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Studies on the Terpenoids and Related Alicyclic Compounds. XXXII.[1] A Synthesis of Chiral Dimethylcyclopropane Derivatives, Versatile Chiral Synthons for Casbane, Lathyrane, and Ingenane-Type Diterpenoids, from (+)-3-Carene

TSUYOSHI SATOH, TERUYOSHI OKUDA, YOUHEI KANEKO, and KOJI YAMAKAWA*

Faculty of Pharmaceutical Sciences, Science University of Tokyo, Ichigaya-Funagawara-machi, Shinjuku-ku, Tokyo 162, Japan

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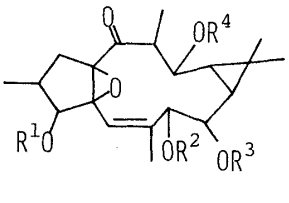
A synthesis of chiral dimethylcyclopropane derivatives, useful for the synthesis of casbane, lathyrane, and ingenane-type diterpenoids, from easily available (+)-3-carene is described. The silyl enol ether (**8**) was derived from (−)-*cis*-4-caranone (**7b**), which was obtained from (+)-3-carene (**6**). Ozonolysis of **8** gave **9a** and **10**. The right half segment (**11b**) for a synthesis of crotonitenone (**3**) was formed from **9a** in three steps. The epoxide (**12**) was isomerized to a mixture of the allylic alcohols (**13a**) and (**14a**), which was transformed to the ketone (**20**) in five steps. Methylation of **20** followed by phosphorylation and reduction gave (+)-*cis*-4-caranone (**23**) in about 40% overall yield from **12**. The methylester (+)-(**32b**) and its enantiomer (−)-(**34b**) were synthesized from (+)-**6**. Ozonolysis of a mixture of the silyl enol ether (**30**) and (**31**) followed by methylation with diazomethane gave **32a**, which was hydrolyzed to give the desired (+)-**32b**. The enantiomer (−)-**34b** was derived from **32a** in five steps.

Keywords——carene; caranone; casbane; ingenane; lathyrane; diterpenoid; ozonolysis; silyl enol ether; oxirane isomerization; chiral synthon

The plants belonging to *Euphorbiaceae* have many kinds of biological activity. Recent systematic investigations of the plants for biologically active substances have resulted in the discovery of several new classes of diterpenoid[2] such as ingol esters (**1**),[3] lathyrols (**2**),[4] crotonitenone (**3**),[5] ingenol esters (**4**),[6] and phorbol esters (**5**).[7] These diterpenoids are the cytotoxic, irritant, piscicidal, or cocarcinogenic principles of the plants.



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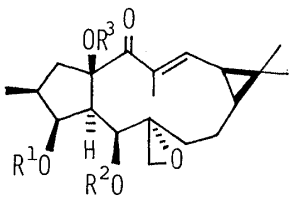

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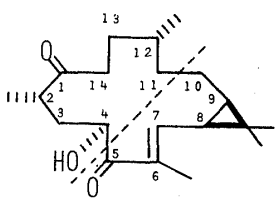

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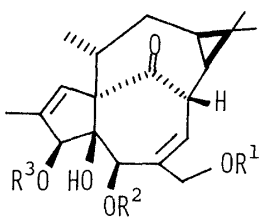

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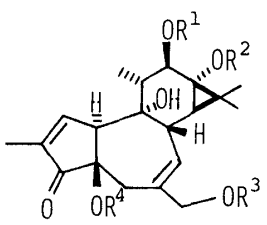

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Fig. 1

The structures of these diterpenoids are characterized by a dimethylcyclopropane ring as a common feature. In the course of a project directed toward the total synthesis of these diterpenoids, we needed to investigate several chiral dimethylcyclopropane derivatives from optically active monoterpenoids having a dimethylcyclopropane moiety. The ideal synthetic intermediate should be readily available in optically active form and should contain appropriate functional groups that would elaborate a single enantiomer or both enantiomers of the diterpenoids. In this paper, we describe the synthesis of both enantiomers of a segment of these diterpenoids from easily available (+)-3-carene (**6**).

Synthesis of the Right Half Segment (9a and 11b) of Crotonitenone (3)

Fot the project directed toward a synthesis of crotonitenone (**3**), we selected 2,2-dimethyl-3-(2-methyl-2-methoxycarbonylethyl)-*cis*-cyclopropane carbaldehyde (**9a**) and the propanedithioacetal of 2,2-dimethyl-3-(2-methyl-3-tetrahydropyranyloxypropyl)-*cis*-cyclopropane carbaldehyde (**11b**) as electrophilic and nucleophilic right half segments (from C5 to C10 of **3**; dotted line).

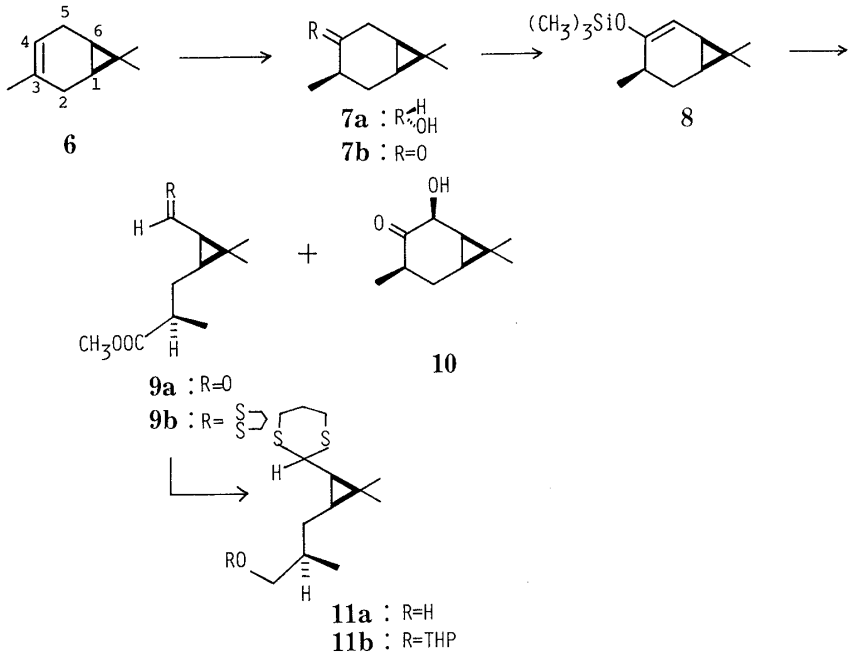

Chart 1

Hydroboration-oxidation of (+)-3-carene (**6**) with diborane in tetrahydrofuran (THF) followed by treatment with hydrogen peroxide gave *cis*-caran-*trans*-4-ol (**7a**)[8] in 67% yield. Oxidation of **7a** by Swern's[9] method gave (−)-*cis*-4-caranone (**7b**)[8] in 87% yield. To cleave the C4–C5 bond, **7b** was transformed to the enol silyl ether and then ozonolyzed. The ketone (**7b**) was treated with lithium diisopropylamide (LDA) at −78 °C followed by trimethylchlorosilane[10] to give **8** in 93% yield; no positional isomer could be detected. Ozonolysis[11] of **8** was carried out at −78 °C in a mixture of methanol and dichloromethane. The ozonide was reduced with dimethyl sulfide and acidic and neutral products were separated. The acidic product was methylated with diazomethane to give a methyl ester (**9a**) in 56% yield. A keto-alcohol (**10**) (19% yield) was separated as a neutral product and the structure was determined by infrared (IR), nuclear magnetic resonance (NMR), and mass spectroscopy. The aldehyde (**9a**) is an ideal chiral synthon for a synthesis of crotonitenone (**3**) as an electrophilic right half segment. The aldehyde (**9a**) was transformed to a nucleophilic right half segment (**11b**) in three steps. Treatment of **9a** with 1,3-propanedithiol and BF_3–OEt_2 in

dichloromethane gave a thioacetal **9b** in 83% yield. The methylester of **9b** was reduced with lithium aluminum hydride to give **11a** in 88% yield. The alcohol group of **11a** was protected with dihydropyran to afford **11b** in 95% yield. The thioacetal (**11b**) is another good chiral synthon for a synthesis of crotonitenone (**3**). The synthesis of **3** is now under investigation in our laboratory.

Synthesis of (+)-*cis*-4-Caranone (23)

For the synthesis of lathyrols (**2**), the enantiomers of **9a** and **11b** are ideal chiral starting materials. As (−)-3-carene is very rare in nature, the effective chemical transformation of (+)-3-carene (**6**) to its enantiomer or some other derivative is required. We report here a successful route to (+)-*cis*-4-caranone (**23**) (enantiomer of (−)-(**7b**)) from (+)-3-carene (**6**).

Caran-*trans*-epoxide (**12**) was easily prepared from **6** according to the reported procedure.[12] To remove the methyl group at the C-3 position of **12** by ozonolysis, the allylic

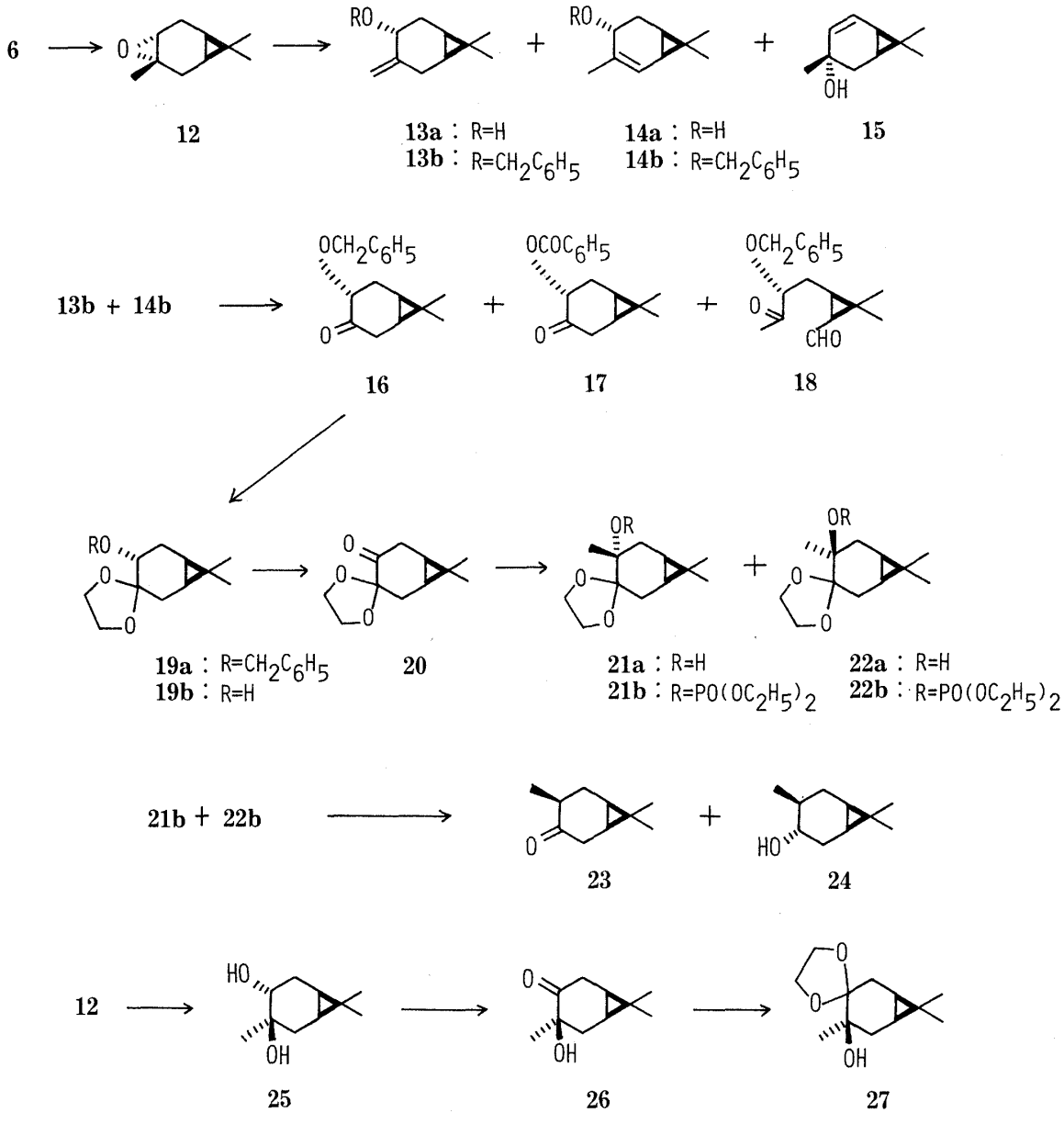

Chart 2

TABLE I. Isomerization of the Oxirane (**12**) into Allylic Alcohols (**13a**), (**14a**), and (**15**)

Reagent	Solvent	Conditions	Allylic alcohols (ratio)[a]			Total yield (%)
			13a	**14a**	**15**	
$Al(OCH(CH_3)_2)_3$	Toluene	Reflux 5.5 h	1	Trace	0	31
$Al(OCH(CH_3)_2)_3$	Heptane–pyridine	Reflux 23 h	1	Trace	0	42
$LiN(C_2H_5)_2$	Ether	Room temp. 5 h	0	1	1	70
$LiN(CH(CH_3)_2)_2$	Ether	Room temp. 1 h	2	1	3	62
$LiN(C_6H_{11})_2$	Ether	Room temp. 1.5 h	3	2	4	98
$PhN(CH_3)Al^{iso}Bu_2$	Benzene	Room temp. 2 h	8	1	0	99

a) The product ratio was determined by NMR spectroscopy.

alcohol (**13a**) was required. In the several known procedures for isomerization of oxiranes to allylic alcohols, three types of reagents were tried as shown in Table I. The method using aluminum isopropoxide[13] gave relatively pure **13a** but the yield was not satisfactory. Lithium dialkylamide[14] gave good yield but the products were an inseparable mixture of **13a**, **14a**, and **15**. Diisobutylaluminum *N*-methylanilide[15] worked well to give a quantitative yield of an inseparable mixture of **13a** and **14a** (8 : 1). The hydroxyl group in **13a** and **14a** was protected with a benzyl group[16] to give an inseparable mixture of **13b** and **14b** in quantitative yield. Ozonolysis of the mixture (**13b** and **14b**) in methanol at $-78\,^{\circ}C$ followed by treatment with dimethyl sulfide gave the desired ketone (**16**) (82% yield), **17** (5% yield) and an unstable keto-aldehyde (**18**) (5% yield). The IR spectrum of **16** shows an absorption band attributable to ketone at $1720\,cm^{-1}$. The IR spectrum of the benzoate (**17**) shows absorption bands attributable to ester and saturated ketone at 1735 and $1720\,cm^{-1}$, respectively. The ketone **16** was treated with 2-ethylenedioxybutane in the presence of a catalytic amount of *p*-toluenesulfonic acid to give **19a** and unchanged **16** in 89 and 10% yields, respectively. The benzyl group of **19a** was hydrogenolyzed with palladium on charcoal to give the desired **19b** almost quantitatively. The alcohol (**19b**) was oxidized with dimethyl sulfoxide and oxalyl chloride[9] to afford the ketone (**20**) as an oil in 96% yield. Methylation of **20** was achieved by the use of methyllithium in THF to afford an inseparable mixture of **21a** and **22a** (about 7 : 1 from gas liquid chromatography (GLC)) in 89% yield. The configuration of the methyl group at C-3 of **21a** and **22a** was determined as follows. The epoxide (**12**) was hydrolyzed with *p*-toluenesulfonic acid in aqueous acetone to give the known diol (**25**)[8b,12] in 85% yield. The secondary hydroxyl group of **25** was oxidized with dimethyl sulfoxide and oxalyl chloride to give the keto-alcohol (**26**) in 77% yield. The ketone group of **26** was protected with an ethylenedioxy group to afford **27** in 39% yield. The ^1H-NMR and ^{13}C-NMR signals of **27** were identical with those of the minor product in the mixture (**21a** and **22a**), so the methyl group at C-3 of the main product (**21a**) is *cis* with respect to the cyclopropane ring. Phosphorylation of the mixture (**21a** and **22a**) was carried out with a slight excess of *n*-butyllithium in a mixture of THF and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), followed by diethyl chlorophosphate, to afford a mixture of **21b** and **22b**. The crude phosphates were reduced with lithium in ethylamine[17] followed by treatment with ammonium chloride to give the desired (+)-*cis*-4-caranone (**23**) in 58% yield and the alcohol (**24**) in 14% yield, respectively. The total yield of (+)-**23** from the epoxide (**12**) was about 40%.

A Synthesis of Both Enantiomers of Methyl-2,2-dimethyl-3-(2-hydroxyethyl)-cyclopropane-*cis*-acetate (32b and 34b)

Chiral synthons of another type for the synthesis of the diterpenoids were examined. Ozonolysis of (+)-3-carene (**6**) gave **28**[18] in good yield. Selective reduction of the aldehyde group of **28** was achieved with lithium tri-*tert*-butoxyaluminum hydride in THF at −50 °C to give a keto-alcohol (**29a**) in 91% yield. The hydroxyl group of **29a** was protected with dihydropyran to give **29b** quantitatively. The enol silyl ether of **29b** was treated with LDA and trimethylchlorosilane to give a mixture of **30** and **31** (12 : 1 from GLC) in 98% yield. When 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was used as a base[19] in this reaction, only **31** was

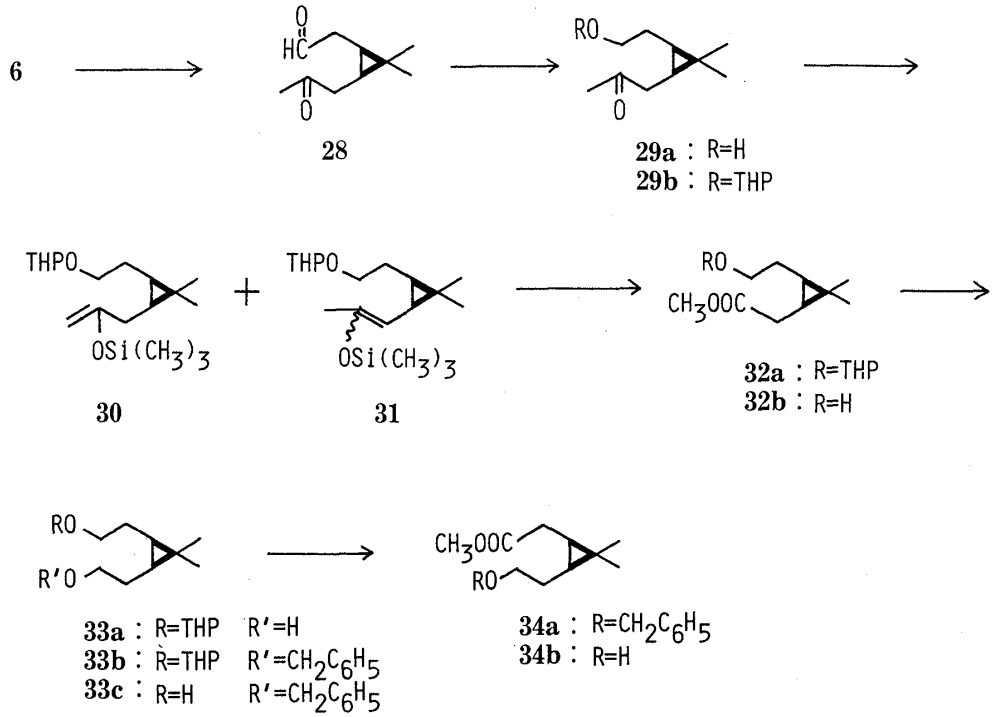

Chart 3

obtained. Ozonolysis of the mixture (**30** and **31**) in a mixture of methanol and dichloromethane at −78 °C followed by treatment with diazomethane gave the desired methylester (**32a**) in 60% yield. The tetrahydropyranyl protecting group of **32a** was hydrolyzed to give **32b** in 96% yield. The alcohol (**32b**) exhibited a positive specific rotation, $[\alpha]_D$ +6.2°. The enantiomer of **32b** was synthesized from **32a** in five steps as follows. Reduction of **32a** with $LiAlH_4$ at 0 °C gave a 98% yield of **33a**, which was protected with a benzyl group to give **33b** in quantitative yield. The tetrahydropyranyl group of **33b** was hydrolyzed to give the alcohol (**33c**) in 92% yield. The alcohol group was oxidized with pyridinium dichromate (PDC)[20] followed by treatment with diazomethane to give the desired methyl ester (**34a**) in 50% yield. The benzyl group of **34a** was hydrogenolyzed with palladium on charcoal to give **34b**, which exhibited a negative specific rotation, $[\alpha]_D$ −6.48°, in 98% yield as an oil.

Both (+)-**32b** and its enantiomer (−)-**34b** are also good chiral starting materials for the synthesis of diterpenoids such as **1**—**4** and the syntheses are currently being studied.

Experimental

All melting points and boiling points are uncorrected. A Shibata GTO-250 glass tube oven was used for bulb-to-bulb distillation, and boiling points are given as the temperature of the heating bath. A JASCO DIP-SL automatic

polarimeter was used for specific rotations. IR spectra were measured in KBr disks or directly on a NaCl plate with a Hitachi 215 spectrometer. Ultraviolet (UV) spectra were measured with a Hitachi 200 spectrometer. NMR spectra were measured in $CDCl_3$ solution with a JEOL JNM-FX-100 pulse Fourier-transform spectrometer (100 MHz) using Me_4Si as an internal standard. Electron impact and in-beam mass spectra (EI-MS and IB-MS) were obtained on a Hitachi M-80 double focusing spectrometer at 70 eV by direct insertion. Wako silica gel C-200 (200 mesh) containing 2% fluorescence reagent 254 was used in column chromatography.

***cis*-Caran-*trans*-4-ol (7a)**——Diborane (22.5 ml; 1 M solution in ether) was added dropwise to a solution of (+)-3-carene (**6**) (4.08 g) in dry THF (25 ml) with stirring at 0 °C under an N_2 atmosphere. The reaction mixture was stirred at 0 °C until **6** could not be detected by GLC. Water (10 ml), 3 N NaOH (6 ml) and 35% H_2O_2 (6 ml) were added to the reaction mixture and the whole was stirred at 40 °C for 1 h. The mixture was saturated with NaCl and extracted twice with ether, then the combined organic layer was washed with sat. brine, dried (Na_2SO_4) and concentrated. The residue was distilled, bp 87 °C (7 mmHg), to give 3.08 g (67%) of **7a** as a colorless oil. IR cm^{-1}: 3350 (OH). NMR δ: 0.92 (3H, d, $J=7$ Hz, 3-CH_3), 0.90, 0.96 (each 3H, s, CH_3), 3.05 (1H, ddd, $J=10$, 9, 7 Hz, 4-H).

(−)-*cis*-4-Caranone (7b)[8]——A solution of dimethyl sulfoxide (4.25 ml) in 10 ml of CH_2Cl_2 was added dropwise to a stirred solution of oxalyl chloride (2.5 ml) in 40 ml of CH_2Cl_2 at −50 °C. The mixture was stirred at −50 °C for 2 min, then **7a** (3.08 g in 15 ml of CH_2Cl_2) was added over a period of 5 min and stirring was continued for 15 min. Triethylamine (14 ml) was added, and after 5 min the reaction mixture was allowed to warm to room temperature. Water (80 ml) was added and the whole was extracted twice with CH_2Cl_2. The combined organic layer was washed with sat. brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography followed by distillation, bp 116 °C (30 mmHg), to give 2.64 g (87%) of **7b** as a colorless oil. IR cm^{-1}: 1710 (CO). NMR δ: 0.84, 1.04 (each 3H, s, CH_3), 0.94 (3H, d, $J=6$ Hz, 3-CH_3). $[\alpha]_D$ −164.0° ($CHCl_3$, $c=4.80$).

The Trimethylsilyl Enol Ether (8)——A solution of **7b** (760 mg) in THF (2 ml) was added dropwise to a solution of LDA in THF [prepared from diisopropylamine (0.84 ml) and *n*-BuLi (1.5 M in hexane; 4 ml) in THF (10 ml) at 0 °C] at −78 °C. The reaction mixture was stirred at −78 °C for 30 min, then trimethylchlorosilane (1.27 ml) was added. The whole was allowed to warm to −10 °C, then diluted with hexane and washed with cold aq. $NaHCO_3$. The hexane solution was dried (Na_2SO_4) and evaporated, and the residue was distilled, bp 81 °C (3 mmHg), to afford 1.044 g (93%) of **8** as a colorless oil. IR cm^{-1}: 1645 (C=C). NMR δ: 0.20 (9H, s, $Si(CH_3)_3$), 0.88 (3H, d, $J=7$ Hz, 3-CH_3), 0.92, 1.04 (each 3H, s, CH_3), 4.76 (1H, m, $W/2=8$ Hz, 5-H). MS *m/z* (% Rel. int.): 224 (M^+, 24), 209 ($M-CH_3$, 36), 73 (100).

Ozonolysis of the Silyl Enol Ether (8)——A solution of **8** (1.12 g) in a mixture of dry MeOH (16 ml) and dry CH_2Cl_2 (4 ml) was treated with ozone at −78 °C until **8** could not be detected by GLC. Dimethyl sulfide (1.42 ml) was added and the mixture was stirred at −10 °C for 1 h, at 0 °C for 1 h, and at room temperature for 1 h. The solvent was evaporated off and the residue was dissolved with ether. This solution was extracted twice with 10 ml of 10% NaOH. The organic layer was washed with sat. brine and after usual work-up gave 157 mg (19%) of **10** as a colorless oil. The alkaline extracts were combined and acidified with 10% HCl, and the solution was extracted with ether. The ether layer was washed with sat. brine and evaporated. The residue was dissolved with 10 ml of ether and treated with a slight excess of diazomethane in ether at 0 °C. Evaporation of the ether gave a residue, which was chromatographed on silica gel and distilled, bp 104 °C (2 mmHg), to give 552 mg (56%) of **9a** as a colorless oil.

Methyl Ester (**9a**): $[\alpha]_D$ −71.56° ($CHCl_3$, $c=3.88$). High-resolution MS: Mol. Wt. 198.1254 for $C_{11}H_{18}O_3$: Observed *m/z* 198.1243. IR cm^{-1}: 2730 (aldehyde), 1735, 1690 (CO). NMR δ: 1.20, 1.32 (each 3H, s, CH_3), 1.21 (3H, d, $J=7$ Hz, CH_3), 1.99 (2H, m, $W/2=20$ Hz, $-CH_2-$), 2.47 (1H, sextet, $J=7$ Hz), 3.68 (3H, s, $COOCH_3$), 9.43 (1H, d, $J=6$ Hz, aldehyde-H). MS *m/z* (% Rel. int.): 198 (M^+, 2), 169 ($[M-CHO]^+$, 14), 138 (47), 109 (100).

Ketol (**10**): High-resolution MS: Mol. Wt. 168.1149 for $C_{10}H_{16}O_2$: Observed *m/z* 168.1147. IR cm^{-1}: 3450 (OH), 1710 (CO). NMR δ: 1.10 (3H, d, $J=7$ Hz, 3-CH_3), 1.12, 1.20 (each 3H, s, CH_3), 3.78 (1H, br d, $J=6$ Hz, 5-H). MS *m/z* (% Rel. int.): 168 (M^+, 42), 125 (13), 100 (98), 82 (100).

2,2-Dimethyl-3-(2-methyl-2-methoxycarbonylethyl)-*cis*-cyclopropane-carbaldehyde 1,3-Dithiopropane Acetal (9b)——A solution of the aldehyde (**9a**) (764 mg) in 10 ml of dry CH_2Cl_2 and 1,3-propanedithiol (1.89 ml) was cooled to −20 °C and 1 drop of BF_3–OEt_2 was added. The solution was stirred at −20 °C for 5 min then allowed to warm to room temperature, and stirring was continued for another 10 min. The reaction mixture was diluted with ether and washed successively with sat. $NaHCO_3$, 5% aq. KOH, and sat. brine. The ether layer was dried and evaporated to give a residue, which was purified by silica gel column chromatography followed by distillation, bp 137—143 °C (2 mmHg), to give 900 mg (83%) of the thioacetal (**9b**) as a colorless oil. $[\alpha]_D$ −40.4° ($CHCl_3$, $c=5.69$). High-resolution MS: Mol. Wt. 288.1216 for $C_{14}H_{24}O_2S_2$: Observed *m/z* 288.1239. IR cm^{-1}: 1735 (CO). NMR δ: 1.06, 1.07 (each 3H, s, CH_3), 1.19 (3H, d, $J=7$ Hz, CH_3), 2.80 (4H, m, $W/2=8$ Hz), 3.68 (3H, s, $COOCH_3$). MS *m/z* (% Rel. int.): 288 (M^+, 56), 245 ($[M-C_3H_7]^+$, 11), 213 (28), 182 (37), 147 (55), 119 (100).

2,2-Dimethyl-3-(3-hydroxy-2-methylpropyl)-*cis*-cyclopropane-carbaldehyde 1,3-Dithiopropane Acetal (11a)——$LiAlH_4$ (10 mg) was added to a solution of **9b** (70 mg) in dry ether (2 ml) at 0 °C. The reaction mixture was stirred for 15 min, then quenched with sat. NH_4Cl and treated in the usual way to give a product, which was distilled, bp 174 °C (2 mmHg), to provide 55 mg (88%) of **11a** as a colorless oil. $[\alpha]_D$ −21.15° ($CHCl_3$, $c=3.41$). High-resolution MS: Mol. Wt. 260.1268 for $C_{13}H_{24}OS_2$: Observed *m/z* 260.1301. IR cm^{-1}: 3400 (OH). NMR δ: 0.96 (3H, d, $J=7$ Hz,

CH_3), 1.04, 1.08 (each 3H, s, CH_3), 2.80 (4H, m, $W/2=8$ Hz), 3.52 (2H, m, $W/2=20$ Hz, $-C\underline{H}_2OH$), 3.71 (1H, d, $J=10$ Hz). MS *m/z* (% Rel. int.): 260 (M^+, 45), 217 ($[M-C_3H_7]^+$, 9), 175 (25), 147 (52), 119 (100).

2,2-Dimethyl-3-(3-tetrahydropyranyloxy-2-methylpropyl)-*cis*-cyclopropane-carbaldehyde 1,3-Dithiopropane Acetal (11b)——Pyridinium *p*-toluenesulfonate (PPTS, 45 mg) was added to a solution of **11a** (260 mg) and dihydropyran (255 mg) in dry CH_2Cl_2 (10 ml) and this reaction mixture was stirred at room temperature for 2 h. The mixture was diluted with ether, washed with half-saturated brine and then dried and concentrated. The residue was purified by silica gel column chromatography and distillation, bp 157 °C (3 mmHg), to give 328 mg (95%) of **11b** as a colorless oil. High-resolution MS: Mol. Wt. 344.1842 for $C_{18}H_{32}O_2S_2$: Observed *m/z* 344.1867. NMR δ: 0.96 (3H, dd, $J=7$, 2 Hz, CH_3), 1.04, 1.08 (each 3H, s, CH_3), 2.80 (4H, m, $W/2=8$ Hz, S–$C\underline{H}_2$–), 4.55 (1H, br s). MS *m/z* (% Rel. int.): 344 (M^+, 4), 259 (9), 217 (4), 119 (25), 85 (100).

Allylic Alcohols (13a, 14a, and 15)——a) A solution of **12** (304 mg) and aluminum isopropoxide (490 mg) in 4 ml of toluene was refluxed for 5.5 h. The reaction was quenched by adding 5 ml of 1 N HCl and the whole was extracted with ether. The organic layer was washed with sat. brine, dried and evaporated. The product was purified by silica gel column chromatography to give 95 mg (31%) of a mixture of **13a** with a trace of **14a** as a semisolid.

13a: IR cm^{-1}: 3400 (OH), 1640 (C=C). NMR δ: 0.88, 1.00 (each 3H, CH_3), 4.07 (1H, t, $J=4$ Hz, 3-H), 4.77 (2H, m, $W/2=8$ Hz, vinyl-H).

b) A solution of **12** (304 mg) and aluminum isopropoxide (490 mg) in 4 ml of heptane and pyridine (0.19 ml) was refluxed for 23 h. The same work-up as above gave 129 mg (42%) of a mixture of **13a** with a trace of **14a**.

c) The epoxide (**12**) (304 mg) was added to a solution of lithium diethylamide (5.25 mmol) in 10 ml of ether at 0 °C and the reaction mixture was stirred at room temperature for 5 h. The same work-up as described in a) gave 212 mg (70%) of a 1 : 1 mixture of **14a** and **15**. **14a**: NMR δ: 1.78 (3H, s, 3-CH_3), 3.70 (1H, t, $J=4$ Hz, 4-H), 5.53 (1H, br s, 2-H). **15**: NMR δ: 5.79 (2H, s, 4, 5-H).

d) The epoxide (**12**) (304 mg) was added to a solution of lithium diisopropylamide (5.25 mmol) in 10 ml of ether at 0 °C and the reaction mixture was stirred at room temperature for 1 h. The same work-up as described in a) gave 188 mg (62%) of a mixture of **13a**, **14a**, and **15** in a ratio of 2 : 1 : 3.

e) The same reaction was tried with lithium dicyclohexylamide at room temperature for 1.5 h to give 98% yield of a mixture of **13a**, **14a**, and **15** in a ratio of 3 : 2 : 4.

f) *N*-Methylaniline (6 mmol) was added dropwise with stirring to a solution of diisobutylaluminum hydride (6 mmol) in dry benzene (14 ml) at 0 °C. The solution was stirred at room temperature until evolution of H_2 gas ceased and then recooled to 0 °C. A solution of **12** (456 mg) in 6 ml of dry benzene was added dropwise with stirring to the aluminum amide solution at 0 °C, and then the reaction mixture was stirred at room temperature for 2 h. The mixture was diluted with ether and quenched with ice-cold 1% aq. HCl. The organic layer was separated and washed with sat. brine, then dried and evaporated to give an oily product, which was distilled, bp 74—76 °C (3 mmHg), to give 455 mg (99%) of a mixture of **13a** and **14a** in a ratio of 8 : 1 as a semisolid.

Benzylation of the Alcohols 13a and 14a——Sodium hydride (1.11 g; 50% in mineral oil) was added to a solution of 2.13 g of the mixture of **13a** and **14a** (8 : 1) in dry THF (50 ml) with stirring at room temperature, and the mixture was stirred for 1 h. Tetra-*n*-butylammonium iodide (53 mg) and benzyl bromide (3.33 ml) were added to the solution and the mixture was stirred at room temperature for 9 h, then quenched by adding half-saturated NH_4Cl. The whole was extracted with ether and the organic layer was washed with sat. brine. The solvent was dried and concentrated to give a residue, which was purified by silica gel column chromatography to afford 3.38 g (99%) of an inseparable mixture of **13b** and **14b** as a colorless oil. **13b**: High-resolution MS: Mol. Wt. 242.1669 for $C_{17}H_{22}O$; Observed *m/z* 242.1670. IR cm^{-1}: 1650 (C=C). NMR δ: 0.88, 0.98 (each 3H, s, CH_3), 3.68 (1H, t, $J=4$ Hz, 4-H), 4.24, 4.50 (each 1H, d, $J=12$ Hz, Ph$C\underline{H}_2$), 4.76, 4.88 (each 1H, m, $W/2=5$ Hz, olefin-H), 7.28 (5H, s, aromatic-H). MS *m/z* (% Rel. int.): 242 (M^+, 0.5) 175 (2.5), 151 (7), 134 (8), 91 (100).

Ozonolysis of the Mixture of 13b and 14b——Ozone was passed into a solution of the mixture of **13b** and **14b** (2.32 g) in 70 ml of MeOH at −78 °C until no starting material was detectable. Dimethyl sulfide (3.4 ml) was added to the solution and the mixture was stirred at −10 °C for 1 h. The solvent was evaporated off, and the residue was extracted with ether, washed with sat. brine, dried (Na_2SO_4) and concentrated. The residue was chromatographed on a silica gel column to afford **16** (1.92 g; 82%), **17** (125 mg; 5%), and **18** (135 mg; 5%). **16**: Colorless oil, bp 126 °C (2 mmHg). IR cm^{-1}: 1720 (CO). NMR δ: 0.84, 1.04 (each 3H, s, CH_3), 3.46 (1H, t, $J=3$ Hz), 4.40, 4.49 (each 1H, d, $J=12$ Hz, Ph$C\underline{H}_2$), 7.29 (5H, s, aromatic-H). MS *m/z* (% Rel. int.): 138 ($[M-C_7H_6O]^+$, 31), 170 (17), 91 (100). **17** Oil, High-resolution MS: Mol. Wt. 258.1254 for $C_{16}H_{18}O_3$: Observed *m/z* 258.1254. IR cm^{-1}: 1735, 1720 (CO). NMR δ: 1.02, 1.08 (each 3H, s, CH_3), 4.95 (1H, t, $J=4$ Hz), 7.48 (3H, m, aromatic-H), 8.01 (2H, m, aromatic-H). MS *m/z* (% Rel. int.): 258 (M^+, 1), 136 (25), 121 (17), 105 (100). **18**: Colorless oil, IR cm^{-1}: 1710, 1690 (CO). NMR δ: 1.14, 1.24 (each 3H, s, CH_3), 2.18 (3H, s, $COCH_3$), 3.76 (1H, t, $J=6$ Hz), 4.40, 4.58 (each 1H, d, $J=12$ Hz, Ph$C\underline{H}_2$), 7.28 (5H, s, aromatic-H), 9.50 (1H, d, $J=4$ Hz, aldehyde-H). MS *m/z* (% Rel. int.): 231 ($[M-C_2H_3O]^+$, 3), 123 (4), 91 (100).

Ketalization of 16——A solution of **16** (1.71 g) and *p*-TsOH (666 mg) in 2-ethylenedioxybutane (100 ml; 80% in benzene) was stirred at room temperature for 40 h. The reaction mixture was diluted with ether, washed with sat. brine, dried (Na_2SO_4) and concentrated. The residue was chromatographed on a silica gel column to afford 1.81 g (89%) of **19a** as a colorless oil and 170 mg (10%) of recovered **16**. High-resolution MS: Mol. Wt. 288.1723 for

$C_{18}H_{24}O_3$: Observed *m/z* 288.1710. NMR δ: 0.91, 0.96 (each 3H, s, CH_3), 3.24 (1H, t, $J=8$ Hz), 3.98 (4H, m, $W/2=16$ Hz, OCH_2CH_2O), 4.58, 4.64 (each 1H, d, $J=12$ Hz, $PhCH_2$), 7.26 (5H, s, aromatic-H). MS *m/z* (% Rel. int.): 288 (M^+, 42), 197 (34), 167 (63), 153 (44), 91 (100).

Hydrogenolysis of the Benzyl Ether (19a)——A mixture of **19a** (816 mg) and 10% Pd–C (160 mg) in 15 ml of EtOH was stirred under H_2 for 2.5 h. The Pd–C was filtered off and the filtrate was concentrated to give a residue, which was distilled, bp 113 °C (2 mmHg), to afford 559 mg (99%) of **19b** as a colorless oil. *Anal.* Calcd for $C_{11}H_{18}O_3$: C, 66.67; H, 9.09; Mol. Wt. 198.1254. Found: C 66.57; H, 8.33; M^+ 198.1237. IR cm^{-1}: 3470, 3360 (OH). NMR δ: 0.98, 1.00 (each 3H, s, CH_3), 3.50 (1H, dd, $J=9$, 7 Hz), 4.00 (4H, m, $W/2=7$ Hz, OCH_2CH_2O). MS *m/z* (% Rel. int.): 198 (M^+, 42), 167 (60), 153 (60), 115 (39), 102 (100).

Oxidation of the Alcohol (19b)——A solution of dimethyl sulfoxide (0.83 ml) in 2 ml of CH_2Cl_2 was added dropwise to a stirred mixture of oxalyl chloride (0.51 ml) in 15 ml of CH_2Cl_2 at −50 °C. The mixture was stirred for 2 min and a solution of **19b** (772 mg) in 5 ml of CH_2Cl_2 was added within 5 min. The reaction mixture was stirred at −50 °C for 15 min, then triethylamine (2.73 ml) was added. The reaction mixture was stirred for 5 min then allowed to warm to room temperature. Water (20 ml) was added and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with sat. brine, dried an concentrated. The residue was purified by silica gel column chromatography followed by distillation, bp 105 °C (3 mmHg), to give 736 mg (96%) of **20** as a colorless oil. High-resolution MS: Mol. Wt. 196.1098 for $C_{11}H_{16}O_3$: Observed *m/z* 196.1096. IR cm^{-1}: 1735 (CO). NMR δ: 0.89, 1.04 (each 3H, s, CH_3), 4.04 (4H, m, $W/2=10$ Hz, OCH_2CH_2O). MS *m/z* (% Rel. int.): 196 (M^+, 5), 168 (9), 153 (7), 99 (5), 86 (100).

Methylation of the Ketone (20) with MeLi——A solution of **20** (192 mg) in THF (4 ml) was added dropwise to a solution of 2.63 ml of MeLi (1.64 M in ether) in 5 ml of THF at 0 °C, and the reaction mixture was stirred for 5 min, then diluted with ether and quenched with half-saturated NH_4Cl. The whole was extracted with ether and the extract was washed with sat. brine, dried, and concentrated. The residue was purified by silica gel column chromatography followed by distillation, bp 155 °C (3 mmHg), to afford 167 mg (89%) of a mixture of **21a** and **22a** (about 7 : 1 by GLC) as a colorless oil. **21a**: High-resolution MS: Mol. Wt. 212.1411 for $C_{12}H_{20}O_3$: Observed *m/z* 212.1413. IR cm^{-1}: 3475 (OH). NMR δ: 1.00, 1.06 (each 3H, s, CH_3), 1.10 (3H, s, CH_3), 3.92 (4H, m, $W/2=24$ Hz, OCH_2CH_2O). MS *m/z* (% Rel. int.): 212 (M^+, 36), 197 (3), 167 (100), 153 (50), 116 (37). ^{13}C-NMR δ: 14.42, 16.91, 18.76, 21.39, 22.42, 28.85, 29.34, 31.53, 64.81, 65.01, 72.46, 110.52.

(+)-*cis*-4-Caranone (23)——A solution of the mixture of **21a** and **22a** (318 mg) in 2 ml of THF and 0.5 ml of TMEDA was treated dropwise with 1.5 ml of *n*-BuLi (1.50 M in hexane), with stirring at 0 °C. After 30 min, diethyl chlorophosphate (0.434 ml) was added dropwise to the mixture at 0 °C with stirring. The whole was stirred at room temperature for 2 h, then diluted with ether, washed with sat. brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography to afford the crude phosphates **21b** and **22b** (IR cm^{-1}: 1260 (P=O), 1020 (POC), MS *m/z*: 348 (M^+)). A solution of the crude phosphates (**21b**, **22b**) and *tert*-BuOH (0.55 ml) in THF (6 ml) was added dropwise with stirring to an ice-cold, argon-protected solution of lithium (210 mg) in dry ethylamine (25 ml). After 30 min, the reaction mixture was quenched with NH_4Cl and the $EtNH_2$ was evaporated off. The residue was extracted with ether and the extract was washed with sat. brine, dried and concentrated. The residue was separated by silica gel column chromatography to afford 133 mg (58%) of **23** and 32 mg (14%) of **24**. **23**: Colorless oil, $[\alpha]_D$ +164.1° ($CHCl_3$, $c=4.56$). The IR and NMR spectra of **23** were superimposable upon those of **7b**. **24**: Colorless oil. The IR and NMR spectra of **24** were superimposable upon those of **7a**.

3β,4α-Dihydroxycarane (25)——A mixture of the epoxide (**12**) (1.52 g) and *p*-TsOH (60 mg) in 4 ml of acetone and 3 ml of water was stirred at room temperature for 3 h. Sat. $NaHCO_3$ was added to the reaction mixture and the whole was extracted with ether. After the usual work-up, the crude product was recrystallized from AcOEt–hexane to give 1.44 g (85%) of **25** as colorless prisms, mp 62—63 °C. High-resolution MS: Mol. Wt. 170.1306 for $C_{10}H_{18}O_2$: Observed *m/z* 170.1316. IR cm^{-1}: 3525, 3390, 3220 (OH). NMR δ: 0.69 (2H, m, cyclopropane ring-H), 0.96, 0.98 (each 3H, s, CH_3), 1.19 (3H, d, $J=0.5$ Hz, 3-CH_3), 3.34 (1H, dd, $J=10$, 7 Hz, 4-H).

3β-Hydroxy-4-caranone (26)——A solution of dimethyl sulfoxide (0.32 ml) in 1 ml of CH_2Cl_2 was added dropwise to a stirred solution of oxalyl chloride (0.262 ml) in 4 ml of CH_2Cl_2 at −60 °C. The mixture was stirred at −50 °C for 2 min, then a solution of **25** (340 mg) in 1.5 ml of CH_2Cl_2 and 0.5 ml of dimethyl sulfoxide was added over a period of 5 min and stirring was continued for 15 min. Triethylamine (1.4 ml) was then added and after 5 min, the reaction mixture was allowed to warm to room temperature. The same work-up as described for **7b** gave 258 mg (77%) of **26** as a colorless oil, bp 82 °C (2 mmHg). High-resolution MS: Mol. Wt. 168.1149 for $C_{10}H_{16}O_2$: Observed *m/z* 168.1156. IR cm^{-1}: 3500 (OH), 1715 (CO). NMR δ: 0.83, 1.05 (each 3H, s, CH_3), 1.49 (3H, d, $J=0.5$ Hz, 3-CH_3). MS *m/z* (% Rel. int.): 168 (M^+, 7), 150 (5), 125 (14), 43 (100).

4,4-Ethylenedioxy-3β-hydroxycarane (27)——A solution of **26** (145 mg) and *p*-TsOH (33 mg) in 2-ethylenedioxybutane (9 ml; 80% in benzene) was stirred at room temperature for 6 d. The same work-up as described for **19a** gave 72 mg (39%) of **27** as a colorless oil and 86 mg (59%) of **26**. **27**: bp 108 °C (2 mmHg). High-resolution MS: Mol. Wt. 212.1411 for $C_{12}H_{20}O_3$: Observed *m/z* 212.1387. IR cm^{-1}: 3450 (OH). NMR δ: 0.97, 1.10 (each 3H, s, CH_3), 1.32 (3H, d, $J=0.5$ Hz, 3-CH_3), 3.92 (4H, m, OCH_2CH_2O). ^{13}C-NMR δ: 14.52, 19.05, 20.08, 20.66, 21.88, 28.80, 30.16, 32.84, 64.86, 65.35, 72.90, 111.06. MS *m/z* (% Rel. int.): 212 (M^+, 36), 197 (3), 167 (100), 139 (15), 116

(25).

2,2-Dimethyl-3-(2-hydroxyethyl)-1-(2-oxopropyl)-*cis*-cyclopropane (29a)——Lithium tri-*tert*-butoxyaluminum hydride (1.40 g) was added to a solution of **28** (840 mg) in dry THF at −50 °C with stirring, and stirring was continued at that temperature for 2 h. The reaction mixture was quenched with sat. NH_4Cl. The usual work-up and purification by silica gel column chromatography gave 772 mg (91%) of **29a** as a colorless oil, bp 97 °C (2.5 mmHg). High-resolution MS: Mol. Wt. 170.1305 for $C_{10}H_{18}O_2$: Observed *m/z* 170.1298. IR cm^{-1}: 3400 (OH), 1700 (CO). NMR δ: 0.92, 1.08 (each 3H, s, CH_3), 1.48 (2H, m, $W/2=16$ Hz, $C\underline{H}_2CH_2OH$), 2.18 (3H, s, $COCH_3$), 2.39 (1H, d, $J=6$ Hz, $C\underline{H}_2COCH_3$), 3.62 (2H, t, $J=6$ Hz, $C\underline{H}_2OH$). MS *m/z* (% Re. int.): 170 (M^+, 0.6), 126 (13), 113 (41), 43 (100).

2,2-Dimethyl-3-(2-tetrahydropyranyloxyethyl)-1-(2-oxopropyl)-*cis*-cyclopropane (29b)——Pyridinium *p*-toluenesulfonate (PPTS) (208 mg) was added to a solution of **29a** (1.59 g) and dihydropyran (2.36 g) in dry CH_2Cl_2 (40 ml), and the reaction mixture was stirred overnight at room temperature. The mixture was then diluted with ether, washed with half-saturated brine, dried and concentrated. The residue was purified by silica gel column chromatography followed by distillation, bp 110 °C (3 mmHg), to afford 2.4 g (99%) of **29b** as a colorless oil. IR cm^{-1}: 1720 (CO). NMR δ: 0.92, 1.08 (each 3H, s, CH_3), 2.16 (3H, s, $COCH_3$), 2.36 (2H, d, $J=7$ Hz, $C\underline{H}_2COCH_3$), 3.42 (2H, m, $W/2=20$ Hz), 3.68 (2H, m, $W/2=28$ Hz), 4.56 (1H, br s). MS *m/z* (% Rel. int.): 254 (M^+, 0.08), 239 (0.3), 169 (6), 85 (100).

Trimethylsilyl Enol Ether (30) and (31)——a) Chlorotrimethylsilane (1.44 ml) was added to a solution of **29a** (640 mg) and DBU (1.35 ml) in dry CH_2Cl_2 (8 ml) at 40 °C with stirring. The reaction mixture was stirred at 40 °C for 6.5 h, then diluted with ether. The whole was washed successively with cold 1% HCl, cold sat. $NaHCO_3$ and brine, then dried and concentrated. The residue was distilled, bp 113 °C (3 mmHg), to give 770 mg (94%) of **31** as a colorless oil. IR cm^{-1}: 1665 (C=C), 1120 (Si–O). NMR δ: 0.20 (9H, s, $Si(CH_3)_3$, 0.94, 1.07 (each 3H, s, CH_3), 1.78 (3H, br s, vinyl-CH_3), 4.20 (1H, br d, $J=9$ Hz, olefin-H), 4.56 (1H, br s).

b) A solution of **29a** (355 mg; 1.4 mmol) in 2 ml of dry THF was added to a solution of LDA (2.24 mmol) in dry THF (10 ml) at −78 °C, and the reaction mixture was stirred at that temperature for 30 min. Next, trimethylchlorosilane (0.35 ml) was added rapidly with stirring and the whole was allowed to warm to −10 °C, then diluted with hexane. The solution was washed successively with cold aq. $NaHCO_3$ and sat. brine, then dried and evaporated. The residue was distilled, bp 155 °C (3 mmHg), to give 450 mg (98%) of a mixture of **30** and **31** in a ratio of 12 : 1. IR cm^{-1}: 1630 (C=C), 1120 (Si–O). NMR δ: 0.21 (9H, s, $Si(CH_3)_3$), 0.94, 1.06 (each 3H, s, CH_3), 4.08, 4.14 (each 1H, br s, olefin-H), 4.57 (1H, br s).

Ozonolysis of the Mixture (30 and 31)——Ozone was passed through a solution of the trimethylsilyl enol ether (1.10 g; 12 : 1 mixture of **30** and **31**) in dry MeOH (18 ml) and CH_2Cl_2 (4.5 ml) at −78 °C until the silyl enol ether could no longer be detected. Dimethyl sulfide (1.21 ml) was added and the solution was stirred at −10 °C for 1 h, then at 0 °C for 1 h and finally at room temperature for 1 h. The solvent was evaporated off and the residue was dissolved with ether. The ether layer was extracted twice with 10% aq. NaOH (8 ml). The extract was acidified with 10% HCl at 0 °C and then extracted with ether. The ether layer was washed with sat. brine, dried and evaporated. The residue was dissolved with ether and treated with a slight excess of CH_2N_2. Evaporation of the solvent gave a residue, which was purified by distillation, bp 155 °C (3 mmHg), to give 547 mg (60%) of **32a** as a colorless oil. *Anal.* Calcd for $C_{15}H_{26}O_4$: C, 66.67; H, 9.63. Found: C, 66.15; H, 9.49. IR cm^{-1}: 1740 (CO). NMR δ: 0.94, 1.07 (each 3H, s, CH_3), 2.28 (2H, d, $J=7$ Hz, $C\underline{H}_2COOCH_3$), 3.68 (3H, s, $COOCH_3$), 4.56 (1H, br s). MS *m/z* (% Rel. int.): 186 ($[M-C_5H_8O]^+$, 7), 85 (100).

(+)-Methyl-2,2-dimethyl-3-(2-hydroxyethyl)-cyclopropane-*cis*-1-acetate (32b)——A solution of **32a** (201 mg) and PPTS (19 mg) in EtOH (7 ml) was warmed at 50 °C for 2 h. The solvent was evaporated off and the residue was extracted with ether, washed with half-saturated brine, dried and concentrated. The residue was purified by silica gel column chromatography and distillation, bp 117 °C (3 mmHg), to afford 134 mg (96%) of **32b** as a colorless oil. $[\alpha]_D$ +6.20° ($CHCl_3$, $c=6.45$). High-resolution MS: Mol. Wt. 186.1255 for $C_{10}H_{18}O_3$: Observed *m/z* 186.1261. IR cm^{-1}: 3400 (OH), 1735 (CO). NMR δ: 0.93, 1.07 (each 3H, s, CH_3), 1.52 (2H, dq, $J=7$, 2 Hz, $C\underline{H}_2CH_2OH$), 2.30 (2H, dd, $J=7$, 1.4 Hz, $C\underline{H}_2COOCH_3$), 3.64 (2H, t, $J=7$ Hz, $C\underline{H}_2OH$), 3.68 (3H, s, $COOCH_3$). MS *m/z* (% Rel. int.): 186 (M^+, 3), 168 (13), 156 (24), 109 (37), 41 (100).

2,2-Dimethyl-3-(2-tetrahydropyranyloxyethyl)-1-(2-hydroxyethyl)-*cis*-cyclopropane (33a)——$LiAlH_4$ (46 mg) was added to a solution of **32a** (328 mg) in dry ether (12 ml) at 0 °C with stirring and the reaction mixture was stirred at 0 °C for 40 min. After usual work-up, the crude product was purified by silica gel column chromatography and distillation, bp 166 °C (3 mmHg), to afford 288 mg (98%) of **33a** as a colorless oil. IR cm^{-1}: 3400 (OH). NMR δ: 0.50 (2H, m, $W/2=12$ Hz, cyclopropane-H), 0.93, 1.03 (each 3H, s, CH_3), 3.65 (2H, t, $J=7$ Hz, $C\underline{H}_2OH$), 4.57 (1H, br s). MS *m/z* (% Rel. int.): 158 ($[M-C_5H_8O]^+$, 12), 128 (4), 95 (4), 85 (100).

2,2-Dimethyl-1-(2-benzyloxyethyl)-3-(2-tetrahydropyranyloxyethyl)-*cis*-cyclopropane (33b)——The alcohol (**33a**) (328 mg) was protected with benzyl bromide in the same manner as described for **13a** and **14a** to give 443 mg (99%) of **33b** as a colorless oil. IR cm^{-1}: 1205, 1035 (COC). NMR δ: 0.50 (2H, m, $W/2=12$ Hz, cyclopropane-H), 0.93, 1.02 (each 3H, s, CH_3), 4.50 (2H, s, $C\underline{H}_2Ph$), 4.56 (1H, br s), 7.28 (5H, s, aromatic-H). MS *m/z* (% Rel. int.); 248 ($[M-C_5H_8O]^+$, 14), 157 (7), 91 (49), 85 (100).

(−)-2,2-Dimethyl-3-(2-benzyloxyethyl)-1-(2-hydroxyethyl)-*cis*-cyclopropane (33c)——A mixture of tetrahydro-

pyranyl ether (**33b**) (423 mg) and PPTS (32 mg) was treated in the same way as described for **32a** to give 289 mg (92%) of **33c**, bp 144 °C (3 mmHg), as a colorless oil. $[\alpha]_D$ −3.26° ($CHCl_3$, $c=5.5$). High-resolution MS: Mol. Wt. 248.1775 for $C_{16}H_{24}O_2$: Observed m/z 248.1774. IR cm^{-1}: 3350 (OH). NMR δ: 0.50 (2H, m, $W/2=12$ Hz, cyclopropane-H), 0.91, 1.02 (each 3H, s, CH_3), 1.54 (4H, m, $W/2=20$ Hz, $C\underline{H}_2CH_2OH$ and $C\underline{H}_2CH_2OCH_2Ph$), 3.49 (2H, t, $J=7$ Hz, $C\underline{H}_2OCH_2Ph$), 3.63 (2H, t, $J=7$ Hz, $C\underline{H}_2OH$), 4.50 (2H, s, $C\underline{H}_2Ph$), 7.28 (5H, s, aromatic-H). MS m/z (% Rel. int.): 248 (M^+, 10), 157 (19), 109 (8), 91 (100).

(+)-Methyl-2,2-dimethyl-3-(2-benzyloxyethyl)-cyclopropane-*cis*-1-acetate (34a)——A mixture of **33c** (255 mg) and pyridinium dichromate (PDC; 1.3 g) in dry dimethylformamide (DMF) (5.2 ml) was stirred at room temperature for 6 h, then diluted with ether and washed with water. The ether layer was extracted with 10% NaOH (4 ml) and the extract was acidified with 10% HCl. The solution was extracted with ether, and the extract was washed with sat. brine, dried (Na_2SO_4) and evaporated. The residue was dissolved with ether and treated with a slight excess of CH_2N_2. The reaction mixture was evaporated and the residue was purified by silica gel column chromatography followed by distillation, bp 133 °C (2 mmHg), to give 142 mg (50%) of **34a** as a colorless oil. $[\alpha]_D$ +2.95° ($CHCl_3$, $c=7.1$). High-resolution MS: Mol. Wt. 276.1724 for $C_{17}H_{24}O_3$: Observed m/z 276.1736. IR cm^{-1}: 1730 (CO). NMR δ: 0.92, 1.06 (each 3H, s, CH_3), 1.55 (2H, q, $J=7$ Hz, $C\underline{H}_2CH_2OCH_2Ph$), 2.27 (2H, d, $J=7$ Hz, $C\underline{H}_2COOCH_3$), 3.48 (2H, t, $J=7$ Hz, $C\underline{H}_2OCH_2Ph$), 3.65 (3H, s, $COOCH_3$), 4.50 (2H, s, $C\underline{H}_2Ph$), 7.28 (5H, s, aromatic-H). MS m/z (% Rel. int.): 276 (M^+, 0.2), 245 (1.4), 185 (16), 155 (2.9), 91 (100).

(−)-Methyl-2,2-dimethyl-3-(2-hydroxyethyl)-cyclopropane-*cis*-acetate (34b)——A mixture of **34a** (138 mg) and 10% Pd–C (27 mg) in EtOH (3 ml) was stirred under an H_2 atmosphere at room temperature for 1 h. The catalyst was filtered off and the filtrate was evaporated to give a residue, which was purified by silica gel column chromatography followed by distillation, bp 106 °C (2 mmHg), to give 91 mg (98%) of **34b** as a colorless oil. $[\alpha]_D$ −6.48° ($CHCl_3$, $c=3.6$). The NMR and IR spectra of (−)-**34b** were superimposable upon those of (+)-**32b**.

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