ml of dry methanol was stirred and maintained at 0° while 14 ml of glacial acetic acid was added dropwise over 20 min. After standing for 2 hr the solution was poured into water containing an excess of sodium bicarbonate and the water extracted with ether. Work-up followed by distillation gave 1.9 g (80%) of methyl 1-methyl-4-hydroxy-4-cyanocyclohexanecarboxylate: bp 90–96° (0.08 mm); ir 3430 (OH), 2220 (CN), 1725, 1708 (C═O); nmr 3.69 (s, 3 H), 3.2–1.5 (m, 9 H), 1.21 (s) and 1.19 (s, total of 3H) (a mixture of cis and trans isomers).

Dehydration of 1.1 g (5.6 mmol) of the cyanohydrin in the usual fashion[33] gave 750 mg (75%) of **2i**: bp 53–55° (0.08 mm); ir 2200 (CN), 1722 (C═O), 1635 (C═C); nmr 6.56 (m, 1 H), 3.69 (s, 3 H), 2.9–1.4 (m, 6 H), 1.22 (s, 3 H); mass spectrum, *m/e* 179.

Anal. Calcd for $C_{10}H_{13}O_2N$: C, 67.04; H, 7.31; N, 7.81. Found: C, 67.09; H, 7.31; N, 7.80.

Methyl 1-Methyl-4-carboxamido-3-cyclohexenecarboxylate (2g). A mixture of 165 mg (0.92 mmol) of **2i** in 10 ml of 1 *N* sodium hydroxide containing 15 ml of 30% hydrogen peroxide (w/v) was stirred at 30° for 10 min. The alkaline solution was extracted with chloroform. Work-up gave a white solid which after two recrystallizations from carbon tetrachloride weighed 78 mg (43%) and melted at 120–121°: ir 3365, 3160 (N–H), 1710 (ester C═O), 1665 (amide C═O), 1638 (C═C), 1600 (NH); nmr 6.58 (m, 1 H), 5.5 (br s, 2 H), 3.66 (s, 3 H), 3.0–1.4 (m, 6 H), 1.22 (s, 3 H); mass spectrum, *m/e* 197.

Anal. Calcd for $C_{10}H_{15}O_3N$: C, 60.87; H, 7.69; N, 7.11. Found: C, 60.95; H, 7.63; N, 7.10.

Dimethyl 1-Methyl-3-cyclohexene-1,4-dicarboxylate (2h). Basic hydrolysis of 550 mg (3 mmol) of **2g** with 1 *N* sodium hydroxide gave, after acidification of the solution, filtration, and recrystallization of the solid from acetone, 420 mg (76%) of solid: mp 247–249°; ir 3500–3200 (br OH), 1670 (br C═O), 1640 (C═C); nmr (trifluoroacetic acid) 7.32 (m, 1 H), 3.2–2.6 (m, 6 H), 1.36 (s, 3 H). A mixture of 300 mg of this solid and 1.6 g of silver oxide in 30 ml of 1,2-dimethoxyethane was heated to 45–50°. Excess methyl iodide was added, and stirring and heating were continued for 3 hr. The reaction mixture was filtered, and the filtrate concentrated. Chromatography of the residue on silica, using cyclohexane-ethyl acetate (4:1) as eluent, followed by distillation gave 280 mg (83%) of **2h**: bp 61–63° (0.06 mm); ir 1712 (C═O), 1640 (C═C); nmr 6.92 (m, 1 H), 3.71 (s, 3 H), 3.66 (s, 3 H), 2.9–1.4 (m, 6 H), 1.21 (s, 3 H); mass spectrum, *m/e* 212.

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.24; H, 7.59. Found: C, 62.19; H, 7.62.

Methyl 1-Methyl-3,3,5,5-tetradeuterio-4-oxocyclohexanecarboxylate (3). The ethyl ester[10] of 1-methyl-4-oxocyclohexanecarboxylic acid, 4.5 g (24 mmol), was hydrolyzed by heating in 100 ml of D_2O (99.5% D) containing NaOD formed by addition of 4 g of sodium. Work-up gave 3.0 g (78%) of solid which after recrystallization from benzene-petroleum ether had mp 77.5–79° (lit.[10] mp 78–79°). The deuterium content of this product was shown to be greater than 95 mol % d_4 by mass spectroscopic analysis. Esterification using methyl iodide and silver oxide gave methyl 1-methyl-3,3,5,5-tetradeuterio-4-oxocyclohexanecarboxylate in 90% yield.

Synthesis of Series 1, the 3,5,5-Trideuterio Derivatives of 2. The conversions of **3** to all members of series **1** were conducted as described above for the conversions **4** to **2**. The only changes made were to substitute deuteriums for any exchangeable protons in those reagents which might have promoted exchange of the deuteriums already present. For example acetic acid-*O-d*, methanol-*O-d*, and morpholine-*N-d* were utilized wherever necessary. The deuterium content of the final products **1a–i** were determined by low voltage mass spectral analysis.

The morpholino and acetoxy derivatives **1b** and **1c** were found to have greater than 85% incorporation of three deuterium atoms and the remaining seven members of series **1** all had greater than 95% incorporation of deuterium at positions 3 and 5.

Acknowledgments. The authors thank the National Research Council of Canada for financial support and for a fellowship to B. F. R. (1968–1970).

Stereochemistry of Asymmetric Silicon. XIX. Nucleophilic Substitutions Involving Hydrogen and Carbon as Leaving Groups and Further Demonstration of Stereochemistry Crossover[1-3]

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Abstract: In this paper it is demonstrated that the stereochemistry of nucleophilic replacement of hydrogen and carbon leaving groups from silicon is a sensitive function of the nature of the reagent, the solvent, and, for carbon as a leaving group, the nature of the leaving organic group. Reagents used are all strong nucleophiles.

Although preliminary treatment of a portion of the present work on R_3Si^*H has appeared,[4,5] the data on carbon as a leaving group are completely new and the older work on the reactions of R_3Si^*H with bases is useful for completeness and for demonstrating stereochemistry crossover by comparison with new work never published.

The silicon–hydrogen bond is certainly extremely important from both synthetic and mechanistic standpoints and the latter aspect can receive much clarification by stereochemical studies such as those reported herein. We shall demonstrate a certain sensitivity of stereochemistry to various factors which make it reasonably certain that SN2*-Si and SN2**-Si are not common mechanisms for the silicon–hydrogen bond in R_3Si^*H (R_3Si^* is α-naphthylphenylmethylsilyl).[6]

Perhaps the simplest reaction of R_3Si^*H with a nucleophile is H–D exchange with lithium aluminum deuteride

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(1) For the preceding paper in this series, see L. H. Sommer and D. L. Bauman, *J. Amer. Chem. Soc.*, **91**, 7076 (1969).

(2) In its initial stages, this work was done at the Pennsylvania State University with generous support by Dow Corning Corp.

(3) We thank the National Science Foundation for vital recent support.

(4) For a preliminary communication on isotopic H–D exchange at R_3Si^* with $LiAlH_4$, see L. H. Sommer and C. L. Frye, *J. Amer. Chem. Soc.*, **81**, 1013 (1959).

(5) For preliminary treatment of the nucleophilic displacements on R_3Si^*H with KOH and with *tert*-butoxide anion in *tert*-butyl alcohol solvent, see L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965, pp 104–106.

(6) For a summary of the meaning of the mechanism symbols used in this paper, see ref 5, Chapter 11.

in ether solvent. This proceeds with pure retention of configuration and has been done also with R_3Si^*D and $LiAlH_4$.

$$\begin{aligned}&(+)R_3Si^*H + LiAlD_4 \xrightarrow[\sim 140°,\ 3\ hr]{Et_2O\text{–}n\text{-}Bu_2O} (+)R_3Si^*D\\ &(+)R_3Si^*D + LiAlH_4 \xrightarrow[\sim 140°,\ 3\ hr]{Et_2O\text{–}n\text{-}Bu_2O} (+)R_3Si^*H\end{aligned} \qquad (1)$$

Assignment of a detailed probable mechanism to reactions 1 is clouded by the uncertainty concerning exactly what AlH(D) species is participating in the exchange. Lithium aluminum hydride is unstable under the designated conditions. However, a four-center SNi-Si mechanism involving AlH(D) and Si*H(D) seems most plausible. In support of this conclusion we have effected the D–H exchange shown in reaction 2 with

$$\underset{[\alpha]D\ +36°}{(+)R_3Si^*D} + i\text{-}Bu_2AlH \xrightarrow{hexane} \underset{[\alpha]D\ +31.6°}{(+)R_3Si^*H(D)} \qquad (2)$$

good retention of configuration. The conditions were 36 hr of reflux in hexane solvent. The reactants were used in equimolar amounts and the product was a 50:50 mixture of Si*–H and Si*–D.

The reaction of powdered KOH(s) with R_3Si^*H is not only interesting from a mechanistic standpoint but is also an excellent method for the preparation of optically active R_3Si^*OK. Previously reported preparation of this latter material[7] from R_3Si^*OH and KOH(s) is much less convenient. Reaction 3 proceeds with a

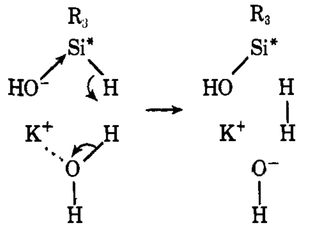
$$\underset{[\alpha]D\ -34°}{(-)R_3Si^*H} + KOH(s) \xrightarrow{xylene} \underset{[\alpha]D\ +72°\ (c\ 8.4,\ xylene)}{(+)R_3Si^*OK + H_2} \qquad (3)$$

predominant stereochemistry of ~92% retention of configuration. The optical purity of the product R_3Si^*OK was judged on the basis of reaction 4 and the

$$\underset{[\alpha]D\ +72°}{(+)R_3Si^*OK} + H_2O \longrightarrow \underset{[\alpha]D\ -17°}{(-)R_3SiOH} \qquad (4)$$

known rotation of optically pure silanol, [α]D 20.5°.[7]

Perhaps the simplest mechanistic rationale of predominant *retention* in reaction 3 (~92%) is indicated in mechanism scheme 5 which takes into account the



(5)

approximately 10% water in the powdered KOH(s) and, we feel, has the advantage of direct formation of H_2, instead of initial formation of KH which would result from a four-center SNi-Si mechanism. For a previous report on another probable six-center SNi-Si mechanism, see Grignard reduction of R_3Si^*OMe with *retention* by *t*-BuMgCl.[8]

Because of relatively slow racemization of the product by alkoxy–alkoxy exchange, it was found possible to obtain an optically active product from reaction of R_3Si^*H with potassium *tert*-butoxide in *tert*-butyl alcohol.[9] Reaction 6 proceeds with a predominant stereochemistry[10] of at least 95% retention of configuration. Optically pure $R_3Si^*O\text{-}t\text{-}Bu$ is assumed to have [α]D 28° on the basis of the product from the reaction of R_3SiCl with *tert*-butyl alcohol.[8]

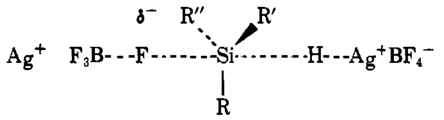
$$\underset{[\alpha]D\ +33°}{(+)R_3Si^*H} + t\text{-}C_4H_9OH \xrightarrow{KO\text{-}t\text{-}C_4H_9} \underset{[\alpha]D\ -26°}{(-)R_3Si^*O\text{-}t\text{-}C_4H_9} \qquad (6)$$

From the SN2-Si stereochemistry rule,[11] and the fact that $(+)R_3Si^*Cl$ gives $(-)R_3Si^*O\text{-}t\text{-}C_4H_9$ (ref 8), it follows that the latter and $(+)R_3Si^*H$ have the same configuration and reaction 6 proceeds with predominant retention of configuration. (($(+)R_3Si^*Cl$ and $(+)R_3Si^*H$ have opposite configurations.[7])

At this point in the discussion, reactions with nucleophiles appear uniformly to give *retention* of configuration with R_3Si^*H. However, it seems appropriate at this point to recall some of our previous work in which Ph_2CHLi, benzhydryllithium, gave 60% *inversion* as the predominant stereochemistry with R_3Si^*H, in line with our conclusion that "charge-delocalized" organometallic reagents favor *inversion* relative to simple alkyl- and aryllithiums.[12] Since H is an extremely "poor" and highly basic leaving group, *retention* of configuration was found with the lesser "charge-delocalized" $PhCH_2Li$ and $Ph(CH_3)CHLi$.[12] In this paper we wish to report that excellent *inversion* of configuration, >97%, results with R_3Si^*H in reaction 7.

$$\underset{[\alpha]D\ +33.2°}{(+)R_3Si^*H} + AgBF_4 \xrightarrow{ether} \underset{[\alpha]D\ -43.7°}{(-)R_3Si^*F} \qquad (7)$$

The result in reaction 7 is an extremely interesting one that is consistent with mechanism model 8 involving



$$Ag^+\ \ F_3B\text{---}\overset{\delta^-}{F}\text{-------}Si(R)(R')(R'')\text{--------}H\text{---}Ag^+BF_4^- \qquad (8)$$

simultaneous electrophilic "pull" on H, thus converting it into a good leaving group, and "push" on Si*. Reaction 7 is thus a nucleophilic displacement on Si* assisted by strong electrophilic catalysis. Stereochemistry crossover here is very interesting and reinforces again our prior conclusion that *retention* reactions (by SNi-Si) have special requirements which must be met. In reaction 7 the *actual* leaving group is "good" and an SN2-Si mechanism takes over.

We next report the first stereochemical data concerning cleavage by a strongly nucleophilic reagent of the silicon–carbon bond. A summary of the data obtained for the cleavages of the silicon–carbon bond with powdered potassium hydroxide in xylene solvent is found in Table I. The silicon compounds are listed in order of decreasing acidity of the conjugate acid of the leaving group. The pK_a values

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[7] L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Amer. Chem. Soc.*, **86**, 3271 (1964).

[8] L. H. Sommer, C. L. Frye, and G. A. Parker, *ibid.*, **86**, 3276 (1964).

[9] For systems involving primary alcohols that give alkoxide–alkoxide exchange with rapid inversion and hence would lead to racemization in the above studies, see L. H. Sommer and H. Fujimoto, *ibid.*, **90**, 982 (1968).

[10] For a precise definition of the method of calculation of predominant stereochemistry, see L. H. Sommer, J. D. Citron, and G. A. Parker, *ibid.*, **91**, 4729 (1969); a predominant stereochemistry of 95% retention means 5% inversion and an optical purity of the product of 90%.

[11] L. H. Sommer, G. A. Parker, N. C. Lloyd, C. L. Frye, and K. W. Michael, *ibid.*, **89**, 857 (1967).

[12] L. H. Sommer and W. D. Korte, *ibid.*, **89**, 5802 (1967).

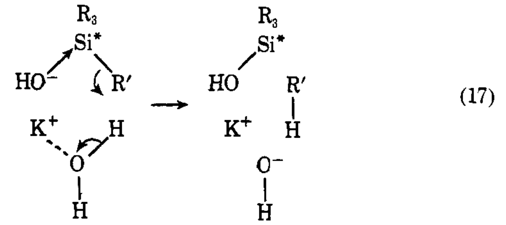
Table I. Stereochemistry of the Cleavage of R_3Si^*R' with Powdered Potassium Hydroxide in Xylene Solvent to give R_3Si^*OK and $R'H$

Reaction	RX[a] reactant	pK_a[b]	Reaction conditions	Product[c]	Predominant stereochemistry[d]	Ref
9	$(-)RC{\equiv}CC_6H_5$[g]	21	4 hr, 60°	(+)ROH	91% Ret	12
10	$(+)RCH(C_6H_5)_2$[g]	35	4 hr, 60°	(+)ROH	97% Inv	12
11	$(+)RC(C_3H_7)(C_6H_5)_2$	*e*	*f*	(+)RH	55% Inv	
12	$(+)RCH_2(C_6H_4$-*o*-Cl)	*e*	19 hr, 125°	(−)RH	65% Ret	
13	$(+)RCH_2C_6H_5$[g]	48	30 hr, 130°	(−)RH	79% Ret	12
14	$(+)RCH_2(C_6H_4$-*p*-$CH_3)$	*e*	40 hr, 134°	(−)RH	65% Ret	
15	$(+)RCH_2(C_6H_4$-*o*-$CH_3)$[g]	*e*	26 hr, 133°	(+)RH	66% Ret	12
16	$(-)RCH(CH_3)(C_6H_5)$[g]	*e*	24 hr, 130°	(−)RH	73% Ret	12

[a] R = α-naphthylphenylmethylsilyl group. [b] The pK_a of the conjugate acid of the leaving group is cited. The values used are estimates cited in ref 13 and 14. [c] The product listed is that from which the stereospecificity was determined. The initial product from the reaction is the potassium silanolate which is readily hydrolyzed with little loss of optical purity to the silanol. In most cases the silanol was contaminated with some hydrocarbon so the silanol was reduced and the silane purified. [d] (Inv = inversion, Ret = retention). A predominant stereochemistry of say 90% inversion means that this is the path taken by 90% of the reaction and that 10% proceeded with retention leading to an optical purity in the product of 80%. [e] Data unavailable. [f] Several temperatures were used for the same reaction: 4 hr at 90°, 14 hr at 110°, and 4 hr at 135°. [g] Compound reported in ref 12.

cited for the hydrocarbons[13,14] are meant to display the trend in acidity rather than providing an exact value since there is still considerable question as to the precise values.[14] Syntheses and properties of new compounds in Table I are given in the Experimental Section. Some of the compounds in Table I have been reported previously.[12]

The two diphenyl-substituted leaving groups, benzhydryl and 1,1-diphenyl-*n*-butyl, were displaced from asymmetric silicon with predominant inversion of configuration, whereas the monophenyl-substituted leaving groups such as benzyl, α-methylbenzyl, and *o*-chlorobenzyl were displaced with various degrees of retention of configuration. Since the benzyl-type leaving groups have only one phenyl group which can assist in the stabilization of an incipient negative charge by electron delocalization through the aromatic ring in the transition state, considerable assistance from the electrophilic portion of the nucleophile may be necessary to break the silicon–carbon bond. The cleavage of the silicon–benzyl bond probably proceeds by the SNi-Si mechanism for which a four-center model seems less plausible than the six-center one, as shown in the model of eq 17, where R′ is a benzyl group.



(17)

The benzhydryl-type leaving groups can stabilize the developing negative charge more effectively because of the charge delocalization through the second phenyl group so a concerted SN2-Si mechanism may be energetically favorable for the cleavage reaction. The decreased stereospecificity of the cleavage of the 1,1-diphenyl-*n*-butyl group from silicon may reflect a decrease in the acidity of the parent hydrocarbon due to the propyl group in the α position. The data obtained for the cleavage of the benzhydryl group from silicon are consistent with the observation of Rodewald[15] that the fluorenyl group can be cleaved from silicon with a high degree of *inversion* stereochemistry.

Phenylacetylene has a pK_a between 15 and 21[14] which, if compared with a pK_a of 35 for diphenylmethane,[14] would make the phenylethynyl group a considerably better leaving group from silicon if only the basicity of the leaving group was considered. However, the essentially 100% retention stereochemistry was more similar to the retention stereochemistry of the benzyl group cleavage from silicon than the almost 100% inversion of configuration obtained when the benzhydrylsilane was cleaved. The stereochemistry and rate of displacement of the phenylethynyl group from asymmetric silicon were actually more similar to that of the methoxy group than that of other carbanion leaving groups. The methoxysilane was cleaved in 1 hr at steam-bath temperature with 91% retention of configuration. The similarity in the mode of cleavage is even more apparent when data concerning solvent effects on the cleavage reaction are considered (see below).

The similar pathway for the cleavage of the phenylethynylsilane and methoxysilane and the different path for the cleavage of the benzhydrylsilane can be explained by considering the ability of the leaving groups to stabilize a developing negative charge in the transition state. The incipient charge in the transition state on the acetylenic carbon is not highly dispersed as in the case of the benzhydryl group, but localized as in the case of the methoxide ion. Therefore, the electrophilic portion of the nucleophile is more important for the stabilization of the charge on the acetylenic carbon than on the benzhydryl carbon. Because of charge localization on the acetylenic carbon in reaction 9 (Table I), a six-center SNi-Si retention mechanism satisfies the requirements for minimum charge separation and stabilization of the negative charge in the nonpolar solvent.

Eaborn and coworkers[16] have shown that there is greater solvent participation in the cleavage of the phenylethynylsilane than in the cleavage of a benzylsilane in polar solvents. The solvent participation is rationalized in terms of the decreased ability of the acetylenic carbon to stabilize the negative charge. In the nonpolar solvent xylene, this solvent assistance

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(13) D. J. Cram, *Chem. Eng. News*, 41, 92 (1963).

(14) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, Chapter 1, and references therein.

(15) L. H. Sommer and P. G. Rodewald, unpublished work.

(16) C. Eaborn and D. R. M. Walton, *J. Organometal. Chem.*, 4, 217 (1965).

Table II. Solvent Effects on the Stereochemistry of the Potassium Hydroxide Cleavage Reactions of α-Naphthylphenylmethylsilyl Derivatives

RX[a] reactant	Solvent	Product[b] isolated	$[\alpha]_D$,[c] deg	Predominant stereochemistry[d]
(+)RH	Xylene	(+)ROH	+17.0	92% Ret
(+)RH	*tert*-Butyl alcohol	(+)ROH	+13.2	83% Ret
(+)RH	Isopropyl alcohol	(+)ROH	+4.2	60% Ret
(+)RH	Methanol	(±)ROH	0.0	Rac
(+)$ROCH_3$	Xylene	(+)ROH	+16.4	91% Ret
(+)$ROCH_3$	*tert*-Butyl alcohol	(+)ROH	+2.2	55% Ret
(+)$ROCH_3$	Isopropyl alcohol	(−)ROH	−8.3	70% Inv
(+)$ROCH_3$	33% DME[e] and 67% *tert*-butyl alcohol	(+)ROH	+4.1	60% Ret
(+)$ROCH_3$	Ethyl alcohol	(±)ROH	0.0	Rac
(−)$RC{\equiv}CC_6H_5$	Xylene	(+)RH[f]	+29.2	91% Ret
(−)$RC{\equiv}CC_6H_5$	Isopropyl alcohol	(−)RH[f]	−8.1	70% Inv

[a] R = α-naphthylphenylmethylsilyl group. [b] The initial product of the reaction, the potassium silanolate, was hydrolyzed to the silanol. [c] Measured in ether solvent unless otherwise noted. [d] (Ret = retention, Inv = inversion, Rac = racemization). See footnote *d*, Table I. [e] DME is dimethoxyethane. [f] The silanol was contaminated with $PhC{\equiv}CH$. Reduction gave a pure product easily isolated.

is probably replaced by assistance from the electrophilic portion of the nucleophile.

Solvent Effects on the Cleavage Reaction. Changing the solvent from the nonpolar xylene to more polar protic solvents, *tert*-butyl alcohol and isopropyl alcohol, altered the stereochemistry of the potassium hydroxide cleavages of α-naphthylphenylmethylsilane, the methoxysilane, and the phenylethynylsilane (Table II). All three leaving groups, hydride, methoxy, and phenylethynyl, were displaced with a high degree of retention of configuration in xylene. When *tert*-butyl alcohol was used, the cleavage of all three silanes showed a considerable decrease in stereospecificity. In isopropyl alcohol the stereochemistry changed from predominant retention to predominant inversion of configuration for the cleavage of the methoxysilane and phenylethynylsilane, and the silane was cleaved with only 60% retention of configuration. A mixture of dimethoxyethane and *tert*-butyl alcohol did not change the stereochemistry significantly from that obtained from the reaction in pure *tert*-butyl alcohol.

These data, coupled with the observation by Bauman[17] that displacement of the phenoxy group, a slightly better leaving group than the methoxy group, changed from 68% retention to 92% inversion of configuration with a change of solvent from xylene to isopropyl alcohol, indicate that at least two stereospecific mechanisms are operative. One, a six-center SNi-Si mechanism leading to retention of configuration, is prevalent in nonpolar solvents when poor leaving groups, methoxy, phenoxy, phenylethynyl, are cleaved from silicon, and the second, an inversion mechanism, most likely the SN2-Si, becomes energetically more favorable in polar solvents, especially for the better leaving groups. Since the dimethoxyethane did not appear to increase the amount of inversion stereochemistry, even though it is considered a good solvent for cation solvation, therefore freeing the anion for nucleophilic attack, the dielectric constant of the solvent may be a key factor in determining the stereochemical outcome of the reaction. A solvent with a large dielectric constant may be necessary for stabilizing the charge in the transition state so that an inversion mechanism with considerable charge separation may compete with a retention mechanism that minimizes charge separation.

When extremely polar solvents, ethanol and methanol, were used, complete racemization of the product of the cleavage occurred. The cleavage reaction itself may be quite stereospecific, but a rapid exchange of hydroxide ion with the silanol formed in the very polar solvents may lead to racemization. This is not meant to imply that all reactions run in pure methanol or ethanol will give racemic products.

Experimental Section

Reactions of α-Naphthylphenylmethylsilane. 1. H–D Exchange with $LiAlH_4$. The deuteride is easily prepared from R_3Si^*Cl using $LiAlD_4$ in ether as the reagent. Reaction is rapid and quantitative giving R_3Si^*D, $[\alpha]_D 35°$ (*c* 11.2, pentane). *Anal.* Calcd for $C_{17}H_{15}SiD$: Si, 11.25; D(–Si), 0.808; mol wt, 249. Found: Si, 11.3; D(–Si), 0.823; mol wt, 251. The hydride, R_3Si^*H, has been reported.[7] The hydride exchange of R_3Si^*D will be described in detail; the reverse isotopic exchange was carried out in essentially the same manner. To 3.0 g (12 mmol) of R_3Si^*D (mp 62–64°), $[\alpha]_D + 35°$ (*c* 10, pentane), were added 3.0 g (0.316 equiv of Al–H) of lithium aluminum hydride, 30 ml of diethyl ether, and 35 ml of di-*n*-butyl ether. The reaction flask was then heated at 138–141° for 3 hr after distillation of Et_2O. Work-up with acetone, followed by treatment with dilute hydrochloric acid and water washing, was followed by drying over sodium sulfate and removal of solvent under vacuum. There was obtained, after silica gel chromatography, 2.75 g (92% recovery) of material, mp 60–63°, $[\alpha]_D$ +34.7° (*c* 8, pentane). The infrared spectrum showed better than 80% conversion to R_3Si^*H, and it will be noted that optical purity was essentially unaltered by the exchange.

H–D Exchange with *i*-Bu_2AlH. Under a dry nitrogen atmosphere in a 50-ml reaction flask, 0.673 g (2.7 mmol) of (+)R_3Si^*D, $[\alpha]_D$ +36°, dissolved in 4.5 ml of *n*-hexane, was combined with 0.50 ml (2.7 mmol) of *i*-Bu_2AlH. After magnetically stirring for 2 hr at room temperature, infrared analysis (using the Si*–D, Si*–H, and Al–H stretching bands) of an aliquot of the clear, colorless solution showed no appreciable development of R_3Si^*H. The solution was then heated at reflux temperature for 1 hr, and infrared analysis after this period indicated approximately 5% of the silicon was in the form of R_3Si^*H. Subsequent analyses of the reaction solution after 13 and 24 hr showed progressive increase in Si–H, decrease in Si–D, and decrease in Al–H. After 24 hr the exchange was nearly complete. After heating for a total of 36 hr, the exchange was judged complete (50% Si–H, 50% Si–D) by the infrared spectrum. The remaining portion of the reaction mixture was then cooled, taken up in pentane solvent, and worked up by washing with cold dilute HCl in a separatory funnel, then washing to neutrality, and drying with sodium sulfate. Removal of solvent gave 0.37 g of the pure, essentially equimolar, mixture of R_3Si^*H and R_3Si^*D, $[\alpha]_D$ 31.6° (*c* 1.5, pentane), confirmed by its infrared spectrum in CCl_4.[18]

2. Cleavage of (−)-α-Naphthylphenylmethylsilane with KOH(s). To a 50-ml erlenmeyer flask were added 4 g (0.07 mol) of powdered

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(17) D. L. Bauman, private communication.

(18) This study was carried out by J. McLick.

potassium hydroxide, containing *ca.* 10% water, 15 ml of dry xylene, and 1.6 g (0.0064 mol) of (−)-α-naphthylphenylmethylsilane (97% optically pure). The flask was then closed with a rubber stopper, fitted with a calcium sulfate drying tube, and heated on the steam bath for 2 hr with occasional swirling of the flask contents; at this point, the evolution of hydrogen had apparently ceased. The supernatant liquid was then decanted into a 2.50-dm polarimeter tube; the flask contents were rinsed with additional dry xylene which was also decanted into the polarimeter tube. Assuming a theoretical yield of potassium silanolate (1.9 g), the specific rotation was found to be $[\alpha]_D$ +72° (*c* 8.4 in xylene). Hydrolysis yielded 1.7 g of (−)-α-naphthylphenylmethylsilanol, $[\alpha]_D$ −17° (*c* 3.6 in ether), the infrared spectrum of which was identical with that of the authentic silanol. Titration of the xylene solution with standard acid indicated a 95% yield of R_3Si^*OK.

3. Reaction with *tert*-Butyl Alcohol. To a 200-ml distillation flask were added 65 ml of dry *tert*-butyl alcohol and 2.3 g (0.059 g-atom) of potassium. The flask was attached to a condenser, protected from atmospheric moisture by a calcium chloride tube, and heated at reflux for 24 hr to dissolve all the alkali metal. At this point, 20.0 g (0.0805 mol) of (+)-α-naphthylphenylmethylsilane (98% optically pure) was added and the solution was heated 4 hr at 88–92° to complete the solvolysis. After adding 100 ml of hexane, the product was washed four times with water, dried over sodium sulfate, and then evacuated free of solvents at the aspirator to give 25.8 g (97% yield) of (−)-α-naphthylphenylmethyl-*tert*-butoxysilane, $[\alpha]_D$ −25.9° (*c* 4.75 in pentane), $n^{34.5}{}_D$ 1.5797. The absence of silanol and unsolvolyzed silane in this residue was indicated by the infrared spectral transparency at 3.00 and 4.7 μ, respectively. Although this material was not analyzed further, its infrared spectrum was virtually identical with that of the (+)-*tert*-butoxysilane (distilled and of the theoretical Si content) obtained by reaction of R_3Si^*Cl with *tert*-butyl alcohol. The latter reaction is, in general, known to proceed with high stereospecificity and inversion.

4. Reaction with Silver Tetrafluoroborate.[19] (+)-α-Naphthylphenylmethylsilane (2.48 g, 0.01 mol), $[\alpha]_D$ +32.6° (*c* 11.1 pentane), was dissolved in 20 ml of anhydrous diethyl ether. The solution was added dropwise to a magnetically stirred solution of 2.17 g (0.011 mol) of $AgBF_4$ in 50 ml of anhydrous diethyl ether, excluding any moisture. During the addition of the silane the color of the solution became deep black and hydrogen was evolved. A silver mirror was formed on the walls of the flask. After the addition of the silane, stirring was continued for 0.5 hr. During this time the silver mirror broke down and was suspended in the completely clear solution. After decanting the supernatant liquid it was freed of ether by evaporation *in vacuo*. In order to remove boron trifluoride etherate, finally high vacuum (1 mm) was applied. The final product, which crystallized after a few minutes standing, was taken up in a few milliliters of *n*-hexane. Crystallization soon occurred in the refrigerator, mp 68°, yield 1.4 g (52%), $[\alpha]_D$ −43.7° (*c* 4.98, ether).

Potassium Hydroxide Cleavages of α-Naphthylphenylmethylsilyl Derivatives. a. Cleavage of α-Naphthylphenylbenzhydrylmethylsilane. A solution of (+)-α-naphthylphenylbenzhydrylmethylsilane (4.00 g, 0.0096 mol), $[\alpha]_D$ +15.4° (*c* 3.7 in chloroform), in xylene (20 ml) was placed in a 100-ml flask, vented to the atmosphere *via* a Gilman trap, and treated with powdered potassium hydroxide (10 g). The mixture was heated on the steam bath for 4 hr. The orange-colored reaction mixture was then cooled and the solution decanted from the excess potassium hydroxide into a polarimeter tube. The material in the solution had $[\alpha]_D$ −61.8° (*c* 16.0 in xylene). This value is based on a quantitative yield of the potassium silanolate. The potassium silanolate was hydrolyzed by pouring the xylene solution into a separatory funnel containing 3% hydrochloric acid (200 ml) and ethyl ether (50 ml) and then washing the organic layer five times with cold water. After drying the organic layer over anhydrous calcium chloride, filtering, and removing the solvent under vacuum, (+)-α-naphthylphenylmethylsilanol (2.40 g, 0.0091 mol), $[\alpha]_D$ + 22.6° (*c* 11.5 in xylene), was obtained. The infrared spectrum of the silanol was identical with the spectrum of the authentic silanol prepared by Frye.[7]

b. Cleavage of α-Naphthylphenyl(1,1-diphenyl-*n*-butyl)methylsilane. A solution of (+)-α-naphthylphenyl(1,1-diphenyl-*n*-butyl)methylsilane (1.57 g, 0.0035 mol), $[\alpha]_D$ +25.4° (*c* 8.0 in carbon tetrachloride), in xylene (20 ml) was mixed with powdered potassium hydroxide (2.5 g) and the mixture heated to 90° for 4 hr, 110° for 14 hr, and finally to 135° for 4 hr. Hydrolysis, as described in the previous experiment, and removal of solvent under vacuum left a material (0.90 g) with $[\alpha]_D$ +2.9° (*c* 3.7 in ethyl ether) which, as indicated by the infrared spectrum, was predominantly the silanol, but contained a considerable quantity of the 1,1-diphenyl-*n*-butane. The silanol was dissolved in dry ethyl ether and di-*n*-butyl ether and treated with lithium aluminum hydride (0.2 g) for 16 hr at 80°. Work-up and subsequent chromatography through a 26 × 0.5 in. column of silica gel gave a material (0.44 g) with $[\alpha]_D$ +3.4° (*c* 3.0 in pentane). The infrared spectrum was consistent with that of α-naphthylphenylmethylsilane[7] except that a small amount of the hydrocarbon was still present.

c. Cleavage of α-Naphthylphenyl(*o*-chlorobenzyl)methylsilane. A solution of (+)-α-naphthylphenyl(*o*-chlorobenzyl)methylsilane (2.58 g, 0.069 mol), $[\alpha]_D$ +1.90° (*c* 10.0 in ethyl ether), in xylene (20 ml) was treated with powdered potassium hydroxide (4.0 g) and the mixture heated at 125° for 19 hr. After having been cooled, the organic material was decanted from the excess potassium hydroxide into a separatory funnel containing 3% hydrochloric acid (100 ml) and ethyl ether (50 ml). The organic layer was washed with water until neutral, dried over sodium sulfate, and filtered. Removal of solvent under vacuum left a material with $[\alpha]_D$ −4.9° (*c* 11.5 in ether) which was composed of a mixture of the silanol and the unchanged *o*-chlorobenzylsilane. Treatment of the product with lithium aluminum hydride in ethyl ether and di-*n*-butyl ether overnight at 80° and hydrolysis following the "standard procedure" gave a mixture of the silane and the benzylsilane. Elution chromatography through a 25 × 0.5 in. column of silica gel with a solvent blend of 10% benzene in pentane separated the two organosilanes. (−)-α-Naphthylphenylmethylsilane (0.73 g, 0.0029 mol) with $[\alpha]_D$ −10.3° (*c* 3.2 in pentane) was obtained. The infrared spectrum was identical with that of the spectrum of the authentic silane.[7]

d. Cleavage of (+)-α-Naphthylphenylbenzylmethylsilane. A solution of (+)-α-naphthylphenylbenzylmethylsilane (4.26 g, 0.0126 mol), $[\alpha]_D$ +5.5° (*c* 3.5 in pentane), in dry xylene (30 ml) was treated with powdered potassium hydroxide (4.0 g). The reaction mixture was maintained at 130° for 30 hr before it was cooled and the organic material treated as described in the previous experiment. The mixture of the silanol and the benzylsilane, which had $[\alpha]_D$ −4.9° (*c* 11.5 in ethyl ether), was treated with lithium aluminum hydride to reduce the silanol to the silane. The silane and the unchanged benzylsilane were separated on a 26 × 0.25 in. column of silica gel with a 10% benzene–pentane solvent blend. The first 25 ml of the eluate contained only a trace of silicon-containing material so it was discarded. The next three 25-ml fractions of eluate contained 0.35, 0.52, and 0.13 g, respectively, of (−)-α-naphthylphenylmethylsilane which crystallized after the solvent was removed under vacuum. The infrared spectra of the three fractions were identical with that of the authentic silane.[7] The largest fraction (0.52 g) had $[\alpha]_D$ −16.1° (*c* 2.9 in pentane). The combined weight of the three fractions, 1.00 g, constituted a 32% yield. Subsequent fractions from elution chromatography gave the essentially pure unchanged benzylsilane with $[\alpha]_D$ +5.5° (*c* 1.7 in pentane).

Duplication of this experiment under essentially identical conditions gave very similar results. Cleavage of (−)-α-naphthylphenylbenzylmethylsilane (3.06 g, 0.0091 mol), $[\alpha]_D$ −4.1° (*c* 4.6 in pentane), and reduction of the silanol yielded, after chromatography, (+)-α-naphthylphenylmethylsilane (0.79 g, 0.0032 mol) with $[\alpha]_D$ +13.3° (*c* 2.6 in pentane).

e. Cleavage of α-Naphthylphenyl(*p*-methylbenzyl)methylsilane. A solution of (+)-α-naphthylphenyl(*p*-methylbenzyl)methylsilane (1.08 g, 0.0031 mol), $[\alpha]_D$ +11.0° (*c* 4.5 in pentane), in xylene (20 ml) was treated with powdered potassium hydroxide (3.0 g), and the mixture was maintained at 134° for 40 hr. After having been cooled to room temperature, the xylene solution was decanted from the excess potassium hydroxide, washed with water, dried over sodium sulfate, and filtered before the solvent was removed under vacuum. The infrared spectrum of the oily material (0.648 g) indicated that most of the material was the silanol. Reduction of the silanol with lithium aluminum hydride and chromatography through silica gel gave (−)-α-naphthylphenylmethylsilane (0.33 g, 0.0013 mol), $[\alpha]_D$ −10.2° (*c* 1.0 in pentane). The infrared spectrum served to identify the product.

f. Cleavage of α-Naphthylphenyl(*o*-methylbenzyl)methylsilane. A mixture of (+)-α-naphthylphenyl(*o*-methylbenzyl)methylsilane (2.11 g, 0.0060 mol), $[\alpha]_D$ +10.2° (*c* 4.2 in pentane), xylene (30 ml), and powdered potassium hydroxide (4.0 g) was maintained at 133° for 26 hr, before it was cooled and the xylene solution decanted from the potassium hydroxide into a separatory funnel containing ethyl ether (50 ml). The organic material was washed with dilute hydrochloric acid and five portions of water and dried over sodium

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(19) This work was carried out by A. Ritter.

Table III. Preparation of New R_3Si^*R' Compounds

R'	$[\alpha]_D$,[a] deg	Found, % C	Found, % H	Calcd, % C	Calcd, % H
$-C(C_3H_7)(C_6H_5)_2$[b]	−25.4 (*c* 8.0, CCl_4)	*c*	*c*	*c*	*c*
$-CH_2(C_6H_4$-*o*-$Cl)$[d]	−1.9 (*c* 10.0, Et_2O)	77.3	5.70	77.3	5.68
$-CH_2(C_6H_4$-*p*-$CH_3)$[e]	−11.0 (*c* 4.5, C_5H_{12})	85.3	6.99	85.2	6.86
$-CH(CH_3)(C_6H_5)$[f]	−32.4 (*c* 11.5, C_5H_{12})	85.5	6.89	85.2	6.86

[a] Product from reaction of R′Li with $(+)R_3Si^*Cl$. [b] Characteristic infrared bands, μ: 3.38, 3.40, 4.50, 6.92, 6.95, 8.40, 8.65. [c] *Anal.* Calcd for $C_{33}H_{32}Si$: Si, 6.15. Found: Si, 6.17. [d] Characteristic infrared bands, μ: 3.38, 6.40, 6.75, 6.80, 7.05, 7.15, 8.34, 8.65, 9.80. [e] Characteristic infrared bands, μ: 3.45, 5.30, 6.21, 6.88, 8.30, 8.60. [f] Characteristic infrared bands, μ: 3.45, 6.90, 8.60, 7.88, 10.0.

sulfate. The material left, after removal of solvent under vacuum, contained a mixture of the silanol and the starting material. Reduction of the silanol with lithium aluminum hydride followed by separation of the silane from the starting material by elution chromatography gave (+)-α-naphthylphenylmethylsilane (0.38 g, 0.00156 mol) which had an infrared spectrum identical with that of the authentic silane. The major fraction (0.24 g) from chromatography had $[\alpha]_D$ +11.0° (*c* 1.8 in pentane).

g. Cleavage of α-Naphthylphenyl(α-methylbenzyl)methylsilane. A mixture of (−)-α-naphthylphenyl(α-methylbenzyl)methylsilane (3.89 g, 0.011 mol), $[\alpha]_D$ −8.8° (*c* 19.0 in pentane), xylene (25 ml), and powdered potassium hydroxide (3.0 g) was heated for 24 hr at 136°. After allowing the mixture to cool, the xylene solution was decanted from the potassium hydroxide into a separatory funnel containing ethyl ether (50 ml). The organic material was washed with dilute hydrochloric acid and four portions of water, dried, and filtered. Analysis of the infrared spectrum of the residue remaining after the solvent had been removed under vacuum indicated that the residue contained almost an equal quantity of the silanol and the α-methylbenzylsilane. The silanol was reduced to the silane by treatment of the mixture with lithium aluminum hydride. Elution chromatography over silica gel with a 10% benzene-pentane solvent blend was used to separate the silane from the α-methylbenzylsilane. (−)-α-Naphthylphenylmethylsilane (0.81 g, 0.0032 mol) was obobtained with $[\alpha]_D$ −4.1° (*c* 4.1 in pentane).

h. Cleavage of α-Naphthylphenyl(phenylethynyl)methylsilane. A mixture of (−)-α-naphthylphenyl(phenylethynyl)methylsilane (1.54 g, 0.0044 mol), $[\alpha]_D$ −8.2° (*c* 7.2 in pentane), xylene (25 ml), and powdered potassium hydroxide (4.0 g) was placed in a 125-ml flask, vented to the atmosphere *via* a Gilman trap. The flask was heated on a steam bath for 4 hr. The dark orange solution was decanted from the potassium hydroxide into a separatory funnel containing ethyl ether (50 ml) and dilute hydrochloric acid (~3%, 50 ml), and the mixture was shaken for 20 sec. After washing the organic layer four times with cold water, the organic material was dried over sodium sulfate and filtered. Analysis of the infrared spectrum of the materials, after removal of the solvent under vacuum, indicated that the product was essentially the pure silanol (0.67 g) with $[\alpha]_D$ 13.8° (*c* 3.0 in ether). Reduction of the silanol with lithium aluminum hydride gave the crude silane, $[\alpha]_D$ +22.3° (*c* 3.3 in pentane). Chromatography through a 24 × 0.5 in. column of silica gel with a 10% benzene-pentane solvent blend (200 ml) afforded (+)-α-naphthylphenylmethylsilane (0.34 g, 0.0014 mol) with $[\alpha]_D$ +26.0° (*c* 1.8 in pentane). The infrared spectrum was identical with that of the authentic silane.[7]

Reactions of α-Naphthylphenylmethylsilyl Derivatives with Potassium Hydroxide in Protic Solvents. a. Cleavage of (−)-α-Naphthylphenylmethylsilane in *tert*-Butyl Alcohol. Powdered potassium hydroxide (4.0 g) was added to a solution of (−)-α-naphthylphenylmethylsilane (0.84 g, 0.0034 mol), $[\alpha]_D$ −33.8° (*c* 5.0 in pentane), in *tert*-butyl alcohol (30 ml). Evolution of a gas, presumed to be hydrogen, began immediately and ceased after 9 min. The alcoholic solution was decanted from undissolved potassium hydroxide into a mixture of dilute hydrochloric acid (~3%, 50 ml) and ethyl ether (100 ml) into a separatory funnel. After shaking the mixture for a few seconds the organic layer was washed five times with 50-ml portions of water, dried over sodium sulfate, and filtered. Removal of solvent under vacuum left essentially pure (−)-α-naphthylphenylmethylsilanol[7] (0.82 g, 0.0031 mol), $[\alpha]_D$ −13.2° (*c* 3.3 in ether). The infrared spectrum served to identify the product.

b. Cleavage of (−)-α-Naphthylphenylmethylsilane in Isopropyl Alcohol. Powdered potassium hydroxide (1.5 g) was added to a solution of (−)-α-naphthylphenylmethylsilane (0.72 g, 0.0029 mol), $[\alpha]_D$ −33.8° (*c* 5.0 in pentane), in reagent grade isopropyl alcohol (20 ml). The flask warmed slightly and evolution of a gas, presumably hydrogen, began immediately and ceased after 3 min. After waiting for 1 min the solution was separated from a slight amount of undissolved potassium hydroxide and treated as described in the preceding experiment. (−)-α-Naphthylphenylmethylsilanol (0.60 g, 0.0024 mol), $[\alpha]_D$ −4.2° (*c* 3.0 in ether), was obtained.

c. Cleavage of (−)-α-Naphthylphenylmethylsilane in Methanol. A solution of (−)-α-naphthylphenylmethylsilane (0.80 g, 0.0032 mol), $[\alpha]_D$ −33.8° (*c* 5.0 in pentane), in purified methanol (20 ml) was treated with powdered potassium hydroxide (4.0 g) by rapidly pouring the entire amount of the hydroxide into the solution and swirling. Within 15 sec, the evolution of the gas had ceased and the solution was treated as described in section a. Essentially pure racemic α-naphthylphenylmethylsilanol was obtained.

d. Cleavage of (+)-α-Naphthylphenylmethylmethoxysilane in *tert*-Butyl Alcohol. Powdered potassium hydroxide (2.5 g) was added to a solution of (+)-α-naphthylphenylmethylmethoxysilane (0.98 g, 0.0035 mol), $[\alpha]_D$ +15.1° (*c* 13.2 in pentane), in purified *tert*-butyl alcohol (20 ml) and the mixture stirred occasionally for 10 min. The alcoholic solution was treated as described in section a and yielded (+)-α-naphthylphenylmethylsilanol (0.81 g, 0.0031 mol) with $[\alpha]_D$ +2.2° (*c* 10.1 in ether). The infrared spectrum of the product was identical with that of the authentic silanol.[7]

e. Cleavage of (+)-α-Naphthylphenylmethylmethoxysilane in Isopropyl Alcohol. A solution of (+)-α-naphthylphenylmethylmethoxysilane (0.99 g, 0.0035 mol), $[\alpha]_D$ +15.0° (*c* 31.1 in pentane), in reagent grade isopropyl alcohol (20 ml) was treated with powdered potassium hydroxide (2.5 g) and stirred for 5 min. The alcoholic solution was decanted from the undissolved potassium hydroxide into a separatory funnel containing 1% hydrochloric acid (100 ml) and ethyl ether (75 ml), and the mixture was shaken for 20 sec. The aqueous layer was discarded, and the organic layer was washed six times with water, dried over sodium sulfate, and filtered. Removal of solvent under vacuum left essentially pure (−)-α-naphthylphenylmethylsilanol (0.84 g, 0.0032 mol), $[\alpha]_D$ −8.3° (*c* 10.6 in ethyl ether). The product was characterized by its infrared spectrum. The silanol was reduced with lithium aluminum hydride. (−)-α-Naphthylphenylmethylsilane (0.68 g) with $[\alpha]_D$ −14.3° (*c* 2.7 in pentane) was obtained.

f. Cleavage of (+)-α-Naphthylphenylmethylmethoxysilane in a Mixture of *tert*-Butyl Alcohol and Dimethoxyethane. (+)-α-Naphthylphenylmethylmethoxysilane (0.71 g, 0.0025 mol), $[\alpha]_D$ +12.5° (*c* 2.8 in pentane), was dissolved in purified *tert*-butyl alcohol (12 ml) and dimethoxyethane (6 ml) and treated with powdered potassium hydroxide (4.0 g). After 10 min, the solution was decanted from the undissolved potassium hydroxide and worked up as described in the previous experiment. The product, (+)-α-naphthylphenylmethylsilanol (0.54 g, 0.0020 mol), $[\alpha]_D$ +4.1° (*c* 3.3 in ethyl ether), was identified by the infrared spectrum.

g. Cleavage of (+)-α-Naphthylphenylmethylmethoxysilane in Ethanol. Powdered potassium hydroxide (2.0 g) was added to a solution of (+)-α-naphthylphenylmethylmethoxysilane (1.06 g, 0.0038 mol), $[\alpha]_D$ +15.1° (*c* 13.2 in pentane), in absolute ethanol (15 ml) and swirled for 90 sec before it was worked up as described in section e. Removal of the solvent under vacuum left the pure racemic silanol.

h. Cleavage of α-Naphthylphenyl(phenylethynyl)methylsilane in Isopropyl Alcohol. A solution of (−)-α-naphthylphenyl(phenylethynyl)methylsilane (1.80 g, 0.0052 mol), $[\alpha]_D$ −8.4° (*c* 7.1 in pentane), in reagent grade isopropyl alcohol (40 ml) was treated with powdered potassium hydroxide (3.0 g). After 5 min of occasional stirring, the red solution was worked up as described in section e. The infrared spectrum of the product, (−)-α-naphthylphenylmethylsilanol (1.37 g), $[\alpha]_D$ −3.6° (*c* 5.5 in ethyl ether), was essentially identical with that of the authentic silanol.[7] The silanol was reduced with lithium aluminum hydride. Chromatography of the crude reduction product through a 26 × 0.5 in. column of silica gel with a 10% benzene-pentane solvent blend gave (−)-α-naphthylphenylmethylsilane (1.00 g; 0.0040 mol), with [α]D −7.4° (c 5.1 in pentane).

Preparation of New Compounds. These were all prepared by standard procedures usually involving reaction of R_3Si^*Cl with R′Li. Table III lists some of their physical properties and appropriate analytical data.

Stereochemistry of Asymmetric Silicon. XX. Hydroxylation and Carbene Insertion Reactions of R_3Si^*H[1,2]

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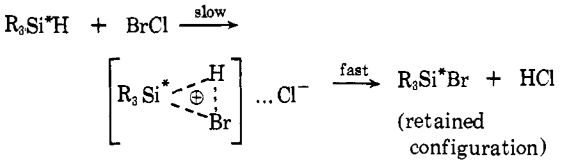
Abstract: Studies on the stereochemistry of the reactions of optically active R_3Si^*H (α-naphthylphenylmethylsilane) with perbenzoic acid (hydroxylation) to give R_3Si^*OH and with dihalocarbenes (insertion) to give $R_3Si^*CHX_2$ are reported. Discussion of mechanism implications of this work leads to the conclusion that both reactions, like the halogenation of R_3Si^*H, involve three-center intermediates which give products with predominant retention of configuration.

In contrast to the preceding paper[2] in this series which dealt with strongly nucleophilic reagents such as KOH(s), $LiAlH_4$, and ROK, the present paper reports studies on R_3Si^*H using perbenzoic acid and halocarbenes. Both of the latter may be regarded as electrophilic in character. They are certainly *not* strong nucleophiles and the stereochemistry of their reactions with optically active R_3Si^*H is of mechanistic interest.

Hydroxylation of R_3Si^*H. Because of the close relationship we believe to exist between the hydroxylation described below and the reactions of R_3Si^*H with Cl_2, Br_2, and BrCl (uncatalyzed by light), it is perhaps appropriate to illustrate our preferred mechanism for halogenation of R_3Si^*H with BrCl as shown in eq 1.[3]



(1)

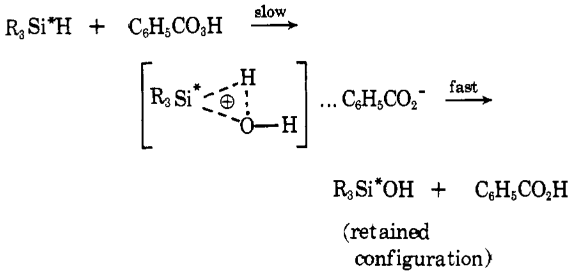
Based on mechanism model 1 we predicted and carried out the hydroxylation of R_3Si^*H with perbenzoic acid as the source of OH^+.

A 49% yield of optically active R_3Si^*OH was obtained from R_3Si^*H using an excess of perbenzoic acid in benzene solvent at room temperature for 12 hr. Pertinent data are given in reaction 2. The predominant stereochemistry of (2) is at least 93% retention of configuration based on an optical purity of the product of ~86%. The method of calculating the per cent predominant stereochemistry has been reported.[4]

$$\underset{[\alpha]\text{D} -35^\circ}{(+)R_3Si^*H} + C_6H_5CO_3H \longrightarrow \underset{[\alpha]\text{D} -23^\circ}{(+)R_3SiOH} + C_6H_5CO_2H \quad (2)$$

Since reaction 2 as formulated involves electrophilic attack on R_3Si^*H by OH^+, it had to be proven that the reaction is *not* in fact a nucleophilic substitution by benzoate anion followed by conversion of the formed benzoate (R_3Si^*OCOPh) to silanol. This latter possibility was excluded by experiments which showed that (a) (+)α-NpPhMeSiOCOPh gives no reaction with perbenzoic acid, and (b) work-up without the use of water still gives the silanol.

The simplest mechanism model for hydroxylation by reaction 2 is analogous to (1) and we have so formulated it in (3) below. Although more complex mechanisms also are possible, we believe that all reasonable variants of (3) share with it the essential feature of electrophilic attack at the silicon–hydrogen bond.



(3)

Dihalocarbene Insertions into R_3Si^*H. There has recently been much interest in carbene (or carbenoid) insertions into Si–X bonds with which X = H,[5] C (ring strained),[6] and Cl.[7]

We wish to report stereochemical studies on such insertions[8] using optically active R_3Si^*H,[9] α-naphthylphenylmethylsilane.

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[1] Current support of this work by the National Science Foundation is gratefully acknowledged. Initial studies were carried out at the Pennsylvania State University with support from Dow Corning Corporation.

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[8] For a preliminary communication on this subject, see: L. H. Sommer, L. A. Ulland, and A. Ritter, *J. Amer. Chem. Soc.*, **90**, 4486 (1968).

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