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Asymmetric Cyclization Reactions. Cyclization of Substituted 4-Pentenals into Cyclopentanone Derivatives by Rhodium(I) with Chiral Ligands

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Abstract: *Asymmetric cyclization of substituted 4-pentenals (**Ia,b,c; IIa,b,c,d**) by Rh(I) with chiral ligands was tested, and substrate (**IId**) with a bulkier substituent at C_4 underwent more stereoselective cyclization by Rh(I)-((+)-DIPMC) to yield substituted cyclopentanone (**IIId**) The Rh(I) with (+)-DIPMC was found to proceed in a different manner from the Wilkinson-catalyzed cyclization*

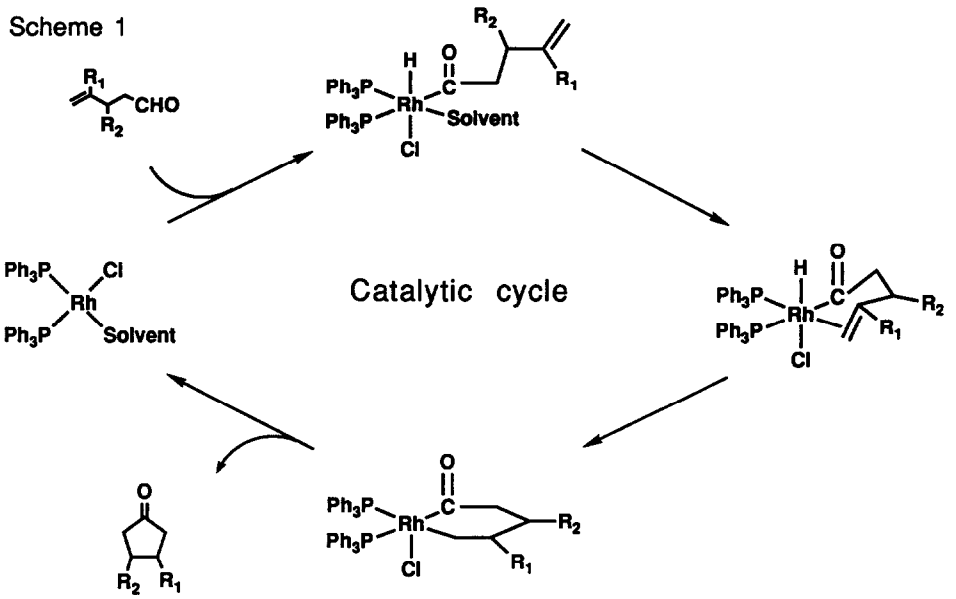
Stereoselective cyclization is one of the indispensable reactions for the synthesis of natural products, and there are several excellent methods for the cyclization. Among them, it is well known that metal-catalyzed cyclization plays an essential role in the synthesis of structurally complex organic molecules.[1] Rh(I)-catalyzed cyclization of 4-pentenals into cyclopentanones was first found by our laboratory.[2a] Further studies evolved this reaction using the Wilkinson complex into the stereocontrolled cyclization of 3,4-disubstituted 4-pentenals to *cis*-3,4-disubstituted cyclopentanones,[2b] and this method has been widely applied to the synthesis of several natural products.[3]

Since the reaction involves clearly the addition of the hydrogen atom and the acyl group of the aldehyde to a coordinated double bond, this cyclization is considered to proceed in the intramolecular hydroacylation mechanism[4] *via* the oxidative addition[5] of the aldehyde to rhodium atom to yield the acylrhodium hydride intermediate; subsequent addition of Rh-H to the coordinated double bond to form the six-membered ring including Rh; then reductive elimination to cyclopentanone (Scheme 1).

The hydroacylation mechanism was supported by the deuterium labeled experiment, in which deuterium of the deuterium aldehyde occupied the β-position of the cyclized cyclopentanone.[6,2b]

On the basis of this practical Rh(I)-catalyzed cyclization under mild reaction conditions, we undertook the asymmetric cyclization by the Rh(I)-complex with chiral ligands. Previously, James and Young[7] reported that on heating (150°C) (±)-2-methyl-2-phenyl-4-pentenal and $Rh(chiraphos)_2Cl$ in PhCN, the (-)-(*S*)-optical isomer with 69% e.e. was obtained (17% yield) *via* the kinetic resolution process. The employed Rh(I) complex is apparently not only unacceptable in chemical yield and optical purity, but also the employed conditions are too

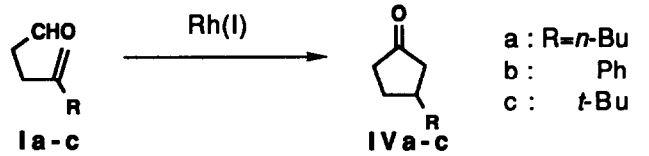
drastic for general application. One reason for the low conversion yield may be attributable to undesirable substituent (quarternary carbon) at the C_2-position of tested substrates.[8]



This paper[9] reports on our study on the asymmetric cyclization of the 4-pentenals without any substituents at the C_2-position with Rh(I)(chiral diphosphine)Cl. A mixture of 4-*n*-butyl-4-pentenal (**Ia**) and Rh(I)-complex which was prepared from RhCl(cyclooctene)$_2$ and chiral phosphine ligands such as BPPM,[10] DIOP,[11] and DIPMC,[12] was stirred in CH_2Cl_2 at room temperature. The employed chiral phosphine ligands possess two diphenylphosphine groups in the molecule. Therefore, the cyclization reaction seemed to differ from the case of the Wilkinson complex. However, preliminary experiments proved that the expected cyclization into the five-membered ring proceeds smoothly in a similar manner to the case of Wilkinson complex. The results are summarized in Table 1. Among the three tested ligands, (+)-DIPMC with the C_2 axis afforded (-)-(*S*)-3-butylcyclopentanone (**IVa**) with 73% e.e. (-)-BPPM resulted in the formation of **IVa** with 46% e.e., and the cyclization using (+)-DIOP with the C_2 axis was only 6% e.e. Glaser *et al*,[13] investigated the asymmetric hydrogenation of methyl α-(N-acyl-N-methylamino)cinnamate using Rh(I)-catalyst with chiral phosphine ligands, and it was found that the stereoselectivity was in order of (+)-DIOP (73% e.e), (1*R*,2*R*)-*trans*-1,2-bis(diphenylphosphinomethyl)cyclobutane (43%e.e), and (+)-DIPMC (26%e.e). The above observation suggests that it is difficult to predict excellent ligand for Rh(I)-catalyzed cyclization from the result of asymmetric hydrogenation.

The absolute stereochemistry of each cyclized product (**IVa**,**b**, and **c**) was determined to be *S*-configuration by comparison with the sign of reported specific rotation.[14] This finding suggests that addition of the hydrogen and the acyl function of the aldehyde to a double bond proceeded in stereochemically common mechanism to yield the *S*-configuration.

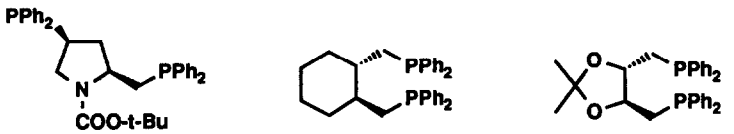
Scheme 2



Ia-c IVa-c

Table 1. Rhodium-catalyzed Cyclization of Prochiral Substrates.

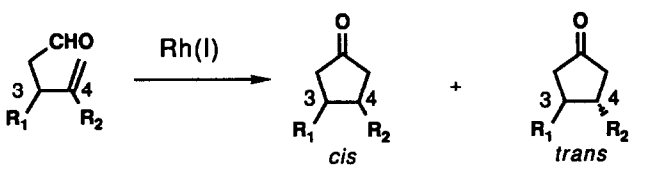
Product	Ligand	Reaction time(h)	Yield (%)	$[\alpha]_D^{25}$ (c, $CHCl_3$)	Optical yield (% e.e.)	Abs. Config.
IVa	(-)-BPPM	71	45	-58.6° (3.30)	46	*S*
IVa	(+)-DIOP	14	64	-0.83° (2.95)	6	*S*
IVa	(+)-DIPMC	2.5	78	-99.3° (5.70)	73	*S*
IVb	(+)-DIPMC	4	71	-70.7° (2.08)	76	*S*
IVc	(+)-DIPMC	4.5	68	-131.6° (1.39)	77	*S*



(-)-BPPM (+)-DIPMC (+)-DIOP

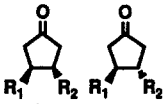
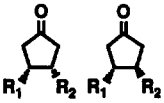
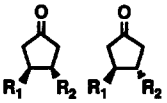
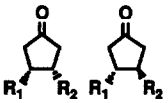
Next, our attention was directed to the cyclization of 3,4-disubstituted 4-pentenals (II) by Rh(I)-complex with chiral ligand. As mentioned previously,[2b] 3,4-disubstituted 4-pentenals are stereoselectively cyclized in good yields to *cis*-3,4-disubstituted cyclopentanones by Rh(I)-complex (Wilkinson), and the *trans*-isomers are not obtained. However, preliminary cyclization of (±)-**IIa** by Rh(I) with (+)-DIOP afforded a mixture of 3,4-*cis*- and *trans*-cyclopentanones[15] in the ratio of 1.20 (*cis*) to 1.00 (*trans*). This result is in sharp contrast to the case of Wilkinson-catalyzed cyclization to afford stereoselectively 3,4-disubstituted *cis*-cyclopentanones. This remarkable difference prompted us to study the cyclization of (3*R*)-**IIa** and (3*S*)-**IIb** by Rh(I) with chiral ligands ((+)-DIPMC or (+)-DIOP).

Scheme 3



IIa(3*R*)	R_1=$CH_2CH_2COCH_3$ R_2=CH_3	(3*R*)-*cis*-**IIIa**	(3*R*)-*trans*-**IIIa**
IIb(3*S*)	R_1=$CH_2CH_2COCH_3$ R_2=CH_3	(3*S*)-*cis*-**IIIb**	(3*S*)-*trans*-**IIIb**
IIc(3*R*)	R_1=$CH_2CH_2COCH_3$ R_2=$CH_2CH_2OCOCH_3$	(3*R*)-*cis*-**IIIc**	(3*R*)-*trans*-**IIIc**
IId(3*S*)	R1=$CH_2CH_2COCH_3$ R_2=$CH_2CH_2OCOCH_3$	(3*S*)-*cis*-**IIId**	(3*S*)-*trans*-**IIId**

Table 2. Rhodium-catalyzed Cyclization of Chiral Substrates.

Substrates	II-b (3S)	II-a (3R)	II-d (3S)	II-c (3R)
Products	IIIb	IIIa	IIId	IIIc
	 cis (3S,4R) trans (3S,4S)	 cis (3R,4S) trans (3R,4R)	 cis (3S,4R) trans (3S,4S)	 cis (3R,4S) trans (3R,4R)
(+)-DIOP				
Yield(%)	79	75		
Ratio	1.91 : 1	1 : 1.30		
(+)-DIPMC				
Yield(%)	79	60	80	88
Ratio	3.13 : 1	1 : 2.24	8.09 : 1	1 : 2.57

The result of Rh(I)-catalyzed cyclization using chiral ligands and chiral substrates is shown in Table 2. Yields in each case are fairly good, and the absolute configuration of the C_3 has a significant effect on the stereochemistry of products. That is to say, (3*S*)-**IIb** was cyclized by Rh(I) with (+)-DIPMC to afford (3*S*,4*R*)-**IIIb**(*cis*) as the main product, in the ratio of 3.13 to 1.00 ((3*S*,4*S*)-**IIIb**(*trans*)). On the other hand, (3*R*)-**IIa** was cyclized to the *trans* configuration ((3*R*,4*R*)-**IIIa**), in the ratio of 2.24 to 1.00 (3*R*,4*S*)-**IIIa**(*cis*)) under the same cyclization conditions. A similar effect of 3*S* and 3*R* on the cyclization was also observed in the case of (+)-DIOP, in which (+)-DIOP cyclized (3*S*)-**IIb** to *cis*-compound and *trans*-compound in the ratio of 1.91 to 1.00, while (3*R*)-**IIa** was cyclized in the ratio of 1.30 (*trans*) to 1.00 (*cis*). It is noteworthy that the absolute stereochemistry of the C_4 of the main products in Rh(I)-catalyzed cyclization using (+)-DIPMC or (+)-DIOP as ligand is *R*-configuration, regardless of the absolute configuration at C_3 of the substrate (**IIa,b**).

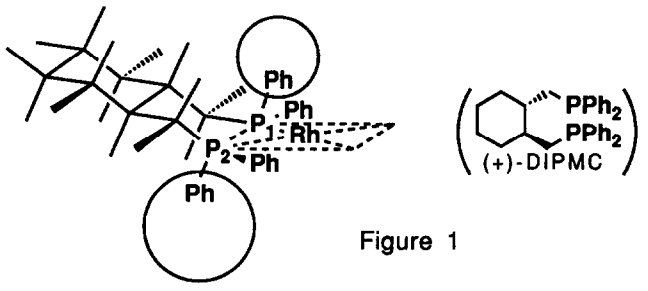


Figure 1

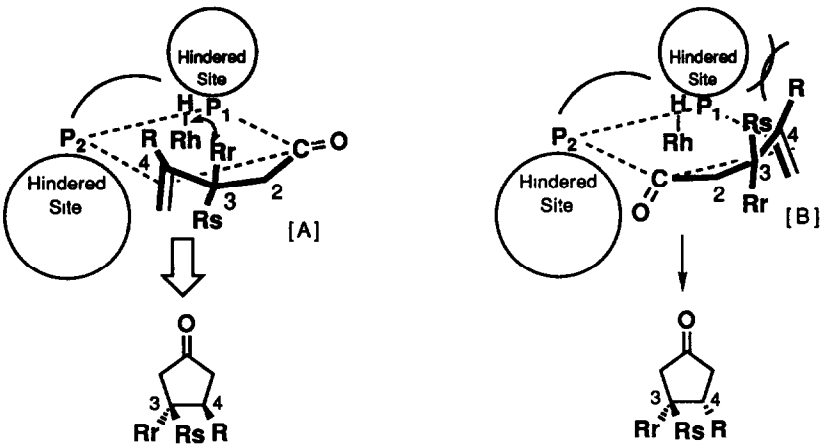


Figure 2

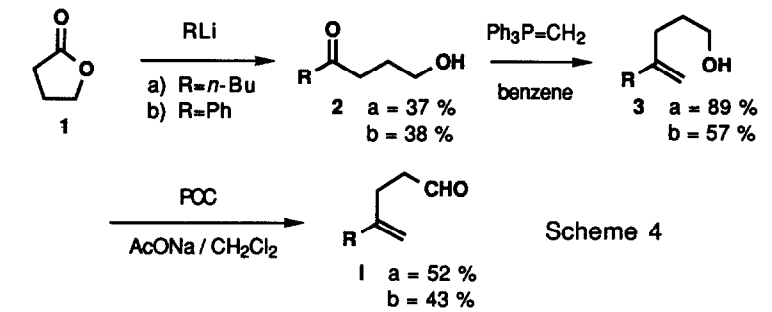
On the basis of the above findings, the following mechanism is tentatively proposed. In (+)-DIPMC, which was more stereoselective than (+)-DIOP, it is likely that this ligand takes a chair-chair conformation as shown in Fig. 1. In this case, it can be assumed that each phosphine (P_1 and P_2) with two phenyl functions coordinates in such a way that a phenyl function of one phosphine (P_1) occupies β-axial bond and that of the other (P_2) occupies α-axial bond. That is to say, the β-side of P_1 and α-side of P_2 may be sterically hindered. Therefore, it is reasonable that, as in Fig.2A, R-substituent in Scheme 2 (Rr and Rs=H) occupies a less hindered β-side of P_2 and subsequent addition of Rh-H to the double bond affords the *S*-configuration.

In 3,4-disubstituted 4-pentenals, preferential cyclization of 3*S* (or 3*R*)-substituent to 3,4-*cis* (or *trans*)-disubstituted cyclopentanone may be rationalized by the following assumption. In **IIa,b**, the methyl function (R_2=Me) approaches to occupy the less hindered space (β-side of P_2), and subsequent cyclization proceeds to afford from **3*S*(IIb)** the 3,4-*cis*-isomer (**IIIb**) or from **3*R*(IIa)** the 3,4-*trans*-isomer (**IIIa**), respectively. However, it is likely that a hindered space (β-side of P_1) allows approach of a small methyl function. This assumption provides rational explanation for the findings that 3,4-*trans*-**IIIb** or 3,4-*cis*-**IIIa** was obtained from **3*S*(IIb)** or **3*R*(IIa)**, respectively, as minor products.

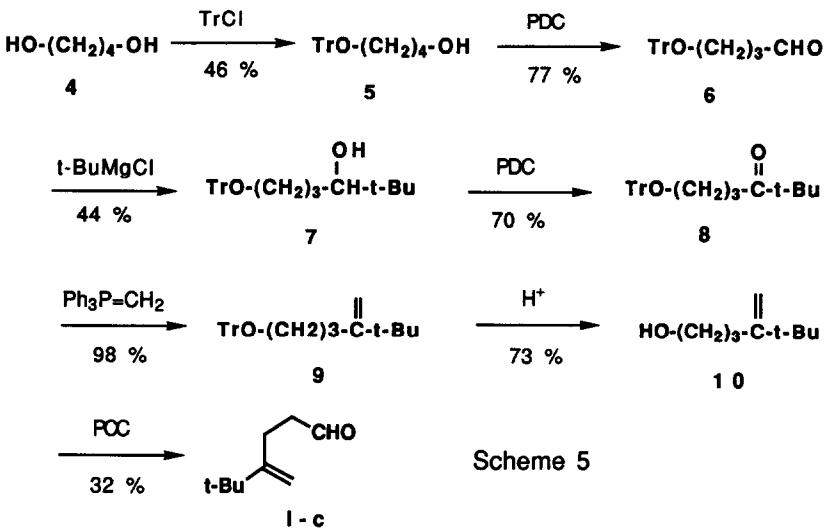
On the basis of the above assumption that the diastereoselectivity of the cyclized products may be correlated to the bulkiness of substituents at C_4, substrates **IIc(3*R*)** and **IId(3*S*)** with a bulkier acetoxyethyl substituent than the methyl function were subjected to Rh(I)-catalyzed cyclization. In accord with our expectation, the bulkiness at C_4 of **IId(3*S*)** raised the diastereoselectivity of cyclization reaction in the ratio of 8.09 (*cis*-**IIId**) to 1 (*trans*-**IIId**).[16] A similar explanation might support the assumption that the substrate **IIc(3*R*)** is preferentially cyclized to the *trans*-isomer. However, this cyclization resulted in low diastereoselectivity. This may be attributable to the steric hinderance between Rh-H and Rr(3*R*)($CH_2CH_2COCH_3$) as in Fig. 2A. The intermediate as shown in Fig. 2B seems to reduce the unfavorable steric hinderance between Rh-H and Rr, although the acetoxyethyl function occupies the hindered site of P_1 and subsequent cyclization affords the *cis* products. The above unfavorable factors of 3*R*-configuration allowing the formation of the *cis*-product may reduce the diastereoselectivity of the cyclization.

Synthesis of substrates

The aldehydes (**Ia,b**) and (**Ic**)) were synthesized by a sequence of reactions as shown in Scheme 4 and 5, respectively. The lactone (**1**) was alkylated with R-lithium (a; R=Bu, b;R=Ph), and the resulting ketone (**2**) was subjected to Wittig reaction and subsequent oxidation with PCC. In this manner, **Ia** and **b** were obtained in 17.1% and 9.3% yields from **1**, respectively. The aldehyde (**Ic**) was also prepared from butanediol (**4**) by conventional method. The aldehydes (**IIc,d**) were synthesized from 10-acetoxymethyllimonene[17] in a manner similar to the case of **IIa,b**.[3]



Scheme 4



Scheme 5

Experimental

Infrared (IR) spectra were measured with a JASCO A-202 spectrometer. ^{1}H and ^{13}C NMR spectra were measured on JEOL JNM-PS-100 and GX-270 spectrometers. Coupling constants are reported in hertz, and the abbreviations br, s, d, t, and m refer to broad, singlet, doublet, triplet, and multiplet, respectively. Mass spectra (MS) were taken on a JEOL JMS-D 300 spectrometer. Each reaction was carried out under an Ar atmosphere and monitored by TLC (Merck, silica gel 60F-254 plates). For gravity column chromatography, silica gel (Merck, Kieselgel 60, 70-230 mesh) was used, and for flash column chromatography, 230-400 mesh silica gel was used. All organic solvent extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Wilkinson-

complex was prepared by Normant procedure (*J. Organomet. Chem. Library* **1**. 1976, 219). Optical rotations were measured using JASCO DIP-360 polarimeter at 25°C.

General procedure of cyclization with Rh(I) complex. Mixture of chlorobis(cyclooctene)rhodium(I) dimer (107 mg, 0.18 mmol) and (1*S*,2*S*)-(+)-*trans*-1,2-bis(diphenylphosphinomethyl)cyclohexane[(+)-DIPMC](143 mg, 0.36 mmol) in CH_2Cl_2 (4 ml) was stirred for 10 min at room temperature, then the aldehyde (3*S*-**IIb**, 100 mg, 0.71 mmol) in CH_2Cl_2 (4 ml) was added dropwise, and the whole was stirred for 19 h. After removal of the solvent, ether (20 ml) was added. The resulting precipitate was filtered off, and the filtrate was concentrated *in vacuo* to leave an oily residue, which was subjected to flash chromatography (20% AcOEt in hexane). Thus, a mixture of *cis*- and *trans*-**IIIb** (79 mg, 79%) was obtained.

4-Oxo-1-octanol (2a). To a stirred solution of γ-lactone (**1**)(10 g, 116 mmol) in ether (120 ml) was added n-butyllithium (70 ml, 112 mmol)(1.6 M in hexane) at -78°C. The whole was stirred for 2 h at the same temperature, and quenched with 10% aqueous NH_4Cl (50 ml), then extracted with ether. The ether extract was washed and dried. The solvent was removed *in vacuo* to leave an oily residue, which was purified by distillation to afford **2a** (6.17 g, 37%) as a colorless oil, bp 81 °C / 0.9 Torr. IR(film) 3420, 1710, 1415, 1380, 1060 cm^{-1}; ^1H NMR($CDCl_3$) δ 0.90 (3H, m, CH_3), 3.63 (2H, m, CH_2O); MS m/z 144 (M^+), 126, 97, 84; HRMS m/z: calcd. for $C_8H_{16}O_2$: 144.11502; found 144.11554.

3-Benzoyl-1-propanol (2b). In a manner similar to the synthesis of **2a**, γ-Lactone (**1**)(8.0 g, 93 mmol) and phenyllithium (23.3 ml, 46.6 mmol)(2.3 M in cyclohexane-ether) afforded **2b** (1.58 g, 38%) as a colorless oil. IR(film) 3420, 1680, 1600, 1445, 1050 cm^{-1}; ^1H NMR($CDCl_3$) δ 3.14 (2H, t, J=6.8 Hz, CH_2CO), 3.74 (2H, J=6.1 Hz, CH_2), 7.32-7.59 (3H, m, aromatic-H), 7.86-8.11(2H, m, aromatic-H); MS m/z 164 (M^+), 146, 120, 105, 77; HRMS m/z: calcd. for $C_{10}H_{12}O_2$: 164.08372; found 164.08350.

4-Butyl-4-penten-1-ol (3a). A mixture of methyltriphenylphosphonium bromide (37.2 g, 104 mmol) and t-BuOK (11.7 g, 104 mmol) in benzene (400 ml) was refluxed for 1.5 h, then cooled to ambient temperature. The ketol (**2a**)(5,0 g, 34.7 mmol) in benzene (20 ml) was added dropwise, and stirred for 1.5 h. The reaction mixture was diluted with aqueous NH_4Cl (200 ml), then extracted with ether. The combined organic layer was washed and dried. Removal of the solvent *in vacuo* afforded an oily residue, which was purified by flash column chromatography (20% AcOEt in hexane) to give **3a** (4.39 g, 89%) as a colorless oil. IR(film) 3350, 1645, 1440, 1060 cm^{-1}; ^1H NMR($CDCl_3$) δ 0.91 (3H, m, CH_3), 3.75 (2H, t, J=6.3 Hz, CH_2O), 4.74 (2H, m, $=CH_2$); MS m/z 142 (M^+), 124, 95, 85; HRMS m/z: calcd. for $C_9H_{18}O_1$: 142.13576; found 142.13537.

4-Phenyl-4-penten-1-ol (3b). In a manner similar to the case of **3a**, **3b** was prepared from **2b** in 55% yield. IR(film) 3340, 1625, 1495, 1440, 1055 cm^{-1}; ^1H NMR($CDCl_3$) δ 3.64 (2H, t, J=6.4 Hz, CH_2O), 5.09 (1H, m, =-H), 5.29 (1H, m, =-H), 7.14-7.47 (5H, m, aromatic-H); MS m/z 162 (M^+), 118; HRMS m/z: calcd. for $C_{11}H_{14}O_1$: 162.10446; found 162.10494.

4-Trityloxy-1-butanol (5). To a stirred solution of 1,4-butanediol (8.0 g, 88.8 mmol) in pyridine (90 ml) was added triphenylmethyl (trityl) chloride (24.7 g, 88.8 mmol) at 0°C, and after being stirred for 3 h at room temperature, the reaction mixture was poured into ice water (ca. 100 ml) containing 10% HCl (50 ml), then neutralized carefully with 10% HCl, and extracted with AcOEt. The AcOEt extract was washed, and dried, then the solvent was removed *in vacuo* to leave an oily residue which was purified by flash column chromatography. The fraction eluted with 50% $CHCl_3$ in hexane afforded **5** (13.6 g, 46%) as a colorless oil. IR(film) 3350, 1590, 1490, 1440 cm^{-1}; ^1H NMR($CDCl_3$) δ 3.11 (2H, t, J=6.0 Hz, CH_2O), 3.62 (2H, t, J=6.0 Hz, CH_2O), 7.19-7.50 (15H, m, aromatic-H); MS m/z 332 (M^+), 244;HRMS m/z: calcd. for $C_{23}H_{24}O_2$: 332.17762; found 332.17738.

4-Trityloxybutan-1-al (6). To a stirred suspension of pyridinium dichromate (PDC, 38.5 g, 100 mmol) in CH_2Cl_2 (200 ml) was added dropwise the alcohol (**5**) (13.6 g, 40.9 mmol) in CH_2Cl_2 (200 ml) at ambient temperature, and the whole was stirred for 22 h, and diluted with ether (200 ml). The precipitate was filtered off by florisil short column, and the filtrate was concentrated *in vacuo* to afford an oily residue, which was purified by flash chromatography. The fraction eluted with 15% ether in hexane afforded **6** (10.4 g, 77%) as a colorless oil. IR(film) 1730, 1600, 1500, 1450, 1440 cm^{-1}; ^1H NMR($CDCl_3$) δ 3.13 (2H, t, J=6.2 Hz, CH_2O), 7.13-

7.45 (15H, m, aromatic-H), 9.77 (1H, t, J=1.5 Hz, CHO); MS m/z 330 (M^+) 243, 183, 165, 105; HRMS m/z: calcd. for $C_{23}H_{22}O_2$: 330.16197; found 330.16145.

2,2-Dimethyl-6-trityloxy-3-hexanol (7). To a stirred solution of **6** (10.4 g, 31.6 mmol) in THF (8 ml) was added dropwise t-BuMgCl (37.4 ml, 41.1 mmol)(1.1M in THF) at 0°C, and the whole was stirred for 1.5 h, quenched with 10% aqueous NH_4Cl (50 ml), then extracted with ether. The ether extracted was washed, and dried, then the solvent was removed *in vacuo*. An oily residue was subjected to flash column chromatography, and the fraction eluted with 10% AcOEt afforded **7** (5.46 g, 44%) as a colorless oil. IR(film) 3470, 1600, 1490, 1450 cm^{-1}; ^1H NMR($CDCl_3$) δ 0.98 (9H, s, CH_3x 3), 3.12 (3H, m, CH_2O, CHO), 7.18-7.50 (15H, m, aromatic-H); MS m/z 388 (M^+), 370, 311, 243; HRMS m/z: calcd. for $C_{27}H_{32}O_2$: 388.24022; found 338.24076.

2,2-Dimethyl-6-trityloxy-3-hexanone (8). In a manner similar to the oxidation of **5** with PDC, **7** (6.11 g, 15.7 mmol) was subjected to PDC (15.1 g, 39.3 mmol) oxidation to afford **8** (4.27 g, 70%) as colorless needles, mp 79 °C (from hexane). IR(Nujol) 1700, 1595, 1445, 1070 cm^{-1}; ^1H NMR($CDCl_3$) δ 1.10 (9H, s, CH_3x 3), 2.57 (2H, t, J=7.5 Hz, CH_2CO), 3.07 (2H, t, J= 6.2 Hz, CH_2O), 7.04-7.53 (15H, m, aromatic-H); MS m/z 386 (M^+), 243; HRMS m/z: calcd. for $C_{27}H_{30}O_2$: 386.22457; found 386.22416.

4-*tert*-Butyl-1-trityloxy-4-pentene (9). In a manner similar to the Wittig reaction of **2**, the ketone (**8**) (4.13 g, 10.0 mmol) gave **9** (4.03 g, 98%) as a colorless oil. IR(film) 1630, 1590, 1450, 1070 cm^{-1}; ^1H NMR($CDCl_3$) δ 1.03 (9H, s, CH_3x 3), 3.10 (2H, t, J=6.2 Hz, CH_2O), 4.67 (1H, d, J=1.2 Hz, =-H), 4.84 (1H, s, =-H), 7.19-7.51 (15H, m, aromatic-H); MS m/z 384 (M^+), 307; HRMS m/z: calcd. for $C_{28}H_{32}O_1$: 384.24530; found 384.24574.

4-*tert*-Butyl-4-penten-1-ol (10). Mixture of **9** (3.54 g, 9.21 mmol), acetone (25 ml), H_2O (5 ml), and 10% HCl (4 ml) was stirred for 20 h at room temperature. After removal of acetone, the reaction mixture was diluted with 5% aqueous $NaHCO_3$ (50 ml), and extracted with AcOEt. The AcOEt extract was washed, and dried, then solvent was removed *in vacuo* to afford an oily residue. After flash column chromatography (30% ether in hexane), **10** (953 mg, 73%) was obtained as a colorless oil. IR(film) 3330, 1630, 1360, 1060, 890 cm^{-1}; ^1H NMR($CDCl_3$) δ 1.09 (9H, s, CH_3x 3), 3.69 (2H, t, J=6.4 Hz, CH_2O), 4.71 (1H, d, J=0.98 Hz, =-H), 4.89 (1H, d, J=0.98 Hz, =-H); MS m/z 142 (M^+), 124; HRMS m/z: calcd. for $C_9H_{18}O_1$: 142.13576; found 142.13533.

4-*n*-Butyl-4-penten-1-al (Ia). To a stirred mixture of pyridinium chlorochromate (PCC, 1.75 g, 8.0 mmol) and sodium acetate (0.13 g, 1.5 mmol) in CH_2Cl_2 (7 ml) was added dropwise **3a** (767 mg) in CH_2Cl_2 (7 ml) at ambient temperature. After being stirred for 1.5 h, the reaction mixture was diluted with ether, and the precipitate was filtered off. The filtrate was concentrated *in vacuo* to leave an oily residue, which was purified by flash column chromatography. The fraction eluted with 10% ether in hexane afforded **Ia** (309 mg, 41%) as a colorless oil. IR(film) 2730, 1730, 1645, 890 cm^{-1}; ^1H NMR($CDCl_3$) δ 0.91 (3H, m, CH_3), 1.14-1.58 (4H, m), 2.03 (2H, m), 2.28-2.68 (4H, m), 4.70 (1H, t, J=0.61 Hz, =-H), 4.78 (1H, d, J=1.2 Hz, =-H), 9.78 (1H, t, J=1.6 Hz, CHO); MS m/z 140 (M^+), 97, 83, 69; HRMS m/z: calcd. for $C_9H_{16}O_1$: 140.12011; found 140.12073.

4-Phenyl-4-penten-1-al (Ib) and 4-tert-Butyl-4-penten-1-al (Ic). In a manner similar to that described for the oxidation of **3a**, **1b** and **1c** were obtained in 43% and 32% yields, respectively. **Ib**: IR(film) 2820, 2820, 1720, 1620, 1490, 890 cm^{-1}; ^1H NMR($CDCl_3$) δ 2.44-3.15 (4H, m), 5.09 (1H, m, =-H), 5.32 (1H, m, =-H), 7.25-7.46 (5H, m, aromatic-H), 9.77 (1H, t, J=1.3 Hz, CHO); MS m/z 160 (M^+), 142, 118; HRMS m/z: calcd. for $C_{11}H_{12}O_1$: 160.08881; found 160.08848. **Ic**; IR(film) 2970, 2730, 1725, 1630, 1390, 1360, 895 cm^{-1}; ^1H NMR($CDCl_3$) δ 1.08 (9H, s, CH_3x 3), 4.62 (1H, t, J=1.3 Hz,=-H), 4.92 (1H, d, J=0.5 Hz, =-H), 9.79 (1H, t, J=1.6 Hz, CHO); MS m/z140 (M^+), 125, 122, 107, 83; HRMS m/z: calcd. for $C_9H_{16}O_1$: 140.12011; found 140.12059.

3-*n*-Butylcyclopentanone (IVa)(Table 1; (+)-DIPMC). IR(film) 1740, 1460, 1405, 1160 cm^{-1}; ^1H NMR($CDCl_3$) δ 0.91 (3H, t, J=6.8 Hz, CH_3), 1.27-1.57 (7H, m), 1.79 (1H, m, CH), 2.06-2.43 (5H, m); MS m/z 140 (M^+), 111, 83; HRMS m/z: calcd. for $C_9H_{16}O_1$: 140.12011; found 140.12047.

3-Phenylcyclopentanone (IVb)(Table 1, (+)-DIPMC). IR(film) 1740, 1600, 1490, 1400, 1135 cm^{-1}; ^1H NMR($CDCl_3$) δ 1.99 (1H, m, CH), 2.23-2.53 (4H, m), 2.68 (1H, m), 3.43 (1H, m), 7.21-7.39 (5H, m, aromatic-H); MS m/z 160 (M^+), 117, 104; HRMS m/z: calcd. for $C_{11}H_{12}O_1$: 160.08881; found 160.08867.

3-*tert*-Butylcyclopentanone (IVc)(Table 1, (+)-DIPMC). IR(film) 1740, 1475, 1405, 1365, 1165 cm^{-1}; ^1H NMR($CDCl_3$) δ 0.92 (9H, s, CH_3x 3), 1.60 (1H, m), 1.82-2.39 (6H, m); MS m/z 140 (M^+), 125, 83, 57; HRMS m/z: calcd. for $C_9H_{16}O_1$: 140.12011; found 140.11986.

Determination of the enantiomeric excess of IVa,b,c. Cyclized products (**IVa**, 60 mg, 0.43 mmol), (2*R*,3*R*)-(-)-butanediol (116 mg, 1.29 mmol), and *p*-toluenesulfonic acid (9 mg) in CH_2Cl_2 (20 ml) were refluxed under azeotropic conditions, and the usual work afforded an oily acetal, which was roughly chromatographed on silica gel using 20% ether in hexane as eluent. In the ^{13}C NMR spectra, two methylene assignable to C_2, C_5 and one methine assignable to C_3 indicated the diastereomer ratio. **IVa**: δ 44.67 (main), 44.98(C_2); 37.64 (main), 38.08 (C_3). **IVb**: δ 45.91 (main), 46.11 (C_2); 43.10 (main), 43.55 (C_3); 38.11 (main), 38.45 (C_5). **IVc**: δ 39.42 (main), 39.69 (C_2); 48.11 (main), 48.67 (C_3); 37.79 (main), 38.15(C_5).

(3*S*)-4-Acetoxyethyl-3-(3'-oxobutyl)-4-penten-1-al (IId) and (3R)-4-acetoxyethyl-3-(3'-oxobutyl)-4-penten-1-al (IIc). IIc; IR(film) 2930, 2720, 1735, 1715, 1640, 1240 cm^{-1}; ^1H NMR($CDCl_3$) δ 2.04 (3H, s, $OCOCH_3$), 2.13 (3H, s, $COCH_3$), 4.20 (2H, t, J=7.0 Hz, CH_2O), 4.92 (2H, t, J=1.2 Hz, =-H x 2), 9.68 (1H, t, J=1.8 Hz, CHO); MS m/z 222 (M^+-H_2O), 180; $[\alpha]_D$ -5.1 (c 1.39, $CHCl_3$). **IIc**: $[\alpha]_D$ +6.5 (c 2.21, $CHCl_3$).

4-Acetoxyethyl-3-(3'-oxobutyl)cyclopentanone (IIId)(Table 2, (+)-DIPMC). IR(film) 2930, 1730, 1710, 1360, 1240 cm^{-1}; ^1H NMR($CDCl_3$) δ 1.36-1.64 (2H, m), 1.77-2.59 (10H, m), 2.06 (3H, s, $OCOCH_3$), 2.17 (3H, s, $COCH_3$), 4.04-4.14 (2H, m, CH_2O); ^{13}C NMR($CDCl_3$) δ 217.73(s), 216.83(s), 207.92(s), 171.03(s), 63.10(t), 62.92(t), 44.95(t), 44.49(t), 43.20(t), 42.89(t), 42.03(d), 41.85(t), 41.54(t), 39.93(d), 38.44(d), 36.29(d), 32.66(t), 30.04(q), 30.01(q), 28.39(t), 27.43(t), 22.79(t), 20.96(q); MS m/z 222 (M^+-H_2O), 183, 182, 141, 123, 99, 96, 81, 43.

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