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# Ring-Opening Reactions of $\alpha,\beta$-Epoxy Silanes with Organocopper Reagents: Reaction at Carbon or Silicon?

Paul F. Hudrlik,* Da Ma, Rama S. Bhamidipati, and
Anne M. Hudrlik

*Department of Chemistry, Howard University,
Washington, D.C. 20059*

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$\alpha,\beta$-Epoxy silanes react with a wide variety of reagents *via* ring opening $\alpha$ to silicon.[1] These reactions have been found to have a variety of uses in organic synthesis.[1] A number of years ago, we introduced a stereospecific synthesis of olefins[2a] and heteroatom-substituted olefins[2bc] based on these ring opening reactions coupled with stereospecific[3,4] $\beta$-elimination reactions of the resulting $\beta$-hydroxy silanes. $\alpha,\beta$-Epoxy silanes also have potential uses for the preparation of homochiral building blocks in asymmetric synthesis due to the effect of silicon on the stereochemistry of epoxidation reactions, particularly the Sharpless asymmetric epoxidation.[5]

$\alpha$-Ring opening of $\alpha,\beta$-epoxy silanes has been observed under both nucleophilic and electrophilic conditions. The reaction was first observed in 1963 using $LiAlH_4$[6] and then in 1975, in a paper that introduced the olefin synthesis,[2a] using organocopper reagents. Additional examples of $\alpha$-ring opening of $\alpha,\beta$-epoxy silanes have been reported with organocopper reagents,[7] as well as with a variety of other reagents including other hydride reagents (*e.g.*, $i$-$Bu_2AlH$,[8] $AlH_3$[6e,9]), stabilized organolithium reagents,[7h,10] $R_3SnLi$,[11] magnesium halides,[12] hydrogen halides,[13] $SiF_4$,[14] $RCO_2H$,[2b,4b,15] ROH/acid,[16] $CH_3CN$/acid,[2b] amines,[2c] azides,[17] KSCN,[6d] and organosulfur reagents.[18]

The reasons for the preference for $\alpha$ opening of the $\alpha,\beta$-epoxy silanes are not completely obvious. The $\alpha$-position is frequently the more hindered, and ring opening at the $\beta$-position (under electrophilic conditions) might be expected to produce a highly stabilized $\beta$-silyl cation.[19] However, as we first pointed out in 1976, the lack of $\beta$-opening, although remarkable, is perhaps less surprising in view of the relative orientation of the C−Si bond and the $\beta$-C−O bond which greatly deviates from the parallel alignment that is favorable for stabilization of a developing positive $\beta$-charge by the silicon.[12a] The high reactivity of $Me_3SiCH_2X$ toward nucleophilic displacements has also been noted.[20] Both the reactivity of $Me_3SiCH_2X$[20c] and the $\alpha$-opening of $\alpha,\beta$-epoxy silanes[6ad,8a,12bc,13c,21] have been rationalized by assuming

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(4) Syn-elimination with basic conditions;[2a,3] anti-elimination with acid conditions;[2a,3] anti-elimination by conversion of the hydroxyl to a good leaving group and treatment with fluoride, *e.g.*, see: (a) Luo, F.-T.; Negishi, E. *J. Org. Chem.* **1983**, *48*, 5144−5146. See also: (b) Croudace, M. C.; Schore, N. E. *J. Org. Chem.* **1981**, *46*, 5357−5363.

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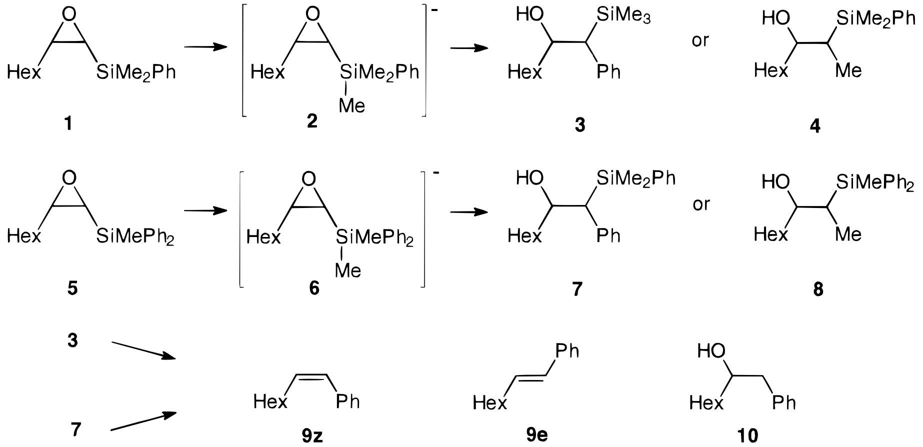
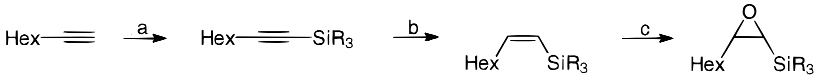
**Scheme 1**



**Scheme 2**



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|---|---|---|---|
| SiR3 = SiMe3 | **11** | **12** | **13** |
| SiR3 = SiMe2Ph | **14** | **15** | **1** |
| SiR3 = SiMePh2 | **16** | **17** | **5** |

(a) RLi, then $R_3SiCl$; (b) *i*-$Bu_2AlH$, then $H_3O^+$; (c) *m*-CPBA

initial coordination of the nucleophile with both silicon and carbon. Coordination of the nucleophile with silicon followed by 1,2-rearrangement to the α-carbon[6d,12b,21b,22] has also been suggested for the α-opening reactions.[23,24]

We report here a test of the latter suggestion (coordination followed by 1,2-rearrangement) for the reactions of α,*β*-epoxy silanes with organocopper reagents.[25] We have studied the reactions of the $PhMe_2Si$ and $Ph_2MeSi$ epoxy silanes **1** and **5** with methylcopper reagents (MeLi/CuI 2:1) (see Scheme 1).[26] If pentacoordinated intermediates **2** and **6** were involved, α-phenyl-*β*-hydroxy silanes **3** and **7** should be formed rather than α-methyl-*β*-hydroxy silanes **4** and **8**, since phenyl is a better migrating group than methyl.[28] The α-phenyl-*β*-hydroxy silanes **3** and **7** might be expected to undergo *β*-elimination or desilylation reactions more rapidly than the α-methyl-*β*-hydroxy silanes **4** and **8**; therefore, 1-phenyl-1-octene (**9**) and 1-phenyl-2-octanol (**10**) might also be formed.

*(Z)*-1-(Trimethylsilyl)-1,2-epoxyoctane (**13**), used as a control and as a starting material for the preparation of comparison samples, and the corresponding phenyldimethylsilyl (**1**) and diphenylmethylsilyl (**5**) epoxides were prepared as shown in Scheme 2.

Our first attempts to prepare comparison samples of α-phenyl-*β*-hydroxy silanes **3** and **7** by ring opening of epoxy silanes **13** and **1** with copper reagents derived from PhLi were unsuccessful. Treatment of epoxy silanes **13** and **1** with PhLi/CuI (2:1) and with PhLi/CuCN (2:1) led to no detectable *β*-hydroxy silanes (**3** and **7**, respectively). In all of the cases, small amounts of 1-phenyl-1-octene (**9**) as well as considerable amounts of biphenyl were present in the products. In the case of the $PhMe_2Si$ epoxide **1**, diphenyldimethylsilane was also observed in the product mixtures.

Early attempts to open α,*β*-epoxy silanes with alkenyl organocopper reagents were reported to be unsuccessful.[7df,29] Alexakis and co-workers have found that such reactions can be carried out with the assistance of $BF_3{\cdot}Et_2O$.[7d−f] We were able to prepare **3** and **7** using the Alexakis procedure. Treatment of epoxy silane **13** with PhLi/CuI (2:1) in the presence of $BF_3{\cdot}Et_2O$ produced the *β*-hydroxy silane **3** in 86% yield. Treatment of epoxy silane **1** with PhLi/CuI (2:1) in the presence of $BF_3{\cdot}Et_2O$ produced the *β*-hydroxy silane **7** in 58% yield. Comparison samples of the olefins **9z** and **9e** were prepared by

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(22) Eisch, J. J.; Chiu, C. S. *J. Organomet. Chem.* **1988**, *358*, C1−C5.

(23) Lowering the transition state energy of an $S_N2$ reaction at the carbon α to silicon has been compared to stabilization of an "anion" at the α-carbon. Overlap involving the empty, antibonding orbitals of the Me-Si bond (in the case of a $Me_3Si$ group) with the filled orbitals of the carbon−metal bond has been invoked: Fleming, I. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; Vol. 3, pp 541−686 (especially pp 545−546).

(24) Rearrangements of α-substituted organosilicon compounds with migration of an organic group from silicon to carbon are well-known: (a) Hudrlik, P. F.; Abdallah, Y. M.; Kulkarni, A. K.; Hudrlik, A. M. *J. Org. Chem.* **1992**, *57*, 6552−6556 and references cited therein. (b) Hudrlik, P. F.; Abdallah, Y. M.; Hudrlik, A. M. *Tetrahedron Lett.* **1992**, *33*, 6743−6746. (c) A precedent for 1,2-rearrangement from silicon to the α-carbon of an epoxy silane is the reactions of some *β*-substituted epoxy (phenyldimethyl)silanes with $EtAlCl_2$, $Me_2AlCl$, $Et_2AlCl$, or $Me_3Al$ which resulted in modest yields of phenyl-substituted olefins: Fleming, I.; Newton, T. W. *J. Chem. Soc., Perkin Trans. 1* **1984**, 119−123. (In contrast, reaction of triphenylsilylethylene oxide with $MeAlCl_2$ resulted in the chlorohydrin from *β*-opening of the epoxide (ref 19b)).

(25) The mechanism of substitution reactions of organocopper reagents is discussed in the following: Lipshutz, B. H.; Sengupta, S. *Org. React.* **1992**, *41*, 135−631.

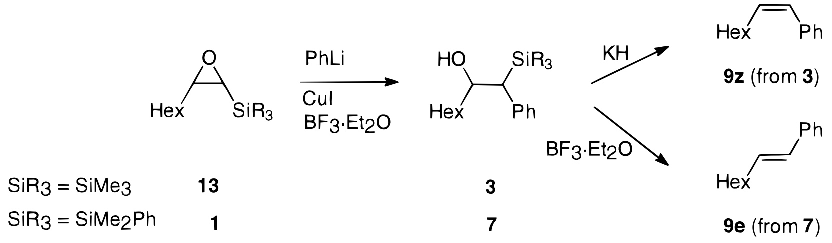
(26) When this work was begun, the only example of reaction of a Ph−Si epoxy silane with an organocopper reagent was in the dissertation of one of the authors.[27] Two additional examples have since been reported.[7k] In these cases, the isolated product was from direct epoxide opening; the possibility of rearrangement was not addressed.

(27) Bhamidipati, R. S. Ph.D. Thesis, Howard University, Washington, DC, 1991.

(28) For example, see ref 24.

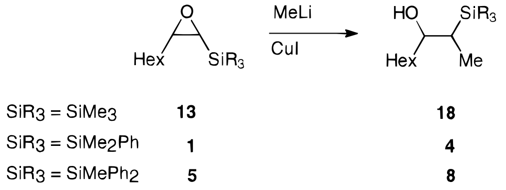
(29) Paquette, L. A.; Yan, T.-H.; Wells, G. J. *J. Org. Chem.* **1984**, *49*, 3610−3617.

**Scheme 3**



$\beta$-elimination reactions of the $\beta$-hydroxy silanes **3** and **7**. A $\beta$-elimination reaction of **3** either with KH/THF or with KH/ether gave (*Z*)-1-phenyl-1-octene (**9z**)[30] accompanied by an unidentified byproduct. A $\beta$-elimination reaction of **7** with $BF_3{\cdot}Et_2O/CH_2Cl_2$ gave (*E*)-1-phenyl-1-octene (**9e**)[31] in 95% yield (see Scheme 3). A sample of (*E*)-1-phenyl-1-octene (**9e**) was also prepared from 1-phenyl-1-octanol by treatment with $CuSO_4$ (78% yield).[32]

Epoxy silanes **13**, **1**, and **5** were each treated with MeLi/CuI (2:1) in ether. The product from epoxy silane **13** was 2-(trimethylsilyl)-3-nonanol (**18**), as expected (76% yield). The product from epoxy silane **1** was shown to be 2-(phenyldimethylsilyl)-3-nonanol (**4**), and the product from epoxy silane **5** was shown to be 2-(diphenylmethylsilyl)-3-nonanol (**8**).



2-(Phenyldimethylsilyl)-3-nonanol (**4**) was isolated after chromatography in 67% yield from the reaction with epoxide **1**. 2-(Diphenylmethylsilyl)-3-nonanol (**8**) was isolated after chromatography in 57% yield from the reaction with epoxide **5**. Compounds **4** and **8** were identified from their IR, $^1$H NMR, $^{13}$C NMR, and mass spectra. In particular, the $^1$H NMR of **4** showed a three-proton doublet at $\delta$ 1.037 ($J = 7$ Hz), and the $^{13}$C NMR (with DEPT) showed four $CH_3$ groups at $\delta$ $-3.890$, $-3.802$, 7.903, and 13.972; the $^1$H NMR of **8** showed a doublet at $\delta$ 1.111 ($J = 7.5$ Hz), and the $^{13}$C NMR (with DEPT) showed three $CH_3$ groups at $\delta$ $-5.080$, 8.041, and 14.012.

The crude products from the reactions of epoxy silanes **1** and **5** with MeLi/CuI were compared by GC and by $^1$H NMR with (*E*)- and (*Z*)-1-phenyl-1-octene (**9e** and **9z**), with 1-phenyl-2-octanol (**10**), and with the α-phenyl-$\beta$-hydroxy silanes (**3** in the case of epoxy silane **1**, and **7** in the case of epoxy silane **5**). In the case of the crude product from epoxy silane **1**, the $^1$H NMR spectrum showed predominantly peaks due to the $\beta$-hydroxy silane **4**, with only a few additional singlets around $\delta$ 0.0. *No signals from the comparison compounds **3**, **9e**, **9z**, or **10** were visible.* The GC trace showed predominantly one peak, with the maximum amount of comparison compounds **3**, **9z**, and **9e** at 2%, <1%, and <1%, respectively. In the case of the crude product from epoxy silane **5**, the $^1$H NMR spectrum showed predominantly peaks due to the $\beta$-hydroxy silane **8**, with a very small multiplet at about $\delta$ 1.5 and two very small singlets about 2.6−2.7. *No signals from the comparison compounds **7**, **9e**, **9z**, or **10** were visible.* The GC trace showed predominantly one peak, with the maximum amount of comparison compounds **7**, **9z**, and **9e** at 2%, <1%, and 4%, respectively.

Diphenyldimethylsilane, which was present in the product mixture from the reaction of the $PhMe_2Si$ epoxide **1** with PhLi/CuI, was not observed in the reaction mixture from epoxide **5** with MeLi/CuI. The formation of diphenyldimethylsilane from the reactions of epoxide **1** with PhLi/CuI and PhLi/CuCN suggests the possibility that pentacoordinated intermediates such as **6** under some conditions are more likely to undergo C−Si bond breaking rather than rearrangement.

These results indicate that the ring-opening reactions of epoxy silanes **1** and **5** with MeLi/CuI give the α-methyl-$\beta$-hydroxy silanes **4** and **8**, respectively, with no detectable α-phenyl-$\beta$-hydroxy silanes **3** or **7** or derived $\beta$-elimination or desilylation products. Consequently, whether or not pentacoordinate intermediates **2** and **6** are formed in these reactions, they do not appear to be part of the product-determining pathway (to products **4** and **8**). Initial coordination of the nucleophile with both carbon and silicon remains a possibility.

## Experimental Section

**General**. All of the reactions were carried out under nitrogen, and liquid transfers were carried out with nitrogen-flushed syringes. The verb "concentrated" refers to removal of solvent on the rotary evaporator. Column chromatography was performed on Florisil (60−100 mesh, Fisher) or on silica gel (60 Å, 200−425 mesh, Fisher). GC analyses were performed with a 10% OV-101 silicone column on 80/100 mesh Gas-chrom Q, 2.6 m × 2.5 mm glass column (column S-3) or a Supelco SPB-1 30 m × 0.25 mm capillary column, film thickness 1.0 μm (column C-4); the retention time of a hydrocarbon is sometimes included. NMR spectra ($^1$H at 300 MHz and $^{13}$C at 75 MHz) were obtained in $CDCl_3$; chemical shifts are reported in $\delta$ relative to TMS ($\delta$ 0.00) for $^1$H NMR measurements unless otherwise specified and to $CDCl_3$ ($\delta$ 77.000) for $^{13}$C NMR measurements. Assignments in the $^{13}$C NMR spectra were made by DEPT 45, 90, and 135. High-resolution mass spectra (HRMS) were determined by the Midwest Center for Mass Spectrometry, University of Nebraska.

Anhydrous ether and THF were distilled from sodium and benzophenone. CuI (Aldrich) was 99.999%. *m*-CPBA (Aldrich, 55−65%) was assumed to be 60%. Methyllithium (low halide) in diethyl ether was obtained from Aldrich. (1-Octynyl)trimethylsilane (**11**)[33] and (1-octynyl)phenyldimethylsilane (**14**)[34] were prepared from 1-octyne by treatment with methyllithium followed by trimethylchlorosilane and phenyldimethylchlorosilane, respectively. (*Z*)-(1-Octenyl)trimethylsilane (**12**)[33,35] and (*Z*)-(1-octenyl)phenyldimethylsilane (**15**)[36] were prepared from octyn-

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[31] Yamane, T.; Kikukawa, K.; Takagi, M.; Matsuda, T. *Tetrahedron* **1973**, *29*, 955−962. Mixer, R. Y.; Young, W. G. *J. Am. Chem. Soc.* **1956**, *78*, 3379−3384.

[32] Tanis, S. P.; Abdallah, Y. M. *Synth. Commun.* **1986**, *16*, 251−259.

[33] Uchida, K.; Utimoto, K.; Nozaki, H. *J. Org. Chem.* **1976**, *41*, 2215−2217.

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ylsilanes **11** and **14**, respectively, by treatment with *i*-$Bu_2AlH$. (*Z*)-1-(Trimethylsilyl)-1,2-epoxyoctane (**13**)[2b,37] was prepared from vinylsilane **12** by treatment with *m*-CPBA. 1-Phenyl-2-octanol (**10**)[38] was prepared from heptanal by treatment with benzylmagnesium chloride and from 1,2-epoxyoctane by treatment with PhLi/CuCN (2:1).

**(*Z*)-1-Phenyldimethylsilyl-1,2-epoxyoctane (1).** To a mixture of 2.11 g (7.34 mmol) of *m*-CPBA and 1.02 g (7.19 mmol) of $Na_2HPO_4$ in 40 mL of dichloromethane was added a solution of 1.24 g (5.03 mmol) of vinylsilane **15** in 2 mL of dichloromethane. The resulting reaction mixture was stirred at rt for 26 h, and then 15 mL of 20% aqueous $NaHSO_3$ was added. The resulting mixture was stirred for 1 h. Then the aqueous layer was separated, 12 mL of 20% NaOH solution was added to the organic layer, and the resulting mixture was stirred for 0.5 h. Water was added, and the organic layer was washed with saturated $NaHCO_3$ followed by water, dried ($MgSO_4$), and concentrated. Chromatography on 75 g of Florisil using petroleum ether/ether (95:5) gave 1.21 g (92% yield) of the epoxy silane **1** as a colorless liquid: $^1H$ NMR $\delta$ 0.388 (3 H, s), 0.408 (3 H, s), 0.869 (3 H, t, $J = 7$ Hz), 1.2−1.5 (10 H, m), 2.402 (1 H, d, $J = 5$ Hz), 3.120 (1 H, crude q), 7.375 (3 H, m), 7.563 (2 H, m); $^{13}C$ NMR $\delta$ −3.289 ($CH_3$), −2.791 ($CH_3$), 13.967 ($CH_3$), 22.495 ($CH_2$), 26.908 ($CH_2$), 29.079 ($CH_2$), 31.373 ($CH_2$), 31.685 ($CH_2$), 50.139 (CH), 57.804 (CH), 127.884 (CH), 129.341 (CH), 133.831 (CH), 137.180 (C); GC/MS *m/z* (tentative assignment, relative intensity) 262 ($M^+$, not visible), 247 ($M^+ - Me$, 4), 233 ($M^+ - Et$, 2), 191 ($M^+ -$ Pent, 17), 137 ($PhMeSiOH^+$, 36), 135 ($PhMe_2Si^+$, 100), 121 ($PhMeSiH^+$, 10), 117 (10), 105 (10), 75 (10); calcd mass for $C_{15}H_{23}OSi$ ($M^+ - Me$) 247.1518, HRMS (*m/z*) 247.1517. GC analysis (column S-3) [100 °C (1 min), 10 °C/min to 250 °C (10 min), $C_{18}H_{38}$ at 15.2 min] showed one major peak at 15.3 min (98%); under these conditions vinylsilane **15** had a retention time of 13.3 min (none was visible).

**1-Phenyl-1-(phenyldimethylsilyl)-2-octanol (7) and (*E*)-1-Phenyl-1-octene (9e).** To a mixture of 0.63 g (3.31 mmol) of CuI in 10 mL of anhydrous ether at −70 °C was added 8.3 mL (6.6 mmol) of phenyllithium (0.8 M in ether) dropwise, and the resulting reaction mixture was stirred at −55 °C for 1 h. Then the mixture was recooled to −78 °C, a solution of 0.26 g (0.99 mmol) of epoxy silane **1** in 4 mL of ether was added, and the resulting mixture was stirred for 0.5 h. Then 0.15 mL (1.22 mmol) of $BF_3 \cdot Et_2O$ in 30 mL of anhydrous ether was added slowly (the temperature was kept below −70 °C), and the resulting mixture was stirred for 1.5 h at −78 °C. Then a mixture of 50 mL of saturated $NH_4Cl$ and 15 mL of ammonium hydroxide was added, and the resulting mixture was stirred at rt for 1 h. The layers were separated, the aqueous layer was extracted twice with ether, and the combined organic layers were dried ($MgSO_4$) and concentrated to give 0.47 g of crude product. Chromatography of a portion (0.24 g) of the crude product on 50 g of Florisil using petroleum ether/ether (9:1) gave 0.10 g (58% yield[39]) of $\beta$-hydroxy silane **7** ($R_f = 0.3$) as a colorless liquid: $^1H$ NMR $\delta$ 0.177 (3 H, s), 0.342 (3 H, s), 0.832 (3 H, crude t, $J = 7$ Hz), 1.1−1.6 (16 H, including OH), 2.393 (1 H, d, $J = 7$ Hz), 4.031 (1 H, m), 7.1−7.5 (10 H, m); $^{13}C$ NMR $\delta$ −3.772 ($CH_3$), −2.379 ($CH_3$), 13.984 ($CH_3$), 22.531 ($CH_2$), 22.630 (small, impurity?), 25.869 ($CH_2$), 29.098 ($CH_2$), 31.748 ($CH_2$), 36.919 ($CH_2$), 44.612 (CH), 72.644 (CH), 125.291 (CH), 127.705 (CH), 128.236 (CH), 129.002 (CH), 129.578 (CH), 134.039 (CH), 134.163 (small, impurity?), 138.276 (C), 140.344 (C); GC/MS *m/z* (tentative assignment, relative intensity) 340 ($M^+$, not visible), 188 ($M^+ - HOSiMe_2Ph$, 28), 135 ($PhMe_2Si^+$, 52), 117 ($Ph\text{-}CH{=}CH{-}CH_2^+$, 60), 104 ($Ph{-}CH{=}CH_2^+$, 100), 91 ($C_7H_7^+$, 20). GC analysis (column S-3) [150 °C (0 min), 10 °C/min to 270 °C (8 min), $C_{18}H_{38}$ at 9.2 min] showed one major peak at 15.35 min (92%) and a minor peak at 12.05 min (4.7%); under these conditions epoxy silane **1** had a retention time of 10.2 min (none was visible).

To a solution of 0.10 g (0.39 mmol) of 1-phenyl-1-(phenyldimethylsilyl)-2-octanol (**7**) in 10 mL of $CH_2Cl_2$ was added 1.8 mL (14.6 mmol) of $BF_3 \cdot Et_2O$, and the resulting reaction mixture was stirred at rt for 1 h. Then 25 mL of saturated $NaHCO_3$ was added, and the resulting mixture was stirred at rt for 10 min. The layers were separated, the aqueous layer was extracted twice with ether, and then the combined organic layers were dried ($MgSO_4$) and concentrated. Flash chromatography on 50 g of silica gel using petroleum ether/ether (9:1) gave 0.07 g (95% yield) of (*E*)-1-phenyl-1-octene (**9e**).[31]

**Reaction of Epoxide 1 with MeLi/CuI**: **2-(Phenyldimethylsilyl)-3-nonanol (4).** To a mixture of 1.18 g (6.20 mmol) of CuI in 10 mL of anhydrous ether at −45 °C was added 12.4 mL (12.4 mmol) of methyllithium (1.0 M) dropwise. The resulting reaction mixture was stirred for 1 h at −45 °C. Then a solution of 0.40 g (1.52 mmol) of epoxy silane **1** in 4 mL of anhydrous ether was added dropwise, and the resulting mixture was stirred [2 h at −45 °C, 23 h (−45 °C → rt)]. Then 50 mL of saturated $NaHCO_3$ was poured into the reaction mixture, the layers were separated, the aqueous layer was extracted three times with ether, and then the combined organic layers were washed with saturated $NaHCO_3$ followed by water, dried ($MgSO_4$), and concentrated. Chromatography on 20 g of Florisil using petroleum ether/ether (95:5) gave 0.28 g (67% yield) of the $\beta$-hydroxy silane **4** as a colorless liquid: $^1H$ NMR ($CH_2Cl_2$ standard) $\delta$ 0.385 (3 H, s), 0.394 (3 H, s), 0.926 (3 H, t, $J = 7$ Hz), 1.037 (3 H, d, $J = 7$ Hz), 1.134 (1 H, m), 1.2−1.6 (11 H including OH, m), 3.798 (1 H, m), 7.4 (3 H, m), 7.6 (2 H, m); $^{13}C$ NMR $\delta$ −3.890 ($CH_3$), −3.802 ($CH_3$), 7.903 ($CH_3$), 13.972 ($CH_3$), 22.540 ($CH_2$), 26.023 (CH), 26.211 ($CH_2$), 29.219 ($CH_2$), 31.777 ($CH_2$), 36.270 ($CH_2$), 72.847 (CH), 127.705 (CH), 128.799 (CH), 133.871 (CH), 136.831 (C); GC/MS *m/z* (tentative assignment, relative intensity) 278 ($M^+$, not visible), 260 ($M^+ - H_2O$, <1), 193 ($M^+ -$ Hex, 1), 152 ($PhMe_2SiOH^+$, 12), 137 ($PhMeSiOH^+$, 100), 135 ($PhMe_2Si^+$, 100), 126 ($Hex\text{-}CH{=}CH{-}Me^+$, 8), 115 (25), 105 ($C_6H_5Si^+$, 15), 75 (30). GC analysis (column S-3) [150 °C (1 min), 10 °C/min to 270 °C (10 min), $C_{18}H_{38}$ at 11.0 min] showed one major peak at 12.48 min (100%).

In a similar experiment, 0.26 g of epoxy silane **1** in 4 mL of anhydrous ether was treated with MeLi/CuI (from 0.59 g of CuI, 10 mL of ether, and 4.4 mL of methyllithium) [2 h at −45 °C, 18 h (-45 °C → rt)] giving 0.26 g (93% crude yield) of **4** as a crude product for comparison with compounds **3**, **9e**, **9z**, and **10** as discussed in the text.

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**Supporting Information Available:** IR data for **1**, **4**, and **7**, experimental details for preparation and/or characterization of **3**, **5**, **8**, **9z**, **16**, **17**, **18**, and $^{13}C$ NMR spectra of **1**, **3**, **4**, **5**, **7**, **8**, **16**, **17**, and **18** (7 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.

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