(Z)-Diethyl 1,2,3,4-tetrahydro-1-(1-methyl-1-phenylmethylidene)naphthalene-3,3-dicarboxylate (18): 55% yield; colorless oil; IR (neat) 1730 (br s), 1270 (s), 1240 (s), 1220 (s), 1180 (s), 760 (s), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$, TMS) δ 1.22 (t, J = 7.1 Hz, 6 H), 2.20 (s, 3 H), 3.12 (s, 2 H), 3.30 (s, 2 H), 4.1–4.2 (m, 4 H), 6.52 (d, J = 7.6 Hz, 1 H), 6.67 (t, J = 7.6 Hz, 1 H), 6.9–7.2 (m, 7 H) ppm; ^{13}C NMR ($CDCl_3$, TMS) δ 14.07, 22.38, 34.34, 35.59, 55.21, 61.53, 124.87, 126.27, 126.38, 127.15, 128.11, 128.22, 128.73, 129.03, 130.23, 134.66, 136.08, 144.90, 171.20 ppm; MS m/z 378 (M^+), 304, 231, 217, 216, 215, 105, 103; HRMS calcd for $C_{24}H_{26}O_4$ 378.1831, found 378.1844.

(E)-Diethyl 1,2,3,4-tetrahydro-1-[1-(trimethylsilyl)-1-phenylmethylidene]naphthalene-3,3-dicarboxylate (19): 43% yield; colorless oil; IR (neat) 1736 (br s), 1259 (s), 837 (s), 760 (m), 703 (m) cm^{-1}; ^1H NMR ($CDCl_3$, TMS) δ −0.17 (s, 9 H), 1.09 (t, J = 7.1 Hz, 6 H), 2.77 (s, 2 H), 3.16 (s, 2 H), 3.9–4.1 (m, 4 H), 6.90–6.98 (m, 2 H), 7.1–7.5 (m, 7 H) ppm; ^{13}C NMR ($CDCl_3$, TMS) δ 0.79, 13.85, 35.59, 36.40, 54.74, 61.36, 125.20, 125.99, 127.37, 127.55, 127.94, 135.52, 139.45, 142.82, 144.27, 144.66, 171.28 ppm; MS m/z 436 (M^+), 421, 363, 333, 273, 245, 205, 178, 164, 149, 119, 107, 91; HRMS calcd for $C_{26}H_{32}O_4Si$ 436.2070, found 436.2048. Anal. Calcd for $C_{26}H_{32}O_4Si$: C, 71.52; H, 7.39. Found: C, 71.50; H, 7.43.

(E)-2,3-Dihydro-1-(1-phenylmethylidene)indene (20):[17,18] mp 71–72 °C (lit.[18] mp 71–72 °C); ^1H NMR ($CDCl_3$, TMS) δ 3.10 (s, 4 H), 6.96 (s, 1 H), 7.18–7.65 (m, 9 H) ppm; ^{13}C NMR ($CDCl_3$, TMS) δ 30.57, 30.75, 118.88, 120.67, 125.13, 126.10, 126.47, 128.02, 128.29, 138.10, 142.43, 143.97, 145.66 ppm; MS m/z 206 (M^+), 205, 204.

3-(Phenylmethyl)indene (21):[19] ^1H NMR ($CDCl_3$, TMS) δ 3.35–3.36 (m, 2 H), 3.89–3.92 (m, 2 H), 6.12–6.14 (m, 1 H), 7.18–7.46 (m, 9 H) ppm; ^1H NMR ($CDCl_3$, TMS) δ 34.36, 37.61, 119.23, 123.62, 124.49, 125.90, 126.00, 128.25, 128.83, 129.89, 139.25, 143.36, 144.44, 145.01 ppm; MS m/z 206 (M^+), 205.

Acknowledgment. We are indebted to the National Science Council of the Republic of China for financial support.

Registry No. 8, 119826-66-3; 9, 120417-24-5; 10, 127530-86-3; 11, 127619-92-5; 12, 127619-93-6; 13, 127619-94-7; 14, 127619-95-8; 15, 127619-96-9; 16, 127619-97-0; 17, 127619-98-1; 18, 127619-99-2; 19, 127620-00-2; 20, 16275-02-8; 21, 22495-71-2; $Pd(PPh_3)_4$, 14221-01-3; allenylmagnesium bromide, 18295-60-8; 2-iodobenzyl bromide, 40400-13-3; diethyl 2-(2-bromobenzyl)malonate, 66192-11-8; propargyl bromide, 106-96-7; 1-bromo-2-butyne, 3355-28-0; 3-bromo-1-(trimethylsilyl)-1-propyne, 38002-45-8; phenylzinc chloride, 28557-00-8.

Supplementary Material Available: ^1H and ^{13}C NMR spectra for compounds 8–10, 12, 13–16, and 18 (21 pages). Ordering information is given on any current masthead page.

(17) Prinzbach, H.; Seip, D.; Englert, G. *Justus Liebigs Ann. Chem.* **1966**, *698*, 57.
(18) Bestmann, H. J.; Hartl, R.; Haberlein, H. *Justus Liebigs Ann. Chem.* **1968**, *718*, 33.
(19) Hubert, A. J.; Reimlinger, H. *J. Chem. Soc. C* **1969**, 944.

Lewis Acid Promoted Ring-Opening Allylation of Epichlorohydrin with Allylic Silanes and Stannanes To Afford 1-Chloro-5-alken-2-ols. A Short Synthesis of (S)-(−)-Ipsenol

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Received February 5, 1990

Epichlorohydrin (1) was allylated in good yields with representative allylic silanes (2, 5, 7, 9) and stannanes (12, 18) in the presence of appropriate Lewis acids. The reaction proceeds with ring opening at the unsubstituted site in 1 and with allylic inversion in the allylating agents to give 1-chloro-5-alken-2-ols cleanly. A short synthesis of (S)-(−)-ipsenol (29) from 1 and an (allenylmethyl)silane (26) demonstrates the utility of this method in organic synthesis.

Allylation of oxiranes is generally carried out under basic conditions by utilizing allyllithium or allylmagnesium reagents in the presence or absence of a copper(I) catalyst.[1] However, if these transformations can also be achieved under nonbasic or weakly acidic conditions, as has been realized in the allylation of aldehydes and ketones with allylic silanes[2] and stannanes,[3] the scope of utilizing oxiranes as synthetic intermediates will be further extended.

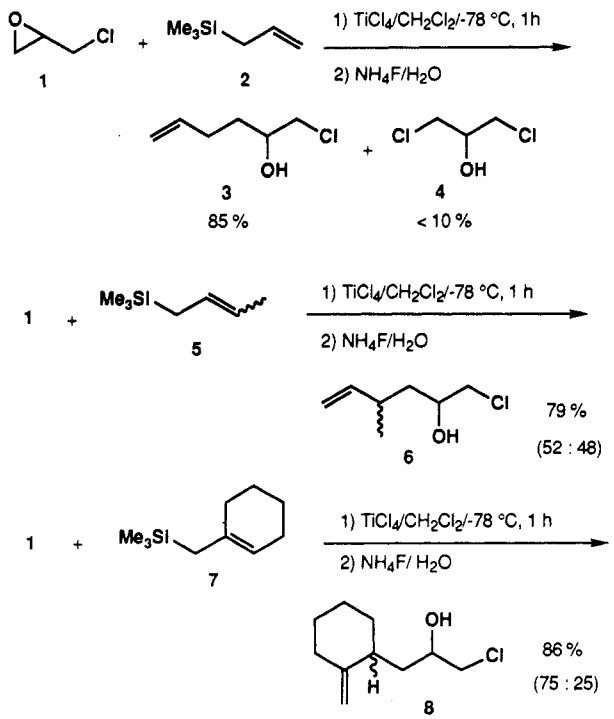
In the literature, however, only two such reactions are described.[4,5] In one report,[4] it is stated that allylative ring opening of ethylene oxide can be performed smoothly with allylsilanes under the influence of $TiCl_4$. Introduction of a methyl substituent (i.e., propylene oxide), however, results in the formation of mixtures of products, and it is suggested that rapid isomerization of the oxirane might be at least in part the cause for the problem.[6]

In the second report,[5] the successful allylation of alkenyloxiranes with allyltin reagents in the presence of $BF_3{\cdot}OEt_2$ is described. The allylative ring opening takes place at the site of the alkenyl substitution. Therefore,

(1) (a) Smith, J. G. *Synthesis* **1984**, 629. (b) Huynh, C.; Derguini-Boumechal, F.; Linstrumelle, G. *Tetrahedron Lett.* **1979**, *20*, 1503. (c) Fabris, H. J. *J. Org. Chem.* **1967**, *32*, 2031.
(2) (a) Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200. (b) Magnus, P. D.; Sarkar, T.; Djuric, S. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 7, Chapter 48. (c) Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, *17*, 1295.
(3) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworth: London, 1987. (b) Naruta, Y.; Ushida, S.; Maruyama, K. *Chem. Lett.* **1979**, 919. (c) Hosomi, A.; Iguchi, H.; Endo, M.; Sakurai, H. *Chem. Lett.* **1979**, 977.
(4) Fleming, I.; Patterson, I. *Synthesis* **1979**, 446.
(5) Naruta, Y.; Maruyama, K. *Chem. Lett.* **1987**, 963.
(6) Intramolecular reactions are exceptional: Molander, G. A.; Andrews, S. W. *J. Org. Chem.* **1989**, *54*, 3114 and references cited therein.

0022-3263/90/1955-4849$02.50/0

Scheme I



it may be argued that these substituents stabilize the incipient positive charge, so that it prevents the isomerization of the starting oxiranes.

In the present study, we anticipated that the presence of an electronegative substituent adjacent to the oxirane ring might also minimize such isomerizations and could alter the directional mode of the ring opening. Indeed, as described below, epichlorohydrin (1) was allylatively opened smoothly at the unsubstituted site with allylic silanes and stannanes in the presence of appropriate Lewis acids.[7] As a result, this method opens a new way to prepare a variety of 1-chloro-5-en-2-ol derivatives.

Now, 1 is commercially available in an enantiomerically pure form of either *R* or *S* configuration[8] and, thus, has become a more convenient chiral C_3 unit in the synthesis of optically active alcohols.[9] Therefore, the present method also provides an additional way to utilize this valuable chiral C_3 synthon. An example of such applications is demonstrated here by a short synthesis of (*S*)-(−)-ipsenol (**29**), and aggregation pheromone of the California engraver beetle ips.[10]

Results and Discussion

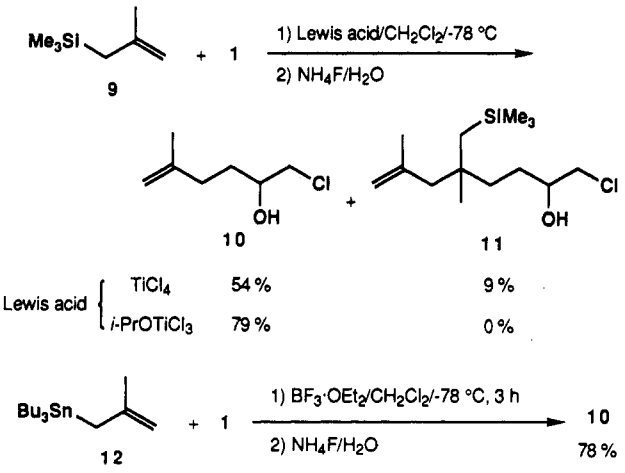
A mixture of 1 and allyltrimethylsilane (2) in dichloromethane was treated with $TiCl_4$ at −80 °C for 1 h. After the reaction was quenched with 30% aqueous NH_4F and the mixture extracted with ether, GC analysis indicated formation of two products in ca. 9:1 ratio. They were easily separated by silica gel chromatography. The major product was found to be the expected 1-chloro-5-hexen-2-ol (3), while the minor one was identified as 1,3-dichloro-2-propanol (4), apparently formed by competitive ring opening of 1 by the chloride ion (Scheme I).

Similarly, crotylsilane 5 and (cyclohexenylmethyl)silane 7 smoothly reacted with 1 to give 6 and 8, respectively. As in generally observed in the electrophilic substitution of allylic silanes and stannanes,[2,3] these reactions proceed with allylic inversion in the allylating agents. Unfortunately, however, the stereoselectivity was found to be poor in both cases (52:48 for 6 and 75:25 for 8 by GC and/or ^1H NMR).

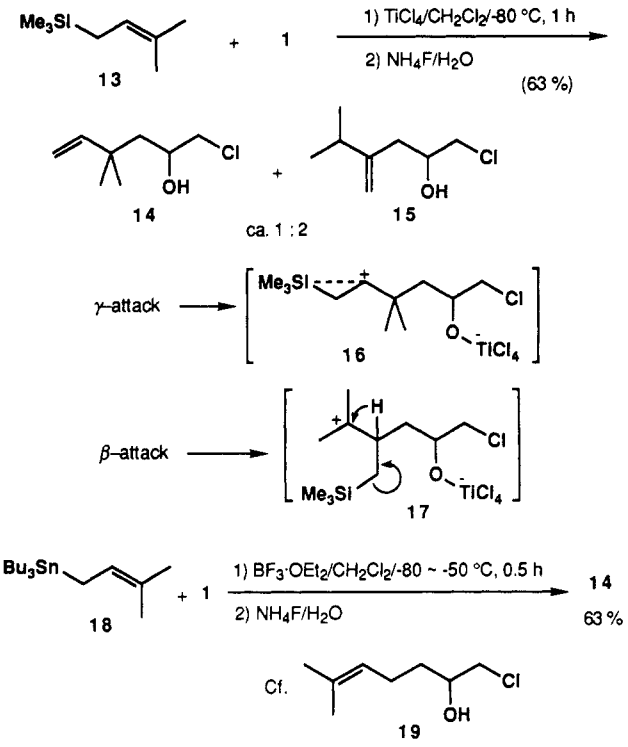
By the same procedure, however, methallylsilane 9 gave somewhat lower yield (54%) of the normal allylation product 10 along with a higher boiling byproduct 11 (9%) as shown in Scheme II. The latter is formed by the reaction of 1 with two molecules of 9. Fortunately, use of a milder Lewis acid, *i*-$PrOTiCl_3$, avoided the undesirable formation of 11. Use of methallyltin reagent 12 in place of 9 and in combination with BF_3·OEt_2 also gave 10 in a reasonable yield.

Prenylsilane 13 also gave two products (Scheme III). The major one was not the normal allylation product 14,

Scheme II



Scheme III



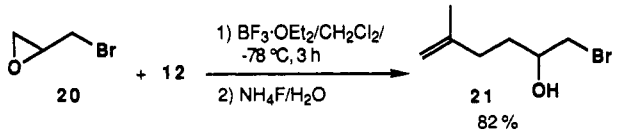
(7) Lewis acid promoted alkynylative ring opening of 1 with alkynyllithium is also known to proceed at the unsubstituted site of the ring: Yamaguchi, M.; Hirao, I. *Tetrahedron Lett.* **1983**, *24*, 391.

(8) Available from Daiso. For the original preparative procedure developed by Takano et al., see ref 9c and d.

(9) (a) Golding, B. T. *Chem. Ind.* **1988**, 617. (b) Jurczak, J.; Pikul, S.; Bauer, T. *Tetrahedron* **1986**, *42*, 447. (c) Takano, S.; Yanase, M.; Sekiguchi, Y.; Ogasawara, K. *Tetrahedron Lett.* **1987**, *28*, 1783. (d) Takano, S.; Yanase, M.; Takahashi, M.; Ogasawara, K. *Chem. Lett.* **1987**, 2017.

(10) (a) Silverstein, R. M.; Rodin, J. O.; Wood, D. L.; Browne, L. E. *Tetrahedron* **1966**, *22*, 1929. (b) Mori, K.; Takigawa, T.; Matsumoto, T. *Ibid.* **1979**, *35*, 933. (c) Ikeda, N.; Arai, I.; Yamamoto, H. *J. Am. Chem. Soc.* **1986**, *108*, 483.

Scheme IV



but an unexpected homoallylic alcohol **15**. Electrophilic attack at the γ-position leads to an intermediate **16**, which is sterically hindered in this substrate, while attack at the β-position give rise to a relatively stable tertiary carbocation **17** and the latter seems to be favored. Hydride shift followed by desilylation of **17** gives **15**. This problem was again solved by using a more nucleophilic prenyltin reagent **18**, which gave only **14** by the normal γ-attack. Although prenylsilane **13** and other γ,γ-disubstituted allylic silanes generally react with electrophiles at the γ-position,[2] there is at least one precedent for such a β-attack pathway.[11] A similar difference in behavior between silicon and tin reagents can also be seen in the Lewis acid promoted reaction of γ-alkoxyallyl derivatives with carbonyl compounds.[12] There is also precedent for the hydride shift–desilylation sequence in some cationic reactions of organosilanes.[13]

It should also be noted that, in contrast to our result with **18**, the copper(I)-catalyzed reaction of prenylmagnesium chloride with **1** is reported to give isomeric 1-chloro-6-methyl-5-hepten-2-ol (**19**) exclusively.[9d] The present method thus complements the conventional one in controlling this type of regiochemistry in the allylation of **1**.

Similarly, epibromohydrin (**20**) reacted nicely with **12** in the presence of BF_3·OEt_2 at −78 °C to afford a good yield of 1-bromo-5-methyl-5-hexen-2-ol (**21**) as shown in Scheme IV. The reaction of **20** and allyltributyltin (**22**) was, however, impractically slow at −78 °C (incomplete even after 5 h), and when the reaction temperature was raised to −35 °C, serious side reactions occurred. Glycidyl tosylate was also less reactive than **1** and mostly recovered unreacted when treated with **2** in the presence of $TiCl_4$ at −80 to −50 °C. Therefore, the success of these reactions seems to depend on a delicate balance of both the reactivity of oxiranes and the nucleophilicity of allylating agents.

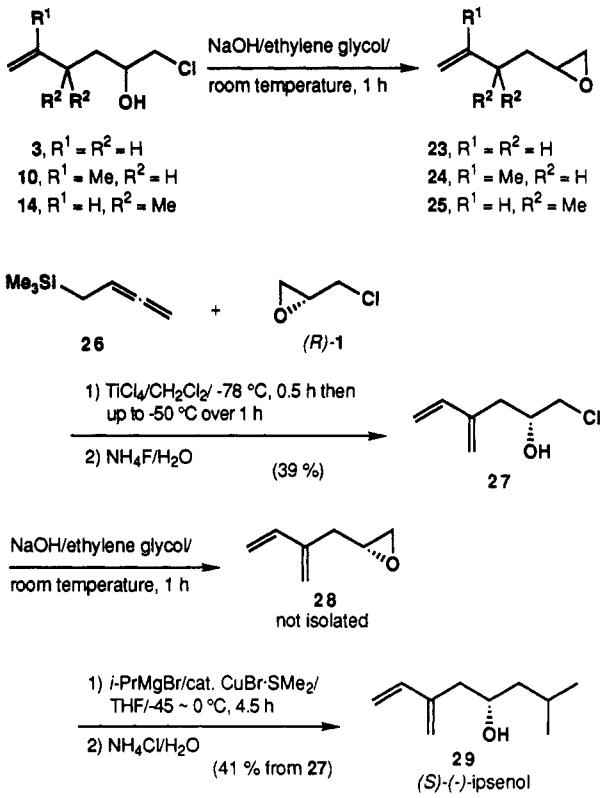
Finally, by taking the advantage of the regiocontrol in this reaction, (*S*)-(−)-ipsenol (**29**)[10] was prepared from 2,3-butadienyltrimethylsilane (**26**) and (*R*)-(−)-**1** in only three steps as shown in Scheme V. Prior to this application, it was confirmed that some of the chlorohydrins prepared (**3**, **10**, **14**) could be smoothly converted to the corresponding oxiranes (**23**–**25**, respectively).

In conclusion, the present reaction enables regioselective three-carbon extension of a variety of allylic silanes and stannanes to give 1-chloro-5-alken-2-ols and is applicable to enantioselective synthesis by employing enantiomerically pure **1**.

Experimental Section

All reactions were run under a slightly positive pressure of argon in oven-dried flasks. ^1H NMR spectra were recorded in $CDCl_3$. IR spectra were recorded on a Hitachi 270-30 spectrophotometer as neat liquids on sodium chloride plates. Capillary GC analyses were performed with an OV-1 column (0.25-mm i.d., 50 m). Bath temperatures and pressures given are from bulb-to-bulb distillations. Dichloromethane was distilled from P_2O_5 just before use. Epichlorohydrin (**1**) was dried over 4-Å molecular sieves and purified by distillation, bp 115–116 °C, while (*R*)-(−)-**1** (≥98% ee) provided by Daiso,[8] $[\alpha]^{26}_D$ −33.8° (*c* 4.89, methanol) (lit.[9d] $[\alpha]^{25}_D$ −33.23° (*c* 5.81, methanol)), was used without further purification. Epibromohydrin (**20**) was purified as described for **1**, bp 135–137 °C. All of the allylic silanes (**2**, **5**, **7**, **9**, **13**) and tins (**12**, **18**, **22**) except for **23** were prepared from the corresponding allyl Grignard reagents and chlorotrimethylsilane[2] or chlorotributyltin.[3] In the case of **5**, the product was a mixture of not only cis and trans isomers but also their regioisomer, and purification by GC–isolation was thus needed. (Allenylmethyl)silane **23**, bp 118–121 °C, was prepared in 64% yield by the copper(I)-catalyzed coupling of (trimethylsilyl)methylmagnesium chloride and propargyl tosylate.[14]

Scheme V



1-Chloro-5-hexen-2-ol (3). Procedure A. To a stirred solution of **1** (0.56 g, 6.0 mmol) and **2** (0.57 g, 5.0 mmol) in dichloromethane (10 mL) in a 50-mL round-bottomed flask was added at −78 °C (a dry ice–methanol bath) a solution of $TiCl_4$ (1.14 g, 6.0 mmol) in the same solvent (5 mL) through the cold inner surface of the flask over a period of 2–3 min. The mixture was stirred at the temperature for 0.5 h and the cold bath removed. Immediately, 30% aqueous NH_4F (1.5 mL) and ether (15 mL) were added, and the mixture stirred vigorously while being allowed to come to room temperature. The organic phase was separated, washed with half-saturated aqueous NaCl, and dried (Na_2SO_4). Chromatographic isolation (silica gel/5–10% ethyl acetate–hexane) and bulb-to-bulb distillation at 95–100 °C (15 Torr) gave 0.54 g (80%) of pure **3**. Its ^1H NMR and IR spectral data agree well with those reported.[1c] A minor product, eluted after **3** during chromatography, was isolated by GC and found to be the dichloro alcohol **4** by spectral comparison with a commercial sample.

1-Chloro-4-methyl-5-hexen-2-ol (6). By procedure A, **5** (cis:trans ≈ 1:1; 0.406 g, 3.16 mmol) was converted to **6**: bath temperature 75–80 °C (4 Torr); 0.37 g (79%); ^1H NMR (60 MHz) δ 1.05 (d, *J* = 6.6 Hz, 3 H), 1.2–1.8 (m, 2 H), 1.9–2.8 (m, 2 H, 1

(11) Hamana, H.; Sugasawa, T. *Tetrahedron Lett.* **1985**, *26*, 921.
(12) In the reaction with Lewis acid activated aldehydes, (γ-alkoxyallyl)tin reagents give normal allylation products: (a) Keck, G. E.; Abbott, D. E.; Wiley, M. R. *Tetrahedron Lett.* **1987**, *28*, 139; (b) Koreeda, M.; Tanaka, Y. *Ibid.* **1987**, *28*, 143. In contrast, (γ-alkoxyallyl)silanes, under similar conditions, are reported to give products derived from the initial electrophilic attack at the β-position: (c) Pornet, J.; Rayadh, A.; Miginiac, L. *Ibid.* **1988**, *29*, 4717.
(13) (a) Sakurai, H.; Imai, T.; Hosomi, A. *Tetrahedron Lett.* **1977**, *18*, 4045. (b) Fleming, I.; Patel, S. K. *Ibid.* **1981**, *22*, 2321.
(14) Montury, M.; Psaume, B.; Gore, J. *Tetrahedron Lett.* **1980**, *21*, 163.

H exchangeable with D_2O), 3.2–4.4 (m, 3 H), 4.6–6.3 (m, 3 H); IR 3400, 3080, 2960, 2930, 1640, 1455, 1435, 1420, 1090, 1050, 1000, 915 cm^{-1}. Anal. Calcd for $C_7H_{13}ClO$: C, 56.57; H, 8.81; Cl, 23.85. Found: C, 56.45; H, 8.99; Cl, 23.77. Capillary GC indicated the product to be a mixture of diastereomers in 48:52 ratio.

2-(3'-Chloro-2'-hydroxypropyl)-1-methylenecyclohexane (8). By procedure A, **7** (1.0 g, 5.0 mmol) was converted to **8**: bath temperature 115–120 °C (8 Torr); 0.79 g (84%); ^1H NMR (60 MHz) δ 0.8–2.0 (m, 8 H), 2.0–2.9 (m, 4 H, 1 H exchangeable with D_2O), 3.2–4.2 (m, 3 H), 4.4–4.9 (m, 2 H); IR 3400, 3080, 2930, 2850, 1645, 1450, 1090, 1070, 1050, 890 cm^{-1}. Anal. Calcd for $C_{10}H_{17}ClO$: C, 63.65; H, 9.08; Cl, 18.79. Found: C, 63.61; H, 9.23; Cl, 18.72. The product was a diastereomeric mixture, and the ratio was estimated by capillary GC to be 75:25.

1-Chloro-5-methyl-5-hexen-2-ol (10). Procedure B. To a stirred solution of **1** (0.51 g, 5.5 mmol) and **12** (1.73 g, 5.0 mmol) in dichloromethane (10 mL) was added at −78 °C $BF_3{\cdot}OEt_2$ (1.56 g, 11.0 mmol) rapidly, and the stirring was continued for 3 h at the temperature. When the mixture was treated with 30% aqueous NH_4F (2 mL) and ether (10 mL) as described in procedure A, solid precipitated. The clear supernatant was separated by filtering the mixture through a layer of tightly packed Na_2SO_4 and evaporated to give almost pure **10**, which was further purified by bulb-to-bulb distillation at 70–75 °C (4 Torr): 0.58 g (78%); ^1H NMR (60 MHz) δ 1.4–1.9 (m, 5 H), 1.9–2.4 (m, 3 H, 1 H exchangeable with D_2O), 3.2–4.2 (m, 3 H), 4.7 (br s, 2 H); IR 3385, 3075, 2935, 1650, 1445, 1380, 1095, 1070, 1040, 890 cm^{-1}. Anal. Calcd for $C_7H_{13}ClO$: C, 56.57; H, 8.81; Cl, 23.85. Found: C, 56.42; H, 8.99; Cl, 23.67. Also by procedure A but with *i*-$PrOTiCl_3$ [prepared freshly by mixing 3:1 ratio of $TiCl_4$ and $(i\text{-}PrO)_4Ti$ in dichloromethane] instead of $TiCl_4$, **1** (0.23 g, 2.5 mmol) and **9** (0.29 g, 2.2 mmol) smoothly reacted to give **10** (0.24 g, 73%).

1-Chloro-5,7-dimethyl-5-[(trimethylsilyl)methyl]-7-octen-2-ol (11). When $TiCl_4$ was used (i.e., by adopting the original procedure A), the reaction of **1** and **9** afforded not only **10** (54%) but also a minor product. This was isolated by chromatography (eluting just before **10**) followed by bulb-to-bulb distillation at 105–110 °C (0.03 Torr) and identified as **11** (8%) by the following spectral properties and analytical data: ^1H NMR (100 MHz) δ 0.05 (s, 9 H), 0.7 (s, 2 H), 1.0 (s, 3 H), 1.1–1.7 (m, 4 H), 1.75 (s, 3 H), 2.0 (s, 2 H), 2.15 (d, J = 4.9 Hz, 1 H), 3.3–3.9 (m, 3 H), 4.5–5.0 (m, 2 H); IR 3400, 3075, 2950, 1640, 1460, 1380, 1250, 1055, 890, 860, 840 cm^{-1}; MS, m/e 276 [$(M-1)^+$, 0.02%]. Anal. Calcd for $C_{14}H_{29}ClOSi$: C, 60.72; H, 10.56. Found: C, 60.47; H, 10.38.

1-Chloro-4,4-dimethyl-5-hexen-2-ol (14). By procedure B but with a longer reaction time (6 h at −78 °C), **18** (1.8 g, 5.0 mmol) was converted to **14**: bath temperature 80–85 °C (4 Torr); 0.66 g (81%); ^1H NMR (60 MHz) δ 1.1 (s, 6 H), 1.4–1.7 (m, 2 H), 2.2 (d, J = 3.8 Hz, 1 H, exchangeable with D_2O), 3.2–4.2 (m, 3 H), 4.7–6.3 (m, 3 H); IR 3400, 3085, 2960, 2935, 1640, 1430, 1415, 1385, 1365, 1080, 1060, 1005, 915 cm^{-1}. Anal. Calcd for $C_8H_{15}ClO$: C, 59.07; H, 9.30; Cl, 21.80. Found: C, 58.91; H, 9.47; Cl, 21.68.

1-Chloro-5-methyl-4-methylenehexan-2-ol (15). When **13** and **1** were reacted by procedure A, two products (total 63%) were isolated by chromatography in ca. 1:2 ratio. The expected product **14** was the minor one. The major product, which eluted just after **14**, was further purified by GC–isolation and identified as **15** by the following spectral properties: ^1H NMR (60 MHz) δ 1.05 (d, J = 7.2 Hz, 6 H), 1.9–2.6 (m, 4 H, 1 H exchangeable with D_2O), 3.3–4.3 (m, 3 H), 4.6–5.1 (m, 2 H); IR 3400, 3090, 2965, 2940, 2870, 1640, 1465, 1430, 1075, 1050, 900 cm^{-1}.

1-Bromo-5-methyl-5-hexen-2-ol (21). By procedure B, **20** (0.75 g, 5.5 mmol) and **12** (1.73 g, 5.0 mmol) reacted to give **21**: bath temperature 85–90 °C (4 Torr); 0.79 g (82%); ^1H NMR (60 MHz) δ 1.3–1.9 (m, 5 H), 1.9–2.5 (m, 3 H, 1 H exchangeable with D_2O), 3.1–4.1 (m, 3 H), 4.7 (br s, 2 H); IR 3400, 3080, 2940, 2840, 1650, 1445, 1425, 1380, 1275, 1225, 1095, 1065, 1060, 1030, 890 cm^{-1}. Anal. Calcd for $C_7H_{13}BrO$: C, 43.54; H, 6.78; Br, 41.39. Found: C, 43.46; H, 6.85; Br, 41.27.

(3-Buten-1-yl)oxirane (23). To a solution of chlorohydrin **3** (0.88 g, 6.54 mmol) in ethylene glycol (7 mL) was added crushed NaOH (0.52 g, 13.1 mmol) (slightly exothermic), and the mixture was stirred at ambient temperature for 1 h. After addition of water (14 mL), product was extracted with pentane (2 × 15 mL). The pentane extract was washed with water (30 mL) and dried (Na_2SO_4). Distillation gave 0.54 g (84%) of **23**: bp 118–120 °C (lit.[15] bp 119–121 °C); ^1H NMR and IR, identical with spectral data of a commercial sample (Aldrich).

(3-Methyl-3-buten-1-yl)oxirane (24). By the same procedure as above, **10** (0.87 g, 5.85 mmol) was converted to **24**, which was purified by bulb-to-bulb distillation at 110–115 °C (130 Torr): 0.49 g (74%); ^1H NMR (100 MHz) δ 1.4–1.8 (m, 5 H), 2.0–2.3 (m, 2 H), 2.35–2.55 (m, 1 H), 2.6–3.0 (m, 2 H), 4.6–4.8 (narrow m, 2 H); IR 3080, 3050, 2975, 2935, 2860, 1650, 1485, 1450, 1415, 1380, 1260, 920, 890, 865, 840 cm^{-1}; Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.79. Found: C, 74.92; H, 10.79.

(2,2-Dimethyl-3-buten-1-yl)oxirane (25). By the same procedure as above, **14** (1.07 g, 6.57 mmol) was converted to **25**, which was purified by bulb-to-bulb distillation at 110–115 °C (115 Torr): 0.65 g (78%); ^1H NMR (100 MHz) δ 1.08 (s, 3 H), 1.10 (s, 3 H), 1.5 (d, J = 5.5 Hz, 2 H), 2.25–2.45 (m, 1 H), 2.6–2.75 (m, 1 H), 2.75–3.0 (m, 1 H), 4.8–5.1 (m, 2 H), 5.6–6.05 (m, 1 H); IR 3085, 3045, 2965, 2925, 2870, 1640, 1470, 1410, 1385, 1365, 1260, 1000, 960, 910, 845, 830, 760, 690 cm^{-1}. Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.07; H, 11.19.

(*S*)-(−)-Ipsenol (29). By procedure A, (*R*)-(−)-**1** (1.94 g, 21.0 mmol) and **26** (2.78 g, 22.0 mmol) reacted to give, after chromatographic isolation, 1-chloro-4-methylene-5-hexen-2-ol (**27**): 1.20 g (39%); ^1H NMR (60 MHz) δ 2.2 (br s, 1 H), 2.55 (d, J = 6 Hz, 2 H), 3.3–4.3 (m, 3 H), 4.6–5.8 (m, 4 H), 6.4 (dd, J = 11 and 17.5 Hz, 1 H); IR 3400, 3090, 2955, 1595, 1430, 1250, 1085, 1060, 1040, 995, 905, 855 cm^{-1}. Chlorohydrin **27** (1.14 g, 7.78 mmol) was converted to (2-methylene-3-buten-1-yl)oxirane (**28**) as described for **23**. Crude **28** obtained as a colorless liquid (0.91 g, not completely evaporated because of its volatility) was immediately used for the next step. Thus, a 1.2 M THF solution of isopropylmagnesium bromide (9.33 mL, 11.2 mmol) was added dropwise at −60 to −50 °C to CuBr–SMe_2 (0.24 g, 1.2 mmol) in THF (2 mL), and the mixture was stirred for 10 min at −50 to −45 °C to give a light purple slurry. A solution of **28** in THF (10 mL) was added within ca. 5 min, and the stirring was continued for 4.5 h while the temperature was allowed to come to −5 °C within the first 0.5 h and then kept at −5 to 0 °C. The reaction was quenched by adding saturated aqueous NH_4Cl, and the product was extracted with ether (50 mL). The ether extract was washed with water (40 mL), dried (Na_2SO_4), and evaporated to give 1.47 g of a colorless liquid. Chromatographic isolation and subsequent bulb-to-bulb distillation at 120–125 °C (13 Torr) (lit.[10b] bp 86–88 °C (15 Torr)) gave the title compound **29**: 0.49 g (41%); $[\alpha]^{25}_D$ −17.2° (*c* 1.28, ethanol) (lit.[10c] $[\alpha]_D$ −17.5° (*c* 1.58, ethanol) for the *S* isomer); 98% ee based on the reported specific rotation value; ^1H NMR (100 MHz) and IR, identical with data reported for the natural product.[10a]

Acknowledgment. Financial support provided by The Kurata Foundation (The Kurata Research Grant) to this work is gratefully acknowledged.

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