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THE PREPARATION AND CHEMISTRY OF (R)-(1-NAPHTHYL)PHENYL-METHYLSILYLMETHYLLITHIUM: STEREOCHEMISTRY AT SILICON IN THE ELIMINATION OF β-HYDROXYSILANES.

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Abstract: (R)-(1-naphthyl)phenylmethylsilylmethyllithium has been prepared from 1-naphthylphenylmethylsilylmethyltri-n-butyltin, which is in turn prepared in four steps from (R)-(1-naphthyl)phenylmethylsilane. The title lithium reagent was reacted with benzaldehyde, pivaldehyde, acrolein and 2-methylcyclohexanone to produce the corresponding β-hydroxysilanes in good yield, but with only a 3-4% diastereomeric excess. Unfortunately, these diastereomers proved impossible to separate. Model studies employing the methyldiphenylsilyl group showed that these β-hydroxysilanes could be protiodesilylated to give the corresponding methyl alcohol. The products from the adduct with pivaldehyde and acrolein were used to investigate the stereochemistry at silicon of the β-elimination of the β-hydroxysilanes. This was found to occur with inversion of configuration at silicon when the elimination is carried out with boron fluoride etherate, sulfuric acid or acetic acid/sodium acetate, but with retention of configuration when carried out with potassium hydride.

The recent advances in asymmetric syntheses[3] and in silicon-mediated transformations[4] have been extraordinary. The combination of these two general developments has, however, been attempted only in a small number of instances[5] despite some early work of Brook and coworkers[6] indicating that some successes along these lines might be possible. Even in the absence of high stereoselectivity in the reactions of chiral organosilanes[7], the presence of the chiral organosilane moiety allows for the potential separation of the formed diastereomers[8], which could lead to silicon-free products of high optical purity. This general approach has been used successfully by Brown and coworkers[9] with certain chiral organoborane reagents.

In our own experience we have used the readily available 1-naphthylphenyl-methylsilyl[10] unit as the chiral silicon group. This unit has not given high diastereoselectivities in its reactions, but we have succeeded in the separation of the formed diastereomers in several cases.[7] We report herein on the preparation of three diastereomeric β-hydroxyalkyl (1-naphthyl)phenylmethylsilanes of the type **1**, attempts at their separation and the stereochemistry at silicon for their elimination.

1

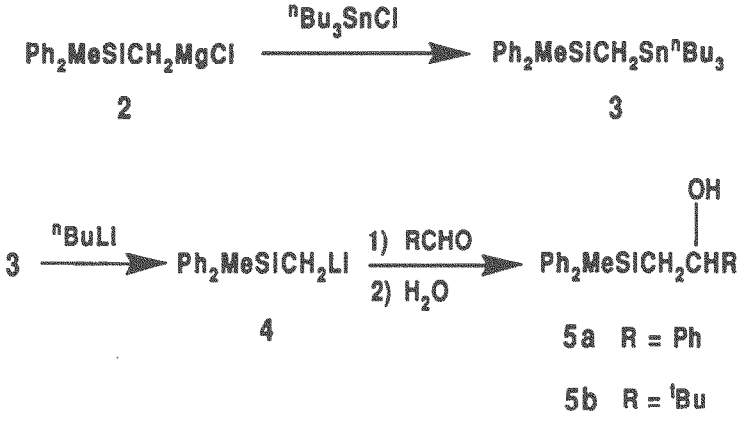
Results and Discussion

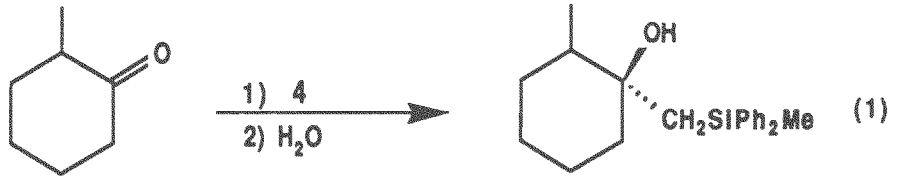
Preparation of β-Hydroxysilanes Optically Active at Silicon.

In order to ascertain that certain reactions would procede we first looked at a model system, namely (chloromethyl)methyldiphenylsilane. This material is readily prepared from (chloromethyl)dimethylchlorosilane and phenylmagnesium bromide. It reacts readily with magnesium turnings to form the Grignard reagent **2**. This reagent, however, reacts very poorly with aldehydes, due in part to its greater steric bulk over that of the more common trimethylsilyl system. Reaction of **2** with tri-n-butyltin chloride gives the tin reagent **3**, which when treated with n-butyllithium in THF at -78° provides the lithium reagent **4**[11], which did react with benzaldehyde in good yield. It was of some concern that the intermediate β-alkoxysilanes would suffer

elimination prior to hydrolysis and that the desired β-hydroxysilanes would not be isolable. This did not prove to be a problem even with the adduct of benzaldehyde. The second question of interest was whether the β-hydroxy methyldiphenylsilyl systems would protiodesilylate in the same manner as the trimethylsilyl systems as reported by Hudrlik and coworkers.[12] This, too, proved to be possible. It was found, however, that the purity of the potassium tert-butoxide is crucial to the success of the reaction, with aged material leading to considerable elimination.

SCHEME I





Having satisfied ourselves that it should be possible to prepare and isolate β-hydroxy-silanes from reagent **1** we prepared this reagent as shown in equation. (Chloromethyl)(1-naphthyl)phenylmethylsilane was prepared by tri-n-butyltin hydride reduction of the dichloride as previously described.[7] Reaction of this material with magnesium turnings provided the Grignard reagent, which was reacted with tri-n-butyltin chloride to give the required precursor in 75 percent yield. The tin reagent **7** was reacted with n-butyllithium in THF at -78°C[11] followed by the addition of the appropriate carbonyl compound to generate the β-hydroxysilanes **8** as diastereomeric mixtures. Unfortunately, it did not prove possible to separate any of these diastereomeric mixtures by crystallization or chromatography. As can be seen from the results shown in Table I, the

diastereoselectivity is extremely low with only about 4% de being observed. As expected the reaction with 2-methylcyclohexanone occurred from the side opposite to that of the methyl group.[11] It was not possible to determine the diastereomeric ratio of this reaction product. The unreacted 2-methylcyclohexanone was checked for optical activity and found to be optically inactive indicating that no kinetic resolution had occurred. Likewise, the β-hydroxysilane was subjected to elimination with boron fluoride etherate and the resulting 1-methylene-2-methylcyclohexane found to be optically inactive.

SCHEME II

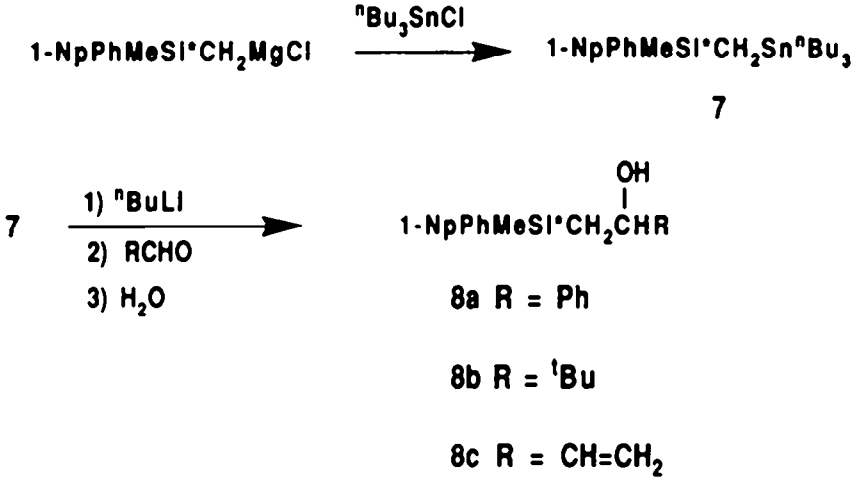


TABLE I. β-HYDROXYSILANES FROM 3 AND 7.

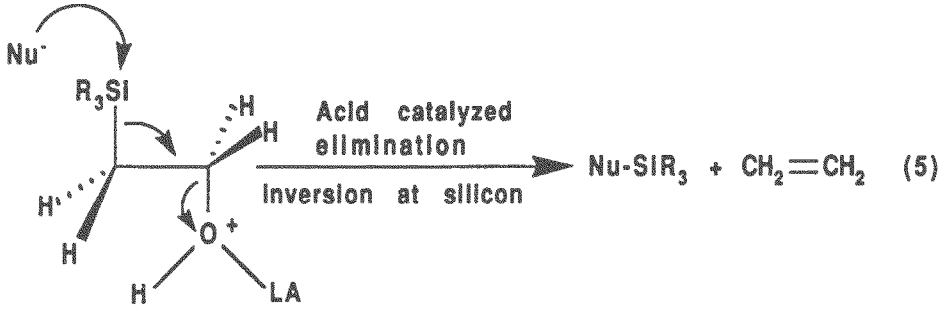
Silane	Carbonyl Compound	Product	% Yield	Diastereomeric Ratio
3	benzaldehyde	5a	61	..
3	pivaldehyde	5b	58	..
3	2-methyl-cyclohexanone	6	59	..
7	benzaldehyde	8a	65	47:53
7	pivaldehyde	8b	81	47:53
7	acrolein	8c	58	46:54
7	2-methyl-cyclohexanone	8d	46	..[a]

a. It was not possible to determine the diastereomeric ratio in this material.

Stereochemisry at Silicon of the Elimination of β-Hydroxysilanes.

The Peterson reaction, which in its original form utilized trimethylsilylmethylmagnesium chloride to convert aldehydes and ketones to their methylene derivatives in a Wittig-type transformation,[13] has been expanded to include the reactions of a wide variety of α-silyl carbanionic species with aldehydes and ketones.[14] The stereochemistry of the elimination of the resulting β-hydroxysilanes, intermediates in the above trans-

formations, have only been studied in terms of the stereochemistry of the olefin. The most authoritative of these studies is that of Hudrlik and Peterson[15], who showed that a single diastereomeric β-hydroxysilane could be converted to either the (Z) or (E) olefin depending on the reaction conditions chosen for the elimination. The effect of reaction conditions on this reaction have also been studied.[16] The results from these and other studies indicate that the acid catalyzed elimination occurs in an anti fashion and that the based catalyzed elimination occurs in a syn manner. This would predict that the acid catalyzed process would occur with inversion of configuration at silicon and the base catalyzed reaction with retention of configuration at silicon. The results of the elimination of β-hydroxysilanes **8b** and **8c** under acid and base conditions are shown in Table II. As can be seen the acid catalyzed elimination does occur with inversion of stereochemistry at silicon and the base (KH) catalyzed reaction occurs with retention of stereochemistry at silicon. These results are in complete agreement with the above assumptions.



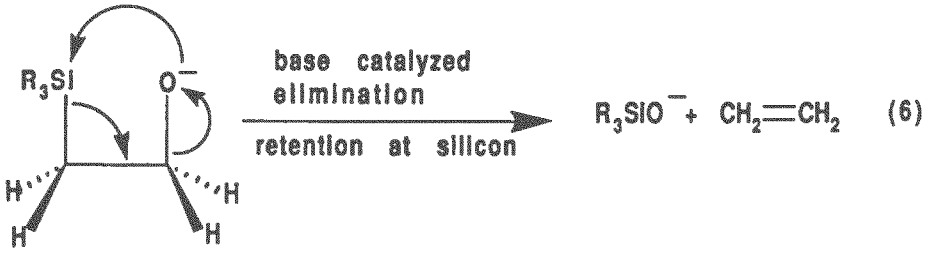


TABLE II. STEREOCHEMISTRY OF THE ELIMINATION OF β-HYDROXYSILANES

β-Hydroxy-silane	Reaction Conditions	Product	$[\alpha]_D$	Stereo-chemistry	(%)
8b	BF_3Et_2O/CH_2Cl_2	(R) R_3Si^*F	-40.9°	Inversion	(87)
8c	HOAc/NaOAc	(R) R_3Si^*OAc	-16°	Inversion	(89)
8c	H_2SO_4/THF/H_2O	(R) R_3Si^*OH	-15°	Inversion	(91)
8c	KH/THF then H_2O	(S) R_3Si^*OH	+19°	Retention	(95)

Experimental Section

General Considerations

All reactions were carried out in a standard apparatus consisting of a two- or three-necked flask equipped with a magnetic stirring bar, condenser and no-air stopper. The apparatus was dried in an oven at 120°C for a minimum of four hours and cooled under an atmosphere of nitrogen or flame-dried under a flow of nitrogen and cooled under a nitrogen atmosphere. All reactions were conducted in a nitrogen atmosphere. ^{1}H NMR, ^{13}C NMR and ^{29}Si NMR spectra were recorded on a Jeol FX90Q spectrophotometer with internal tetramethylsilane as standard and deuterochloroform as a lock. (Chloromethyl)methyldiphenylsilane was prepared by the reaction of phenylmagnesium bromide on (chloromethyl)dimethylchlorosilane and (S)-(1-naphthyl)phenylmethylsilane by the published procedure.[10] All solvents were dried by accepted means prior to use.

Preparation of (+)-1-Naphthylphenylmethyl(chloromethyl)silane.

A standard apparatus was charged with 2 g (6 mmol) of (+)-(1-naphthyl)phenylmethyl(dichloromethyl)-silane, 0.3 g of azoisobutyl nitrile, and 10 mL of dry hexane. To this was added 3.2 mL (12 mmol) of tri-n-butyltin hydride. The reaction mixture was stirred for 24 h, the solvent removed, and the tri-n-butyltin chloride distilled at reduced pressure. The residue was chromatographed on silica gel (hexane) to give 0.26 g (60%) of the title compound: mp 57-57.5°C; $[\alpha]D^{25}$ +6.98° (c 2.17, hexane); ^{1}H NMR δ 7.85-6.97 (m, 12H), 3.25 (s, 2H), 0.80 (s, 3H); ^{13}C NMR δ 136.9, 135.3, 135.0, 134.5, 133.5, 131.8, 130.9, 129.9, 128.1, 125.9, 125.5, 125.1, 29.7, -4 0.

Preparation of (Chloromethyl)methyldiphenylsilane.

A standard apparatus was charged with 5.10 g (210 mmol) of magnesium turnings, 300 mL of dry ether. To this was added 31.4 g (200 mmol) of bromobenzene in 100 mL of dry ether at rate so as to maintain a gentle reflux. The Grignard was allowed to form overnight, after which time was added 16.35 g (100 mmol) of (chloromethyl)methyldichlorosilane followed by refluxing for 24 h. The mixture was hydrolyzed with 10% ammonium chloride (300 mL). The two layers were separated and the aqueous layer extracted with ether (2 x 200 mL). The combined organic layer was dried over anhydrous sodium sulfate. The solvents were removed at reduced pressure. The residue was distilled at reduced pressure to give 14.31 g (58%) of the title compound: bp 96-98°C/0.2 mm ; nD^{20} 1.5810; ^{1}H NMR δ 7.60-7.26 (m, 10H), 3.20 (s, 2H), 0.68 (s, 3H); ^{13}C NMR δ 134.5, 134.0, 129.8, 127.9, 28.7, -5.66; ^{29}Si NMR δ -8.9.

Preparation of Methyldiphenyl(tri-n-butylstannylmethyl)silane.

A standard apparatus was charged with 0.27 g (11 mmol) of magnesium turnings in 10 mL of THF. To this was added 2.47 g (10 mmol) of (chloromethyl)methyldiphenylsilane. The mixture was heated just below the reflux temperature for 12 h. To the solution 3.25 g (10 mmol) of tri-n-butyltin chloride in 3 mL of THF was added dropwise followed by refluxing for 24 h. The cooled reaction mixture was dilute with more THF and hydrolyzed with 10% aqueous ammonium chloride. The aqueous layer was separated and extracted with hexane, the combined ethereal fractions were washed with water, dried over magnesium sulfate. After solvent removal at reduced pressure, the residue was distilled to gave 4.01 g (80%) of the title compound: bp 168-170°C/ 0.05 mm; ^{1}H NMR δ 7.57-7.22 (m,10H), 1.42-0.59 (m, 27H), 0.55 (s, 3H), 0.25 (s, 2H); ^{13}C NMR δ 139.79, 134.15,

128.79, 127.71, 29.11, 27.38, 13.62, 10.53, -1.33, -9.78; ^{29}Si NMR δ -5.9; Anal. Calcd. for $C_{26}H_{42}SiSn$: C, 62.28; H, 8.44. Found: C, 62.36; H, 8.46.

Preparation of 1-Phenyl-2-(Methyldiphenylsilyl)ethanol: Representative procedure.

Following the procedure of Seitz and Zapata[35] with some modifications, the standard apparatus was charged with a solution of 3.0 g (6.0 mmol) of methyldiphenyl(tri-n-butylstannylmethyl)silane in 8 mL of dry THF. The reaction mixture was cooled to 0°C and 4.0 mL (6.0 mmol) of n-butyllithium in hexane was added dropwise. After 30 min the reaction was cooled to -78°C and a solution of 0.61 g (6.0 mmol) of benzaldehyde in 2 mL of dry THF was added dropwise. The reaction was stirred at -78°C for 2 h, water was added and the mixture was extracted with diethyl ether (3 x 75 mL). The combined organic extracts were washed with water and dried over anhydrous sodium sulfate. The solvents were removed at reduced pressure. Filtration of the crude product over silica gel chromatography with hexane gave 2.08 g (100%) of tetra-n-butyltin. Elution with a mixture of ethyl acetate/hexane (1:1 v:v) gave 1.17 g (61%) of the title compound; ^{1}H NMR δ 7.42-7.08 (m, 15H), 4.65 (dd, 1H, J=7.1, 7.6 Hz), 2.45 (s, 1H), 1.64 (dd, 2H, J=7.6, 7.1 Hz), 0.34 (s, 3H); ^{13}C NMR δ 146.02, 136.81, 136.65, 134.26, 134.10, 128.79, 127.98, 127.49, 127.0, 125.54, 71.64, 25.81, -4.04; ^{29}Si NMR δ -9.2; Anal. Calcd. for $C_{21}H_{22}SiO$: C, 79.20; H, 6.96. Found: C, 79.17; H, 7.01.

Preparation of 1-(Methyldiphenylsilyl)-3,3-dimethyl-2-butanol.

Following general procedure above, 3.0 g (6.0 mmol) of methyldiphenyl(tri-n-butyl-stannylmethyl)silane was reacted with 4.05 mL (6.0 mmol) of n-butyllithium. The anion was quenched by the addition of 0.52 g (6 mmol) of pivalaldehyde, afforded 1.05 g (58%) of the title compound. n_D^{20} 1.550; ^{1}H NMR δ 7.62-7.24 (m, 10H), 3.54 (d, 1H, J=3.9 Hz), 3.43 (d, 1H, J=4.2), 1.34-1.22 (m, 3H), 0.87 (s, 9H), 0.66 (s, 3H); ^{13}C NMR δ 137.87, 137.22, 134.55, 129.09, 127.85, 77.00, 35.97, 25.50, 17.30, -3.31; ^{29}Si NMR δ -7.1; Anal. Calcd. for $C_{19}H_{26}SiO$: C, 76.45; H, 8.78. Found: C, 76.56; H, 8.83.

Preparation of (Z)-1-(Methyldiphenylsilylmethyl)-2-methylcyclohexanol.

Following general procedure above, 3.0 g (6.0 mmol) of methyldiphenyl(tri-n-butyl-stannylmethyl)silane was reacted with 4.05 mL (6.0 mmol) of n-butyllithium. The anion was quenched by the addition of 0.67 g (6.0 mmol) of 2-methylcyclohexanone, afforded 1.15 g (59%) of the title compound; ^{1}H NMR δ 7.62-7.25 (m, 10H), 1.86-1.17 (m, 12H), 0.86 (d, 3H, J=5.6), 0.70 (s, 3H); ^{13}C NMR δ 138.19, 138.00, 134.36, 128.96, 127.72, 73.88, 41.23, 40.23, 30.83, 28.29, 25.50, 22.11, 15.22, -2.14; ^{29}Si NMR δ - 10.9; Anal. Calcd. for $C_{21}H_{28}SiO$: C,77.72; H, 8.70. Found: C, 77.66; H, 8.75.

Preparation of 1-Phenylethanol from 1-Phenyl-2-(Methyldiphenyl-silyl)ethanol: Representative procedure.

Following the procedure of Hudrlik and coworkers,[12] a 50-mL standard apparatus was charged with a 5% solution of potassium tert-butoxide in 19:1 (DMSO/H_2O) and 0.43 g (1.35 mmol) of 1-phenyl-2-(methyldiphenyl-silyl)ethanol. The reaction mixture was stirred at room temperature for 12 h, water was added and the mixture was extracted with diethyl ether (3 x 50 mL). The combined organic extracts were washed with water and dried over anhydrous sodium sulfate. The solvents were removed at reduced pressure. Filtration of the crude over silica gel chromatography with hexane gave 0.12 g (72%) of the title compound; ^{1}H NMR δ 7.24 (s, 5H, aromatic hydrogens), 4.71 (q, 1H, J=3.7 Hz), 3.21 (d, 1H, J=3.7 Hz), 1.36 (d, 3H, J=6.4 Hz); ^{13}C NMR δ 145.58,

127.82, 126.62, 125.05, 69.36, 24.67.

Preparation of 3,3-Dimethyl-2-butanol from 1-(Methyl-diphenylsilyl)-3,3-dimethyl-2-butanol.

Following the procedure above, a 5% solution of potassium tert-butoxide in 19:1 (DMSO/H2O) and 0.41 g (1.37 mmol) of 1-(methyldiphenylsilyl)-3,3-dimethyl-2-butanol was stirred at room temperature for 48 h. Purification of the crude material gave 0.10 g (74%) of the title compound. IR (neat) 3400, and 1100 cm-1; ^{1}H NMR δ 3.36 (q,1H, J=6.4 Hz), 2.79 (bs, 1H), 1.02 (d, 3H, J=6.3 Hz), 0.80 (s, 9H); ^{13}C NMR δ 75.00, 34.58, 25.26, 17.52; MS 102(3), 69(39), 57(100), 56(79).

Preparation of Trans-1,2-Dimethylcyclohexanol from (Z)-1-(Methyl-diphenylsilylmethyl)-2-Methylcyclohexanol.

Following the procedure above, a 5% solution of potassium tert-butoxide in 19:1 (DMSO/H2O) and 0.65 g (2 mmol) of (Z)-1-(methyldiphenylsilylmethyl)-2-methylcyclohexanol was stirred at room temperature for 48 h. Purification of the crude material gave 0.18 g (68%) of the title compound. IR (neat) 3450, 1170; ^{1}H NMR δ 1.65-1.20 (m, 10H), 1.06 (s, 3H), 0.89 (d, 3H, J=5.4 Hz); ^{13}C NMR δ 70.82, 40.16, 39.78, 30.46, 28.46, 25.75, 21.90 14.97.

Preparation of (-)-1-Naphthylphenylmethyl(tri-n-butylstannylmethyl)-silane.

A standard apparatus was charged with 2.2 g (89 mmol) of magnesium turnings in 80 mL of THF. To this was added 26.25 g (89 mmol) of (+)-(1-naphthyl)phenylmethyl(chloromethyl)silane. The mixture was heated at just below the reflux temperature for 12 h. To the solution was added 29 g (89 mmol) of tri-n-butyltin chloride in 15mL of THF dropwise followed by refluxing for 48 h. The cooled reaction mixture was hydrolyzed with 10% ammonium chloride (30 mL). The aqueous layer was separated and extracted with hexane, the combined organic layers were washed with water and dried over $MgSO_4$. After solvent removal at reduced pressure, the by-product, 1-naphthylphenyldimethylsilane, was distilled at 168°C/0.02 mm. The residue was filtered using a short column of silica gel eluting with hexane to gave 37.27 g (75%) of the title compound, $[\alpha]_D^{25}$ -24.9° (c, 4.14, cyclohexane), $[\alpha]_D^{25}$ -23.3° (c 2.27, cyclo-hexane); ^{1}H NMR δ 7.81-7.23 (m, 12H), 1.26-0.48 (m, 29H), 0.68 (s, 3H); ^{13}C NMR δ 140.66, 137.02, 134.53, 134.05, 133.56, 130.04, 128.79, 127.76, 125.43, 125.22, 125.0, 29.0, 27.32, 13.62, 10.31, 0.35, -8.75; ^{29}Si NMR δ -5.5; Anal. Calcd. for $C_{30}H_{44}SiSn$: C, 65.34; H, 8.04. Found: C, 65.44; H, 8.08.

Preparation of 1-Phenyl-2-(1-Naphthylphenylmethylsilyl)ethanol.

Following the general procedure above, 3.31 g (6.0 mmol) of (-)-1-naphthylphenylmethyl(tri-n-butyl-stannylmethyl)-silane was reacted with 4.05 mL (6.0 mmol) of n-butyllithium. The resulting anion was quenched by the addition of 0.61 g (6.0 mmol) of benzaldehyde, provided 1.44 g (65%) of the title compound as a 47/53 mixture of diastereomers which resisted separation. The diastereomeric ratio was determined observing the Si-CH_3 signals in the ^{1}H NMR. The major impurities, (1-naphthyl)phenyldimethylsilane and tetrabutyltin, were removed by flash chromatography eluting with hexane; ^{1}H NMR δ 7.65-7.11 (m, 17H, aromatic hydrogens), 4.74 (dd of one diastereomer, 1H, J=3.9, 4.2 Hz), 4.65 (dd of the other diastereomer, 1H, J=4.2, 4.2 Hz), 2.02-1.88 (m for both diastereomers, 3H), 0.61 (s of one diastereomer, 3H), 0.47 (s of other diastereomer, 3H); ^{13}C NMR δ 146.13, 137.84, 137.68, 136.92, 135.18, 134.97, 134.32, 133.40, 130.36, 130.25, 129.06, 128.95, 128.19, 127.87, 127.44, 127.27, 125.70, 125.49, 125.00, 72.23, 26.83, -1.93; ^{29}Si

NMR δ -8.5, -8.7 (for both diastereomers); Anal. Calcd. for $C_{25}H_{24}SiO$: C, 81.48; H, 6.54. Found: C, 81.33; H, 6.62.

Preparation of 1-(1-Naphthylphenylmethylsilyl)-3,3-dimethyl-2-butanol.

Following the general procedure above, 3.31 g (6.0 mmol) of (-)-1-naphthylphenylmethyl(tri-n-butylstannyl-methyl)silane was reacted with 4.05 mL (6.0 mmol) of n-butyllithium. The resulting anion was quenched by the addition of 0.65 g (6.0 mmol) of pivalaldehyde, provided 1.69 g (81%) of the title compound as a 47/53 mixture of diastereomers, which resisted separation. It was impossible to determine the diastereomeric ratio using the Si-CH_3 signal in ^1H NMR because they showed the same chemical shift. The ^{29}Si NMR spectrum showed 2 peaks corresponding to the mixture of diastereomers, the relative intensities of these signals were used to determine the ratio of diastereomers. The major impurities, (1-naphthyl)phenyldimethylsilane and tetra-n-butyltin, were removed by flash chromatography eluting with hexane; ^1H NMR δ 7.84-7.26 (m, 12H, aromatic hydrogens), 3.49 (dd of one diastereomer, 1H, J=3.7, 3.7 Hz), 3.38 (dd of the other diastereomer, 1H, J=3.7, 3.4 Hz), 1.53-1.41 (m for both diastereomers, 2H), 1.25 (bs for both diastereomers, 1H), 0.61 (s for both diastereomers, 3H), 0.80 (s, 9H); ^{13}C NMR δ 138.70, 137.78, 137.03, 136.86, 135.29, 135.08, 134.75, 134.59, 134.32, 133.40, 130.25, 129.01, 128.47, 127.92, 125.59, 125,32, 125.11, 77.23, 35.94, 25.37, 17.90, -1.44 and-1.82 (for both diastereomers); ^{29}Si NMR δ -6.2 and -6.4 (for both diastereomers); Anal. Calcd. for $C_{23}H_{28}SiO$: C, 79.26; H, 8.10. Found: C, 79.00; H, 8.17.

Preparation of (Z)-1-(1-Naphthylphenylmethylsilyl)-2-methyl-cyclohexanol.

Following the general procedure above, 3.31 g (6.0 mmol) of (-)-1-naphthylphenylmethyl(tri-n-butylstannylmethyl)silane was reacted with 4.05 mL (6.0 mmol) of n-butyllithium. The resulting anion was quenched by the addition of 0.67 g (6.0 mmol) of 2-methyl-cyclohexanone, provided 1.04 g (46%) of the title compound as a mixture of diastereomers which resisted separation. It was not possible to determine the diastereomeric ratio using the Si-CH_3 signal in ^1H or ^{29}Si NMR spectrum because they showed the same chemical shift. The major impurities, 1-naphthylphenyldimethylsilane and tetra-n-butyltin, were removed by flash chromatography eluting with hexane or distillation; ^1H NMR δ 7.96-7.23 (m, 12H), 2.12-1.29 (m, 12H), 0.87-0.77 (m, 6H); ^{13}C NMR δ 138.87, 136.75, 135.62, 135.29, 134.97, 134.86, 134.26, 133.45, 130.15, 128.90, 128.63, 127.82, 125.38, 125.16, 125.00, 74.02, 41.30, 39.89, 30.79, 28.51, 28.30, 25.37, 22.07, 15.24, 0.02; ^{29}Si NMR δ -10.4; Anal. Calcd. for $C_{25}H_{30}SiO$: C, 80.16; H, 8.07. Found: C, 80.03; H, 8.15

Preparation of 1-(1-Naphthylphenylmethylsilyl)-3-buten-2-ol.

Following the general procedure above, 3.31 g (6.0 mmol) of (-)-(1-naphthyl)phenylmethyl-(tri-n-butylstannyl-methyl)silane were reacted with 4.05 mL (6.0 mmol) of n-butyllithium. The anion was quenched by the addition of 0.40 g (6.0 mmol) of acrolein, providing 1.11 g (58%) of the title compound as a 46/54 mixture of diastereomers which resisted separation. It proved impossible to determine the diastereomeric ratio using the Si-CH_3 signal in ^1H NMR because they showed the same chemical shift. The ^{29}Si NMR spectrum showed 2 peaks corresponding to the mixture of diastereo-mers, the relative intensities of these signals were used to determine the ratio of diastereomers. The major impurities, 1-naphthylphenyldimethylsilane and tetra-n butyltin, were removed by flash chromatography eluting with hexane; ^1H NMR δ 7.89-7.12 (m, 12H), 6.00-5.58 (m, 1H), 4.93-4.77 (m, 2H), 4.32-4.07 (m, 1H), 1.75-1.65 (m, 3H), 0.76 (s, 3H); ^{13}C NMR δ 142.88, 137.78, 137.57, 136.81, 134.91, 134.42, 134.26, 133.29, 130.22, 128.95, 128.84, 128.30, 127.76, 125.54, 125.22,

124.94, 113.24, 113.08, 70.61, 24.29, -1.50, -1.60; ^{29}Si NMR δ -8.4, -8.5.

Reaction of 1-(1-Naphthylphenylmethylsilyl)-3,3-dimethyl-2-butanol with Boron Fluoride Etherate.

Following the procedure of Hudrlik and Peterson[15] a 50-mL standard apparatus was charged with 0.87 g (2.5 mmol) of 1-(1-naphthylphenylmethylsilyl)-3,3-dimethyl-2-butanol in 10 mL of dichloromethane. The reaction mixture was cooled to 0°C and 0.18 mL (1.5 mmol) of boron trifluoride etherate was added dropwise. The solution was stirred at room temperature for 1 h. The mixture was added to a saturated sodium bicarbonate solution overlaid with pentane; the organic layer was washed with two additional portions of the saturated sodium bicarbonate solution and was dried over anhydrous magnesium sulfate. The solvents were removed at reduced pressure. Filtration of the crude product through silica gel with hexane and then crystallization from hexane gave 0.47 g (70%) of (R)-(-)-1-naphthylphenylmethylfluorosilane: mp 61-64°C, $[\alpha]_D^{25}$ -40.9° (c 9.12, ether), [lit.[17] mp 67.5-68°C $[\alpha]_D^{25}$ -46.9° (c 9.12, ether)]; ^{1}H NMR δ 8.07-7.28 (m, 12H), 0.84 (d, 3H, J=7.3 Hz); ^{13}C NMR δ 136.65, 135.29, 134.80, 134.64, 133.94, 133.45, 133.34, 132.69, 132.00, 131.34, 130.58, 128.95, 128.07, 127.87, 126.35, 125.76, 125.00, -0.95, -1.66; ^{29}Si NMR δ 15.8.

Reaction of 1-(1-Naphthylphenylmethylsilyl)-3-buten-2-ol with Acetic Acid/Sodium Acetate.

Following the procedure of Hudrlik and Peterson[15] a 50-mL standard apparatus was charged with 15 mL of acetic acid saturated with sodium acetate and 0.23 g (0.7 mmol) of 1-(1-naphthylphenylmethylsilyl)-3-buten-2-ol. The reaction mixture was stirred at 80°C for 3 days, cooled to room temperature, and poured into a saturated sodium bicarbonate solution overlaid with pentane. The layers were separated, and pentane layer was washed with saturated sodium bicarbonate solution and was dried over anhydrous magnesium sulfate. The solvents were removed at reduced pressure. Filtration of the crude product over silica gel with hexane gave 0.136 g (65%) of (R)-(-)-1-naphthylphenylmethylacetoxysilane: $[\alpha]_D^{25}$ -16° (c 8.6, pentane), [lit.[18] $[\alpha]_D^{25}$ +18° (c 8.6, pentane) for the S isomer)]; ^{1}H NMR δ 7.80-7.20 (m, 12H), 2.00 (s, 3H), 0.80 (s, 3H); ^{13}C NMR δ 171.20, 136.60, 135.40, 134.70, 134.60, 134.94, 133.45, 133.34, 132.69, 132.00, 131.34, 130.58, 128.95, 128.07, 127.87, 126.35, 125.77, 125.20, 51.20, 2.00.

Reaction of 1-(1-Naphthylphenylmethylsilyl)-3-buten-2-ol with Sulfuric Acid.

Following the procedure of Hudrlik and Peterson[15] a 50-mL standard apparatus was charged with two drops of concentrated sulfuric acid in 10 mL of THF and 0.49 g (1.54 mmol) of 1-(1-naphthylphenylmethylsilyl)-3-buten-2-ol. The reaction mixture was reflux for 2 days, cooled to room temperature, and poured into a saturated sodium bicarbonate solution overlaid with ether. The layers were separated, and ether layer was washed with the saturated sodium bicarbonate solution and was dried over anhydrous magnesium sulfate. The solvents were removed at reduced pressure. Filtration of the crude product over silica gel with hexane/ethyl acetate (1:1, v:v) gave 0.25 g (60%) of (R)-(+)-1-naphthylphenylmethylsilanol: $[\alpha]_D^{25}$ -15° (c 5.46, ether), [lit.[17] $[\alpha]_D^{25}$ -16.5° (c 5.46, ether) for the R isomer)]; ^{1}H NMR δ 7.70-7.20 (m, 12H), 3.00 (bs, 1H), 0.82 (s, 3H); ^{13}C NMR δ 138.70, 137.78, 137.03, 136.86, 135.29, 135.08, 134.75, 134.59, 134.32, 133.40, 130.25, 129.01, 128.47, 127.92, 125.59, 125,32, 125.11, -2.10.

Reaction of 1-(1-Naphthylphenylmethylsilyl)-3-buten-2-ol with Potassium Hydride.

Following the procedure of Hudrlik and Peterson[15] a 50-mL standard apparatus was charged with

potassium hydride (0.10 g of a 50% slurry in oil, ca.1.25 mmol) and 4 mL of pentane, the solution was stirred and the liquid was removed. To the residue were added 5 mL of THF and 0.30 g (1.00 mmol) of 1-(1-naphthyl-phenylmethylsilyl)-3-buten-2-ol. The reaction mixture was reflux for 2 days, cooled to room temperature, and poured into 10% sodium bicarbonate solution overlaid with ether. The layers were separated, and ether layer was washed with saturated sodium bicarbonate solution and was dried over anhydrous magnesium sulfate. The solvents were removed at reduced pressure. Filtration of the crude product over silica gel with hexane/ethyl acetate (1:1, v:v) gave 0.15 g (58%) of (S)-(+)-(1-naphthyl)phenylmethyl-silanol: $[\alpha]_D^{25}$ +19° (c 6.66, ether), [lit.[17] $[\alpha]_D^{25}$ +20.0° (c 6.66, ether) for the S enantiomer)].

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