

Mechanistic Study on the Base-Promoted Reaction of Allylphenylsilanes to Alkenylsilanols[#]

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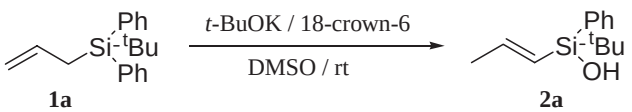
On treatment of allylphenylsilanes with *t*-BuOK and 18-crown-6 in DMSO, isomerization of the olefinic double bond and subsequent substitution of the phenyl group with a hydroxy group took place smoothly to afford alkenylsilanol derivatives in good yields. The reaction mechanism was investigated using ^{18}O-labeled sulfoxide. We found that a (methylsulfinyl)methyl anion generated from DMSO participated in this reaction.

Temporary silicon connection pioneered by Stork achieved regiospecific and stereoselective formation of C–C bonds by bringing together two reaction partners by means of an eventually removable silicon atom.[1] The silicon-tethered reaction has been established as an efficient method for the stereoselective construction of ring systems by numerous types of reactions, such as ionic, radical, photochemical, and cycloaddition reactions.[2] Alkenylsilanols are considered to be useful synthetic units for silyl-tethered reactions. Furthermore, alkenylsilanols have been utilized as sila-analogs of the Katsuki–Sharpless asymmetric epoxidation,[3] and in accelerating the Simmons–Smith reaction, as observed with allylic alcohols.[4] Palladium-catalyzed cross coupling has been achieved with silanols.[5] Also the organic chemistry of silanols involving preparative methods as well as applications towards organic synthesis was reported by Hirabayashi and Mori.[6] However, little attention has been given to the synthetic utilization of silanols because of their instability to moisture, heat, acid, and base, which has made syntheses and isolation difficult. Although a number of synthetic methods for alkenylsilanols have been reported, there remains a lack of excellent synthetic method for the preparation of alkenylsilanols.[7] In order to overcome the above-mentioned drawbacks, we have developed a simple base-promoted protocol for the preparation of alkenylsilanols from readily available allylsilanes under *t*-BuOK and 18-crown-6 in DMSO (Scheme 1).[8] Anderson and co-workers reported also the formation of silanols by treating alkenylsilanes with *t*-BuOK and 18-crown-6 in undried THF.[9] They proposed that hydroxide anions could form pentavalent silicon species, and this reaction was followed by the substitution of a phenyl group with a hydroxy group.

In this reaction, the origin of the hydroxy oxygen was of great interest and studies on the reaction mechanism were important from the viewpoint of organosilicon chemistry. We report herein the mechanism of the base-promoted reaction of allylphenylsilanes in detail.

At the outset, we used several solvents to promote the reaction of allyl-*t*-butyldiphenylsilane **1a** (Table 1). On treatment of **1a** with 1.5 molar amounts of *t*-BuOK in THF, isomerization of the olefinic double bond took place at room temperature to afford corresponding alkenylsilane **4a** in 82% yield (Entry 1). The isomerization was completed in 15 min when DMF was used as solvent (Entry 2). In marked contrast, in DMSO the reaction course was dramatically changed to give alkenylsilanol derivative **2a** in 80% yield (Entry 3). Addition of 18-crown-6 improved the yield of **2a** to 89% (Entry 4).



1a **2a**

Scheme 1.

Among the bases tested, KH (yield of **2a**: 67%), NaH (12%), and *n*-BuLi (0%) were not effective. However, when *n*-BuLi was employed in DMSO, isomerized alkenylsilane **4a** was obtained in 80% yield.

Thus, the base-promoted preparation of **2a** was accomplished by adding *t*-BuOK and 18-crown-6 to allylsilane **1a** in DMSO at room temperature, and the effect of silyl substituent was examined under the optimized reaction conditions (Table 2). Allylsilanes **1** bearing a sterically hindered silyl group also afforded the corresponding silanols **2** in good yields. Allyltriphenylsilane **1c** gave **2c** in 71% yield when the reaction was carried out initially at −45 °C and gradually warmed to room temperature (Entry 3). When allyldimethylphenylsilane was employed, the major product was a disiloxane, which was formed by dehydration of dimethylphenylsilanol (Entry 4). These results indicate that a *t*-butyldiphenylsilyl group is the best for the synthesis of **2**.

The results with other allyl-*t*-butyldiphenylsilanes are shown in Table 3. Transformation of 2-methyl-2-propenylsilane **1e** into the corresponding alkenylsilanol **2e** was achieved in 62% yield (Entry 2). When 2-butenylsilane **1f** was employed, the corresponding alkenylsilanol **2f** and allylsilanol **5f** were obtained each in 20% yield and silanol **3a** was obtained in 50% yield (Entry 3). Isomerization using 3-methyl-2-butenylsilane **1g** did not occur but rather gave 3-methyl-2-butenylsilanol **5g** in 22% yield (Entry 4). Isomerization of

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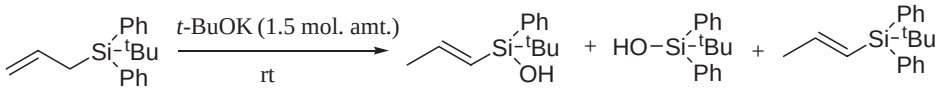
Table 1. Effect of Solvent

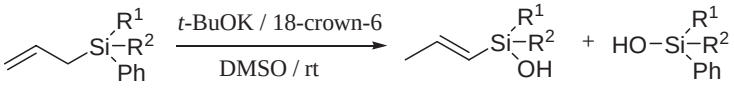


1a **2a** **3a** **4a**

Entry	Solvent	Time/min	Yield of **2a**/%	Yield of **3a**/%	Yield of **4a**/%
1	THF	12	0	0	82
2	DMF	15	0	0	90
3	DMSO	25	80	7	0
4	DMSO[a)]	15	89	10	0

a) 18-crown-6 (0.36 molar amount) was added.

Table 2. Effect of Silyl Group

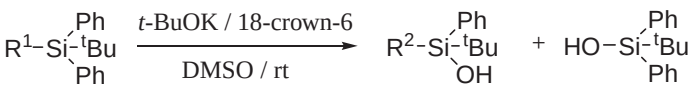


1 **2** **3**

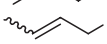
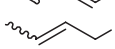
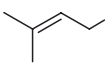
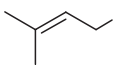
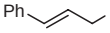
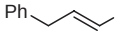
Entry	R^1	R^2	Allylsilane	Yield of **2**/%	Yield of **3**/%
1	*t*-Bu	Ph	**1a**	**2a**: 89	**3a**: 10
2	*i*-Pr	*i*-Pr	**1b**	**2b**: 52	**3b**: 29
3	Ph	Ph	**1c**	**2c**: 71[a)]	**3c**: 19
4	Me	Me	**1d**	**2d**: 0	**3d**: 44[a),b)]

a) The reaction was carried out initially at −45 °C in a mixture of DMSO and THF (v/v = 1/4) and gradually warmed to rt. b) Isolated as disiloxane produced by dehydration of the silanol.

Table 3. Effect of Allyl Substituents



1 **2** **3a**

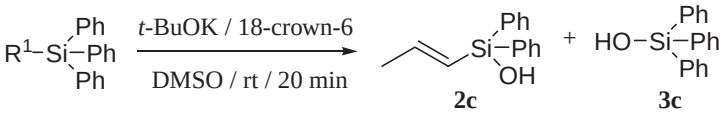
Entry	R^1	Allylsilane	Conditions	R^2	Yield of **2**/%	Yield of **3a**/%
1		**1a**	rt/15 min		**2a**: 89	10
2		**1e**	rt/70 min		**2e**: 62	20
3		**1f**	rt/30 min		**2f**: 20	50
					**5f**: 20	
4		**1g**	rt/55 min		**5g**: 22	54
5		**1h**	50 °C/20 min		**2h**: 97	0
6		**1i**	rt/80 min		**2i**: 0	99

the olefinic double bond was dependent on the stability of the double bond. Although the present transformation generally proceeded smoothly at room temperature, 3-silylcyclohexene **1h** required heating at 50 °C for 20 min (Entry 5). The substitution of the phenyl group with a hydroxy group on the silicon atom is the rate-determining step as the isomerization of the double bond took place smoothly at room temperature. Among these results, the allyl group was a good leaving group in comparison with the vinyl group. Cinnamylsilane **1i** afforded only silanol **3a** because the cinnamyl moiety was a good leaving group (Entry 6).

The reactivity of allylsilane **1c** was compared with that of alkenylsilane **4c** (Table 4). Whereas alkenylsilanol **2c** was obtained in good yield using alkenylsilane **4c** at room temperature, **1c** afforded **2c** in low yield. This result proved that the allyl moiety is a good leaving group.

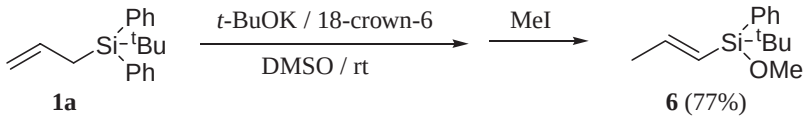
It should be noted that corresponding silyl ether **6** was obtained in high yield by a one-pot procedure when the present reaction was quenched by the addition of methyl iodide (Scheme 2).

Table 4. Comparison of Allylsilane with Vinylsilane in Reactivity



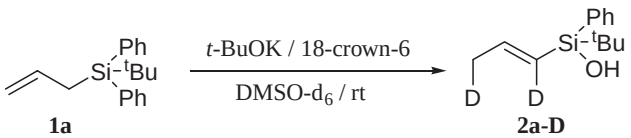
2c **3c**

Entry	R^1	Silane	Yield of **2c**/%	Yield of **3c**/%
1		**1c**	23	70
2		**4c**	68	26



1a **6** (77%)

Scheme 2.



1a **2a-D**

D content: α:70%, γ:87%

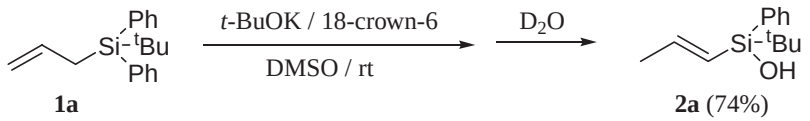
Scheme 3.

Use of DMSO-d_6 as solvent led to the incorporation of deuterium at both α and γ positions to silicon (Scheme 3). On the other hand, deuterium was not incorporated at the alkenyl moiety when the reaction mixture was treated with D_2O (Scheme 4). Only deuterium exchange of the hydroxy group occurred. These results suggest that a (methylsulfinyl)-methyl anion generated from DMSO took part in the isomerization of the double bond.

In order to clarify the participation of a (methylsulfinyl)-methyl anion, other sulfoxides were examined (Table 5). When dibutyl sulfoxide and dodecyl methyl sulfoxide were used, the yield of **2a** decreased (Entries 2 and 3). This reduction of yield could be brought about by steric hindrance of the α-carbanions of these sulfoxides. It is noted that **2a** was not obtained at all when di-*t*-butyl sulfoxide was used.

Finally, a labeling experiment was performed. ^{18}O-Labeled dibutyl sulfoxide **7** was obtained by treating dibutyl sulfide with *N*-bromosuccinimide in $H_2{}^{18}O$–MeOH solution (Scheme 5). GC-MS analysis of the sulfoxide showed that its ^{18}O content was 90%. When the reaction was carried out under standard reaction conditions employing **7** as solvent, ^{18}O-labeled silanol (**2a-^{18}O**) was obtained (Scheme 6).

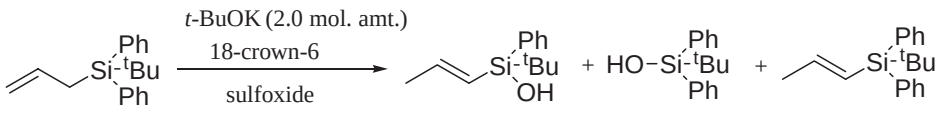
The combination of *t*-BuOK with DMSO is used to cleave C–Si bonds.[10,11] The present transformation was found to pro-



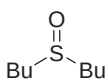
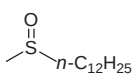
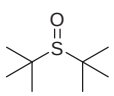
1a **2a** (74%)

Scheme 4.

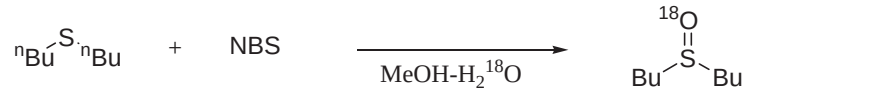
Table 5. Effect of Sulfoxide



1a **2a** **3a** **4a**

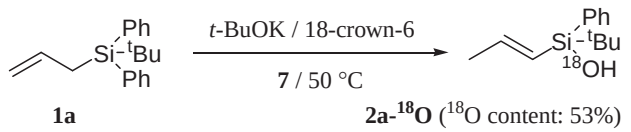
Entry	Sulfoxide	Conditions	Yield of **2a**/%	Yield of **3a**/%	Yield of **4a**/%
1	DMSO	rt/15 min	89	10	0
2		50 °C/4 h	49	24	19
3[a)]		50 °C/4 h	39	9	45
4		50 °C/4 h	0	0	93

a) THF was used as solvent.



(1.0 mol. amt.) (1.1 mol. amt.) (^{18}O content: 95%) **7** (88%, ^{18}O content: 90%)

Scheme 5.



1a **2a-^{18}O** (^{18}O content: 53%)

Scheme 6.

ceed via initial isomerization of the olefinic double bond followed by substitution of the phenyl group with a hydroxy group. The fact that treatment with methyl iodide furnished corresponding silyl ether **6** in good yield (Scheme 2) suggests that a silanolate anion would be formed in the present reaction.

On the basis of our experimental data, we propose the following mechanism for the reaction of **1a** (Scheme 7). Initially, base-catalyzed isomerization of the olefinic double bond took place smoothly to afford alkenylsilane **4a**.[12] Attack of a (methylsulfinyl)methyl anion to the silicon atom, followed by proton abstraction from DMSO, gave sulfonium salt **8** via penta-coordinate silicate species. The nucleophilic attack of **8** by a nucleophile afforded silanolate intermediate **9**. When an allylsilane bearing a less sterically hindered silyl substituent was employed, (methylsulfinyl)methyl anion easily attacked the silyl moiety, leading to the elimination of the allyl group to form silanol **3**.

Conclusion

In conclusion, we have designed a facile method for the preparation of alkenylsilanols from allylsilanes by use of *t*-BuOK in DMSO. In addition, we have elucidated the reaction mechanism on the basis of labeling experiments.

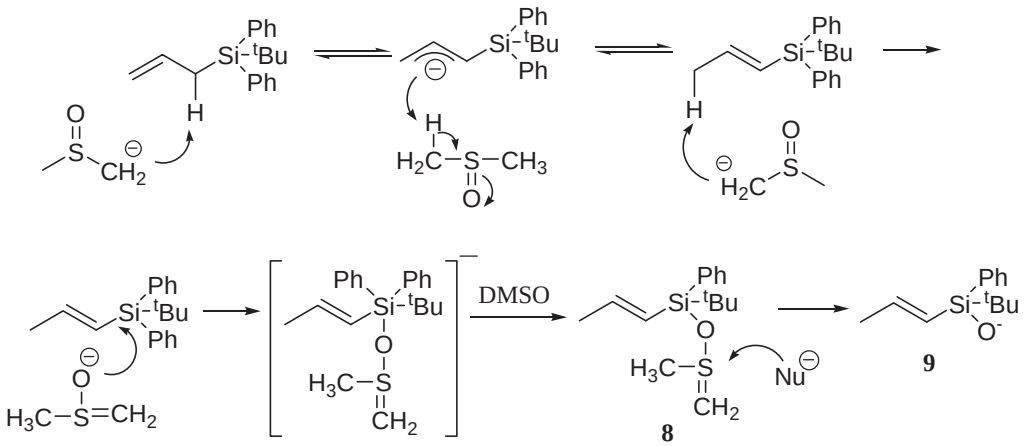
Experimental

NMR spectra were measured in $CDCl_3$ on an AL400 instrument (JEOL, 400 MHz for ^{1}H, 100 MHz for ^{13}C). Tetramethylsilane (TMS) (δ 0) served as an internal standard for ^{1}H NMR and $CDCl_3$ was used as an internal standard (δ 77.0) for ^{13}C NMR. Analytical thin-layer chromatography (TLC) was performed on commercial Merck plates coated with silica gel 60 F-254. Visualization was accomplished with UV light. All reagents were commercially available from Wako Pure Chemical Industries Ltd., Japan.

***t*-Butyldiphenyl-2-propenylsilane (1a).** Allylmagnesium chloride was prepared from allyl chloride and magnesium in THF according to standard procedure. *t*-Butylchlorodiphenylsilane (25 g, 90.96 mmol) was added to the Grignard reagent (150 mL, 181.91 mmol, 1.21 mol L^{-1}) at room temperature. After being stirred at reflux for 3.5 h, the reaction mixture was quenched by adding 1 mol dm^{-3} HCl solution at 0 °C. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to dryness. Purification of the crude mixture by column chromatography (SiO_2, hexane/EtOAc = 30/1, v/v) gave *t*-butyldiphenyl-2-propenylsilane (**1a**) in 91% yield.

Colorless oil. $R_f = 0.6$ (hexane/EtOAc = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.60 (4H, m), 7.37–7.32 (6H, m), 5.77 (1H, ddt, J = 17.0, 10.0, 7.8 Hz), 4.90 (1H, dd, J = 17.0, 3.1 Hz), 4.79 (1H, dd, J = 10.0, 3.1 Hz), 2.18 (2H, dd, J = 7.8, 1.2 Hz), 1.07 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 134.6, 134.4, 129.0, 127.5, 114.5, 27.9, 18.9, 18.6. IR (neat) 2928, 2859, 1470, 1427, 1157, 1104, 895, 820, 764, 732, 697, 624, 613, 578, 482, 425 cm^{-1}. MS(EI) m/z (%) 280 (5), 223 (100), 182 (50), 146 (60). Found: C, 81.55; H, 8.90%. Calcd for $C_{19}H_{24}Si$: C, 81.36; H, 8.62%.

Diisopropylphenyl-2-propenylsilane (1b). A dibutyl ether solution of PhLi (154 mL, 324 mmol, 2.10 mol L^{-1}) was added to a solution of dichlorodiisopropylsilane (50.0 g, 270 mmol) in THF (100 mL) at 0 °C. After being stirred at room temperature for 2 h, allylmagnesium chloride (360 mL, 540 mmol, 1.50 mol L^{-1}), generated by the reaction of allyl chloride and magnesium in another flask, was added to the reaction mixture at 0 °C. After being stirred at reflux for 3 h, the reaction was quenched by adding 1 mol dm^{-3} HCl solution at 0 °C. The aqueous layer



Scheme 7.

was extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to dryness. Purification of the crude mixture by column chromatography (SiO_2, hexane/EtOAc = 30/1, v/v) gave allyldiisopropylphenylsilane (**1b**) in 85% yield.

Colorless oil. $R_f = 0.8$ (hexane/EtOAc = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (2H, d, $J = 6.1$ Hz), 7.38–7.34 (3H, m), 5.91 (1H, dddd, $J = 16.8$, 10.0, 8.1, 8.0 Hz), 4.98 (1H, d, $J = 16.8$ Hz), 4.86 (1H, d, $J = 10.0$ Hz), 1.94 (2H, d, $J = 8.1$ Hz), 1.29 (2H, dq, $J = 7.6$, 7.1 Hz), 1.05–0.94 (12H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 135.1, 133.7, 128.7, 127.5, 113.2, 27.6, 18.6, 18.5, 18.4, 18.3, 10.8, 10.6. IR (neat) 2930, 2855, 1472, 1419, 1110, 888, 820, 764, 739, 710, 611, 573, 423 cm^{-1}. MS(EI) m/z (%) 232 (10), 190 (100), 153 (50), 146 (30), 112 (50). Found: C, 77.90; H, 10.70%. Calcd for $C_{15}H_{24}Si$: C, 77.51; H, 10.41%.

Triphenyl-2-propenylsilane (1c). White crystals; mp 95.4–96.6 °C (hexane). $R_f = 0.6$ (hexane/EtOAc = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.51 (6H, m), 7.44–7.32 (9H, m), 5.88 (1H, dddd, $J = 15.3$, 10.0, 7.8, 2.1 Hz), 4.93 (1H, dd, $J = 15.3$, 1.6 Hz), 4.87 (1H, d, $J = 10.0$ Hz), 2.39 (2H, d, $J = 7.8$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 134.5, 133.7, 129.5, 127.8, 115.0, 21.3. IR (neat) 3039, 1627, 1485, 1427, 1155, 1110, 1044, 1027, 996, 932, 892, 771, 728, 695, 588, 472, 434 cm^{-1}. MS(EI) m/z (%) 300 (60), 259 (50), 223 (100), 146 (50), 69 (10). Found: C, 83.77; H, 6.89%. Calcd for $C_{21}H_{20}Si$: C, 83.94; H, 6.71%.

Dimethylphenyl-2-propenylsilane (1d). Colorless oil. $R_f = 0.8$ (hexane/EtOAc = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.48 (2H, m), 7.34–7.32 (3H, m), 5.77 (1H, ddt, $J = 18.9$, 8.5, 7.8 Hz), 4.84 (1H, d, $J = 18.9$ Hz), 4.83 (1H, d, $J = 8.5$ Hz), 1.74 (2H, d, $J = 7.8$ Hz), 0.27 (3H, s), 0.26 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 134.5, 133.5, 128.9, 127.7, 113.3, 23.86, −3.4. IR (neat) 3069, 2957, 1629, 1427, 1248, 1192, 1155, 1113, 1035, 991, 931, 893, 831, 816, 725, 696, 645, 568, 466 cm^{-1}. MS(EI) m/z (%) 176 (70), 135 (100), 99 (70), 58 (30). Found: C, 75.24; H, 9.33%. Calcd for $C_{11}H_{16}Si$: C, 74.93; H, 9.15%.

***t*-Butyl(2-methyl-2-propenyl)diphenylsilane (1e).** Colorless oil. $R_f = 0.4$ (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.60 (4H, m), 7.40–7.24 (6H, m), 4.56 (2H, d, $J = 5.7$ Hz), 2.20 (2H, s), 1.38 (3H, s), 1.05 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 136.2, 134.9, 129.0, 127.4, 110.8, 27.8, 22.2, 18.6. IR (neat) 2928, 2855, 1615, 1427, 1103, 819, 799, 733, 697, 676, 607, 526, 498, 461, 443, 427 cm^{-1}. MS(EI) m/z (%) 294 (5), 237 (100), 182 (30), 160 (50). Found: C, 81.33; H, 9.02%. Calcd for $C_{20}H_{26}Si$: C, 81.57; H, 8.90%.

2-Butenyl-*t*-butyldiphenylsilane (1f). Colorless oil. $R_f = 0.8$ (hexane/EtOAc = 40/1). ($E/Z = 3/1$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.58 (4H, m), 7.40–7.34 (6H, m), 5.38–5.23 (2H, m), 2.12–2.04 (2H, m), 1.52 (E, 2.25H, d, $J = 7.3$ Hz), 1.42 (Z, 0.75H, d, $J = 6.6$ Hz), 1.05 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.0, 134.7, 128.9, 127.6, 126.4 (E), 125.7 (Z), 124.8 (E), 122.7 (Z), 27.8, 18.5, 18.0 (E), 16.9 (E), 12.7 (Z), 12.0 (Z). IR (neat) 2929, 2856, 1471, 1426, 1104, 963, 820, 753, 735, 697, 665, 651, 604, 512, 481, 458, 411 cm^{-1}. MS(EI) m/z (%) 294 (5), 237 (100), 182 (40), 160 (40). Found: C, 81.25; H, 8.77%. Calcd for $C_{20}H_{26}Si$: C, 81.57; H, 8.90%.

***t*-Butyl(3-methyl-2-butenyl)diphenylsilane (1g).** Colorless oil. $R_f = 0.8$ (hexane/EtOAc = 40/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.57 (4H, m), 7.38–7.30 (6H, m), 5.16 (1H, t, $J = 8.1$ Hz), 2.02 (2H, d, $J = 8.1$ Hz), 1.55 (3H, s), 1.38 (3H, s), 1.06 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 135.0, 128.8, 127.7, 127.3, 119.3, 28.0, 25.8, 18.4, 17.6, 12.6. IR (neat) 2927, 2855, 1470, 1426, 1103, 819, 729, 697, 669, 605, 505, 481, 456, 418, 401 cm^{-1}. MS(EI) m/z (%) 308 (10), 251 (100), 182 (40), 174 (50). Found: C, 82.09; H, 9.33%. Calcd for $C_{21}H_{28}Si$: C, 81.75; H, 9.15%.

3-(*t*-Butyldiphenylsilyl)-1-cyclohexene (1h). 3-Chloro-1-cyclohexene (1.65 g, 14.12 mmol) was added to a solution of tributylstannyl chloride (1.31 g, 4.03 mmol) and magnesium (0.29 g, 12.10 mmol) in THF (10 mL) at reflux. After being stirred at reflux for 3.5 h, the reaction was quenched by adding 1 mol dm^{-3} HCl solution at 0 °C. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to dryness. Purification of the crude mixture by distillation (130–145 °C, 7 Torr) gave 3-(tributylstannyl)-1-cyclohexene in 93% yield as colorless oil. An ether solution of MeLi (3.4 mL, 3.88 mmol, 1.14 mol L^{-1}) was added to a solution of the allylstannane (1.44 g, 3.88 mmol) in THF (30 mL) at −90 °C. After being stirred at −90 °C for 2 h, *t*-butyldiphenylchlorosilane (2.13 g, 7.74 mmol) was added to the reaction mixture at −90 °C. After being stirred at −78 °C for 1.5 h, the reaction was quenched by adding 1 mol dm^{-3} HCl solution at 0 °C. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to dryness. Purification of the crude mixture by column chromatography (SiO_2, hexane/EtOAc = 50/1, v/v) gave 3-(*t*-butyldiphenylsilyl)-1-cyclohexene (**1h**) in 70% yield.

White crystals; mp 81.4–82.5 °C (hexane). $R_f = 0.4$ (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (2H, dd, $J = 1.3$, 6.5 Hz), 7.57 (2H, dd, $J = 1.5$, 6.3 Hz), 7.38–7.30 (6H, m), 5.88 (1H, d, $J = 10.0$ Hz), 5.68–5.65 (1H, m), 2.39–2.36 (1H, m), 1.97–1.93 (2H, m), 1.87–1.83 (1H, m), 1.69–1.65 (2H, m), 1.45–1.39 (1H, m), 1.11 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 134.6, 128.8, 128.4, 127.3, 126.2, 29.0, 25.2, 25.1, 23.69, 23.3, 19.0. IR (neat) 2922, 2854, 2360, 1461, 1425, 1102, 889, 821, 737, 717, 698, 626, 599, 536, 501, 482, 467, 437 cm^{-1}. MS(EI) m/z (%) 320 (15), 263 (15), 240 (100), 186 (50), 183 (30). Found: C, 81.33; H, 9.02%. Calcd for $C_{22}H_{28}Si$: C, 82.43; H, 8.80%.

3-Phenyl-2-propenyl-*t*-butyldiphenylsilane (1i): Prepared according to the method for the preparation of **1h**. Colorless oil. $R_f = 0.4$ (hexane/EtOAc = 40/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.60 (4H, m), 7.37–7.31 (6H, m), 7.19–7.12 (5H, m), 6.23–6.21 (2H, m), 2.33 (2H, d, $J = 7.1$ Hz), 1.09 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 138.2, 135.9, 134.3, 129.8, 129.1, 128.4, 127.5, 126.2, 125.5, 114.5, 28.0, 18.6, 18.2. IR (neat) 2928, 2856, 1470, 1154, 1104, 998, 961, 819, 733, 697, 604, 520, 481 cm^{-1}. MS(EI) m/z (%) 357 (5), 299 (100), 240 (50), 222 (40), 183 (30). Found: C, 84.69; H, 7.65%. Calcd for $C_{25}H_{28}Si$: C, 84.21; H, 7.91%.

Typical Procedure for Preparation of (*E*)-*t*-Butylphenyl-1-propenylsilanol (2a). A solution of *t*-butyldiphenyl-2-propenylsilane (**1a**) (49.0 mg, 0.17 mmol) in DMSO (0.5 mL) and 18-crown-6 (16.6 mg, 0.06 mmol) were successively added to potassium *t*-butoxide (35.3 mg, 0.31 mmol) at room temperature. After being stirred at room temperature for 15 min, the reaction was quenched by adding 1 mol dm^{-3} HCl solution. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to dryness. Purification of the crude mixture by column chromatography (SiO_2, hexane/EtOAc = 7/1, v/v) gave (*E*)-*t*-butylphenyl-1-propenylsilanol (**2a**) in 89% yield ($E/Z = 97/3$).

Colorless oil. $R_f = 0.4$ (hexane/EtOAc = 7/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.55 (2H, m), 7.43–7.32 (3H, m), 6.32 (1H, dq, $J = 18.6$, 6.2 Hz), 5.92 (1H, dq, $J = 18.6$, 1.7 Hz), 2.35–2.29

(1H, br), 1.87 (3H, dd, $J = 6.2$, 1.7 Hz), 0.95 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 134.4, 129.0, 127.3, 127.1, 124.4, 26.6, 25.5, 18.4. IR (neat) 3376, 2929, 2856, 1618, 1471, 1427, 1390, 1361, 1111, 985, 939, 819, 761, 735, 698, 608, 492, 476 cm^{-1}. MS(EI) m/z (%) 220 (5), 163 (100), 137 (20), 123 (90). Found: C, 71.01; H, 8.96%. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15%.

(*E*)-Diisopropyl-1-propenylsilanol (2b). Colorless oil. $R_f = 0.5$ (hexane/EtOAc = 7/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24 (1H, dq, $J = 17.8$, 5.3 Hz), 5.57 (1H, dq, $J = 17.8$, 1.6 Hz), 1.93–1.82 (1H, br), 1.85 (3H, dd, $J = 5.3$, 1.6 Hz), 1.28–1.18 (2H, m), 1.08–0.92 (12H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4, 125.3, 22.8, 17.2, 12.7. IR (neat) 3365, 2928, 2850, 1618, 1472, 1425, 1390, 1362, 1111, 985, 939, 819, 765, 610, 495 cm^{-1}. MS(EI) m/z (%) 172 (10), 129 (100), 76 (40). Found: C, 63.10; H, 11.99%. Calcd for $C_9H_{20}OSi$: C, 62.72; H, 11.70%.

(*E*)-Diphenyl-1-propenylsilanol (2c). White crystals; mp 135.2–137.4 °C (hexane). $R_f = 0.4$ (hexane/EtOAc = 7/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.57 (4H, m), 7.42–7.32 (6H, m), 6.28 (1H, dq, $J = 18.6$, 6.0 Hz), 5.98 (1H, d, $J = 18.6$ Hz), 3.01–2.82 (1H, br), 1.86 (3H, d, $J = 6.0$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 135.1, 134.9, 134.5, 129.7, 127.8, 127.7, 126.2, 22.7. IR (neat) 3246, 3068, 2360, 2324, 1427, 1117, 997, 831, 736, 709, 694, 506 cm^{-1}. MS(EI) m/z (%) 240 (45), 199 (100), 163 (20), 147 (15), 123 (70). Found: C, 74.66; H, 6.99%. Calcd for $C_{15}H_{16}OSi$: C, 74.95; H, 6.71%.

***t*-Butyl-(2-methyl-1-propenyl)phenylsilanol (2e).** Colorless oil. $R_f = 0.4$ (hexane/EtOAc = 7/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.59 (2H, m), 7.40–7.33 (3H, m), 5.51 (1H, s), 2.08–1.93 (1H, br), 1.92 (3H, s), 1.72 (3H, s), 0.94 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 135.2, 134.8, 129.6, 127.7, 117.7, 26.6, 25.9, 24.0, 18.4. IR (neat) 3421, 2929, 2856, 1617, 1471, 1427, 1361, 1111, 1007, 939, 807, 737, 698, 607, 502, 447 cm^{-1}. MS(EI) m/z (%) 177 (100), 122 (50). Found: C, 72.01; H, 9.11%. Calcd for $C_{14}H_{22}OSi$: C, 71.73; H, 9.46%.

(*E*)-(1-Butenyl)-*t*-butylphenylsilanol (2f). Colorless oil. $R_f = 0.4$ (hexane/EtOAc = 7/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.57 (2H, m), 7.41–7.40 (3H, m), 6.37 (1H, dt, $J = 18.7$, 6.3 Hz), 5.88 (1H, dd, $J = 18.7$, 1.1 Hz), 2.18 (2H, dq, $J = 7.6$, 6.3 Hz), 2.12–2.04 (1H, br), 0.96 (3H, t, $J = 7.6$ Hz), 0.95 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 136.0, 134.5, 129.3, 127.5, 121.7, 27.8, 26.0, 18.4, 17.9. IR (neat) 3411, 2929, 2856, 2360, 1471, 1427, 1391, 1361, 1112, 998, 819, 737, 698, 606, 503, 486, 431 cm^{-1}. MS(EI) m/z (%) 177 (100), 122 (50). Found: C, 71.50; H, 9.56%. Calcd for $C_{14}H_{22}OSi$: C, 71.73; H, 9.46%.

(*E*)-(2-Butenyl)-*t*-butylphenylsilanol (5f). Colorless oil. $R_f = 0.4$ (hexane/EtOAc = 7/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.57 (2H, m), 7.41–7.40 (3H, m), 5.42–5.36 (2H, m), 2.48–2.36 (1H, br), 1.85 (2H, d, $J = 7.1$ Hz), 1.56 (3H, d, $J = 5.1$ Hz), 0.93 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 134.1, 129.5, 127.4, 125.5, 125.0, 27.8, 27.0, 19.1, 18.6. IR (neat) 3411, 2929, 2856, 2360, 1471, 1427, 1391, 1361, 1112, 998, 819, 737, 698, 606, 503, 486, 431 cm^{-1}. MS(EI) m/z (%) 177 (100), 122 (50). Found: C, 71.52; H, 9.56%. Calcd for $C_{14}H_{22}OSi$: C, 71.73; H, 9.46%.

***t*-Butyl(3-methyl-2-butenyl)phenylsilanol (5g).** Colorless oil. $R_f = 0.4$ (hexane/EtOAc = 7/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.57 (2H, m), 7.40–7.34 (3H, m), 5.30 (1H, dd, $J = 7.6$, 1.3 Hz), 2.39–2.28 (1H, br), 1.83 (2H, dd, $J = 12.2$, 7.6 Hz), 1.64 (3H, s), 1.57 (3H, s), 0.96 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8, 134.2, 130.7, 129.4, 127.5, 118.2, 26.1, 25.8, 18.5, 17.8, 13.9. IR (neat) 3414, 2929, 2856, 1471, 1427, 1361, 1111, 998, 819, 737, 698, 606, 502, 487, 431 cm^{-1}. MS(EI) m/z (%) 248 (20), 191 (100), 179 (20), 123 (20). Found: C, 72.90; H, 10.11%. Calcd for $C_{15}H_{24}OSi$: C, 72.52; H, 9.74%.

***t*-Butyl(1-cyclohexenyl)phenylsilanol (2h).** Colorless oil. $R_f = 0.4$ (hexane/EtOAc = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.60 (2H, m), 7.38–7.31 (3H, m), 6.30 (1H, m), 2.20–2.11 (2H, m), 2.11–2.04 (2H, m), 2.02–1.94 (1H, br), 1.65–1.55 (4H, m), 1.00 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 135.7, 134.5, 134.4, 129.2, 127.5, 28.0, 26.9, 25.7, 22.9, 22.2, 18.88. IR (neat) 3419, 2927, 2855, 1609, 1471, 1427, 1361, 1061, 936, 800, 738, 696, 612, 553, 506, 478 cm^{-1}. MS(EI) m/z (%) 260 (10), 203 (100), 123 (30). Found: C, 74.03; H, 9.60%. Calcd for $C_{16}H_{24}OSi$: C, 73.79; H, 9.29%.

***t*-Butyldiphenylsilanol (3a).** Colorless oil. $R_f = 0.4$ (hexane/EtOAc = 7/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.70 (4H, m), 7.40–7.35 (6H, m), 2.35–2.29 (1H, br), 1.06 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1, 134.7, 129.6, 127.7, 26.6, 19.1. IR (neat) 3445, 2929, 2856, 1674, 1598, 1471, 1112, 820, 741, 700, 607, 505 cm^{-1}. MS(EI) m/z (%) 256 (5), 199 (100). Found: C, 74.88; H, 7.95%. Calcd for $C_{16}H_{20}OSi$: C, 74.95; H, 7.86%.

(*E*)-*t*-Butyldiphenyl-1-propenylsilane (4a). A solution of *t*-butyldiphenyl-2-propenylsilane (**1a**) (48.1 mg, 0.17 mmol) in DMF (0.5 mL) was added to potassium *t*-butoxide (38.5 mg, 0.34 mmol) at room temperature. After being stirred at room temperature for 15 min, the reaction was quenched by adding 1 mol dm^{-3} HCl solution. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to dryness. Purification of the crude mixture by column chromatography (SiO_2, hexane/EtOAc = 25/1, v/v) gave **4a** in 90% yield.

Colorless oil. $R_f = 0.5$ (hexane/EtOAc = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.57 (4H, m), 7.39–7.30 (6H, m), 6.08–6.03 (2H, m), 1.90 (3H, dd, $J = 2.9$, 1.5 Hz), 1.07 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 136.2, 135.1, 128.9, 127.5, 124.6, 27.3, 23.0, 18.1. IR (neat) 2958, 2928, 2856, 1617, 1457, 1192, 1104, 1049, 819, 697, 605, 506, 486 cm^{-1}. MS(EI) m/z (%) 223 (100), 183 (40), 146 (15), 105 (25). Found: C, 81.41; H, 8.84%. Calcd for $C_{19}H_{24}Si$: C, 81.36; H, 8.62%.

(*E*)-*t*-Butylphenyl-1-propenylsilyl Methyl Ether (6). A solution of *t*-butyldiphenyl-2-propenylsilane (**1a**) (47.4 mg, 0.17 mmol) in DMSO (0.5 mL) and 18-crown-6 (13.4 mg, 0.05 mmol) were successively added to potassium *t*-butoxide (28.4 mg, 0.25 mmol) at room temperature. After being stirred at that temperature for 20 min, the reaction was quenched by adding methyl iodide (119.9 mg, 0.84 mmol). After stirring the reaction mixture for 10 min, water was added. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to dryness. Purification of the crude mixture by column chromatography (SiO_2, hexane/EtOAc = 40/1, v/v) gave *t*-butylphenyl-1-propenylsilyl methyl ether (**6**) in 77% yield.

Colorless oil. $R_f = 0.4$ (hexane/EtOAc = 40/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.53 (2H, m), 7.42–7.30 (3H, m), 6.35 (1H, dq, $J = 18.8$, 6.1 Hz), 5.84 (1H, d, $J = 18.8$ Hz), 3.50 (3H, s), 1.84 (3H, d, $J = 6.1$ Hz), 0.92 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 135.2, 134.1, 129.3, 127.5, 123.1, 51.7, 26.0, 23.0, 18.3. IR (neat) 2930, 2856, 1617, 1472, 1427, 1188, 1082, 988, 823, 734, 700, 611, 503 cm^{-1}. MS(EI) m/z (%) 177 (100), 137 (40), 107 (20). Found: C, 71.49; H, 9.61%. Calcd for $C_{14}H_{22}OSi$: C, 71.73; H, 9.46%.

Dibutyl Sulfoxide-^{18}O (7). A solution of dibutyl sulfide (10.00 g, 68.36 mmol) in dried methanol (20 mL) and water-^{18}O

(2.00 g, 100.00 mmol) was added to *N*-bromosuccinimide (13.14 g, 75.19 mmol) and the temperature was kept at 10 °C. After being stirred and keeping the reaction mixture at 0 °C for 45 min, CH_2Cl_2 was added. The organic layers were washed successively with sat. $NaHCO_3$, brine, dried over anhydrous Na_2SO_4, and concentrated to dryness. Purification of the crude mixture by distillation (122–125 °C, 3 Torr) gave dibutyl sulfoxide-^{18}O (**6**) in 88% (^{18}O content: 90%) yield as colorless crystals.

Colorless crystals. mp 32.3–34.1 °C. $R_f = 0.2$ (hexane/EtOAc = 1/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.69 (4H, t, $J = 7.7$ Hz), 1.79–1.71 (4H, m), 1.59–1.42 (4H, m), 0.97 (6H, t, $J = 7.3$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.0, 23.1, 21.7, 12.7. IR(neat) 2656, 2928, 2871, 1466, 1412, 983, 920, 736, 427 cm^{-1}. MS(EI) m/z (%) 164 (30), 146 (50), 108 (60), 89 (100), 61 (60). Found: C, 59.01; H, 11.55%. Calcd for $C_8H_{18}{}^{18}OS$ (^{18}O content: 90%): C, 59.14; H, 11.73%.

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