similar conclusion. X-ray crystallographic analysis of diterpenediol 1 confirmed the proposed structure. When the title compound was recrystallized from acetone, one solvent molecule was incorporated per two diterpene diol molecules (mp 76–81 °C). The X-ray analysis of the latter revealed that two molecules of compound 1 are arranged together by hydrogen bonds between both of the 7α-hydroxyl groups and both of the hydroxymethyl groups. Each time, such a dimeric entity is linked to the acetone carbonyl by one 7α-hydroxyl function (Figure 1). The structure was solved by YZARC[16] and refined by the SHELX 76 program[17] on the basis of 2918 reflections selected from 6241 measured reflections and for which $I > 2.5\ \sigma(I)$. The incident radiation was Mo Kα (λ = 0.7107 Å). The final R value was 0.139. Crystal data: $C_{20}H_{32}O_2 \cdot 0.5CH_3COCH_3$; monoclinic; space group $P2_1$; cell dimensions a = 14.167 (5) Å, b = 22.721 (14) Å, c = 12.965 (5) Å, β = 101.32 (3)°; V = 4092.1 (32) Å^3; Z = 8. Atomic coordinates and equivalent isotropic temperature factors, interatomic distances, and bond angles are included in the supplementary material. Among natural substances of the pimaradienediol, isopimaradienediol, or sandaracopimaradienediol type, the title product is the only one containing OH functions at the 7,18-positions instead of the more common 2,18-,[9] 3,18-,[10] or 3,19-diol[11] combinations. The 7-position in these types of natural products is rarely hydroxylated. Some 7α-hydroxylated 8(14),15-sandaracopimaradienes, including 8(14),15-sandaracopimaradiene-1β,7α-diol and 8(14),15-sandaracopimaradiene-7α-ol, were isolated from *Zexmenia* species.[12] Recently however, the corresponding methyl ester analogue of 1, methyl 7α-hydroxysandaracopimarate, was isolated from *Juniperus communis*[14] and was also obtained by photooxidation of methyl isopimarate.[15]

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Registry No. 1, 82190-51-0.

Supplementary Material Available: Tables containing atomic coordinates and equivalent isotropic temperature factors, interatomic distances, and bond angles (5 pages). Ordering information is given on any current masthead page.

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Palladium-Catalyzed Carbonylation of Vinyl Halides: A Route to the Synthesis of α-Methylene Lactones

Larry D. Martin and J. K. Stille*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

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α-Methylene γ-lactones were synthesized in high yields by the palladium-catalyzed carbonylation reactions of alkyl-substituted 3-bromobut-3-en-1-ols under mild conditions. The bromo alcohols were obtained by the reaction of [1-(trimethylsilyl)vinyl]magnesium bromide with various epoxides followed by conversion of the trimethylsilyl group to bromide. By starting with optically active epoxides such as (*R*)-1,2-epoxypropane or (2*R*,3*R*)-2,3-epoxybutane, the corresponding lactones could be obtained virtually optically pure. The carbonylation reaction is selective in that it generates only γ-lactones when there is a choice of two vinylic iodides or two alcohols that could lead either to the five- or six-membered rings.

Introduction

As a consequence of the wide range of biological activity, particularly the cytotoxic and antitumor activity,[1] fungitoxicity,[2] and plant growth inhibition[3] possessed by α-methylene-γ-butyrolactones, this class of compounds has been the object of considerable synthetic activity.[4] The transition metal assisted syntheses of unsaturated lactones have been developed more recently, some of the most useful transformations depending on carbonylation reactions. Many of the carbonylation reactions leading to γ-lactones are stoichiometric; the synthesis of a wide variety of butenolides, for example, requiring molar quantities of sodium tetracarbonylcobaltate[5] or dicobalt octacarbonyl,[6] although moderate turnovers have been realized with these cobalt carbonyls.[5,7] Stoichiometric or greater quantities of nickel tetracarbonyl are required to convert homopropargyl alcohols (**3**)[8] or alcoholic vinyl bromides (**1**)[9] to the corresponding α-methylene γ-lactones (**2**). More

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0022-3263/82/1947-3630$01.25/0

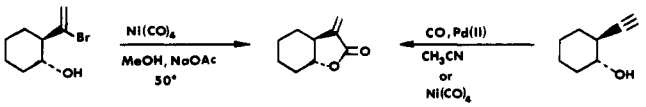
Table I. Palladium-Catalyzed Carbonylation of Halo Alcohols to α-Methylene γ-Lactones[a]

halo alcohol	$[\alpha]^{25}_D$ (c)[b]	rctn time, h	α-methylene γ-lactone (R, R')	$[\alpha]^{25}_D$ (c)[b]	% yield
1	rac	72	2	rac	72
10a	rac	96	11a (H, CH_3)	rac	58
		48			88
(R)-10a	−10.8 (7.26)	72	(R)-11a (H, CH_3)	+33.8 (5.82)	73
10b	rac	48	11b (H, C_2H_5)	rac	62
10c	rac	48			93
(S,R)-10c	+5.23 (17.45)	48	(S,R)-11c (CH_3, CH_3)	+75.7 (8.17)	85
14		24[c]	15		55

[a] Carbonylations were run at 35 psig CO, 70 °C in CH_3CN with 1 mol % $(Ph_3P)_4Pd$ (6). [b] Rotations in CH_2Cl_2. [c] 2 mol % 6.

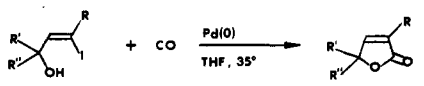
recently, the carbonylation of an E/Z mixture of 1 was carried out with large excesses of nickel carbonyl and long heating to give only moderate yields of 2.[10]

In one of the more useful and well-studied transition-metal-catalyzed lactone synthesis, α-methylene γ-lactones (2) have been obtained from the palladium-catalyzed carbonylation of homopropargyl alcohols (3).[11] Our in-



1 2 3

terest in this synthetic methodology stemmed from the fact that butenolides (5) could be prepared by the palladium-catalyzed carbonylation of iodo alcohols (4) under mild conditions in excellent yields.[12] The report[9] that vinyl



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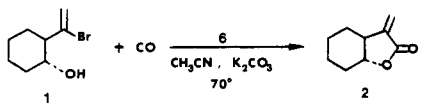
bromides such as 1 could be converted to α-methylene γ-lactones with a 6:1 ratio of nickel carbonyl to substrate, but that palladium would not catalyze this conversion, was inconsistent with our results[12] obtained in the butanolide synthesis. Thus, the palladium-catalyzed carbonylation of a series of 3-bromohomoallylic alcohols was undertaken as a synthetic route to α-methylene γ-lactones.

Results and Discussion

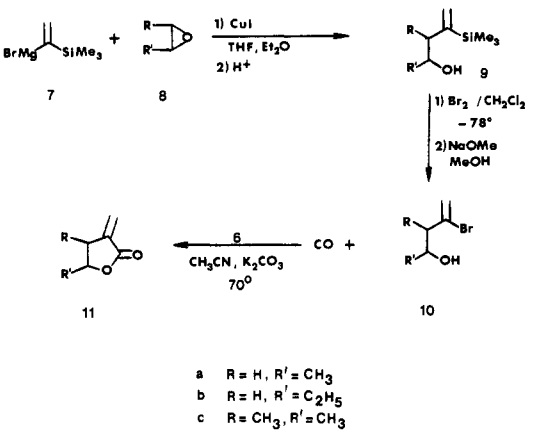
The carbonylation of the vinyl iodides to yield butenolides was successfully catalyzed by a palladium(0) species generated in situ by the reduction of dichlorobis(triphenylphosphine)palladium(II) with hydrazine.[12] By use of this procedure for the catalyst generation and the reaction conditions (THF, 25–35 °C, 1–3 atm CO, K_2CO_3) that gave high yields of butenolides, only a trace of 2-(*trans*-2-hydroxycyclohexyl)propenoic acid lactone (2) was obtained from *trans*-2-(α-bromovinyl)cyclohexanol (1). Tetrakis(triphenylphosphine)palladium(0) (6) in tetrahydrofuran at 70 °C did not catalyze the carbonylation. Of the various solvents tried, the highest yields of 2 could be obtained in acetonitrile with 6 as the catalyst (Table I).

Scheme I. Synthesis of α-Methylene γ-Lactones



1 2

Synthesis of α-Methylene γ-Lactones. The general procedure for the synthesis of 3-bromo-3-butenols utilized the reaction of epoxides (8) with the Grignard reagent (7) obtained from (α-bromovinyl)trimethylsilane[13] (Scheme I). The vinylsilanes (9) were converted to the vinyl bromides (10) by the addition of bromine followed by elimination with base.[14]



7 8 9 11 10

a R = H, R' = CH_3
b R = H, R' = C_2H_5
c R = CH_3, R' = CH_3

Carbonylation of both 4-bromo-4-penten-2-ol (**10a**) and 5-bromo-5-hexen-3-ol (**10b**), obtained by this procedure, to γ-methyl- and γ-ethyl-α-methylene γ-lactones **11a** and **11b**, respectively, also could be carried out in high yields with tetrakis(triphenylphosphine)palladium(0) (**6**) in acetonitrile (Table I). Long reaction times apparently lead to the decomposition of the lactone product, since higher yields of lactone **11a** were obtained at half of the reaction time.

Because the ring-opening reaction of the epoxide by the vinyl Grignard reagent is both regio- and stereospecific,[15] and the carbonylation reaction does not involve an asymmetric carbon, this general procedure held promise for the synthesis of a number of optically active lactones from optically active epoxides.

Thus, the synthetic sequence utilizing (*R*)-1,2-epoxypropane[16] [(*R*)-**8a**] and *trans*-(2*R*,3*R*)-2,3-epoxybutane[17]

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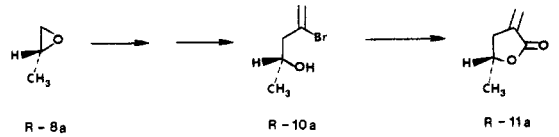
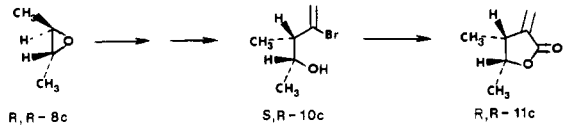
[(*R*,*R*)-8c] and Grignard reagent 7 followed by conversion of the trimethylsilyl group to bromide gave the optically active alcoholic vinyl bromides (*R*)-**10a** and (*S*,*R*)-**10c**. Carbonylation of these substrates under the standard reaction conditions provided good yields of the optically active α-methylene γ-lactones, (*R*)-**11a** and (*R*,*R*)-**11c**.

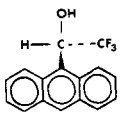


R-8a R-10a R-11a



R,R-8c S,R-10c R,R-11c

A chiral solvent, 2,2,2-trifluoro-1-(9-anthryl)ethanol (**12**)[18a] was employed to determine the enantiomeric purity of the optically active lactones by observing the effect of this shift reagent on the methyl doublet in the ^{1}H NMR spectrum of **11a**. Racemic **11a** could not be totally resolved into two doublets; however, a "triplet" was observed at a 5:1 ratio of **12** to **11a**. When the ^{1}H NMR spectrum of (*R*)-**11a** was observed in the presence of **9**, only a doublet was observed, indicating an ee ≥ 95%. This doublet corresponded to the downfield portion of the "triplet", which when interpreted by solvation model **13**[18] indicates the *R* configuration. This NMR method unfortunately could not be used for lactone **11c**. On the basis of the results obtained in the conversion of (*R*,*R*)-**8c** to lactone **11c**, however, a high optical yield would be expected.



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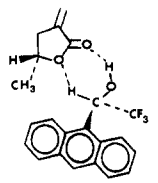

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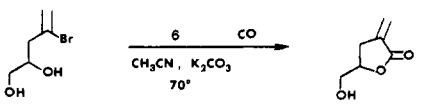
The propensity of the carbonylation reaction to generate five- rather than six-membered lactones when there is a choice available is illustrated by the carbonylation reaction of the bromo diol. The carbonylation of 4-bromo-4-pentene-1,2-diol (**14**) only generated a γ-lactone (**15**). Treatment of 3-bromo-2-methyl-3-butene-1,2-diol (**16**), however, with carbon monoxide under the standard reaction conditions failed to produce any lactone.



14 15

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Experimental Section

General Procedures. Proton NMR spectra were obtained on a Varian EM-360 and are reported in parts per million (δ) relative to Me_4Si; ^{13}C NMR spectra were obtained on a JEOL FX-100 and are reported in parts per million (δ) relative to Me_4Si. Analyses on unknown compounds were conducted by Micro-Tech Laboratories. Literature procedures were employed for the syntheses of (α-bromovinyl)trimethylsilane,[13] silyl alcohols,[9,14] bromo alcohols **1** and **10**,[14] (*R*)-1,2-epoxypropane ([α]$_D$ +12.4° (neat), lit.[12] [α]$_D$ 11.57),[16] *trans*-(2*R*,3*R*)-2,3-epoxybutane ([α]$_D$ +59.3 (neat), lit.[17] [α]$_D$ for 2*S*,3*S* enantiomer, −47.02°), and tetrakis(triphenylphosphine)palladium (**6**).[19]

Silyl Alcohols 9. The general synthetic procedure outlined in Scheme I is illustrated with 1,2-epoxypropane as the starting epoxide. To a mixture of 2.0 g (82 mmol) of magnesium in 20 mL of anhydrous THF was added 10 μL (0.16 mmol) of methyl iodide to activate the magnesium. After the mixture was stirred for 30 min at room temperature, a water bath was place around the reaction flask and 6.0 g (33.5 mmol) of (α-bromovinyl)trimethylsilane[13] was slowly added via syringe (~15 min). The reaction mixture was stirred for 1 h and then transferred, via double-tipped needle, to a −78 °C mixture of 0.1 g (0.5 mmol) of cuprous iodide in 100 mL of anhydrous ether. After the mixture had been stirred at −78 °C for 15 min, 1.945 g (33.49 mmol) of 1,2-epoxypropane (**8a**) in 2 mL of ether was added via syringe over a 15-min period. The mixture was allowed to slowly warm to room temperature overnight. The reaction was quenched with 50 mL of 1 N HCl. The organic layer was separated, and the aqueous layer was extracted 3 times with methylene chloride. The organic layers were combined and dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was distilled with a Kugelrohr apparatus to yield 2.067 g (13.05 mmol, 39.0%) of 4-(trimethylsilyl)pent-4-en-2-ol (**9a**): ^{1}H NMR (CCl_4) δ 0.13 (s, 9 H, $SiCH_3$), 1.13 (d, *J* = 6 Hz, 3 H, CH_3), 2.25 (br d, *J* = 6 Hz, 2 H, CH_2), 2.57 (s, 1 H, OH), 3.77 (sextet, *J* = 6 Hz, 1 H, CHOH), 5.45 (d, *J* = 3 Hz, 1 H, =CH), 5.65 (br m, 1 H, =CH); ^{13}C NMR ($CDCl_3$) δ −1.41 ($Si(CH_3)_3$), 22.76 (CH_3), 46.46 (CH_2C=), 65.79 (CHOH), 127.15 (CH_2=), 148.93 (C=); (*R*)-**9a** [α]$_D$ −8.4° (26.84, CH_2Cl_2). Anal. $C_8H_{18}SiO$: C, H.

***trans*-2-[1-(Trimethylsilyl)vinyl]cyclohexanol**:[9] ^{1}H NMR (CCl_4) δ 0.10 (s, 9 H, $SiCH_3$), 0.97–2.30 (v br m, 9 H, ring H's), 3.40 (br m, 2 H, CHOH), 5.38 (d, *J* = 3 Hz, 1 H, =CH), 5.60 (d, *J* = 3 Hz, 1 H, =CH).

5-(Trimethylsilyl)hex-5-en-3-ol (9b):[9] ^{1}H NMR (CCl_4) δ 0.17 (s, 9 H, $SiCH_3$), 1.03 (t, *J* = 6 Hz, 3 H, CH_3), 1.53 (pentet, *J* = 6 Hz, 2 H, CH_3CH_2), 2.50 (br d, *J* = 6 Hz, 2 H, CH_2C=), 3.50 (v br m, 2 H, CHOH), 5.52 (d, *J* = 3 Hz, 1 H, =CH), 5.68 (br m, 1 H, =CH).

4-(Trimethylsilyl)-3-methylpent-4-en-2-ol (9c). By use of the general procedure for the synthesis of **9a**, **9c** was obtained in a 37% yield: ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 9 H, $SiCH_3$), 1.05 (d, *J* = 6 Hz, 3 H, $(CHCH_3)$ 1.15 (d, *J* = 6 Hz, 3 H, CH_3CHOH), 1.80 (br s, 1 H, OH), 2.32 (br pentet, *J* = 6 Hz, 1 H, $HCC=CH_2$) 3.75 (pentet, *J* = 6 Hz, 1 H, CHOH), 5.38 (d, *J* = 2 Hz, 1 H, $C=CH_2$), 5.55 (d, *J* = 2 Hz, 1 H, $C=CH_2$); ^{13}C NMR ($CDCl_3$) δ −1.24 ($Si(CH_3)_3$), 16.05 (CH_3), 21.48 (CH_3), 45.53 ($CHC=CH_2$), 69.88 (CHOH), 124.23 ($=CH_2$), 155.53 (C=); (*S*,*R*)-**9c** [α]$_D$ +15.7° (7.25, CH_2Cl_2). Anal. $C_9H_{20}SiO$: C, H.

4-(Trimethylsilyl)pent-4-ene-1,2-diol. This compound was prepared in a 63% yield by the general procedure described for **9a**: ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 9 H, $SiCH_3$), 2.27 (br d, *J* = 6 Hz, 2 H, $=CCH_2$), 3.23–4.00, 3.37 (m, s, 5 H, CH_2OH, CHOH, OH's), 5.33 (m, 1 H, =CH), 5.55 (br m, 1 H, =CH); ^{13}C NMR ($CDCl_3$) δ −1.47 ($Si(CH_3)_3$), 39.81 (CH_2C=), 65.91 (CH_2OH), 70.58 (CHOH), 126.92 (CH_2=), 147.82 (>C=CH_2). Anal. $C_8H_{18}SiO_2$: C, H.

Conversion of Vinylsilanes (9) to Vinyl Bromides (10). The procedure using bromination followed by elimination with

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base[14] was employed with the substitution of methylene chloride for pentane as the extraction solvent.

4-Bromopent-4-en-2-ol (10a). This compound was obtained in a 68% yield: ^{1}H NMR (CCl_4) δ 1.09 (d, J = 6 Hz, 3 H, CH_3), 2.37 (br d, J = 6 Hz, 2 H, =CCH_2), 3.57 (s, 1 H, OH), 3.84 (hextet, J = 6 Hz, 1 H, CHOH), 5.27 (br s, 1 H, =CH), 5.47 (br s, 1 H, =CH); ^{13}C NMR ($CDCl_3$) δ 22.23 (CH_3), 50.73 (CH_2C=), 65.21 (CHOH), 118.98 (CH_2=), 130.36 (>C=CH_2). Anal. C_5H_9OBr: C, H, Br.

***trans*-2-(α-Bromovinyl)cyclohexanol (1):**[9] ^{1}H NMR (CCl_4) δ 1.0–2.4 (v br m, 9 H, ring H's), 3.45 (br m, 2 H, CHOH), 5.44 (br s, 1 H, =CH), 5.68 (br s, 1 H, =CH).

5-Bromohex-5-en-3-ol (10b):[9] ^{1}H NMR (CCl_4) δ 0.73 (t, J = 6 Hz, 3 H, CH_3), 1.23 (pentet, J = 6 Hz, 2 H, CH_3CH_2), 2.27 (d, J = 6 Hz, 2 H, CH_2C=), 2.37 (s, 1 H, OH), 3.57 (pentet, J = 6 Hz, 1 H, CHOH), 5.27 (br s, 1 H, HC=), 5.47 (br s, 1 H, HC=).

4-Bromo-3-methylpent-4-en-2-ol (10c). This compound was obtained in a 60% yield by using the general procedure:[13] ^{1}H NMR ($CDCl_3$) δ 1.18 (d, J = 6 Hz, 3 H, CH_3), 1.22 (d, J = 6 Hz, 3 H, CH_3), 2.17 (s, 1 H, OH), 2.35 (br, pentet, J = 6 Hz, 1 H, CHC=CH_2), 3.96 (pentet, J = 6 Hz, 1 H, CHOH), 5.47 (d, J = 2 Hz, 1 H, C=CH_2), 5.67 (d, J = 2 Hz, 1 H, C=CH_2); ^{13}C NMR ($CDCl_3$) δ 14.98 (CH_3), 21.28 (CH_3CHOH), 51.31 (CH), 69.28 (CHOH), 117.26 (H_2C=), 137.86 (BrC=); $[\alpha]_D$ +5.23° (17.45, CH_2Cl_2). Anal. $C_6H_{11}BrO$: C, H, Br.

4-Bromopent-4-ene-1,2-diol (14). This compound was obtained in a 31% yield: ^{1}H NMR ($CDCl_3$) δ 2.3 (br m, 4 H, CH_2C=, OH), 3.2–4.1 (v br m, 3 H, CH_2OH, CHOH), 5.15 (br s, 1 H, =CH), 5.35 (br s, 1 H, =CH); ^{13}C NMR ($CDCl_3$) δ 45.07 (CH_2C=), 65.39 (CH_2OH), 69.54 (CHOH), 119.57 (CH_2=), 129.44 (BrC=). Elemental analysis $C_5H_9O_2Br$: C, H, Br.

Carbonylation of Bromo Alcohols to Lactones (Table I). Samples of 19.0 mg (0.0164 mmol) of tetrakis(triphenylphosphine)palladium(0) and 350 mg (2.5 mmol) of potassium carbonate were placed in a Fischer-Porter pressure bottle containing a magnetic stirring bar. The atmosphere of the reaction vessel was exchanged for carbon monoxide by evacuation followed by pressurization to 32 psig. The process was repeated 3 times. A sample of 295.8 mg (1.792 mmol) of 4-bromopent-4-en-2-ol (**10a**) in a 5 mL of acetonitrile was added via syringe. The reaction vessel was placed into a 70 °C bath, and the pressure was maintained at 32 psig for 48–72 h. The reaction mixture was cooled to room temperature and then the pressure was released. Ether (~10 mL) was added, and the mixture was filtered through a Celite pad. The precipitate was washed twice with 10-mL portions of ether, and the solvent was removed from the combined organic fractions under reduced pressure. The crude lactone was then purified via Kugelrohr distillation, yielding 116.6 mg (1.040 mmol, 58%) of lactone **11a**:[18] ^{1}H NMR (CCl_4) δ 1.37 (d, J = 6 Hz, 3 H, CH_3), 2.40 (d of m, J^d = 17 Hz, 1 H), 3.07 (d of m, J^d = 17 Hz, 1 H, last 2 peaks, CH_2C=), 4.55 (sextet, J = 6 Hz, 1 H, CHO), 5.50 (t, J = 3 Hz, 1 H, =CH), 6.03 (t, J = 3 Hz, 1 H, =CH);[18,21] (*R*)-**11d** $[\alpha]_D$ +33.8° (5.82, CH_2Cl_2).

2-(*trans*-2-Hydroxycyclohexyl)propenoic Acid Lactone (2):[9] ^{1}H NMR (CCl_4) δ 1.0–2.6 (m, 9 H, ring H's), 3.4–3.9 (m, 1 H, CHO), 5.30 (d, J = 3 Hz, 1 H, =CH), 5.94 (d, J = 3 Hz, 1 H, =CH) (lit.[22]).

4,5-Dihydro-5-ethyl-3-methylene-2(3*H*)-furanone (11b):[9] ^{1}H NMR (CCl_4) δ 1.00 (t, J = 7 Hz, 3 H, CH_3), 1.67 (pentet, J = 7 Hz, 2 H, CH_3CH_2), 2.47 (d of m, J^d = 16 Hz, 1 H), 3.03 (d of m, J^d = 16 Hz, 1 H, last 2 peaks CH_2C=), 4.32 (pentet, J = 7 Hz, 1 H, CHO), 5.45 (t, J = 3 Hz, 1 H, C=CH), 5.93 (t, J = 3 Hz, 1 H, C=CH).

***cis*-4,5-Dihydro-4,5-dimethyl-3-methylene-2(3*H*)-furanone (11c):** ^{1}H NMR (CCl_4) δ 1.00 (d, J = 7 Hz, 3 H, CH_3), 1.10 (d, J = 7 Hz, 3 H, CH_3), 2.97 (m, 1 H, CHC=), 4.50 (pentet, J = 7 Hz, 1 H, CHO), 5.28 (d, J = 3 Hz, 1 H, C=CH), 5.97 (d, J = 3 Hz, 1 H, C=CH); ^{13}C NMR ($CDCl_3$) δ 13.48 (CH_3), 16.34 (CH_3), 37.67 (CH_3CH-C=CH_2), 77.57 (CH_3CHO), 120.98 (=CH_2), 140.65 (C=), 170.43 (C=O). (4*R*,5*R*)-**11c** $[\alpha]_D$ 7.57° (8.17, CH_2Cl_2). Anal. $C_7H_{10}O_2$: C, H.

4,5-Dihydro-5-(hydroxymethyl)-3-methylene-2(3*H*)-furanone (15): IR ν_{CO} 1760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.85–3.18 (m, 2 H, CH_2C=C), 3.52–4.25 (m, 2 H, CH_2OH), 4.52–4.98 (m, CHO), 5.75 (t, J = 2 Hz, 1 H, C=CH), 6.32 (t, J = 2 Hz, C=CH); ^{13}C NMR ($CDCl_3$) δ 28.87 (CH_2), 64.00 (CH_2OH), 77.66 (CHO), 122.41 (=CH_2), 134.41 (C=), 170.79 (C=O). Anal. $C_6H_8O_3$: C, H.

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Registry No. (±)-**1**, 78631-34-2; (±)-**2**, 61248-47-3; **6**, 14221-01-3; (±)-**8a**, 16033-71-9; (*R*)-**8a**, 15448-47-2; (±)-**8b**, 55555-96-9; (±)-**8c**, 6189-41-9; (*R*,*R*)-**8c**, 1758-32-3; (±)-**9a**, 82166-53-8; (*R*)-**9a**, 82112-54-7; (±)-**9b**, 82112-55-8; (±)-**9c**, 82166-54-9; (*S*,*R*)-**9c**, 82112-56-9; (±)-**10a**, 82112-57-0; (*R*)-**10a**, 82166-49-2; (±)-**10b**, 82112-58-1; (±)-**10c**, 82112-59-2; (*S*,*R*)-**10c**, 82166-50-5; (±)-**11a**, 82166-51-6; (*R*)-**11a**, 62322-49-0; (±)-**11b**, 82112-60-5; (±)-**11c**, 82112-61-6; (*R*,*R*)-**11c**, 82166-52-7; **14**, 82112-62-7; **15**, 82112-63-8; (α-bromovinyl)trimethylsilane, 13683-41-5; cyclohexene oxide, 286-20-4; (±)-*trans*-2-[1-(trimethylsilyl)vinyl]cyclohexanol, 82112-64-9; glycidol, 556-52-5; 4-(trimethylsilyl)pent-4-ene-1,2-diol, 82112-65-0.

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