Regioselective Opening of Terminal Epoxides with 2-(Trialkylsilyl)allyl Organometallic Reagents

Larry E. Overman* and Paul A. Renhowe

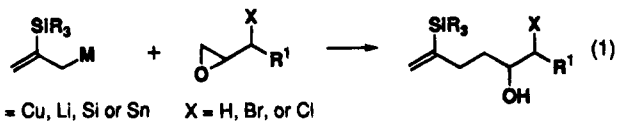
Department of Chemistry, University of California, Irvine, California 92717-2025

Received March 9, 1994®

Terminal epoxides react with 2-(trialkylsilyl)allyl organometallics (Sn, Si, Li, Cu) with varying degrees of efficiency depending upon the nature of the epoxide. The combination of [2-(trimethylsilyl)allyl]tributylstannane (**4**) and $EtAlCl_2$ is optimum and provides 1-substituted 4-(trimethylsilyl)-4-penten-1-ol products in good yield.

Nucleophilic ring opening of epoxides with organometallic reagents has found widespread application in the formation of carbon–carbon σ bonds.[1] Among the most common reagents employed are organomagnesium, organolithium, organocopper, organozinc, organoaluminum, and organoboron compounds.[2] In some cases, the basicity of these reagents can promote undesired side reactions. A useful alternative, which often avoids these problems, is the Lewis acid-promoted addition of less basic carbon nucleophiles.[2b] For the specific case of allylation, a limited number of allylsilanes[3] and allylstannanes[4] are reported to react with epoxides under Lewis acidic conditions to give bishomoallylic alcohols in useful yields.

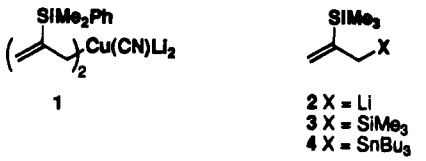
In our recent synthesis of the marine acetogenin, (+)-isolaurepinnacin, we were faced with the task of opening an α-bromo 1,2-epoxide with a 2-(trimethylsilyl)allyl organometallic (eq 1, X = Br).[5] During these studies we



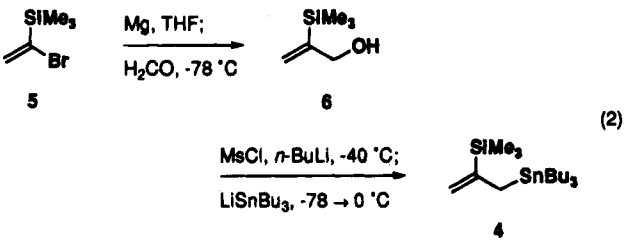
investigated the reaction of several 2-silylallyl organometallics with terminal epoxides (eq 1). Detailed herein are the results of these studies, which highlight particular advantages of the $EtAlCl_2$-promoted reaction of epoxides with allylstannanes.

Results and Discussion

Our studies focused on the reactions of the allylic nucleophiles **1-4** with representative epoxides. The allylcuprate **1** and allyllithium **2** were explored initially. The general procedure of Fleming for silylcupration of allene was employed to generate allylcuprate **1** conveniently in multigram quantities.[6] The allyllithium reagent **2** was prepared from the allylstannane **4**. Although similar allylstannanes have been reported in the literature,[7] the existing methods for their synthesis proved difficult to scale up.



A readily scaled synthesis of allylstannane **4** is outlined in eq 2. An improvement of the method of Chan[8] was employed to prepare 2-(trimethylsilyl)-2-propen-1-ol (**6**).



In this procedure, a standardized solution of monomeric formaldehyde in THF was prepared as described by Schlosser,[9] and a slight deficiency of this reagent was then added at −78 °C to the Grignard reagent derived from **5**. These conditions minimized the formation of polyether byproducts, which are difficult to separate from **6**. After some optimization, generation of the mesylate derivative of **6** at low temperature,[10] followed by reaction of this intermediate with $LiSnBu_3$, provided stannane **4** in 54% overall yield from the commercially available bromide **5**. Stannane **4** was easily purified in multigram quantities by reversed-phase column chromatography on C-18 silica gel.[11]

Results of the reactions of the higher order cyanocuprate **1** and the allyllithium reagent **2** with a representative set of epoxides are summarized in Table 1. Allylcuprate **1** reacted smoothly with 1,2-epoxyhexane to afford **7** and in moderate yield with epichlorohydrin to

® Abstract published in *Advance ACS Abstracts,* June 15, 1994.

(1) Bartók, M.; Láng, K. L. In *The Chemistry of Functional Groups: The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulphur Analogues*; Patai, S., Ed.; John Wiley and Sons Ltd.: New York, 1980; Supplement E, Part 2, Chapter 14, pp 609–681.

(2) (a) Klunder, J. M.; Posner, G. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Pattenden, G., Eds.; Pergamon: Oxford, 1991; Vol. 3, Chapter 1.5, pp 223–226. (b) Yamaguchi, M. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Schreiber, S. L., Eds.; Pergamon: Oxford, 1991; Vol. 1, Chapter 1.11, pp 342–345.

(3) (a) Fleming, I.; Paterson, I. *Synthesis* **1979**, 446. (b) Hayashi, T.; Kabeta, K.; Yamamoto, T.; Tamao, K.; Kumada, M. *Tetrahedron Lett.* **1983**, *24*, 5661.

(4) Imai, T.; Nishida, S. *J. Org. Chem.* **1990**, *55*, 4849

(5) Berger, D.; Overman, L. E.; Renhowe, P. A. *J. Am. Chem. Soc.* **1993**, *115*, 9305.

(6) Fleming, I.; Rowley, M. *Tetrahedron* **1989**, *45*, 413.

(7) (a) Lee, E.; Yu, S.-G.; Hur, C.-U.; Yang, S.-M. *Tetrahedron Lett.* **1988**, *29*, 6969. (b) Desponds, O.; Schlosser, M. *J. Organomet. Chem.* **1991**, *409*, 93.

(8) (a) Chan, T. H.; Ong, B. S. *J. Org. Chem.* **1978**, *43*, 2994. (b) Chan, T. H.; Mychajlowskij, W.; Ong, B. S.; Harpp, D. *J. Org. Chem.* **1978**, *43*, 1526.

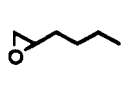
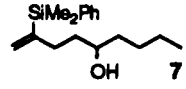
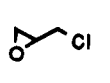
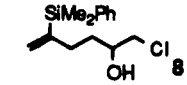
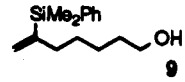
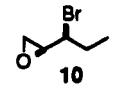
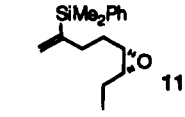
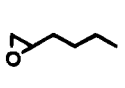
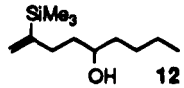
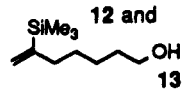
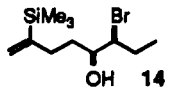
(9) Schlosser, M.; Coffinet, D. *Synthesis* **1971**, 380.

(10) Westmijze, H.; Vermeer, P. *Synthesis* **1979**, 390.

(11) Farina, V. *J. Org. Chem.* **1991**, *56*, 4985.

0022-3263/94/1959-4138$04.50/0

Table 1. Reaction of the Higher Order Cuprate 1 and Allyllithium Reagent 2 with Terminal Epoxides

epoxide	product(s)	reaction conditions[a] nucleophile	temp, °C	additive, eq	yield, %
	 7	1	-78 → 25	none	81
	 8	1	-40	none	60
	 9	1	-78 → -30	$BF_3{\cdot}OEt_2$, 1.0	53
 10	 11	1	-78 → -40	none	36
	 12	2	-78	none	62
	 12 and 13	2	-78	$BF_3{\cdot}OEt_2$, 1.4	12: 55 13: 12
	12	2[b]	-78	$BF_3{\cdot}OEt_2$, 1.4	40
10	 14	2	-78	none	37
10	14 and 13	2	-78	$BF_3{\cdot}OEt_2$, 1.3	14: 50 13: 16
10	14	2[b]	-78	$BF_3{\cdot}OEt_2$, 1.3	51

[a] One equiv of the allylic nucleophile was employed, and the solvent was THF unless noted otherwise. Reactions were performed at least three times, and mean yields are reported. [b] Solvent was 2,5-dimethyltetrahydrofuran.

provide **8**. Addition of $BF_3{\cdot}OEt_2$[12] to this latter reaction resulted in ring opening of THF to provide **9**. The β-bromo alkoxide generated from the reaction of bromo epoxide **10**[5] with **1** was apparently not stable even at low temperature, since the rearranged epoxide **11** was isolated in 36% yield when this reaction was conducted at −78 → −40 °C. Epoxide **11** was also formed when this reaction was carried out solely at −78 °C.

The allyllithium reagent **2** also reacted smoothly with 1,2-epoxyhexane to give a moderate yield of alcohol **12**, while in the presence of $BF_3{\cdot}OEt_2$ the yield of **12** was decreased slightly due to competitive opening of THF (Table 1). Utilization of the more stable 2,5-dimethyltetrahydrofuran as the solvent shut down this undesired side reaction; however, the yield of **12** was still low. Qualitatively similar results were obtained in the reaction of lithium reagent **2** with bromo epoxide **10**.

Results obtained from the reaction of several epoxides with the allylsilane **3**[13] and allylstannane **4** are collected in Table 2. Attempted reaction of 1,2-epoxyhexane with allylsilane **3** in CH_2Cl_2 at −78 °C in the presence of 1 equiv of $TiCl_4$ resulted only in chloride opening to form chlorohydrin **15**[14] in 55% yield. However, treatment of epichlorohydrin with **3** under the same conditions (or with $EtAlCl_2$) provided the allylated chlorohydrin **16** in high yield. This result is consistent with the earlier success of Imai and Nishida[4] in reacting α-chloro epoxides with simple allylsilanes. Perhaps most surprisingly, reaction of **3** with epibromohydrin in the presence of $TiCl_4$ provided, in 90% yield, only the product of chloride opening, 3-bromo-2-chloropropan-1-ol (**17**).[15] Similarly, the α-bromo epoxide **10**[5] experienced only chloride opening to form **18** when treated with allylsilane **3** and $TiCl_4$. In an attempt to minimize chloride opening, we examined less reactive Lewis acids such as $TiCl_4$–Ph_3P, (3:1) $TiCl_4$–

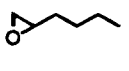
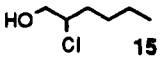
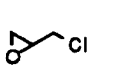
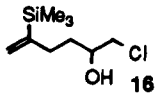
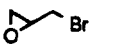
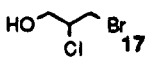
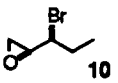
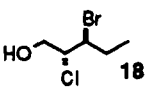
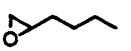
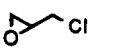
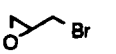
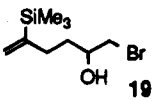
(12) Kurth, M. J.; Abreo, M. A. *Tetrahedron Lett.* **1987**, *28*, 5631.

(13) Watanabe, H.; Saito, M.; Sutou, N.; Kishimoto, K.; Inose, J.; Nagai, Y. *J. Organomet. Chem.* **1982**, *225*, 343.

(14) Nakai, H.; Kurono, M. *Chem. Lett.* **1977**, 995.

(15) Hirano, D. S.; Geigert, J.; Lee, T. D. *J. High Resolut. Chromatogr. Chromatogr. Commun.* **1983**, *6*, 38.

Table 2. Reaction of the Allylsilane 3 and the Allylstannane 4 with Terminal Epoxides

		reaction conditions[a]		
epoxide	product(s)	nucleophile, eq	additive, eq	yield, %
	 **15**	**3**, 0.9	$TiCl_4$, 1.0	55
	 **16**	**3**, 0.9	$TiCl_4$, 1.0	85
	16	**3**, 0.9	$EtAlCl_2$, 1.0	87
	 **17**	**3**, 0.9	$TiCl_4$, 1.0	90
 **10**	 **18**	**3**, 10.0	$TiCl_4$, 1.0	77
10	**14**	**3**, 10.0	$BF_3{\cdot}OEt_2$, 2.0	24
	**12**	**4**, 1.5	$EtAlCl_2$, 1.1	92
	**16**	**4**, 1.5	$EtAlCl_2$, 1.1	100
	 **19**	**4**, 1.5	$EtAlCl_2$, 1.1	90
10	**14**	**4**, 1.5	$EtAlCl_2$, 1.1	88
10	**14** and **18**	**4**, 2.0	$TiCl_4$, 1.0	**14**: 39 **18**: 25
10	**14**	**4**, 2.0	$BF_3{\cdot}OEt_2$, 2.0	37
10	**10**	**4**, 2.0	$SnCl_4$, 1.0	95

[a] Reactions were performed in CH_2Cl_2 at −78 °C at least three times, and mean yields are reported.

$Ti(OiPr)_4$, and $EtAlCl_2$; however, only **18** was produced in each case. By using 10 equiv of the allylsilane nucleophile and $BF_3{\cdot}OEt_2$ as the Lewis acid, the desired allylated product **14** was formed, albeit in low yield.

As expected, the more reactive[4,16] allylstannane nucleophile **4** minimized competitive epoxide opening with chloride. As summarized in Table 2, reactions of 1,2-epoxyhexane, epichlorohydrin, epibromohydrin, and bromo epoxide **10** with [2-(trimethylsilyl)allyl]tributyltin (**4**) in the presence of 1.1 equiv of $EtAlCl_2$ proceeded in excellent yield to provide the allylated products **12**, **16**, **19**, and **14**. Advantages of using $EtAlCl_2$ to promote the reaction of allylstannane **4** with epoxides is apparent in the results in the study of the reaction of **4** with **10**. Use of $SnCl_4$, rather than $EtAlCl_2$, resulted in a 95% recovery of the starting epoxide **10**, while use of $BF_3{\cdot}OEt_2$ provided **14** in low yield only. With $TiCl_4$, **14**, and the product of chloride opening **18** were formed in a 8:5 ratio.

In summary, highly functionalized vinylsilane alcohols and vinylsilane halohydrins can be prepared in high yields from the reaction of [2-(trimethylsilyl)allyl]tributyltin (**4**) with terminal epoxides and terminal α-halo epoxides. $EtAlCl_2$ is the optimum Lewis acid for these reactions. Although our studies focused solely on [2-(tri-

(16) Hagen, G.; Mayr, H. *J. Am. Chem. Soc.* **1991**, *113*, 4954.

methylsilyl)allyl]stannanes, we anticipate that the allylstannane–$EtAlCl_2$ combination will be generally useful for epoxide allylations.

Experimental Section

Preparation of 1-Chloro-5-(dimethylphenylsilyl)-5-hexen-2-ol (8) from the Reaction of Epichlorohydrin with Higher Order Allyl Cuprate 1. Following the general procedure of Fleming,[6] 2.95 g (10.0 mmol) of chlorodimethylphenylsilane was treated with an excess of lithium shot (0.17 g, 24.0 mmol) in dry THF (20 mL) at 0 °C. The rapidly stirred mixture was allowed to warm to 23 °C over 18 h. The resulting dark red mixture was filtered under argon through a Schlenk filter, and the filtrate was cooled to −78 °C in a dry ice/acetone bath. This solution was then cannulated into a −78 °C slurry of 448 mg (5.00 mmol) of CuCN and dry THF (7 mL). The resulting mixture was warmed to 0 °C with stirring over 30 min. The resulting solution was cooled to −78 °C, and 0.50 mL (10 mmol) of allene was added. The resulting solution was maintained at −78 °C for 1 h. Epichlorohydrin 0.32 mL (4.1 mmol) was then added, and the solution was warmed to −35 °C. After 4 h, the solution was quenched at −35 °C with saturated aqueous NH_4Cl solution (pH 8 with NH_4OH). The layers were separated, and the H_2O layer was extracted with Et_2O (3 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated. The resulting yellow residue was purified on silica gel (3:1 hexane–Et_2O) to yield 0.40 g (60%) of **8** as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.53–7.50 (m, 2H), 7.37–7.35 (m, 3H), 5.72–5.71 (m, 1H), 5.47–5.46 (m, 1H), 3.70–3.66 (m, 1H), 3.47 (dd, J = 11.0, 3.3 Hz, 1H), 3.35 (dd, J = 11.0, 7.0 Hz, 1H), 2.36–2.13 (m, 2H), 2.01 (d, J = 4.6 Hz, 1H), 1.59–1.50 (m, 2H), 0.39 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.5, 138.1, 133.9, 129.1, 127.8, 126.5, 70.9, 50.3, 33.3, 31.7, −2.95, −3.10; IR (film) 3406, 3050, 2956, 1588, 1431, 1250, 1113, 1063; MS (CI, NH_3) m/e calcd for $C_{14}H_{25}ClNOSi$ 286.1394, found 286.1394 (M + NH_4), 253, 191, 155, 135.

General Procedure for the Reaction of Epoxides with Allyllithium 2. Preparation of 2-(Trimethylsilyl)-1-nonen-5-ol (12). A solution of stannane **4** (240 mg, 0.58 mmol) in dry THF (1.2 mL) was cooled to −78 °C, and a solution of n-BuLi (0.27 mL, 0.58 mmol, 2.2 M in hexanes) was added dropwise. The resulting yellow solution was maintained at −78 °C for 15 min, after which time it was transferred by cannula into a −78 °C solution of 1,2-epoxyhexane (56 μL, 0.47 mmol) and 0.3 mL of dry THF. The resulting solution was maintained for 1 h at −78 °C and then was quenched at this temperature with H_2O (2 mL). The layers were separated, and the H_2O layer was extracted with Et_2O (3 × 5 mL). The combined organic layers were washed with brine (2 × 5 mL), dried ($MgSO_4$), filtered, and concentrated. Purification of the residue on silica gel (3:1 pentane–Et_2O) provided 62 mg (62%) of **12** as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 5.58 (apparent t, J = 2.7, 1.3 Hz, 1H), 5.33 (d, J = 2.8 Hz, 1H), 3.64–3.56 (m, 1H), 2.35–2.12 (m, 2H), 1.65–1.25 (m, 9H), 0.91 (br t, J = 7.1, 6.7 Hz, 3H), 0.09 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.2, 124.0, 71.8, 37.2, 36.6, 32.1, 27.8, 22.7, 14.1, −1.44; IR (film) 3381, 2956, 2931, 2863, 1638, 1456, 1406, 1250, 1050; MS (EI) m/e calcd for $C_{11}H_{23}OSi$ 199.1518, found 199.1519 (M − Me), 181, 130, 91, 75. Anal. Calcd for $C_{12}H_{26}OSi$: C, 67.22; H, 12.22. Found: C, 67.10; H, 12.20.

General Procedure for the Reaction of Epoxides with Allylsilane 3. Preparation of 1-Chloro-5-(trimethylsilyl)-5-hexen-2-ol (16). To a solution of epichlorohydrin (0.10 mL, 1.3 mmol), allylsilane **3**[13] (0.20 g, 1.1 mmol), and dry CH_2Cl_2 (2.2 mL) at −78 °C was added $TiCl_4$ (1.3 mL, 1.3 mmol, 1 M in THF) over a period of 30 min. The resulting yellow solution was maintained at −78 °C for 2.5 h, at which time the reaction was quenched with H_2O (5 mL). The layers were separated, and the H_2O layer was extracted with Et_2O (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried ($MgSO_4$), filtered, and concentrated. The residue was purified on silica gel (2:1 pentane–Et_2O) to give 190 mg (85%) of **16** as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 5.59 (s, 1H), 5.36–5.35 (m, 1H), 3.84–3.80 (m, 1H), 3.65 (dd, J = 6.0, 3.0 Hz, 1H), 3.50 (dd, J = 11.0, 3.0 Hz, 1H), 2.36–2.18 (m, 2H), 2.00–1.80 (br s, 1H), 1.70–1.62 (m, 2H), 0.10 (s 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.3, 124.4, 71.1, 50.4, 33.3, 31.6, −1.50; IR (film) 3419, 2956, 1636, 1431, 1250, 1063; MS (EI) m/e calcd for $C_8H_{16}ClOSi$ 191.0659, found 191.0661 (M − Me), 191, 115, 93, 81, 75.

General Procedure for the Reaction of Epoxides with Allylstannane 4. Preparation of (5S,6S)-6-Bromo-5-hydroxy-2-(trimethylsilyl)-1-octene (14). To a −78 °C solution of allylstannane **4** (310 mg, 1.9 mmol), epoxide **10**[5] (1.13 g, 2.80 mmol), and dry CH_2Cl_2 (5 mL) was added $EtAlCl_2$ (0.22 mL, 2.1 mmol), and the resulting solution was maintained at −78 °C for 19 h. The reaction then was quenched at −78 °C with saturated aqueous NH_4Cl (5.0 mL) and allowed to warm to 23 °C over 1 h. The layers were separated, and the aqueous layer was extracted with Et_2O (2 × 10 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), filtered, and concentrated. Purification of the residue on silica gel (9:1 pentane–Et_2O) provided 460 mg (88%) of **14**, as a light yellow oil: ^1H NMR (500 MHz, $CDCl_3$) δ 5.58 (s, 1H), 5.35 (s, 1H), 4.03–3.99 (m, 1H), 3.54–3.48 (m, 1H), 2.34–2.27 (m, 1H), 2.23–2.17 (m, 1H), 1.95 (apparent quint, J = 7.0 Hz, 2H), 1.86 (d, J = 8.5 Hz, 1H), 1.75–1.62 (m, 2H), 1.05 (t, J = 7.0 Hz, 3H), 0.09 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.5, 124.4, 73.2, 67.2, 35.0, 31.8, 29.1, 12.6, −1.44; IR (film) 3450 (broad), 2956, 2899, 2879, 1248, 924, 837, 757, 690 cm^{-1}; MS (EI) m/e calcd for $C_{11}H_{24}BrOSi$ 278.0701, found 278.0696 (M), 199, 157, 139, 109, 73; $[\alpha]^{25}_D$ −12.4°, $[\alpha]_{577}$ −11.3°, $[\alpha]_{546}$ −12.3°, $[\alpha]_{435}$ −21.5°, $[\alpha]_{405}$ −25.2° (c 1.10, $CHCl_3$). Anal. Calcd for $C_{11}H_{23}BrOSi$: C, 47.31; H, 8.30. Found: C, 47.36; H, 8.31.

Preparation of [2-(Trimethylsilyl)allyl]tributylstannane (4). To a −50 °C solution of the alcohol **6**[7] (4.00 g, 31 mmol) and dry THF (50 mL) was added n-BuLi (2.5 M in hexane, 12.3 mL, 31 mmol) dropwise. The reaction then was maintained at −50 °C for 30 min, methanesulfonyl chloride (2.4 mL, 31 mmol) was then added, and the reaction was maintained for an additional 30 min at −50 °C.

According to the procedure of Still,[17] $(n\text{-Bu})_3SnLi$ was prepared from freshly prepared $(n\text{-Bu})_3SnH$[18] (8.30 mL, 31 mmol) and n-BuLi (2.5 M in hexane, 12.3 mL, 31 mmol) in dry THF (100 mL) at 0 °C. The stannyllithium solution was then cooled to −78 °C and cannulated into the cold solution of crude mesylate. The resulting solution was allowed to warm to 23 °C over several hours and then was quenched with H_2O (50 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 × 25 mL). The combined organic layers were washed with brine (50 mL), dried ($MgSO_4$), filtered, and concentrated. Purification of the residue on reversed-phase silica gel[11] (4:1 MeCN–CH_2Cl_2 → 3:2 MeCN–CH_2Cl_2) provided 8.80 g (71%) of **4** as a clear liquid: ^1H NMR (500 MHz, $CDCl_3$) δ 5.36–5.32 (m, 1H), 5.09–5.04 (m, 1H), 1.89 (t, J = 31.5 Hz, 2H), 1.55–1.26 (m, 12H), 0.90–0.83 (m, 15H), 0.07 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.0, 120.0, 29.1, 27.4, 17.1, 13.7, 9.70, −1.61; IR (film) 2960, 2926, 2870, 1601, 1462, 1418, 1245, 1073; MS (EI) m/e calcd for $C_{18}H_{40}SiSn$ − Me 389.1686, found 389.1691 (M − Me), 347, 291, 235, 177, 121.

2-(Dimethylphenylsilyl)-1-nonen-5-ol (7): ^1H NMR (300 MHz, $CDCl_3$) δ 7.54–7.49 (m, 2H), 7.39–7.31 (m, 3H), 5.73–5.71 (m, 1H), 5.45–5.44 (d, J = 2.7 Hz, 1H), 3.51–3.47 (m, 1H), 2.32–2.10 (m, 2H), 1.52–1.42 (m, 2H), 1.39–1.21 (m, 7H), 0.89 (br t, 6.8 Hz, 3H), 0.39 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.3, 138.3, 133.9, 129.0, 127.8, 126.0, 71.6, 37.1, 36.6, 32.0, 27.8, 22.7, 14.0, −2.88; IR (film) 3356, 3050, 2956, 2931, 2863, 1425, 1250, 1113, 1050; MS (CI, NH_3) m/e calcd for $C_{17}H_{32}NOSi$ 294.2253, found 294.2253 (M + NH_4), 261, 199, 192, 161, 135.

6-(Dimethylphenylsilyl)-6-hepten-1-ol (9): ^1H NMR (300 MHz, $CDCl_3$) δ 7.53–7.50 (m, 2H), 7.36–7.34 (m, 3H), 5.68 (t, J = 1.3 Hz, 1H), 5.41 (d, J = 2.9 Hz, 1H), 3.57 (t, J = 6.6, Hz, 2H), 2.13 (br t, J = 7.8, 7.0 Hz, 2H), 1.53–1.43 (m, 2H), 1.39–

(17) Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481.
(18) Kuivila, H. G.; Beumel, O. F. *J. Am. Chem. Soc.* **1961**, *83*, 1246.

1.24 (m, 5H), 0.37 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.2, 138.4, 133.9, 128.9, 127.7, 125.8, 62.9, 35.9, 32.5, 28.5, 25.4, −2.96; IR (film) 3356, 3050, 2938, 2863, 1431, 1250, 1113, 1050; MS (EI) *m/e* calcd for $C_{14}H_{21}OSi$ 233.1362, found 233.1364 (M − Me), 191, 173, 137, 75.

(3*R*, 4*S*)-7-(Dimethylphenylsilyl)-3,4-epoxy-7-octene (11): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52−7.50 (m, 2H), 7.36−7.35 (m, 3H), 5.73−5.72 (m, 1H), 5.47−5.46 (m, 1H), 2.88−2.81 (m, 2H), 2.35−2.18 (m, 2H), 1.62−1.35 (m, 4H), 0.99 (t, J = 7.5 Hz, 3H), 0.39 (s 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.4, 138.0, 133.9, 129.0, 127.8, 126.1, 58.4, 56.9, 32.3, 27.1, 21.0, 10.6, −3.05; IR (film) 2969, 1456, 1431, 1250, 1113; MS (EI) *m/e* calcd for $C_{15}H_{21}OSi$ 245.1362, found 245.1364 (M − Me), 183, 141, 135, 75; $[\alpha]^{25}_D$ −2.65°, $[\alpha]_{577}$ −3.07°, $[\alpha]_{546}$ −3.99°, $[\alpha]_{435}$ −5.23°, $[\alpha]_{405}$ −6.13° (*c* 1.68, $CHCl_3$). Anal. Calcd for $C_{16}H_{24}OSi$: C, 73.79; H, 9.29. Found: C, 73.88; H, 9.28.

6-(Trimethylsilyl)-6-hepten-1-ol (13): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.55−5.54 (m, 1H), 5.31−5.30 (m, 1H), 3.65 (t, J = 6.6 Hz, 2H), 2.14 (br t, J = 7.6, 6.8 Hz, 2H), 1.63−1.54 (m, 2H), 1.49−1.33 (m, 5H), 0.08 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3, 123.8, 63.0, 36.0, 32.7, 28.8, 25.6, −1.44; IR (film) 3419, 2938, 2863, 1638, 1419, 1338, 1250, 1050; MS (EI) *m/e* calcd for $C_9H_{19}OSi$ 171.1205, found 171.1208 (M − Me), 153, 143, 81, 75. Anal. Calcd for $C_{10}H_{22}OSi$: C, 64.45; H, 11.90. Found: C, 64.52; H, 11.87.

1-Bromo-5-(trimethylsilyl)-5-hexen-2-ol (19): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.58 (apparent d, J = 1.3 Hz, 1H), 5.36 (apparent d, J = 2.6 Hz, 1H), 3.83−3.76 (m, 1H), 3.55 (dd, J = 10.0, 3.3 Hz, 1H), 3.40 (dd, J = 10.0, 7.0 Hz, 1H), 2.38−2.15 (m, 3H), 1.71−1.64 (m, 2H), 0.09 (s 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.3, 124.4, 70.7, 40.5, 34.3, 31.7, −1.47; IR (film) 3419, 2956, 1688, 1425, 1250, 1050; MS (EI) *m/e* calcd for $C_8H_{16}BrOSi$ 235.0154, found 235.0155 (M − Me), 195, 171, 155, 81, 75.

(2*R*, 3*S*)-3-Bromo-2-chloro-1-pentanol (18): ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.30 (apparent dt, J = 6.7, 6.4, 2.6, 2.3 Hz, 1H), 4.11−4.06 (m, 1H), 4.03−3.91 (m, 2H), 2.04−1.86 (m, 3H), 1.07 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 64.7, 63.5, 59.1, 29.7, 11.3; IR (film) 3318, 2975, 2938, 2881, 1638, 1463, 1238, 1069, 1038; MS (EI) *m/e* calcd for C_5H_9BrO 163.9837, found 163.9841 (M − HCl), 134, 103, 85, 67, 55; $[\alpha]^{25}_D$ +37.9°, $[\alpha]_{577}$ +39.1°, $[\alpha]_{546}$ +44.7°, $[\alpha]_{435}$ +76.7°, $[\alpha]_{405}$ +92.6° (*c* 2.03, $CHCl_3$).

Acknowledgment. This investigation was supported by NSF Grant CHE-90-03812. NMR and mass spectra were determined at Irvine with spectrometers purchased with the assistance of NSF Shared Instrumentation Grants.

Supplementary Material Available: General experimental procedure for preparing **6** and copies of ^{1}H and ^{13}C NMR spectra of **4**, **7**−**9**, **17**, **19**, and **16** (17 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.