Preparation of Silafunctional Allylsilanes by Palladium-Catalyzed Silylation of Allylic Chlorides with 1,1-Dichloro-1-phenyl-2,2,2-trimethyldisilane[1]

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Unsymmetrically substituted disilane, 1,1-dichloro-1-phenyl-2,2,2-trimethyldisilane ($PhCl_2SiSiMe_3$), was found to be an effective reagent for palladium-catalyzed allylic silylation of allylic chlorides substituted at the α and/or γ positions. The silylation proceeded under mild conditions in the presence of a palladium catalyst coordinated with the 1,1′-bis(diphenylphosphino)ferrocene (dppf) ligand to give the corresponding allylphenyldichlorosilanes in high yields. The stereochemistry of the catalytic silylation demonstrated overall inversion which is consistent with the stereochemical results previously reported on stoichiometric reactions. Use of (*R*)-2-[(*S*)-1,1′-bis(diphenylphosphino)ferrocenyl]ethylamine ((*R*)-(*S*)-BPPFA) as a chiral ligand for the silylation gave optically active allylsilanes of up to 61% ee.

Introduction

Allylsilanes are useful reagents in organic synthesis, reacting with a wide variety of electrophiles in a regiospecific manner.[2,3] In particular, those containing functional groups on the silyl group have received increasing attention owing to their unique reactivity.[4] The silafunctionalized allylsilanes have been prepared mainly by silylation of allyl–metals[2] or hydrosilylation of 1,3-dienes.[2] Although the preparation by palladium-catalyzed allylic silylation of allylic chlorides with methylchlorodisilanes has been reported, it suffers the lack of general applicability because it requires a high reaction temperature (120–170 °C) and the allylic substrate is limited to those lacking substituents at the α or γ position.[5,6] We have previously found that unsymmetrically substituted disilanes, $PhCl_2SiSiMe_3$ and $Cl_3SiSiMe_3$, are highly reactive toward the silylation of π-allylpalladium complexes to give silafunctional allylsilanes stereospecifically in high yields,[7,8] and it prompted us to study the catalytic silylation by use of the reactive unsymmetrically substituted disilanes. Here we report that the palladium-catalyzed silylation of α- and γ-substituted allylic chlorides with $PhCl_2SiSiMe_3$ proceeds under mild conditions to give corresponding silafunctional allylsilanes in high yields.

Results and Discussion

Disilanes including 1,1-dichloro-1-phenyl-2,2,2-trimethyldisilane ($PhCl_2SiSiMe_3$) were examined for their reactivity in the palladium-catalyzed allylic silylation of allylic chlorides **1** (Scheme I). The reaction conditions and results are summarized in Table I. The reaction of 3-chlorocyclohexene (**1a**) with $PhCl_2SiSiMe_3$ in THF in the presence of 1 mol % of a palladium catalyst generated in situ from bis(μ-chloro)bis(η^3-allyl)dipalladium(II) and triphenylphosphine proceeded at 40 °C to substitute the chloride in **1a** with the phenyldichlorosilyl group, producing 3-(phenyldichlorosilyl)cyclohexene (**2**). The allylsilane was isolated as phenyldiethoxysilyl derivative **3** in 70% yield by treatment of the reaction mixture with ethanol and triethylamine (entry 1). The introduction of a phenyldichlorosilyl group rather than a trimethylsilyl group on the allylic substrate is as expected from our previous results on the stoichiometric reaction of $PhCl_2SiSiMe_3$ with (π-allyl)palladium complexes.[7] Ferrocenylbis(phosphine), 1,1′-bis(diphenylphosphino)ferrocene (dppf),[9] is a more efficient ligand than triphenylphosphine for the silylation which led to a higher yield (84%) of **3** in a shorter reaction time (entry 2). The allylic silylation of linear allylic chlorides, (*E*)-1-chloro-2-butene (**1b**) and (*E*)-2-chloro-3-pentene (**1c**), was also successful with $PhCl_2SiSiMe_3$ (entries 6 and 9). Thus, the reaction of **1b** gave a 92% yield of a regioisomeric mixture of allylsilanes which consisted of 3-silyl-1-butene (**4**) and (*E*)-1-silyl-2-butene (**5**) in a ratio of 18 to 82, and the reaction of **1c** proceeded quantitatively to give 2-silyl-3-pentene (**6**) as a 90:10 mixture of *E* and *Z* isomers.

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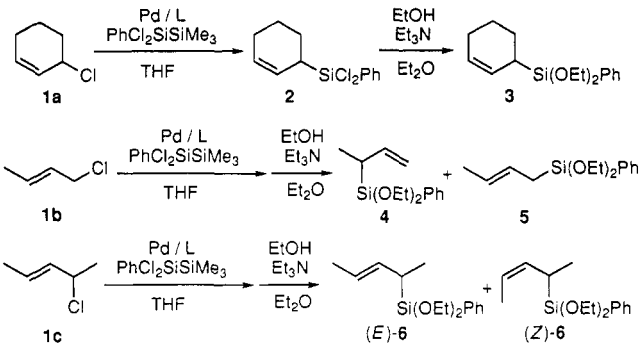
Scheme I



Fluorine-substituted unsymmetric disilane, 1,1-difluoro-1-phenyl-2,2,2-trimethyldisilane ($PhF_2SiSiMe_3$), exhibited comparable reactivity to $PhCl_2SiSiMe_3$, the silylation of chloride **1b** giving a high yield of (phenyldifluorosilyl)-butenes (entry 7). On the other hand, symmetrically substituted disilanes were less reactive than unsymmetrically substituted ones. The silylation of **1a** did not take place at all with hexamethyldisilane or 1,1,2,2-tetrachloro-1,2-dimethyldisilane under similar reaction conditions (entries 4 and 5). Of the symmetric disilanes, 1,1,2,2-tetrachloro-1,2-diphenyldisilane was most reactive, which gave a 68% yield of 1-silyl-2-butene **5** in the reaction of monosubstituted chloride **1b** (entry 8), though only a low yield (17%) of allylic silane **3** was formed in the reaction of α,γ-disubstituted chloride **1a** (entry 3).

The palladium-catalyzed silylation was found to proceed with inversion of configuration with respect to the chiral carbon center where the silylation took place (Scheme II). Thus, the reaction of *cis*-3-chloro-5-carbomethoxy-1-cyclohexene (**1d**)[10] (*cis*:*trans* = 88:12) with $PhCl_2SiSiMe_3$ in the presence of Pd–dppf catalyst at 60 °C gave *trans*-3-(phenyldichlorosilyl)-5-carbomethoxy-1-cyclohexene (**7**) (*cis*:*trans* = 15:85) in quantitative yield. The *trans* stereochemistry was assigned by the ^1H NMR spectra of alcohol **9**[11] which was obtained by oxidative cleavage of the carbon–silicon bond in **8** with hydrogen peroxide according to the procedures reported by Tamao.[12] The oxidation has been established to proceed with retention of configuration.[12d] Similarly, starting with *trans*-**1d**[10] (*cis*:*trans* = 21:79), *cis*-**7** (*cis*:*trans* = 59:41) was obtained preferentially. The silylation with Pd–PPh_3 catalyst gave essentially the same stereochemical results as that with Pd–dppf, where *cis*-**1d** (*cis*:*trans* = 88:12) led to *trans*-**7** (*cis*:*trans* = 15:85) and *trans*-**1d** (*cis*:*trans* = 21:79) led to *cis*-**7** (*cis*:*trans* = 65:35).

This catalytic silylation must proceed via the (π-allyl)-palladium intermediate which is formed by the oxidative addition of allylic chlorides to a palladium(0) species. The stereochemistry upon oxidative addition to palladium(0) complexes coordinated with phosphine ligands has been reported to be inversion with allylic halides[13] as well as allylic esters.[14] It is deduced from the overall inversion of configuration observed here in the catalytic silylation that the stereochemistry upon silylation of (π-allyl)-palladium is retenion, indicating that the silyl group attacks the palladium atom of the (π-allyl)palladium intermediate to form the palladium–silyl bond and reductive elimination gives the allylsilane. The retention of configuration upon silylation has been also observed in the stoichiometric reaction of (π-allyl)palladium complexes with disilanes including $PhCl_2SiSiMe_3$ in the presence of a phosphine ligand.[7] The palladium-catalyzed silylation of allylic acetates with tris(trimethylsilyl)aluminum has been reported to proceed with the same stereochemistry.[6b]

The allylic silylation was applied to catalytic asymmetric synthesis of optically active functionalized allylsilanes by incorporation of chiral phosphine ligands on the palladium catalyst (Scheme III). The results are summarized in Table II. Of the chiral phosphine ligands examined, chiral ferrocenylbis(phosphine), (*R*)-2-[(*S*)-1,1′-bis(diphenylphosphino)ferrocenyl]ethylamine ((*R*)-(*S*)-BPPFA),[15] which is a chiral version of the dppf ligand and is one of the most enantioselective ligands especially in catalytic asymmetric reactions via a (π-allyl)palladium intermediate,[16] brought about the highest catalytic activity in the reaction of allylic chloride **1a** with $PhCl_2SiSiMe_3$. Optically active allylsilane (*R*)-**3** was formed in 93% yield in the reaction at 40 °C for 0.5 h, though the enantiomeric purity of (*R*)-1-cyclohexen-3-ol (**10**)[17] obtained by the oxidation was not high (10% ee) (entry 1). The catalytic silylation was much slower with the BINAP[18] ligand (entry 2), and no silylation products were formed with other chiral bis(phosphine) ligands such as chiraphos[19] or DIOP[20] (entries 3 and 4).

The highest enantioselectivity was observed in the asymmetric silylation of linear allylic chloride (*E*)-1-chloro-2-butene (**1b**). The reaction of **1b** with $PhCl_2SiSiMe_3$ in the presence of (*R*)-(*S*)-BPPFA–Pd catalyst at room temperature for 4 h gave a 99% yield of allylsilanes consisting of 3-(phenyldiethoxysilyl)-1-butene (**4**) and (*E*)-1-(phenyldiethoxysilyl)-2-butene (**5**) in a ratio of 21 to 79, the oxidation of the former giving (*S*)-1-buten-3-ol (**11**)[21] of 61% ee (entry 5). Optically active allylsilane was also obtained in the asymmetric silylation of (*E*)-2-chloro-3-pentene (**1c**), which gave (*E*)-2-(phenyldiethoxysilyl)-3-pentene (**6**) (25% ee) and its Z isomer **6** (39% ee) in a ratio of 75 to 25 (entry 6).

To summarize, we have established a convenient method for the preparation of silafunctional allylsilanes which was performed by the palladium-catalyzed allylic silylation with unsymmetrically substituted disilanes and the catalytic asymmetric allylic silylation was demonstrated by means of a chiral catalyst. The stereochemistry of the

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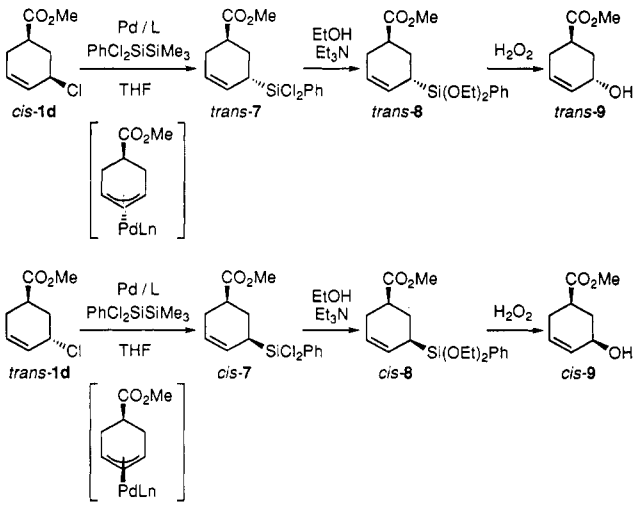
Table I. Silylation of Allylic Chlorides 1 with 1,1-Dichloro-1-phenyl-2,2,2-trimethyldisilane Catalyzed by Palladium–Phosphine Complexes[a]

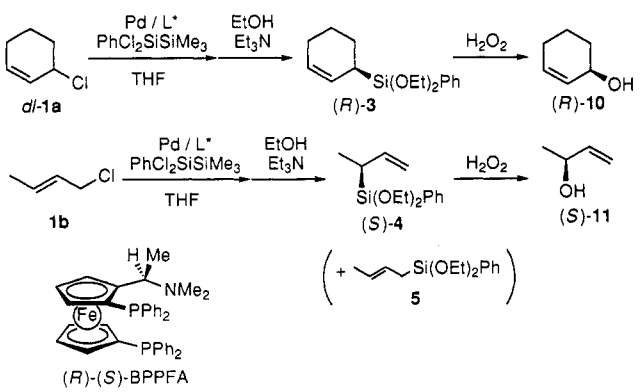
entry	1	disilane	ligand[b]	temp (°C)	time (h)	product	yield (%)[c]
1	**1a**	$PhCl_2SiSiMe_3$	PPh_3	40	20	**3**	70
2	**1a**	$PhCl_2SiSiMe_3$	dppf	40	4	**3**	84
3	**1a**	$PhCl_2SiSiCl_2Ph$	dppf	40	20	**3**	17
4	**1a**	$MeCl_2SiSiCl_2Me$	dppf	40	20		0
5	**1a**	$Me_3SiSiMe_3$	dppf	60	170		0
6	**1b**	$PhCl_2SiSiMe_3$	dppf	rt	23	**4, 5**	92 (18:82)[d,e]
7	**1b**	$PhF_2SiSiMe_3$	dppf	rt	55	*f*	92 (23:77)[e,g]
8	**1b**	$PhCl_2SiSiCl_2Ph$	dppf	rt	54	**4, 5**	68 (0:100)[d,e]
9	**1c**	$PhCl_2SiSiMe_3$	dppf	60	15	**6**	99 (90:10)[e,h]
10	*cis*-**1d**[i]	$PhCl_2SiSiMe_3$	dppf	60	22	**7**	99 (15:85)[j]
11	*cis*-**1d**[i]	$PhCl_2SiSiMe_3$	PPh_3	60	69	**7**	20 (15:85)[j]
12	*trans*-**1d**[k]	$PhCl_2SiSiMe_3$	dppf	60	16	**7**	99 (59:41)[j]
13	*trans*-**1d**[k]	$PhCl_2SiSiMe_3$	PPh_3	60	16	**7**	90 (65:35)[j]

[a] All reactions were carried out in THF under nitrogen. 1:disilane:catalyst = 1:1.4–1.6:0.01. [b] P:Pd = 2.2:1. [c] Isolated yield by bulb-to-bulb distillation. [d] The ratio of **4** to **5**. [e] Determined by GLC analysis. [f] Isolated as (phenyldimethylsilyl)butenes. [g] The ratio of 2-(phenyldimethylsilyl)-3-butene to (*E*)-1-(phenyldimethylsilyl)-2-butene. [h] The ratio of (*E*)-**6** to (*Z*)-**6**. [i] *cis*:*trans* = 88:12. [j] The ratio of *cis*-**7** to *trans*-**7**. [k] *cis*:*trans* = 21:79.

Scheme II



Scheme III



palladium-catalyzed silylation was also established to be overall inversion.

Experimental Section

General Considerations. Optical rotations were measured with a JASCO DIP-370 polarimeter. ^1H NMR spectra were measured with a JEOL JNM-EX-270 (270-MHz) or JNM-EX-90 (90-MHz) spectrometer with $CDCl_3$ as the solvent and $SiMe_4$ as the internal standard unless otherwise noted. Low-resolution mass spectra (LRMS) and high-resolution mass spectra (HRMS) were recorded with a JEOL JMS-DX-303. GLC analysis and preparative GLC were performed on a Shimadzu GC-8A or Shimadzu GC-4A gas chromatograph, equipped with a 1-m column packed with Silicone OV-1 (5% on Chromosorb WAW).

Table II. Asymmetric Silylation of Allylic Chlorides 1 with 1,1-Dichloro-1-phenyl-2,2,2-trimethyldisilane Catalyzed by Chiral Palladium–Phosphine Complexes[a]

entry	1	ligand[b]	temp (°C)	time (h)	product	yield (%)[c]	% ee (config)
1	**1a**	(*R*)-(*S*)-BPPFA	40	0.5	**3**	93	10 (*R*)[d]
2	**1a**	(*R*)-BINAP	60	44	**3**	80	7 (*R*)
3	**1a**	(*S*,*S*)-chiraphos	60	43		0	
4	**1a**	(+)-DIOP	60	24		0	
5	**1b**	(*R*)-(*S*)-BPPFA	20	4	**4, 5**	99 (21:79)[e,f]	61 (*S*)[g]
6	**1c**	(*R*)-(*S*)-BPPFA	60	9	**6**	60 (75:25)[f,h]	25,[i] 39[j]

[a] See footnote *a* in Table I. [b] P:Pd = 2.2:1. [c] Isolated yield by bulb-to-bulb distillation. [d] (*R*)-**3**: $[\alpha]_D^{20}$ +8.4 (*c* 1.5, benzene). [e] The ratio of **4** to **5**. [f] Determined by GLC analysis. [g] The enantiomeric purity of **4**. $[\alpha]_D^{20}$ –6.1 (*c* 0.8, benzene) for a 29:71 mixture of (*S*)-2-(phenyldimethylsilyl)-3-butene and (*E*)-1-(phenyldimethylsilyl)-2-butene (see Experimental Section). [h] The ratio of (*E*)-**6** to (*Z*)-**6**. [i] The enantiomeric purity of (*E*)-**6**. Absolute configuration was not determined. [j] The enantiomeric purity of (*Z*)-**6**. Absolute configuration was not determined.

Infrared spectra were obtained with a Hitachi 270-30 spectrometer. Preparative medium pressure liquid chromatography (MPLC) was performed with a silica gel prepacked column CIG Si-10 (Kusano). HPLC analysis was performed on a Shimadzu LC-9A liquid chromatograph system with chiral stationary phase columns, Sumitomo Chemical Co. Ltd., Sumichiral OA series. Benzene, ether, and THF were distilled from benzophenone ketyl under nitrogen before use. Ethanol was distilled from magnesium ethoxide under nitrogen. Triethylamine was dried over calcium hydride and distilled under nitrogen. Chlorotrimethylsilane was distilled from sodium metal and stored in the presence of sodium metal under argon.

Preparation of Disilanes. 1,1-Dichloro-1-phenyl-2,2,2-trimethyldisilane.[8] A mixture of 135 g (0.458 mol) of chlorotriphenylsilane and 12.7 g (1.83 mol) of lithium shot in 1000 mL of THF was stirred at room temperature for 15 h under nitrogen. The mixture turned a deep greenish color. The silyllithium solution obtained was added dropwise under nitrogen to a solution of 87 mL (0.687 mol) of chlorotrimethylsilane in 170 mL of THF. The mixture was stirred by a mechanical stirrer at room temperature for 20 h and hydrolyzed with 200 mL of water. The mixture was extracted with ether, and the organic layer was dried over magnesium sulfate. Removal of solvent followed by recrystallization from ethanol gave 117 g (77%) of 1,1,1-triphenyl-2,2,2-trimethyldisilane as white crystals. ^1H NMR: δ 0.13 (s, 9 H), 7.0–7.4 (m, 15 H).

Hydrogen chloride was bubbled through a solution of 50.1 g (0.151 mmol) of 1,1,1-triphenyl-2,2,2-trimethyldisilane in 150 mL of benzene. To the solution was added a catalytic amount (about 20 mg) of aluminum trichloride which was freshly sublimed before use. The mixture was warmed, then the reaction occurred, and benzene was spontaneously refluxed. The reaction mixture was stirred for 4 h under bubbling hydrogen chloride. The progress was checked by GLC. When the second dephenylation was

complete, the reaction was quenched by addition of 0.5 mL of acetone. The mixture was filtered through a glass micro fiber filter and concentrated by distillation. First distillation under reduced pressure (bp 73 °C/73 mmHg) gave 3.91 g (12%, 18.8 mmol) of 1,1,1-trichloro-2,2,2-trimethyldisilane. The residue was distilled under reduced pressure (bp 92 °C/1.8 mmHg) to give 28.2 g (75%) of 1,1-dichloro-1-phenyl-2,2,2-trimethyldisilane. ^{1}H NMR: δ 0.15 (s, 9 H), 7.4–7.55 (m, 3 H), 7.65–7.75 (m, 2 H). IR (neat): 2964, 1432, 1252, 1110, 843, 738, 694 cm^{-1}.

1,1-Difluoro-1-phenyl-2,2,2-trimethyldisilane.[22] To a solution of 899 mg (3.60 mmol) of 1,1-dichloro-1-phenyl-2,2,2-trimethyldisilane in 8.0 mL of ether was added at 0 °C 496 mg (3.60 mmol) of $CuF_2 \cdot 2H_2O$ under an argon atmosphere. The mixture was stirred at the same temperature for 11 h. Pentane was added, and copper salts were filtered off. Removal of solvent followed by bulb-to-bulb distillation (bath temperature 100–120 °C/105 mmHg) gave 708 mg (91%) of 1,1-difluoro-1-phenyl-2,2,2-trimethyldisilane. ^{1}H NMR (CCl_4/TMS): δ 0.14 (s, 9 H), 7.2–7.6 (m, 5 H). IR (neat): 3076, 2962, 1594, 1432, 1252, 1122, 878, 842, 815, 743, 704 cm^{-1}.

Palladium-Catalyzed Silylation of Allylic Halides with $PhCl_2SiSiMe_3$. All reactions were carried out under a nitrogen atmosphere. Reaction conditions and results are summarized in Table I. Typical procedures for the isolation of the silylation products as phenyldichlorosilanes (method A) and phenyldiethoxysilanes (method B) are shown below.

Method A. A mixture of 1.9 mg (0.005 mmol) of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ and 6.3 mg (0.011 mmol) of dppf or 2.9 mg (0.022 mmol) of triphenylphosphine in 2.0 mL of THF was stirred at room temperature for 10 min. To the catalyst solution was added successively at a given temperature 1 mmol of allylic halide 1 and 324 mg (1.3 mmol) of $PhCl_2SiSiMe_3$, and the mixture was stirred at the same temperature for a given period. The solvent was evaporated and the residue was distilled (bulb-to-bulb) to give allylic phenyldichlorosilanes. To a solution of the dichlorosilane obtained above in 10 mL of ether were added dropwise at 0 °C ethanol (3 equiv to dichlorosilyl product) and triethylamine (2.4 equiv), and then ammonium salts were precipitated. The mixture was stirred at room temperature for 2 h and filtered through a Celite pad. Removal of the solvent followed by bulb-to-bulb distillation gave allylic phenyldiethoxysilanes.

Method B. To the reaction mixture resulting from the silylation carried out in the same manner as method A were added successively at 0 °C 10 mL of ether, 0.23 mL (3.9 mmol) of ethanol, and 0.43 mL (3.1 mmol) of triethylamine. The mixture was stirred at room temperature for 2 h and filtered through a Celite pad. Removal of the solvent followed by bulb-to-bulb distillation gave allylic phenyldiethoxysilanes.

Silylation of 1a (Method A). 3-(Phenyldichlorosilyl)-cyclohexene (2): ^{1}H NMR δ 1.46–1.57 (m, 1 H), 1.61–1.81 (m, 2 H), 1.89–2.15 (m, 3 H), 2.25–2.33 (m, 1 H), 5.67–5.78 (m, 1 H), 5.82–5.90 (m, 1 H), 7.40–7.55 (m, 3 H), 7.70–7.80 (m, 2 H); ^{13}C NMR ($CDCl_3$/$CHCl_3$) δ 21.8, 22.7, 24.9, 30.4, 122.9, 126.5, 128.5, 129.8, 131.8, 134.2. Anal. Calcd for $C_{12}H_{14}Cl_2Si$: C, 56.03; H, 5.49. Found: C, 55.96; H, 5.49. 3-(Phenyldiethoxysilyl)cyclohexene (3): ^{1}H NMR δ 1.23 (t, J = 6.9 Hz, 3 H), 1.26 (t, J = 6.9 Hz, 3 H), 1.43–1.94 (m, 7 H), 3.84 (q, J = 6.9 Hz, 2 H), 3.85 (q, J = 6.9 Hz, 2 H), 5.60–5.70 (m, 1 H), 5.82 (d, J = 10.2 Hz, 1 H), 7.30–7.45 (m, 3 H), 7.60–7.70 (m, 2 H); ^{13}C NMR δ 18.3, 22.2, 22.8, 24.4, 24.9, 30.9, 58.7, 58.9, 126.3, 126.4, 127.6, 129.9, 133.0, 134.7; LRMS m/e 276 (M^+), 195, 167; HRMS calcd for $C_{16}H_{24}O_2Si$ 276.1546, found 276.1554. Anal. Calcd for $C_{16}H_{24}O_2Si$: C, 69.52; H, 8.75. Found: C, 69.31; H, 8.79.

Silylation of 1b (Method B). The products were obtained as a mixture of 3-(phenyldiethoxysilyl)-1-butene (4) and (*E*)-1-(phenyldiethoxysilyl)-2-butene (5). The ratio was determined by GLC analysis. Analytical data for the isomeric mixture are as follows. Anal. Calcd for $C_{14}H_{22}O_2Si$: C, 67.15; H, 8.86. Found: C, 67.06; H, 8.94. 4: ^{1}H NMR δ 1.11 (d, J = 7.3 Hz, 3 H), 1.23 (t, J = 6.9 Hz, 6 H), 2.03 (quint, J = 7.3 Hz, 1 H), 3.84 (q, J = 6.9 Hz, 4 H), 4.87 (d, J = 17.2 Hz, 1 H), 4.91 (d, J = 10.6 Hz, 1 H), 6.01 (ddd, J = 17.2, 10.6, and 7.3 Hz, 1 H), 7.25–7.45 (m, 3 H), 7.5–7.65 (m, 2 H). 5: ^{1}H NMR δ 1.23 (t, J = 6.9 Hz, 6 H), 1.58 (d, J = 7.9 Hz, 3 H), 1.60 (d, J = 4.9 Hz, 2 H), 3.83 (q, J = 6.9 Hz, 4 H), 5.25–5.5 (m, 2 H), 7.25–7.45 (m, 3 H), 7.5–7.65 (m, 2 H).

The ethoxysilanes 4 and 5 were converted into known[23] 3-(phenyldimethylsilyl)-1-butene and (*E*)-1-(phenyldimethylsilyl)-2-butene by the following procedure. To a solution of 1.15 g (4.59 mmol) of the 21:79 mixture of 4 and 5 in 15 mL of ether was added at room temperature 7.4 mL (14 mmol) of methyllithium in ether. The reaction mixture was stirred overnight and hydrolyzed with 10% hydrochloric acid. The mixture was extracted with ether and dried over $MgSO_4$. Removal of solvent followed by bulb-to-bulb distillation gave 865 mg (95%) of a 29:71 mixture of 3-(phenyldimethylsilyl)-1-butene and (*E*)-1-(phenyldimethylsilyl)-2-butene. 3-(Phenyldimethylsilyl)-1-butene: ^{1}H NMR δ 0.25 (s, 6 H), 1.05 (d, J = 7.3 Hz, 3 H), 1.84 (quint, J = 7.3 Hz, 1 H), 4.80 (d, J = 17.3 Hz, 1 H), 4.86 (d, J = 10.5 Hz, 1 H), 5.86 (ddd, J = 17.3, 10.5, and 7.3 Hz, 1 H), 7.28–7.39 (m, 3 H), 7.45–7.55 (m, 2 H). (*E*)-1-(Phenyldimethylsilyl)-2-butene: ^{1}H NMR δ 0.25 (s, 6 H), 1.62 (d, J = 5.9 Hz, 3 H), 1.64 (d, J = 6.6 Hz, 2 H), 5.19–5.30 (m, 2 H), 7.28–7.39 (m, 3 H), 7.45–7.55 (m, 2 H).

The products obtained by the silylation of **1b** with $PhF_2SiSiMe_3$ were isolated as 2-(phenyldimethylsilyl)-3-butene and (*E*)-1-(phenyldimethylsilyl)-2-butene after treatment with methyllithium in a similar manner.

Silylation of 1c (Method B). The allylsilanes 6 were obtained as a mixture of *E* and *Z* isomers. The ratio was determined by GLC analysis. Analytical data for the isomeric mixture are as follows. Anal. Calcd for $C_{15}H_{24}O_2Si$: C, 68.13; H, 9.15. Found: C, 67.76; H, 9.27. (*E*)-2-(Phenyldiethoxysilyl)-3-pentene (6): ^{1}H NMR δ 1.08 (d, J = 7.3 Hz, 3 H), 1.25 (t, J = 6.9 Hz, 3 H), 1.64 (t, J = 6.6 Hz, 3 H), 1.94 (quint, J = 7.3 Hz, 1 H), 3.39 (q, J = 6.9 Hz, 4 H), 5.29 (dq, J = 15.5 and 6.6 Hz, 1 H), 5.52 (dd, J = 15.5 and 7.3 Hz, 1 H), 7.25–7.45 (m, 3 H), 7.60–7.70 (m, 2 H). (*Z*)-2-(Phenyldiethoxysilyl)-3-pentene (6): ^{1}H NMR δ 1.08 (d, J = 7.3 Hz, 3 H), 1.24 (t, J = 6.9 Hz, 3 H), 1.51 (t, J = 5.3 Hz, 3 H), 2.24 (dq, J = 10.2 and 7.3 Hz, 1 H), 3.39 (q, J = 6.9 Hz, 4 H), 5.20–5.40 (m, 2 H), 7.25–7.45 (m, 3 H), 7.60–7.70 (m, 2 H).

Silylation of 1d (Method A). The products 7 were obtained as a mixture of *cis* and *trans* isomers, the ratio of which was determined by ^{1}H NMR spectra. Both isomers were treated with EtOH and Et_3N to give *cis*- and *trans*-8, respectively. The isomers of 8 were separated by preparative GLC. The stereochemistry of each isomer was determined by conversion into known alcohol 9 (*vide infra*). *trans*-5-Carbomethoxy-3-(phenyldichlorosilyl)-cyclohexene (7): ^{1}H NMR δ 2.05–2.60 (m, 5 H), 2.63–2.79 (m, 1 H), 3.68 (s, 3 H), 5.66–5.91 (m, 2 H), 7.37–7.57 (m, 3 H), 7.65–7.80 (m, 2 H). *cis*-5-Carbomethoxy-3-(phenyldichlorosilyl)cyclohexene (7): ^{1}H NMR δ 2.05–2.60 (m, 5 H), 2.63–2.79 (m, 1 H), 3.67 (s, 3 H), 5.66–5.91 (m, 2 H), 7.37–7.57 (m, 3 H), 7.65–7.80 (m, 2 H). *trans*-5-Carbomethoxy-3-(phenyldiethoxysilyl)cyclohexene (8): ^{1}H NMR δ 1.24 (t, J = 6.9 Hz, 3 H), 1.26 (t, J = 6.9 Hz, 3 H), 1.89–2.24 (m, 5 H), 2.59–2.65 (m, 1 H), 3.64 (s, 3 H), 3.85 (q, J = 6.9 Hz, 2 H), 3.86 (q, J = 6.9 Hz, 2 H), 5.62–5.69 (m, 1 H), 5.78–5.83 (m, 1 H), 7.33–7.42 (m, 3 H), 7.61–7.65 (m, 2 H); ^{13}C NMR δ 18.3, 23.7, 24.8, 27.0, 37.2, 51.5, 58.9, 59.0, 123.7, 126.5, 127.8, 130.1, 132.3, 134.7, 176.2; LRMS m/e 334 (M^+), 195; HRMS calcd for $C_{18}H_{26}O_4Si$ 334.1600, found 334.1590. Anal. Calcd for $C_{18}H_{26}O_4Si$: C, 64.64; H, 7.83. Found: C, 64.77; H, 7.83. *cis*-5-Carbomethoxy-3-(phenyldiethoxysilyl)cyclohexene (8): ^{1}H NMR δ 1.23 (t, J = 6.9 Hz, 3 H), 1.26 (t, J = 6.9 Hz, 3 H), 1.52–1.65 (m, 1 H), 1.98–2.20 (m, 4 H), 2.39–2.49 (m, 1 H), 3.65 (s, 3 H), 3.84 (q, J = 6.9 Hz, 2 H), 3.86 (q, J = 6.9 Hz, 2 H), 5.64–5.71 (m, 1 H), 5.85 (d, J = 10.2 Hz, 1 H), 7.32–7.45 (m, 3 H), 7.60–7.64 (m, 2 H); ^{13}C NMR δ 18.3, 24.6, 26.0, 27.6, 40.0, 51.6, 58.9, 124.5, 126.1, 127.8, 130.1, 132.1, 134.7, 176.6; LRMS m/e 334 (M^+), 195;

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HRMS calcd for $C_{18}H_{26}O_4Si$ 334.1600, found 334.1618. Anal. Calcd for $C_{18}H_{26}O_4Si$: C, 64.64; H, 7.83. Found: C, 64.77; H, 7.83.

Palladium-Catalyzed Asymmetric Silylation of Allylic Halides with $PhCl_2SiSiMe_3$. The asymmetric silylation was carried out in essentially the same manner as method A or B. The reaction conditions and results are summarized in Table II. The enantiomeric purities and absolute configurations were determined by conversion into alcohols (*vide infra*).

Oxidation of Allylic Diethoxysilanes to Allylic Alcohols and Determination of the Enantiomeric Purities. General Procedure. To a mixture of 1 mmol of allylic phenyldiethoxysilane, 116 mg (2.0 mmol) of potassium fluoride, and 200 mg (2.0 mmol) of potassium hydrogen carbonate in 1.0 mL of THF and 1.0 mL of methanol was added dropwise 0.28 mL (2.5 mmol) of 30% hydrogen peroxide, aqueous solution, and the mixture was stirred overnight. Aqueous sodium thiosulfate was added to quench the excess hydrogen peroxide. The mixture was extracted with ether and the ether layer was dried over magnesium sulfate. Removal of solvent followed by column chromatography on silica gel (hexane:ethyl acetate = 3:1) gave product alcohol.

The enantiomeric purities of the alcohols were determined by HPLC analysis of their 3,5-dinitrophenyl carbamate derivatives obtained by the following procedure. A mixture of alcohol (2 mg), 3,5-dinitrophenyl isocyanate (5 mg), and pyridine (5 μL) in toluene (0.5 ml) was stirred at 60–70 °C for 30 min. The mixture was evaporated, diluted with chloroform, and filtered. The filtrate was analyzed by HPLC with a chiral stationary phase column, Sumichiral OA-4100 (hexane:1,2-dichloroethane:ethanol = 100:20:1).

Oxidation of 3. Yield: 36%. (*R*)-2-Cyclohexen-1-ol (**10**):[17] $[\alpha]_D^{20}$ + 13.1 (*c* 0.5, chloroform); 10% ee; ^{1}H NMR δ 1.45–2.18 (m, 7 H), 4.21 (bs, 1 H), 5.7–5.8 (m, 1 H), 5.8–5.9 (m, 1 H).

Oxidation of 4 and 5. Yield: 15%. (*S*)-3-Buten-2-ol (**11**):[23] ^{1}H NMR δ 1.27 (d, J = 7 Hz, 3 H), 2.58 (bs, 1 H), 4.29 (quint, J = 7 Hz, 1 H), 5.04 (d, J = 10 Hz, 1 H), 5.20 (d, J = 18 Hz, 1 H), 5.91 (ddd, J = 18, 10, and 7 Hz, 1 H). (*E*)-2-Buten-1-ol: ^{1}H NMR δ 1.71 (d, J = 5.0 Hz, 3 H), 2.15 (bs, 1 H), 4.06 (d, J = 5.0 Hz, 2 H), 5.56–5.80 (m, 2 H).

Oxidation of 6. Yield: 40%. (*E*)-3-Penten-2-ol:[24] ^{1}H NMR δ 1.35 (d, J = 7 Hz, 3 H), 1.53 (bs, 1 H), 1.69 (d, J = 7 Hz, 3 H), 4.26 (quint, J = 7 Hz, 1 H), 5.52 (dd, J = 16 and 7 Hz, 1 H), 5.67 (dq, J = 16 and 7 Hz, 1 H). (*Z*)-3-Penten-2-ol (**12**):[24] ^{1}H NMR δ 1.35 (d, J = 7 Hz, 3 H), 1.53 (bs, 1 H), 1.68 (d, J = 7 Hz, 3 H), 4.69 (quint, J = 7 Hz, 1 H), 5.40–5.65 (m, 2 H).

Oxidation of 8. *trans*-5-Carbomethoxy-2-cyclohexen-1-ol (**9**):[11] yield, 34%; ^{1}H NMR δ 1.79–1.90 (m, 1 H), 1.95–2.45 (m, 4 H), 2.72–2.90 (m, 1 H), 3.70 (s, 3 H), 4.22–4.35 (m, 1 H), 5.78–5.97 (m, 2 H). *cis*-5-Carbomethoxy-2-cyclohexen-1-ol (**9**):[11] yield, 41%; ^{1}H NMR δ 1.65–1.82 (m, 1 H), 2.00 (bs, 1 H), 2.00–2.20 (m, 3 H), 2.65–2.80 (m, 1 H), 3.70 (s, 3 H), 4.22–4.36 (m, 1 H), 5.67–5.82 (AB, 2 H).

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