Stereoselective Construction of Acyclic Structures with Four Consecutive Asymmetric Centers

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(Received November 22, 1989)

All the eight possible diastereomers of 6,8-dihydroxy-5,7-dimethyltridecane, taken as the model example for the construction of four consecutive asymmetric centers, were stereoselectively synthesized from two common starting materials, α-hydroxy-β-methyl-γ,δ-unsaturated acids (**1a** and **1b**), wherein a newly introduced stereoselective epoxidation of β-methylhomoallylic alcohols and the subsequent alkylative opening of epoxide rings were utilized as key steps.

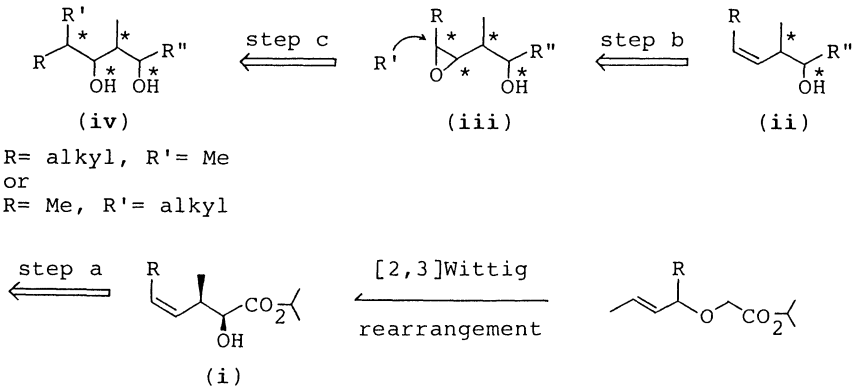
Consecutive asymmetric centers with methyl and hydroxyl groups arranged in an alternating way on an acyclic carbon chain has frequently appeared in some classes of acetogenins such as macrolides and polyethers, reflecting the incorporation of propionate in their biosynthetic route.

Efforts devoted to the total syntheses of these natural products have promoted the development of many useful methodologies for acyclic stereocontrol including those for consecutive asymetric centers.[1] For example, related to their first total synthesis of rifamycin S which bore eight consecutive asymmetric carbon atoms of the above type in its *ansa* chain part,[2] Kishi et al. have developed two different methodologies for the construction of three consecutive asymmetric centers, which could lead to the selective preparation of any diastereomer out of possible four.[2c,3] Though the *ansa* chain part of rifamycin S was then successively synthesized by different groups by different stereoselective methodologies,[4] their interest was mainly focused on the particular configuration of the above *ansa*-macrolide, and no methodology which enabled the stereocontrolled construction of any desired configuration of four or more consecutive asymmetric centers has been reported until recently when Stork et al. have described a general approach to the stereoselective construction of contiguous chiral carbons via butenolide intermediates.[5,6]

The present authors have also communicated recently a new general approach to the stereoselective construction of four consecutive asymmetric centers, where eight diastereomers of 5,7-dimethyl-6,8-tridecanediol have been chosen as model targets.[7] Full details of the study will be described here.

Results and Discussion

The basic strategy is represented by Scheme 1 in retrosynthetic manner. The most crucial step in this approach was the stereocontrolled epoxidation of homoallylic alcohols (step b) and much consideration was given to this point in connection with the choice of starting materials. Although *trans*- as well as *cis*-β-methylhomoallylic alcohols were considered to serve as the possible starting materials in principle, the author adopted the cis compounds from the following reasons: i) Sato et al. recently reported that the epoxidation of β-methyl-*trans*-homoallylic alcohols exhibited poor diastereoselection.[8] ii) Kinoshita et al. reported that the reaction of hydroxyl-protected β-methyl-γ,δ-*cis*-epoxy alcohol derivatives with 2-lithio-1,3-dithiane proceeded with high regioselectivity, while the corresponding trans-epoxy compounds showed poor regioselectivity.[9] iii) The starting β-



Scheme 1.

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methyl-*cis*-homoallylic alcohols (**ii**) were considered to be derived from γ,δ-unsaturated α-hydroxy-β-methyl carboxylic acid (**i**) which was easily obtained by [2,3]Wittig rearrangement of *trans*-alkenyloxyacetic acid ester.[10]

For the epoxidation of β-methyl-*cis*-homoallylic alcohols, Mihelich et al. have already shown that a $VO(acac)_2$-*t*-butyl hydroperoxide (TBHP) system generally gave epoxides *anti* to the β-methyl group with high diastereoselectivity.[11] The remaining problem was, therefore, the *syn*-selective epoxidation of the same substrate. The *cis*-homoallylic alcohol of this type is considered to take preferred conformation with the β-hydrogen atom in the plane of the double bond as depicted by Fig. 1. Therefore, if the hydroxyl group was protected with a bulky protective group to shield the top face of the double bond and if a bulky and poorly oxygenophilic epoxidizing agent was chosen, the reagent would be forced to approach the double bond from its bottom face, giving the desired *syn*-selectivity. This was realized as described below by a combination of *O*-triisopropylsilylation and WO_5-HMPA oxidation.

The next problem was the opening of the epoxide rings (step c) by methylation or butylation to work out the remaining two chiral centers with desired regio- and stereochemistry. It was recognized that regiochemistry in this reaction was quite dependent on reaction conditions and substrates, and in the present study also, much elaboration had been required until optimum conditions for each substrate were obtained.

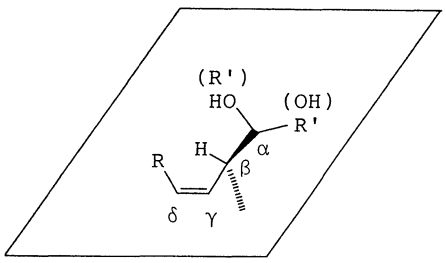
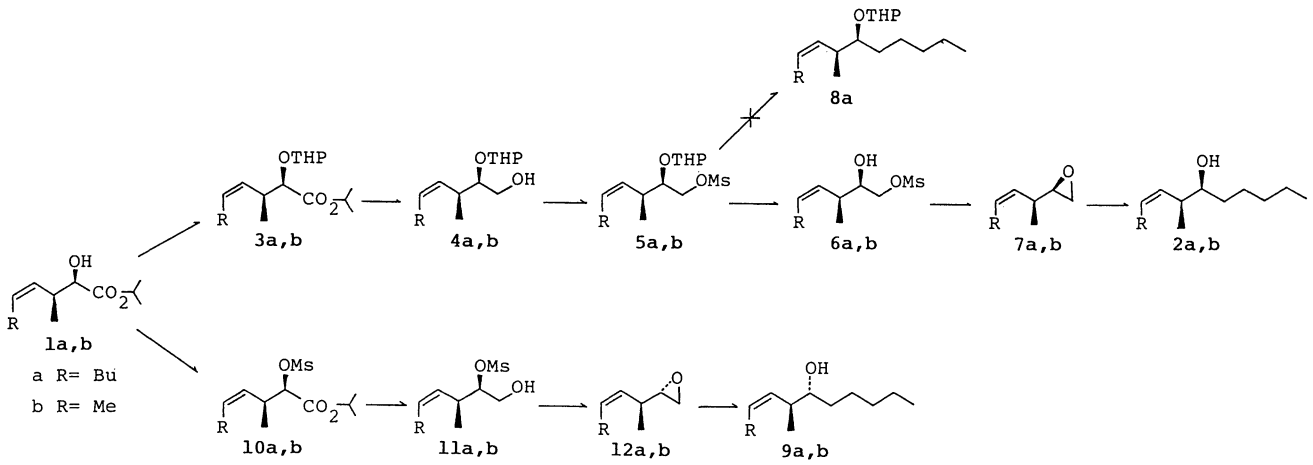


Fig. 1.

Preparation of β-Methyl-*cis*-homoallylic Alcohols. The preparation of *syn*-β-methylhomoallylic alcohols (**2a** and **2b**) proceeded uneventfully by conventional methodology as described below (Scheme 2). [2,3]-Wittig rearrangement product (**1a**) was first converted to the corresponding THP ether (**3a**)[12] in 94% yield. Compound (**3a**) was then reduced by $LiAlH_4$ and the resulting alcohol (**4a**) was treated with methanesulfonyl chloride and triethylamine to give the methanesulfonate (**5a**) in 69% yield. As the replacement of the methanesulfonyloxyl group by a butyl group by using $LiCuBu_2$ or LiBu failed, an indirect method was adopted. The sulfonate (**5a**) was converted to the epoxide (**7a**) in 95% yield by treatment with a catalytic amount of *p*-toluenesulfonic acid in methanol, followed by cyclization of the resulting hydroxy methanesulfonate (**6a**) with aqueous NaOH. The reaction of the epoxide (**7a**) with $LiCuBu_2$ at −20 °C proceeded smoothly to give the desired *syn*-homoallylic alcohol (**2a**) in 81% yield. Another (*Z*)-homoallylic alcohol (**2b**) was also prepared from **1b** in the same manner except that the volatile epoxide (**7b**) was used for the next reaction without purification, as a pentane extract of the reaction mixture.

Next, **1a** and **1b** were transformed into the α,β-*anti*-β-methyl-*cis*-homoallylic alcohols (**9a** and **9b**), with the inversion of stereochemistry at the α-carbon atom. This time, **1a** was first converted to the methanesulfonate (**10a**) in 83% yield. Reduction of **10a** with $LiAlH_4$ followed by Fisher's work up[13] gave a mixture of the alcohol (**11a**) and the anti-epoxide (**12a**) in 61% and 34% yields, respectively. Compound (**12a**) is considered to be partly formed from **11a** during the work-up under basic conditions. Treatment of **11a** with aqueous KOH gave **12a** in 81% yield. Butylation of **12a** with $LiCuBu_2$ gave α,β-*anti*-β-methyl-*cis*-homoallylic alcohol (**9a**) in 82% yield. No contamination with *syn*-homoallylic alcohol (**2a**) was detected in the product. Compound (**1b**) was also transformed into **9b** in the same manner as described for **9a** except



Scheme 2.

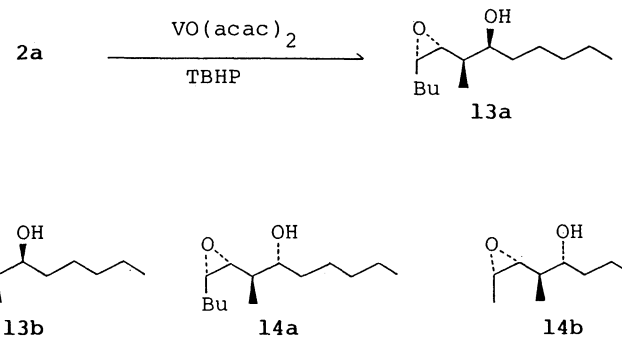
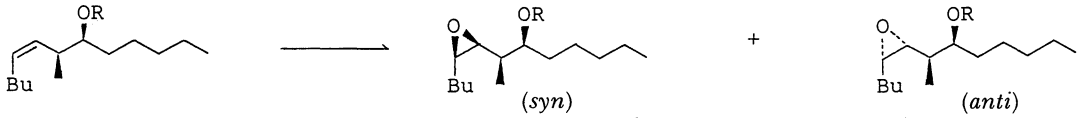


Fig. 2.

Table 1. Epoxidation of Silyl Ether Derivatives of Homoallylic Alcohols



15a R=*t*-BuMe$_2$Si
18a R=Et$_3$Si
19a R=*i*-Pr$_3$Si

16a R=*t*-BuMe$_2$Si
20a R=*i*-Pr$_3$Si

17a R=*t*-BuMe$_2$Si
21a R=*i*-Pr$_3$Si

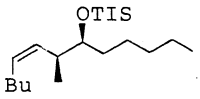
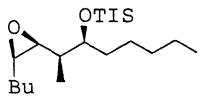
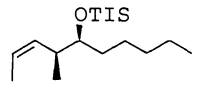
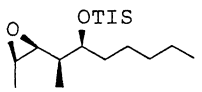
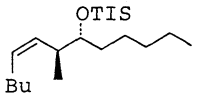
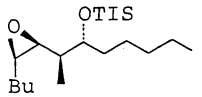
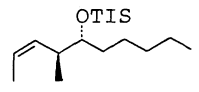
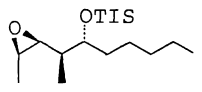
Substrate	Oxidizing agent	*syn* : *anti*
15a	MoO_5·HMPA	5 1
15a	WO_5·HMPA	5.5 1
18a	WO_5·HMPA	—
19a	WO_5·HMPA	10.8 1

that the intermediary epoxide (**12b**) was used for the next reaction without purification because of its high volatility.

Epoxidation of *cis*-Homoallyulic Alcohols. The *cis*-homoallylic alcohols (**2a**, **2b**, **9a**, and **9b**) thus obtained was first converted to *β,γ-anti-β*-methyl-*γ,δ-cis*-epoxy alcohols (**13a**, **13b**, **14a**, and **14b**), respectively, by using Mihelich procedure.[11] In all these cases, the epoxidation proceeded smoothly with high *anti*-selectivity (>30 : 1) and good yields (Fig. 2).

Then, our efforts were directed to *syn*-selective epoxidation of the same substrates (**2a**, **2b**, **9a**, and **9b**) as mentioned above. On considering the conformation represented by Fig. 1, these compounds were modified with trialkylsilyl protecting groups. The epoxidation of the *t*-butyldimethylsilyl (TBDMS) ether (**15a**) was first examined. The reaction with $MoO_2(acac)_2$-TBHP system did not give the desired product but only the deprotected compound (**2a**) was obtained.[14] On the other hand, the treatment of **15a** with MoO_5·HMPA and with WO_5·HMPA[15] in 1,2-dichloroethane at room temperature gave the *syn*-epoxide (**16a**) as the major isomer in a ratio of 5 : 1 and in a ratio of 5.5 : 1, respectively (Table 1). The low reaction temperature (0 °C) did not improve the diastereoselectivity. The triethylsilyl (TES) ether protection (**18a**) was cleaved under the reaction conditions using MoO_5·HMPA or WO_5·HMPA. Then, **2a** was protected with more stable and more bulky triisopropylsilyl (TIS) group.[16] The reaction of the TIS ether

Table 2. *Syn*-Selective Epoxidation of Triisopropylsilyl Ethers of *β*-Methylhomoallylic Alcohols

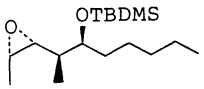
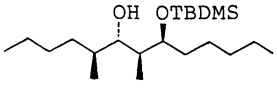
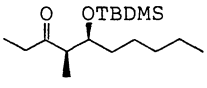
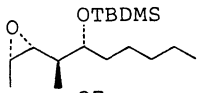
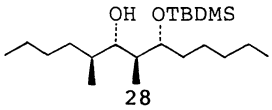
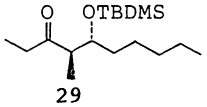
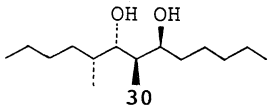
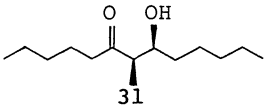
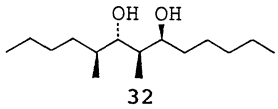
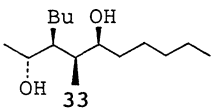
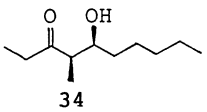
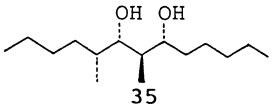
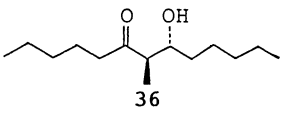
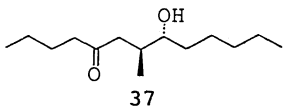
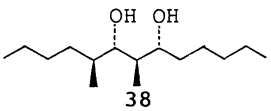
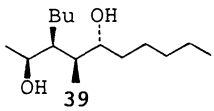
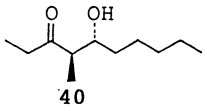
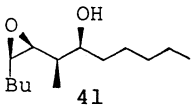
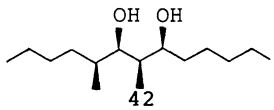
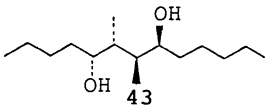
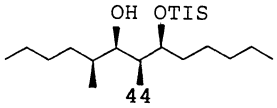
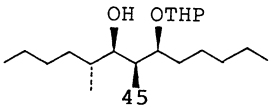
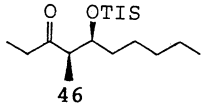
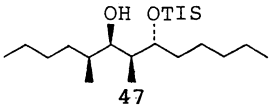
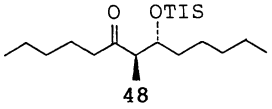
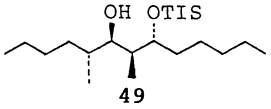
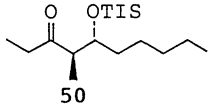
Substrate	The major epoxy silyl ether	Yield/%	Selectivity
 **19a**	 **20a**	80	10.8 : 1
 **19b**	 **20b**	89	16.7 : 1
 **22a**	 **23a**	74	8.2 : 1
 **22b**	 **23b**	67	7.4 : 1

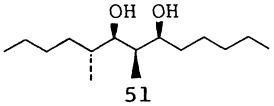
(**19a**) and WO_5·HMPA in dichloroethane at room temperature proceeded smoothly with high *syn*-selectivity (10.8 : 1) and good chemical yield. The results are shown in Table 2 together with the examples of other three TIS ethers (**19b**, **22a**, and **22b**). The resulting *syn*-epoxy silylethers (**20a**, **20b**, **23a**, and **23b**) were easily purified by column chromatography.

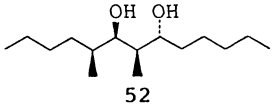
Thus, all the possible diastereomers of γ,δ-*cis*-epoxy-β-methyl alcohol were obtained stereoselectively in the form of free alcohols (*anti*-epoxide series) or of corresponding TIS ethers (*syn*-epoxide series).

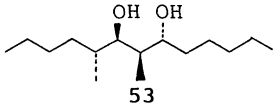
Regioselective Alkylation of γ,δ-*cis*-Epoxy Alcohols and Their Silyl Ethers. With these epoxy alcohols (**13a**, **13b**, **14a**, and **14b**) and epoxy silylethers (**20a**, **20b**, **23a**, and **23b**) in hand, our attention was

Table 3. Opening of γ,δ-*cis*-Epoxy Alcohols and Their Silyl Ethers

Entry	Substrate	Temp	Yield/% 1,3-Diol	1,4-Diol	Hydroxy ketone
1	 24	rt	 25 (80)		 26 (19)
2	 27	rt	 28 (46)		 29 (49)
3	**13a**	rt	 30 (78)		 31 (14)
4	**13b**	rt	 32 (55)	 33 (8)	 34 (4)
5	**14a**	rt	 35 (72)		 36
					 37 (18)
6	**14b**	rt	 38 (56)	 39 (4)	 40 (7)
7	 41	rt	 42 (26)	 43 (58)	
8	**20a**	reflux (THF)	 44 (45)		
9	**20b**	rt	 45 (78)		 46 (6)
10	**23a**	reflux (THF)	 47 (59)		 48 (16)
11	**23b**	rt	 49 (88)		 50 (1)

 51

 52

 53

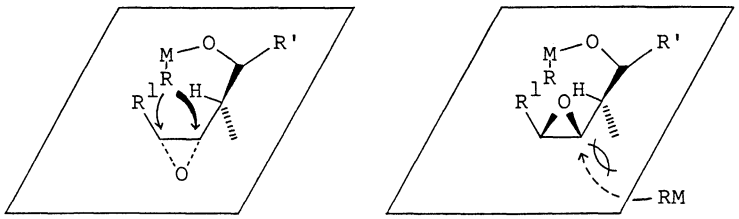


Fig. 3.

next focused on the regioselective opening of epoxide rings giving the desired 1,3-diols.

Sato et al., recently reported that the reaction of the trimethylsilyl ether of γ-trimethylsilyl-γ,δ-*trans*-epoxy-β-methyl alcohol with vinylmagnesium bromide in the presence of copper(I) iodide gave a 1,3-diol highly regioselectively, whereas the same epoxy alcohol without protection gave a mixture of 1,3- and 1,4-diols.[8] Therefore, we first examined the ring-opening reaction of the hydroxyl-protected epoxy alcohol (**24**) with 2-lithio-1,3-dithiane according to Kinoshita's procedure.[9] However **24** did not react even under the forced conditions. The alkylation of the same substrate using cuprates or alkyl metal-Lewis acid systems also failed.[17] Only the higher order mixed cuprate in ether[18] was found to be effective for the regio- and stereoselective ring opening. However, the reaction at 0 °C was slow and the yield of **25** was unsatisfactory (57%). At 20 °C, the undesired ketone (**26**, 15%) was formed as a by-product besides the desired **25** (60%), though the starting material was entirely consumed. As this undesired epoxy-ketone rearrangement was considered to be brought about by Lewis acidic lithium ion, we examined various additives in order to suppress the effect of the lithium ion and found that the addition of tributylphosphine could improve the yield of **25** up to 80%, though a considerable amount (19%) of **26** was still formed (Table 3, entry 1). Unlike **24**, treatment of diastereomeric **27** with $Li_2Cu(CN)Bu_2$ even in the presence of tributylphosphine gave the undesired ketone (**29**) as a major product (49%) together with the 1,3-diol derivative (**28**, 46%). Then we examined the direct alkylation of the parent, OH-nonprotected epoxy alcohols (**13a**, **13b**, **14a**, and **14b**). Treatment of **13a** with $Li_2Cu(CN)Me_2$ at room temperature gave the 1,3-diol (**30**) as a major product (78%) with the formation of a small amount of the ketone (**31**, 14%) (entry 3), unlike the alkylation of *trans*-epoxy alcohol.[8] Other three β,γ-*anti*-epoxy alcohols (**13b**, **14a**, and **14b**) were also converted in the same manner to the corresponding 1,3-diols (**32**, **35**, and **38**) in good yields, though a small amount of respective 1,4-diols and ketones were formed (entries 4, 5, and 6).

In the series of β,γ-*syn*-epoxy alcohols, however, nonprotected forms gave poor regioselectivity, as exemplified by the reaction of the epoxy alcohol (**41**) where the undesired 1,4-diol (**43**) was the predominant product (entry 7). When the corresponding triisopropylsilyl (TIS) ethers (**20a**, **20b**, **23a**, and **23b**) were used as substrates (entries 8—11), 1,3-diol derivatives became the almost exclusive products and the formation of regioisomeric 1,4-diols were not observed. Among these compounds, **20a** and **23a** having terminal butyl group were reluctant to react with $Li_2Cu(CN)Me_2$ at room temperature, and the alkylative opening was effected at an elevated temperature in THF, though the appreciable amount of starting materials (**20a**, 54%; **23a**, 19%) were recovered.

The difference in the regioselectivity of epoxide-ring opening between non-protected *anti*- and *syn*-epoxy alcohols may be explained as follows. In both cases, the hydrogen atom at the β-position is considered to be synperiplanar to the δ-substituent (R^1) to minimize the steric repulsion between R^1 and substituent at the β-carbon atom and, therefore, *syn*- and *antio*-epoxy alcohols are considered to take the preferred conformation **A** and **B**, respectively, as depicted in Fig. 3. In the conformer **A**, the nucleophile anchored to alkoxide anion can attack the proximate γ-carbon atom in an intramolecular fashion, leading to the undesired 1,4-diol. In the conformer **B**, however, the anchored nucleophile can not attack either epoxy carbon in an intramolecular fashion. The intermolecular attack of the nucleophile at the γ-carbon atom was also disturbed by an eclipsing interaction of the approaching nucleophile with β-methyl group, and therefore the attack at the δ-carbon atom leading to 1,3-diols is preferred.

The monosilyl ethers (**25**, **44**, **45**, **47**, and **49**) obtained here were easily hydrolyzed to the corresponding 1,3-diols (**32**, **42**, **51**, **52**, and **53**), respectively, by treatment with *n*-Bu_4NF in THF at room temperature. Thus, stereoselective synthesis of all the possible eight diastereomers (**30**, **32**, **35**, **38**, **42**, **51**, **52**, and **53**) of 5,7-dimethyltridecane-6,8-diol were successfully attained.

Experimental

Melting points are uncorrected. ^1H NMR spectra were recorded with JEOL JNM GX400 spectrometer in $CDCl_3$ using TMS as the internal standard. IR spectra were recorded on Hitachi 260-10 infrared spectrophotometer.

Isopropyl (2*R,3*S**,4*Z*)-2-(2-Tetrahydropyranyloxy)-3-**

methyl-4-nonenoate (3a). A solution of isopropyl (2*R**, 3*S**,4*Z*)-2-hydroxy-3-methyl-4-nonenoate[10] (**1a**, 144.9 mg) in CH_2Cl_2 (5 ml) was treated with dihydropyran (120 μl) and a catalytic amount of pyridinium *p*-toluenesulfonate.[12] The mixture was stirred overnight under nitrogen atmosphere at room temperature. The solution was concentrated under vacuum and chromatographed on silica gel with hexane-ethyl acetate (20 : 1), giving the product (**3a**, 191.9 mg, 93%) as an oil.

Found: C, 69.16; H, 10.23%. Calcd for $C_{18}H_{32}O_4$: C, 69.19; H, 10.32%.

(2*R,3*S**,4*Z*)-2-(2-Tetrahydropyranyloxy)-3-methyl-4-nonen-1-ol (4a).** A solution of $LiAlH_4$ in THF (1 mol dm^{-3}, 675 μl) was added to a solution of **3a** (191.9 mg) in dry THF (4 ml) at 0 °C. After stirring for 10 min at the same temperature, the reaction mixture was carefully quenched according to the Fisher's procedure.[13] The resulting solution was filtered through Celite and evaporated in vacuo to give 164.9 mg of the crude product, which was used in the next reaction without purification.

(2*R,3*S**,4*Z*)-2-(2-Tetrahydropyranyloxy)-3-methyl-4-nonennyl Methanesulfonate (5a).** The crude alcohol (**4a**, 164.9 mg) in CH_2Cl_2 (5 ml) was treated with methanesulfonyl chloride (64.6 μl) and triethylamine (125 μl), and the solution was stirred at room temperature for 1 h. The mixture was filtered, concentrated, and chromatographed over silica gel with hexane-ethyl acetate (10 : 1) to give the methanesulfonate (**5a**, 142.6 mg, 69% from **3a**).

Found: C, 57.32; H, 8.95%. Calcd for $C_{16}H_{31}O_5S$: C, 57.28; H, 9.31%.

(2*R,3*S**,4*Z*)-1,2-Epoxy-3-methyl-4-nonene (7a).** A solution of **5a** (142.6 mg) in methanol (3 ml) containing a catalytic amount of *p*-toluenesulfonic acid was stirred at room temperature for 10 min. Ether and water were added to the reaction mixture. The organic layer was separated and concentrated to give the corresponding alcohol (**6a**) which was used for the following reaction without purification. Aqueous NaOH (2.138 mol dm^{-3}, 260 μl) was added to a solution of **6a** in methanol (3 ml). After 1 h, the mixture was extracted with ether with the addition of water, and the extract was concentrated and chromatographed on silica gel with hexane-ether (20 : 1) to give **7a** (62.1 mg, 95%) as an oil; ^{1}H NMR δ=0.89 (t, 3H, *J*=6.8 Hz), 1.09 (d, 3H, *J*=6.8 Hz), 1.25—1.35 (m, 4H), 2.00—2.10 (m, 2H), 2.30—2.40 (m, 1H), 2.52 (dd, 1H, *J*=2.4 and 4.9 Hz), 2.72 (dd, 1H, *J*=3.9 and 4.9 Hz), 2.75—2.80 (m, 1H), 5.22 (dd, 1H, *J*=9.8 and 11.2 Hz), 5.44 (dt, 1H, *J*=7.3 and 11.2 Hz).

Found: C, 77.68; H, 11.61%. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76%.

(6*R,7*R**,8*Z*)-7-Methyl-8-tridecen-6-ol (2a).** To an ethereal solution of lithium dibutylcuprate (8.42 mmol) at −20 °C was added an ethereal solution of the epoxide (**7a**, 1.08 g) at −20 °C. The reaction was run overnight at the same temperature and then quenched by the addition of a mixture of saturated aqueous NH_4Cl and concd aqueous ammonia (9 : 1, 40 ml). After stirring for 30 min at room temperature, the mixture was extracted with ether, and the extract was dried over Na_2SO_4 and concentrated in vacuo, yielding an oil that was chromatographed on silica gel with hexane-ethyl acetate (20 : 1) to afford **2a** (1.21 g, 81%) as an oil; ^{1}H NMR δ=0.89 (t, 3H, *J*=6.8 Hz), 0.90 (t, 3H, *J*=6.8 Hz), 0.99 (d, 3H, *J*=6.8 Hz), 1.20—1.40 (m, 10H), 1.40—1.60 (m, 3H), 2.00—2.10 (m, 2H), 2.50—2.60 (m, 1H), 3.35—3.40 (m, 1H), 5.20 (ddt, 1H, *J*=9.8 and 11.2 Hz), 5.41 (ddt, 1H, *J*=7.3 and 11.2 Hz).

Found: C, 78.89; H, 13.25%. Calcd for $C_{14}H_{28}O$: C, 79.18; H, 13.29%.

Isopropyl (2*R,3*S**,4*Z*)-2-(2-Tetrahydropyranyloxy)-3-methyl-4-hexenoate (3b).** The compound was prepared from isopropyl (2*R**,3*S**,4*Z*)-2-hydroxy-3-methyl-4-hexenoate (**1b**)[10] in a similar manner to that described for **3a**. Yield: 92%.

Found: C, 66.50; H, 9.54%. Calcd for $C_{15}H_{26}O_4$: C, 66.64; H, 9.69%.

(2*R,3*S**,4*Z*)-2-(2-Tetrahydropyranyloxy)-3-methyl-4-hexenyl Methanesulfonate (5b).** The compound was prepared from **3b** in a similar manner to that described for **5a**. Overall yield: 91%.

Found: C, 53.68; H, 8.15%. Calcd for $C_{11}H_{20}O_5S$: C, 53.40; H, 8.27%.

(2*R,3*S**,4*Z*)-2-Hydroxy-3-methyl-4-hexenyl Methanesulfonate (6b).** A solution of **5b** (2.32 g) in MeOH (10 ml) containing a catalytic amount of *p*-toluenesulfonic acid was stirred for 1 h. To the solution was added a small amount of triethylamine and the mixture was concentrated. The residue was chromatographed on silica gel with hexane-ethyl acetate (1 : 1) to give **6b** (1.53 g, 93%) as an oil; ^{1}H NMR δ=1.07 (d, 3H, *J*=6.8 Hz), 1.64 (dd, 3H, *J*=2.0 and 6.8 Hz), 2.27 (br s, 1H), 2.60—2.70 (m, 1H), 3.05 (s, 3H), 3.65 (ddd, 1H, *J*=2.4, 7.3, and 8.3 Hz), 4.11 (dd, 1H, *J*=7.3 and 10.3 Hz), 4.32 (dd, 1H, *J*=2.4 and 10.3 Hz), 5.18 (ddq, 1H, *J*=2.0, 8.3, and 10.7 Hz), 5.55 (ddq, 1H, *J*=2.0, 6.4, and 10.7 Hz).

(2*Z*,4*R,5*R**)-4-Methyl-2-decen-5-ol (2b).** To a mixture of a solution of **6b** (1.408 g) in pentane (15 ml) and water (8 ml) was added aqueous KOH (1 mol dm^{-3}, 7.4 ml). After the solution was stirred vigorously for 1 h, the organic layer was separated, dried over alumina, and concentrated carefully at atmospheric pressure to a small bulk. To an ethereal solution of lithium dibutylcuprate (13.4 mmol) was added at −20 °C the above concentrate which contained the epoxide (**7b**) formed. The reaction was run overnight at this temperature and the mixture was worked up in the usual manner to give, after chromatography on silica gel with hexane-ethyl acetate (4 : 1), **2b** (775 mg, 67%) as an oil; ^{1}H NMR δ=0.89 (t, 3H, *J*=6.8 Hz), 0.99 (d, 3H, *J*=6.8 Hz), 1.20—1.60 (m, 9H), 1.64 (dd, 3H, *J*=1.5 and 6.8 Hz), 2.50—2.60 (m, 1H), 3.35—3.45 (m, 1H), 5.24 (ddq, 1H, *J*=1.5, 9.8, and 10.7 Hz), 5.51 (dq, 1H, *J*=6.8 and 10.7 Hz).

Found: C, 77.34; H, 12.95%. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02%.

Isopropyl (2*R,3*S**,4*Z*)-2-Methylsulfonyloxy-3-methyl-4-nonenoate (10a).** Triethylamine was added dropwise to a solution of the ester (**1a**, 160.9 mg) and methanesulfonyl chloride (70.9 μl) in CH_2Cl_2 (5 ml) and the mixture was stirred at room temperature for 1 h. Filtration followed by removal of solvent and chromatography on silica gel with hexane-ethyl acetate (30 : 1) gave the methanesulfonate (**10a**, 179.0 mg, 83%) as an oil; ^{1}H NMR δ=0.90 (t, 3H, *J*=6.8 Hz), 1.05 (d, 3H, *J*=6.8 Hz), 1.28 (d, 3H, *J*=5.9 Hz), 1.29 (d, 3H, *J*=5.9 Hz), 1.30—1.40 (m, 5H), 2.00—2.10 (m, 1H), 3.11 (s, 3H), 3.10—3.20 (m, 1H), 4.77 (d, 1H, *J*=5.4 Hz), 5.10 (m, 1H, *J*=5.9 Hz), 5.27 (ddt, 1H, *J*=2.0, 9.8, and 10.7 Hz), 5.48 (ddt, 1H, *J*=1.0, 7.8, and 10.7 Hz).

Found: C, 54.87; H, 8.27%. Calcd for $C_{14}H_{26}O_5S$: C, 54.88; H, 8.55%.

(2*R,3*S**,4*Z*)-2-Methylsulfonyloxy-3-methyl-4-nonen-1-ol**

(11a). A solution of $LiAlH_4$ in THF (1 mol dm^{-3}, 760 μl) was added to a solution of **10a** (179.0 mg) in dry THF (4 ml) at 0 °C. After stirring for 10 min at the same temperature, the reaction mixture was carefully quenched according to the Fisher's procedure. The resulting solution was filtered through Celite and evaporated in vacuo to give a mixture of two compounds as an oil. The mixture was chromatographed on silica gel first with hexane-ether (20 : 1) to give the epoxide (**12a**, 30.8 mg, 34%) and then with hexane-ethyl acetate (1 : 1) to give the alcohol (**11a**, 89.5 mg, 61%).

Found: C, 52.86; H, 9.03%. Calcd for $C_{11}H_{22}O_4S$: C, 52.77, H, 8.85%.

(2*R,3*R**,4*Z*)-1,2-Epoxy-3-methyl-4-nonene (12a).** Aqueous KOH (1 mol dm^{-3}, 7.24 ml) was added to a solution of **11a** (1.510 g) in MeOH (15 ml). After the solution was stirred for 1 h at room temperature, water and ether were added to the mixture. The separated organic layer was dried over Na_2SO_4, concentrated in vacuo, and chromatographed on silica gel with hexane-ether (20 : 1) to give **12a** (753 mg, 81%) as an oil; ^{1}H NMR δ=0.89 (t, 3H, J=5.4 Hz), 1.01 (d, 3H, J=7.3 Hz), 1.20—1.40 (m, 4H), 2.03 (m, 2H), 2.54 (dd, 1H, J=2.9 and 4.9 Hz), 2.58 (m, 1H), 2.70 (dd, 1H, J=3.9 and 4.9 Hz), 2.85 (ddd, 1H, J=2.4, 3.9, and 4.9 Hz), 5.19 (ddt, 1H, J=1.5, 9.3, and 10.7 Hz), 5.45 (ddt, 1H, J=1.0, 7.3, and 10.7 Hz).

Found: C, 77.60; H, 11.68%. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76%.

(6*R,7*S**,8*Z*)-7-Methyl-8-tridecen-6-ol (9a).** The compound was prepared from **12a** in a similar manner to that described for **2a**. Yield: 82%.

An oil; ^{1}H NMR δ=0.89 (t, 3H, J=6.8 Hz), 0.90 (t, 3H, J=6.8 Hz), 0.96 (d, 3H, J=6.8 Hz), 1.20—1.60 (m, 14H), 2.00—2.10 (m, 2H), 3.25—3.35 (m, 1H), 5.22 (dd, 1H, J=10.3 and 11.2 Hz), 5.53 (dt, 1H, J=7.8 and 11.2 Hz).

Found: C, 78.97; H, 13.25%. Calcd for $C_{14}H_{28}O$: C, 79.18; H, 13.29%.

Isopropyl (2*R,3*S**,4*Z*)-2-Methylsulfonyloxy-3-methyl-4-hexenoate (10b).** The compound was prepared from **1b** in a similar manner to that described for **10a**. Yield: 87%.

An oil; ^{1}H NMR δ=1.05 (d, 3H, J=6.8 Hz), 1.27 (d, 3H, J=6.3 Hz), 1.28 (d, 3H, J=6.3 Hz), 1.65 (dd, 3H, J=1.5 and 6.8 Hz), 3.11 (s, 3H), 3.10—3.20 (m, 1H), 4.78 (d, 1H, J=5.4 Hz), 5.05—5.15 (m, 1H), 5.30 (ddq, 1H, J=1.5, 9.8, and 10.7 Hz), 5.58 (ddq, 1H, J=1.0, 6.8, and 10.7 Hz).

Found: C, 49.92; H, 7.58%. Calcd for $C_{11}H_{20}O_5S$: C, 49.98; H, 7.63%.

(2*R,3*S**,4*Z*)-2-Methylsulfonyloxy-3-methyl-4-hexen-1-ol (11b).** A solution of $LiAlH_4$ in THF (1 mol dm^{-3}, 97 μl) was added to a solution of **10b** (23.4 mg) in dry THF (2 ml) at 0 °C. After stirring for 10 min, aqueous HCl (2 mol dm^{-3}, 60 μl) was carefully added to the reaction mixture. The mixture was extracted with ether and the extract was dried over Na_2SO_4, concentrated, and chromatographed on silica gel with hexane-ethyl acetate (1 : 1) to give **11b** (18.3 mg, 99%) as an oil; ^{1}H NMR δ=1.08 (d, 3H, J=6.8 Hz), 1.65 (dd, 3H, J=2.0 and 6.8 Hz), 2.06 (br s, 1H), 2.80—2.95 (m, 1H), 3.12 (s, 3H), 3.71 (dd, 1H, J=7.3 and 12.7 Hz), 3.87 (dd, 1H, J=2.7 and 12.7 Hz), 4.50—4.60 (m, 1H), 5.20 (ddq, 1H, J=2.0, 9.8, and 10.7 Hz), 5.57 (dq, 1H, J=6.8 and 10.7 Hz).

Found: C, 45.77; H, 7.69%. Calcd for $C_8H_{16}O_4S$: C, 46.14; H, 7.74%.

(2*Z*,4*R,5*S**)-4-Methyl-2-decen-5-ol (9b).** The compound was prepared from **11b** in a similar manner to that described for **2b**. Yield: 52%.

An oil; ^{1}H NMR δ=0.89 (t, 3H, J=6.8 Hz), 0.96 (d, 3H, J=6.8 Hz), 1.20—1.60 (m, 9H), 1.65 (dd, 3H, J=2.0 and 6.8 Hz), 2.45—2.60 (m, 1H), 3.30—3.40 (m, 1H), 5.26 (ddq, 1H, J=2.0, 9.8, and 10.7 Hz), 5.61 (dq, 1H, J=6.4 and 10.7 Hz).

Found: C, 77.21; H, 12.94%. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02%.

(6*R,7*S**,8*S**,9*R**)-8,9-Epoxy-7-methyl-6-tridecanol (13a).** To a solution of **2a** (69.8 mg) in dry CH_2Cl_2 (3.5 ml) containing oxobis(2,4-pentanedionato)vanadium(IV) (1.7 mg, 2 mol%) was added an anhydrous *t*-butyl hydroperoxide solution (6.15 mol dm^{-3}, 80 μl) in dichloroethane at −20 °C. The mixture was gradually warmed to room temperature and stirred overnight. After a small amount of Me_2S was added, the mixture was concentrated in vacuo to give an oily residue. Chromatography on silica gel with hexane-ethyl acetate (9 : 1) gave **13a** (63.6 mg, 85%) as an oil; ^{1}H NMR δ=0.89 (t, 3H, J=6.8 Hz), 0.93 (t, 3H, J=7.3 Hz), 0.96 (d, 3H, J=7.3 Hz), 1.20—1.70 (m, 15H), 1.80 (br s, 1H), 2.89 (dd, 1H, J=4.4 and 9.3 Hz), 2.90—3.00 (m, 1H), 3.65—3.75 (m, 1H).

Found: C, 73.29; H, 12.13%. Calcd for $C_{14}H_{28}O_2$: C, 73.63; H, 12.36%.

(2*R,3*S**,4*S**,5*R**)-2,3-Epoxy-4-methyl-5-decanol (13b).** The compound was prepared from **2b** in a similar manner to that described for **13a**. Yield: 81%.

An oil; ^{1}H NMR δ=0.89 (t, 3H, J=6.8 Hz), 0.96 (d, 3H, J=6.8 Hz), 1.29 (d, 3H, J=5.4 Hz), 1.20—1.40 (m, 6H), 1.40—1.60 (m, 3H), 1.90 (br s, 1H), 2.88 (dd, 1H, J=4.4 and 9.3 Hz), 3.10 (dq, 1H, J=4.4 and 5.4 Hz), 3.65—3.75 (m, 1H).

Found: C, 70.78; H, 11.81%. Calcd for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90%.

(6*R,7*R**,8*R**,9*S**)-8,9-Epoxy-7-methyl-6-tridecanol (14a).** The compound was prepared from **9a** in a similar manner to that described for **13a**. Yield: 95%.

An oil: ^{1}H NMR δ=0.88 (t, 3H, J=6.8 Hz), 0.93 (t, 3H, J=6.8 Hz), 0.95 (d, 3H, J=7.3 Hz), 1.20—1.65 (m, 15H), 2.51 (br s, 1H), 2.86 (dd, 1H, J=4.4 and 9.3 Hz), 2.90—3.00 (m, 1H), 3.60—3.70 (m, 1H).

Found: C, 73.51; H, 12.21%. Calcd for $C_{14}H_{28}O_2$: C, 73.63; H, 12.36%.

(2*R,3*S**,4*S**,5*S**)-2,3-Epoxy-4-methyl-5-decanol (14b).** The compound was prepared from **9b** in a similar manner to that described for **13a**. Yield: 94%.

An oil; ^{1}H NMR δ=0.90 (t, 3H, J=6.8 Hz), 0.95 (d, 3H, J=6.8 Hz), 1.30 (d, 3H, J=5.9 Hz), 1.20—1.80 (m, 9H), 2.40 (br s, 1H), 2.86 (dd, 1H, J=4.4 and 9.8 Hz), 3.05 (dq, 1H, J=4.4 and 5.9 Hz), 3.65—3.75 (m, 1H).

Found: C, 70.69; H, 11.83%. Calcd for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90%.

(2*Z*,4*R,5*R**)-4-Methyl-5-triisopylsiloxy-2-decene (19b).** Triisopropylsilyl triflate (128 μl) and 2,6-lutidine (110 μl)[16] were added at room temperature to a solution of **2b** (64.1 mg) in dry CH_2Cl_2 (1 ml). The mixture was stirred for 1 h at room temperature, and concentrated in vacuo. Column chromatography of the residue with hexane gave the corresponding TIS ether (**19b**, 89.0 mg, 73%) as an oil; ^{1}H NMR δ=0.89 (t, 3H, J=6.8 Hz), 0.94 (d, 3H, J=6.8 Hz), 1.00—1.15 (m, 21H), 1.20—1.60 (m, 8H), 1.61 (d, 3H, J=4.9 Hz), 2.55—2.65 (m, 1H), 3.70 (dt, 1H, J=4.9 and 6.3 Hz), 5.30—5.45 (m, 2H).

Found: C, 73.40; H, 13.00%. Calcd for $C_{20}H_{42}OSi$: C, 73.54; H, 12.96%.

(6*R,7*R**,8*Z*)-7-Methyl-6-triisopropylsiloxy-8-tridecene**

(19a). The compound was prepared from **2a** in a similar manner to that described for **19b**. Yield: 76%.

An oil; ^{1}H NMR δ=0.85—0.92 (m, 6H), 0.93 (d, 3H, J=6.4 Hz), 0.96—1.20 (m, 21H), 1.20—1.60 (m, 12H), 2.00—2.10 (m, 2H), 2.50—2.60 (m, 1H), 3.68 (dt, 1H, J=4.9 and 6.4 Hz), 5.25—5.40 (m, 2H).

Found: C, 74.77; H, 13.01%. Calcd for $C_{23}H_{48}OSi$: C, 74.92; H, 13.12%.

(6*R,7*S**,8*Z*)-7-Methyl-6-triisopropylsiloxy-8-tridecene (22a).** The compound was prepared from **9a** in a similar manner to that described for **19b**. Yield: 85%.

An oil; ^{1}H NMR δ=0.85—0.90 (m, 6H), 0.90—1.15 (m, 24H), 1.20—1.50 (m, 12H), 1.95—2.10 (m, 2H), 2.55—2.65 (m, 1H), 3.65—3.70 (m, 1H), 5.30—5.40 (m, 2H).

(2*Z*,4*R,5*S**)-4-Methyl-5-triisopropylsiloxy-2-decene (22b).** The compound was prepared from **9b** in a similar manner to that described for **19b**. Yield: 74%.

An oil; ^{1}H NMR δ=0.85—0.90 (m, 3H), 0.95—1.15 (m, 21H), 1.02 (d, 3H, J=5.9 Hz), 1.20—1.60 (m, 8H), 1.61 (dd, 3H, J=1.5 and 6.4 Hz), 2.60—2.70 (m, 1H), 3.70 (dt, 1H, J=3.4 and 6.4 Hz), 5.30—5.50 (m, 2H).

Found: C, 73.51; H, 12.82%. Calcd for $C_{20}H_{42}OSi$: C, 73.54; H, 12.96%.

(2*R,3*S**,4*S**,5*S**)-2,3-Epoxy-4-methyl-5-(triisopropylsiloxy)decane (20b).** A mixture of **19b** (7.1 mg) and WO_5-HMPA[14] (30 mg) in $ClCH_2CH_2Cl$ (500 µl) was stirred overnight at room temperature. After removal of the solvent in vacuo, the residue was dissolved in ether and filtered through a short silica-gel column to remove inorganic material. The filtrate was concentrated to give a mixture of two diastereomers in the ratio of 16.7:1. The mixture was chromatographed at medium pressure by using Lobar column, LiChroprep Si 60 supplied by E. Merck, with hexane-ethyl acetate (300:1) to give the epoxide (**20b**, 89%) as an oil in a pure form. ^{1}H NMR δ=0.88 (t, 3H, J=6.8 Hz), 0.95—1.20 (m, 24H), 1.20—1.70 (m, 9H), 1.29 (d, 3H, J=5.4 Hz), 2.99 (dd, 1H, J=4.4 and 9.3 Hz), 3.07 (dt, 1H, J=4.4 and 5.4 Hz), 3.88 (ddd, 1H, J=2.0, 4.4, and 8.8 Hz).

Found: C, 70.20; H, 12.11%. Calcd for $C_{20}H_{42}O_2Si$: C, 70.11; H, 12.35%.

(6*R,7*R**,8*R**,9*S**)-8,9-Epoxy-7-methyl-6-(triisopropylsiloxy)tridecane (20a).** The compound was prepared from **19a** in a similar manner to that described for **20b**. The ratio of **20a** and its *anti*-isomer before chromatography was 10.8:1. Yield: 80%.

An oil; ^{1}H NMR δ=0.88 (t, 3H, J=6.8 Hz), 0.92 (t, 3H, J=6.8 Hz), 1.00—1.20 (m, 24H), 1.20—1.60 (m, 15H), 2.90—3.00 (m, 1H), 3.01 (dd, 1H, J=3.9 and 9.3 Hz), 3.85—3.90 (m, 1H).

Found: C, 71.67; H, 12.46%. Calcd for $C_{23}H_{48}O_2Si$: C, 71.81; H, 12.58%.

(6*R,7*S**,8*S**,9*R**)-8,9-Epoxy-7-methyl-6-(triisopropylsiloxy)tridecane (23a).** The compound was prepared from **22a** in a similar manner to that described for **20b**. The ratio of **23a** and its *anti*-isomer before chromatography was 8.2:1. Yield: 74%.

An oil; ^{1}H NMR δ=0.89 (t, 3H, J=6.8 Hz), 0.92 (t, 3H, J=6.8 Hz), 0.95—1.10 (m, 21H), 1.11 (d, 3H, J=6.8 Hz), 1.20—1.70 (m, 15H), 2.89 (dd, 1H, J=3.9 and 8.8 Hz), 2.90—3.00 (m, 1H), 3.75—3.85 (m, 1H).

Found: C, 71.57; H, 12.41%. Calcd for $C_{23}H_{48}O_2Si$: C, 71.81; H, 12.58%.

(2*R,3*S**,4*S**,5*R**)-2,3-Epoxy-4-methyl-5-(triisopropylsiloxy)decane (23b).** The compound was prepared from **22b** in a similar manner to that described for **20b**. The ratio of **23b** and its *anti*-isomer before chromatography was 7.4:1. Yield: 67%.

An oil: ^{1}H NMR δ=0.89 (t, 3H, J=6.8 Hz), 0.95—1.10 (m, 21H), 1.12 (d, 3H, J=6.5 Hz), 1.20—1.65 (m, 9H), 1.29 (d, 3H, J=5.4 Hz), 2.91 (dd, 1H, J=3.9 and 9.3 Hz), 3.10 (dq, 1H, J=3.9 and 5.9 Hz), 3.75—3.85 (m, 1H).

Found: C, 70.02; H, 12.06%. Calcd for $C_{20}H_{42}O_2Si$: C, 70.11; H, 12.35%.

(2*R,3*S**,4*R**,5*R**)-2,3-Epoxy-4-methyl-5-(*t*-butyldimethylsiloxy)decane (24).** A solution of *t*-butyldimethylsilyl chloride (67.3 mg) in dry DMF (1 ml) and a solution of imidazole (68.4 mg) in the same solvent (1 ml) were added at room temperature to **13b** (58.3 mg). The mixture was stirred overnight at room temperature and diluted with ether. The ethereal solution was washed with water, dried over Na_2SO_4, concentrated, and chromatographed on silica gel with hexane-ethyl acetate (100:1) to give the silyl ether (**24**, 75.1 mg, 80%) as an oil; ^{1}H NMR δ=0.07 (s, 6H), 0.85—0.90 (m, 6H), 0.90 (s, 9H), 1.27 (d, 3H, J=5.4 Hz), 1.20—1.40 (m, 7H), 1.40—1.60 (m, 2H), 2.82 (dd, 1H, J=4.4 and 9.8 Hz), 3.08 (dt, 1H, J=5.4 and 9.8 Hz), 3.82 (m, 1H).

Found: C, 68.16; H, 11.80%. Calcd for $C_{17}H_{36}O_2Si$: C, 67.94; H, 12.07%.

(5*R,6*S**,7*R**,8*S**)-5,7-Dimethyl-6,8-tridecanediol (30).** Dry ether (1 ml) was added to copper(I) cyanide (41.5 mg) and the slurry was cooled to −20 °C. Ethereal MeLi (1.09 mol dm^{-3}, 850 µl), dimethyl sulfide (37.4 µl), and tributylphosphine (125.5 µl) were successively added dropwise to this producing a clear solution, and the mixture was then warmed to 0 °C. The epoxide (**13a**, 21.1 mg) was dissolved in dry ether (500 µl) and added to the above solution of the cuprate. The mixture was stirred for 48 h at room temperature and then quenched by the addition of a 30% H_2O_2 solution (300 µl). After 5 min, saturated aqueous NH_4Cl and ether were added to the reaction mixture and then extracted with ether. The extract was dried over Na_2SO_4. After filtration, ether was removed in vacuo, yielding a mixture of three compounds as an oil (22.3 mg). The mixture was chromatographed at medium pressure by using a Lobar column with hexane-ethyl acetate (4:1) to give **30** (17.6 mg, 78%) and **31** (2.9 mg, 14%).

30: A white solid: mp 58.5—59.0 °C; ^{1}H NMR δ=0.85 (d, 3H, J=7.3 Hz), 0.88—0.95 (m, 9H), 1.20—1.80 (m, 16H), 2.34 (br s, 2H), 3.49 (dd, 1H, J=4.4 and 7.8 Hz), 3.87 (ddd, 1H, J=2.0, 2.4, and 8.8 Hz).

Found: C, 73.77; H, 13.06%. Calcd for $C_{15}H_{32}O_2$: C, 73.71; H, 13.20%.

31: An oil; ^{1}H NMR δ=0.86—1.0 (m, 6H), 1.12 (d, 3H, J=5.8 Hz), 1.20—1.80 (m, 14H), 2.40—2.65 (m, 3H), 3.60—3.70 (br s, 1H), 3.75—3.85 (m, 1H). IR 1700 cm^{-1} (C=O).

(5*R,6*R**,7*S**,8*R**)-5,7-Dimethyl-6,8-tridecanediol (32).** The epoxide (**24**, 19.9 mg) was treated with $LiCu(CN)Bu_2$ in a similar manner to that described for the preparation of **30**, giving a mixture of two compounds (**25** and **26**) as an oil (23.1 mg). To this mixture dissolved in THF (1 ml), was added a tetrabutylammonium fluoride solution in THF (1 mol dm^{-3}, 127 µl) and the reaction mixture was stirred for 30 min. After filtration, THF was removed in vacuo. The residue was chromatographed on preparative TLC with hexane-ethyl acetate (4:1) to give the diol (**32**, 11.9 mg, 74%) as an oil; ^{1}H NMR δ=0.86—0.92 (m, 9H), 0.94 (d, 3H, J=7.3

Hz), 1.00—1.90 (m, 16H), 2.46 (br s, 2H), 3.34 (dd, 1H, J=5.4 and 6.4 Hz), 3.92 (ddd, 1H, J=2.0, 2.4, and 8.3 Hz).

Found: C, 73.42; H, 13.15%. Calcd for $C_{15}H_{32}O_2$: C, 73.71; H, 13.20%.

(5*R,6*S**,7*R**,8*R**)-5,7-Dimethyl-6,8-tridecanediol (35).** The compound was prepared from **14a** in a similar manner to that described for **30**. Yield: 72%.

An oil; ^{1}H NMR δ=0.75 (d, 3H, J=6.8 Hz), 0.84 (d, 3H, J=6.8 Hz), 0.90 (t, 6H, J=6.8 Hz), 1.20—1.80 (m, 16H), 3.23 (br s, 2H), 3.51 (dd, 1H, J=2.0 and 9.3 Hz), 3.64 (dt, 1H, J=2.4 and 7.8 Hz).

Found: C, 73.47; H, 12.99%. Calcd for $C_{15}H_{32}O_2$: C, 73.71; H, 13.20%.

(5*R,6*R**,7*S**,8*S**)-5,7-Dimethyl-6,8-tridecanediol (38).** The compound was prepared from **14b** in a similar manner to that described for **30**. Yield 56%.

An oil; ^{1}H NMR δ=0.77 (d, 3H, J=6.8 Hz), 0.85—0.95 (m, 6H), 0.99 (d, 3H, J=6.8 Hz), 1.10—1.70 (m, 16H), 2.95 (br s, 2H), 3.42 (dd, 1H, J=2.4 and 8.8 Hz), 3.63 (dt, 1H, J=2.4 and 7.8 Hz).

Found: C, 73.53; H, 13.10%. Calcd for $C_{15}H_{32}O_2$: C, 73.71; H, 13.20%.

(5*R,6*S**,7*R**,8*R**)-5,7-Dimethyl-6-hydroxy-8-(triisopropylsiloxy)tridecane (44).** To a suspension of copper(I) cyanide (25.4 mg) in dry THF (1 ml) was added methyllithium in ether (1.09 mol dm^{-3}, 534 µl) at room temperature. A solution of **20a** (23 mg) in dry THF (500 µl) was added to the above solution of the cuprate. The reaction mixture was refluxed for 24 h, then cooled to room temperature, and quenched by the addition of a 30% H_2O_2 solution (160 µl). After 5 min, a saturated NH_4Cl solution and ether were added to the mixture. The organic layer was separated and dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and the residue was chromatographed at medium pressure by using Lobar column with hexane-ethyl acetate (300 : 1) to give **44** (10.8 mg, 45%) and the recovered **20a** (12.5 mg, 54%).

An oil; ^{1}H NMR δ=0.89 (t, 6H, J=6.8 Hz), 0.90 (d, 3H, J=7.3 Hz), 0.95 (d, 3H, J=6.4 Hz), 1.00—1.20 (m, 21H), 1.20—1.40 (m, 10H), 1.40—1.80 (m, 6H), 2.98 (s, 1H), 3.45 (dd, 1H, J=2.9 and 7.8 Hz), 3.98 (ddd, 1H, J=2.0, 2.0, and 10.3 Hz).

(5*R,6*S**,7*S**,8*R**)-5,7-Dimethyl-6,8-tridecanediol (42).** A tetrabutylammonium fluoride solution in THF (1 mol dm^{-3}, 96 µl) was added to a solution of the alcohol (**44**, 19.2 mg) in THF (1 ml) and the reaction mixture was stirred for 1 h. After filtration, THF was removed in vacuo. The residue was chromatographed on preparative TLC with hexane-ethyl acetate (4 : 1) to give the diol (**42**, 9.4 mg, 80%) as an oil; ^{1}H NMR δ=0.88 (d, 3H, J=7.3 Hz), 0.88 (t, 6H, J=7.3 Hz), 0.96 (d, 3H, J=6.4 Hz), 1.20—1.80 (m, 16H), 2.72 (br s, 1H), 2.82 (br s, 1H), 3.45 (dd, 1H, J=1.5 and 7.3 Hz), 3.75—3.85 (m, 1H).

Found: C, 73.58; H, 13.10%. Calcd for $C_{15}H_{32}O_2$: C, 73.71; H, 13.20%.

(5*R,6*S**,7*R**,8*S**)-5,7-Dimethyl-6-hydroxy-8-(triisopropylsiloxy)tridecane (47).** The compound (**47**) was prepared from **23a** in a similar manner to that described for **44**. Yield: 59%.

An oil; ^{1}H NMR ^{1}H NMR δ=0.89 (t, 6H, J=6.8 Hz), 1.00 (d, 3H, J=6.4 Hz), 1.05 (d, 3H, J=6.8 Hz), 1.00—1.15 (m, 21H), 1.15—1.40 (m, 14H), 1.50—1.70 (m, 1H), 1.70—1.90 (m, 1H), 3.62 (dd, 1H, J=1.5 and 9.3 Hz), 3.77 (d, 1H, J=6.4 Hz), 3.92 (ddd, 1H, J=2.0, 2.4, and 10.3 Hz).

Found: C, 71.78; H, 12.90%. Calcd for $C_{24}H_{52}O_2Si$: C, 71.93; H, 13.08%.

(5*R,6*R**,7*R**,8*S**)-5,7-Dimethyl-6-,8-tridecanediol (51).** The compound was prepared from **20b** in a similar manner to that described for **32**. Yield: 68%.

An oil; ^{1}H NMR δ=0.80 (d, 3H, J=6.4 Hz), 0.85—0.95 (m, 9H), 1.00—1.45 (m, 14H), 1.50—1.60 (m, 1H), 1.60—1.70 (m, 1H), 2.50 (br s, 2H), 3.47 (dd, 1H, J=1.5 and 9.3 Hz), 3.80—3.85 (m, 1H).

Found: C, 73.57; H, 13.09%. Calcd for $C_{15}H_{32}O_2$: C, 73.71; H, 13.20%.

(5*R,6*S**,7*S**,8*S**)-5,7-Dimethyl-6-,8-tridecanediol (52).** The compound was prepared from **47** in a similar manner to that described for **42**. Yield: 81%.

A white solid; mp 61.0—61.5 °C; ^{1}H NMR δ=0.89 (t, 6H, J=6.3 Hz), 0.99 (d, 3H, J=6.8 Hz), 1.00 (d, 3H, J=6.8 Hz), 1.15—1.40 (m, 12H), 1.40—1.75 (m, 4H), 2.36 (br s, 1H), 2.49 (br s, 1H), 3.60—3.65 (m, 2H).

Found: C, 73.61; H, 13.15%. Calcd for $C_{15}H_{32}O_2$: C, 73.71; H, 13.20%.

(5*R,6*R**,7*R**,8*R**)-5,7-Dimethyl-6-,8-tridecanediol (53).** The compound was prepared from **23b** in a similar manner to that described for **32**. Yield: 75%.

A white solid; mp 56.0—56.5 °C; ^{1}H NMR δ=0.78 (d, 3H, J=6.8 Hz), 0.85—0.95 (m, 6H), 0.99 (d, 3H, J=7.3 Hz), 1.00—1.70 (m, 16H), 2.33 (br s, 2H), 3.63 (dd, 1H, J=1.5 and 9.3 Hz), 3.60—3.70 (m, 1H).

Found: C, 73.59; H, 13.17%. Calcd for $C_{15}H_{32}O_2$: C, 73.71; H, 13.20%.

Support by the Grand-in-Aid for Special Project Research (No. 61224009) from the Ministry of Education, Science and Culture, is gratefully acknowledged.

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