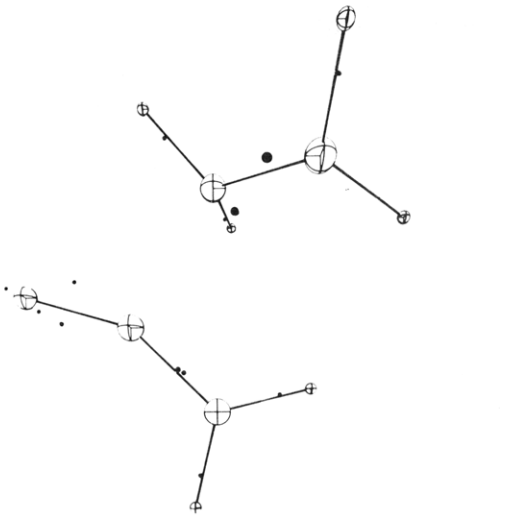

Figure 12. The nuclei and centroids of charge are represented in scale for point XVII (R_{23} = 1.90 Å, R_{14} = 2.69 Å).

Figures 10 and 11 which give the charge centroids for points VII and X, respectively.

The "two-step" path is seen to justify its name when one considers the progression of the LMO centroids. Of the two centroids which shift to form the C_1C_4 and C_2C_3 bonds in cyclobutanone only the ethylene centroid is significantly displaced until R_{23} = 1.9 Å (point XVII, in Figure 12).

Since the SCF ground-state MO configuration contributes overwhelmingly (>90%) to the 55 configuration expansion for the (2s + 2a) activated complex, the LMO's derived from these MO's serve as a valid description. For point XVII, however, this M0 configuration contributes only 70% to the same expansion, while the configurations of the mono- and diexcitations from the HOMO to the LUMO contribute 7 and 15%. Even so, one might expect that the LMO's derived from this SCF configuration would give a qualitatively correct description for this point.

Conclusions

(1) The cause for the stereochemistry of the ketene plus ethylene reaction cannot be attributed to orbital symmetry rules since there is no symmetry forbidden pathway. This can be seen by inspection of the AO coefficients of the two HOMO's and two LUMO's for the activated complexes along the two concerted paths, showing a change in symmetry elements from reactant-like to product-like. A more stringent test of forbiddeness of a pathway is the need for the interaction of the configurations which cross near the transition state, which is not found for the synchronous (2s + 2s) path. This conclusion is independent of the SCF basis set used.

(2) The apparent antarafacial addition of ketene can be explained through electrostatic potential diagrams of ketene and of the supermolecule during the initial stages of approach. The electrophilic and nucleophilic regions are expected to be independent of the basis set, as far as their positions are concerned.

(3) The approach of the molecules is such that a bond is almost formed between the central carbon of ketene and a carbon of ethylene, just before the CH_2 groups rotate toward bonding. This bonding is strong enough to prevent rotation of the ethylene CH_2 group, thus preserving suprafacial stereoproducts. Although there is a certain amount of charge separation in the terminal CH_2 groups, this reaction can be described as a nonsynchronous concerted reaction.[7] This conclusion is dependent on the basis set used since the STO-3G basis tends to favorize the formation of single bonds and cyclic isomers.

Acknowledgment. I thank G. Leroy for his hospitality and use of his laboratory where most of the calculations were carried out. I also thank M. Sana and D. Peeters for the use of their DENPOT program. I also thank K. Krogh-Jespersen for carrying out the calculations with the GAUSSIAN 82 program.

Registry No. CH_2=C=O, 463-51-4; CH_2=CH_2, 74-85-1.

Intramolecular [2 + 2] Photocycloaddition of 4-Substituted Cyclopent-2-en-1-ones

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The intramolecular [2 + 2] photocycloaddition of 4-(3,4-pentadienyl)cyclopent-2-en-1-ones has been shown to yield the expected straight cycloaddition product, a tricyclo[4.2.1.$0^{4,9}$]nonanone, and a novel product, a tricyclo[4.3.1.$0^{4,10}$]decenone, with a bridgehead double bond. The reaction course can be controlled by side-chain substituents and by the temperature of the reaction.

The synthetic approaches to di- and triquinane compounds have attracted the interest of many workers in the past decade and the synthetic developments in this area of chemistry have been reviewed this year by Paquette.[1] Also, the methods for construction of five-membered rings onto preexisting cyclic compounds have been evaluated by Ramaiah.[2] In these reviews more than 18 methods for cyclopentaneannulation have been discussed, and most recently Trost has presented his development of the formal equivalent of a 1,3-dipolar cycloaddition of a zwitterionic form of trimethylenemethane in the synthesis of carbocycles.[3]

One synthetic route which offers much promise for the synthesis of polyfunctionalized di- and triquinanes is the

(1) Paquette, L. A. "Topics in Current Chemistry"; Springer-Verlag: New York, 1984; Vol. 119.

(2) Ramaiah, M. *Synthesis* **1984**, 529.

(3) Trost, B. M. *Chimia* **1984**, *38*, 319 and references therein.

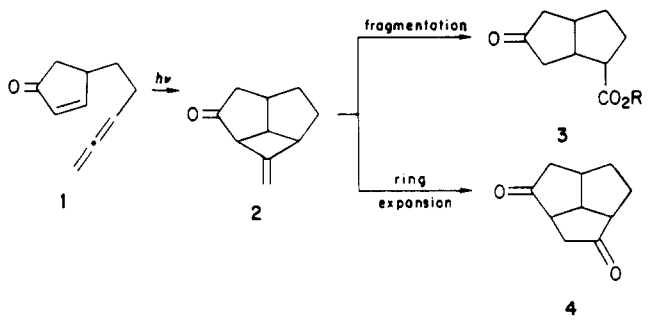
0022-3263/85/1950-3155$01.50/0

Table I. Photochemical Ring Closure Results[a]

starting compd	temp; solvent; concn	irrad time; % convrsn	products 11, %	products 12, %	ratio 11:12
1	20 °C; Et_2O; 3 mM	13.5 h; 100%	75	25	3:1
	−76 °C; Et_2O; 1.6 mM	34 h; 93%	81	12	6.8:1
9a	20 °C; Et_2O; 8 mM	15 h; 100%	52	48	1.1:1
	−78 °C; Et_2O; 0.9 mM	16 h; 72%	43	29	1.5:1
9b	20 °C; heptane; 5.1 mM −76 °C	16 h; 97%	50	47	1.1:1
10a	20 °C; Et_2O; 2.6 mM	6.5 h; 100%	87	13	6.7:1
	−78 °C; Et_2O; 1.5 mM	12 h; 96%	96		100:0
10b	20 °C; Et_2O; 1.5 mM	30 h; 96%	83	13	6.4:1
	−78 °C; Et_2O; 1.4 mM	44 h; 100%	92	8	11.5:1

[a] All analyses were obtained by using capillary GC analysis.

intramolecular [2 + 2] photocycloaddition of 4-(3,4-pentadienyl)-2-cyclopenten-1-ones **1**.[4] This latter synthetic route leads to ring system **2** which by ring fragmentation can serve as a precursor to substituted bicyclo[3.3.0]octane compounds **3** and by ring expansion to the triquinane

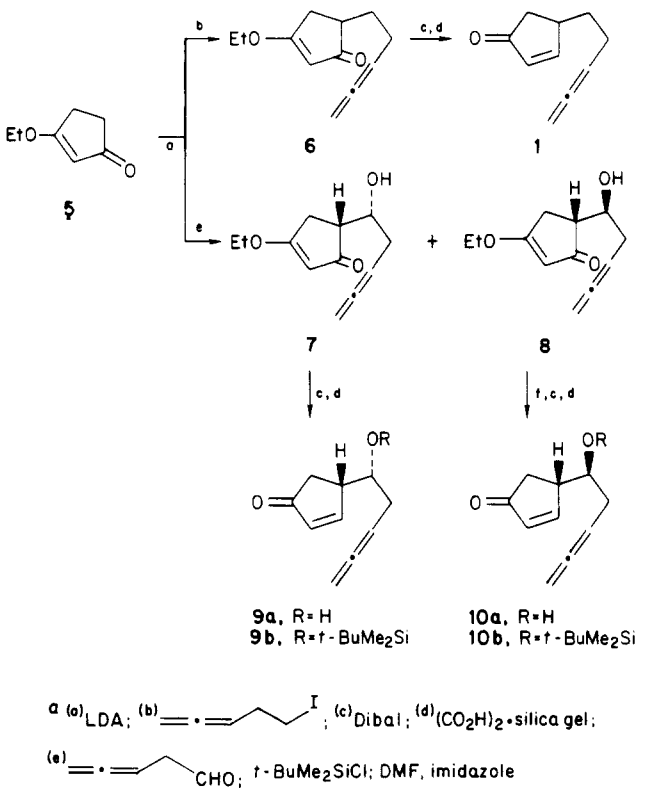


skeleton **4**. The photochemistry of **1** and its side-chain substituted derivatives has been evaluated to assess the synthetic potential of this photochemical process.

As shown in Scheme I, the starting 4-substituted 2-cyclopenten-1-ones were readily prepared by treatment of the lithium enolate of 3-ethoxy-2-cyclopenten-1-one (**5**)[5] with 1-iodopenta-3,4-diene[6] or 3,4-pentadienal.[7] The alkylation to form **6** proceeded in a modest yield of 24% even when HMPT was used as a cosolvent. The product **6** upon Dibal reduction followed by hydrolysis using acidic wet silica gel[8] yielded the allene **1**. The aldol reaction yielded, after flash chromatography, 45% of anti isomer **7** and 24% of syn isomer **8**. The anti isomer **7** could be reduced and hydrolyzed directly to yield the cyclopentenone **9a**. However, it was necessary to protect the hydroxyl group of the syn isomer **8** as a *tert*-butyldimethylsilyl ether for the reduction to be successful; this material upon hydrolysis yielded the cyclopentenone **10b**. The stereochemistry of the hydroxyl groups was established by X-ray crystallographic determination of subsequent photoproducts.

The results of the irradiation[9] of these enones at 20 °C and −75 °C are listed in Table I. Two reaction pathways were followed in the intramolecular [2 + 2] photocycloaddition reaction of these compounds. For example, with the parent system **1**, the first of these pathways was the expected straight cycloaddition[9,10] to give a tricyclo[4.2.1.$0^{4,9}$]nonanone derivative (**11a**); the alternate, novel pathway is cycloaddition of the terminal carbon atom of the allene to α-carbon of the enone to give a tricyclo[4.3.1.$0^{4,10}$]decenone bridgehead olefin derivative (**12a**).[11] The structural assignments were made on the basis of ^1H NMR and off-resonance ^{13}C NMR data (see Experimental Section). Substitution at C-1 of the side chain had a large effect on the product distribution. Irradiation of the unsubstituted enone **1** at room temperature gave a 3:1 mixture of straight cycloadduct **11a** to bridgehead olefin adduct **12a**. The ratios of products obtained in the room temperature irradiations of anti and syn isomers **9a** and **10a** were 1.1:1 and 6.7:1, respectively. Very similar product ratios were obtained with the corresponding *tert*-butyl-

Scheme I



(4) For a recent survey on the synthetic aspects of [2 + 2] photocycloaddition of α,β-unsaturated carbonyl compounds, see: Baldwin, S. W. "Organic Photochemistry"; Padwa, A., Ed.; Marcel Dekker, Inc.; New York, 1981; Vol. 5, pp 123–226.

(5) Oppolzer, W.; Buford, S. C. *Helv. Chim. Acta* **1980**, *63*, 788.

(6) Dauben, W. G.; Shapiro, G. *J. Org. Chem.* **1984**, *49*, 4252.

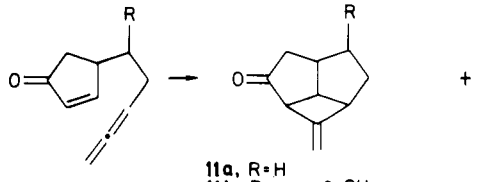
(7) Cresson, P.; Atlani, M. *C. R. Seances Acad. Sci., Ser. C* **1967**, *265*, 942.

(8) Huet, F.; Lechevallier, A.; Pellet, M.; Conia, J. M. *Synthesis* **1978**, 63.

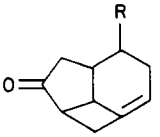
(9) The systems studied have 1,6-unsaturation as defined by numbering from C-α of the enone until the first unsaturated atom of the allene function is reached. Cycloadditions involving bonding between the central allenic carbon with C-α of the enone are straight, while bonding involving the central allenic carbon and C-β of the enone are called crossed.

(10) Only straight cycloaddition has been reported for the intramolecular photocycloaddition of allenes, see: (a) Becker, D.; Harel, Z.; Birnbaum, D. *J. Chem. Soc., Chem. Commun.* **1975**, *10*, 377. (b) Becker, D.; Nagler, M.; Harel, Z.; Gillon, A. *J. Org. Chem.* **1983**, *48*, 2584. (c) Reference 6.

(11) Dauben, W. G.; Shapiro, G.; Luders, L. *Tetrahedron Lett.*, in press.



11a, R=H
11b, R=α- or β-OH
11c, R=α- or β-OSiMe$_2$-t-Bu

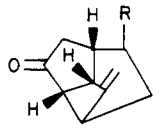


12a, R=H
12b, R=α- or β-OH
12c, R=α- or β-OSiMe$_2$-t-Bu

dimethylsilyl ethers **9b** and **10b**, ruling out any hydrogen bonding effects. The stereochemical orientation of the hydroxyl group in the photoproducts of the straight adduct configuration was established by X-ray crystal structure studies of the crystalline L-Selectride reduction product from the adduct **11b**-α-OH.[12]

From the regiochemical results of the cycloaddition of olefins to enones, it has been shown that the "rule of five" can be partially or totally invalidated by appropriate structural modifications, such as ring size and substitution. Thus, it is not surprising that the cycloaddition of an allene is not a regiospecific reaction in this present study. Generally, only substitution at the internal position of an olefin addend plays a role.[13] There are a few cases where regio- and stereoselectivity of the intramolecular photocycloaddition is affected by side-chain methyl substituents.[14] This selectivity obtained is generally considered in terms of a "product development control" where the favored product is that which is least sterically crowded since it is suggested that this substituent repulsion is felt more severely in the final ring closure, the first bonding being reversible.[15] To see if this same rationale could be applied in the present study, MM2 calculations[16] were performed on cycloaddition products. The results are listed in Table II.

The straight cycloadducts **11** are more stable than the corresponding bridgehead olefins **12**, and the photoproducts in which the hydroxyl group occupies an exo (or β) position are more stable than their corresponding endo (or α) isomers. However, this endo destabilization is more pronounced in the highly cupped straight product than for the bridgehead olefins. This trend in calculated product energy difference is in accord with the observed product ratios and is consistent with the aforementioned arguments for selectivity. It is also of interest that the strain energy for the crossed products **13–15** are higher than that for the isolated products, i.e., ΔH_f (kcal/mol) = 3.63, −36.40, and −35.73, respectively.



13, R=H
14, R=α-OH
15, R=β-OH

Finally, the effect of temperature on the product distribution is noteworthy. The increased selectivity gained in the −75 °C irradiations, particularly of **1** and **10a**, is in line with the mechanistic suggestions. These results are only of qualitative significance and the product energy control provides only a partial, but useful, explanation of the yield variances.

Experimental Section[17]

General Procedure for Analytical Irradiations. Analytical irradiations were generally performed on solutions of the given enone at a concentration of 1 mg/L in ether. The solutions were purged with nitrogen prior to irradiation. The irradiations were monitored by capillary GC without internal standard; however, there is little material loss when the irradiations are filtered through uranium glass. Low-temperature irradiations were performed by placing the Pyrex irradiation tube containing the sample into a Pyrex Dewar filled with methanol in which the temperature was controlled by means of a Cryocool immersion cooler. This apparatus was then irradiated in a Rayonet photochemical reactor fitted with 350-nm lamps or with a 450-W Hanovia lamp fitted with a water-cooled probe.

General Procedure for Preparative Irradiations. Preparative irradiations were generally performed on solutions of the given enone in dry, distilled ether at room temperature. The solutions were placed with a magnetic stirring bar into a Pyrex immersion-well irradiation vessel containing a water-cooled probe. The system was purged with nitrogen, and a slow nitrogen flow was continued throughout the duration of the irradiation. A 450-W Hanovia lamp fitted with a uranium glass filter was used as the light source. The reaction was monitored by capillary GC. Alternatively, a solution of the enone was placed in a Pyrex tube, purged with nitrogen, and irradiated in a Rayonet photochemical reactor fitted with 350-nm bulbs.

3-Ethoxy-5-(3,4-pentadienyl)cyclopent-2-en-1-one (6). To a stirred solution of diisopropylamine (1.04 g, 10.5 mmol) in 9 mL of THF, cooled in an ice bath, was added *n*-butyllithium (7.30 mL, 1.2 *M* in hexane, 8.70 mmol). The solution was stirred for 10 min and cooled to −78 °C and 3-ethoxycyclopent-2-en-1-one (1.00 g, 7.93 mmol)[5] in 9 mL of THF was added. The solution was stirred for 15 min, and HMPT (1.34 g, 7.50 mmol) was added followed by 1-iodo-3,4-pentadiene (2.30 g, 8.05 mmol) in HMPT (1.44 g). The resulting mixture was maintained at −78 °C for 4 h and allowed to warm to room temperature overnight. Saturated aqueous ammonium chloride solution and hexane were added, and the organic phase was separated, washed with saturated aqueous sodium sulfite and sodium chloride solution, and dried. The solvent was removed by using a rotary evaporator and the residual oil was purified by flash chromatography (20–50% ethyl acetate–hexane gradient) to yield 350 mg (24%) of product: IR 1955, 1700, 1600, 1435, 1380, 1350 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.18 (s, 1), 5.03 (quintet, 1, J = 6.7 Hz), 4.60 (dt, 2, J = 6.7, 3.0 Hz),

(12) Analysis performed by Dr. F. Hollander, University of California, Berkeley, X-ray Crystallographic Facility (CHEXRAY).
(13) Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 1292, 1299.
(14) (a) Hoye, T. R.; Martin, S. J.; Peck, D. R. *J. Org. Chem.* **1982**, *47*, 331. (b) Birch, A. M.; Pattenden, G. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1195. (c) Wender, P. A.; Howbert, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 688. (d) Oppolzer, W.; Wylie, R. *Helv. Chim. Acta* **1980**, *63*, 1198.
(15) Oppolzer, W. *Acc. Chem. Res.* **1982**, *15*, 135.
(16) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 5219.

(17) General Methods. Solvents were dried and/or distilled under a nitrogen atmosphere prior to use when this was deemed necessary from sodium benzophenone ketyl for ethyl ether and tetrahydrofuran (THF) from CaH_2 for triethylamine, diisopropylamine, and hexamethylphosphoramide (HMPT), and from P_2O_5 for dichloromethane. Reagents were purified by the standard procedures when appropriate.[18] All reactions involving organometallic reagents were performed by using oven-dried glassware under nitrogen atmosphere. Capillary gas chromatographic analysis for monitoring irradiations and analyzing product mixtures was performed with Hewlett-Packard 5880A or 5790A instruments equipped with a series 5880A Level Four integrating recorder. A J&W Scientific Durabond-1 (a cross-linked polymethylsiloxane similar to SE-30) capillary column (L = 30 m, i.d. = 0.25 mm, film thickness = 0.25 μm) was used in all cases. Flash chromatography was performed by the method of Still.[19] ^{1}H NMR spectra were recorded on a UCB-250 (250 MHz, FT) spectrometer. ^{13}C NMR spectra were recorded on a BVX 300 (76 MHz) and a UCB-200 (51 MHz) spectrometer. Mass spectral analyses were performed on a Kratos MS-50 instrument. Elementary analyses were performed by the Microanalytical Laboratory operated by the College of Chemistry, University of California, Berkeley.
(18) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: New York, 1966.
(19) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

Table II. Calculated Enthalpies of Products

adduct series	ΔH_f (kcal mol^{-1}) 11	12	$\Delta H_f(12) - \Delta H_f(11)$ (kcal mol^{-1})	exptl prod ratio 11	12
1	−0.68	2.05	2.73	3	1
9a	−39.84	−37.91	1.93	1	1
10a	−41.50	−38.37	3.13	6	1

3.96 (q, 2, J = 7.0 Hz), 2.72 (ddd, 1, J = 1.0, 7.2, 14.2 Hz), 2.65 (m, 1), 2.28 (ddd, 1, J = 1.0, 7.2, 14.2 Hz), 1.80–2.10 (m, 4), 1.34 (t, 3, J = 7.0 Hz); mass spectrum, exact mass calcd for $C_{12}H_{16}O_2$ m/e 192.1150, found m/e 192.1148.

4-(3,4-Pentadienyl)cyclopent-2-en-1-one (1). To a stirred solution of **6** (301 mg, 1.57 mmol) in 5 mL of dichloromethane was added Dibal (1.72 mL, 1.00 M in hexane) at ice-bath temperature. The reaction mixture was stirred at 0 °C for 3 h, and saturated aqueous sodium sulfate solution was added until the aluminum salts began to precipitate. Ethyl acetate was added, the reaction mixture was filtered, and the salts were rinsed with dichloromethane. The solvent was removed by rotary evaporation to yield a yellow oil which was dissolved in 15 mL of 2 N THF–HCl (2:1, v/v), the solution stirred for 1 h, and ethyl acetate-hexane was added. The organic layer was separated, washed with saturated aqueous sodium bicarbonate and sodium chloride solutions, and dried. The solvent was removed by using a rotary evaporator and the residual oil was purified by flash chromatography (10–25% ethyl acetate–hexane) to give 199 mg (86% over two steps) of **1** as a pale yellow oil: UV_{max} (methylcyclohexane) 215 nm (ϵ 9032); IR 1995, 1715, 1585, 1410, 1250, 1185 cm^{-1}; ^{1}H NMR δ 7.57 (dd, 1, J = 2.5, 5.7 Hz), 6.09 (dd, 1, J = 2.0, 5.7 Hz), 5.05 (quintet, 1, J = 6.7 Hz), 4.63 (dt, 2, J = 6.7, 3.2 Hz), 2.88–3.00 (m, 1), 2.48 (dd, 1, J = 1.0, 6.3, 19.8 Hz), 2.00 (m, 3), 1.35–1.70 (m, 2); mass spectrum, exact mass calcd for $C_{10}H_{12}O$ m/e 148.0888, found m/e 148.0893.

Preparative Irradiation of 1. A solution of the enone **1** (149 mg, 1.00 mmol) in 330 mL of dry distilled ether was irradiated under the standard conditions for 13.5 h. After this time GC analysis showed complete consumption of the enone and a 3:1 mixture of photoproducts **11a** and **12a**. The solvent was removed by using a rotary evaporator to give 146 mg of the mixture of products as an oil. Pure samples of each product were obtained by preparative GLC (no separation could be obtained by TLC or flash chromatography). 5-Methylenetricyclo[4.2.1.0^{4,9}]nonan-3-one (**11a**): IR 2970, 1740, 1665, 1270 cm^{-1}; ^{1}H NMR δ 5.08 (dt, 1, J = 1.0, 2.5 Hz), 4.90 (dt, 1, J = 1.0, 3.0 Hz), 3.39 (m, 2), 3.17 (q, 1, J = 8.4 Hz), 2.81 (quintet, 1, J = 8.4 Hz), 2.56 (ddd, 1, J = 1.0, 8.7, 17.8 Hz), 2.58 (d, 1, J = 17.8 Hz), 2.08 (m, 1), 1.63–1.85 (m, 2), 1.45–1.60 (m, 1); ^{13}C NMR δ 147.8, 110.5, 52.4, 48.1, 47.9, 42.6, 37.7, 33.5, 32.5 (carbonyl off scale); mass spectrum, exact mass calcd for $C_{10}H_{12}O$ m/e 148.0888, found m/e 148.0881. Tricyclo[4.3.1.0^{4,10}]dec-6-en-3-one (**12a**): IR ($CHCl_3$) 1735, 1210 cm^{-1}; ^{1}H NMR δ 5.48 (t, 1, J = 2.4 Hz), 3.40 (m, 1), 3.19 (m, 1), 2.72 (t, 1, J = 7.1 Hz), 2.62 (d, 1, J = 12.3 Hz), 2.55 (m, 1), 2.27 (d, 1, J = 14.9 Hz), 2.23 (d, 1, J = 14.9 Hz), 2.05–2.14 (m, 2), 1.70 (m, 2); mass spectrum, exact mass calcd for $C_{10}H_{22}O$ m/e 148.0888, found m/e 148.0887.

3,4-Pentadienal. To a stirred solution of ethyl 3,4-pentadienoate[6] (20.0 g, 0.16 mol) in 100 mL of dry, distilled dichloromethane was added Dibal (230 mL, 1.0 M in dichloromethane via cannula at −80 to −90 °C over a period of 30 min. The solution was sitrred at −80 to −90 °C for 1 h. The mixture was transferred via cannula into 500 mL of a mechanically stirred solution of 5% HCl at 0 °C. The mixture was stirred for 1 h, and the organic phase was separated and was washed with cold 10% HCl solution (2 × 500 mL) and saturated aqueous sodium chloride solution, and dried. The solvent was removed by distillation using a 19-cm Vigreux column (100 mmHg, 25 °C). Ether was added to the product and the solution was further concentrated to give 8.5 g (65%) of the allenic aldehyde as a yellow oil (to which was added a small quantity of hydroquinone stabilizer): IR (thin film) 1965, 1735, 1265 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.55 (t, 1, J = 3.0 Hz), 5.25 (quintet, 1, J = 7.0 Hz), 4.70 (dt, 2, J = 7.0, 3.0 Hz), 2.90–3.21 (m, 2).

***anti*- and *syn*-3-Ethoxy-5-(1-hydroxy-3,4-pentadienyl)-cyclopent-2-en-1-ones (7 and 8).** To a stirred solution of diisopropylamine (8.30 g, 82.0 mmol) in 250 mL of THF was added *n*-BuLi (65.0 mL, 1.2 M in hexanes, 78.0 mmol) at 0 °C. The solution was stirred for 10 min and cooled to −78 °C, and 3-ethoxycyclopent-2-enone[5] (9.0 g, 71.4 mmol) in 40 mL of THF was added by cannula over a period of 15 min. The solution was stirred for 30 min and 3,4-pentadienal (8.0 g, 97.6 mmol) in 15 mL of ether was added. The reaction was allowed to proceed for 10 min and quenched by the addition of aqueous saturated ammonium chloride solution, and the mixture was allowed to warm to room temperature. The organic phase was separated, washed with aqueous saturated ammonium chloride and sodium chloride solution, and dried. The solvent was removed by using a rotary evaporator to give a viscous orange oil. The crude product was purified by flash chromatography (20–60% ethyl acetate–hexane gradient) to yield 6.7 g (45%) of the less polar anti diastereomer **7** and 3.6 g (24%) of the more polar syn diastereomer **8**, both as dark yellow oils. The properties of **7** are as follows: IR (thin film) 3430, 1955, 1680, 1590 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 5.21 (s, 1), 5.16 (quintet, 1, J = 7.0 Hz), 4.61 (dt, 2, J = 6.7, 3.0 Hz), 4.00 (q, 2, J = 7.0 Hz), 3.75 (m, 1), 2.53–2.80 (m, 4), 2.23–2.40 (m, 2), 1.35 (t, 3, J = 7.0 Hz); ^{13}C NMR δ ($CDCl_3$) 209.1, 208.8, 189.7, 103.6, 85.3, 74.3, 72.0, 67.9, 48.1, 34.3, 31.7, 13.9; UV_{max} (MeOH) 239 nm (e 10927). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 68.98; H, 7.81. The properties of **8** are as follows: IR (thin film) 3400, 1955, 1690, 1595 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 5.25 (s, 1), 5.10 (quintet, 1, J = 7.0 Hz), 4.66 (dt, 2, J = 6.6, 3.0 Hz), 4.21 (s, br, 1), 4.02 (q, 2, J = 7.0). 2.18–2.87 (m, 6), 1.36 (t, 3, J = 7.0 Hz); UV_{max} (MeOH) 239 nm (ϵ 16890); mass spectrum, exact mass calcd for $C_{12}H_{16}O_3$ m/e 208.1099, found m/e 208.1101.

***anti*-4-(1-Hydroxy-3,4-pentadienyl)cyclopent-2-en-1-one (9a).** To a stirred solution of **7** (1.11 g, 5.33 mmol) in 50 mL of dichloromethane was added Dibal (21.3 mL, 1.0 M in hexane, 21.3 mmol) at ice-bath temperature. The reaction mixture was stirred at 0 °C for 0.5 h, 0.5 g of methanol was added, and aqueous saturated sodium sulfate solution was added until the aluminum salts began to precipitate. The mixture was diluted with hexane and filtered, and the salts were rinsed with dichloromethane. The combined organic solvents were evaporated and the residual oil was added to wet silica gel (15 mL of dichloromethane–0.8 mL of 10% oxalic acid–3 g of 70–230-mesh ASTM silica gel). The mixture was stirred for 1 h, neutralized with 50 mg of solid sodium bicarbonate, and filtered through a coarse frit. The silica gel was rinsed with dichloromethane, and the combined organic fractions were concentrated on a rotary evaporator to give a yellow oil. The crude product was purified by flash chromatography (40–60% ethyl acetate–hexane gradient) to give 760 mg (87%) of the enone as a pale yellow oil: UV_{max} (EtOH) 221 nm (ϵ 10600); IR (thin film) 3440, 2930, 1960, 1720, 1595 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 7.80 (dd, 1, J = 5.7, 2.5 Hz), 6.20 (dd, 1, J = 5.7, 2.0 Hz), 5.13 (quintet, 1, J = 6.8 Hz), 4.71 (dt, 2, J = 6.8, 2.9 Hz), 3.60–3.66 (m, 1), 3.03–3.11 (m, 1), 2.43 (dd, 1, J = 18.7, 6.6 Hz), 2.01–2.40 (m, 4); mass spectrum, exact mass calcd for $C_{10}H_{12}O_2$ m/e 164.0837, found m/e 164.0833.

***anti*-4-[1-[(*tert*-Butylidimethylsilyl)oxy]-3,4-pentadienyl]cyclopent-2-en-1-one (9b).** To a stirred solution of **9a** (200 mg, 1.2 mmol) in 10 mL of DMF were added a solution of imidazole (164 mg, 2.41 mmol), a catalytic amount of 4-(dimethylamino)pyridine, and *tert*-butyldimethylsilyl chloride (216 mg, 1.43 mmol) in 5 mL of DMF. The solution was stirred at room temperature for 24 h, 10% ethyl acetate–hexane solution was added, and the solution washed with water. The organic layer was washed with saturated aqueous sodium chloride solution and dried, and the solvent was removed on a rotary evaporator. The crude product was purified by flash chromatography (10% ethyl acetate–hexane) to give 211 mg (62%) of the product: UV_{max} (MeOH) 221 nm (ϵ 10280); IR (thin film) 2950, 1960, 1720, 1590, 1260, 1090 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 7.70 (dd, 1, J = 5.7, 2.5 Hz), 6.17 (dd, 1, J = 5.7, 2.1 Hz), 5.10 (quintet, 1, J = 6.8 Hz), 4.65 (dt, 2, J = 6.7, 2.7 Hz), 3.69 (q, 1, J = 5.7 Hz), 3.11–3.19 (m, 1),

2.39 (dd, 1, J = 18.8, 6.6 Hz), 2.14–2.30 (m, 2), 2.05 (dd, 1, J = 18.7, 2.5 Hz), 0.85 (s, 9), 0.04 (s, 3), 0.01 (s, 3). Anal. Calcd for $C_{16}H_{26}O_2Si$: C, 69.01; H, 9.41. Found: C, 69.14; H, 9.50.

***syn*-3-Ethoxy-5-[1-[(*tert*-butyldimethylsilyl)oxy]-3,4-pentadienyl]cyclopent-2-en-1-one.** As described for the preparation of **9b**, 1.10 g (5.29 mmol) of **8** was silylated and the product purified by flash chromatography (30–50% ethyl acetate–hexane) to give 1.13 g (64%) of product: IR (thin film) 2940, 1960, 1700, 1600, 1100 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 5.22 (s, 1), 5.03 (quintet, 1, J = 7.0 Hz), 4.65 (dt, 2, J = 6.6, 2.6 Hz), 4.30–4.34 (m, 1), 4.02 (q, 2, J = 7.0 Hz), 2.82 (dd, J = 2.7, 1.0 Hz) and 2.75 (dd, J = 2.7, 1.0 Hz), sum of previous two bands = 1 H, 2.58–2.63 (m, 1), 2.48 (dd, J = 7.3, 1.0 Hz) and 2.41 (dd, J = 7.3, 1.0 Hz), sum of two previous bands = 1 H, 2.09–2.25 (m, 2), 1.39 (t, 3, J = 7.0 Hz), 0.79 (s, 9), 0.03 (s, 3), –0.05 (s, 3); UV_{max} (MeOH) 239 nm (ϵ 17 200). Anal. Calcd for $C_{18}H_{30}O_3Si$: C, 67.03; H, 9.38. Found: C, 67.07; H, 9.48.

***syn*-4-[1-[(*tert*-Butyldimethylsilyl)oxy]-3,4-pentadienyl]cyclopent-2-en-1-one (10b).** To a stirred solution of 3-ethoxy-5-[1-(*tert*-butyldimethylsilyl)oxy]-3,4-pentadienyl]cyclopent-2-en-1-one (913 mg, 2.83 mmol) in 10 mL of dry dichloromethane was added Dibal (5.6 mL, 1.0 M in dichloromethane, 5.6 mmol) at ice-bath temperature. The reaction mixture was stirred for 2 h, and saturated aqueous Na_2SO_4 solution was added until the aluminum salts began to precipitate. Hexane was added, the reaction mixture was filtered through a coarse frit, and the salts were washes with dichloromethane. The solvent was removed by using a rotary evaporator, and wet, acidic silica gel was added directly to the residual oil. The mixture was stirred for 1.5 h, neutralized with 50 mg of solid sodium bicarbonate, and filtered through a coarse frit. The silica gel was rinsed with dichloromethane, and the combined organic fractions were concentrated to give a yellow oil. The crude product was purified by flash chromatography (10% ethyl acetate–hexane) to give 551 mg (70%) of the enone as a colorless oil: UV_{max} (MeOH) 221 nm (ϵ 9400); IR (thin film) 2950, 1960, 1720, 1590, 1255, 1100 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 7.51 (dd, 1, J = 3.2, 2.5 Hz), 6.18 (dd, 1, J = 3.6, 2.1 Hz), 5.06 (quintet, 1, J = 7.1 Hz), 4.66 (dt, 2, J = 6.7, 2.7 Hz), 3.89–3.94 (m, 1), 3.17 (quintet, 1, J = 2.8 Hz), 2.33 (d, 1, J = 2.8 Hz), 2.30 (d, 1, J = 2.8 Hz), 2.11–2.22 (m, 2), 0.81 (s, 9), 0.03 (s, 3), –0.03 (s, 3). Anal. Calcd for $C_{16}H_{26}O_2Si$: C, 69.01; H, 9.41. Found: C, 69.11; H, 9.50.

***syn*-4-(1-Hydroxy-3,4-pentadienyl)cyclopent-2-en-1-one (10a).** To a stirred solution of **10b** silyl ether (500 mg, 1.80 mmol) in 3.0 Ml of THF was added tetrabutylammonium fluoride (3.4 mL, 1.0 M solution in THF, 3.4 mmol) at 0 °C. The solution was allowed to warm to room temperature over 3 h and was stirred for an additional 24 h. Ethyl acetate–hexane (1:1) was added, and the organic layer was extracted with water and saturated aqueous sodium chloride solution, filtered through a pad of silica gel, and dried. Solvent was removed on a rotary evaporator and the yellow oil was purified by flash chromatography (50% ethyl acetate–hexane) to give 216 mg (73%) of product as a colorless oil: UV_{max} (MeOH) 222 nm (ϵ 6660); IR (thin film) 3420, 2920, 1960, 1700, 1585 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 7.62 (dd, 1, J = 5.7, 2.5 Hz), 6.24 (dd, 1, J = 5.7, 2.1 Hz), 5.12 (quintet, 1, J = 6.9 Hz), 4.75 (dt, 2, J = 6.7, 2.9 Hz), 3.86–3.88 (m, 1), 3.12–3.17 (m, 1), 2.38 (dd, 1, J = 18.9, 6.7 Hz), 2.16–2.38 (m, 4); mass spectrum, exact mass calcd for $C_{10}H_{12}O_2$ m/e 164.0837, found m/e 164.0838.

Preparative Irradiation of *anti*-4-(1-Hydroxy-3,4-pentadienyl)cyclopent-2-en-1-one (9a). A solution of the enone **9a** (1.0 g, 6.1 mmol) in 330 mL of dry, distilled ether was irradiated under the standard conditions for 9.5 h. GC analysis showed complete consumption of the enone and a 1:1 mixture of photoproducts. The solvent was removed on a rotary evaporator to give 1 g of cloudy white oil. The crude product was purified by flash chromatography (15–70% ethyl acetate–hexane gradient) to give 471 mg (47% isolated yield) of the higher R_f photoproduct **11b**-α-OH and 309 mg (31% isolated yield) of the lower R_f photoproduct **12b**-α-OH. The properties of **11b**-α-OH are as follows: IR (thin film) 3440, 2960, 1735, 1670 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 4.95 (dt, 1, J = 2.9, 1.0 Hz), 4.84 (dt, 1, J = 2.9, 1.0 Hz), 4.30 (q, 1, J = 6.8 Hz), 3.29 (m, 2), 3.16 (ddd, 1, J = 14.5, 8.0, 1.4 Hz), 2.41–2.98 (m, 3), 2.13–2.40 (m, 2), 1.69–1.78 (m, 1); ^{13}C NMR δ ($CDCl_3$) 217.8, 149.4, 109.9, 76.1, 54.6, 44.3, 42.9, 40.7, 39.7, 39.4; mass spectrum, exact mass calcd for $C_{10}H_{12}O_2$ m/e 164.0837, found

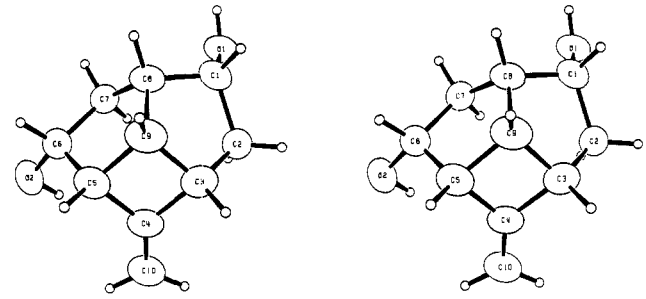


Figure 1.

m/e 164.0840. The properties of **12b**-α-OH are as follows: IR (thin film) 3420, 2940, 1730, 1590 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 5.42 (t, 1, J = 2.3 Hz), 4.17–4.09 (m, 1), 3.44–3.57 (m, 1), 2.43–2.77 (m, 5), 2.26 (d, 2, J = 9 Hz), 1.80–1.96 (m, 2); ^{13}C NMR δ ($CDCl_3$) 222.3, 134.2, 117.3, 67.2, 49.1, 44.4, 43.5, 38.8, 37.3, 30.3. Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 72.97; H, 7.46.

3,8-Dihydroxy-5-methylenetricyclo[4.2.1.0^{4,9}]nonane. To a stirred solution of 8-hydroxy-5-methylenetricyclo[4.2.1.0^{4,9}]-nonan-3-one (339 mg, 2.07 mmol) in 7 mL of THF was added L-Selectride (5.2 mL, 1.0 M, 5.2 mmol) at –78 °C under nitrogen. The reaction mixture was stirred for 2.5 h at this temperature and was warmed to –30 °C. Water (2.5 mL), 3.0 M aqueous NaOH solution (3.0 mL), and 30% H_2O_2 (3.0 mL) were added. Ether was added, and the aqueous layer was separated and extracted with ether. The combined organic layers were dried and concentrated on a rotary evaporator to give 321 mg of crude product as a white solid. The solid was recrystallized from ethyl acetate–hexane to give 210 mg of the diol as clear, colorless, tabular crystals. The mother liquor was concentrated and the residue was purified by flash chromatography (70% ethyl acetate–dichloromethane) to give an additional 78 mg of pure crystalline diol (84% yield overall): mp 118–119 °C; IR ($CHCl_3$) 3430, 2970, 1665 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 4.99 (d, 1, J = 2.2 Hz), 4.97 (d, 1, J = 2.2 Hz), 4.27–4.33 (m, 2), 3.27 (t, br, 1, J = 7.0 Hz), 3.09–3.24 (m, 1), 2.85 (q, 1, J = 7.0 Hz), 2.68 (quintet, 1, J = 7.0 Hz), 2.00–2.34 (m, 4), 1.72–1.80 (m, 2); mass spectrum, exact mass calcd for $C_{10}H_{14}O_2$ m/e 166.0994, found m/e 166.0991.

The structure of this crystalline material was determined by X-ray crystallographic analysis. The numerical data for this analysis are given in the Supplementary Material section in this manuscript and the ORTEP stereodiagram of this determined structure is shown in Figure 1.

Preparative Irradiation of *anti*-4-[1-[(*tert*-Butyldimethylsilyl)oxy]-3,4-pentadienyl]cyclopent-2-en-1-one (9b). A solution of enone **9b** (187 mg, 0.67 mmol) in 200 mL of dry, distilled ether was irradiated under the standard conditions for 9 h. GC analysis indicated 100% conversion to two photoproducts in a 1:1 ratio. The solvent was removed on rotary evaporator to give 170 mg of the photoproduct mixture as a yellow oil. The mixture was purified by flash chromatography (0–10% ethyl acetate–hexane gradient) to yield 91 mg of the higher R_f photoproduct **11c**-α-*t*-**BuMe$_2$Si** ether and 73 mg of **12c**-α-*t*-**BuMe$_2$Si** ether as colorless oils. The properties of **11c**-α-*t*-**BuMe$_2$Si** ether are as follows: IR (thin film) 2950, 1740, 1670, 1255, 1120 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 4.95 (t, 1, J = 2.0 Hz), 4.81 (t, 1, J = 2.0 Hz), 4.29 (q, 1, J = 6.4 Hz), 3.36 (m, 1), 3.27 (m, 1), 3.13 (q, 1, J = 7.7 Hz), 2.82–2.85 (m, 1), 2.74 (d, 1, J = 1.0 Hz), 2.33 (dt, 1, J = 8.8, 1.7 Hz), 2.09–2.21 (m, 1), 1.66–1.76 (m, 1), 0.85 (s, 9), 0.02 (s, 6); ^{13}C NMR δ ($CDCl_3$) 216.6, 147.9, 110.4, 81.5, 53.6, 46.7, 45.8, 44.5, 41.4, 41.3, 25.7, 17.8, –4.6, –4.7. Anal. Calcd for $C_{16}H_{26}O_2Si$: C, 69.01; H, 9.41. Found: C, 69.07; H, 9.54. The properties of **12c**-α-*t*-**BuMe$_2$Si** ether are as follows: IR (thin film) 2950, 1740, 1260, 1120 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 5.40 (dd, 1, J = 4.7, 2.0 Hz), 4.14 (m, 1), 3.45 (m, 1), 3.05–3.25 (m, 1), 2.51–2.71 (m, 4), 2.31 (d, 1, J = 3.0 Hz), 2.28 (d, 1, J = 5.4 Hz), 1.64–2.25 (m, 1), 0.90 (s, 9), 0.05 (s, 6); ^{13}C NMR δ ($CDCl_3$) 222.2, 134.1, 118.0, 67.9, 48.9, 43.6, 37.8, 37.7, 31.3, 25.8, 18.1, –4.7, –4.8. Anal. Calcd for $C_{16}H_{26}O_2Si$: C, 69.01; H, 9.41. Found: C, 69.00; H, 9.56.

Preparative Irradiation of *syn*-4-(1-Hydroxy-3,4-pentadienyl)cyclopent-2-en-1-one (10a). A solution of enone **10a** (200 mg, 1.22 mmol) in 200 mL of dry, distilled ether was irradiated under the standard conditions for 6.5 h. GC analysis indicated

100% conversion to two photoproducts in a 6.7:1 ratio. The solvent was removed on a rotary evaporator to give 182 mg of the photoproduct mixture as a yellow oil. The mixture was mixture was purified by flash chromatography (20–70% ethyl acetate–hexane gradient) to yield 130 mg of the higher R_f photoproduct **11b**-β-OH and 23 mg of the lower R_f photoproduct **12b**-β-OH as colorless oils. The properties of **11b**-β-OH are as follows: IR ($CHCl_3$) 3450, 2960, 1740, 1665 cm^{-1}; ^1H NMR δ ($CDCl_3$) 5.04 (t, 1, J = 2.7 Hz), 4.92 (t, 1, J = 2.7 Hz), 4.23–4.24 (m, 1), 3.43–3.53 (m, 1), 3.39 (m, 1), 2.55–2.62 (m, 2), 2.32–2.53 (m, 1), 1.89–2.14 (m, 2), 1.66 (d, 2, J = 11.0 Hz); ^{13}C NMR δ ($CDCl_3$) 217.1, 149.8, 110.4, 76.6, 54.4, 44.8, 43.2, 41.3, 40.5, 39.9; mass spectrum, exact mass calcd for $C_{10}H_{12}O_2$ m/e 164.0837, found m/e 164.0841. The properties of **12b**-β-OH are as follows: IR (thin film) 3410, 2920, 1735 cm^{-1}; ^1H NMR δ ($CDCl_3$) 5.44 (dd, 1, J = 4.3, 2.0 Hz), 4.17 (m, 1), 3.47 (m, 1), 3.05–3.20 (m, 1), 2.56–2.73 (m, 4), 2.33 (d, 2, J = 8.0 Hz), 1.80–1.96 (m, 2); ^{13}C NMR δ ($CDCl_3$) 221.9, 134.3, 117.3, 67.4, 49.1, 43.5, 38.9, 37.4, 37.3, 30.4. Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.11; H, 7.40.

Preparative Irradiation of *syn*-4-[1-[(*tert*-Butyldimethylsilyl)oxy]-3,4-pentadienyl]cyclopent-2-en-1-one (10b). A solution of enone **10b** (441 mg, 1.58 mmol) in 330 mL of dry, distilled ether was irradiated for 18 h. GC analysis indicated 100% conversion to two photoproducts in a 6.6:1 ratio. The solvent was removed by rotary evaporation to give 431 mg of the photoproduct mixture. The mixture was purified by flash chromatography (0–10% ethyl acetate–hexane gradient) to give 315 mg of the higher R_f photoproduct **11c**-β-t-**BuMe$_2$Si** ether and 30 mg of the lower R_f photoproduct **12c**-β-t-**BuMe$_2$Si** ether as colorless oils. The properties of **11c**-β-t-$BuMe_2Si$ ether are as follows: IR (thin film) 2950, 1740, 1670, 1260, 1100 cm^{-1}; ^1H NMR δ ($CDCl_3$) 5.02 (t, 1, J = 2.2 Hz), 4.89–4.91 (m, 1), 4.12 (q, 1, J = 5.4 Hz), 3.37–3.48 (m, 1), 3.26–3.34 (m, 2), 2.61–2.69 (m, 1), 2.53 (dd, 1, J = 9.0, 1.0 Hz), 2.30 (dd, 1, J = 16.0, 1.0 Hz), 1.80–2.04 (m, 2), 0.86 (s, 9), 0.03 (s, 6); ^{13}C NMR δ ($CDCl_3$) 216.8, 147.9, 110.5, 81.6, 53.7, 46.8, 45.9, 44.6, 41.5, 41.4, 25.7, 17.9, −4.6, −4.7. Anal. Calcd for $C_{16}H_{26}O_2Si$: C, 69.01; H, 9.41. Found: C, 68.96; H, 9.54. The properties of **12c**-β-t-$BuMe_2Si$ ether are as follows: IR (thin film) 2950, 1740, 1260, 1090 cm^{-1}; ^1H NMR δ ($CDCl_3$) 5.44 (dd, 1, J = 4.6, 2.2 Hz), 4.12 (m, 1), 3.41–3.47 (m, 1), 3.07–3.16 (m, 1), 2.61–2.71 (m, 1), 2.52 (d, 2, J = 5.8 Hz), 2.43–2.47 (m, 1), 2.34 (d, 1, J = 3.8 Hz), 2.30 (d, 1, J = 5.7 Hz), 1.85–1.97 (m, 1), 0.87 (s, 9), 0.05 (s, 6); ^{13}C NMR δ ($CDCl_3$) 222.3, 134.0, 117.9, 67.8, 48.9, 43.7, 38.9, 37.9, 37.8, 31.3, 25.7, 18.0, −4.6, −4.8. Anal. Calcd for $C_{16}H_{26}O_2Si$: C, 69.01; H, 9.41. Found: C, 69.02; H, 9.52.

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Registry No. 1, 97253-59-3; 6, 97253-58-2; 7, 97253-60-6; 8, 97253-61-7; **9a**, 97253-62-8; **9b**, 97253-63-9; 8 (TBDMS), 97253-64-0; **10a**, 97253-66-2; **10b**, 97253-65-1; **11a**, 97253-67-3; **11b** (isomer 1), 97253-69-5; **11b** (isomer 2), 97334-51-5; **11c** (isomer 1), 97253-71-9; **11c** (isomer 2), 97335-05-2; **12a**, 97253-68-4; **12b** (isomer 1), 97253-70-8; **12b** (isomer 2), 97334-52-6; **12c** (isomer 1), 97253-72-0; **12c** (isomer 2), 97334-53-7; 1-iodo-3,4-pentadiene, 32442-48-1; 3,8-dihydroxy-5-methylenetricyclo[4.2.1.$0^{4,9}$]nonane, 97253-73-1; 3-ethoxycyclopent-2-en-1-one, 22627-70-9; 3,4-pentadienal, 4009-55-6.

Supplementary Material Available: Tables of atomic positional and crystal and data collection parameters (6 pages). Ordering information is given on any current masthead page.

Synthesis of Karahanaenone

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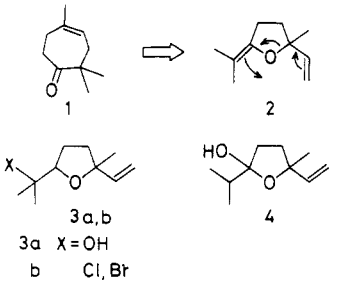
Karahanaenone (1) has been prepared from dehydrolinalyl acetate. Electrochemical epoxidation of dehydrolinalyl acetate provided the corresponding epoxide **6a** (75%) which was converted to keto acetate **7a** (82%) by an electrogenerated acid-catalyzed rearrangement. Hydrogenation followed by alkaline hydrolysis gave 6-hydroxy-2,6-dimethyl-7-octen-3-one (**7c**) (86%), which was subjected to thermal dehydration at 200 °C to give **1** (85%) via Claisen type rearrangement of the intermediate 2-methyl-2-ethenyl-5-propylidenetetrahydrofuran (**2**). An alternative route to **1** via thermolysis of the xanthate of 1-(5-ethenyl-5-methyl-2-tetrahydrofuranyl)-1-methylethanol (**10b**) is also described.

Karahanaenone (1) was isolated as a key flavor of a hop oil by Naya and Kotake[1] and has been synthesized by a number of investigators using cationic rearrangements[2,3] and cyclizations[4], a Diels–Alder approach,[5,6] and by a Cope [3, 3] sigmatropic rearrangement.[7,8] As far as a convenient precursor of **1** is concerned, tetrahydrofuran derivative **2** is promising because Claisen rearrangement of **2** would provide **1**. Demole demonstrated that the collidine-promoted dehydrobromination of **3b** leads to **1**,[9] most likely

Scheme I



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