1-Adamantyl Hydrodisulfide (6). A 30-mL portion of 2.4 M HCl in MeOH was added to a solution of 2.1 g (8.7 mmol) of acetyl adamantyl disulfide (5) in 60 mL of MeOH, and the total volume then was brought to 100 mL with MeOH. The resulting solution was allowed to stand at room temperature for 16 h. The MeOH was removed under reduced pressure, the residue dissolved in hexane, washed four times with water, and dried. The hexane was removed under reduced pressure, yielding 1.6 g (92%) of crude 1-adamantyl hydrodisulfide (6). Molecular distillation at 50 mtorr with a bath temperature of 45 °C gave 1.0 g of 6 (58%) as a colorless liquid: n^{27}_D 1.5824; mp below 25 °C; mass spectrum (direct probe), 200 ($M^{+\cdot}$) [calcd 200]; 135 (base peak); IR 2500 cm^{-1} (S-H); ^1H NMR δ 2.58 (1 H, s, H-S), 1.7-1.0 (15 H, H of adamantyl group); ^{13}C NMR δ 46.73 (s, C-1), 41.56 (t, C-2), 36.16 (t, C-4), 29.82 (d, C-3). Titration of a 28.3-mg portion of 6 with 0.100 N I_2 required 1.45 mL of titrant; equiv wt 195 (calcd 200; 98% purity).

Anal. Calcd for $C_{10}H_{16}S_2$: C, 59.95; H, 8.05. Found: C, 59.77; H, 8.32.

1-Adamantyl 2,4-Dinitrophenyl Disulfide (9). A solution of 0.236 g (1.00 mmol) of 2,4-dinitrobenzenesulfenyl chloride in Et_2O was added to a solution of 0.168 g (1.00 mmol) of 1-adamantanethiol in Et_2O. Crystals of 9 precipitated from the reaction mixture, and three recrystallizations from MeOH gave 0.23 g (63% yield) of 9 that had a constant melting point of 162-163 °C.

Anal. Calcd for $C_{16}H_{18}N_2O_4S_2$: C, 52.44; H, 4.95; S, 17.50. Found: C, 52.57; H, 5.03; S, 17.61.

The same material (9) could be obtained from the reaction of crude samples of 6 with 2,4-dinitrochlorobenzene in methanol and a drop of Et_3N in yields of ca. 50%, mp 161-162 °C. The identity of the materials was determined by identity of the IR spectra, melting points, and an undepressed mixture melting point.

NMR Studies of Chlorinolysis Reactions. To solutions of 1-adamantyl disulfide (6; 0.17 g, 0.50 mmol in 1.5 mL of $CDCl_3$) was added 0.5 mL of 1.0 M solutions of either Cl_2 or SO_2Cl_2 in CCl_4 in one portion. Solutions of Cl_2 were prepared by bubbling Cl_2 gas into CCl_4 at ca. 0 °C and were analyzed by iodometric titration. Solutions of SO_2Cl_2 in CCl_4 were prepared by dissolving the required amount of freshly distilled SO_2Cl_2 in dry CCl_4 and were not analyzed. The resulting solutions then were subjected to either analysis by GC or by NMR.

Acknowledgment. This investigation was supported by PHS Grant CA 30321 awarded by the National Cancer Institute, DHHS.

Heteroatom Cyclopentene Annulation. Synthesis of Guaiane Ring System

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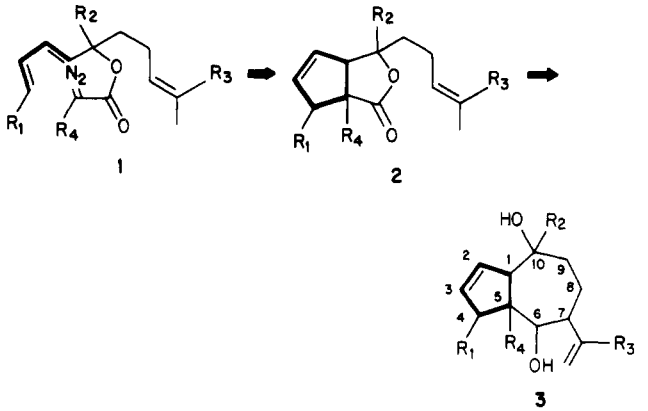
Received January 29, 1985

While the intramolecular cyclopentene annulation of dienic diazo ketones has proven very useful in the synthesis of cyclopentanoid terpenes,[2,3] it has not been possible to extend this process to the preparation of bicyclo[5.3.0]-decanones due to the interfering *inter*molecular reactions of the conformationally mobile precursory diazo ketones.[4]

Scheme I



R_1 = H or CH_3; R_2 = H or CH_3; R_3 = H or CH_3 or CO_2R; R_4 = H or CH_3 or CO_2R

In order to establish this methodology as a tool in the synthesis of perhydroazulene sesquiterpenes of both guaiane or pseudoguaiane types, we sought a reaction sequence that would bypass the formation of a seven-membered ring during the cyclopropanation and, at the same time, allow a facile elaboration of any intermediate to the required bicyclo[5.3.0]decane ring system (Scheme I).

A solution to this problem was envisioned in the combination of the [4 + 1] annulation methodology which incorporates a heteroatom tether (e.g., 1 → 2) with the ene reaction or an equivalent closure[5] between an aldehyde generated from 2 and an appropriate olefinic appendage. This sequence, described herein, proceeds with reasonable steric control of all six chiral centers in 3: the ring junction, controlled by the fusion of two five-membered rings, remains cis; the stereochemistry at C6-C7 is dictated by the transition state of the olefin-aldehyde closure; the C4 center is controlled during the cyclopentene formation *or* by isomerization of the olefin, and the C10 center is controlled by oxidative manipulations at a more advanced stage of synthesis. Additionally, based on the selection of substituents in 1 (R_1 or R_4), the *regiochemistry* of 3 and thus the structural type of either guaianes or pseudoguaianes can be entered selectively (Scheme I).

Following the completion of a model study dealing with the synthesis of simple bicyclic lactones of type 2,[6] we prepared diazo ester 6 in three steps from readily available sorbyl aldehyde and the Grignard reagent derived from 4-methylpent-3-enyl bromide,[7] followed by esterification and diazo transfer reaction[8] (Scheme II). The exposure of 6 to $CuSO_4$ in refluxing benzene gave cyclopropanes **7a** and **7b** (1.7:1) in excellent yield after chromatography. The major isomer was subjected to thermolysis (Vycor, 600 °C) and subsequent decarbomethoxylation to give **9a** and **9b** (1.7:1). It should be noted that both cyclopropanes **7a** and **7b** can *eventually* be used in the synthesis of the same target molecule since the incipient C10 stereocenter will

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(3) Hudlicky, T.; Short, R. P.; Ranu, B. C.; Revol, J. M. *J. Org. Chem.* **1983**, *48*, 4453. Ranu, B. C.; Kavka, M.; Higgs, L. A.; Hudlicky, T. *Tetrahedron Lett.* **1984**, 2447.
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(5) We have not established whether the cyclization of olefin-aldehyde system in 2 is a true ene reaction or simply a Lewis acid catalyzed cationic closure. For simplicity the term ene, as used in this paper, refers to the *product* of a formal ene reaction.
(6) Hudlicky, T.; Govindan, S. V.; Reddy, D. B.; Kulp, T.; Still, B. *J. Org. Chem.* **1983**, *48*, 3422. Govindan, S. V.; Hudlicky, T.; Koszyk, F. J. *J. Org. Chem.* **1983**, *48*, 3581.
(7) Prepared from ethyl cyclopropylcarboxylate (i, MeMgI; ii, HBr, 48%). Oppolzer, W., private communication.
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0022-3263/85/1950-4166$01.50/0

Table I. ^{1}H NMR Assignment of Lactones 8 and 9[a]

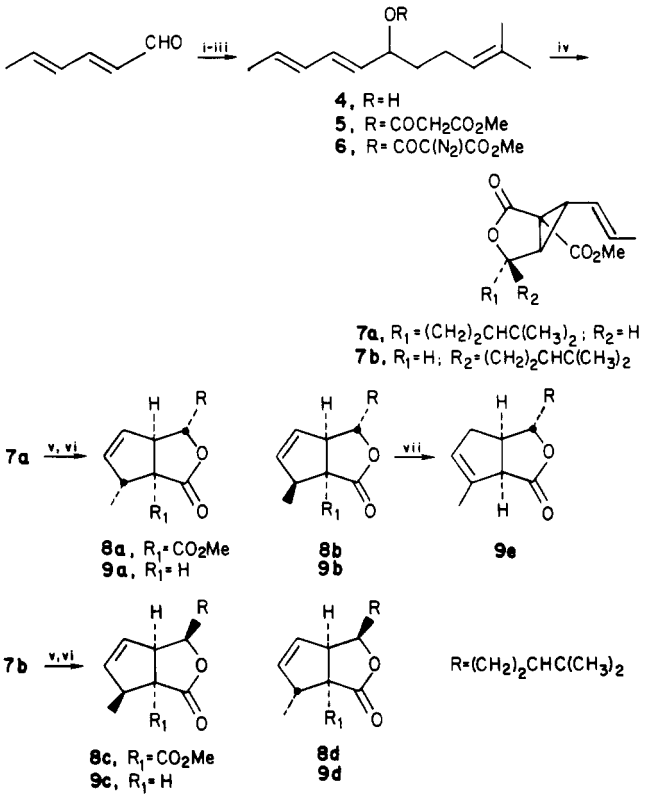
	8a	8b	8c	8d	9a	9b	9c	9d
H1	3.59 m	b	3.52 m	3.77 m	3.1–3.3	3.32 m	2.89–3.29	3.60 m
H2	5.67 dt (6, 1.8)	5.73 dt (7, 3)	5.82 dt (5.4, 2)	5.73 dt (6, 1.5)	5.69 dt (5, 1.7)	5.81 dt (5.5, 2.2)	5.86 m	5.75 dt (6.5, 1.5)
H3	5.53 dt (6, 2.3)	5.55 tt (7, 1.8)	5.60 dt (5.4, 2)	5.53 dt (6,2)	5.60 dt (5, 1.7)	5.59 dt (5.5, 1.5)	5.68 m	5.60 dt (6.5, 2)
H4	3.64 q br (7.5	3.41 ddq (1.8, 3, 8)	3.85 m	3.60 m	3.1–3.3	3.14 m	2.89–3.29	3.1–3.3
H5					3.1–3.3	2.80 dd (1.5, 7.5)	2.89–3.29	3.1–3.3
H7	5.10 t br (7)	5.10 t br (7)	5.12 t br (7.5)	5.13 t br (6.5)	5.10 t br (8)	5.11 t br (7)	5.13 m	5.12 t br (7.5)
H8's	2.15 q (7)	2.13 q (7)	2.08 m	2.20 m	2.13 q br (8)	2.15 q br (7)	2.15 q br (8)	2.17 m
H9's	1.83 m	c	c	c	c	c	c	c
H10	4.15 ddd (4, 6, 8)	4.29 dd (8, 10.5)	4.36 m	4.60 ddd (5.5, 6.5, 9)	4.18 ddd (2.5, 6, 7.5)	4.32 ddd (1.5, 5, 5)	4.37 m	4.45 ddd (5.6, 7.5, 9.4)
H12	1.63 br	1.63 br	1.60 br	1.63 br	1.64 br	1.65 br	1.62 br	1.63 br
H13	1.70 d (1)	1.70 d (1)	1.68 br	1.70 br	1.71 br	1.73 br	1.69 br	1.70 br
H14	1.23 d (7.5)	1.01 d (8)	1.45 d (6)	1.32 d (7)	1.24 d (6.5)	1.14 d (7.5)	1.38 d (6.5)	1.27 d (8)
COOMe	3.80 s	3.84 s	3.80 s	3.80 s				

[a] m = multiplet, s = singlet, d = doublet, t = triplet, q = quartet, br = broad. Values of J (Hz) given in parentheses. [b] Obscured by COOMe. [c] Obscured.

later be destroyed by oxidation. The stereochemistry of the C4-methyl, controlled at this stage with only 64:36 selectivity, can be fully controlled by isomerization of either isomer to **9e** ($RhCl_3$, EtOH).[9,19] Surprisingly, the minor isomer of cyclopropane **7b** gave, upon identical treatment, a 3:1 mixture of bicyclic lactones **8c** and **8d** epimeric at C4, where the *major* product had the C4 configuration of **8b**. Wel also observed this steric reversal in the model series and lack an adequate explanation of its origin.[6] Decarbomethoxylation of the esters gave lactones **9c** and **9d**. Since the C10 center will later be destroyed, lactones **9a** and **9d** and lactones **9b** and **9c** can be combined for further synthetic elaborations, yielding approximately 1:1 selectivity in the preparation of guaiane synthons **9** having the C4 stereochemistry of either 5-*epi*-kessane or bulnesene type of sesquiterpenoids.[10] In practical application, this selectivity will be increased by choosing **9a** and **9d** for the elaboration to kessane-type targets, while all four isomers may be subjected to isomerization to **9e** for the production of bulnesene-type terpenes. The utility of lactone **9e** can be recognized in potential oxidations or hydrogenations that are known to proceed stereoselectively to give the β-orientation of the C4 substituent.[11]

We now had a reasonable entry to the bicyclic lactones **9** which were equipped with the necessary olefinic appendage for further transformations to perhydroazulene skeleton. Although all four isomers of **9** may eventually be used in a convergent manner since C4 and C10 centers may become sp^2 hybridized at some stage of the synthesis, we performed, for the purpose of completeness, a detailed spectral analysis of all diastereomers. The chemical shift of protons and carbons listed in Tables I and II of these compounds may aid us in future encounters of diastereomers in this series. The primary synthetic thrust, however, utilized for the moment only the major isomer, **9a**. Lactone **9a** was reduced with DIBAL to **10** which was obtained as a single diastereomer (Scheme III). The stereochemistry of this substance was assigned on the basis of its ^{1}H NMR spectrum, which showed a triplet (J = 3.5 Hz) for the acetal proton. This triplet reduced to a doublet after D_2O exchange. The value of this coupling indicates a cis relationship of the acetal and the ring-junction protons. This stereochemical arrangement would also be expected on the basis of the approach of hydride from the less hindered face.

Scheme II[a]



[a] Reagents: i, $LiCH_2CH_2CHC(CH_3)_2/Et_2O$; ii, $ClCOCH_2CO_2Me/Et_3N/CH_2Cl_2/0$ °C; iii, TsN_3/CH_3CN; iv, $CuSO_4$/benzene; v, 610 °C/Vycor/$PbCO_3$; vi, LiI/DMF/Δ; vii, $RhCl_3$/EtOH.

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(10) For recent synthetic accomplishments, see: Rigby, J. H.; Wilson, J. Z. *J. Am. Chem. Soc.* **1984**, *106*, 8217 and references therein. See also: ApSimon, J., Ed. "The Total Synthesis of Natural Products"; Wiley: New York, 1973, 1983; Vols. 2, 5.

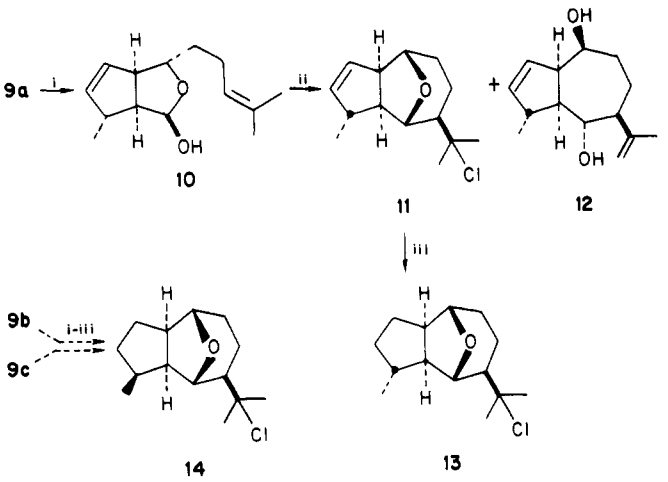
(11) Piers, E.; Cheng, K. F. *J. Chem. Soc., Chem. Commun.* **1969**, 562.

Table II. ^{13}C NMR Assignment of Lactones 8 and 9

	8a	8b	8c[a]	8d	9a	9b	9c	9d
C1	46.6	48.5	52.9	46.5	42.2	44.6	44.8	42.4
C2	127.4	128.6	127.8	123.7	129.3	129.2	129.6	125.7
C3	136.7	136.1	135.2	138.9	138.3	138.1	136.7	139.8
C4	58.1	52.9	59.9	56.8	45.7	49.5	47.2	46.3
C5	63.19	63.5			53.20	50.7	54.3	50.7
C6	170.4	168.5			172.1			
C7	122.4	122.3	123.9	122.9	122.9	122.6	124.1	122.9
C8	23.6	23.7	26.8	24.6	23.7	23.7	27.0	24.6
C9	35.7	35.3	31.0	31.8	36.6	36.5	30.6	32.1
C10	83.3	82.4	79.9	80.0	83.8	83.4	79.8	80.1
C11	132.7	132.8		133.0	133.0			
C12	17.3	17.3	17.6	17.7	17.7	17.7	17.7	17.7
C13	25.3	25.3	25.5	25.6	25.7	25.7	25.7	25.7
C14	16.3	16.9	21.5	15.4	16.4	21.1	22.1	15.7
COOMe	52.7[b]	52.5	52.7	53.0				

[a] Missing resonances not detected in the spectrum. [b] Carbonyl resonance not detected in the ^{13}C NMR spectra.

Scheme III[a]



[a] Reagents: i, diisobutylaluminum hydride/toluene/−78 °C; ii, $SnCl_4$/benzene, 6 °C; iii, H_2/PtO_2.

Exposure of this material to several Lewis acid systems[12] gave traces of diol **12** and a good yield of cyclic chloro ether **11**.[13] The preparation of this chloro ether was eventually optimized by using Et_2AlCl in CH_2Cl_2. We suspect that an acid-catalyzed aldehyde–olefin closure is taking place rather than a true ene reaction, since we were not able to obtain **12** (or **11**) by thermolysis of lactol **10** in toluene. Chloro ether **11** was finally hydrogenated to **13**, which may eventually be elaborated further to 5-*epi*-kessane-type sesquiterpenes, should such targets become desirable.

This study served to demonstrate the initial feasibility of synthesis of [5.3.0] bicyclic systems by the application of a tandem cyclopentene annulation/ene reaction[5] sequence. The entire sequence leading to **13** proceeds in nine steps and in fair overall yield. The preliminary results indicate that *either* configuration at C4 is accessible directly, as in the case of **13**, or possibly via lactone **9e** or **9b**, whose transformations and final hydrogenations would yield **14**, possessing the necessary C4 configuration of bulnesene sesquiterpenes.

Our goal at this point is the detailed study and eventual control of the aldehyde–olefin closure and the establishment of whether this closure resembles a cationic cyclization or a true ene reaction. We also intend to synthesize **14** on a scale large enough to permit its conversion to bulnesene. Experiments directed toward the modification of general substrate **1** where the C10 substituent is already present or where the olefinic fragment contains a carboxylate for elaboration to α-methylene lactones have been initiated. We will report on their outcome in due course.

Experimental Section

All nonhydrolytic reactions were carried out in a nitrogen or argon atmosphere, using standard techniques for the exclusion of air and moisture. Glassware used for moisture-sensitive reactions was flame-dried with an internal inert gas sweep.

All solvents were distilled prior to use. THF, toluene, and benzene were distilled from sodium benzophenone ketyl, ether from LAH, and CH_2Cl_2 from CaH_2.

Infrared spectra were recorded on neat samples, unless otherwise specified, and ν_{max} is expressed in cm^{-1}. Chemical shifts are expressed in δ units, and the coupling constants are indicated in parentheses and expressed in hertz; multiplicities of the signals are indicated as follows: d for doublet, t for triplet, q for quartet, m for multiplet, and any combinations as appropriate. Unspecified signals are singlets. The abbreviation br next to signal multiplicity connotes broad.

Flash chromatography was performed by the procedure of Still and co-workers,[20] using Kiesel gel 60 (230–400 mesh) by EM reagents. Mass spectra were recorded on a Du Pont 20-491 or a Varian MAT-112 instrument (low resoltuion) or on a double focusing Du Pont 21-110C instrument (exact mass).

1-(4-Methyl-3-pentenyl)-2,4-hexadien-1-ol (4). (4-Methyl-3-pentenyl)lithium was generated by the procedure of Lansbury and co-workers.[14] A solution of 7.44 g (45.62 mmol) of 5-bromo-2-methyl-2-pentene in 80 mL of ether was stirred at −78 °C, and 37 mL (73.39 mmol) of 1.98 M *tert*-butyllithium in pentane was added over 15 min. Stirring was continued for 5 min at −78 °C. A solution of 3.22 g (33.54 mmol) of 2,4-hexadienal in 10 mL of ether was added via pressure-equalized additon funnel over 5 min. The syringe and the wall of the addition funnel were washed with 10 mL of ether. The solution was warmed to room temperature and hydrolyzed with 30 mL of brine. The aqueous layer was extracted twice with ether. The combined organic extracts were washed with brine, dried, and evaporated. The residue was purified by flash chromatography on a 34-mm column with 3:17 ether–hexane as eluant, which gave 3.82 g (73%) of **4** as a greenish yellow oil: IR 3375, 1650; ^1H NMR 1.6 (s br, 3 H), 1.7 (s br, 3 H), 1.72 (d br, 3 H, J = 6), 4.05 (q br, 1 H, J = 6), 5.07 (t br, 1 H, J = 6), 5.37–6.60 (m's, 4 H); ^{13}C NMR 17.7 (q), 18.0 (q), 24.2 (t), 25.7 (q), 37.5 (t), 72.1 (d), 124.3 (d) [quaternary olefinic carbon obscured], 129.0 (d), 130.6 (d), 131.4 (d), 133.8 (d); mass spectrum, m/e (relative intensity) 180 (M^+, 15.7), 165 (20), 137 (54.3), 123 (30), 110 (71.4), 97 (71.4), 83 (38.6), 79 (37.1), 69 (100), 55 (91.4), 41 (92.9); mass spectrum, calcd for $C_{12}H_{20}O$ 180.1514, found 180.1511.

(12) Among the systems tried were $TiCl_4$, $SnCl_4$, BF_3·Et_2O, ZnI_2, and silica gel in benzene, methylene chloride, and chloroform.

(13) Evidence for the presence of small amounts of diol **12** was obtained from ^1H NMR and IR spectra of aliquots of the reactions (δ 4.9, excocyclic CH_2, and 3500 cm^{-1}).

(14) Lansbury, P. T.; Haddon, V. R.; Stewart, R. C. *J. Am. Chem. Soc.* **1974**, *96*, 896.

Methyl 1-(4-Methyl-3-pentenyl)-2,4-hexadien-1-yl Malonate (5). A solution of 4.03 g (22.36 mmol) of 1 in 30 mL of methylene chloride was cooled and stirred in an ice bath and treated to a sequential addition of methyl malonate monochloride (3.46 g, 25.35 mmol) and 4-(*N*,*N*-dimethylamino)pyridine (0.27 g, 10 mol %). Triethylamine (2.94 g, 29.07 mmol) was then added dropwise via a disposable syringe. The solution was stirred at 0 °C for 3 h and at room temperature for 18 h. Solvent was evaporated, and the residue was swirled with 75 mL of water and 150 mL of ether. The aqueous layer was extracted twice with ether. The combined organic extracts were washed twice with cold 5% aqueous hydrochloric acid, four times with saturated aqueous sodium bicarbonate, and once with brine and dried. Evaporation of solvent gave a residue, which was purified by flash chromatography on a 34-mm column using 1:4 ether–hexene as eluant to obtain 3.8 g (60.7%) of the ester **5**: IR 1760, 1740; ^{1}H NMR 1.6 (s br, 3 H), 1.70 (d, 3 H, J = 2), 1.77 (d br, 3 H, J = 6), 3.33 (s, 2 H), 3.73 (s, 3 H), 5.03 (t br, 1 H, J = 6), 5.20–6.60 (m's, 5 H); ^{13}C NMR 17.6 (q), 17.9 (q), 23.9 (t), 25.6 (q), 34.7 (t), 41.8 (t), 52.2 (q), 75.8 (d), 123.5 (d), 128.0 (d), 130.9 (d), 130.9 (d), 132.30 (s), 133.5 (d), 165.7 (s), 166.9 (s); mass spectrum, m/e (relative intensity) 280 (M^+, 25.7), 253 (54.3), 161 (72.6), 146 (54.3), 119 (54.3), 96 (100), 69 (97.1); mass spectrum, calcd for $C_{16}H_{24}O_4$ 280.1675, found 280.1665.

Methyl 1-(4-Methyl-3-pentenyl)-2,4-hexadien-1-yl Diazomalonate (6). A solution of 3.18 g (11.35 mmol) of ester **2** in 25 mL of acetonitrile was stirred with 2.46 g (12.49 mmol) of tosyl azide and 1.16 g (11.48 mmol) of triethylamine at room temperature for 48 h. The solution was taken up in 200 mL of ether and washed three times with 10% aqueous potassium hydroxide, water, and brine and dried. Evaporation of solvent gave 3.98 g of a deep yellow oil, which contained 88:12 mixture of the diazo ester **6** and tosyl azide (ratio based on ^{1}H NMR integration) and which was chromatographically inseparable. This crude product was used as such in the next step: IR 2140, 1765, 1750; ^{1}H NMR (of diazo ester) 1.6 (s br, 3 H), 1.7 (s $C_{16}H_{22}N_2O_4$ 3 H), 1.76 (d br, 3 H, J = 6), 3.83 (s, 3 H,) 5.07 (t br, 1 H, J = 6), 5.2–6.5 (m's, 5 H), (tosyl azide) 2.47 (s, Ar methyl) 7.4 and 7.83 (d each, J = 9); ^{13}C NMR (of diazo ester) 17.6 (q), 17.9 (q), 23.9 (t), 25.6 (q), 34.7 (t), 52.3 (q), 65.8 (s), 76.2 (d), 123.4 (d), 127.8 (d), 130.8 (d), 131.2 (d), 132.2 (s), 134.0 (d), 160.3 (s), 161.6 (s); mass spectrum, m/e (relative intensity) 306 (M^+, 45.01), 280 (39.4), 223 (100), 161 (39.4), 155 (66.2), 91 (100); mass spectrum, calcd for $C_{16}H_{22}N_2O_4$ 306.1579, found 306.1570.

1-Oxo-3α-(4-methyl-3-pentenyl)-4a-carbomethoxy-4-prop-1-en-1-yl-1,3,3a,4a-tetrahydrocyclopropa[*c*]furan (7a) and 1-Oxo-3β-(4-methyl-3-pentenyl)-4a-carbomethoxy-4-prop-1-en-1-yl-1,3,3a,4a-tetrahydrocyclopropa[*c*]furan (7b). The mixture of diazo ester **6** and tosyl azide (88:12, 3.63 g) was dissolved in 10 mL of benzene and added over 15 min to a stirred, refluxing mixture of 7.6 g of anhydrous copper sulfate and 0.31 g of cupric acetylacetonate in 70 mL of benzene. The mixture was refluxed for 9 h, cooled, and filtered. Evaporation of solvent gave a greenish oil, which consisted of tosyl azide and the isomeric lactones **7a** and **7b**. Careful flash chromatography on a 34-mm column using 1:4 ether–hexane as eluant yielded 0.99 g of **7a** and 0.56g of **7b**.

7a: Kugelrohred at 145 °C (bath) (0.15 mm); colorless oil; IR 1780, 1730; ^{1}H NMR 1.61 (s br, 3 H), 1.70 (s br, 3 H), 1.72 (dd, 3 H, J = 1.3, 7), 2.15 (q br, 2 H, J = 7.5), 2.30 (dd, 1 H, J = 5.4, 8.7), 2.60 (d, 1 H, J = 5.4), 3.83 (s, 3 H), 4.33 (dd, 1 H, J = 6.6), 5.07 (t br, J = 7.6), 5.32 (ddq, 1 H, J = 8.7, 15, 1.3), 5.8 (dq, 1 H, J = 15, 7); ^{13}C NMR 17.3 (q), 17.7 (q), 22.4 (t), 25.3 (q), 32.03 (s), 34.6 (d), 35.2 (t), 37.2 (d), 52.3 (q), 77.8 (d), 122.2 (d), 122.7 (d), 131.3 (d), 132.7 (s), 165.1 (s), 169.1 (s); mass spectrum, m/e (relative intensity) 190 (57.7), 174 (16.9), 161 (14.1), 148 (93.0), 133 (46.5), 116 (100) [mass peak was not observed]. Anal. Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97; M_r, 278.1518. Found: C, 68.81; H, 8.24; M_r, 278.1513.

7b: IR (in $CHCl_3$) 1780, 1730; ^{1}H NMR 1.60 (s br, 3 H), 1.70 (s br, 3 H), 1.72 (dd, 3 H, J = 1.2, 7), 2.10 (m, 2 H), 2.35 (m, 1 H), 2.75 (dd, 1 H, J = 3.8, 5), 3.8 (s, 3 H), 4.60 (m, 1 H), 5.10 (t br, 1 H, J = 6), 5.35 (m, 1 H), 5.83 (m, 1 H); ^{13}C NMR 17.7 (q), 17.9 (q), 24.0 (t), 25.6 (q), 32.1 (t), 34.3 (d), 34.3 (d), 52.4 (q), 77.4 (d), 122.8 (d), 123.3 (d), 130.1 (s), 131.5 (d), 165.4 (s), 169.4 (s); mass spectrum, m/e (relative intensity) 278 (M^+, 1.3), 260 (2.0), 246 (5.4), 228 (4.8), 205 (5.4), 160 (13.6), 135 (16), 105 (31.4), 93 (22.7), 79 (48.2), 69 (100); mass spectrum, calcd for $C_{16}H_{22}O_4$ 278.1518, found 278.1510.

1-Oxo-3α-(4-methyl-3-pentenyl)-6α-methyl-6aα-carbomethoxy-1,3,3aα,6a-tetrahydrocyclopenta[*c*]furan (8a) and the C6 Epimer (8b). Cyclopropane **7a** (0.81 g, 3.68 mmol) was pyrolyzed at 610 °C (0.0007 mm) through a horizontal Vycor type precoated with lead carbonate. The pyrolysate was collected in a trap cooled with liquid nitrogen. The trap and the tube were washed with methylene chloride, and the solution was filtered through a short column of silica gel. The crude product was chromatographed on a 25 mm wide flash column using 15:85 ether–hexane as eluant to obtain 0.15 g of **8a** and 0.09 g of **8b**.

8a: colorless oil; IR (in $CHCl_3$) 1770, 1740; ^{1}H NMR 1.23 (d, 3 H, J = 7.5), 1.70 (d, 3 H, J = 1), 1.63 (s br, 3 H), 1.83 (m, 1 H), 2.15 (q, 2 H, J = 7), 3.59 (m, 1 H), 3.64 (q br, 1 H, J = 7.5), 3.80 (s, 3 H), 4.15 (ddd, 1 H, J = 4, 6, 8), 5.10 (t br, 1 H, J = 7), 5.53 (dt, 1 H, J = 6, 2.3), 5.67 (dt, 1 H, J = 6, 1.8) [one of the methylene protons obscured under methyls]; ^{13}C NMR 16.17 (q), 17.34 (q), 23.57 (t), 25.3 (q), 35.7 (t), 46.6 (d), 52.7 (q), 58.1 (d), 63.2 (s), 83.3 (d), 122.4 (d), 127.4 (d), 132.7 (s), 136.7 (d), 170.4 (s); mass spectrum, m/e (relative intensity) 278 (M^+, 13.9), 246 (3.8), 219 (3.3), 138 (20.1), 122 (27.8), 95 (100), 82 (63.4), 79 (42.9); mass spectrum, calcd for $C_{16}H_{22}O_4$ 278.1518, found 278.1510.

8b: IR (in $CHCl_3$) 1780, 1730; ^{1}H NMR 1.01 (d, 3 H, J = 8), 1.63 (s br, 3 H), 1.70 (d, 3 H, J = 1), 2.13 (q, 2 H, J = 7), 3.41 (ddq, 1 H, J = 1.8, 3.8), 3.84, (s, 3 H), 4.29 (dd, 1 H, J = 8, 10.5), 5.10 (t br, 1 H, J = 7), 5.55 (d t, 1 H, J = 7, 3), 5.73 (dt, 1 H, J = 7, 1.8) [ring-junction methine proton and methylene β to lactone are obscured]; ^{13}C NMR 16.9 (q), 17.3 (q), 23.7 (t), 25.3 (q), 35.3 (t), 48.5 (d), 52.5 (q), 52.9 (d), 63.5 (s), 82.4 (d), 122.3 (d), 128.6 (d), 132.8 (s), 136.1 (d), 168.5 (s); mass spectrum, m/e (relative intensity) 278 (M^+, 12.8), 246 (3.9), 173 (3.9), 160 (9.9), 153 (9.9), 138 (42.8), 122 (17.6), 107 (31.9), 95 (100), 82 (85.6), 79 (54); mass spectrum, calcd for $C_{16}H_{22}O_4$ 278.1518, found 278.1513.

1-Oxo-3α-(4-methyl-3-pentenyl)-6α-methyl-1,3,3aα,6aα-tetrahydrocyclopenta[*c*]furan (9a) and the C6 Epimer (9b). **9a**. **8a** (108 mg, 0.39 mmol), 265 mg (1.94 mmol) of lithium iodide, and 2.5 mL of anhydrous DMF were refluxed for 3 h. The solution was cooled, quenched with 5 mL of cold 3 M HCl, and extracted five times with ether. The combined ether extracts were washed with five 1-mL portions of water and once with brine and dried. Evaporation of solvent gave a crude product, which was filtered through a short column of 1 g of silica gel using 8 mL of hexane and 10 mL of 10% ether–hexane as eluants. This yielded 77 mg (90%) of **9a**, which was Kugelrohred at 152 °C (bath) (0.005 mm) to give a colorless oil; IR (in $CHCl_3$) 1755; ^{1}H NMR 1.24 (d, 3 H, J = 6.5), 1.64 (s br, 3 H), 1.71 (s br, 3 H), 2.13 (q br, 2 H, J = 8), 3.1–3.3 (m's, 3 H), 4.18 (ddd, 1 H, J = 2.5, 6, 7.5), 5.10 (t br, 1 H, J = 8), 5.60 (dt, 1 H, J = 5, 1.7), 5.69 (dt, 1 H, J = 5, 1.7) [methylene protons β to lactone obscured]; ^{13}C NMR 16.4 (q), 17.7 (q), 23.7 (q), 25.7 (q), 36.6 (t), 42.2 (d), 45.7 (d), 53.2 (d), 83.8 (d), 122.9 (d), 129.3 (d), 133.0 (s), 138.3 (d), 177.1 (s); mass spectrum, m/e (relative intensity) 220 (M^+, 2.1), 205 (0.6), 192 (2.4), 181 (2.5), 163 (2.6), 110 (30.4), 95 (38.5), 80 (100). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15; M_r, 220.1463. Found: C, 76.00; H, 9.14; M_r, 220.1467.

9b. **8b** (30.5 mg, 0.11 mmol) was decarbomethoxylated as detailed for **8a** → **9a** to obtain 20 mg (83.0%) of **9b** as a pale yellow oil: IR (in $CHCl_3$), 1770; ^{1}H NMR 1.14 (d, 3 H, J = 7.5), 1.65 (s br, 3 H), 1.73 (s br, 3 H), 2.15 (q br, 2 H, J = 7), 2.80 (dd, 1 H, J = 1.5, 7.5), 3.14 (m, 1 H), 3.32 (m, 1 H), 4.32 (ddd, 1 H, J = 1.5, 5.5), 5.11 (t br, 1 H, J = 7), 5.59 (dt, 1 H, J = 5.5, 1.5), 5.81 (dt, 1 H, J = 5.5, 2.2) [methylene protons β to lactone obscured]; ^{13}C NMR 17.7 (q), 21.1 (q), 23.7 (t), 25.7 (q), 36.5 (t), 44.6 (d), 49.5 (d), 50.7 (d), 83.4 (d), 122.6 (d), 129.2 (d), 138.1 (d); mass spectrum, m/e (relative intensity) 220 (M^+, 5.2), 192 (3.0), 163 (4.7), 95 (44.9), 80 (100); mass spectrum, calcd for $C_{14}H_{20}O_2$ 220.1463, found 220.1469.

1-Oxo-3β-(4-methyl-3-pentenyl)-6β-methyl-6aα-carbomethoxy-1,3,3aα,6a-tetrahydrocyclopenta[*c*]furan (8c) and the C6 Epimer (8d). Cyclopropyl lactone **7b** (0.78 g, 3.54 mmol) was pyrolyzed at 610 °C (0.05 mm) as described for the conversion **7a** → **8a,b**. Recovery of the products by extraction with methylene chloride, followed by solvent removal, gave a residue, which was chromatographed (flash column, 24 mm wide) with 1:4 ether–hexane as eluant. This yielded 0.05 g of **8d** and 0.15 g of **8c**.

8d: IR 1760, 1730; ^{1}H NMR 1.32 (d, 3 H, J = 7), 1.63 (s br, 3 H), 1.70 (s br, 3 H), 2.20 (m, 2 H), 3.60 (m, 1 H), 3.77 (m, 1 H), 3.80 (s, 3 H), 4.60 (ddd, 1 H, J = 5.5, 6.5, 9), 5.13 (t br, 1 H, J = 6.5), 5.53 (dt, 1 H, J = 6.2), 5.73 (dt, 1 H, J = 6, 1.5) [methylene β to lactone obscured]; ^{13}C NMR 15.4 (q), 17.7 (q), 24.6 (t), 25.6 (q), 31.8 (t), 46.5 (d), 56.8 (d), 80.0 (d), 122.9 (d), 123.7 (d), 133.0 (s), 138.9 (d) [lactone carbon and carbon adjacent to lactone were too weak to be observed]; mass spectrum, m/e (relative intensity) 278 (M^+, 3.8), 260 (5.8), 246 (7.1), 218 (8.6), 161 (25.4), 138 (100), 119 (25.1), 110 (27.3), 106 (46.9), 79 (86.8); mass spectrum, calcd for $C_{16}H_{22}O_4$ 278.1518, found 278.1507.

8c: IR (in $CHCl_3$) 1765, 1730; ^{1}H NMR 1.45 (d, 3 H, J = 6), 1.60 (s br, 3 H), 1.68 (s br, 3 H), 2.08 (m, 2 H), 3.52 (m, 1 H), 3.80 (s, 3 H), 3.85 (1 H, m), 4.36 (m, 1 H), 5.12 (t br, 1 H, J = 7.5), 5.60 (dt, 1 H, J = 5.4, 2), 5.82 (dt, 1 H, J = 5.4, 2) [methylene β to lactone oxygen obscured]; ^{13}C NMR 17.6 (q), 21.5 (q), 25.5 (q), 26.8 (t), 31.0 (t), 52.9 (d), 59.9 (d), 79.9 (d), 123.9 (d), 127.8 (d), 135.2 (d) [singlets obscured]; mass spectrum, m/e (relative intensity) 278 (M^+, 32.8), 246 (20), 222 (19.1), 138 (48.1), 120 (25.8), 105 (100); mass spectrum, calcd for $C_{16}H_{22}O_4$ 278.1518, found 278.1510.

1-Oxo-3β-(4-methyl-3-pentenyl-)-6β-methyl-1,3,3aα,6aα-tetrahydrocyclopenta[*c*]furan (9c) and the C6 Epimer (9d). **8d** (50 mg, 0.18 mmol), 125 mg of lithium iodide (0.92 mmol), and 1 mL of anhydrous DMF were refluxed for 3 h and worked up as described for **8a** → **9a** conversion. The crude material was filtered through 1 g of silica gel to obtain 28 mg (70.8%) of **9d**. In a similar fashion, 142.1 mg of **8c** was decarbomethoxylated to obtain 45 mg (40.2%) of **9c**.

9d: IR (in $CHCl_3$) 1770; ^{1}H NMR 1.27 (d, 3 H, J = 8), 1.63 (s br, 3 H), 1.70 (s br, 3 H), 2.17 (m, 2 H), 3.10–3.30 (m's, 2 H), 3.60 (m, 1 H), 4.45 (ddd, 1 H, J = 5.6, 7.5, 9.4), 5.12 (t br, 1 H, J = 7.5), 5.60 (dt, 1 H, J = 6.5, 2) 5.75 (dt, 1 H, J = 6.5, 2) [methylene β to lactone oxygen obscured]; ^{13}C NMR 15.7 (q), 17.7 (q), 24.6 (t), 25.7 (q), 32.1 (t), 42.4 (d), 46.3 (d), 50.7 (d), 80.1 (d), 122.9 (d), 125.7 (d), 139.8 (d) [quaternary carbons were too weak to observe]; mass spectrum, m/e (relative intensity) 220 (M^+, 5.1), 205 (1.6), 192 (4.9), 163 (7.7), 95 (39.8), 80 (100); mass spectrum, calcd for $C_{14}H_{20}O_2$ 220.1463, found 220.1469.

9c: IR (in $CHCl_3$) 1760; ^{1}H NMR 1.38 (d, 3 H, J = 6.5), 1.62 (s br, 3 H), 1.69 (s br, 3 H), 2.15 (q br, 2 H, J = 8), 2.89–3.29 (m's, 3 H), 4.37 (m, 1 H), 5.13 (m, 1 H), 5.68 (m, 1 H), 5.86 (m, 1 H); ^{13}C NMR 17.7 (q), 22.1 (q), 25.7 (q) 27.0 (t), 30.6 (t), 44.8 (d), 47.2 (d), 54.3 (d), 79.8 (d), 124.1 (d), 129.6 (d), 136.7 (d) [quaternary carbons obscured]; mass spectrum, m/e (relative intensity) 220 (M^+, 23.4), 205 (4.3) 177 (9.8), 175 (12.7), 164 (14.7), 151 (17.0), 107 (35.8), 93 (58.5), 80 (100); mass spectrum, calcd for $C_{14}H_{20}O_2$ 220.1463, found 220.1459.

1-Hydroxy-3α-(4-methyl-3-pentenyl)-6α-methyl-1,3,3aα,6aα-tetrahydrocyclopenta[*c*]furan (*10*). **9a** (45 mg, 0.20 mmol) in 2 mL of anhydrous toluene was stirred and cooled at −78 °C, and a solution of DIBAL-H in toluene (0.15 mL; 25 wt% solution in toluene; 0.225 mmol)[15] was added dropwise via a disposable syringe. Stirring was continued for 1 h at −78 °C. Methanol (0.5 mL) and saturated aqueous ammonium chloride (1 mL) were added, and the reaction mixture was extracted three times with ether. The combined ether extracts were washed with brine and dried. Evaporation of solvents gave 37 mg (81.5%) of **10**, which was homogeneous by TLC and spectral criteria: colorless oil; IR 3435; ^{1}H NMR 1.14 (d, 3 H, J = 6.5), 1.62 (s br, 3 H), 1.70 (s br, 3 H), 2.10 (q br, 2 H, J = 8), 2.80 (m, 1 H), 2.97 (m, 1 H), 3.15 (ddd, 1 H, J = 2, 3, 8), 3.25 (d, 1 H, J = 3.5, disappears on D_2O exchange), 3.80 (dt, 1 H, J = 3.4, 6.8), 5.14 (t br, 1 H, J = 8), 5.39 (t, 1 H, J = 3.5), 5.58 (complex AB pattern, 2 H); ^{13}C NMR 15.8 (q), 17.7 (q), 24.9 (t), 25.7 (q), 37.9 (t), 40.5 (d), 53.1 (d), 56.7 (d), 85.2 (d), 100.7 (d), 124.1 (d), 131.1 (d), 137.1 (d) [olefinic singlet not detected]; mass spectrum, m/e (relative intensity) 222 (M^+, 6.2) 205 (34.1), 179 (17.0), 161 (8.4), 123 (75.7), 110 (38.5), 95 (100), 81 (76.8); mass spectrum, calcd for $C_{14}H_{22}O_2$ 222.1620, found 222.1614.

(1β,5β)-4β-Methyl-6α,10α-epoxy-7α-(2-(2-chloropropyl))-bicyclo[5.3.0]dec-2-ene (11) from the Lewis Acid Catalyzed Cyclization of Lactol 10 Using $SnCl_4$.[16] **10** (100 mg, 0.45 mmol) was dissolved in 40 mL of anhydrous benzene, and the solution was stirred and cooled in an ice–water bath (8–10 °C). Stannic chloride (16 μL, 0.068 mmol) was added in one lot, and the stirring continued for 6 min. The reaction was quenched with 160 μL of water, washed three times with brine, and dried. Evaporation of benzene gave a crude material, which was chromatographed on 1 g of silica gel packed in a 5-in. disposable pipette. Elution with 3% ether–hexane led to the isolation of 12 mg of a mixture of unidentified products and 45 mg (42%) of the ene product 11.

Using Et_2AlCl.[17] **10** (20 mg, 0.09 mmol) was dissolved in 3 mL of anhydrous methylene chloride. A solution of diethylaluminum chloride (40μL; 25 wt % solution in toluene; 0.08 mmol) was then added, and the reaction mixture was stirred at the room temperature for 2 h. The reaction mixture was then slowly added to a rapidly stirred solution of aqueous potassium hydroxide (25%; 0.8 mL). The products were taken up in pentane, and the pentane solution was washed with saturated aqueous sodium bicarbonate and brine and dried. The crude material, after solvent removal, was chromatographed on 1 g of silica gel to obtain 8 mg of **11**.

11: colorless oil; IR 1650; ^{1}H NMR 1.10 (d, 3 H, J = 6.5), 1.58 (s br, 3 H), 1.62 (s br, 3 H), 1.75 (m, 2 H), 2.00 (d br, 1 H, J = 11), 3.02 (m, 1 H), 3.1–3.2 (m's, 2 H), 3.98 (s br, 1 H), 4.5, (s br, 1 H), 5.55 (m's, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.9 (CH_3), 18.2 (CH_2), 29.7 (CH_2), 30.7 (CH_3), 31.1 (CH_3), 32.7 (CH_2), 34.1 (CH_2) 37.5 (CH) 42.3 (CH), 47.9 (CH), 51.6 (CH), 71.9 (C), 77.0 (CH), 83.7 (CH); mass spectrum, m/e (relative intensity) 204 (M^+, 51.5), 123 (75.0), 107 (33.4), 93 (100), 79 (51.1); mass spectrum, calcd for $C_{14}H_{20}O$ 204.1514, found 204.1519 (M^+ − HCl). Anal. Calcd for $C_{14}H_{21}OCl$: C, 70; H, 8.75. Found: C, 70.03; H, 9.01. The material gave a positive Beilstein test.[18]

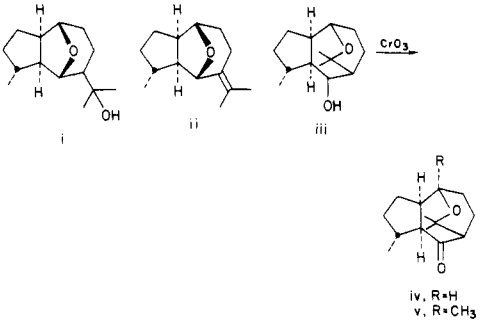
1-Oxo-3α-(4-methyl-3-pentenyl)-6-methyl-1,3,3aα,6aα-tetrahydrocyclopenta[*c*]furan (9e). Lactone **9a** (30 mg, 0.14 mmol) was dissolved in 1 mL of EtOH containing 2 mg of $RhCl_3 \cdot 3H_2O$. The solution was refluxed for 8 h and then kept at room temperature overnight, whereupon the solvent was removed and the residue filtered through a short plug of silica gel to give essentially quantitative yield of **9e**: IR (neat) 1775; ^{1}H NMR ($CDCl_3$) 1.2 (m, 3 H), 1.6 (s, 3 H), 1.69 (s, 3 H), 1.85 (s, 3 H), 2.1 (m, 2 H), 2.6 (m, 2 H), 3.5 (br, 1 H), 4.05 (m, 1 H), 5.1 (s br, 1 H), 5.5 (s br, 1 H); ^{13}C NMR ($CDCl_3$) 14.0 (CH_3), 17.5 (CH_3), 24.0 (CH_2), 25.2 (CH_3), 25.7 (CH_2), 36.0 (CH_2), 37.3 (CH_2), 44.7 (CH), 56.3 (CH), 86.7 (CH), 123.3 (CH), 126.3 (CH) [lactone carbonyl and quaternary olefinic carbons not detected]; mass spectrum (70 eV), m/e (relative intensity) 220 M^+ (15), 137 (10), 133 (25), 120

(15) Adapted from: Corey, E. J.; Weinshenker, N. M.; Schaaf, T. K.; Huber, W. *J. Am. Chem. Soc.* **1969**, *91*, 5675.

(16) Marshall, J. A.; Andersen, N. H.; Johnson, P. C. *J. Org. Chem.* **1970**, *35*, 186.

(17) Adapted from: Snider, B. B.; Karras, M.; Price, R. T.; Rodini, D. J. *J. Org. Chem.* **1982**, *47*, 4538.

(18) Compounds i, ii, and iii were initially considered as candidates for the structure of **13** (vis **11**). All of these substances would have given M^+ of 206, consistent with either ii or the loss of H_2O from i or iii. Structures



i and ii were finally excluded on the basis of careful analysis of ^{1}H and ^{13}C NMR spectra. Structure iii was eliminated after the comparison of spectral data (especially the chemical shifts of methyl groups) of its presumed oxidation product iv with spectra of v which is known (Liu, H.-J.; et al. *Tetrahedron Lett.* **1977**, 3699). We thank Prof. Hsing-Jang Liu of the University of Alberta for kindly providing us with spectra of v for this comparison.

(19) Similar isomerization was also attempted using **9b**. On the basis of one trial, this material was recovered unchanged. The isomerization may be performed at a latter stage.

(20) Still, C. W.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(19), 119 (19), 109 (12), 108 (11), 107 (56), 106 (31), 105 (39), 96 (30), 95 (52), 94 (59), 93 (49), 92 (18), 91 (49), 87 (19), 82 (29), 81 (86), 80 (100), 79 (95), 77 (36), 69 (40), 67 (24).

(1β,5β)-4β-Methyl-6α,10α-epoxy-7α-(2-(2-chloropropyl))-bicyclo[5.3.0]decane (13). Chloro ether **11** (10 mg) was dissolved in 5 mL of ethanol containing 2 mg of PtO_2 and hydrogenated with a Parr hydrogenator (16 psi, 1 h). The catalyst was removed by filtration of the solution through 1 g of silica (flash chromatography grade) using hexane and 97:3 hexane–Et_2O as eluants. Evaporation gave quantitative yield of **13**: IR ($CHCl_3$) 1100, 1000; ^1H NMR ($CDCl_3$) 1.07 (d, 3 H, J = 7), 1.58 (s, 3 H), 1.61 (s, 3 H), 1.2–1.8 (m, 8 H), 1.95 (m, 1 H), 2.05 (m, 1 H), 2.42 (t, 1 H, J = 7), 2.86 (t, 1 H, J = 7), 3.99 (s br, 1 H), 4.47 (s br, 1 H); ^{13}C NMR ($CDCl_3$) 14.8 (CH_3), 18.2 (CH_2), 29.7 (CH_2), 30.7 (CH_3), 31.1 (CH_3), 32.7 (CH_2), 34.1 (CH_2), 37.5 (CH), 47.3 (CH), 47.9 (CH), 51.6 (CH), 71.9 (C), 77.0 (CH), 83.7 (CH); mass spectrum (70eV), m/e (relative intensity) 206 (M^+ – HCl) (34), 191 (21), 151 (20), 150 (13), 149 (18), 135 (38), 125 (100), 124 (46), 123 (71), 121 (22), 109 (49), 107 (52), 96 (27), 95 (86), 94 (33), 93 (50), 83 (37), 82 (82), 81 (99), 80 (20), 79 (57), 77 (32), 71 (21), 69 (98), 68 (63), 62 (97).

Acknowledgment. We are indebted to the National Science Foundation (CHE-8102944) for generous financial support, to Dr. James Hudson (University of Texas, Austin) for assistance with exact mass measurements, and to the ACS-Project Seed sponsorship for J. Meyers. The skillful assistance of Barry Colwell and John Meyers in the preparation of reagents and starting materials is gratefully appreciated.

Registry No. **4**, 97635-09-1; **5**, 97635-10-4; **6**, 97635-11-5; **7a**, 97635-12-6; **7b**, 97673-25-1; **8a**, 97635-13-7; **8b**, 97673-26-2; **8c**, 97673-28-4; **8d**, 97673-29-5; **9a**, 97635-14-8; **9b**, 97673-27-3; **9c**, 97673-30-8; **9d**, 97673-31-9; **9e**, 97635-18-2; **10**, 97635-15-9; **11**, 97635-16-0; **13**, 97635-17-1; $Li(CH_2)_2CH{=}C(CH_3)_2$, 64504-53-6; $ClCOCH_2CO_2Me$, 37517-81-0; sorbyl aldehyde, 142-83-6.

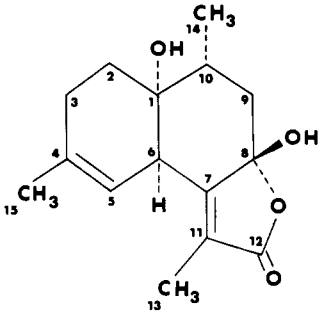
Communications

Verocephol, a Unique Amorphane Sesquiterpene γ-Lactol

Summary: The investigation of *Verbesina sphaerocephala* afforded an amorphane γ-lactol; the structure was established by interpretation of spectral data and X-ray diffraction analysis.

Sir: In our continuing search for biologically active sesquiterpene lactones from the Compositae family, we have isolated from the leaves of *Verbesina sphaerocephala* Asa Gray, collected in Soyotlán, Jalisco, México, a new γ-lactol. Verocephol (**1**) is the first representative having an amorphane skeleton[1] with a γ-lactol which, under acetylation conditions, is epimerized into the more common cadinane sesquiterpene framework.

Verocephol (**1**) [$C_{15}H_{20}O_4$, M^+ 264, mp 198–200 °C, $[\alpha]^{20}_D$ +316° (*c* 1.0, MeOH)] was isolated from air-dried plant material extracted with $CHCl_3$, after exhaustive silica gel chromatography, preparative silica gel GF-254 TLC, and crystallization with ethyl acetate–hexane.

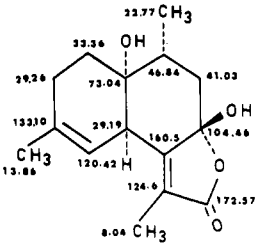


1

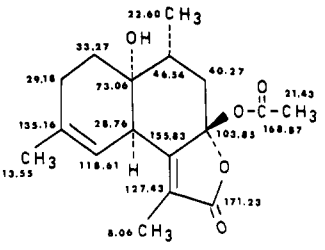
The presence of an α,β-unsaturated γ-lactone was indicated by UV (EtOH) absorption at 220 nm (ε 19600) and by an IR band (Nujol suspension) at 1750 cm^{-1}. Also hydroxyl groups absorptions were observed at 3470 and 3250 cm^{-1}.

(1) Coates, R. M. *Fortschr. Chem. Org. Naturst.* **1976**, *33*, 73.

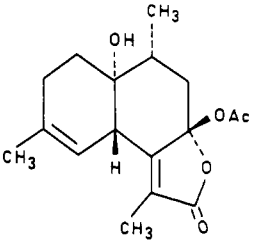
Chart I



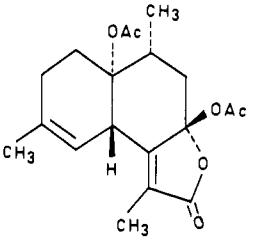
1
(^{13}C NMR in $CDCl_3$ + DMSO-d_6)



2
(^{13}C NMR in $CDCl_3$)



3



4

Table I. ^1H NMR Spectral Data of Verocephol and Derivatives[a]

		1	2	3	4	
CH_3 14	d	0.91	0.95	0.97	1.00	J = 7.0 Hz
CH_3 15	br s	1.65	1.67	1.67	1.68	
CH_3 13	s	1.79	1.87	1.76	1.83	
H 6	m	3.43	3.49	4.97	4.90	$w_{1/2}$ = 9 Hz
H 5	br s	5.08	4.94	5.07	4.95	$w_{1/2}$ = 6 Hz
$CH_3C(O)$–	s		1.93	1.91	1.94	
$CH_3C(O)$–					1.96	

[a] 80 MHz, $CDCl_3$, and **1** in $CDCl_3$–DMe_2SO-d_6; d, doublet; br s, broad singlet; s, singlet; δ from Me_4Si.

On treatment with acetyl chloride and pyridine, compound **1** (Chart I) was converted into the monoacetate derivative **2** whereas acetylation upon reflux with acetic anhydride–pyridine produced the mono- and diacetate β H-6 epimers **3** and **4** with a cadinane skeleton where the

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