Diastereoselective Cyclization of 6-Octen-1-als with Rhodium(I)-Complex

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In Rh(I) (Wilkinson)-catalyzed cyclization of 6-octen-1-als, the formation of cis-cyclohexanols is in contrast to Lewis acid-catalyzed cyclization, which affords predominantly the trans-cyclohexanols. However, 6-octen-1-als with a cyclic acetal (1,3-dioxane or 1,3-dioxolane) at the C_3-position were stereoselectively cyclized to only the trans-products. The aldehyde with a chiral protecting group ((4R,6R)-dimethyl-1,3-dioxane with the C_2-axis) at the C_3-position was diastereoselectively cyclized to the trans-cyclohexanol, and on a basis of the absolute stereochemistry of the cyclized product, the cyclization mechanism is tentatively proposed. The effect of 4R-methyl-1,3-dioxane at the C_3-position was also examined.

Previously, we showed that in Rh(I)(Wilkinson)-catalyzed cyclization[1] of 6-octen-1-als with methyl substituents at the C_2- or C_3-position,[2] a mixture of cis- and trans-cyclohexanol derivatives was obtained, whereas 7-methyl-6-octen-1-al without any substituent underwent decarbonylation. 4-Oxa-analogues also afforded a similar result. The formation of cis-cyclohexanols as the main product is in contrast to Lewis acid-catalyzed cyclization[3] to afford predominantly the trans-cyclohexanol.
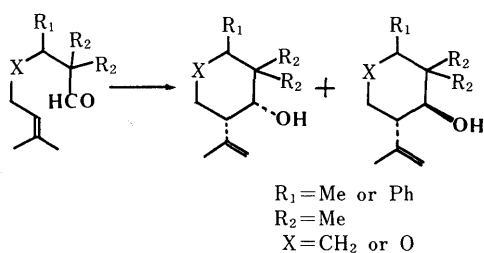

Chart 1

Now, we report on Rh(I)-catalyzed diastereoselective cyclization of 6-octen-1-als with a chiral protecting group at the C_3-position. The effect of a cyclic acetal at the C_3-position was also examined. Interestingly, the aldehyde (1a, $n=0$) with a cyclic acetal (1,3-dioxolane) at the C_3-position was stereoselectively cyclized to only the trans-alcohol (2a, $n=0$, 60%), and the cis-alcohol was not obtained at all. Similarly, the aldehyde (1b, $n=1$) with a cyclic acetal (1,3-dioxane) was also stereoselectively cyclized to the trans-alcohol (2b, $n=1$, 55%). This stereocontrolled trans-cyclization prompted us to examine cyclization of the aldehydes with a chiral protecting group. When the aldehyde (3) with (4R,6R)-dimethyl-1,3-dioxane (with the C_2 axis) at the C_3-position was heated at reflux in $CHCl_3$ in the presence of equimolar Wilkinson-complex, only one trans-alcohol (4) ($[\alpha]_D^{25}$ − 19.79° ($c=1.02$, EtOH)) was obtained in 60% yield, similarly to the case of 1. The result of proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy using a shift reagent (Eu(DME))[4] indicated that 4 should be >99% de. Thus, it was concluded that this cyclization proceeded in a diastereoselective manner. Removal of the protecting group in 4 with 5% aqueous AcOH/tetrahydrofuran (THF) at 40 °C for 5 h afforded the optically active ketone (5, 75%) ($[\alpha]_D^{25}$ − 11.64° ($c=1.62$, EtOH)). The absolute stereochemistry of (−)-5 was de-
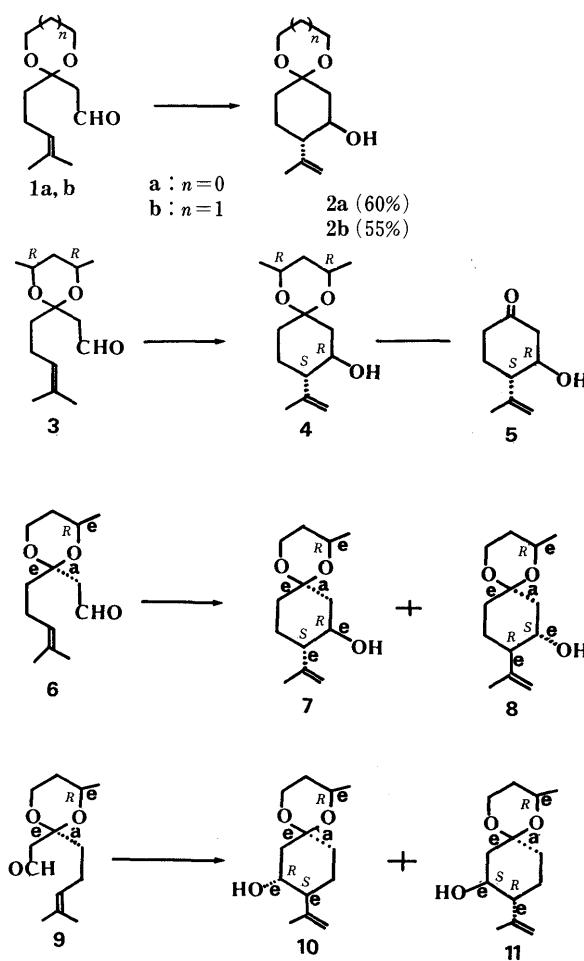

Chart 2

termined to be (3R,4S) by comparison with (+)-5, in which the absolute stereochemistry was established from the circular dichroism (CD) spectrum to be (3S,4R).[5] The formation of (3R,4S)-(−)-5 allows us tentatively to propose the following mechanism. As shown in Fig. 1, the environment of the aldehyde function in the chair form indicated by the full line seems to provide sterically better conditions for cyclization than the dotted-line chair form, in which the axial methyl at C_4, may interfere with the access of the bulky Rh(I)-complex. There are two possible pathways (Chart 3) in this cyclization. Consideration of

a Dreiding stereomodel suggests that conformation 1A involves a steric repulsion between the C_4-H_2 and $C_{6'}$-Me(ax). However, the $C_{6'}$-Me(ax) in conformation 2A occupies a sterically more hindered position between C_4 and C_5. The above difference in steric hinderance causes the reaction to proceed *via* the sterically less hindered 1A to afford the (3R,4S)-product.

Next, Rh(I)-catalyzed cyclization was examined on two aldehydes (6 and 9) with 4R-methyl-1,3-dioxane at the C_3-position, which were prepared from methyl 3-oxo-7-methyl-6-octenoate and R-1,3-butanediol (see Syntheses of Substrates). Each aldehyde (6 and 9) afforded two diastereomeric *trans*-alcohols 7 ($[\alpha]_D^{25}$ +2.06° (c = 1.65, EtOH),

Fig. 1

path 1
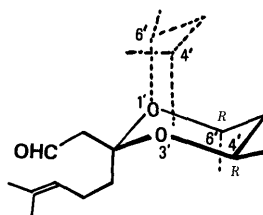
1A

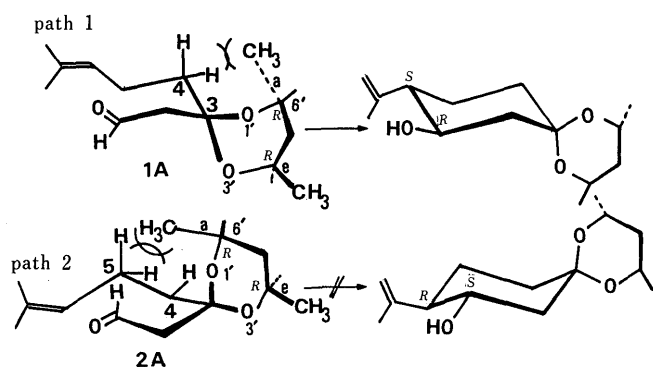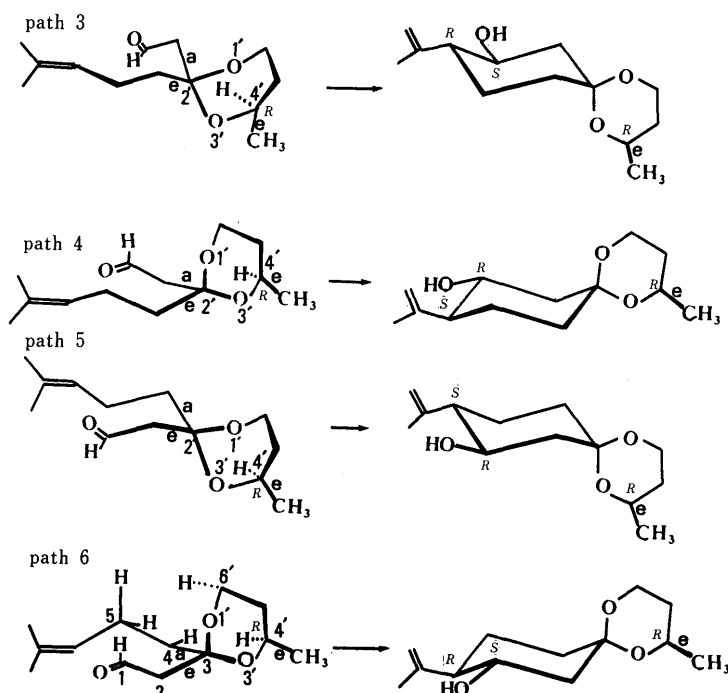path 2

2A

Chart 3

42%) and 8 ($[\alpha]_D^{25}$ -42.30° (c = 1.68, EtOH), 7%), and 10 ($[\alpha]_D^{25}$ +6.24° (c = 5.00, EtOH), 40%) and 11 ($[\alpha]_D^{25}$ -41.63° (c = 3.18, EtOH), 12%), respectively. Independent deprotection of the less polar, main products 7 and 10 from these aldehydes afforded (-)-5 (3R,4S) ($[\alpha]_D^{25}$ -11.64° (c = 1.05, EtOH) from 7, and -11.25° (c = 1.82, EtOH) from 10).[6] In the cyclization of 6 and 9, the formation of the (3R,4S)-*trans*-alcohol as the main product may be rationalized in terms of the following mechanism. In the cyclization of 6 (axial formylmethyl in 1,3-dioxane ring), path 4 may be more favorable than path 3, because the $C_{4'}$-H (axial) close to the aldehyde function in path 3 may hinder the access of the bulky Rh(I)-complex to the aldehyde function. In 9, path 5 (equatorial formylmethyl in the 1,3-dioxane ring) seems to be more favorable than path 6, because the $C_{6'}$-H (axial) in path 6 is subject to steric repulsion involving C_4-H and C_5-H. Thus, the chiral protecting group with the C_2-axis seems to be effective for diastereoselective cyclization.

Syntheses of Substrates Reaction of the dianion (12), prepared from the sodium salt of methyl acetoacetate and BuLi, with 1-bromo-3-methyl-2-butene afforded the ketone (13) in 78% yield, and this was converted to the acetals using ethylene glycol for 1a, 1,3-propanediol for 1b, (R)-1,3-butanediol for 6 and 9, and (2R,4R)-pentanediol for 3 under standard conditions (p-toluenesulfonic acid/benzene). Reduction of the acetals with LiAlH$_4$ followed by oxidation with pyridinum chlorochromate (PCC) in CH$_2$Cl$_2$ yielded the corresponding aldehydes. Acetalization using (2R,4R)-pentanediol with the C_2-axis afforded only one acetal (19). However, acetalization using (R)-1,3-butanediol gave the acetal (16) as a mixture of two diastereomers, which showed a single spot on thin layer chromatography (TLC). Reduction of 16 with LiAlH$_4$ coupled with careful silica-gel column chromatography afforded the polar fraction (17) and the less polar fraction (18) on TLC. Configurations of 17 and 18 were determined by comparison of the ^{1}H-NMR spectra of the correspond-

path 3

path 4

path 5

path 6

Chart 4

$$CH_3COCH_2COOCH_3 \longrightarrow CH_2^-COCH^-COOCH_3$$

Chart 5
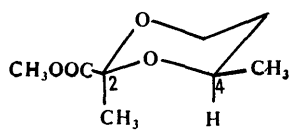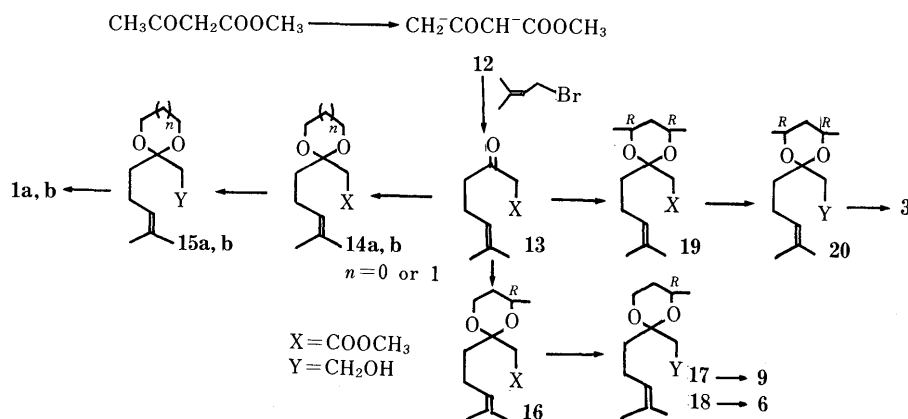
Fig. 2

ing aldehydes (9 and 6) with those of the two (R)-1,3-butanedioxy acetals of methyl pyruvate. On the basis of the findings that, in (R)-1,3-butanedioxy acetals of methyl pyruvate (Fig. 2), the signal of the axial methyl group (δ 1.51) at C_2 in the less polar fraction is observed upfield from the equatorial methyl signal (δ 1.65) at C_2 in the polar fraction, the formylmethyl function [C_2-H_2:δ 2.54 (2H, d, $J = 2.9$ Hz)] in the less polar aldehyde (6) was assigned to be axial, and that of the more polar aldehyde (9) [the C_2-H_2: δ 2.93 (2H, dd, $J = 1.5$, 3.2 Hz)] was assigned to be equatorial.

Experimental

Infrared (IR) spectra were measured with a JASCO A-202 spectrometer. ^{1}H-NMR spectra were measured on JEOL JNM-PS-100 and GX-270 spectrometers. Mass spectra (MS) were taken on a JEOL JMS-D 300 spectrometer. Optical rotations were measured on a JASCO DIP-4 polarimeter. For column chromatography, silica gel (Merck, Kieselgel 60, 70—230 mesh) was used. TLC was performed on Silica gel 60 F_{254} plates (Merck). All organic solvent extracts were washed with brine and dried over anhydrous sodium sulfate. Ratios of solvent systems in column chromatography refer to v/v. Each product was obtained as a colorless oil.

General Procedure of Rh(I) (Wilkinson)-Catalyzed Cyclization A mixture of Wilkinson complex (4.56 mmol) and the aldehyde (4.56 mmol) in $CHCl_3$ (300 ml) was heated at reflux for 4 h under an N_2 atmosphere. After removal of the solvent in vacuo, the residue was diluted with ether, and the precipitate was filtered off. The ether layer was concentrated in vacuo to leave an oily residue, which was purified by column chromatography on silica gel.

Compound 2a,b from 1a,b 2a: 60% yield. IR (neat): 3450, 1640 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.74 (3H, m, Me), 3.55—3.81 (1H, m, CHO–), 3.96 (4H, s, OCH$_2$CH$_2$O), 4.93 (2H, m, =CH$_2$). MS m/z: 198 (M$^+$), 180, 115. 2b: 55% yield. IR (neat): 3430, 1640 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.72 (3H, m, Me), 3.49—3.77 (1H, m, CHO–), 3.84—4.00 (4H, m, OCH$_2$ × 2), 4.89—4.94 (2H, m, =CH$_2$). MS m/z: 212 (M$^+$), 194, 167.

Compound 10 and 11 from 9 10: The less polar fraction, $[\alpha]_D^{25} + 6.24°$ ($c = 5.00$, EtOH). 40% yield. IR(neat): 3400, 1640 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.17 (3H, d, $J = 6$ Hz, Me), 1.72 (3H, s, Me), 4.88—4.89 (1H, m, =–H), 4.91—4.92 (1H, m, =–H). MS m/z: 226 (M$^+$), 208, 181, 143. 11: The more polar fraction, $[\alpha]_D^{25} - 41.63°$ ($c = 3.18$, EtOH). 12% yield. IR (neat): 3400, 1640 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.18 (3H, d, $J = 6$ Hz, Me), 1.72 (3H, s, Me), 4.88—4.89 (1H, m, =–H), 4.92—4.94 (1H, m, =–H). MS m/z: 226 (M$^+$), 208, 181, 143.

Compound 7 and 8 from 6 7: The less polar fraction, $[\alpha]_D^{25} + 2.06°$

($c = 1.65$, EtOH). 42% yield. IR (neat): 3400, 1640 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.17 (3H, d, $J = 6$ Hz, Me), 1.72 (3H, s, Me), 4.88—4.90 (1H, m, =–H), 4.91—4.93 (1H, m, =–H). MS m/z: 226 (M$^+$), 208, 181. 8: The more polar fraction, $[\alpha]_D^{25} - 42.30°$ ($c = 1.68$, EtOH). 7% yield. IR (neat): 3400, 1640 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.18 (3H, d, $J = 6$ Hz, Me), 1.72 (3H, s, Me), 4.88—4.90 (1H, m, =–H). 4.92—4.94 (1H, m, =–H). MS m/z: 226 (M$^+$), 208, 181, 143.

Compound 4 from 3 $[\alpha]_D^{25} - 19.79°$ ($c = 1.02$, EtOH). 60% yield. IR (neat): 3450, 1640, 1380 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.19 (3H, d, $J = 6.3$ Hz, Me), 1.24 (3H, d, $J = 6.3$ Hz, Me), 1.61 (3H, d, $J = 0.8$ Hz, =–Me), 3.60—3.72 (1H, m, CHO–), 3.98—4.22 (2H, m, CHO– × 2), 4.92 (2H, m, =CH$_2$). MS m/z: 239 (M$^+ - 1$), 222, 202, 157.

Methyl 7-Methyl-3-oxo-6-octenate (13) Methyl acetoacetate (9.28 g) in THF (20 ml) was added dropwise to a stirred suspension of NaH (3.52 g, 60% dispersion in mineral oil) in THF (200 ml) under ice-water cooling, and the whole was stirred for 0.5 h, then BuLi (1.56 M in hexane) (53.84 ml) was added dropwise at 0 °C. After 10 min, 1-bromo-3-methyl-2-butene (13.12 g) in THF (16 ml) was added dropwise to the dianion solution at 0 °C, and the whole was stirred for 0.5 h at 0 °C, then for 1 h at room temperature. The reaction was quenched with 5% aqueous HCl (50 ml), diluted with brine (100 ml), and then extracted with ether. The ether extract was washed, and dried, then removal of the solvent in vacuo afforded an oily residue, which was subjected to silica gel column chromatography. The fraction eluted with hexane–AcOEt (50 : 1) gave 13 (11.50 g, 78%) as a colorless oil. IR (neat): 1740, 1710, 1620 cm^{-1}. ^{1}H-NNR (CDCl$_3$) δ: 1.62 (3H, s, Me). 1.68 (3H, s, Me), 3.45 (2H, s, CH$_2$CO), 3.74 (3H, s, OMe), 5.03 (1H, m, =–H). MS m/z: 184 (M$^+$), 166, 59.

Methyl 3,3-Ethylenedioxy-7-methyl-6-octenate (14a) A mixture of the keto-ester (13) (3.68 g) and ethylene glycol (3.72 g) in benzene (100 ml) was refluxed in the presence of p-toluenesulfonic acid (trace) with azeotropic removal of H_2O. The reaction mixture was washed, and dried, then removal of the solvent in vacuo afforded an oily residue, which was chromatographed on silica gel. The fraction eluted with hexane–AcOEt (50 : 1) afforded 14a (3.74 g, 82%) as a colorless oil. IR (neat): 1735, 1650 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.62 (3H, s, Me), 1.68 (3H, s, Me), 2.67 (2H, s, CH$_2$CO), 3.69 (3H, s, OMe), 4.00 (4H, s, OCH$_2$CH$_2$O), 5.12 (1H, m, =–H). MS m/z: 228 (M$^+$), 169, 59.

3,3-Ethylenedioxy-7-methyl-6-octen-1-ol (15a) Compound 14a (1.87 g) in ether (10 ml) was added dropwise to a stirred suspension of LiAlH$_4$ (240 mg) in ether (40 ml) at room temperature, and the mixture was refluxed for 11 h. Usual work-up afforded an oily residue, which was purified by column chromatography on silica gel. The fraction eluted with hexane–AcOEt (20 : 1) afforded 15a (1.03 g, 63%) as a colorless oil. IR (neat): 3400, 1650 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.64 (3H, s, Me), 1.71 (3H, s, Me), 3.75 (2H, m, CH$_2$O), 5.10 (1H, m, =–H). MS m/z: 200 (M$^+$), 182.

3,3-Ethylenedioxy-7-methyl-6-octen-1-al (1a) Compound 15a (1.03 g) in CH$_2$Cl$_2$ (11 ml) was added dropwise to a stirred solution of PCC (1.63 g) and AcONa (0.13 g) in CH$_2$Cl$_2$ (8 ml) at room temperature under an N$_2$ atmosphere. After 4 h, the reaction mixture was diluted with ether (100 ml), and the supernatant was separated from the black gum by decantation. The organic layer was passed through a short column of florisil, and the solvent was removed in vacuo to leave an oily residue, which was subjected to column chromatography on silica gel. The fraction eluted with hexane–AcOEt (30 : 1) afforded 1a (0.51 g, 52%) as a colorless oil. IR (neat): 2850, 1720, 1640 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.61 (3H, s, Me), 1.68 (3H, s, Me), 4.01 (4H, s, OCH$_2$CH$_2$O), 5.08 (1H, m,

=-H), 9.75 (1H, t, $J=2.9$ Hz, CHO). MS m/z: 198 (M$^+$), 180.

Methyl 7-Methyl-3,3-(1,3-propanedioxy)-6-octenate (14b) Compound **14b** was prepared from **13** and 1,3-propanediol in 69% yield, in a manner similar to that described for the synthesis of **14a**. IR (neat): 1735, 1640 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.63 (3H, s, Me), 1.70 (3H, s, Me), 3.67 (3H, s, OMe), 3.83—4.03 (4H, m, OCH$_2$ ×2), 5.17 (1H, m, =-H). MS m/z: 242 (M$^+$), 183, 169.

7-Methyl-3,3-(1,3-propanedioxy)-6-octen-1-ol (15b) Compound **15b** was obtained by reduction of **14b** in 60% yield, in a manner similar to that described for reduction of **14a**. IR (neat): not measured. ^{1}H-NMR (CDCl$_3$) δ: 1.62 (3H, s, Me), 1.70 (3H, s, Me), 3.09 (1H, br s, OH), 5.13 (1H, m, =-H). MS m/z: 214 (M$^+$), 196, 131.

7-Methyl-3,3-(1,3-propanedioxy)-6-octen-1-al (1b) PCC oxidation of **15b** afforded **1b** in 58% yield, in a manner similar to that described for oxidation of **15a**. ^{1}H-NMR (CDCl$_3$) δ: 1.62 (3H, s, Me), 1.70 (3H, s, Me), 9.84 (1H, t, $J=2.9$ Hz, CHO). IR and MS were not measured.

Methyl 3,3-[(R)-1,3-Butanedioxy]-7-methyl-6-octenate (16) Compound **16** was obtained from **13** and (R)-1,3-butanediol in 65% yield, in a manner similar to that described for the preparation of **14a**. IR (neat): 1740, 1650 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.16 (3H, d, $J=6.1$ Hz, Me), 1.63 (3H, s, Me), 1.68 (3H, s, Me), 3.69 (3H, s, OMe), 5.06—5.19 (1H, m, =-H). MS m/z: 256 (M$^+$), 173.

3S,3,3-[(R)-1,3-Butanedioxy]-7-methyl-6-octen-1-ol (17) and 3R,3,3-[(R)-1,3-Butanedioxy]-7-methyl-6-octen-1-ol (18) In a manner similar to that described for reduction of **14a**, reduction of **16** (4.17 g) with LiAlH$_4$ (620 mg) afforded a mixture (3.60 g) of **17** and **18**, which could be separated by silica-gel column chromatography to give the less polar fraction (**18**) (1.06 g, 23%) and the more polar fraction (**17**) (2.45 g, 67%). **18**: [α]$_D^{25}$ −4.53° ($c=2.78$, EtOH). IR (neat): 3450, 1670 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.18 (3H, d, $J=6.1$ Hz, Me), 1.62 (3H, d, $J=0.8$ Hz, Me), 1.70 (3H, s, Me), 5.09—5.15 (1H, m, =-H). MS m/z: 228 (M$^+$), 210, 145. **17**: [α]$_D^{25}$ +4.38° ($c=3.19$, EtOH), IR (neat): 3400, 1670 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.16 (3H, d, $J=6.1$ Hz, Me), 1.62 (3H, s, Me), 1.68 (3H, d, $J=1.0$ Hz, Me), 5.08—5.15 (1H, m, Me). MS m/z: 228 (M$^+$), 210, 145.

3S,3,3-[(R)-1,3-Butanedioxy]-7-methyl-6-octen-1-al (9) and 3R,3,3-[(R)-1,3-Butanedioxy]-7-methyl-6-octen-1-al (6) PCC oxidation of **17** and **18** afforded **9** and **6** in 60% yield, respectively, in a manner similar to that described for oxidation of **15a**. **9**: [α]$_D^{25}$ +6.46° ($c=4.70$, EtOH). IR (neat): 2860, 1720 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.18 (3H, d, $J=5.7$ Hz, Me), 1.61 (3H, s, Me), 1.67 (3H, s, Me), 2.93 (2H, dd, $J=1.5$, 3.2 Hz, CH$_2$CHO), 5.02—5.19 (1H, m, =-H), 9.66 (1H, t, $J=3.2$ Hz, CHO). MS m/z: 226 (M$^+$), 55. **6**: [α]$_D^{25}$ −4.66° ($c=3.00$, EtOH). IR (neat): 2860, 1720 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.18 (3H, d, $J=6.1$ Hz, Me), 1.56 (3H, s, Me), 1.66 (3H, s, Me), 2.54 (2H, d, $J=2.9$ Hz, CH$_2$CHO), 5.11 (1H, m, =-H), 9.90 (1H, t, $J=2.9$ Hz, CHO). MS m/z: 226 (M$^+$), 55.

Methyl 7-Methyl-3,3-[(2R,4R)-2,4-pentanedioxy]-6-octenate (19) Compound **19** was obtained from **13** and (2R,4R)-pentanediol in 70% yield, in a manner similar to that described for the preparation of **14a**. [α]$_D^{25}$ −10.41° ($c=1.69$, EtOH). IR (neat): 1735, 1640 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.17 (3H, s, Me), 1.19 (3H, s, Me), 1.62 (3H, d, $J=0.5$ Hz, =-Me),

1.68 (3H, d, $J=1.1$ Hz, =-Me), 2.70 (2H, dd, $J=4.5$, 1.8 Hz, CH$_2$CO), 3.67 (3H, s, COOMe), 3.95—4.07 (2H, m, CHO − ×2), 5.14 (1H, m, =-H). MS m/z: 270 (M$^+$), 239, 197.

7-Methyl-3,3-[(2R,4R)-2,4-pentanedioxy]-6-octen-1-ol (20) Compound **20** was obtained from **19** in 83% yield, in a manner similar to that described for the reduction of **14a**. [α]$_D^{25}$ −26.30° ($c=1.11$, EtOH). IR (neat): 3450, 1640, 1145 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.19 (3H, d, $J=1.2$ Hz, Me), 1.21 (3H, d, $J=1.2$ Hz, Me), 1.61 (3H, d, $J=1.0$ Hz, Me), 1.68 (3H, d, $J=1.0$ Hz, Me), 3.72—3.86 (2H, m, CH$_2$O−), 3.99—4.18 (2H, m, CHO− ×2), 5.11 (1H, m, =-H). MS m/z: 240 (M$^+$), 224, 197, 120.

7-Methyl-3,3-[(2R,4R)-2,4-pentanedioxy]-6-octen-1-al (3) Compound **3** was obtained by the oxidation (65% yield) of **20**, in a manner similar to that described for PCC oxidation of **15a**. [α]$_D^{25}$ −19.04° ($c=1.05$, EtOH). IR (neat): 1725, 1640, 1145 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.19 (3H, d, $J=3.0$ Hz, Me), 1.22 (3H, d, $J=3.0$ Hz, Me), 1.60 (3H, d, $J=0.5$ Hz, =-Me), 1.68 (3H, d, $J=1.1$ Hz, =-Me), 2.69 (2H, dd, $J=3.1$, 1.3 Hz, CH$_2$-CHO), 3.99—4.07 (2H, m, CHO− ×2), 5.09 (1H, m, =-H), 9.78 (1H, m, CHO). MS m/z: 240 (M$^+$), 220, 197.

(3R,4S)-3-Hydroxy-4-isopropenylcyclohexanone (5) A mixture of **4** (21 mg), 5% aqueous AcOH (2 ml), and THF (2 ml) was stirred for 5 h at 40 °C. After removal of the solvent *in vacuo*, the residue was diluted with ether, and the ether layer was washed and dried. The solvent was evaporated off *in vacuo* to afford the oily residue, which was purified by preparative TLC. [α]$_D^{25}$ −11.64° ($c=1.62$, EtOH). Similarly, **7** and **10** were converted to **5** ([α]$_D^{25}$ −11.64° from **7**, and −11.25° from **10**, respectively). IR (neat): 3400, 1710, 1640 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.76 (3H, t, $J=1.0$ Hz, =-Me), 3.73 (1H, m, CHO−), 4.99 (2H, m, =CH$_2$). MS m/z: 154 (M$^+$), 136, 110.

References and Notes

1) For Rh(I) (Wilkinson)-catalyzed cyclization of 6-octen-1-al (citronellal): K. Sakai and O. Oda, *Tetrahedron Lett.*, **1972**, 4375. For Rh(I)-catalyzed cyclization of 4-penten-1-als: K. Sakai, J. Ide, O. Oda and N. Nakamura, *ibid.*, **1972**, 1287; K. Sakai, Y. Ishiguro, K. Funakoshi, K. Ueno and H. Suemune, *ibid.*, **25**, 961 (1984); R. C. Larock, K. Oertle and G. F. Potter, *J. Am. Chem. Soc.*, **102**, 190 (1980); C. F. Lochow and R. G. Miller, *ibid.*, **98**, 1281 (1976).

2) K. Funakoshi, N. Togo, I. Koga, and K. Sakai, *Chem. Pharm. Bull.*, **37**, 1990 (1989).

3) It is well known that Lewis acid-catalyzed cyclization of citronellal affords the *trans*-alcohol. Y. Nakatani and K. Kawashima, *Synthesis*, **1978**, 147; S. Sakane, K. Maruoka and H. Yamamoto, *Tetrahedron*, **42**, 2203 (1986).

4) P. V. Dermaco, T. K. Elzey, R. B. Lewis and E. Wenkert, *J. Am. Chem. Soc.*, **92**, 5734 (1970).

5) The absolute stereochemistry of (+)-5 ([α]$_D^{25}$ +3.0 (27% ee), which was obtained from **11** contaminated with **10**, was determined from the CD spectrum ([θ]^{24} = +47.28 (289 nm, MeOH), Δε = +1.43 × 10^{-2}) to be (3S,4R).

6) Deprotection of **8** and **11** with 5% aqueous AcOH afforded (+)-5.