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Reactions of (Triphenylsilyl)ethylene Oxide with Grignard Reagents (and with $MgBr_2$). A Reinvestigation

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Reactions of (triphenylsilyl)ethylene oxide (**1**) with simple Grignard reagents such as EtMgBr and PhMgBr have been reported to yield crystalline hydroxysilanes assigned as the α-hydroxy silanes expected from *β* opening of the epoxide. Reinvestigation of these reactions showed that the hydroxysilanes were the *β*-hydroxy silanes **4** and **7** expected from a rearrangement−trapping sequence; a bromohydrin, assigned as the α-bromo-*β*-hydroxy silane **9** from α opening, and (triphenylsilyl)acetaldehyde (**8**) were also formed.

Many ring-opening reactions of α,*β*-epoxy silanes are known. In most cases, ring opening occurs at the carbon α to the silicon to give *β*-hydroxy silanes.[1] However, in 1961, the reactions of triphenylsilylethylene oxide (**1**) with simple Grignard reagents (*e.g.*, EtMgBr, PhMgBr) were reported to give products of *β* opening (*e.g.*, α-hydroxy silanes **2** and **5**).[2] (Similar reactions were reported for (tribenzylsilyl)ethylene oxide.[2]) Moreover, the reaction of **1** with $MgBr_2$ to give (triphenylsilyl)acetaldehyde (**8**)[3] appears to take place by a mixture of α- and *β*-opening pathways: reaction of α-deuterio(triphenylsilyl)ethylene oxide with $MgBr_2$ gave **8** with deuterium scrambled between the aldehyde and α carbons.[4]

Most of the studies of ring opening of α,*β*-epoxy silanes have been carried out using *trimethylsilyl* epoxides. Although the vast majority of ring-opening reactions of α,*β*-epoxy silanes give α opening, *β* opening has been observed in some other cases as well, *e.g.*, with sterically hindered substrates such as epoxy silanes having the $(i\text{-Pr})_3Si$ group.[5] Because of the synthetic utility of epoxysilanes[1] and because phenyl-substituted silicon groups have been shown to increase the synthetic versatility of organosilicon compounds (phenyl substitution on silicon allows the stereospecific replacement of the silicon group by OH ($RSiMe_2Ph \rightarrow ROH$),[6] we have reinvestigated the reactions of epoxysilane **1** with Grignard reagents and with $MgBr_2$.

We have previously shown that reactions of Grignard reagents with various α,*β*-epoxy *trimethyl*silanes give *β*-hydroxy silanes that are isomeric with those expected from direct α opening.[8] The reactions were felt to occur by an α-opening pathway: magnesium halide-promoted rearrangement of the epoxides to α-silyl carbonyl compounds and trapping with the Grignard reagents. Bromohydrins, shown to be α-bromo *β*-hydroxy silanes, were obtained from some of these reactions using shorter reaction times.[8] The reactions of magnesium halides with α,*β*-epoxy trimethylsilanes have also been studied[9,10] and have resulted in halohydrins,[9a,b,d,f,g] α-silyl carbonyl compounds,[9a,c−f] and in a few cases, silyl enol ethers[9a,c,f] (presumably from rearrangement of the α-silyl carbonyl compounds). In most cases, the products could be accounted for by α opening of the epoxy silanes.[11] However, reaction of an α-alkyl-substituted epoxy trimethylsilane with a Grignard reagent gave an α-hydroxy silane (presumably from *β* opening) along with the expected *β*-hydroxy silane (1:6 ratio). When the reaction was run with added $MgBr_2$, the *β*-hydroxy silane was obtained in good yield.[8]

Relatively few reactions have been carried out with epoxy silanes having aryl-substituted silicon groups. In addition to the above-mentioned Grignard reactions, other ring-opening reactions of (triphenylsilyl)ethylene oxide (**1**) include examples of both α and *β* ring opening. Reactions with $LiAlH_4$[3a] and with $(i\text{-Bu})_2AlH$[4,12,13] have been reported to result in α opening; although with a large excess of $LiAlH_4$, the product of *β* opening was observed as a minor product.[3a] Reaction with Me_2CuLi resulted in a mixture with predominant α opening (88:12), while addition of $BF_3{\cdot}Et_2O$ reversed the regioselectivity.[14] Reactions with HCl,[4] $(i\text{-Bu})_3Al$,[12b] lithiated sulfones,[15] and $MeAlCl_2$[16] have resulted in predominantly the product of *β* ring opening.

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1996.

[1] Review: Hudrlik, P. F.; Hudrlik, A. M. In *Advances in Silicon Chemistry*; Larson, G. L., Ed.; JAI Press: Greenwich, CT, 1993; Vol. 2, pp 1−89.

[2] Wende, A.; Gesierich, A. *Plaste u. Kautschuk* **1961**, *8*, 301−303; *Chem. Abstr.* **1962**, *56*, 5993f.

[3] (a) Eisch, J. J.; Trainor, J. T. *J. Org. Chem.* **1963**, *28*, 2870−2876. (b) Wilt, J. W.; Kolewe, O.; Kraemer, J. F. *J. Am. Chem. Soc.* **1969**, *91*, 2624−2631. (c) Brook, A. G.; MacRae, D. M.; Bassindale, A. *J. Organomet. Chem.* **1975**, *86*, 185−192.

[4] Eisch, J. J.; Galle, J. E. *J. Org. Chem.* **1976**, *41*, 2615−2621.

[5] Lipshutz, B. H.; Lindsley, C.; Susfalk, R.; Gross, T. *Tetrahedron Lett.* **1994**, *35*, 8999−9002.

[6] (a) Fleming, I.; Henning, R.; Plaut, H. *Chem. Commun.* **1984**, 29−31. (b) Fleming, I.; Sanderson, P. E. J. *Tetrahedron Lett.* **1987**, *28*, 4229−4232. (c) The alkoxy group on silicon has also been used for this purpose; see ref 7.

[7] Tamao, K.; Najako, E.; Ito, Y. *J. Org. Chem.* **1987**, *52*, 4412−4414.

[8] Hudrlik, P. F.; Hudrlik, A. M.; Misra, R. N.; Peterson, D.; Withers, G. P.; Kulkarni, A. K. *J. Org. Chem.* **1980**, *45*, 4444−4448.

[9] (a) Hudrlik, P. F.; Misra, R. N.; Withers, G. P.; Hudrlik, A. M.; Rona, R. J.; Arcoleo, J. P. *Tetrahedron Lett.* **1976**, 1453−1456. (b) Hudrlik, P. F.; Hudrlik, A. M.; Rona, R. J.; Misra, R. N.; Withers, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 1993−1996. (c) Obayashi, M.; Utimoto, K.; Nozaki, H. *Tetrahedron Lett.* **1977**, 1807−1810. (d) Obayashi, M.; Utimoto, K.; Nozaki, H. *Tetrahedron Lett.* **1978**, 1383−1386. (e) Obayashi, M.; Utimoto, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1760−1764. (f) Obayashi, M.; Utimoto, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2646−2652. (g) Okamoto, S.; Shimazaki, T.; Kobayashi, Y.; Sato, F. *Tetrahedron Lett.* **1987**, *28*, 2033−2036.

[10] (a) Ashwell, M.; Jackson, R. F. W. *J. Chem. Soc., Chem. Commun.* **1988**, 645−647. (b) Hewkin, C. T.; Jackson, R. F. W. *Tetrahedron Lett.* **1990**, *31*, 1877−1880. (c) Ashwell, M.; Clegg, W.; Jackson, R. F. W. *J. Chem. Soc., Perkin Trans. 1* **1991**, 897−908. (d) Hewkin, C. T.; Jackson, R. F. W. *J. Chem. Soc., Perkin Trans. 1* **1991**, 3103−3111.

[11] An exception is reactions of epoxides substituted in the α position with SO_2Ph which usually give (α-bromoacyl)silanes.[10]

[12] (a) Eisch, J. J.; Galle, J. E. *J. Organomet. Chem.* **1988**, *341*, 293−313. (b) Eisch, J. J.; Liu, Z.-R.; Singh, M. *J. Org. Chem.* **1992**, *57*, 1618−1621.

[13] The product of *β* opening was obtained from the reaction of α-methyl(triphenylsilyl)ethylene oxide and $(i\text{-Bu})_2AlH$.[12a]

[14] Chauret, D. C.; Chong, J. M. *Tetrahedron Lett.* **1993**, *34*, 3695−3698.

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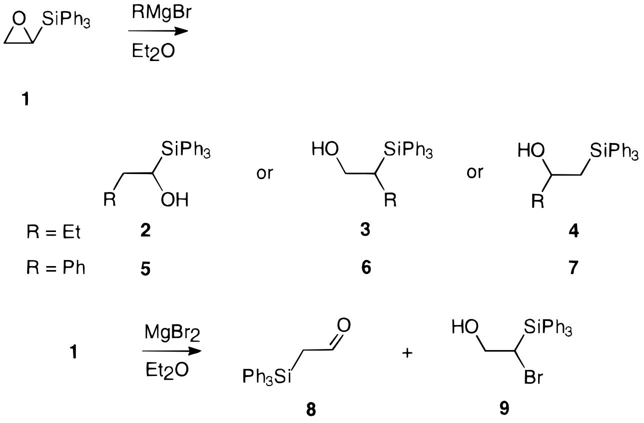
Most of the reported examples of β opening of epoxy *trimethyl*silanes have involved conformationally biased systems[17] or sterically hindered substrates or reagents.[18] The regiochemistry of ring opening of triphenylsilyl and trialkylsilyl epoxides has not been directly compared, although organocopper reagents with $BF_3{\cdot}Et_2O$[14] and lithiated sulfones[15] appear to give more β opening with the triphenylsilyl epoxide.

The β-hydroxy silanes obtained from the direct α opening of α,β-epoxy silanes have been useful in synthesis. They have generally been formed in very high diastereomeric purity and have been used in a stereospecific synthesis of olefins and heteroatom-substituted olefins[1] that we introduced a number of years ago.[9b,24,25] They have also been used in syntheses of alcohols[26] and diols.[7] The β-hydroxy trimethylsilanes obtained from the Grignard reactions of α,β-epoxy silanes have been also obtained in rather high diastereomeric purity (97%, stereochemistry consistent with trapping the α-silyl aldehyde with Cram's rule selectivity[27]) and are also potentially useful synthetic intermediates.[8]

Results and Discussion

We treated epoxide **1** with EtMgBr (ether, reflux, 1–2 h) and obtained a mixture of products from which a crystalline hydroxysilane (assigned as **4**) was isolated by chromatography in 25% yield. Recrystallization produced crystals of mp 74–75 °C (14%). (A mp of 57 °C was obtained for the α-hydroxy silane reported from the reaction of **1** with EtMgBr.[2]) Similarly, we treated **1** with PhMgBr and obtained a mixture of products from which a crystalline hydroxysilane (assigned as **7**) was isolated by chromatography in 24% yield (mp 124–125 °C). Purification produced crystals of mp 126–128 °C. (A mp of 128 °C was obtained for the α-hydroxy silane reported from the reaction of **1** with PhMgBr.[2]) These products were assigned as β-hydroxy silanes **4** and **7**, respectively, from the rearrangement–trapping sequence rather than α-hydroxy silanes (**2**, **5**) from β opening of the epoxides or the β-hydroxy silanes (**3**, **6**) from direct α opening of the epoxides.



The structure of the β-hydroxy silane **4** was supported by the following features of the ^1H and 2-D ($^1H-^1H$) NMR spectra: (1) appearance of C*H*OH as a one-proton multiplet at δ 3.85 that becomes an apparent quintet upon addition of D_2O, (2) presence of coupling between that C*H*OH multiplet and each of two high-field (δ 1.50, 1.72) two-proton multiplets, (3) absence of coupling of the two high-field multiplets with each other. These observations rule out the isomeric α-hydroxy silane **2** (product of β opening) and the β-hydroxy silane **3** (product of direct α opening). In addition, a ^{13}C NMR DEPT experiment indicated that the hydroxyl is attached to a CH rather than a CH_2 (CH at lower field (δ 70.445) and two CH_2's at higher field (δ 33.588 and 22.737)).

The β-hydroxy silane **7** was distinguished from the isomers **5** and **6** by the chemical shifts in the ^1H NMR spectrum, especially the one-proton multiplet at low field (δ 4.94 (becomes dd upon addition of D_2O)) and the two one-proton multiplets at higher field (δ 1.94 (dd), 2.12 (dd)) that displayed a geminal coupling of 15 Hz. In addition, a ^{13}C NMR DEPT experiment indicated that the hydroxyl was attached to a CH rather than a CH_2 (CH at lower field (δ 71.650) and a CH_2 at higher field (δ 25.782)).[28]

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[15] Jankowski, P.; Wicha, J. *Chem. Commun.* **1992**, 802–803.

[16] Eisch, J. J.; Chiu, C. S. *Heteroatom. Chem.* **1994**, *5*, 265–274.

[17] (a) Fristad, W. E.; Bailey, T. R.; Paquette, L. A. *J. Org. Chem.* **1978**, *43*, 1620–1623. (b) Fristad, W. E.; Bailey, T. R.; Paquette, L. A. *J. Org. Chem.* **1980**, *45*, 3028–3037. (c) Davis, A. P.; Hughes, G. J.; Lowndes, P. R.; Robbins, C. M.; Thomas, E. J.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1934–1941. (d) Lambert, J. B.; Wang, G.; Finzel, R. B.; Teramura, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7838–7845. (e) Adiwidjaja, G.; Flörke, H.; Kirschning, A.; Schaumann, E. *Tetrahedron Lett.* **1995**, *36*, 8771–8774.

[18] With epoxides having alkyl substitution at the α position and no substitution at the β position, α opening has been observed under acidic conditions,[19] but β or mixtures of α and β ring opening have been observed under more nucleophilic conditions.[20] A few other examples of β opening or mixtures of α and β ring opening have been observed.[22]

[19] For example, see: (a) Reference 9a ($MgBr_2$). (b) Reference 9b (HBr). (c) Reference 9b (ROH/acid). (d) Shimizu, M.; Yoshioka, H. *Tetrahedron Lett.* **1989**, *30*, 967–970 (SiF_4).

[20] Products of β opening have been observed using organocopper reagents,[21a,b] lithiated allylsilanes,[21c] and azide.[21d]

[21] (a) Rona, R. J. Ph.D. Thesis, Rutgers University, 1978. (b) Knochel, P.; Normant, J. F. *Tetrahedron Lett.* **1984**, *25*, 4383–4386. (c) Schaumann, E.; Kirschning, A. *J. Chem. Soc., Perkin Trans. 1* **1990**, 419–421. (d) Chakraborty, T. K.; Reddy, G. V. *Tetrahedron Lett.* **1991**, *32*, 679–682.

[22] The major product observed was that of β opening using hindered lithiated sulfones,[23a,b] MeOH/alumina,[23c] and metal salts with α-bromoepoxy silanes.[23d] A minor product of β opening was observed using HCl[23e] and lithiated allylsilanes.[21c] Products derived from apparent β opening have been obtained by hydrolysis of α,β-epoxy silanes (or presumed epoxide intermediates) in which the β carbon had a cation-stabilizing group[23f–i] and in the $BF_3{\cdot}Et_2O$-promoted rearrangement of a $PhMe_2Si$ epoxide.[23j] In the last case, the absence of a good nucleophile in the medium may have contributed to the regiochemistry. A few ring-opening reactions of epoxysilanes having other more hindered silyl groups have been reported to result in β or mixtures of α and β ring opening.[5,14]

[23] (a) Jankowski, P.; Marczak, S.; Masnyk, M.; Wicha, J. *J. Organomet. Chem.* **1991**, *403*, 49–62. (b) Jankowski, P.; Marczak, S.; Masnyk, M.; Wicha, J. *J. Chem. Soc., Chem. Commun.* **1991**, 297–298. (c) Hudrlik, P. F.; Nagendrappa, G.; Kulkarni, A. K.; Hudrlik, A. M. *Tetrahedron Lett.* **1979**, 2237–2240. (d) Horiuchi, Y.; Taniguchi, M.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1995**, *36*, 5353–5356. (e) Berti, G.; Canedoli, S.; Crotti, P.; Macchia, F. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1183–1188. (f) Boyd, D. R.; Berchtold, G. A. *J. Org. Chem.* **1979**, *44*, 468–470. (g) Van Epp, J. E., Jr.; Boyd, D. R.; Berchtold, G. A. *J. Org. Chem.* **1981**, *46*, 1817–1820. (h) Ochiai, M.; Sumi, K.; Fujita, E.; Shiro, M. *Tetrahedron Lett.* **1982**, *23*, 5419–5422. (i) Kuwajima, I.; Urabe, H. *Tetrahedron Lett.* **1981**, *22*, 5191–5194. (j) Fleming, I.; Newton, T. W. *J. Chem. Soc., Perkin Trans. 1* **1984**, 119–123.

[24] Hudrlik, P. F.; Peterson, D.; Rona, R. J. *J. Org. Chem.* **1975**, *40*, 2263–2264.

[25] Hudrlik, P. F.; Hudrlik, A. M.; Kulkarni, A. K. *Tetrahedron Lett.* **1985**, *26*, 139–142.

[26] (a) Hudrlik, P. F.; Hudrlik, A. M.; Kulkarni, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 6809–6811. (b) Hudrlik, P. F.; Holmes, P. E.; Hudrlik, A. M. *Tetrahedron Lett.* **1988**, *29*, 6395–6398.

[27] See also Hudrlik, P. F.; Kulkarni, A. K. *J. Am. Chem. Soc.* **1981**, *103*, 6251–6253.

[28] β-Hydroxy silane **7** has been previously prepared from the reaction of triphenylsilyllithium with styrene oxide[29a,b] and from the reduction of α-(triphenylsilyl)acetophenone with $LiAlH_4$.[29c] The melting point (mp 131–133 °C;[29a,c] mp 135–137 °C[29b]) was reported, but no spectral data are available.

The structures of **4** and **7** were confirmed by independent synthesis from (triphenylsilyl)acetaldehyde (**8**). The aldehyde **8** was prepared by treatment of epoxide **1** with $MgBr_2$ (benzene/reflux).[3] As mentioned above, in the reaction of **1** with $MgBr_2$, a mixture of α- and β-opening pathways appears to take place (scrambling with a deuterated substrate), while in reactions of epoxy *trimethyl*silanes with $MgBr_2$, intermediate bromohydrins derived from α opening have been detected. We have studied the reaction of **1** with $MgBr_2$ using conditions analogous to those used for the epoxy trimethylsilanes to see if bromohydrins could be detected. The reaction of **1** with $MgBr_2$ was carried out in ether (0 °C → reflux) and was monitored by ^1H NMR and GC analysis of aliquots. As the reaction progressed, the amount of epoxide **1** decreased, and peaks assigned to aldehyde **8** and to a bromohydrin were observed. The reactions appeared to be quite clean, with peaks due mainly to the above-mentioned compounds as well as to small amounts of 1,2-dibromoethane (from preparation of the $MgBr_2$). From a preparative experiment, the crude product appeared to be a 40:60 mixture of aldehyde **8** and bromohydrin, with a small amount of epoxide **1** remaining. The bromohydrin was isolated by vacuum liquid chromatography (off-white crystals, mp 103−105 °C, 22% yield) and shown to have structure **9**, a product of α opening. The structure was assigned by spectral methods; in particular, the ^1H NMR spectrum in $CDCl_3/D_2O$ showed three doublets of doublets (1 proton each, at δ 3.96, 4.10, and 4.22). Two of the signals (δ 3.96, 4.10) displayed a geminal coupling ($J = 12.88$ Hz), and these two were more complex in the absence of D_2O, indicating the OH was attached to a CH_2. In addition, the ^{13}C NMR DEPT spectrum showed a higher field (δ 43.582) CH and a lower field (δ 64.673) CH_2, consistent with structure **9**.

In early attempts to isolate and purify β-hydroxy silane **7** from the reactions of PhMgBr with epoxide **1** and with silyl aldehyde **8**, the ^1H NMR spectra of the purified products indicated that phenol was present; GC analysis indicated the amount of phenol was comparable to the amount of product **7**. The phenol impurity could be removed by washing with base. In order to better understand the reactions of epoxide **1** with Grignard reagents, we examined the crude products. In the reaction of **1** with PhMgBr (after washing with base), we were able to detect β-hydroxy silane **7**, silyl aldehyde **8**, bromohydrin **9**, 1-phenylethanol, and biphenyl. All products were identified by GC and GC/MS (EI) and by comparison of the ^1H NMR spectra with those of the pure compounds. [Aldehyde **8** was somewhat unstable to our GC conditions; the GC/MS (EI) suggested that it yielded (or contained) triphenylsilanol, and distinguishing these compounds from epoxysilane **1** by GC was difficult (although they could be identified by ^1H NMR and mass spectra).]

We also followed the reaction of **1** with PhMgBr by taking aliquots and analyzing by ^1H NMR and by GC. After 1 h at 0 °C, the ^1H NMR spectrum suggested a 4:4:3 ratio of epoxy silane **1**, 1-phenylethanol, and phenol, and the GC suggested that biphenyl was present in amounts comparable to phenol and 1-phenylethanol. Little or none of β-hydroxy silane **7** was visible. After 1 h at room temperature, the product mixture was similar, except that less of **1** was present, and small amounts of bromohydrin **9** and β-hydroxy silane **7** were present. After 1 h at reflux, the amount of β-hydroxy silane **7** was comparable to the amounts of phenol, 1-phenylethanol, and biphenyl; small amounts of aldehyde **8** and bromohydrin **9** were present, and essentially no epoxysilane **1** remained. The amounts of phenol, 1-phenylethanol, and biphenyl changed very little during the course of the experiment. The reaction appeared quite clean, in that essentially no signals other than those due to the compounds mentioned (and traces of solvent) were present in the ^1H NMR spectra.

The presence of biphenyl was not surprising, but the presence of phenol and 1-phenylethanol suggested a reaction of the Grignard reagent with oxygen (reactions were run under nitrogen) or with a peroxide impurity in the ether (although the ether had been distilled from Na/benzophenone). A control reaction of PhMgBr in ether gave 1-phenylethanol, phenol, and biphenyl in comparable amounts. Similar reactions using undistilled anhydrous ether from two different suppliers gave similar results.

The crude product from the reaction of epoxide **1** with EtMgBr was also examined by GC, GC/MS (EI), and ^1H NMR. Considerable amounts of β-hydroxy silane **4**, bromohydrin **9**, and aldehyde **8** were found, along with small amounts of triphenylvinylsilane. Ethanol and 2-butanol, the products corresponding to phenol and 1-phenylethanol in the reaction of **1** with PhMgBr, would have been removed by the workup. As in the case for the reaction of **1** with PhMgBr, the reaction mixtures appeared clean in that essentially no signals other than those due to the compounds mentioned (and sometimes solvent or small amounts of epoxide **1**) were present in the ^1H NMR spectra.

Since the composition of products from Grignard reactions with epoxides can be influenced by the order of addition of reagents, the reactions of epoxide **1** with EtMgBr and with PhMgBr were run with the order of addition reversed (epoxide added to Grignard reagent), and the crude products were analyzed by ^1H NMR, GC, and GC/MS. The crude product mixtures appeared to be essentially identical to those resulting from the previous order of addition (Grignard reagent added to epoxide).

These results show that the crystalline hydroxy silanes isolated from the reactions of EtMgBr and PhMgBr with epoxide **1** are the β-hydroxy silanes **4** and **7** expected from a rearrangement−trapping sequence and not the α-hydroxy silanes reported.[2] (They also call into question the β opening reported for the reaction of (tribenzylsilyl)-ethylene oxide with Grignard reagents.[2]) In addition, a bromohydrin from α opening was isolated from the reactions of **1** with $MgBr_2$. Consequently, these reactions are analogous to those of trimethylsilyl epoxides.

Experimental Section

General Procedures. All reactions were carried out under nitrogen, and transfers of liquids were carried out with nitrogen-flushed syringes. Melting points are uncorrected. NMR spectra (^1H at 300 MHz and ^{13}C at 75 MHz) were obtained in $CDCl_3$ with TMS (δ 0.00) and $CDCl_3$ (δ 77.000) as internal standards for ^1H and ^{13}C NMR, respectively. Assignments in ^{13}C NMR spectra were made by DEPT 45, 90, and 135. GC analyses were performed with a 30-m capillary SPB-1 column; the retention time of a hydrocarbon is sometimes included. Column chromatography was performed on Florisil

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(29) (a) Gilman, H.; Aoki, D.; Wittenberg, D. *J. Am. Chem. Soc.* **1959**, *81*, 1107−1110. (b) Gilman, H.; Trepka, W. J. *J. Org. Chem.* **1962**, *27*, 1414−1418. (c) Lutsenko, I. F.; Baukov, Yu. I.; Dudukina, O. V.; Kramarova, E. N. *J. Organomet. Chem.* **1968**, *11*, 35−48.

(60–100 mesh, Fisher). Elemental analyses were carried out by Desert Analytics, Tucson, AZ.

Anhydrous ether and THF were freshly distilled from sodium/benzophenone. Magnesium was purchased as magnesium chips (99.98%) from Aldrich. (Triphenylsilyl)ethylene oxide (**1**)[2,30] was prepared by treatment of triphenylvinylsilane with *m*-chloroperbenzoic acid. (Triphenylsilyl)acetaldehyde (**8**)[3] was prepared by treatment of **1** with magnesium bromide etherate in benzene (reflux, 1.25 h).

Reaction of (Triphenylsilyl)ethylene Oxide (1) with Magnesium Bromide Etherate: Isolation of 2-Bromo-2-(triphenylsilyl)ethanol (9). Magnesium bromide was prepared from 0.292 g (12 mmol) of magnesium and 0.85 mL (1.85 g, 9.9 mmol) of 1,2-dibromoethane in 7 mL of anhydrous ether. A 4-mL portion of the lower layer was added to an ice-cooled solution of 0.604 g (2.00 mmol) of epoxy silane **1** in 10 mL of anhydrous ether. The mixture was stirred at 0 °C for 30 min and at room temperature for 30 min and was then heated at reflux for 1 h. The reaction mixture was then added to 40 mL of saturated NH_4Cl overlaid with 70 mL of ether. The organic layer was extracted with saturated $NaHCO_3$, water, and saturated NaCl and then dried ($MgSO_4$). The solvent was removed on a rotary evaporator, giving 0.75 g of a light yellow crystalline solid, mp 85–90 °C. Purification by vacuum liquid chromatography[31] (0.50 g of crude product in 2 mL of toluene applied to 20 g of silica gel (200–425 mesh) using a 5 × 13 cm funnel with 20 mL fractions of petroleum ether followed by 20% ether in petroleum ether) gave aldehyde **8** (0.13 g) and bromohydrin **9** (0.133 g of mp 99–101 °C and 0.12 g of mp 103–105 °C). The bromohydrin was further purified by vacuum liquid chromatography (5 × 10 cm funnel, 20 mL fractions of 20% ether in petroleum ether), giving 0.11 g (22% adjusted yield) of bromohydrin **9** as off-white needles, mp 103–105 °C: IR (KBr) 3369 (br), 3050, 1427, 1110, 1051, 997, 742, 698 cm^{-1}; ^1H NMR (D_2O added) δ 3.96 (dd, $J = 12.88$, 9.69 Hz, 1 H), 4.10 (dd, $J = 12.88$, 2.90 Hz, 1 H), 4.22 (dd, $J = 9.68$, 2.90 Hz, 1 H), 7.35–7.5 (complex, 9 H), 7.6–7.7 (6 H) [in the absence of D_2O, an additional peak at 2.22 (dd, $J = 8.87$, 4.48 Hz, 1 H); multiplets at 3.96 and 4.10 more complex]; ^{13}C NMR δ 43.582 (CH), 64.673 (CH_2), 128.068 (CH), 130.181 (CH), 131.920 (C), 136.145 (CH); GC/MS (CI, NH_3) *m/z* (tentative assignment, relative intensity) 400, 402 [$(M + NH_4)^+$, 92, 100], 322 (80), 320 [$(Ph_3SiCH_2CHO + NH_4)^+$, 50], 294 [$(Ph_3SiOH + NH_4)^+$, 14], 276 (Ph_3SiOH^+, 30), 216 [$(Ph_2SiOH + NH_3)^+$, 20]; GC/MS (EI) *m/z* 276 (Ph_3SiOH^+, 30), 260 (30), 259 (Ph_3Si^+, 100), 199 (Ph_2SiOH^+ 40), 181 (20), 155 (10), 122 ($PhSiOH^+$, 20), 105 ($C_6H_5Si^+$, 10), 77 ($C_6H_5^+$, 10), 51 (10). GC analysis [150 °C (1 min), 10 °C/min to 270 °C (5 min), $C_{24}H_{50}$ at 8.20 min] showed the major peak at 10.94 min (97%) and a minor peak at 8.607 min (2%, aldehyde **8**). Anal. Calcd for $C_{20}H_{19}BrOSi$: C, 62.66; H, 5.00. Found: C, 62.92; H, 5.04.

Reaction of (Triphenylsilyl)ethylene Oxide (1) with Ethylmagnesium Bromide: Isolation of 1-(Triphenylsilyl)-2-butanol (4). Ethylmagnesium bromide in ether (from 0.49 g (20 mmol) of magnesium, 20 mL of anhydrous ether, and 1.4 mL (2.03 g, 19 mmol) of bromoethane) was transferred to an ice-cooled solution of 0.604 g (2.00 mmol) of epoxy silane **1** in 7 mL of anhydrous ether. The reaction mixture was stirred at 0 °C for 40 min and was heated at reflux for 1 h. The mixture was allowed to cool to room temperature and was then added to 30 mL of saturated NH_4Cl overlaid with 50 mL of ether. The organic layer was extracted with saturated $NaHCO_3$, water, and saturated NaCl and then dried ($MgSO_4$). The solvent was removed on the rotary evaporator to give 0.63 g of light yellow liquid that partially solidified. Chromatography on Florisil using 30% ether in pentane gave 150 mg (25% yield) of β-hydroxy silane **4** as a colorless liquid that solidified. Recrystallization from ligroin (bp 60–80 °C) gave 90 mg (14% yield) of **4** as white crystals, mp 74–75 °C: IR (KBr) 3587, 3061, 2912, 1427, 1108, 728, 700 cm^{-1}; ^1H NMR δ 0.88 (t, $J = 7.4$ Hz, 3 H), 1.32 (d, $J = 4.0$ Hz, 1 H, exchanged with D_2O), 1.50 (m, 2 H), 1.72 (appears as overlapping doublets, $J = 5.5$, 8.6 Hz, 2 H), 3.85 (m, 1 H, on addition of D_2O, becomes an apparent quintet), 7.3–7.4 (9 H), 7.5–7.6 (6 H); ^{13}C NMR δ 9.986 (CH_3), 22.737 (CH_2), 33.588 (CH_2), 70.445 (CH), 127.914 (CH), 129.478 (CH), 135.048 (C), 135.693 (CH); 2-D (^1H–^1H) NMR (δ correlated with δ) 0.88 with 1.50; 1.50 with 0.88 and 3.85; 1.72 with 3.85; 3.85 with 1.50 and 1.72; GC/MS (CI, NH_3) *m/z* (tentative assignment, relative intensity) 350 [$(M + NH_4)^+$, 31], 332 (M^+, 38), 294 [$(Ph_3SiOH + NH_4)^+$, 10], 276 (Ph_3SiOH^+, 100), 216 [$(Ph_2SiOH + NH_3)^+$, 12]; GC/MS (EI) *m/z* 276 (Ph_3SiOH^+, 10), 259 (Ph_3Si^+, 70), 199 (Ph_2SiOH^+, 100), 181 (20), 155 (10), 122 ($PhSiOH^+$, (10), 105 ($C_6H_5Si^+$, 10), 77 ($C_6H_5^+$, 10). GC analysis [150 °C (1 min), 10 °C/min to 270 °C (5 min), $C_{24}H_{50}$ at 8.83 min] showed a major peak at 9.36 min (100%).

Reaction of (Triphenylsilyl)acetaldehyde (8) with Ethylmagnesium Bromide: Isolation of 1-(Triphenylsilyl)-2-butanol (4). Ethylmagnesium bromide in ether (from 0.146 g (6.00 mmol) of magnesium, 7 mL of anhydrous ether, and 0.37 mL (0.540 g, 5.00 mmol) of bromoethane) was added slowly to 0.150 g (0.496 mmol) of aldehyde **8** in 10 mL of anhydrous ether. The reaction was stirred at room temperature for 1 h and then added to 40 mL of saturated NH_4Cl overlaid with 40 mL of ether. The organic layer was washed with saturated $NaHCO_3$, water, and saturated NaCl and then dried (Na_2SO_4). The solvent was removed on a rotary evaporator, giving 0.19 g of a colorless liquid that solidified. Chromatography on Florisil using 20% ether in petroleum ether gave 0.117 g (73% yield) of β-hydroxy silane **4** as white crystals, mp 70–71 °C. The IR, ^1H NMR, 2-D ^1H–^1H NMR, ^{13}C NMR with DEPT (45/90/135), GC/MS (CI, NH_3), and GC/MS (EI) of this sample were equivalent to those of the sample of **4** prepared from epoxy silane **1** and EtMgBr. GC analysis [150 °C (1 min), 10 °C/min to 270 °C (5 min), $C_{24}H_{50}$ at 8.91 min] showed a major peak at 9.53 min (99%). Anal. Calcd for $C_{22}H_{24}OSi$: C, 79.47, H, 7.27. Found: C, 79.59, H, 7.30.

Reaction of (Triphenylsilyl)ethylene Oxide (1) with Phenylmagnesium Bromide: Isolation of 1-Phenyl-2-(triphenylsilyl)ethanol (7). Phenylmagnesium bromide in ether (from 0.851 g (35.0 mmol) of magnesium, 15 mL of anhydrous ether, and 3.2 mL (4.77 g, 30 mmol) of bromobenzene) was transferred to an ice-cooled solution of 0.604 g (2.00 mmol) of epoxy silane **1** in 10 mL of anhydrous ether. The reaction mixture was stirred at 0 °C for 15 min and was then heated at reflux for 1 h. The cooled mixture was added to 40 mL of saturated NH_4Cl overlaid with 50 mL of ether. The organic layer was washed twice with 5% NaOH, with saturated $NaHCO_3$, water, and saturated NaCl and then dried ($MgSO_4$). The solvent was removed on the rotary evaporator to give 1.00 g of yellow liquid that partially solidified. Chromatography on Florisil using 30% ether in petroleum ether gave 0.18 g (24% yield) of β-hydroxy silane **7** as white crystals, mp 124–125 °C. The product was further purified by triturating with 10 mL of pentane, giving 0.124 g of white crystals, mp 126–128 °C (lit.[29a,c] mp 131–133 °C, lit.[29b] mp 135–137 °C): IR (KBr) 3567, 3049, 1426, 1108, 728, 700 cm^{-1}; ^1H NMR δ 1.74 (d, $J = 3.5$ Hz, 1 H, exchanged with D_2O), 1.94 (dd, $J = 15.0$, 4.6 Hz, 1 H), 2.12 (dd, $J = 15.0$, 9.6 Hz, 1 H), 4.94 (m, 1 H; in the presence of D_2O, dd, $J = 9.6$, 4.6 Hz, 1 H), 7.2–7.6 (complex, 15 H); ^{13}C NMR δ 25.782 (CH_2), 71.650 (CH), 125.476 (CH), 127.321 (CH), 127.893 (CH), 128.418 (CH), 129.476 (CH), 134.929 (C), 135.792 (CH), 136.241 (small, impurity), 146.789 (C); GC/MS (CI, NH_3) *m/z* (tentative assignment, relative intensity) 398 [$(M + NH_4)^+$, 10], 380 (M^+, 10), 363 ($M^+ - OH$, 10), 294 [$(Ph_3SiOH + NH_4)^+$, 10], 276 (Ph_3SiOH^+, 100), 216 (10); GC/MS (EI) *m/z* 362 ($M^+ - H_2O$, 2), 301 (20), 259 (Ph_3Si^+, 63), 199 (Ph_2SiOH^+, 100), 181 (27), 105 ($C_6H_5Si^+$, 17), 104 (18), 77 ($C_6H_5^+$, 16). GC analysis [70 °C (5 min), 10 °C/min to 270 °C (10 min), $C_{28}H_{58}$ at 24.17 min] showed a major peak at 26.05 min (92%).

Reaction of (Triphenylsilyl)acetaldehyde (8) with Phenylmagnesium Bromide: Isolation of 1-Phenyl-2-(Triphenylsilyl)ethanol (7). Phenylmagnesium bromide in ether (from 0.150 g (6.20 mmol) of magnesium, 7 mL of anhydrous ether, and 0.5 mL (0.745 g, 4.8 mmol) of bromobenzene) was slowly transferred to an ice-cooled solution of 0.150 g (0.496 mmol) of aldehyde **8** in 10 mL of anhydrous ether.

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(30) Eisch, J. J.; Trainor, J. T. *J. Org. Chem.* **1963**, *28*, 487–492.

(31) Pelletier, S. W.; Chokshi, H. P.; Desai, H. K. *J. Nat. Prod.* **1986**, *49*, 892–900.

The reaction mixture was stirred at 0 °C for 15 min, heated at reflux for 1 h, and added to 40 mL of saturated NH_4Cl overlaid with 40 mL of ether. The organic layer was washed with saturated $NaHCO_3$, two portions of 5% NaOH, water, and saturated NaCl and then dried ($MgSO_4$). The solvent was removed on the rotary evaporator, giving 0.30 g of a crude product that solidified. Recrystallization from pentane gave 0.090 g (48% yield) of β-hydroxy silane **7** as white crystals, mp 134−135 °C (lit.[29a,c] mp 131−133 °C, lit.[29b] mp 135−137 °C). The IR spectrum of this sample is very similar to that of a sample of **7** prepared from epoxy silane **1** except the latter had a larger peak at 1043 cm^{-1}. The ^1H NMR, ^{13}C NMR (except for a small peak at δ 136.241 which was present only in the spectrum of the product from epoxysilane **1** and PhMgBr), DEPT(45/90/135), GC/MS (CI, NH_3), and GC/MS (EI) spectra were essentially identical to those of a sample of **7** prepared from **1**. GC analysis [70 °C (5 min), 10 °C/min to 270 °C (5 min), $C_{28}H_{58}$ at 24.16 min] showed a major peak at 26.13 min (94%).

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