetrahedron Lett.* **1981**, *22*, 2071−2074.

(11) (a) Rasser, F.; Anke, T.; Sterner, O. *Phytochemistry* **2000**, *54*, 511−516. (b) Xie, J.-L.; Li, L.-P.; Dai, Z. Q. *J. Org. Chem.* **1992**, *57*, 2313−2316. (c) Sterner, O.; Anke, T.; Sheldrick, W. S.; Steglich, W. *Tetrahedron* **1990**, *46*, 2389−2400. (d) Cimino, G.; Giulio, A. D.; Rosa, S. D.; Stefano, S. D. *Tetrahedron* **1989**, *45*, 6479−6484. (e) Abell, C.; Leech, A. P. *Tetrahedron Lett.* **1988**, *29*, 4337−4340.

(12) (a) Harmata, M.; Bohnert, G. J. Org. Lett. **2003**, *5*, 59−61. (b) Mehta, G.; Sreenivas, K. *Tetrahedron Lett.* **2002**, *43*, 703−706. (c) Ishii, S.; Zhao, S.; Mehta, G.; Knors, C. J.; Helquist, P. J. *Org. Chem.* **2001**, *66*, 3449−3458.

(13) (a) Strunz, G. M.; Bethell, R.; Dumas, M. T.; Boyonski, N. *Can. J. Chem.* **1997**, *75*, 742−753. (b) Arnone, A.; Gregorio, C. D.; Nasini, G.; Pava, O. V. D. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1523−1526. (c) Zhao, S. K.; Helquist, P. *J. Org. Chem.* **1990**, *55*, 5820−5821. (d) Gibbs, R. A.; Bartels, K.; Lee, R. W. K.; Okamura, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 3717−3725. (e) Paquette, L. A.; Lin, H.-S.; Gunn, B. P.; Coghlan, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 5818−5826. (f) Moens, L.; Baizer, M. M.; Little, R. D. *J. Org. Chem.* **1986**, *51*, 4497−4498.

(14) (a) Barrero, A. F.; del Moral, J. Q.; Lara, A. *Tetrahedron* **2000**, *56*, 3717- 3723. (b) Fukushi, Y.; Yajima, C.; Mizutani, J.; Tahara, S. *Phytochemistry* **1998**, *49*, 593−600. (c) Ganguly, R. N.; Trivedi, G. K.; Bhattacharya, S. *Indian J. Chem.* **1978**, *16B*, 23−26. (d) Golsmith, D. In *The Total Synthesis of Natural Products*; Ap-Simon, J., Ed.; John Wiley & Sons: New York, 1992; Vol. 8, pp 1−243.

(15) (a) Singh, V. *Acc. Chem. Res.* **1999**, *32*, 324−333. (b) Singh, V.; Prathap, S. *Tetrahedron* **1996**, *52*, 14287−14296.

(16) (a) Demuth, M.; Hisken, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 973−975. (b) Demuth, M.; Schaffner, K. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 820−836.

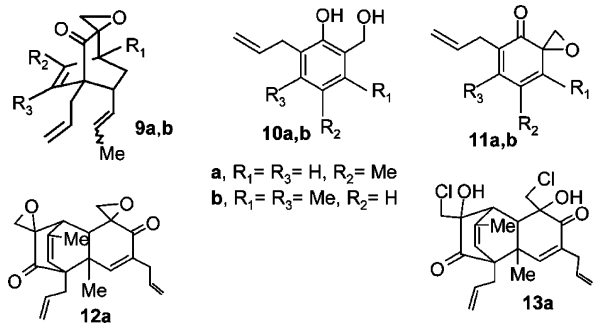


FIGURE 2. Precursors and potential intermediates.

the other would be introduced in the *endo* position by virtue of the cycloaddition, thus keeping both the tethers in appropriate stereochemical disposition required for ring-closing metathesis. Further, both carbocyclic systems **5** and **6** are generated in a single step from the tricyclic precursor **7** via modulation of chemical reactivity in the excited states. Moreover, the key precursors **8** and **9** are generated from simple aromatics, thus generating molecular complexity in the very beginning of the synthetic route, which is one of the important aspects of development of methodology.[1]

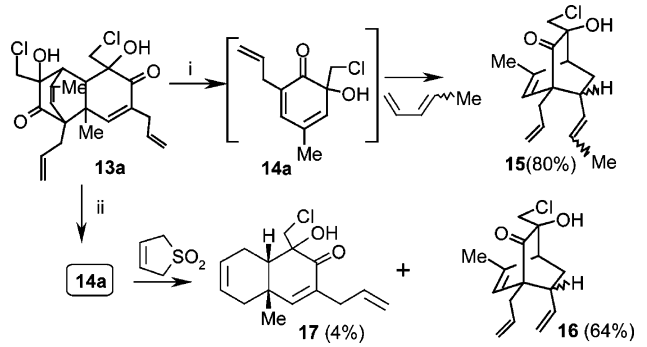
Results and Discussion

Synthesis of Tricyclo[5.2.2.0^{1,5}]undecanes. Toward the realization of the above strategy, it was necessary to devise a new method for the synthesis of tricyclic systems of type **7** and **8** since they are not readily accessible.[17] In the beginning, we considered to develop a synthesis of the keto-epoxide **9a** from the aromatic precursor **10a** via its oxidation to the spiroepoxydienone **11a** and subsequent interception with 1,3-pentadiene. Therefore, the compound **10a**, readily prepared from *p*-cresol, was oxidized with aqueous sodium *m*-periodate in presence of excess 1,3-pentadiene at 0−5 °C following a procedure earlier developed in our laboratory.[15b] However, it did not give the desired adduct **9a**, and instead the dimer **12a** was obtained (Figure 2). Moreover, an attempt to generate the dienone **11a** by retro Diels−Alder reaction of **12a** and interception with 1,3-pentadiene was also futile and gave a mixture of products containing small amounts of 2-hydroxy-3-allyl-5-methyl benzaldehyde.

In order to circumvent the aforementioned problems, the epoxy-dimer **12a** was prepared by periodate oxidation of **10a** and converted into chloro-hydroxy derivative **13a** with a view to generate **14a** and intercept with 1,3-pentadiene. Indeed, pyrolysis of the chloro-hydroxy dimer **13a** in the presence of 1,3-pentadiene led to the desired adduct **15** in excellent yield (80%) as a mixture of *endo* and *exo* isomers, having *endo* as a major isomer (Scheme 2). Similarly, the pyrolysis of the **13a** in the presence of the butadiene sulfone, a source of butadiene, gave the adduct **16** in addition to a small amount of *cis*-decalin derivative **17**, the latter formed as a result of Cope rearrangement of the adduct.

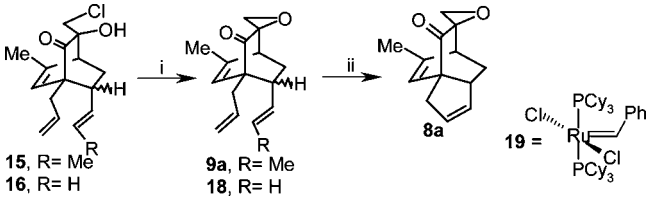
The adduct **15** was efficiently converted to the keto-epoxide **9a** (*endo*/*exo* mixture). Treatment of **9a** with first generation

SCHEME 2[a]



[a] Reagents and conditions: (i) 95−100 °C, *o*-dichlorobenzene; (ii) 105 °C, *o*-dichlorobenzene.

SCHEME 3[a]



[a] Reagents and conditions: (i) aq KOH, $CHCl_3$, CTAB, **9a** (87%), **18** (90%); (ii) **19**, CH_2Cl_2, rt, (55% from **9a**, 35% from **18**).

Grubbs catalyst **19** in dichloromethane ensued a smooth ring-closing metathesis[18,19] and gave the desired product **8a** in good yield (55%), along with some unreacted starting material (mostly the *exo* isomer). Similarly, the adduct **16** was also converted into the keto-epoxide **18**, which upon ring-closing metathesis furnished the same tricyclic keto-epoxide **8a** in good yield (Scheme 3).

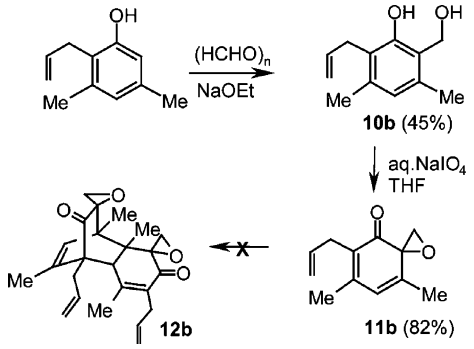
The structure of the cyclized product **8a** was deduced from its spectroscopic features and comparison with its precursor. The ^{1}H NMR (300 MHz, $CDCl_3$) spectrum showed signals for three olefinic protons at δ 5.80−5.75 (m, 1H), 5.65−5.61 (m, 1H), and 5.40 (br m, 1H) (as compared to six in its precursor), clearly indicating that ring-closing metathesis (RCM) had occurred. Moreover, the ^{1}H NMR spectrum exhibited a signal for only one methyl group at δ 1.90 (d, J = 1.5 Hz), which further suggested that RCM had taken place. The methylene protons of the oxirane ring appeared as an AB quartet at δ 3.20 (part of an AB pattern merged with a multiplet, J_{AB} = 6 Hz, 1H) and 2.83 (part of an AB pattern, J_{AB} = 6 Hz, 1H). In addition, other signals appeared at 3.22−3.16 (m merged with AB system, 1H), 2.41−2.22 (merged m, 3H), and 1.40−0.98 (m, 1H). The ^{13}C NMR spectrum displayed signals at δ 203.4 (CO), 145.9, 132.0, 130.4, and 125.0 for the carbonyl and four olefinic carbons, respectively. Other carbons gave signals at 62.09, 57.36, 51.55, 48.13, 44.79, 33.83, 26.14, and 20.09, thus accounting for all 13 carbon atoms. These spectral features suggested the gross structure of the cyclized product. However, it was difficult to ascertain the stereochemistry of the oxirane ring. Hence, the structure **8a** was confirmed through

(17) (a) Buchi, G.; Hauser, A.; Limacher, J. *J. Org. Chem.* **1977**, *42*, 3323−3324. (b) Yamada, Y.; Nagaoka, H.; Kimura, M. *Synthesis* **1977**, 581−582. (c) Demuth, M. Hinsken, W. *Helv. Chim. Acta*, **1988**, *71*, 569−576. (d) Hariprakash, H. K.; Subbarao, G. S. R. *Tetrahedron Lett.* **1997**, *38*, 5343−5346. (e) Singh, V.; Alam, S. Q. *J. Chem. Soc., Chem. Commun.* **1999**, 2518−2519.

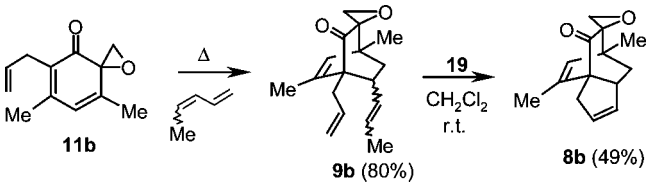
(18) (a) *Hand Book of Metathesis*; Grubbs, R. H., Ed.; Wiely-VCH: Weinheim, Germany, 2003. (b) *Alkene Metathesis in Organic Synthesis*; Furstner, A., Ed.; Springer-Verlag: Germany, 1998.

(19) (a) Katz, T. *Angew. Chem. Int. Ed.* **2005**, *44*, 3010−3019. (b) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem. Int. Ed.* **2003**, *42*, 4592−4633. (c) Schmidt, B. *Angew. Chem. Int. Ed.* **2003**, *42*, 4996−4999.

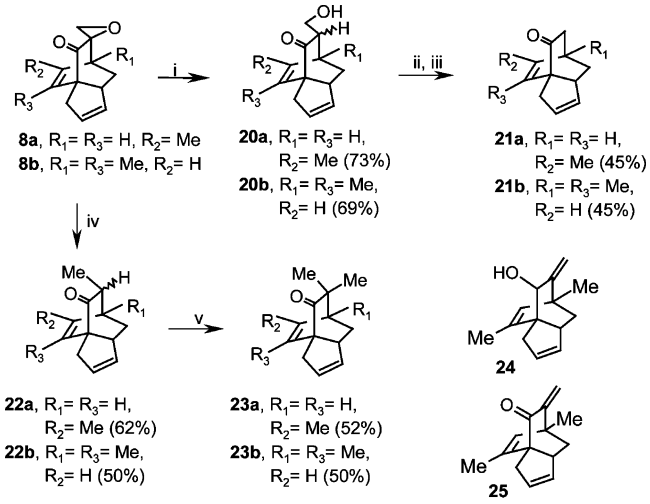
SCHEME 4



SCHEME 5



SCHEME 6[a]



[a] Reagents and conditions: (i) Zn, NH_4Cl, $MeOH/H_2O$; (ii) Jones oxidation; (iii) aq THF, Δ; (iv) Zn, NH_4Cl, dry dioxane, Δ; (v) NaH/THF, MeI, Δ.

a single-crystal X-ray structure determination (see Supporting Information).

Having checked the approach, we adopted it to the synthesis of the tricyclic compound **8b** containing dimethyl groups. Thus, 2-allyl-3,5-dimethylphenol, easily prepared from 3,5-dimethylphenol, was subjected to hydroxymethylation with aqueous formaldehyde and sodium hydroxide. However, it gave a complex mixture of polymeric products. After considerable experimentation, treatment of 2-allyl-3,5-dimethylphenol with *p*-formaldehyde in the presence of sodium ethoxide[20] furnished the desired product **10b** in moderate yield (Scheme 4). In order to prepare the dimer **12b**, the phenol **10b** was oxidized with sodium *m*-periodate. However, it did not furnish the desired dimer, and instead the monomer **11b** was isolated in excellent yield, whose structure was readily revealed from its spectroscopic features.

It was indeed surprising to isolate the cyclohexadienone **11b**, especially since spiroepoxycyclohexadienones are known to have only fleeting existence during the oxidation and instantaneously dimerize.[21] It was interesting to note that the spiroepoxycyclohexa-2,4-dienone **11b** was quite stable, unlike many others, and did not show propensity to undergo Diels−Alder dimerization, although heating at high temperatures (∼140 °C) led to decomposition. It appears that the steric hindrance due to the presence of the allyl and methyl groups prevents the dimerization of **11b**.

Fortunately, heating a solution of the cyclohexadienone **11b** and 1,3-pentadiene (*cis* + *trans*) in *o*-dichlorobenzene in a sealed tube at 100 °C followed by chromatography afforded the adduct **9b** in good yield (80%) as a mixture of *endo* and *exo* isomers containing *endo* as a major isomer. The mixture of adducts was then treated with first generation Grubbs' catalyst **19**, which gave the cyclized product **8b** in 49% yield (Scheme 5).

The contiguous presence of oxirane ring and carbonyl group in tricyclic compounds **8a,b** provided opportunity for further manipulation. Thus, reduction of the keto-epoxide **8a** with activated zinc and ammonium chloride in aqueous methanol[15,22] at ambient temperature (∼30 °C) gave the β-keto alcohol **20a** as the major product (73%) (*syn*/*anti* mixture, ^{1}H NMR), along with very minor amount of the ketone **22a** (Scheme 6). The keto-alcohol **20a** was oxidized with Jones' reagent[23a] and the resulting β-keto-acid was decarboxylated[23b] in refluxing aqueous THF to give the desired compound **21a** in moderate yields (45% for two steps). Alternatively, the reduction of the epoxy-ketone **8a** with activated zinc in refluxing dry dioxane containing ammonium chloride furnished the ketone **22a** as a major product (62%, *syn*/*anti* mixture) as a result of deoxygenation of the oxirane ring, along with the minor compound **20a** (Scheme 6). Alkylation of the ketone **22a** with methyl iodide in the presence of NaH−THF gave the tricyclic system **23a** (52%) (Scheme 6). Similarly, reduction of the keto-epoxide **8b** with Zn in aqueous methanol gave the β-keto-alcohol **20b** as a major product and minor amounts of **22b** (5%) and the trienol **24** (19%). The keto-alcohol **20b** was converted into the tricyclic compound **21b**. Further, compound **8b** was also reduced with Zn−NH_4Cl in dry dioxane to give **22b** along with minor amounts of the trienol **24** (25%) and the keto-alcohol **20b** (15%). The compound **22b** was then alkylated to give the tricyclic compound **23b**. The trienol **24** was oxidized with PDC to give the trienone **25**.

Further, we considered functionalization of the five-membered ring in **21a,b** via allylic oxidation.[24] Thus, the ketone **21a** was treated with PDC in the presence of ^{t}BuOOH in dry benzene (Scheme 7). However, it did not give the expected enones **27** and/or its regioisomer, and instead the enone **26a** was obtained (62%). Attempts for allylic oxidation with PCC and CrO_3−dimethyl pyrazole also gave the same enone as a major

(20) Finn, S. R.; Lewis J. J.; Negson, N. J. L. *J. Soc. Chem. Ind.* **1950**, 129−132.

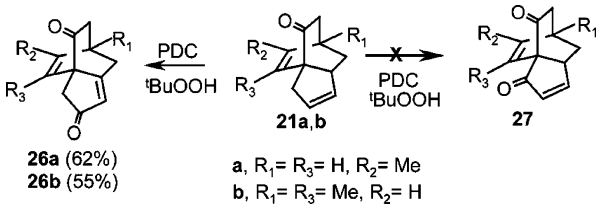
(21) (a) Adler, E.; Bransen, S.; Miyake, H. *Acta Chem. Scand.* **1971**, *25*, 2055−2069. (b) Adler, E.; Holmberg, K. *Acta Chem. Scand.* **1974**, *28B*, 465−472.

(22) (a) Singh, V.; Deota, P. T.; Bedekar, A. V. *J. Chem. Soc., Perkin Trans. 1*, **1992**, 903−912. (b) Singh, V.; Deota, P. T. *J. Chem. Res.* **1989**, 390−391.

(23) (a) Harrison, I. T.; Harrison, S. *Compendium of Organic Synthetic Methods*; Wiley-Interscience: New York, 1971. (b) House, H. O. *Modern Synthetic Reactions*; W. A. Benzamin: Menlo Park, CA, 1972.

(24) Bullman Page, P. C.; McCarthy, T. J. In *Comprehensive Organic Synthesis*; Ley, S.V., Ed.; Pergamon Press: New York, 1991; Vol. 7, pp 83−117.

SCHEME 7



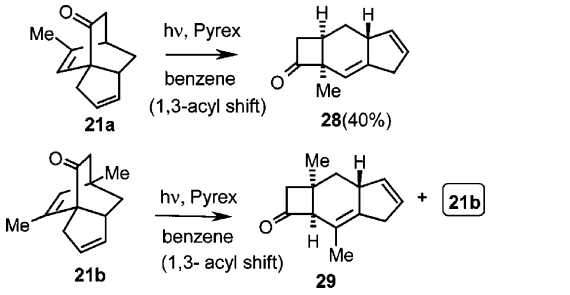
product, and oxidation with SeO_2 gave a complex mixture. Similarly, the oxidation of **21b** also gave the dienone **26b**. It was indeed intriguing to note the formation of **26a,b** during the oxidation especially, since the double bond migrated to afford the more highly substituted alkenes. The structure of the enones **26a,b** was clearly revealed from their spectral data and comparison with the spectral features of the precursors.

It may be mentioned that tricyclic compounds of type **8** and **20**−**26** having a β,γ-unsaturated carbonyl chromophore are not readily available, and the present methodology provides a novel and efficient route to such systems.

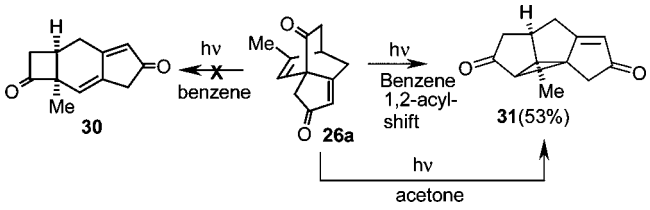
Studies on Photochemical Reactions of Tricyclic System 21a,b and Congeners upon Singlet and Triplet Excitation. Photochemical reactions of β,γ-enones have generated interest for a long time,[25] an interest that is further enhanced recently as a result of their synthetic potential.[16,26,27] In general, β,γ-enones undergo two unique reactions, namely, the 1,2-acyl shift (or the oxa-di-π-methane rearrangement) and the 1,3-acyl shift.[25−27] Demuth and co-workers have examined oxa-di-π-methane reaction of several types of β,γ-enones and demonstrated its synthetic potential.[16,25b,d] Though the photoreactions of β,γ-enones are quite characteristic of their excited states, i.e., 1,2-shift from lowest triplet (T_1) and 1,3-shift from singlet (S_1) or higher triplet (T_2), small changes in the structure of the chromophore and substituents are known to control the outcome in a subtle fashion. Moreover, selective population of excited states is also required for specific photochemical reaction.[25a,27a,b] Keeping the above in mind, photoreaction of tricyclic chromophoric systems **21a,b**−**26** was explored under direct and sensitized irradiation.

Toward the synthesis of the sterpurane framework, photochemical reaction of the tricyclic ketone **21a** was explored upon direct irradiation. Thus, a solution of the ketone **21a** in benzene was irradiated with a mercury vapor lamp (125 W, Applied Photophysics) for 30 min in a Pyrex immersion well (Scheme 8). Removal of solvent and careful chromatography

SCHEME 8



SCHEME 9



of the photolysate gave the desired tricyclic compound **28** in moderate yield (40%) along with a very minor amount of decarbonylated product and some unreacted starting material. The photoproduct, however, appeared to be relatively unstable.

The structure of compound **28** was deduced from its spectral data and comparison with the spectral features of its precursor **21a**. Thus, the IR spectrum of the compound showed an absorption band at 1770 cm^{-1}, which is characteristic of a carbonyl group present in a four-membered ring. Its ^1H NMR spectrum (300 MHz) showed characteristic signals at δ 5.91−5.60 (m, 2H) and 5.30 (br s, 1H) for the three olefinic protons. The appearance of an upfield signal at δ 1.30 (s, 3H) for methyl protons also suggested that the desired structural reorganization had occurred. Other signals were observed at δ 3.20−2.96 (merged m, 4H), 2.86−2.76 (dd, J_1 = 18 Hz, J_2 = 5 Hz, 1H), 2.40−2.30 (m, 1H), 2.15−2.07 (d of dd, J_1 = 13.5 Hz, J_2 = 4.0 Hz, J_3 = 1.5 Hz, 1H), and 1.12−1.00 (d of superimposed dd, J_1 = 13.5 Hz, $J_2 \approx$ 4.0 Hz, 1H). The ^{13}C NMR spectrum (75 MHz) showed resonances at δ 211.7 for carbonyl carbon and 146.1, 133.2, 129.8, and 118.1 for the four olefinic carbons. It further showed signals at δ 62.8, 45.9, 40.1, 38.7, 31.0, 26.01, and 21.1, thus accounting for all 12 carbon atoms.

The irradiation of **21b** under similar conditions also led to the formation of 1,3-acyl shift product **29** (IR and ^1H NMR). However, the photoproduct could not be separated from its starting material. The photochemical reaction of the dienone **26a** upon singlet excitation was indeed surprising, as its direct irradiation in benzene did not give the 1,3-acyl shift product **30**, but instead the triquinane **31** was obtained as a result of oxa-di-π-methane rearrangement (Scheme 9). The absence of 1,3-acyl migration in the direct irradiation of **26a** is presumably due the absorption of light by the α,β-enone chrompore present in **26a**; apparently the compound **31** is formed by self-sensitization via oxa-di-π-methane reaction. The sensitized irradiation of **26a** in acetone also gave the triquinane **31**.

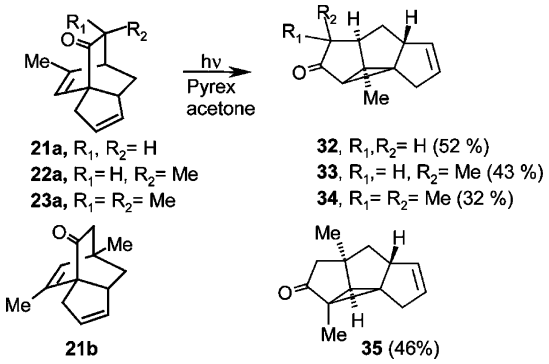
Toward synthesis of triquinane framework, we first examined the photochemical reaction of **21a** upon triplet-sensitized irradiation. Thus, a solution of the compound **21a** in degassed dry acetone (as both solvent and sensitizer) was irradiated in a Pyrex immersion well under nitrogen for 1 h. Removal of solvent and chromatography furnished the tetracyclic compound **32** in moderate yield (52%) as a result of 1,2-acyl shift

(25) (a) Schuster, D. I. In *Rearrangement in Ground and Excited States*; de Mayo, P., Ed; Academic Press, New York, 1980; Vol. 3, pp 167 and references cited therein. (b) Houk, K. N. *Chem. Rev.* **1976**, *76*, 1−74. (c) Coffin, R. L.; Givens, R. S.; Carlson, R. G. *J. Am. Chem. Soc.* **1974**, *96*, 7554−7556. (d) Hixon, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531−551. (e) Givens, R. S.; Oettle, W. F. *J. Chem. Soc., Chem. Commun.* **1969**, 1164−1165.

(26) (a) Zimmerman, H. E.; Armesto, D. *Chem. Rev.* **1996**, *96*, 3065 and references therein. (b) Demuth, M. In *Organic Photochemistry*; Padwa, A., Ed.; Marcell Dekker, Inc.: New York, 1991; Vol. 11, pp 37−97. (c) Padwa, A.; Zhi, L.; Fryxel, Z. E. *J. Org. Chem.* **1991**, *56*, 1077−1083. (d) Schaffner, K.; Demuth, M. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer-Verlag: Berlin, 1986; Vol. 4, pp 61.

(27) (a) Armesto, D.; Ortiz, M. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 7739−7741. (b) Armesto, D.; Ortiz, M. J.; Agarrabeitia, A. R.; Martin-Fontecha, M. *Org. Lett.* **2005**, *7*, 2687−2690. (c) Armesto, D.; Ortiz, M. J.; Agarrabeitia, A. R. In *Organic Photochemistry and Photobiology*; Horspool, W. M., Lenci, F., Eds.; CRC Press: Boca Raton, FL, 2004; Chapter 77. (d) Singh, V. In *Organic Photochemistry and Photobiology*; Horspool, W. M., Lenci, F., Eds.; CRC Press: Boca Raton, FL, 2004; Chapters 78 and 79.

SCHEME 10



(Scheme 10). A small amount of starting material was also recovered. Similarly, sensitized irradiation of compounds **22a** and **23a** in acetone using a mercury vapor lamp gave the corresponding ODPM products **33** and **34** in 43% and 32% yields, respectively (Scheme 10). Sensitized irradiation of **21b** also gave the tetracyclic product **35** as a result of 1,2-acyl shift.

Conclusion

In summary, an efficient synthesis of various tricyclo-[5.2.2.0^{1,5}]undecanes **8a**,**b** and **20**−**26** belonging to duprezianes and a stereoselective entry to the triquinane and sterpurane frameworks has been described. The methodology involved ring-closing metathesis on appropriately designed bicyclo[2.2.2]octenones and photochemical transformations of the resulting tricyclic systems. The bridged bicyclic precursors having suitable olefinic appendages were assembled from simple starting materials via the in situ generation of cyclohexa-2,4-dienones followed by their interception with acyclic dienes. Photochemical reactions of tricyclo[5.2.2.0^{1,5}]undecanes **21a,b** upon direct irradiation led to the formation of 1,3-acylshift products **28** and **29**, whereas direct irradiation of **26a** gave the triquinane **31** as a result of oxa-di-π-methane reaction. Triplet sensitized irradiation of **21a,b**, **22a**, **23a**, and **26a** gave triquinane frameworks, **32**, **35**, **33**, **34**, and **31**, respectively, in a single stereoselective step. The present methodology also demonstrates creation of structural diversity from simple aromatic precursors. Further application of the methodology toward synthesis of natural products is underway.

Experimental Section

6-Allyl-4-methyl-2-hydroxymethylphenol (10a). To a solution of 2-allyl-4-methylphenol (50 g, 0.338 mol) in aqueous sodium hydroxide (1 M, 500 mL) was added formaldehyde (35% w/v; 138 mL, 1.69 mol), and the mixture was stirred for 24 h at room temperature. The reaction mixture was cooled in a crushed ice bath, acidified with dilute hydrochloric acid, and then extracted with ethyl acetate (4 × 100 mL). The organic layer was separated and dried over anhydrous sodium sulfate. Removal of solvent and column chromatography (petroleum ether/ethyl acetate 90:10) gave the compound **10a** (45 g, 75%) as a colorless solid. Mp: 62−63 °C. IR (neat) ν_{max}: 3407, 3347 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.88 (s, 1H), 6.72 (s, 1H), 6.04−5.96 (m, 1H), 5.12−5.07 (m, 2H), 4.76 (s, 2H), 3.7 (d, J = 6 Hz, 2H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 137.0, 130.6, 129.2, 126.9, 126.7, 124.6, 115.9, 64.6, 34.4 and 20.5. Mass (*m*/*z*): 178 (M^+). Analysis: found C, 74.04; H, 8.17; calcd for $C_{11}H_{14}O_2$ C, 74.13; H, 7.92.

6,9-Bis-spiroepoxy-1,4-diallyl-2,12-dimethyl-tricyclo[6.2.2.0^{2,7}]-dodec-3,11-dien-5,10-dione (12a). To a solution of the 6-allyl-4-methyl-2-hydroxymethylphenol **10a** (20 g, 0.112 mol) in acetonitrile (50 mL) was added an aqueous solution of sodium *m*-periodate (48 g, 0.224 mol, 400 mL water) dropwise at ∼10 °C, and the reaction mixture was stirred for 1 h. After further stirring for 3 h at room temperature, the product was filtered, washed with water (3 × 100 mL), and dried to give the epoxy dimer **12a** as a pale yellow solid (13.8 g, 70%), which was recrystallized from petroleum ether/ethyl acetate (10:2). Mp: 115−116 °C. IR (neat) ν_{max}: 1732, 1692 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.29 (s, 1H), 5.84−5.66 (m, 2H), 5.51−5.49 (t, J = 1.5 Hz, 1H), 5.16−5.04 (m, 4H), 3.15 (part of an AB system, J = 6.5 Hz, 1H), 3.08−2.88 (complex m, 3H), 2.95 (part of AB system partly merged with m, J = 6.5 Hz, IH), 2.81 (s, 2H), 2.6 (t, J = 1.6 Hz, 1H), 2.24−2.14 (merged m, 2H), 1.88 (d, J = 1.5 Hz, 3H), 1.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.7, 192.3, 146.4, 143.5, 139.4, 134.5, 125.9, 118.6, 117.5, 62.0, 58.9, 58.2, 57.9, 53.2, 48.4, 46.5, 45.9, 33.8, 30.7, 23.9, 21.0. Mass (*m*/*z*): 352 (M^+). Analysis: found C, 74.95; H, 6.81; requires C, 74.97; H, 6.86 for $C_{22}H_{24}O_4$.

6,9-Bis-chloromethyl-1,4-diallyl-6,9-dihydroxy-2,12-dimethyl-tricyclo[6.2.2.0^{2,7}]dodec-3,11-dien-5,10-dione (13a). To a solution of epoxy dimer **12a** (10 g, 28.41 mmol) in dioxane (100 mL) was slowly added concd HCl (25 mL) at ∼10 °C with stirring. After stirring for 1 h, a yellow precipitate was obtained. The reaction mixture was filtered, and the precipitate was washed with water and dried to give the compound **13a** (10.7 g, 89%), which was recrystallized from chloroform to give a colorless solid. Mp: 122−123 °C. IR (neat) ν_{max}: 3466, 1736, 1703 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.07 (s, 1H), 5.81−5.55 (m, 2H), 5.32 (t, J = 1.6 Hz, 1H), 5.15−5.03 (merged m, 4H), 4.23 (br s, 1H, OH), 3.74−3.44 (merged m, 6H), 3.11−2.72 (br m, 4H), 2.06 (dd, J_1 = 13.5 Hz, J_2 = 9.0 Hz, 1H), 1.77 (d, J = 1.8 Hz, 3H), 1.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.9, 197.1, 144.7, 144.4, 136.7, 134.1, 134.0, 125.5, 118.7, 117.9, 74.0, 67.1, 61.7, 53.9, 49.9, 46.6, 46.5, 45.1, 34.1, 30.7, 23.7 and 21.0. Mass (*m*/*z*): 447.10 ($M^+ + Na^+$). Analysis: found C, 61.33; H, 6.89; requires C, 61.11; H, 6.55 for $C_{22}H_{26}O_4Cl_2$.

1-Allyl-3-chloromethyl-3-hydroxy-5-methyl-7-propenyl-bicyclo-[2.2.2]oct-5-en-2-one (15). A solution of the dimer **13a** (1 g, 2.35 mmol) and 1,3-pentadiene (mixture of *cis* and *trans*) (1.5 mL, excess) in *o*-dichlorobenzene (2 mL) was heated at 105−110 °C in a sealed tube for 7 h. The reaction mixture was then charged as such on silica gel. Elution with petroleum ether first gave *o*-dichlorobenzene. Further elution with petroleum ether/ethyl acetate (96:4) gave an inseparable *endo*/*exo* mixture of adducts **15** (1.03 g, 78%) as a colorless liquid. Repeated chromatography of the mixture of adducts on silica gel (100−200 mesh) furnished the major isomer in pure form. IR (neat) ν_{max}: 3476, 1720 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): signals for the major isomer, δ 5.8−5.64 (m, 2H), 5.48−5.36 (m, 1H), 5.16−5.04 (merged m, 3H), 3.58 (part of an AB system, J_{AB} = 12.0 Hz, 2H), 2.95 (br m, 1H), 2.45−2.31 (m, 3H), 2.19−2.10 (m, 1H), 1.93−1.75 (d, merged with m, J = 1.2 Hz, total 5H), 1.6 (two sets of d dd, J = 1.8 Hz, total 3H). ESI HRMS: calcd for $C_{16}H_{21}O_2ClNa$ [M^+ + Na] 303.1128, found 303.1128.

11-Methyl-8-spiroepoxy-tricyclo[5.2.2.0^{1,5}]undec-3,10-dien-9-one (8a). To a solution of the adduct **15** (5 g, 17.82 mmol) in chloroform (500 mL) containing cetyltrimethylammonium bromide (CTAB) (0.35 g) as a phase transfer catalyst was added an aqueous solution of potassium hydroxide (1.25 g, 22.3 mmol in 100 mL water). The reaction mixture was stirred at ambient temperature for 5 h, after which the organic phase was separated and the aqueous layer was extracted with chloroform (3 × 40 mL). The combined organic extract was washed with brine (1 × 30 mL) and dried over anhydrous sodium sulfate. Removal of solvent in vacuo followed by chromatography (petroleum ether/ethyl acetate (97:3) of the residue gave an inseparable mixture of keto-epoxide **9a** (3.78 g, 87%) as a colorless liquid [IR (neat) ν_{max}: 1733 cm^{-1}, HRMS: calcd for $C_{16}H_{20}O_2Na$ [M^+ + Na] 267.1361, found 267.1363] which was directly subjected to the ring-closing metathesis as described below.

To a degassed solution of compound **9a** (0.5 g, 2.05 mmol) in dichloromethane (205 mL, 0.01 M) was added Grubbs catalyst **19** (68 mg, 4 mmol %), and the reaction mixture was stirred at ambient temperature under nitrogen. Removal of solvent under reduced pressure followed by column chromatography of the residue with petroleum ether/ethyl acetate (97:3) first gave the unreacted starting material (0.18 g, 36%, mostly the *exo* isomer). Continued elution with petroleum ether/ethyl acetate (96:4) gave the cyclized compound **8a** as a colorless solid (0.227 g, 55%). Mp: 70−72 °C. IR (neat) ν_{max}: 1736 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.8−5.75 (m, 1H), 5.65−5.61, (m, 1H), 5.4 (br m, 1H), 3.22−3.16 (m partly merged with an AB system, 1H), 3.20 (part of an AB system merged with m, J_{AB} = 6.0 Hz, 1H), 2.98−2.88 (m of d, J = 16 Hz, 1H), 2.83 (part of an AB system, J_{AB} = 6.0 Hz, 1H), 2.41−2.22 (merged m, 3H), 1.90 (d, J = 1.5 Hz, 3H), 1.40−0.98 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.4, 145.9, 132.0, 130.4, 125.0, 62.0, 57.3, 51.5, 48.1, 44.7, 33.8, 26.1, and 20.0. ESI HRMS: calcd for $C_{13}H_{14}O_2Na$ [M$^+$ + Na] 225.0891, found 225.0896.

1-Allyl-3-chloromethyl-3-hydroxy-5-methyl-7-vinylbicyclo-[2.2.2]oct-5-en-2-one (16) and 4-Allyl-2-chloromethyl-2-hydroxy-6-methylbicyclo[4.4.0]dodeca-4,8-dien-3-one (17). A mixture of the dimer **13a** (1 g, 2.35mmol) and butadiene sulfone (8 g, excess, added at regular intervals over a period of 7 h) in *o*-dichlorobenzene was heated at 105 °C for 7 h. The solvent was distilled off, and the residue was chromatographed on silica gel. Elution with petroleum ether gave some *o*-dichlorobenzene. Continued elution with petroleum ether/ethyl acetate (97:3) furnished the adduct **16** as a mixture of *endo* and *exo* isomers(0.8 g, 64%) and **17** as a minor product (0.05 g, 4%).

Data for 16 (mixture of *endo*, *exo*). IR ν_{max}: 1720, 3476 cm^{-1}. ^{1}H NMR($CDCl_3$, 400 MHz): δ, 5.84−5.40 (m merged with s, total 3H), 5.09−4.94(m, total 4H), 3.62−3.42 (two sets of AB system, J_{AB} = 7.5 Hz, total 2H), 2.98 (br m, 1H), 2.80, 2.72 (two s, total 1H), 2.53−2.40(merged m, total 3H), 2.25−2.20 (m, 1H), 1.97 (two sets of d, J = 1.5 Hz, total 3H), 1.26−1.19 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.8, 145.1, 137.9, 133.8, 124.1, 118.4, 117.2, 75.0, 54.8, 503, 47.9, 44.5, 33.3, 26.7, 21.1. HRMS: calcd for $C_{15}H_{19}O_2ClNa$ [M$^+$ + Na] 289.0766, found 289.0729 [M$^+$ + Na].

Data for 17. Mp: 59−61 °C. IR ν_{max}: 3457, 1669 cm^{-1}. ^{1}H NMR($CDCl_3$, 400 MHz): δ, 6.64 (s 1H), 5.85−5.71(m, 3H), 5.11−5.06 (m, 2H), 3.93 (part of an AB system, J_{AB} = 11 Hz, 1H), 3.54 (part of an AB system, J_{AB} = 11 Hz, 1H), 3.06−2.97 (m, 2H), 2.70 (s, 1H), 2.44−2.37 (m, 2H), 2.03−1.97 (d with structure, J = ~13.5 Hz, 1H), 1.24 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 196.9, 156.9, 135.1,134.3, 125.7, 124.6, 116.9, 46.4, 38.7, 36.8, 33.9, 33.4, 27.5, 22.5. Analysis: found C, 67.30; H, 7.40; calcd C, 67.53; H, 7.17 for $C_{15}H_{20}ClO_2$.

Transformation of 1-Allyl-3-chloromethyl-3-hydroxy-5-methyl-7-vinylbicyclo[2.2.2]oct-5-en-2-one (16) into 8a. A solution of the adduct **16** (0.478 g, 1.79mmol) was treated with aqueous KOH (2.34 mmol, 10 mL) in the presence of cetyltrimethylammonium bromide (0.035 g) as described earlier. Usual workup and chromatography gave the keto-epoxide **18** [(0.352 g, 85%), IR ν_{max}: 1732, cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.93−5.40 (two sets of m and s, total 3H); 5.16−4.97(m, 4H), 3.10 (two set of part of AB system, J_{AB} = 6.2 Hz, total, 1H), 2.87 (two set of part of AB system, J_{AB} = 6.2 Hz, total, 1H), 2.60−2.23 (cluster of m, total 5H), 2.10−1.8 (multiplet overlapped with two sets of d, J = 1.5 Hz, total 4H), 1.45−1.38 (m, 1H). MS calcd for $C_{15}H_{18}O_2Na$ (M$^+$ + Na) 253.266, found 253.116 (M$^+$ + Na)]. The keto-epoxide (0.487 g, 2.10 mmol) was then treated with Grubbs first generation catalyst **19** (0.066 g, 4 mol %) in degassed dichloromethane (215 mL) for 24 h. Removal of solvent followed by chromatography [petroleum ether/ethyl acetate (97:3)] gave the tricyclic compound **8a** (0.234 g, 55%) as a solid which was found to be identical with the sample prepared earlier.

6-Allyl-3,5-dimethyl-2-hydroxymethyl Phenol (10b). Sodium ethoxide was prepared by adding freshly cut sodium (2.84 g, 0.124 mol) to dry ethanol (90 mL) dropwise at ~5 °C. To this solution were added slowly 2-allyl-3,5-dimethylphenol (20 g, 0.123 mol) and *p*-formaldehyde (13.28 g, 0.148 mol) and stirring was continued. After completion of reaction (TLC), the reaction mixture was neutralized with NH_4Cl and extracted with ethyl acetate (4 × 40 mL). The combined extract was washed with brine (2 × 10 mL) and dried. The solvent was removed under vacuum, and the residue was chromatographed on silica gel. Elution with petroleum ether/ethyl acetate (92:8) gave the compound **10b** (10.7 g, 45%) as a solid. Mp: 80−82 °C. IR (neat) ν_{max}: 3286 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (br s, 1H), 6.54 (s, 1H), 5.99−5.90 (m, 1H), 5.01−4.96 (m, 2H), 4.86 (s, 2H), 3.4 (s with str, J = 4.0 Hz, 2H), 2.5−2.3 (br s, 1H), 2.2 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.6, 137.4, 136.1, 133.2, 123.8, 123.1, 120.3, 114.7, 60.7, 30.3, 19.3 and 19.0. ESI HRMS: calcd for $C_{12}H_{16}O_2Na$ [M$^+$ + Na] 215.1048, found 215.1054.

2-Allyl-3,5-dimethyl-6-spiroepoxycyclohexa-2,4-dienone (11b). To a solution of phenol **10b** (10 g, 52.08 mmol) in acetonitrile (25 mL) was added a solution of sodium *m*-periodate (22.3 g, 0.104 mol in ~220 mL water) at ~10 °C. The reaction mixture was stirred for 2 h at room temperature, filtered, and extracted with ethyl acetate (4 × 50 mL). The combined organic layer was then washed with brine (2 × 30 mL) and dried. The solvent was evaporated, and the residue was purified by column chromatography. Elution with petroleum ether/ethyl acetate (94:6) gave the compound **11b** (8.11 g, 82%) as a low-melting solid. IR (neat) ν_{max}: 1654 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.2 (s, 1H), 5.8−5.7 (m, 1H), 5.02−4.9 (m, 2H), 3.22−3.16 (AB pattern overlapped with m, 4H), 2.1 (s, 3H), 1.8 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.1, 150.1, 143.7, 134.8, 129.7, 129.4, 115.0, 58.3, 57.8, 29.3, 20.58 and 16.0. HRMS: calcd for $C_{12}H_{15}O_2$ [M$^+$ + H] 191.1072, found 191.1080.

7,10-Dimethyl-8-spiroepoxy-tricyclo[5.2.2.0^{1,5}]undec-3,10-dien-9-one (8b). A solution of cyclohexadienone **11b** (1 g, 5.263 mmol) and 1,3-pentadiene (mixture of *cis* and *trans*) (2 mL, excess) in *o*-dichlorobenzene (1.5 mL) was heated in a sealed tube at 100 °C for 5 h. The reaction mixture was then was charged as such on silica gel and chromatographed. Elution with petroleum ether/ethyl acetate (97:3) gave the adduct **9b** (1.09 g, 80%) as a mixture of isomers [IR (neat) ν_{max}: 1730 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.04−5.88 (m, 2H), 5.48−5.36 (m, 1H), 5.28−5.04 (complex m, 3H), 3.1−3.06 (part of an AB system, J_{AB} = 6.0 Hz, 1H), 2.92−2.88 (part of an AB system, J_{AB} = 6.0 Hz, 1H), 2.76−2.5 (m, 1H), 2.4−2.28 (m, 1H), 2.24−2.14 (m, 2H), 1.9−1.74 (m, 2H), 1.68−1.52 (m, 4H), 1.22−1.04 (two sets of dd, 1H), 0.9 (s, 3H). HRMS: calcd for $C_{17}H_{22}O_2Na$ [M$^+$ + Na] 281.1517, found 281.1517] which was subjected to ring-closing metathesis as described below.

To a degassed solution of the adduct **9b** (0.5 g, 1.938 mmol) in dichloromethane (195 mL, 0.01 M) was added Grubbs catalyst **19** (63 mg, 4 mmol %), and the mixture was stirred at ambient temperature under nitrogen. Removal of solvent under reduced pressure followed by column chromatography of the residue with petroleum ether/ethyl acetate (97:3) first gave the unreacted starting material (0.18 g, 36%). Continued elution with petroleum ether/ethyl acetate (96:4) gave the desired compound **8b** as a colorless liquid (0.205 g, 49%), which solidifies upon keeping in the refrigerator. Mp: 86−88 °C. IR (neat) ν_{max}: 1734 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.03 (br m, 1H), 5.83−5.78 (m, 1H), 5.65−5.62 (m, 1H), 3.24−3.16 (m, 1H), 3.12 (part of an AB system, J_{AB} = 6 Hz, 1H), 2.9 (part of an AB system, J_{AB} = 6 Hz, 1H), 2.76 (m of d, J = 14.6 Hz, 1H), 2.55 (dd, J_1 = 14.6 Hz, J_2 = 3.0 Hz, 1H), 2.13 (dd, J_1 = 11.7 Hz, J_2 = 10.2 Hz, 1H), 1.74 (d, J = 1.5 Hz, 3H), 1.37 (dd, J_1 = 11.7 Hz, J_2 = 8.8 Hz, 1H), 1.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.4, 136.0, 135.9, 132.2, 130.2, 65.0, 59.8, 48.8, 48.3, 39.1, 35.8, 29.8, 20.0 and 17.9. HRMS: calcd for $C_{14}H_{17}O_2$ [M$^+$ + H] 217.1229, found 217.1221.

11-Methyl-tricyclo[5.2.2.0^{1,5}]undec-3,10-dien-9-one (21a). To a solution of the adduct **8a** (3 g, 14.85 mmol) in MeOH/H_2O (6:1, 105 mL) were added zinc (activated, 18 g, excess) and NH_4Cl (3.5 g, 65.4 mmol). The reaction mixture was stirred at ambient

temperature (~30 °C). After completion of reaction (TLC, 8 h), the reaction mixture was filtered through a celite bed and washed with ethyl acetate (5 × 50 mL). The filtrate was concentrated under vacuum; the residue was diluted with water (15 mL) and extracted with ethyl acetate (4 × 25 mL). The combined extract was washed with brine and dried. The solvent was evaporated under reduced pressure and the residue was chromatographed. Elution with petroleum ether/ethyl acetate (96:4) first gave the compound **22a** as a liquid (*syn*/*anti* mixture, 0.28 g, 10%). Further elution with petroleum ether/ethyl acetate (80:20) gave the β-keto alcohol **20a** as a liquid (*syn*/*anti* mixture, 2.21 g, 73%) [IR (neat) ν_{max}: 3418, 1714 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.77−5.72 (m, 1H), 5.63−5.55 (m, 1H), 5.29−5.23 (m, 1H), 3.84−3.68 (two sets of m, total 1H), 3.63−3.52 (two sets of m, total 1H), 3.29 (br s, 1H), 3.06−2.66 (m, 3H), 2.34−2.09 (m, 3H), 1.85 (d, J = 1.4 Hz, 3H), 1.40−1.25 (m, 1H). HRMS: calcd for $C_{13}H_{16}O_2Na$ [M^+ + Na] 227.1048, found 227.1051]. The keto-alcohol thus obtained was then subjected to oxidation and decarboxylation as described below.

To a solution of the β-keto-alcohol **20a** (1 g, 4.90 mmol) in acetone (30 mL) at ~5 °C was added freshly prepared Jones' reagent dropwise. After completion of reaction (TLC), acetone was removed under vacuum without heating. The residue was diluted with water (20 mL) and extracted with ether (5 × 25 mL). The extract was combined and dried, and the solvent was removed under vacuum to give a β-keto-acid, which was subjected to decarboxylation without further purification. The carboxylic acid thus obtained, was dissolved in THF/H_2O mixture (1:1, 40 mL) and refluxed for 12 h. The reaction mixture was saturated with sodium chloride, extracted with ether (4 × 30 mL), and dried. The solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography. Elution with petroleum ether/ethyl acetate (97:3) gave the compound **21a** as a colorless liquid (0.384 g, 45% after 2 steps). IR (neat) ν_{max}: 1724 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.78−5.74 (m, 1H), 5.63−5.59 (m, 1H), 5.27 (br s, 1H), 3.06−2.96 (br m, 1H), 2.87−2.78 (m of d, J = 15.0 Hz, 1H), 2.71−2.67 (m, 1H), 2.21 (m of d, J = 15.0 Hz, 1H), 2.16−2.00 (m, 3H), 1.83 (d, J = 1.5 Hz, 3H), 1.39−1.31 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 210.5, 148.4, 132.6, 130.5, 123.1, 62.3, 46.7, 38.7, 38.3, 33.9, 28.8 and 19.5. HRMS: calcd for $C_{12}H_{15}O$ 175.1123 [M^+ + H], found 175.1124.

7,10-Dimethyl-tricyclo[5.2.2.0^{1,5}]undec-3,10-dien-9-one (21b). To a solution of the adduct **8b** (3 g, 13.89 mmol) in MeOH/H_2O (6:1, 105 mL) were added zinc (activated, 18 g, excess) and NH_4-Cl (3.5 g, 65.4 mmol). The reaction mixture was stirred at ambient temperature (~30 °C). After completion of reaction (TLC, 10 h) the reaction medium was filtered on a celite bed and washed with ethyl acetate (5 × 35 mL). The filtrate was concentrated under vacuum, and the residue was diluted with water (15 mL) and extracted with ethyl acetate (4 × 25 mL). The combined extract was washed with brine and dried. The solvent was removed under reduced pressure, and the residue was purified by column chromatography. Elution with petroleum ether/ethyl acetate (97:3) gave minor compounds **22b** as a liquid (*syn*/*anti* mixture, 0.14 g, 5%) and the enol **24** (0.53, 19%). Further elution with petroleum ether/ethyl acetate (80:20) gave the β-keto alcohol **20b** as a liquid as a major product (*syn*/*anti* mixture, 2.09 g, 69%. IR (neat) ν_{max}: 3492, 1717 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.03,5.90 (two sets of br s, total 1H), 5.81−5.76 (m, 1H), 5.63−5.55 (m, 1H), 3.91−3.8 (m, 1H), 3.64−3.56 and 3.56−3.46 (two sets of dd, total 1H), 3.1−2.9 (m merged with s, total 2H), 2.74−2.46 (m, 2H), 2.12−1.82 (m, total 2H), 1.68 (two sets of d, J = 1.5 Hz, total 3H), 1.38−1.20 (m merged with two singlets, total 4H). ^{13}C NMR (75 MHz, $CDCl_3$) (*syn*/*anti* mixture): δ 214.2, 212.9, 139.3, 136.9, 134.0, 132.8, 132.5, 132.0, 130.3, 65.9, 65.2, 62.7, 61.6, 54.3, 52.8, 48.4, 46.4, 39.7, 39.6, 39.5, 34.5, 29.6, 29.4, 22.1, 21.6, 19.6, 19.3.

The β-keto-alcohol **20b** thus obtained (2 g, 9.194 mmol) was dissolved in acetone (40 mL), and freshly prepared Jones' reagent was added to it dropwise at ~5 °C. After completion of reaction (TLC), acetone was removed under vacuum. The residue was diluted with water (20 mL) and extracted with ether (4 × 30 mL). The extract was combined and dried, and the solvent was removed under vacuum to give the crude acid, which was subjected to decarboxylation without further purification. The carboxylic acid was dissolved in a THF/H_2O mixture (1:1, 60 mL) and refluxed for 12 h. The reaction mixture was saturated with sodium chloride, extracted with ether (4 × 30 mL), and dried. The solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography. Elution with petroleum ether/ethyl acetate (97:3) gave the compound **21b** as a thick liquid (0.776 g, 45% after 2 steps). IR (neat) ν_{max}: 1726 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.0−5.96 (br m, 1H), 5.81−5.75 (m, 1H), 5.63−5.57 (m, 1H), 3.06−3.01 (m, 1H), 2.63 (m of part of an AB system, J_{AB} = 16.8 Hz, 1H), 2.52 (d of part of an AB system, J_{AB} = 16.8 Hz, J_2 = 3.6 Hz, 1H), 2.04 (part of an AB system, J_{AB} = 18 Hz, 1H), 1.9−1.82 (merged m, 2H), 1.68 (d, J = 2 Hz, 3H), 1.38−1.3 (m, 1H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.8, 137.6, 133.9, 132.4, 130.1, 65.7, 47.7, 45.9, 38.1, 37.9, 29.4, 24.0 and 19.4. HRMS: calcd for $C_{13}H_{17}O$ [M^+ + H] 189.1279, found 189.1283.

8,11-Dimethyl-tricyclo[5.2.2.0^{1,5}]undec-3,10-dien-9-one (22a). To a suspension of activated zinc (12 g, excess) and ammonium chloride (3.5 g excess) in dry dioxane (50 mL) was added the keto-epoxide **8a** (2 g, 9.90 mmol) in dry dioxane (50 mL), and the reaction mixture was refluxed till completion of reaction (TLC, 8 h). The reaction mixture was filtered through a celite bed, and the bed was washed with EtOAc (3 × 20 mL). The filtrate was evaporated under reduced pressure; the residue was diluted with water (20 mL) and extracted with EtOAc (4 × 30 mL). The combined organic layer was washed with brine (20 mL) and dried, and solvent was evaporated under reduced pressure. Column chromatography of the crude residue on silica gel with petroleum ether/EtOAc (96:4) gave the title compound **22a** (*syn*/*anti* mixture, 1.15 g, 62%) as a volatile liquid. IR (neat) ν_{max}: 1724 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 5.78−5.73 (m, 1H), 5.60−5.56 (m, 1H), 5.26 (d, J = 1.6 Hz, 1H), 2.94−2.86 (br t, 1H), 2.86−2.78 (m of d, J = 15.0 Hz, 1H), 2.48 (br m, 1H), 2.24−2.16 (m, 2H), 2.1−2.04 (m, 1H), 1.83 (d, J = 1.6 Hz, 3H), 1.25 (m, 1H), 1.1 (d, J = 7.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 213.3, 149.1, 132.5, 130.7, 123.7, 62.6, 46.8, 44.5, 42.0, 34.2, 24.5, 19.7 and 15.7. HRMS: calcd for $C_{13}H_{16}ONa$ [M^+ + Na] 211.1099, found 211.1090. Elution with petroleum ether/EtOAc (80:20) gave the alcohol **20a** (*syn*/*anti* mixture, 0.36 g, 18%).

8,8,11-Trimethyl-tricyclo[5.2.2.0^{1,5}]undec-3,10-dien-9-one (23a). Sodium hydride (0.75 g, 60% w/w suspension, excess) was placed in a dry two-necked flask and washed with dry petroleum ether, and dry THF (10 mL) was added. A solution of the compound **22a** (0.5 g, 2.66 mmol) in THF (10 mL) was added to the reaction mixture, which was refluxed for 1 h. The reaction mixture was brought to ambient temperature; methyl iodide (1.5 mL, excess) was added and refluxed for 6 h after which it was cooled (0 °C) and quenched by addition of cold water. The reaction mixture was saturated with NaCl, the organic layer was separated, and the aqueous layer was extracted with ether (3 × 20 mL). The combined organic layer was washed with sodium thiosulfate (1 × 20 mL) and dried. The solvent was evaporated under reduced pressure, and the residue was chromatographed on silica gel. Elution with light petroleum ether/EtOAc (98:2) gave the title compound **23a** as a volatile liquid (0.28 g, 52%). IR (neat) ν_{max}: 1726 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 5.78 (m, 1H), 5.60 (m, 1H), 5.20 (br s, 1H), 3.05 (m, 1H), 2.8 (d, J = 16.0 Hz, 1H), 2.3−2.2 (merged m, 3H), 1.85 (s, 3H), 1.25 (m, 1H), 1.09 (s, 3H), 1.04 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 215.0, 149.1, 132.8, 130.5, 122.0, 62.3, 50.5, 46.5, 44.4, 34.3, 25.8, 25.5, 24.5 and 21.2. HRMS: calcd for $C_{14}H_{19}O$ [M^+ + H] 203.1436, found 203.1431.

7,8,10-Trimethyl-tricyclo[5.2.2.0^{1,5}]undec-3,10-dien-9-one (22b). To a suspension of activated zinc (12 g, excess) and ammonium chloride (3.5 g excess) in dry dioxane (50 mL) was added the keto-epoxide **8b** (2 g, 9.26 mmol) in dry dioxane (50 mL), and the

reaction mixture was refluxed till completion of reaction (TLC, 7 h). The reaction mixture was filtered through a celite bed and washed with EtOAc (3 × 30 mL). The filtrate was evaporated under reduced pressure; the residue was diluted with water (20 mL) and extracted with EtOAc (4 × 30 mL). The combined organic layer was washed with brine (20 mL) and dried, and the solvent was removed under reduced pressure. Column chromatography of the residue on silica gel [petroleum ether/EtOAc (97:3)] gave the title compound **22b** (*syn*/*anti* mixture, 0.935 g, 50%) as a liquid. IR (neat) ν_{max}: 1725 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.10 (br m, 1H), 5.75−5.74 (m, 1H), 5.59−5.54 (m, 1H), 2.96−2.87 (m, 1H), 2.64 (m of part of an AB system, J_{AB} = 16.0 Hz, 1H), 2.50 (dd of part of an AB system, J_{AB} = 16.0 Hz, J_2 = 3.0 Hz, 1H), 1.96 (dd, J_1 = 11.2 Hz, J_2 = 8.7 Hz, 1H), 1.82−1.72 (merged m, 1H), 1.67 (d, J = 2.0 Hz, 3H), 1.26−1.20 (merged m, 1H), 1.18 (s, 3H), 1.06 (d, J = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 213.3, 139.3, 133.9, 132.3, 130.3, 65.4, 48.0, 47.5, 40.4, 33.2, 29.7, 22.1, 19.6 and 13.1. HRMS: calcd for $C_{14}H_{18}ONa$ [M^+ + Na] 225.1255, found 225.1254.

Further elution with petroleum ether/ethyl acetate (93:7) gave the enol **24** (0.467 g, 25%). IR (neat) ν_{max}: 3405 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.74−5.68 (merged m, 2H), 5.60−5.56 (m, 1H), 5.12 (d, J = 2.4 Hz, 1 H), 4.80 (d, J = 2.4 Hz, 1H), 3.9 (s, 1H), 3.08−3.0 (m, 1H), 2.56 (m of part of an AB system, J_{AB} = 16.0 Hz, 1H), 2.42 (d of part of an AB system, J_{AB} = 16.0 Hz, J_2 = 3.5 Hz, 1H), 1.9 (br s, 1H), 1.76−1.64 (m merged with d, 4H), 1.36−1.28 (dd, J_1 = 11.5 Hz, J_2 = 8.0 Hz, 1H), 1.2 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.2, 140.1, 134.6, 133.6, 129.8, 106.2, 72.9, 58.7, 42.5, 41.8, 40.9, 31.3, 21.7 and 19.7. HRMS: calcd for $C_{14}H_{19}O$ [M^+ + H] 203.1436, found 203.1438

Elution with petroleum ether/ethyl acetate (80:20) furnished the alcohol **20b** (*syn*/*anti* mixture, 0.303 g, 15%).

7,8,8,10-Tetramethyl-tricyclo[5.2.2.0^{1,5}]undec-3,10-dien-9-one (23b). Sodium hydride (0.70 g, 60% w/w suspension, excess) was placed in a dry two-necked flask and washed with dry petroleum ether, and dry THF (10 mL) was added. A solution of the compound **22b** (0.4 g, 1.98 mmol) in tetrahydrofuran (10 mL) was added to the reaction mixture, which was refluxed for 1 h. The reaction mixture was then brought to ambient temperature; methyl iodide (1.5 mL, excess) was added and refluxed for 6 h. The reaction mixture was cooled (0 °C) and quenched by addition of cold water. The reaction mixture was saturated with sodium chloride, the organic layer was separated, and the aqueous layer was extracted with ether (3 × 20 mL). The combined organic layer was washed with sodium thiosulfate (1 × 20 mL) and dried. The solvent was evaporated under reduced pressure, and the residue was chromatographed on silica gel. Elution with light petroleum ether/EtOAc (98:2) gave the title compound **23b** as a volatile liquid (0.214 g, 50%). IR (neat) ν_{max}: 1726 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.94 (br m, 1H), 5.79−5.75 (m, 1H), 5.60−5.56 (m, 1H), 3.02−2.95 (m, 1H), 2.61 (m of part of AB system, J_{AB} = 16.6 Hz, 1H), 2.51 (d of part of an AB system, J_{AB} = 16.6 Hz, J_2 = 2.7 Hz, 1H), 2.03 (dd, J_1 = 12.4 Hz, J_2 = 9.7 Hz 1H), 1.65 (d merged with signal due to H_2O, 3H), 1.26 (dd, J_1 = 12.4 Hz, J_2 =8.5 Hz, 1H), 1.13 (s, 3H), 1.01 (s, 3H), 0.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.0, 138.9, 132.6, 132.3, 130.3, 65.1, 47.4, 46.6, 43.6, 35.7, 30.3, 24.6, 21.8, 19.4 and 19.2. HRMS: calcd for $C_{15}H_{21}O$ [M^+ + H] 217.1592, found 217.1598.

7,10-Dimethyl-tricyclo[5.2.2.0^{1,5}]dodec-3,8(12),10-trien-9-one (25). To a suspension of PDC (2 g, 5.35 mmol) in 25 mL dry dichloromethane was added the compound **24** (0.5 g, 2.48 mmol), and the reaction mixture was stirred at ambient temperature (∼25 °C). After completion of reaction (TLC), the reaction mixture was filtered through a celite pad and washed with ethyl acetate (3 × 15 mL). The solvent was evaporated, and the residue was purified by chromatography. Elution with petroleum ether/ethyl acetate (97:3) gave compound **25** (0.445 g, 90%). IR (neat) ν_{max}: 1715 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): 5.94 (br m, 1H), 5.88 (d, J = 1.5 Hz, 1H), 5.83−5.77 (m, 1H), 5.63−5.59 (m, 1H), 5.2 (d, J = 1.2 Hz, 1H), 3.04−2.95 (m, 1H), 2.76 (m of part of an AB system, J_{AB} = 15.0 Hz, J_2 = 3.2 Hz, 1H), 2.56 (d of part of an AB system, J_{AB} = 15.0 Hz, 1H), 1.9 (superimposed dd, J = 10.5 Hz, 1H), 1.70 (d, J = 1.5 Hz, 3H), 1.43−1.39 (dd, J_1 = 10.5 Hz, J_2 = 8.0 Hz, 1H), 1.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.6, 146.8, 136.2, 135.6, 132.4, 130.5, 113.5, 65.0, 48.2, 41.7, 39.2, 29.9, 20.8 and 19.7. HRMS: calcd for $C_{14}H_{16}ONa$ [M^+ + Na] 223.1099, found 223.1088

11-Methyl-tricyclo[5.2.2.0^{1,5}]undec-4,10-dien-3,9-dione (26a). To a solution of the ketone **21a** (0.5 g, 2.87 mmol) in 50 mL benzene at ∼15 °C were added PDC (5.37 g, 14.36 mmol) and ^{t}BuOOH (2 mL, excess). After the reaction mixture stirred for 15 min, it was brought to ambient temperature and further stirred for 24 h. The reaction mixture was diluted with ether (10 mL), filtered through a celite bed, and washed with ethyl acetate (2 × 10 mL). The filtrate was concentrated under reduced pressure, and the residue was chromatographed on silica gel. Elution with petroleum ether/ethyl acetate (80:20) furnished the enone **26a** (0.335 g, 62%) as a solid, which was recrystallized from petroleum ether/ethyl acetate. Mp: 126−128 °C. IR (neat) ν_{max}: 1712, 1652 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.87 (br m, 1H), 5.67 (br m, 1H), 3.34 (d, J = 20 Hz, 1H), 3.08−3.02 (m, 1H), 2.72 (m of AB system, J_{AB} = 18.0 Hz, 2H), 2.36 (m of d, J = 18.0 Hz, 1H), 2.24 (d, J = 20.0 Hz, 1H), 2.18−2.11 (m of d, J = 18.0 Hz, 1H), 1.94 (d, J = 1.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 207.7, 204.8 (CO), 177.0, 147.3, 125.8, 122.5, 64.1, 38.8, 37.6, 37.5, 31.2 and 20.3. HRMS: calcd for $C_{12}H_{12}O_2Na$ [M^+ + Na] 211.0735, found 211.0745.

7,10-Dimethyl-tricyclo[5.2.2.0^{1,5}]undec-4,10-dien-3,9-dione (26b). Oxidation of the ketone **21b** (0.5 g, 2.66 mmol) in 50 mL benzene at ∼15 °C with PDC (5.37 g, 14.36 mmol) and ^{t}BuOOH (2 mL, excess) as described above followed by chromatography [petroleum ether/ethyl acetate (80:20)] furnished the enone **26b** (0.295 g, 55%) as a solid, which were recrystallized from petroleum ether/ethyl acetate. Mp: 120−121 °C. IR (neat) ν_{max}: 1710, 1655 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.02 (br m, 1H), 5.82 (t, 1H, J = 1.8 Hz), 3.25−3.19 (part of an AB system, J_{AB} = 18.0 Hz, 1H), 2.62−2.45 (m, total 3H), 2.2 (d of part of an AB system, J_{AB} = 18.0 Hz, J_2 = 3.0 Hz, 1H), 2.06 (part of an AB system, J_{AB} = 18.0 Hz, 1H), 1.76 (d, J = 1.5 Hz, 3H), 1.42 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 207.5, 204.7, 177.6, 136.3, 135.6, 125.4, 67.5, 46.4, 39.5, 36.5, 33.8, 23.3 and 18.2. HRMS: calcd for $C_{13}H_{14}O_2$-Na [M^+ + Na] 225.0891, found 225.0902.

1-Methyl-tricyclo[7.2.0.0^{3,7}]undec-2,5-dien-11-one (28). A solution of **21a** (0.1 g, 0.575 mmol) in benzene (110 mL) was irradiated with a mercury vapor lamp (125 W, Applied Photophysics) in a Pyrex immersion well for 30 min. Benzene was evaporated under reduced pressure and the photolysate was chromatographed. Elution with petroleum ether/ethyl acetate (98:2) afforded the 1,3-acyl shift product **28** (0.04 g, 40%) as a colorless liquid, which was very sensitive. IR (neat) ν_{max}: 1770 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.91−5.60 (m, 2H), 5.30 (br s, 1H), 3.20−2.96 (merged m, 4H), 2.86−2.76 (dd, J_1 = 18.0 Hz, J_2 = 5.0 Hz, 1H), 2.4−2.3 (m, 1H), 2.15−2.07 (d of dd, J_1 = 13.5 Hz, J_2 = 4.0 Hz, J_3 = 1.5 Hz, 1H), 1.30 (s, 3H), 1.12−1.00 (d of superimposed dd, J_1 = 13.5 Hz, J_2 = 4.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 211.7, 146.1, 133.2, 129.8, 118.1, 62.8, 45.9, 40.1, 38.7, 31.0, 26.0 and 21.1. HRMS: calcd for $C_{12}H_{15}O$ [M^+ + H] 175.1123, found 175.1126.

2-Methyl-tetracyclo[6.3.0.0.^{1,3}0^{2,6}]undec-8-en-4,10-dione (31). A solution of **26a** (0.1 g, 0.532 mmol) in benzene (110 mL) was irradiated with a mercury vapor lamp (125 W, Applied Photophysics) in a Pyrex immersion well for 30 min. Benzene was evaporated under reduced pressure, and the photolysate was chromatographed. Elution with petroleum ether/ethyl acetate (65:35) afforded the oxa-di-π-methane product **31** (0.053 g, 53%) as a solid. Mp: 127−128 °C. IR (neat) ν_{max}: 1704, 1682 cm^{-1} (five-membered ring CO, α,β-unsaturated enone). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.0 (s, 1H), 3.2−3.02 (merged m, 2H), 2.86−2.74 (m, 1H), 2.62 (part

of an AB system, J_{AB} = 19.0 Hz, 1H), 2.40 (part of an AB system, J_{AB} = 19.0 Hz, 1H), 2.31 (d, J = 17.0 Hz, 1H), 2.21 (br s, 1H), 2.08 (d, J = 17.0 Hz, 1H), 1.57 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 211.4, 206.9, 188.1, 126.3, 57.8, 50.6, 49.5, 48.5, 45.3, 41.4, 37.2 and 14.0. HRMS: calcd for $C_{12}H_{12}O_2Na$ [M^+ + Na] 211.0735, found 211.0735.

Similarly, irradiation of **26a** (0.075 g, 0.398 mmol) in degassed acetone (110 mL) with a mercury vapor lamp (125 W, Applied Photophysics) in a Pyrex immersion well for 1 h under nitrogen, followed by removal of solvent and chromatography with petroleum ether/ethyl acetate (65:35), afforded product **31** (0.041 g, 54%).

2-Methyl-tetracyclo[6.3.0.0.^{1,3}0^{2,6}]undec-9-en-4-one (32). A solution of **21a** (0.1 g, 0.575 mmol) in degassed acetone (110 mL) was irradiated with a mercury vapor lamp (125 W, Applied Photophysics) in a Pyrex immersion well for 1 h, under nitrogen. Acetone was removed under vacuum, and the reaction mixture was chromatographed. Elution with petroleum ether/ethyl acetate (97:3) gave some unreacted starting material (0.01 g, 10%). Further elution with petroleum ether/EtOAc (94:6) afforded product **32** (0.052 g, 52%) as a colorless liquid. IR (neat) ν_{max}: 1726 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.81−5.76 (m, 1H), 5.73−5.68 (m, 1H), 3.06 (m, 1H), 2.66−2.56 (merged m, 2H), 2.44−2.32 (m of an AB system, J_{AB} = 18.0 Hz, 2H), 1.9−1.76 (m, 3H), 1.74−1.62 (m, 1H), 1.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 215.7, 134.3, 128.7, 50.7, 49.5, 48.4, 47.3, 46.3, 45.3, 44.5, 34.2 and 13.6. HRMS: calcd for $C_{12}H_{15}O$ [M^+ + H] 175.1123, found 175.1118.

2,5-Dimethyl-tetracyclo[6.3.0.0.^{1,3}0^{2,6}]undec-9-en-4-one (33). Irradiation of a solution of **22a** (0.075 g, 0.399 mmol) in degassed acetone (110 mL) in a Pyrex immersion well for 50 min as described above followed by removal of solvent and chromatography [petroleum ether/ethyl acetate (95:5)] afforded product **33** (0.032 g, 43%) as a colorless liquid. IR (neat) ν_{max}: 1725 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.76−5.73 (m, 1H), 5.71−5.67 (m, 1H), 2.78−2.70 (m, 1H), 2.63 (dd, J_1 = 10.0 Hz, J_2 = 3.5 Hz, 1H), 2.5−2.24 (merged m, 4H), 2.02 (dd, J_1 = 12.5 Hz, J_2 = 3.5 Hz, 1H), 1.56−1.44 (m merged with signal due to H_2O present in $CDCl_3$, 1H), 1.4 (s, 3H), 0.85 (d, J = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 212.2, 134.5, 128.6, 51.2, 49.2, 48.8, 46.1, 45.0, 39.0, 34.2, 29.7, 13.4, 9.7. HRMS: calcd for $C_{13}H_{17}O$ [M^+ + H] 189.1279, found 189.1282.

2,5,5-Trimethyl-tetracyclo[6.3.0.0.^{1,3}0^{2,6}]undec-9-en-4-one (34). A solution of **23a** (0.075 g, 0.371 mmol) in degassed acetone (110 mL) was irradiated for 50 min as described earlier. Acetone was removed under vacuum and the reaction mixture was chromatographed. Elution with petroleum ether/ethyl acetate (98:2) gave some unreacted starting material (0.011 g, 15%). Further elution with petroleum ether/EtOAc (96:4) afforded product **34** (0.024 g, 32%) as a colorless liquid. IR (neat) ν_{max}: 1726 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.79−5.74 (m, 1H), 5.72−5.68 (m, 1H), 2.8−2.7 (m, 1H), 2.38 (m of AB system, J_{AB} = 17.0 Hz, 2H), 2.16 (d, J = 6.4 Hz, 1H), 2.02 (dd, J_1 = 13.0 Hz, J_2 = 6.4 Hz, 1H), 1.93 (s, 1H), 1.56−1.48 (m, 1H), 1.4 (s, 3H), 1.12 (s, 3H), 0.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.8, 134.6, 128.7, 57.3, 51.3, 49.2, 45.2, 44.6, 40.5, 34.3, 29.1, 18.0, 14.5. HRMS: calcd for $C_{14}H_{19}O$ [M^+ + H] 203.1436, found 203.1444.

3,6-Dimethyl-tetracyclo[6.3.0.0.^{1,3}0^{2,6}]undec-9-en-4-one (35). A solution of **21b** (0.1 g, 0.532 mmol) in degassed acetone (110 mL) was irradiated for 1 h as described earlier. Acetone was removed under vacuum, and the residue was chromatographed. Elution with petroleum ether/ethyl acetate (97:3) first gave some unreacted starting material (0.012 g, 12%). Further elution with petroleum ether/ethyl acetate (95:5) afforded the product **35** (0.046 g, 46%) as a colorless liquid. IR (neat) ν_{max}: 1720 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.80−5.76 (m, 1H), 5.74−5.70 (m, 1H), 2.94−2.88 (m, 1H), 2.54 (m of d, J = 12.3 Hz, 1H), 2.30−2.20 (merged m, 2H), 2.05 (part of an AB system, J_{AB} = 18.4 Hz, 1H), 1.90−1.85 (m, 2H), 1.55 (m of superimposed dd, J_1 = J_2 = 7.2 Hz, J_3 = 1.2 Hz, 1H), 1.35 (s, 3H), 1.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 216.5, 134.3, 128.0, 54.5, 53.3, 51.2, 50.1, 49.4, 46.4, 44.9, 36.0, 24.9, 12.4. HRMS: calcd for $C_{13}H_{17}O$ [M^+ + H] 189.1279, found 189.1283.

Acknowledgment. We thank CSIR New Delhi for continuing financial support. G.D.P. is thankful to CSIR New Delhi for a fellowship. Thanks are due to DST for creating the National Single-Crystal X-ray Facility.

Supporting Information Available: ^{13}C NMR spectra of compounds **8a,b**, **10a,b**, **11b**, **12a**, **13a**, **16**, **17**, **21a,b**−**23a,b**, **24**, **25**, **26a,b**, **28**, and **31**−**35**; ^{1}H NMR spectrum of compound **15**; CIF data of compound **8a**; and ORTEP diagram of **8a**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO062416M