Elimination Reactions of α,β-Dihydroxysilanes: Stereospecific Synthesis of Silyl Enol Ethers from Vinylsilanes

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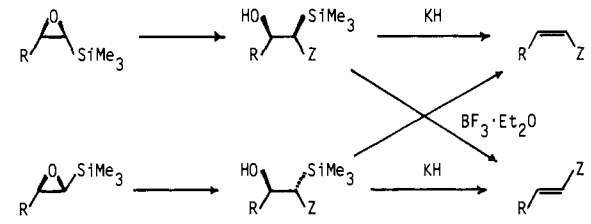
Abstract: α,β-Dihydroxysilanes were prepared from vinylsilanes by osmium tetroxide catalyzed hydroxylation, and in a few cases by acid-catalyzed hydrolysis of the corresponding α,β-epoxysilanes. When α,β-dihydroxysilanes are treated with base, elimination reactions occur via both α- and β-oxidosilanes. With sodium hydride in ether, the α-oxidosilane pathway leading to silyl enol ethers is nearly the exclusive process. This reaction is shown to be highly stereospecific and preferentially anti. The overall process (osmium tetroxide catalyzed hydroxylation followed by treatment with sodium hydride in ether) provides a synthetically useful method for conversion of vinylsilanes to silyl enol ethers with overall retention of double-bond configuration.

Silyl enol ethers have become one of the more useful and versatile functional groups available to the synthetic organic chemist.[1] In their initial applications to synthesis, their stereochemistry (*E*/*Z*) was of little importance. However, in recent years a number of applications have been developed in which this stereochemistry is crucial. One topic of considerable current interest is the use of silyl enol ethers[2] (or other enol derivatives such as metal enolates) of defined stereochemistry in aldol condensations and related processes for the synthesis of acyclic molecules of defined stereochemistry.[3] Silyl enol ethers can also be used in stereospecific vinyl substitution reactions with organometallic reagents,[4] and in various cycloaddition reactions.[1] Many methods exist for the preparation of silyl enol ethers (and generation of metal enolates), but few provide stereochemical control. Although some types of silyl enol ethers can be obtained in high isomeric purity, there is a need for general methods for preparing these intermediates with known, *predictable* stereochemistry.

For some time we have been developing a new method for preparing heteroatom-substituted olefins of known stereochemistry using organosilicon compounds.[5] This method is based on the finding that α,β-epoxysilanes undergo regio- and stereospecific α opening by a variety of nucleophiles to produce diastereomerically pure β-hydroxysilanes,[5,6] and that these β-hydroxysilanes undergo stereospecific syn or anti β-elimination reactions under basic or acidic conditions, respectively.[6,7] (See Scheme I.)

With a view toward extending this method to the generation of stereoisomerically pure enolate anions and silyl enol ethers, we prepared α,β-dihydroxysilanes **2** and **6** (by hydrolysis of α,β-epoxysilanes **1** and **5**, respectively) and treated these compounds with KH (to effect β-elimination to give enolates) followed by Me_3SiCl (to trap the presumed enolates as silyl enol ethers). However, under these conditions, cis–trans mixtures of the silyl enol ethers

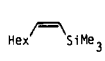
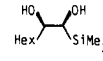
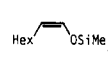
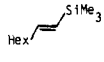
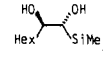
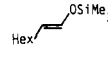
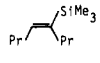
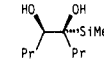
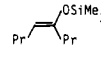
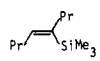
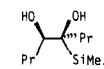
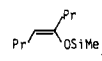
Scheme I



with KH: -Z = -R,[6] -NR_2,[5b] -NHAc,[5a] -OMe,[5] -SPh[5b]

with BF_3·Et_2O: -Z = -R,[6] -OAc,[5a] -OSO_2Me,[5b] -SPh,[5b] -F,[5b] -Br[5a]

Table I. Preparation of Silyl Enol Ethers from Vinylsilanes via α,β-Dihydroxysilanes

vinylsilane (isomeric purity[a])		dihydroxysilane (yield)		silyl enol ether	(yield, isomeric purity[a])
	7 (>99% Z)		6 (70%)		3 (73%, >99% Z)
	8 (>99% E)		2 (48%)		4 (65%, 99% E)
	9 (>99% E)		10 (67%)		11 (77%, >98% E[b])
	12 (~93% Z)		13 (62%)		14 (75%, 91% Z[b])
	15		17 (67%)		18 (77%)
	19		20 (62%)		21 (81%)

[a] The isomeric purities were determined by VPC unless otherwise indicated. [b] Compounds **11** and **14** were not separable by VPC; their ratios were determined by NMR.[19]

(1) For reviews, see: (a) Rasmussen, J. K. *Synthesis* **1977**, 91–110. (b) Fleming, I. *Chimia* **1980**, *34*, 265–271. (c) Brownbridge, P. *Synthesis* **1983**, 1–28, 85–104. (d) Colvin, E. W. "Silicon in Organic Synthesis"; Butterworths: London, 1981; pp 198–287. (e) Weber, W. P. "Silicon Reagents for Organic Synthesis"; Springer-Verlag: Berlin, 1983; pp 206–272.

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(3) For reviews, see: (a) Bartlett, P. A. *Tetrahedron* **1980**, *36*, 2–72. (b) Heathcock, C. H. *Science* **1981**, *214*, 395–400. (c) Evans, D. A.; Takacs, J. M.; McGee, L. R.; Ennis, M. D.; Mathre, D. J.; Bartroli, J. *Pure Appl. Chem.* **1981**, *53*, 1109–1127. (d) Evans, D. A. *Aldrichim. Acta* **1982**, *15*, 23–32. (e) Masamune, S.; Choy, W. *Aldrichim. Acta* **1982**, *15*, 47–64. (f) Evans, D. A.; Nelson, J. V.; Taber, T. R. *Top. Stereochem.* **1982**, *13*, 1–115. (g) Mukaiyama, T. *Org. React.* **1982**, *28*, 203–331. (h) Heathcock, C. H. In "Comprehensive Carbanion Chemistry", Part B; Buncel, E., Durst, T., Eds.; Elsevier: Amsterdam, 1984; pp 177–237.

(4) Hayashi, T.; Katsuro, Y.; Kumada, M. *Tetrahedron Lett.* **1980**, *21*, 3915–3918.

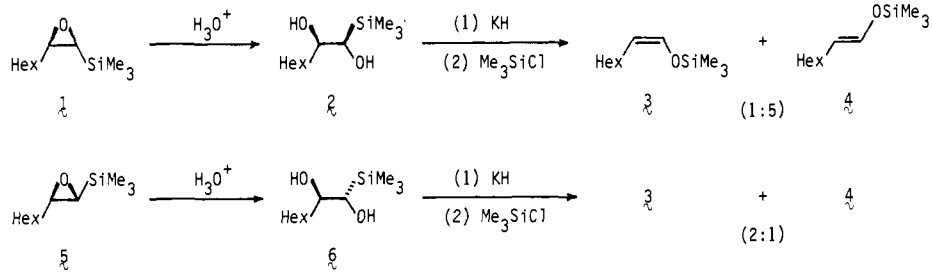
(5) (a) Hudrlik, P. F.; Hudrlik, A. M.; Rona, R. J.; Misra, R. N.; Withers, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 1993–1996. (b) Hudrlik, P. F.; Hudrlik, A. M.; Kulkarni, A. K.; Jain, S.; Rona, R. J., unpublished work.

(6) Hudrlik, P. F.; Peterson, D.; Rona, R. J. *J. Org. Chem.* **1975**, *40*, 2263–2264.

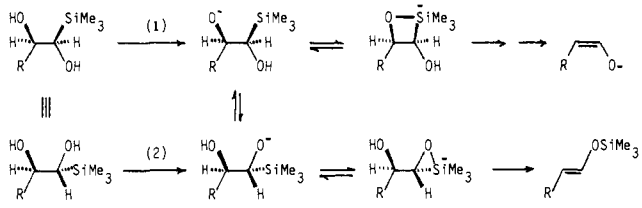
(7) Hudrlik, P. F.; Peterson, D. *J. Am. Chem. Soc.* **1975**, *97*, 1464–1468.

0002-7863/85/1507-4260$01.50/0

Scheme II



Scheme III



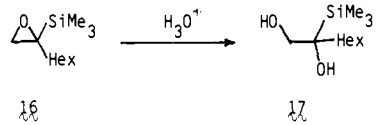
(**3** and **4**) were formed, with the *unexpected* isomer predominating in each case.[8] (See Scheme II.)

In a preliminary communication,[8] we concluded that these elimination reactions took place by two competing pathways: (1) β-elimination of a β-oxidosilane (expected to be syn[6,7]) and (2) Brook rearrangement of an α-oxidosilane with elimination of a β leaving group (e.g., hydroxyl) as in Scheme III. Quenching the elimination reaction of **2** with saturated aqueous $NaHCO_3$ (rather than Me_3SiCl) provided a ~1:5 mixture of octanal and trans silyl enol ether **4**, in support of this conclusion, and of an anti stereochemistry for the elimination reaction of path (2). Further support was obtained from experiments with cyclic α,β-dihydroxysilanes.[9]

We have now found that when α,β-dihydroxysilanes are treated with NaH (rather than KH) in ether, the α-oxidosilane pathway (2) takes place almost exclusively, and that silyl enol ethers can be obtained in high isomeric purity. This convincingly demonstrates that these elimination reactions take place with anti stereochemistry. We have also found that, although some of the precursor α,β-dihydroxysilanes can be prepared by hydrolysis of the corresponding α,β-epoxysilanes, a more generally satisfactory method is osmium tetroxide catalyzed hydroxylation of the corresponding vinylsilanes. Thus, a variety of vinylsilanes can be converted to silyl enol ethers with overall retention of double-bond geometry.[10] (See Table I.)

Results

α,β-Dihydroxysilanes **2** and **17** could be successfully prepared by acid-catalyzed hydrolysis of α,β-epoxysilanes **1** and **16**, respectively, but in general, hydrolysis of the other epoxysilanes we investigated gave low yields of the dihydroxysilanes (at best),



accompanied by carbonyl compounds. This approach to α,β-dihydroxysilanes is complicated by the fact that the dihydroxysilanes are sensitive to acid, undergoing β-elimination reactions to give enols, resulting ultimately in the carbonyl compounds.[11]

We did find, however, that the cis epoxide **1** was sufficiently more reactive than the trans epoxide **5** so that a mixture of **1** and **5** could be used to prepare α,β-dihydroxysilane **2**. [Mixtures of **1** and **5** (about 85% **1**) are readily available from the reaction of heptanal with the organolithium reagent derived from (chloromethyl)trimethylsilane.[12]]

We have found that α,β-dihydroxysilanes can be more generally prepared by osmium tetroxide catalyzed hydroxylation of the corresponding vinylsilanes using trimethylamine *N*-oxide in pyridine as oxidizing agent, a procedure developed by Ray and Matteson for the hydroxylation of hindered olefins.[13,14] Since numerous methods exist for the synthesis of isomerically pure vinylsilanes of diverse structural types,[15,16] a wide variety of diastereomerically pure α,β-dihydroxysilanes should be available.

In order to use α,β-dihydroxysilanes as intermediates for the preparation of isomerically pure silyl enol ethers (or enolate anions), it was necessary to find elimination conditions under which only one of the pathways of Scheme III operates. We therefore studied the reactions of α,β-dihydroxysilane **2** with KH, NaH, and LiH, in THF and/or ether, quenching the reaction mixtures with saturated aqueous $NaHCO_3$. We expected the progression from KH to NaH to LiH, and from THF to ether, would favor the α-oxidosilane pathway (2) since a three-membered-ring intermediate (or transition state) should be more easily formed than a four, and because β-elimination reactions of unactivated β-hydroxysilanes normally do not take place with sodium or lithium as the counterion unless dipolar solvents are present.[7,17]

Treatment of **2** with KH in ether or with NaH in THF (followed by aqueous workup) gave mixtures of trans silyl enol ether **4** and octanal. Analogous results were obtained with the diastereomeric dihydroxysilane **6**. Treatment of **2** with LiH in THF resulted in no reaction. However, treatment with NaH in ether resulted in trans silyl enol ether **4** (99% trans, containing 2.8% octanal), indicating that predominately the α-oxidosilane pathway (2) was operating. This was confirmed by subjecting the opposite diastereomer, α,β-dihydroxysilane **6**, to NaH in ether. Cis silyl enol ether **3** was obtained (>99% cis, containing 1.5% octanal).[18]

(8) Preliminary communication: Hudrlik, P. F.; Schwartz, R. H.; Kulkarni, A. K. *Tetrahedron Lett.* **1979**, 2233–2236.

(9) Hudrlik, P. F.; Nagendrappa, G.; Kulkarni, A. K.; Hudrlik, A. M. *Tetrahedron Lett.* **1979**, 2237–2240.

(10) Hudrlik, P. F.; Hudrlik, A. M.; Kulkarni, A. K. "Abstracts of Papers", 186th National Meeting of the American Chemical Society, Washington, DC, August 31, 1983; American Chemical Society: Washington, DC, 1983; ORGN 170.

(11) (a) Robbins, C. M.; Whitham, G. H. *Chem. Commun.* **1976**, 697–698. (b) Hudrlik, P. F.; Arcoleo, J. P.; Schwartz, R. H.; Misra, R. N.; Rona, R. J. *Tetrahedron Lett.* **1977**, 591–594. (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.

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(13) Ray, R.; Matteson, D. S. *Tetrahedron Lett.* **1980**, *21*, 449–450.

(14) There is one previous example of the hydroxylation of a vinylsilane with osmium tetroxide; no elimination reactions were investigated. Richer, J.-C.; Poirier, M. A.; Maroni, Y.; Manuel, G. *Can. J. Chem.* **1978**, *56*, 2049–2052.

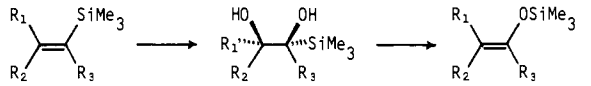
(15) Review: Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761–786.

(16) Hudrlik, P. F.; Kulkarni, A. K.; Jain, S.; Hudrlik, A. M. *Tetrahedron* **1983**, *39*, 877–882.

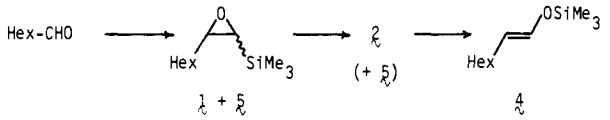
(17) Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780–784.

(18) In an attempt to maximize the β-oxidosilane pathway, α,β-dihydroxysilane **2** was treated with KH in THF. When this reaction mixture was carefully neutralized with aqueous $NaHCO_3$, only octanal was formed (as expected for the β-oxidosilane pathway). However, when the reaction mixture was treated with Me_3SiCl before workup, a mixture of silyl enol ethers (**3** and **4**) was formed. There are a number of possible explanations for this (for example, cleavage of silyl ether by the KOH generated in the α-oxidosilane elimination step, or cis–trans isomerism of the enolates (or enols?) formed in the β-oxidosilane elimination step). At present we have no plans to investigate this further.

These reactions constitute a new synthesis of silyl enol ethers of defined stereochemistry, summarized in Table I. Vinylsilanes **7**, **8**, **9**, **12**, **15**, and **19** were converted to dihydroxysilanes **6**, **2**, **10**, **13**, **17**, and **20**, respectively, with osmium tetroxide and trimethylamine oxide, and then to silyl enol ethers **3**, **4**, **11**, **14**, **18**, and **21**, respectively, by treatment with sodium hydride in ether. A small amount of carbonyl compound generally accompanied the silyl enol ethers. Whether this was from cleavage of the silyl ethers or operation of the β-oxidosilane pathway (1) was not determined. The stereoisomeric purity of the silyl enol ethers was very high, reflecting the stereoisomeric purity of the starting vinylsilanes.[19] The overall process provides a method for converting vinylsilanes to silyl enol ethers with preservation of double-bond geometry.



As mentioned above, α,β-dihydroxysilane **2** can also be prepared by selective hydrolysis of the mixture of epoxysilanes (**1** and **5**) which is obtained from heptanal and the lithium reagent from (chloromethyl)trimethylsilane. Treatment of **2** obtained in this manner (66% yield) with sodium hydride in ether led to trans silyl enol ether **4** in 77% yield and 98% isomeric purity. Thus, an aldehyde could be converted to a trans silyl enol ether having one more carbon atom.



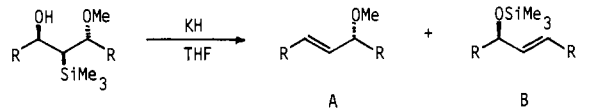
Discussion

Base-induced elimination reactions of β-hydroxysilanes are known to take place in a highly stereospecific syn manner.[5-7] The base-induced elimination reactions of α,β-dihydroxysilanes described here are not consistent with such a pathway, but with a pathway involving formation of the alkoxide α to silicon (α-oxidosilane) and rearrangement of silicon from carbon to oxygen (Brook rearrangement)[21] with anti elimination of the leaving group (hydroxyl)[22] β to silicon[8] (as in Scheme III, path(2)).

Elimination reactions of α-oxidosilanes with a β leaving group were first proposed by Brook in 1967, to account for the formation of silyl enol ethers in the reactions of acylsilanes with diazomethane[23a] and with Wittig reagents.[23b,24] Most of these reactions yielded simple products with no stereochemistry. However, in two examples, reactions of benzoyltriphenylsilane with Wittig reagents gave the silyl enol ethers as *Z* isomers only, and an anti stereochemistry was postulated for the elimination reaction.[23b]

More recently, this type of elimination reaction has been used in several synthetic methods. Reich has developed an efficient, regiospecific synthesis of silyl enol ethers (generally as mixtures of *E* and *Z* isomers) using reactions in which α-oxidosilanes with a β leaving group are presumably involved,[25] and Vedejs has developed a novel method for reductive elimination of sulfur α to carbonyl using this type of reaction.[26,27] Our work provides the first definitive evidence that such reactions proceed in a preferentially anti manner, and that they can be stereospecific.[28]

These reactions may be related to some other anti elimination reactions involving silicon. Yamamoto has recently reported that base-induced reactions of several β-hydroxy-β′-alkoxysilanes yield mixtures of products from syn β-elimination (giving A) and from another elimination reaction (giving B).[29] The latter process, which occurred in a preferentially anti manner, can be viewed as a homologue (β-oxidosilane with a β′ leaving group) of the reactions (α-oxidosilane with a β leaving group) described here.



The above reactions (of α- and β-oxidosilanes with a β leaving group) may be viewed as elimination reactions of β-functional organosilicon compounds induced by an internal nucleophile (alkoxide). It is therefore instructive to compare the analogous elimination reactions induced by an *external* nucleophile. Of these, the best known are the fluoride-induced elimination reactions of β-functional organosilicon compounds, first reported by Cunico,[30] who found that silyl vinyl halides reacted with fluoride to give acetylene, with the trans isomer reacting faster than the cis. Chan has applied these elimination reactions to the preparation of a variety of strained and sensitive alkenes,[31] and the reactions have become widely used. From the work of Miller,[32] Fleming,[33] and Negishi,[34] it is clear that these β-elimination reactions take place with anti stereochemistry.

Silyl enol ethers of known stereochemistry have most often been prepared by silylation of the corresponding enolates. In the last several years a number of methods for preparing either the *E* or *Z* enolates with high stereoselectivity have been developed. Reactions of simple ketones with lithium amides such as LDA or LiTMP in THF usually generate predominantly *E* enolates;[20,35,36] the corresponding reactions in THF–HMPA yield predominantely

(19) The stereochemistry of the silyl enol ethers was confirmed by NMR. In the trisubstituted cases (silyl enol ethers **11** and **14**), the olefinic proton of the *E* isomer **11** (sharp triplet at δ 4.60) appeared at lower field than that of the *Z* isomer **14** (triplet at δ 4.43), in accord with expectation.[20]

(20) (a) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324–2336. (b) Nakamura, E.; Hashimoto, K.; Kuwajima, I. *Tetrahedron Lett.* **1978**, 2079–2082. (c) Heathcock, C. H.; Buse, C. T.; Kleschick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. *J. Org. Chem.* **1980**, *45*, 1066–1081.

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(22) A referee has suggested that Me_3SiO^- may be the leaving group. Although Me_3SiO^- would be a somewhat better leaving group than HO^-, its formation would require an intermolecular silylation process by a catalytic amount of $Me_3SiOSiMe_3$ (or Me_3SiOR), a rather poor silylating agent. Since the stereochemical conclusions would be unaffected, we do not intend to explore this possibility.

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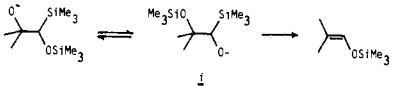

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Z enolates.[35] Similar reactions have been carried out with esters[20c,35a,b] and other carbonyl compounds.[38] The use of more hindered amide bases has been shown to produce enolates with very high stereoselectivity: Masamune has shown that very bulky $(R_3Si)_2NLi$ reagents convert ketones to *Z* enolates, which were converted to *Z* silyl enol ethers of extremely high isomeric purity.[37,39] In contrast, Corey has recently reported that ketones react with lithium di-*tert*-alkylamides in the presence of Me_3SiCl to form *E* silyl enol ethers in high purity.[40] Although the success of some of these methods is impressive, the reasons for the high stereoselectivity are not obvious and the empirical nature of these results makes one cautious about extending these reactions to new cases.[41]

There are few methods for preparing silyl enol ethers with predictable stereochemistry. *Z* silyl enol ethers have been prepared from 1-(trimethylsilyl)allylic alcohols by rearrangements of the corresponding lithium alkoxides;[42] the stereochemistry results from the preferred internal coordination of the siloxyallyllithium intermediate. A few silyl enol ethers have been prepared in a stereospecific manner by pyrolysis of cycloadducts of vinylsilanes with nitrile oxides,[43] retro-Diels-Alder reactions,[44] and acid-catalyzed rearrangements of α,β-epoxysilanes.[45]

The stereospecific preparation of silyl enol ethers described here has a number of features of synthetic interest: (1) The stereochemistry and regiochemistry of the silyl enol ethers are highly predictable. (2) The silyl enol ethers are obtained in excellent isomeric purities, corresponding to those of the starting vinylsilanes. (3) Vinylsilanes of a number of structural types are readily available from a number of methods.[15] (4) Vinylsilanes are stable to many synthetic reagents and are easily carried through a long synthetic sequence.

Since silyl enol ethers are readily convertible to enolates with retention of configuration,[20a,46] this work provides a general route to enolates of known geometry. Moreover, since silyl enol ethers are readily hydrolyzed to carbonyl compounds, this work provides a new method to convert vinylsilanes to aldehydes and ketones.

A potentially more efficient process for converting vinylsilanes to aldehydes and ketones would be osmium tetroxide catalyzed hydroxylation followed by acid-catalyzed β-elimination. This should be especially useful with a cyclic vinylsilane, since the classic method to convert vinylsilanes to ketones, the Stork–Colvin hydrolysis of the derived α,β-epoxysilanes,[47] is not applicable in such cases.[48,49] In a preliminary experiment, α,β-dihydroxysilane **20** was readily converted to cyclohexanone upon treatment with sulfuric acid in THF. The conversion of vinylsilanes to aldehydes and ketones by osmylation–elimination might also find use in acyclic cases where the compounds are sensitive to peracid.

Summary. This work demonstrates that base-induced elimination reactions of α,β-dihydroxysilanes can take place almost exclusively by an α-oxidosilane β-leaving group pathway leading to silyl enol ethers (Scheme III, path (2)) and that this reaction is stereospecifically anti. α,β-Dihydroxysilanes are easily prepared from vinylsilanes by hydroxylation with osmium tetroxide; hence these reactions provide a general stereospecific method for preparing silyl enol ethers from vinylsilanes with overall retention of double-bond geometry. In addition, since silyl enol ethers are excellent precursors to enolates or to carbonyl compounds, this work provides a potentially general method for preparing enolates of known geometry, and a new method for converting vinylsilanes (including cyclic vinylsilanes) to aldehydes and ketones.

Experimental Section

All reactions except the hydrolysis of the epoxysilanes were carried out under an inert (nitrogen or argon) atmosphere. Melting points were determined on a Fisher-Johns hot stage melting point apparatus. Infrared (IR) spectra were taken on a Perkin-Elmer 1320 infrared spectrometer. Proton nuclear magnetic resonance (NMR) spectra were obtained on a Perkin-Elmer R-600 NMR spectrometer; reported chemical shifts are in ppm (δ) relative to $CHCl_3$ (δ 7.26). NMR spectra of compounds **11** and **14** were also taken on a Nicolet NT-200 NMR spectrometer. Vapor phase chromatographic (VPC) analyses were obtained on a Varian Aerograph 90-P instrument with a 10 ft × 0.25 in. 10% SE-30 column, using helium as the carrier gas at the column temperature indicated; the retention time of a hydrocarbon standard under the conditions is included. High-resolution mass spectra were determined by the Midwest Center for Mass Spectrometry, University of Nebraska.

Materials. Pyridine was distilled over barium oxide. *tert*-Butyl alcohol was distilled over sodium. Anhydrous ether was distilled from sodium–benzophenone. (*Z*)-1-(Trimethylsilyl)-1-octene (**7**)[16,50] (>99% *Z*) was prepared from 1-(trimethylsilyl)-1-octyne by treatment with diisobutylaluminum hydride followed by hydrolysis (80% yield).[32] (*E*)-4-(Trimethylsilyl)-4-octene (**9**)[16,51] (>99% *E*) was prepared from 4-octyne by chloroplatinic acid catalyzed hydrosilylation with $MeSiCl_2H$ followed by treatment with MeMgI (79% yield). (*E*)-1-(Trimethylsilyl)-1-octene (**8**) (>99% *E*) and (*Z*)-4-(trimethylsilyl)-4-octene (**12**) (~93% *Z*) were prepared by Wurtz–Fittig reactions on the corresponding vinyl iodides as described in ref 16. 2-(Trimethylsilyl)-1-octene (**15**)[52] (81.5% yield) and 1-(trimethylsilyl)cyclohexene (**19**)[53] (79% yield) were prepared by Wurtz–Fittig reactions on the corresponding vinyl bromide and vinyl chloride, respectively. A mixture of epoxides **1** and **5** was prepared by the reaction of heptanal with $Me_3SiCHLiCl$.[12]

(*Z*)-1-(Trimethylsilyl)-1-octene (3). To a solution of 1.38 g (7.5 mmol) of vinylsilane **7** (>99% *Z*), 1.125 g (10.2 mmol) of trimethylamine *N*-oxide dihydrate, 0.6 mL of pyridine, 4.5 mL of water, and 15 mL of *tert*-butyl alcohol was added 0.3 mL of a 2.5% solution (w/v) of osmium tetroxide in *tert*-butyl alcohol (Aldrich). The reaction mixture was heated at reflux for 24 h and cooled to room temperature, and then 6 mL of 20% aqueous $NaHSO_3$ was added. The resulting mixture was concentrated on the rotary evaporator (room temperature) to remove most of the *tert*-butyl alcohol, saturated with NaCl, and extracted five times with ether. The combined ether layers were washed with saturated NaCl, dried ($MgSO_4$), concentrated, and evaporatively distilled (bulb-to-bulb, oven temperature 95–100 °C, oil pump vacuum), giving 1.14 g (70%) of α,β-dihydroxysilane **6** as a colorless liquid: IR (film) 3400, 2950, 1250, 840 cm^{-1}; NMR ($CDCl_3$) δ 0.08 (s, Me_3Si), 0.8–1.5 (13 H), 1.99 (2 H, br s, OH), 3.40 (1 H, d, J = 3 Hz), 3.80 (1 H, m).

Sodium hydride (144 mg of a 50% dispersion in oil) was stirred (under argon) with two portions of petroleum ether, and each time the liquid was

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(38) For example, (a) aldehydes: Bock, P. L.; Boschetto, D. J.; Rasmussen, J. R.; Demers, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2814–2825. (b) Hydrazones: Davenport, K. G.; Eichenauer, H.; Enders, D.; Newcomb, M.; Bergbreiter, D. E. *J. Am. Chem. Soc.* **1979**, *101*, 5654–5659. (c) Thioamides: Tamaru, Y.; Harada, T.; Nishi, S.; Mizutani, M.; Hioki, T.; Yoshida, Z. *J. Am. Chem. Soc.* **1980**, *102*, 7606–7608.

(39) Silyl enol ethers with the *Z* configuration have also been prepared from reactions of ketones with ethyl (trimethylsilyl)acetate in the presence of tetrabutylammonium fluoride.[20b]

(40) Corey, E. J.; Gross, A. W. *Tetrahedron Lett.* **1984**, *25*, 495–498.

(41) With simple ketones, it has been shown that the *E* enolates are kinetically formed, while the *Z* enolates are thermodynamically more stable.[35c,40]

(42) Kuwajima, I.; Kato, M. *Chem. Commun.* **1979**, 708–709. Kuwajima, I.; Kato M.; Mori, A. *Tetrahedron Lett.* **1980**, *21*, 2745–2748. Kato, M.; Mori, A.; Oshino, H.; Enda, J.; Kobayashi, K.; Kuwajima, I. *J. Am. Chem. Soc.* **1984**, *106*, 1773–1778.

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(46) Stork, G.; Hudrlik, P. F. *J. Am. Chem. Soc.* **1968**, *90*, 4464–4465.

(47) Stork, G.; Colvin, E. *J. Am. Chem. Soc.* **1971**, *93*, 2080–2081. Stork, G.; Jung, M. E. *J. Am. Chem. Soc.* **1974**, *96*, 3682–3684.

(48) Hydrolyses of α,β-epoxysilanes to form aldehydes and ketones[47] have been shown to involve initial epoxide ring opening to the α,β-dihydroxysilanes (as used in the preparation of diols **2** and **17** above) followed by acid-catalyzed β-elimination.[11] Because of the stereochemical requirements of the latter process (anti elimination of Si and OH),[6,7] the α,β-dihydroxysilanes (trans diols) resulting from ring opening of epoxides of *cyclic* vinylsilanes are relatively stable to acid, while those obtained by osmylation of cyclic vinylsilanes (cis diols) have the opposite stereochemistry and are therefore able to undergo the acid-catalyzed elimination.

(49) Cyclic vinylsilanes having $-SiMe(OEt)_2$ groups can be easily oxidized to ketones with 30% H_2O_2; vinylsilanes with the more commonly used Me_3Si groups are inert to these conditions. Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, *2*, 1694–1696. Tamao, K.; Kumada, M.; Maeda, K. *Tetrahedron Lett.* **1984**, *25*, 321–324.

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removed by pipet. Anhydrous ether (15 mL) was added followed by a solution of 218 mg (1 mmol) of the above α,β-dihydroxysilane (**6**) in 5 mL of anhydrous ether. The reaction mixture was stirred overnight (~18 h). Then 5 mL of saturated $NaHCO_3$ was added, the layers were separated, and the aqueous layer was extracted with ether. The combined ether layers were washed with water, dried ($MgSO_4$), concentrated, and evaporatively distilled (bulb-to-bulb, oven temperature 60–65 °C, oil pump vacuum), giving 146 mg (73%) of (*Z*)-1-(trimethylsiloxy)-1-octene (**3**)[4,54] as a colorless liquid: IR (film) 2950, 1650, 1250, 1085, 840 cm^{-1}. The NMR spectrum was equivalent to that reported.[54] VPC analysis (120 °C, $C_{12}H_{26}$ = 5.5 min) showed peaks at 1.9 min (1.5%, octanal), 4.2 min (98%, **3**), and 5.2 min (~0.5%, **4**).

(*E*)-1-(Trimethylsiloxy)-1-octene (4). In a procedure analogous to that used to convert **7** to **6**, 1.38 g (7.5 mmol) of vinylsilane **8** (>99% *E*) was converted to 0.785 g (48%) of α,β-dihydroxysilane **2**: IR (film) 3400, 2950, 1250, 840 cm^{-1}; NMR ($CDCl_3$) δ 0.08 (s, Me_3Si), 0.8–1.5 (13 H), 2.1 (2 H, br, OH), 3.15 (1 H, d, *J* = 6 Hz), 3.62 (1 H, m).

α,β-Dihydroxysilane **2** (218 mg, 1 mmol) was converted to (*E*)-1-(trimethylsiloxy)-1-octene (**4**)[4] (130 mg, 65% yield) by a procedure analogous to that used to convert **6** to **3** except that the reaction time was 24 h. The product (**4**) had IR (film) 2950, 1650, 1250, 1160, 840 cm^{-1}; NMR ($CDCl_3$) δ 0.14 (s, Me_3Si), 0.7–1.5 (11 H), 1.9 (2 H, m), 4.96 (1 H, m), 6.17 (1 H, d, *J* = 12 Hz). VPC analysis (120 °C, $C_{12}H_{26}$ = 3.4 min) showed a peak at 1.4 min (2.8%, octanal) and two peaks (97.2%) at 2.8 min (**3**) and 3.7 min (**4**) in a ratio of 1.2:98.8.

(*E*)-4-(Trimethylsiloxy)-4-octene (11). In a procedure analogous to that used to convert **7** to **6**, 1.38 g (7.5 mmol) of vinylsilane **9** (>99% *E*) was converted to 1.1 g (67%) of α,β-dihydroxysilane **10**. The product (**10**) solidified and had mp 68–70 °C: IR ($CHCl_3$) 3500, 2950, 840 cm^{-1}; NMR ($CDCl_3$) δ 0.07 (s, Me_3Si), 0.7–1.6 (14 H), 2.05 (2 H, OH), 3.70 (1 H, m).

α,β-Dihydroxysilane **10** (218 mg, 1 mmol) was converted to (*E*)-4-(trimethylsiloxy)-4-octene (**11**) (154 mg, 77% yield) by a procedure analogous to that used to convert **6** to **3**, except that the reaction time was 5 h. The product (**11**) had IR (film) 2950, 1655, 1250, 910, 840 cm^{-1}; NMR (200 MHz) ($CDCl_3$) δ 0.16 (s, Me_3Si), 0.86 (6 H, t, *J* = 7 Hz), 1.2–2.1 (8 H, m), 2.36 (m, corresponding to ~6% of 4-octanone), 4.60 (1 H, sharp t, *J* = 7.6 Hz); mass spectrum *m/z* (rel intensity) 200.1598 (M^+, 14) (calcd for $C_{11}H_{24}OSi$, 200.1596), 185 (9), 171 (100), 145 (9), 75 (15), 73 (57). VPC analysis (120 °C, $C_{11}H_{24}$ = 1.8 min) showed peaks at 1.0 min (4.5%, 4-octanone) and 1.7 min (95.5%, **11**).

(*Z*)-4-(Trimethylsiloxy)-4-octene (14). Vinylsilane **12** (920 mg, 5 mmol, ~93% *Z*) was converted to α,β-dihydroxysilane **13** (678 mg, 62% yield) by a procedure analogous to that used to convert **7** to **6** except that the reaction temperature and time were 55 °C and 48 h, respectively. The product (**13**) had IR (film) 3400, 2950, 1250, 840 cm^{-1}; NMR ($CDCl_3$) δ 0.07 (s, Me_3Si), 0.7–1.6 (14 H), 1.94 (2 H, br s, OH), 3.60 (1 H, m).

α,β-Dihydroxysilane **13** (218 mg, 1 mmol) was converted to (*Z*)-4-(trimethylsiloxy)-4-octene (**14**) (150 mg, 75% yield) by a procedure analogous to that used to convert **10** to **11**. The product (**14**) had IR (film) 2950, 1665, 1250, 960, 840 cm^{-1}; NMR (200 MHz) ($CDCl_3$) δ 0.16 (s, Me_3Si), 0.88 (6 H, t, *J* = 7 Hz), 1.2–2.1 (8 H, m), 2.36 (m, corresponding to ~6% of 4-octanone), 4.43 (1 H, t, *J* = 7 Hz), 4.60 (t, corresponding to 9% of **11**); mass spectrum *m/z* (rel intensity) 200.1592 (M^+, 13) (calcd for $C_{11}H_{24}OSi$, 200.1596), 185 (14), 171 (100), 145 (29), 75 (23), 73 (75). VPC analysis (120 °C, $C_{11}H_{24}$ = 1.8 min) showed peaks at 1.0 min (6%, 4-octanone) and 1.7 min (94%, **14** (and **11**)).

2-(Trimethylsiloxy)-1-octene (18). In a procedure analogus to that used to convert **7** to **6**, 1.38 g (7.5 mmol) of vinylsilane **15** was converted to 1.1 g (67%) of α,β-dihydroxysilane **17**, a colorless liquid which solidified (mp 50–51 °C, lit.[8] mp 53–54 °C): IR (film) 3400, 2950, 1250, 840 cm^{-1}; NMR ($CDCl_3$) δ 0.04 (s, Me_3Si), 0.7–1.5 (13 H), 2.07 (2 H, br s, OH), 3.62 (2 H, m).

α,β-Dihydroxysilane **17** (109 mg, 0.5 mmol) was converted to 2-(trimethylsiloxy)-1-octene (**18**)[4] (77 mg, 77% yield) by a procedure analogous to that used to convert **6** to **3** except that the reaction time was 4 h. The product (**18**) had IR (film) 2900, 1600, 1240, 1010, 840 cm^{-1}; NMR ($CDCl_3$) δ 0.17 (s, Me_3Si), 0.7–1.5 (11 H), 1.98 (2 H, m), 4.01 (2 H, s). VPC analysis (150 °C, $C_{11}H_{24}$ = 1.0 min) showed peaks at 0.7 min (5.5%, 2-octanone) and 1.2 min (94.5%, **18**).

1-(Trimethylsiloxy)cyclohexene (21). In a procedure analogous to that used to convert **7** to **6**, 1.155 g (7.5 mmol) of vinylsilane **19** was converted to 874 mg (62%) of α,β-dihydroxysilane **20**, a white solid mp 84–85 °C (lit.[9] mp 85–86 °C). The product (**20**) had IR ($CHCl_3$) 3540, 2950, 1030, 830 cm^{-1}; NMR ($CDCl_3$) δ 0.04 (s, Me_3Si), 1.0–2.0 (–$(CH_2)_4$–, m), overlapping with 1.80 (br s, OH), 3.59 (1 H, apparent t, *J* = 7 Hz).

α,β-Dihydroxysilane **20** (94 mg, 0.5 mmol) was converted to 1-(trimethylsiloxy)cyclohexene (**21**) (69 mg, 81% yield) by a procedure analogous to that used to convert **10** to **11**. IR and NMR spectra of **21** corresponded to those of an authentic sample. VPC analysis (120 °C, $C_{11}H_{24}$ = 3.9 min) showed peaks at 1.2 min (3.5%, cyclohexanone) and 2.9 min (96.5%, **21**).

(*E*)-1-(Trimethylsiloxy)-1-octene (4) via Epoxysilane 1. To an ice-cooled mixture of 1.4 g (7 mmol) of epoxysilanes **1** and **5** (86:14 by VPC) in 22 mL of THF and 11 mL of water was added 6 mL of 1 M H_2SO_4. The resulting mixture was stirred at ice temperature for 3 h and at room temperature for 2 h. Saturated $NaHCO_3$ (35 mL) was added, and stirring was continued for 0.5 h. The resulting mixture was extracted three times with ether, and the combined ether extracts were washed with water, dried ($MgSO_4$), concentrated, and chromatographed on 60 g of Florisil. Elution with petroleum ether removed unreacted epoxide (mostly **5**) and a small amount of octanal. Elution with methylene chloride and with 10% ether in methylene chloride gave 1.012 g (66%) of α,β-dihydroxysilane **2**.

α,β-Dihydroxysilane **2** (110 mg, 0.5 mmol) was converted to (*E*)-1-(trimethylsiloxy)-1-octene (**4**) (78 mg, 77% yield) by a procedure analogous to that used to convert **10** to **11**. VPC analysis (155 °C, $C_{11}H_{24}$ = 1.5 min) showed a peak at 1.1 min (2%, octanal) and two peaks (98%) at 1.80 min (**3**) and 2.05 min (**4**) in a ratio of 2:98.

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Registry No. 1, 62427-11-6; **2**, 72256-58-7; **3**, 71985-42-7; **4**, 71985-43-8; **5**, 62427-09-2; **6**, 72264-34-7; **7**, 57365-48-7; **8**, 57365-47-6; **9**, 64997-08-6; **10**, 96454-27-2; **11**, 96454-28-3; **12**, 83511-19-7; **13**, 96454-29-4; **14**, 96454-30-7; **15**, 63883-63-6; **16**, 62427-10-5; **17**, 63408-33-3; **18**, 55314-45-9; **19**, 17874-17-8; **20**, 72256-54-3; **21**, 6651-36-1; OsO_4, 20816-12-0; NaH, 7646-69-7.

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