

Hydroalumination and Related Reactions of Phenyl 1-(Trimethylsilyl)propadienyl Sulfide Followed by Quenching with Carbonyl Compounds

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Phenyl 1-(trimethylsilyl)propadienyl sulfide undergoes a hydroalumination with diisobutylaluminum hydride (DIBAH) or lithium butyl(diisobutyl)aluminum hydride (BL-DIBAH). The adduct anion derived from DIBAH is regioselectively trapped with carbonyl compounds at the position α to the phenylthio moiety to give 1,3-dienes as Peterson olefination products; the anion derived from BL-DIBAH is trapped at the position γ to the phenylthio moiety to give 3-buten-1-ols. Silylmetalation and stanylaluminum on the same acceptor have been also briefly investigated as equivalent reactions.

In the preceding paper of this series, we have reported that 1-silyethenyl sulfides show only a limited reactivity toward organolithiums in the sequential reactions consisting of Michael type addition and Peterson olefination.¹⁾ We came to select a 1-silylpropadienyl sulfide since this cumulative acceptor was expected to form adduct anion intermediates with a much higher stabilization. The synthetic applications of propadienylsilanes are quite limited to the use as nucleophilic reagents.²⁾ Michael type addition is rarely known.

Results and Discussion

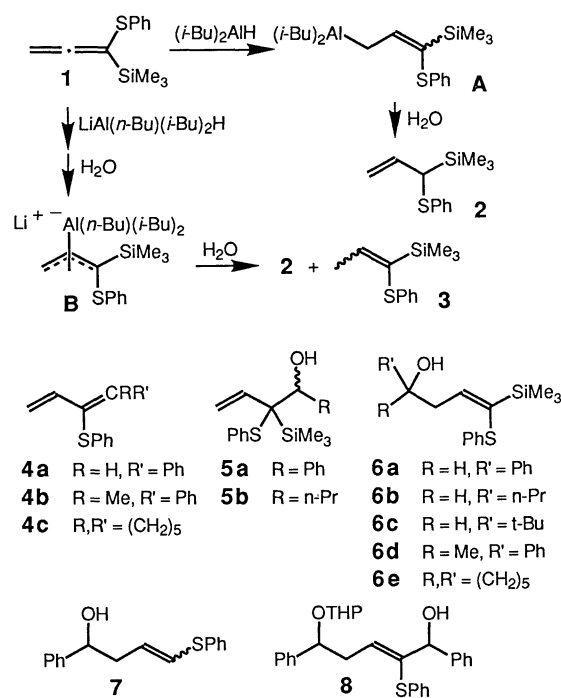
Phenyl 1-(trimethylsilyl)propadienyl sulfide (**1**) used as the acceptor in the present work was prepared in 87% yield by deprotonation of phenyl 1-propynyl sulfide³⁾ with lithium diisopropylamide (LDA) at -78°C and subsequent silylation with chlorotrimethylsilane.

Although no reaction was observed between allenylsilane **1** and diisobutylaluminum hydride (DIBAH) in hexane,⁴⁾ a slow reaction took place in tetrahydrofuran (THF) at room temperature to give, after hydrolytic work-up, 48% yield of phenyl 1-trimethylsilyl-2-propenyl sulfide (**2**) after 24 h (Scheme 1). In this reaction, some of the starting compound **1** was recovered even when two equivalents of DIBAH were employed. A quantitative recovery of **1** resulted in a similar reaction in 1,2-dimethoxyethane (DME) showing highly solvent-sensitive nature of this reaction, and the use of a catalytic amount of copper(I) iodide was totally ineffective.

The exclusive formation of **2** by the regioselective reaction at the less hindered double bond of allene **1** accords with the previously reported selectivity.⁴⁾ Trapping of the adduct anion intermediate with benzaldehyde gave, after work-up with Rochell solution (aqueous potassium sodium tartrate), 1-phenyl-2-phenylthio-1,3-butadiene (**4a**, 39%) and alcohol **5a** (31%). Since alcohol **5a** was quantitatively converted into butadiene **4a** by heating under reflux in

ethanol, both **4a** and **5a** are the products produced from the regioselective carbonyl trapping reaction. Butadiene **4a** actually the only product (62%) when the reaction mixture of **1**, DIBAH, and benzaldehyde was treated with dilute hydrochloric acid. Accordingly, it is most likely that the (3-silylallyl)aluminum **A** was involved as the initial adduct intermediate since allylaluminums are known to react with carbonyl compounds via an allyl rearrangement (Scheme 1).^{5,6)} However, the regioselective water quenching of **A** through allyl rearrangement was surprising.

An aluminate complex, lithium butyl(diisobutyl)aluminum hydride (BL-DIBAH), was found to show a higher reactivity to propadienylsilane **1** than DIBAH, but regiochemical outcome of this reaction was rather poor. Thus, comparable yields of **2** (20%) and phenyl



Scheme 1.

1-trimethylsilyl-1-propenyl sulfide (**3**, 21%) were obtained in the reaction of **1** with BL-DIBAH (1.2 equiv) after hydrolytic quenching. The quenching with benzaldehyde afforded, after hydrolytic work-up with Rochell solution, a single isomer of 1-phenyl-4-phenylthio-4-trimethylsilyl-3-buten-1-ol (**6a**, 62%) along with the recovered **1** (21%).

A considerably ionized species **B** was presumably involved in the reaction of **1** with BL-DIBAH because the aluminum-carbon bond in **B** should be less covalent than in **A** (Scheme 1). The different regioselectivity in the cases of the hydrolytic quenching and the quenching with benzaldehyde can be explained by steric factors. There are several examples known for the reaction of hetero-substituted lithium allylaluminates or crotylaluminates with carbonyl compounds, where the carbonyl addition took place at the position substituted by the hetero substituents.⁷ Our regioselective carbonyl addition at the unsubstituted terminal carbon atom makes a striking contrast with these precedents. This reverse selectivity would probably have arisen from a high steric congestion at the substituted carbon atom of **B**.

Hydroalumination of **1** with DIBAH or BL-DIBAH and trapping of the resulting adducts were performed by using several carbonyl compounds to give 2-phenylthio-1,3-butadienes **4a-c** (or the corresponding alcohols **5a, b**) or 4-phenylthio-4-trimethylsilyl-3-buten-1-ols **6a-e**, and the results are summarized in Scheme 1 and Table 1.

The *Z*-geometry of olefin part of **6a** was determined on the basis of the following observation: Only *Z*-isomer of **7** was formed in 57% yield upon treatment of **6a** with tetrabutylammonium fluoride (TBAF) in hexamethylphosphoric triamide (HMPA), and this

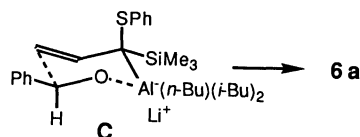


Fig. 1. High *E*-selectivity in the reaction of **B** with benzaldehyde leading to **6a**.

isomer underwent a gradual isomerization in chloroform solution into thermodynamically more stable *E*-isomer of **7** (¹H NMR). The six-membered transition state **C** shown in Fig. 1 would be responsible for the observed exclusive *Z*-selectivity.

The anion resulting from the desilylation of **6** could be trapped with an aldehyde. Thus, after protection of the hydroxyl moiety as a tetrahydropyranyl (THP) ether, vinylsilane **6a** was desilylated with TBAF in the presence of benzaldehyde to afford adduct **8** in 57% yield.

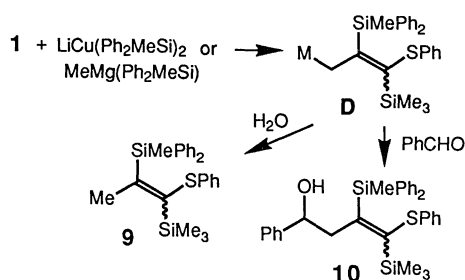
We further examined several reactions which are synthetic equivalent of the above hydroalumination. Thus, methyl(methyldiphenylsilyl)magnesium, prepared from methylmagnesium iodide and (methyldiphenylsilyl)lithium,⁸ reacted with **1** in the presence of a catalytic amount of copper(I) iodide in THF at room temperature to give, after hydrolytic quenching, a single isomer of phenyl 2-(methyldiphenylsilyl)-1-trimethylsilyl-1-propenyl sulfide (**9**) in 62% yield (Scheme 2). However, attempted alkylation of the resulting anion **D** (M=MgMe) with benzaldehyde or methyl iodide was unsuccessful.

On the other hand, the reaction of **1** with lithium (methyldiphenylsilyl)cuprate⁹ in THF at 0 °C afforded the same compound **9** in 57% yield after hydrolytic

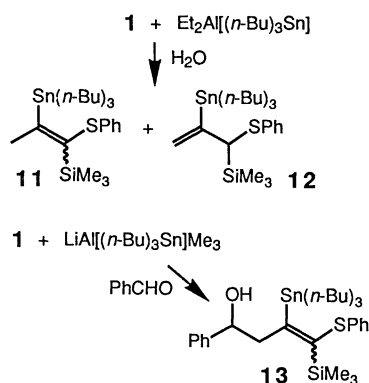
Table 1. Hydroalumination and Related Reactions of Propadienylsilane **1** Followed by Quenching with Carbonyl Compounds or Water

Nucleophile ^{a)}	Conditions	Electrophile ^{a)}	Conditions	Work-up	Product (yield/%) ^{b)}
(<i>i</i> -Bu) ₂ AlH (2)	THF rt, 24 h	None		Rochell soln	2 (48)
(<i>i</i> -Bu) ₂ AlH (2)	THF rt, 24 h	PhCHO(3)	rt, 2 h	Rochell soln	4a (39)+ 5a (31)+ 9 ^{c)}
(<i>i</i> -Bu) ₂ AlH (2)	THF rt, 2 h	PhCHO(3)	rt, 2 h	Dilute HCl	4a (62)+(26) ^{c)}
(<i>i</i> -Bu) ₂ AlH (2)	THF rt, 36 h	PhCOMe(2)	rt, 3 h	Dilute HCl	4b (21)
(<i>i</i> -Bu) ₂ AlH (2)	THF rt, 24 h	Cyclohexanone(2)	rt, 1 h	Dilute HCl	4c (6)
(<i>i</i> -Bu) ₂ AlH (2)	THF rt, 24 h	<i>n</i> -PrCHO(3)	0 °C, 1 h	Dilute HCl	5b (58)
LiAl(<i>n</i> -Bu)(<i>i</i> -Bu) ₂ H (1)	DME rt, 4 h	None		Rochell soln	2 (20)+ 3 (21)
LiAl(<i>n</i> -Bu)(<i>i</i> -Bu) ₂ H (1.2)	DME rt, 3 h	PhCHO(2)	rt, 2 h	Dilute HCl	6a (62)+(21) ^{c)}
LiAl(<i>n</i> -Bu)(<i>i</i> -Bu) ₂ H (1.2)	DME rt, 3 h	<i>n</i> -PrCHO(2)	rt, 2 h	Dilute HCl	6b (44)+(14) ^{d)}
LiAl(<i>n</i> -Bu)(<i>i</i> -Bu) ₂ H (1)	DME rt, 3 h	<i>t</i> -BuCHO(1.5)	rt, 2 h	Dilute HCl	6c (57)
LiAl(<i>n</i> -Bu)(<i>i</i> -Bu) ₂ H (1.2)	DME 0 °C, 1 h	PhCOMe(1.5)	0 °C, 1 h	Dilute HCl	6d (37)+(11) ^{c)}
LiAl(<i>n</i> -Bu)(<i>i</i> -Bu) ₂ H (1.2)	DME 0 °C, 1 h	Cyclohexanone(2)	rt, 2 h	Dilute HCl	6e (51)+(12) ^{c)}
MeMg(Ph ₂ MeSi) (1.3)	THF 0 °C, 3 h ^{b)}	None		Aq NH ₄ Cl	9 (62)
LiCu(Ph ₂ MeSi) ₂ (1.2)	THF 0 °C, 3 h	None		Aq NH ₄ Cl	9 (57)
LiCu(Ph ₂ MeSi) ₂ (1.2)	THF 0 °C, 3 h	PhCHO(2)	rt, 12 h	Aq NH ₄ Cl	10 (51) ^{e)}
Et ₂ Al[(<i>n</i> -Bu) ₃ Sn] (3)	THF rt, 12 h ^{b)}	None		Dilute HCl	11 (17)+ 12 (20)
LiAl[(<i>n</i> -Bu) ₃ Sn]Me ₃ (3)	THF 0 °C, 1 h	PhCHO(3)	0 °C, 1.5h	Dilute HCl	13 (25)

a) The number in parentheses is the amount of reagent used (in equivalent). b) Yield of isolated products. c) Yield/% of the recovered **1**. d) Yield/% of a mixture of **2** and **3**. e) Yield/% of **3**. f) A catalytic amount of copper(I) iodide was used. g) Obtained as a 1:1 mixture of two geometrical isomers (¹H NMR). h) A catalytic amount of copper(I) cyanide was used.



Scheme 2.



Scheme 3.

work-up. In contrast with the poor reactivity of the adduct anion **D** ($M=\text{MgMe}$) derived from **1** and methyl(methyldiphenylsilyl)magnesium, the adduct anion **D** ($M=\text{Li}$) showed a higher reactivity toward an aldehyde so that it could be trapped with benzaldehyde to afford alcohol **10** (51%) as a 1:1 mixture of two geometrical isomers.

Stannylation of allene **1** could be carried out by employing diethyl(tributylstannyl)aluminum, prepared from diethylaluminum chloride and (tributylstannyl)lithium,¹⁰ where two regioisomeric adducts **11** and **12** were obtained in 17 and 20% yields, respectively, after hydrolytic quenching (Scheme 3). The stereochemical assignment of stereochemically pure **11** could not be made only on the basis of spectral data. Trapping of the adduct anion with benzaldehyde was unsuccessful, mixture of complex products having resulted.

When an aluminate complex such as lithium (tributylstannyl)trimethylaluminate, prepared from trimethylaluminum and (tributylstannyl)lithium, was used, quenching of the resulting adduct anion with benzaldehyde proceeded regioselectively to give **13**, albeit in 25% yield.

Experimental

General and Materials. For the instruments used for the record of spectral data and the general experimental procedures, see Ref. 1. Phenyl 1-trimethylsilyl-2-propenyl sulfide (**2**), (*Z*)-1-phenyl-4-phenylthio-4-trimethylsilyl-3-

buten-1-ol (**6a**), and (*Z*)-2,2-dimethyl-5-hexen-3-ol (**6c**) are all known compounds.¹⁰

Phenyl 1-(Trimethylsilyl)propadienyl Sulfide (1). To the LDA solution freshly prepared from butyllithium (1.6 M in hexane, 22.5 ml, 36 mmol; 1 M = 1 mol dm⁻³) and diisopropylamine (5.6 ml, 36 mmol) in dry THF (40 ml) was added dropwise at -78°C a solution of phenyl 1-propynyl sulfide (4.44 g, 30 mmol) in THF (10 ml). After 1 h, this solution was slowly transferred with the aid of a Teflon tube into a cooled solution (-78°C) of chlorotrimethylsilane (5.1 ml, 36 mmol) in THF (30 ml). After 1 h at -78°C , saturated aqueous ammonium chloride was added and the mixture was extracted with diethyl ether (50 ml \times 3). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was subjected to vacuum distillation to give **1** (5.74 g, 87%): Pale yellow liquid; bp $55\text{--}57^\circ\text{C}/106$ Pa (bulb-to-bulb); IR (neat) 2177, 1250, 874, and 841 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) $\delta=0.15$ (9H, s, Me_3Si), 4.51 (2H, s, $=\text{CH}_2$), and 7.1–7.4 (5H, s, Ph); $^{13}\text{C NMR}$ (CDCl_3) $\delta=-1.53$ (q, Me_3Si), 73.18 (t, 3-C), 92.89 (s, 1-C), 127.07, 128.77, 131.66 (each d, Ph), 135.30 (s, Ph), and 209.60 (s, 2-C); MS m/z (rel intensity, %) 220 (M^+ , 65), 115 (12), 103 (25), 77 (20), and 73 (base peak). No satisfactory result of analytical data was obtained due to the instability of **1**.

Phenyl 1-Trimethylsilyl-1-propenyl Sulfide (3). To a solution of DIBAH (1 M in hexane, 1 ml, 1 mmol) in DME (5 ml) was added at 0°C butyllithium (1.6 M in hexane, 0.63 ml, 1 mmol). After 5 min, **1** (0.22 g, 1 mmol) in DME (2 ml) was added, the mixture was stirred at room temperature for 4 h, and poured into aqueous potassium sodium tartarate, and then extracted with diethyl ether (20 ml \times 2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed over silica gel with hexane to give **3** (0.046 g, 21%) and then **2** (0.045 g, 20%). **3**: Colorless liquid; IR (neat) 2956, 1589, 1248, and 839 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) $\delta=0.03$ (9H, s, Me_3Si), 1.91 (3H, d, $J_{3-2}=6.5$ Hz, Me), 6.68 (1H, q, $J_{2-3}=6.5$ Hz, $=\text{CH}$), and 7.13 (5H, m, Ph); $^{13}\text{C NMR}$ (CDCl_3) $\delta=-1.18$ (Me_3Si), 17.18 (Me), 125.24 (2-C), 127.95, 128.89, 135.01, 138.13 (each Ph), and 148.01 (1-C); MS m/z (rel intensity, %) 222 (M^+ , 85), 167 (base peak), and 73 (68). HRMS Found: m/z 222.0892. Calcd for $\text{C}_{12}\text{H}_{18}\text{SSi}$: M, 222.0889.

1-Phenyl-2-phenylthio-1,3-butadiene (4a) and 1-Phenyl-2-phenylthio-2-trimethylsilyl-3-buten-1-ol (5a). To a solution of **1** (0.22 g, 1 mmol) in dry THF (5 ml) was added at 0°C DIBAH (1 M in hexane, 2 ml, 2 mmol). After 24 h at room temperature, benzaldehyde (0.318 g, 3 mmol) was added and stirring was continued for 2 h. Aqueous potassium sodium tartarate was added and the mixture was extracted with diethyl ether (20 ml \times 3). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed on silica gel by using hexane–ethyl acetate (20:1 v/v) to give **4a** (0.093 g, 39%) and **5a** (0.103 g, 31%), and allene **1** was recovered in 9% yield (0.02 g).

When the above reaction mixture was quenched with dilute hydrochloric acid, **4a** (0.148 g, 62%) was obtained together with the unreacted **1** (0.058 g, 26%) after silica-gel chromatography using hexane–ethyl acetate (5:1 v/v).

4a (a 1:2 mixture of *E*- and *Z*-isomers): Colorless liquid; IR (neat) 3059, 1581, 1477, 1439, and 916 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) *E*-isomer: $\delta=5.30$ (1H, dt, $J_{4-3}=10.7$, $J_{\text{gem}}=J_{4-1}=1.5$ Hz,

one of 4-H), 5.83 (1H, dd, $J_{4-3}=17.3$ and $J_{\text{gem}}=1.5$ Hz, the other of 4-H), 6.86 (1H, ddd, $J_{3-4}=17.3$ and 10.7, and $J_{3-1}=1.0$ Hz, 3-H), 6.96 (1H, br s, 1-H), and 7.1–7.4 (10H, m, Ph); Z-isomer: $\delta=5.18$ (1H, dt, $J_{4-3}=10.8$, $J_{\text{gem}}=J_{4-1}=0.8$ Hz, one of 4-H), 5.69 (1H, dd, $J_{4-3}=16.7$ and $J_{\text{gem}}=0.8$ Hz, the other of 4-H), 6.55 (1H, ddd, $J_{3-4}=16.7$ and 10.8, and $J_{3-1}=0.8$ Hz, 3-H), 7.1–7.4 (9H, m, Ph and 1-H), and 7.70 (2H, d, Ph); ^{13}C NMR (CDCl_3) $\delta=117.73$, 120.05, 125.42, 126.46, 127.58, 127.64, 128.12, 128.28, 128.30, 128.87, 128.98, 129.34, 129.89, 129.92, 131.27, 131.77, 135.94, 136.04, 136.21, 137.98, and 139.77; MS m/z (rel intensity, %) 238 (M^+ , 65), 129 (base peak), 128 (84), 127 (27), 104 (24), and 77 (25). HRMS Found: m/z 238.0816. Calcd for $\text{C}_{16}\text{H}_{14}\text{S}$: M, 238.0816.

5a: Pale yellow liquid; IR (neat) 3350, 1580, 1475, and 1430 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=-0.04$ (9H, s, Me_3Si), 2.95 (1H, d, $J=2.6$ Hz, OH), 5.05 (1H, d, $J_{1-\text{OH}}=2.6$ Hz, 1-H), 5.20 (1H, dd, $J_{4-3}=11.3$ and $J_{\text{gem}}=1.1$ Hz, one of 4-H), 5.36 (1H, dd, $J_{4-3}=17.3$ and $J_{\text{gem}}=1.1$ Hz, the other of 4-H), 5.88 (1H, dd, $J_{3-4}=17.3$ and 11.3 Hz, 3-H), and 7.2–7.7 (10H, m, Ph); ^{13}C NMR (CDCl_3) $\delta=-0.42$ (Me_3Si), 57.65 (2-C), 77.02 (1-C), 116.63 (4-C), 129.43, 129.62, 129.91, 130.09, 130.53, 130.59, 130.97, 136.81, 138.51, and 142.37 (3-C and Ph); MS m/z (rel intensity, %) 328 (M^+ , 5), 238 (24), 129 (38), 128 (27), 110 (41), 109 (28), 107 (22), and 105 (base peak). No satisfactory analytical data was available due to its instability.

4-Phenyl-3-phenylthio-1,3-pentadiene (4b). The same procedure as above employing **1** (1 mmol) and DIBAH (2 mmol) was followed by the addition of acetophenone (0.24 g, 2 mmol) in THF (2 ml). After 3 h at room temperature, the reaction mixture was treated with dilute hydrochloric acid and extracted with diethyl ether (20 ml \times 3). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed on silica gel with hexane to give **4b** (0.052 g, 21%): Pale yellow liquid; IR (neat) 3080, 1580, 1480, 1440, and 1025 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=2.25$ (3H, s, Me), 4.85 (1H, br d, $J_{1-2}=10.5$ Hz, one of 1-H), 5.51 (1H, br d, $J_{1-2}=16.5$ Hz, the other of 1-H), 6.31 (1H, dd, $J_{2-1}=16.5$ and 10.5 Hz, 2-H), and 6.9–7.3 (10H, m, Ph); ^{13}C NMR (CDCl_3) $\delta=24.97$ (Me), 117.10, 124.92, 126.60, 127.44, 128.16, 128.32, 128.52, 128.77, 128.85, 134.16, 142.48, and 149.77 (each olefinic C and Ph); MS m/z (rel intensity, %) 252 (M^+ , 67), 226 (22), 218 (30), 143 (base peak), 142 (25), 141 (23), 128 (79), 115 (29), 109 (28), 103 (20), and 91 (26). HRMS Found: m/z 252.0974. Calcd for $\text{C}_{17}\text{H}_{16}\text{S}$: M, 252.0975.

1-Cyclohexylidene-2-propenyl Phenyl Sulfide (4c). The same procedure as above employing **1** (1 mmol) and DIBAH (2 mmol) was followed by the addition of cyclohexanone (0.2 g, 2 mmol) in THF (2 ml). After 1 h at room temperature, the reaction mixture was treated with dilute hydrochloric acid and extracted with diethyl ether (20 ml \times 3). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed on silica gel with hexane, and the eluent containing **4c** was further purified by preparative thin layer chromatography (**4c**: 0.014 g, 9%): Pale yellow liquid; IR (neat) 2980, 1570, 1485, 1445, 1250, and 845 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=1.4$ –1.8 (6H, m, CH_2), 2.5–2.9 (4H, m, CH_2), 5.11 (1H, dd, $J_{\text{cis}}=11.2$ and $J_{\text{gem}}=2.4$ Hz, one of $=\text{CH}_2$), 5.66 (1H, dd, $J_{\text{trans}}=16.0$ and $J_{\text{gem}}=2.4$ Hz, the other of $=\text{CH}_2$), 6.87 (1H, dd, $J_{\text{trans}}=16.0$ and $J_{\text{cis}}=11.2$ Hz, =CH), and 7.15 (5H, br s, Ph); ^{13}C NMR

(CDCl_3) $\delta=26.65$, 28.32, 28.41, 31.85, 34.60 (each CH_2), 117.22, 122.13, 124.56, 126.45, 128.66, 131.96, 138.07, and 154.24 (each olefinic C and Ph); MS m/z (rel intensity, %) 230 (M^+ , base peak), 125 (13), 121 (18), 105 (11), 93 (12), and 91 (24). HRMS Found: m/z 230.1098. Calcd for $\text{C}_{15}\text{H}_{18}\text{S}$: M, 230.1070.

3-Phenylthio-3-trimethylsilyl-1-hepten-4-ol (5b). The same procedure as above employing **1** (1 mmol) and DIBAH (2 mmol) was followed by the addition of butanal (0.216 g, 3 mmol) in THF (2 ml). After 1 h at 0 °C, the reaction mixture was treated with dilute hydrochloric acid and extracted with diethyl ether (20 ml \times 3). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed on silica gel with hexane–ethyl acetate (20:1 v/v) to give **5b** (0.171 g, 58%): Pale yellow liquid; ^1H NMR (CDCl_3) $\delta=0.19$ (9H, s, Me_3Si), 0.92 (3H, t, $J=6.0$ Hz, *n*-Pr), 1.2–1.8 (4H, m, *n*-Pr), 2.56 (1H, d, $J=3.5$ Hz, OH), 3.7–3.9 (1H, m, 4-H), 6.90 (1H, dd, $J_{1-2}=17.5$ and $J_{\text{gem}}=1.1$ Hz, one of 1-H), 5.03 (1H, dd, $J_{1-2}=11.0$ and $J_{\text{gem}}=1.1$ Hz, the other 1-H), 5.82 (1H, dd, $J_{2-1}=17.5$ and 11.0 Hz, 2-H), and 7.1–7.6 (5H, m, Ph); ^{13}C NMR (CDCl_3) $\delta=-1.12$ (q, Me_3Si), 14.21 (q, *n*-Pr), 20.61, 36.52 (each t, *n*-Pr), 55.37 (s, 2-C), 73.09 (d, 1-C), 114.21 (t, 4-C), 128.61, 131.78 (each d, Ph), 135.16 (s, Ph), 136.62, and 138.18 (each d, Ph and 3-C); MS m/z (rel intensity, %) 294 (M^+ , 20), 204 (base peak), 175 (68), 161 (31), 111 (47), 110 (22), 95 (27), and 77 (20). HRMS Found: 294.1483. Calcd for $\text{C}_{16}\text{H}_{26}\text{OSSi}$: 294.1472.

General Procedure for Addition of BL-DIBAH to 1 Followed by Quenching with Carbonyl Compounds. As a typical procedure, the reaction leading to **6a** is presented below: To a solution of DIBAH (1 M in hexane, 1.2 ml, 1.2 mmol) in dry DME (5 ml) was added at 0 °C butyllithium (1.6 M in hexane, 0.75 ml, 1.2 mmol). After 10 min, a solution of **1** (0.22 g, 1 mmol) in DME (2 ml) was added and stirring was continued at room temperature for 3 h. Benzaldehyde (0.212 g, 2 mmol) in DME (2 ml) was added. The mixture was stirred at room temperature for 2 h, poured into dilute hydrochloric acid, and extracted with diethyl ether (20 ml \times 3). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed on silica gel by using hexane–ethyl acetate (20:1 v/v) to give **6a** (0.203 g, 62%) and a mixture of **2** and **3** (0.048 g, 21%).

The eluent employed in the silica-gel column chromatography for the purification of **6b**–**e** was hexane–ethyl acetate (20:1 v/v) in all cases. Reaction conditions and results are listed in Table 1.

(Z)-1-Phenylthio-1-trimethylsilyl-1-hepten-4-ol (6b): Colorless liquid; IR (neat) 3400, 1245, and 840 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=-0.04$ (9H, s, Me_3Si), 0.8–1.0 (3H, m, *n*-Pr), 1.2–1.5 (5H, m, *n*-Pr and OH), 2.5–2.6 (2H, m, 3-H), 3.70 (1H, m, 4-H), 6.66 (1H, t, $J_{2-3}=6.6$ Hz, 2-H), and 7.0–7.3 (5H, m, Ph); ^{13}C NMR (CDCl_3) $\delta=-0.83$ (Me_3Si), 14.28, 19.06, 39.09, 39.82 (each *n*-Pr and 3-C), 71.37 (4-C), 125.52, 128.40, 128.90, 136.69, 137.79 (each Ph and 2-C), and 148.89 (1-C); MS m/z (rel intensity, %) 294 (M^+ , 18), 222 (32), 167 (31), 98 (36), and 73 (base peak). HRMS Found: m/z 294.1472. Calcd for $\text{C}_{16}\text{H}_{26}\text{OSSi}$: M, 294.1472.

(Z)-2-Phenyl-5-phenylthio-5-trimethylsilyl-4-penten-2-ol (6d): Pale yellow liquid; IR (neat) 3400, 1245, and 840 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=0.00$ (9H, s, Me_3Si), 1.64 (3H, s, Me),

1.92 (1H, br s, OH), 3.00 (2H, d, $J_{3-4}=6.9$ Hz, 3-H), 6.60 (1H, t, $J_{4-3}=6.9$ Hz, 4-H), and 7.1–7.5 (10H, m, Ph); ^{13}C NMR (CDCl_3) $\delta=-0.80$ (Me_3Si), 30.28 (Me), 45.26 (3-C), 74.84 (2-C), 125.07, 125.56, 127.02, 128.44, 128.57, 128.86, 131.01, 137.36, 137.63 (each Ph and 4-C), and 147.74 (5-C); MS m/z (rel intensity, %) 342 (M^+ , 7), 223 (20), 222 (base peak), 167 (33), 121 (80), and 73 (81). HRMS Found: m/z 342.1475. Calcd for $\text{C}_{20}\text{H}_{26}\text{OSSi}$: M, 342.1476.

(Z)-1-(3-Phenylthio-3-trimethylsilyl-2-propenyl)-1-cyclohexanol (6e): Pale yellow liquid; IR (neat) 3400, 1250, and 845 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=-0.03$ (9H, s, Me_3Si), 1.1–1.6 (10H, m, CH_2), 2.58 (2H, d, $J=7.0$ Hz, CH_2), 6.74 (1H, t, $J=7.0$ Hz, CH), and 7.0–7.3 (5H, m, Ph); ^{13}C NMR (CDCl_3) $\delta=-0.68$ (Me_3Si), 22.49, 25.91, 38.05, 43.45 (each CH_2), 72.15 (CH), 125.46, 128.46, 128.86, 136.90, 137.89, and 148.17 (each olefinic C and Ph); MS m/z (rel intensity, %) 320 (M^+ , 5), 222 (59), 167 (39), 99 (32), 81 (35), and 73 (base peak). HRMS Found: m/z 320.1136. Calcd for $\text{C}_{18}\text{H}_{28}\text{OSSi}$: 320.1629.

1-Phenyl-4-phenylthio-3-buten-1-ol (7). To a solution of **6a** (0.117 g, 0.36 mmol) in HMPA (1 ml) were added water (0.1 ml) and TBAF (1 M in THF, 0.5 ml, 0.5 mmol). After stirred for 1.5 h at room temperature, the mixture was poured into water and extracted with diethyl ether (15 ml \times 2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed on silica gel by using hexane–ethyl acetate (5:1 v/v) to give **(Z)-7** (0.052 g, 57%), which gradually changed into **(E)-7** in chloroform solution. **(Z)-7:** Pale yellow liquid; IR (neat) 3350, 1580, 1470, 1430, and 730 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=2.18$ (1H, br s, OH), 2.70 (2H, dt, $J_{2-1}=J_{2-3}=7.2$ Hz and $J_{2-4}=1.0$ Hz, 2-H), 4.68 (1H, t, $J_{1-2}=7.2$ Hz, 1-H), 5.80 (1H, dt, $J_{3-4}=9.4$ and $J_{3-2}=7.2$ Hz, 3-H), 6.31 (1H, dt, $J_{4-3}=9.4$ and $J_{4-2}=1.0$ Hz, 4-H), and 7.1–7.4 (10H, m, Ph); MS m/z (rel intensity, %) 256 (M^+ , 10), 150 (36), 107 (39), 79 (78), 78 (29), and 77 (base peak). **(E)-7:** ^1H NMR (CDCl_3) $\delta=2.10$ (1H, br s, OH), 2.57 (2H, dt, $J_{2-1}=J_{2-3}=6.6$ and $J_{2-4}=0.8$ Hz, 2-H), 4.74 (1H, t, $J_{1-2}=6.6$ Hz, 1-H), 5.86 (1H, dt, $J_{3-4}=15.0$ and $J_{3-2}=6.6$ Hz, 3-H), 6.20 (1H, dt, $J_{4-3}=15.0$ and $J_{4-2}=0.8$ Hz, 4-H), and 7.2–7.4 (10H, m, Ph).

1,5-Diphenyl-2-phenylthio-5-[2-(tetrahydropyran)oxy]-2-penten-1-ol (8, a 3:2 mixture of two diastereomers): To a solution of **6a** (0.282 g, 0.86 mmol) in dichloromethane (3 ml) were added 3,4-dihydro-2H-pyran (0.126 g, 1.5 mmol) and pyridinium *p*-toluenesulfonate (0.025 g, 0.1 mmol). After stirred at room temperature for 12 h, the reaction mixture was poured into water and extracted with diethyl ether (15 ml \times 2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed on silica gel with hexane–ethyl acetate (20:1 v/v) to give the THP ether (0.331 g, 93%). To a mixture of this product (0.131 g, 0.32 mmol) and benzaldehyde (0.05 g, 0.5 mmol) in THF (3 ml) was added TBAF (1 M in THF, 0.03 ml, 0.03 mmol). The mixture was stirred at room temperature for 12 h, poured into water, and extracted with diethyl ether (15 ml \times 2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed on silica gel with hexane–ethyl acetate (5:1 v/v) to give **8** (0.081 g, 57%): Pale yellow liquid; IR (neat) 3450, 1585, 1480, 1455, and 1030 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=1.3$ –1.9 (6H, m, THP), 2.35 (1H, br s, OH), 2.86 (2H, t, $J_{4-5}=J_{4-3}=6.2$ Hz, 4-H), 3.2–3.9 (2H, m, THP), 4.7–4.8 (2H, m, THP and 5-H), 5.10, 5.13 (1H, each

s, 1-H), 6.27, 6.41 (1H, each dt, $J_{3-4}=6.2$ and $J_{3-1}=3.3$ Hz, 3-H), and 7.1–7.4 (15H, m, Ph); ^{13}C NMR (CDCl_3) $\delta=19.09$, 19.19, 25.40, 25.51, 30.57, 37.02, 38.50, 61.88, 61.97, 62.10, 76.10, 76.35, 76.38, 95.02, 95.19, 97.49, and signals for aromatic and olefinic carbons.

Phenyl 2-(Methyldiphenylsilyl)-1-trimethylsilyl-1-propenyl Sulfide (9). Methylmagnesium iodide (1.3 M diethyl ether, 1 ml, 1.3 mmol) was added at 0 °C to methyldiphenylsilyllithium (0.32 M in THF, 4.1 ml, 1.3 mmol). Copper(I) iodide (0.01 g) and **1** (0.22 g, 1 mmol) were added after 15 min at 0 °C. After 3 h at 0 °C, the mixture was poured into aqueous ammonium chloride and extracted with diethyl ether (20 ml \times 2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed on silica gel by using hexane to give **9** (0.201 g, 62%) as a single isomer: Colorless liquid; IR (neat) 1583, 1429, 1250, 841, and 789 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=0.10$ (9H, s, Me_3Si), 0.73 (3H, s, MePh_2Si), 2.00 (3H, s, Me), and 6.8–7.5 (15H, m, Ph); ^{13}C NMR (CDCl_3) $\delta=-1.59$ (Me_3Si), 1.24 (MePh_2Si), 26.47 (Me), 125.18, 127.54, 128.07, 128.65, 129.13, 135.13, 138.25, 139.71 (each 2-C and Ph), and 148.01 (1-C); MS m/z (rel intensity, %) 418 (M^+ , 70), 310 (12), 259 (14), 198 (20), 197 (base peak), 105 (36), and 73 (26), HRMS Found: m/z 418.1648. Calcd for $\text{C}_{25}\text{H}_{30}\text{SSi}_2$: M, 418.1689.

3-(Methyldiphenylsilyl)-1-phenyl-4-phenylthio-4-trimethylsilyl-3-buten-1-ol (10). A mixture of copper(I) iodide (0.23 g, 1.2 mmol) and (methyldiphenylsilyl)lithium (0.34 M in THF, 7.5 ml, 2.4 mmol) was stirred at 0 °C for 20 min. To this solution was added **1** (0.22 g, 1 mmol) in THF (2 ml). After stirring at 0 °C for 3 h, benzaldehyde (0.212 g, 2 mmol) was added, the mixture was stirred at room temperature for 12 h, poured into aqueous ammonium chloride, and extracted with diethyl ether (20 ml \times 2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed on silica gel with hexane to give **10** (0.267 g, 51%) as a 1:1 mixture of two isomers: Pale yellow viscous liquid; IR (neat) 2956, 1583, 1430, 1250, and 1026 cm^{-1} ; ^1H NMR (CDCl_3) $\delta=0.04$ (9H, s, Me_3Si), 0.66, 0.67 (3H, each s, MePh_2Si), 2.5–2.9 (2H, m, OH and one of 2-H), 3.28 (1/2H, dd, $J_{\text{gem}}=16.0$ and $J_{2-1}=6.0$ Hz, the other of 2-H), 3.29 (1/2H, each dd, $J_{\text{gem}}=16.0$ and $J_{2-1}=4.9$ Hz, the other of 2-H), 5.20 (1/2H, dd, $J_{1-2}=10.5$ and 4.9 Hz, 1-H), 5.32 (1H, dd, $J_{1-2}=8.8$ and 6.0 Hz, 1-H), and 6.9–7.8 (20H, m, Ph); ^{13}C NMR (CDCl_3) $\delta=-2.24$, -1.53 (each q, MePh_2Si), 0.29 (q, Me_3Si), 45.24, 46.42 (each t, 2-C), 78.59 (d, 1-C), 125.71, 125.89, 127.71, 128.07, 128.30, 128.72, 130.01, 130.25, 134.66, 134.77 (each d, Ph), 138.25, 144.30, 144.60 (each s, 3-C and Ph), 170.13, and 170.54 (each s, 4-C); MS m/z (rel intensity, %) 446 (M^+-78 , 23), 338 (32), 337 (base peak), 231 (62), 152 (16), and 73 (22).

When the reaction mixture, obtained above after the reaction with **1**, was quenched with aqueous ammonium chloride, a mixture of two stereoisomeric adducts **9** was obtained in 57% yield after silica-gel column chromatography.

Phenyl 2-Tributylstannyl-1-trimethylsilyl-1-propenyl Sulfide (11) and **Phenyl 2-Tributylstannyl-1-trimethylsilyl-2-propenyl Sulfide (12).** To a solution of anhydrous tin(II) chloride (0.569 g, 3 mmol) in dry THF (5 ml) was added at -10 °C butyllithium (1.6 M in hexane, 5.6 ml, 9 mmol). After 30 min at -10 °C, diethylaluminum chloride (2 M in toluene, 1.5 ml, 3 mmol) was added and stirring was

continued for 15 min. Copper(I) cyanide (0.004 g, 0.005 mmol) and **1** (0.22 g, 1 mmol) in THF (5 ml) were added. The mixture was stirred at -10°C for 30 min and further 12 h at room temperature. Quenching with dilute hydrochloric acid was followed by extraction with diethyl ether (20 ml \times 2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed on silica gel by using hexane to give **11** (0.16 g, contaminated by tetrabutyltin) and **12** (0.102 g, 20%). Product **11** was further purified by preparative TLC (0.087 g, 17%).

11: Colorless liquid; IR (neat) 1248 and 839 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) $\delta=0.09$ (9H, s, Me_3Si), 0.6–1.7 (27H, m, *n*-Bu), 2.25 (3H, s, Me), and 7.0–7.4 (5H, m, Ph); $^{13}\text{C NMR}$ (CDCl_3) $\delta=1.35$ (Me_3Si), 11.94, 13.82, 27.59, 27.71, 29.36 (each Me and *n*-Bu), 125.12, 126.48, 126.95, 128.60, 128.83, and 140.66 (each Ph and olefinic C); MS *m/z* (rel intensity, %) 455 (M^+-57 , 22), 453 (16), 345 (21), 343 (base peak), 342 (38), 341 (73), 340 (29), 339 (43), 229 (49), 227 (35), 225 (21), 111 (23), and 97 (49). Found: C, 56.01; H, 8.85%. Calcd for $\text{C}_{24}\text{H}_{44}\text{SSiSn}$: C, 56.36; H, 8.67%.

12: Colorless liquid; IR (neat) 1248, 854, and 841 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) $\delta=0.15$ (9H, s, Me_3Si), 0.7–1.7 (27H, m, *n*-Bu), 3.63 (1H, br s, 1-H), 5.15 (1H, dd, $J_{\text{gem}}=1.8$ and $J_{3-1}=0.6$ Hz, one of 3-H), 5.88 (1H, dd, $J_{\text{gem}}=1.8$ and $J_{3-1}=0.6$ Hz, the other of 3-H), and 6.9–7.3 (5H, m, Ph); $^{13}\text{C NMR}$ (CDCl_3) $\delta=1.76$ (q, Me_3Si), 11.24 (t, *n*-Bu), 13.82 (q, *n*-Bu), 27.65, 29.24 (each t, *n*-Bu), 45.30 (d, 1-C), 125.30 (t, 3-C), 125.48, 128.01, 128.83 (each d, Ph), 139.19 (s, Ph), and 156.07 (s, 2-C); MS *m/z* (rel intensity, %) 455 (M^+-57 , 57), 454 (24), 453 (45), 451 (23), 347 (23), 345 (24), 343 (base peak), 342 (38), 341 (75), 340 (29), 339 (43), 229 (43), 227 (32), 179 (23), 177 (26), 111 (22), and 73 (42). Found: C, 56.32; H, 8.78%. Calcd for $\text{C}_{24}\text{H}_{44}\text{SSiSn}$: C, 56.36; H, 8.67%.

1-Phenyl-4-phenylthio-3-tributylstannyl-4-trimethylsilyl-3-buten-1-ol (13). To a solution of anhydrous tin(II) chloride (0.569 g, 3 mmol) in dry THF (5 ml) was added at 0°C butyllithium (1.6 M in THF, 5.6 ml, 9 mmol). Trimethylaluminum (1 M in hexane, 3 ml, 3 mmol) was added after 30 min, stirring was continued at 0°C for 15 min, and copper(I) cyanide (0.004 g, 0.05 mmol) and **1** (0.22 g, 1 mmol) in THF (5 ml) were added. After stirring at 0°C for 1 h, the addition of a solution of benzaldehyde (0.0318 g, 3 mmol) in THF (2 ml) was followed. The mixture was stirred at 0°C for 1.5 h, poured into dilute hydrochloric acid, and extracted with diethyl ether (20 ml \times 3). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The

residue was chromatographed on silica gel with hexane-ethyl acetate (20:1 v/v) to give **13** (0.155 g, 25%) as a single isomer: Pale yellow liquid; IR (neat) 3450, 1590, 1480, 1255, and 850 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) $\delta=0.12$ (9H, s, Me_3Si), 0.83 (9H, t, $J=7.0$ Hz, *n*-Bu), 0.9–1.7 (18H, m, *n*-Bu), 1.92 (1H, d, $J=2.0$ Hz, OH), 2.82 (1H, dd, $J_{\text{gem}}=13.0$ and $J_{2-1}=4.0$ Hz, one of 2-H), 3.10 (1H, dd, $J_{\text{gem}}=13.0$ and $J_{2-1}=10.7$ Hz, the other of 2-H), 4.7–4.9 (1H, m, 1-H), and 7.0–7.5 (10H, m, Ph); $^{13}\text{C NMR}$ (CDCl_3) $\delta=2.24$ (q, Me_3Si), 13.00 (q, *n*-Bu), 13.88, 27.65, 29.41, 50.24 (each t, *n*-Bu and 2-C), 73.65 (d, 1-C), 125.42, 126.07, 127.19, 128.01, 128.95 (each d, Ph), 140.07, 144.60, 148.07 (each s, Ph and 3-C), and 181.30 (s, 4-C); MS *m/z* (rel intensity, %) 573 (M^+-57 , 28), 345 (25), 343 (base peak), 342 (37), 341 (74), 339 (39), 229 (45), 227 (34), 79 (28), and 73 (53). Found: C, 60.29; H, 8.08%. Calcd for $\text{C}_{31}\text{H}_{50}\text{OSSiSn}$: C, 60.37; H, 8.17%.

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