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Mechanistic Studies of the Allylic Rearrangements of α-Silyloxy Allylic Silanes to Silyloxy Vinylic Silanes

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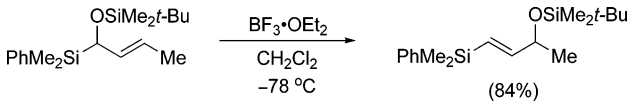
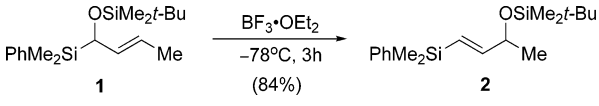


Mechanistic evidence suggests that the Lewis acid-promoted allylic rearrangement of α-silyloxy allylic silanes proceeds along an ionic reaction pathway involving a contact ion pair. The driving force for this transformation is alleviation of steric congestion at the allylic position of the α-silyloxy allylic silane and stabilization of π_{cc} by hyperconjugation.

Although α-oxygenated allylic silanes are useful reagents for organic synthesis,[1,2] their utility has been limited because of their sensitivity toward decomposition. It has been reported that both α-acetoxy allylic silanes and α-hydroxy allylic silanes undergo rearrangements under acidic conditions.[3,4] In this Note, we demonstrate that α-silyloxy allylic silanes undergo rapid allylic rearrangements to provide α-silyloxy vinylic silanes. These reactions are faster than the rearrangements of other α-oxygenated allylic silanes. Mechanistic studies suggest that ionization to form a contact ion pair is rate-determining, and the rate of ionization depends upon steric effects more than it depends upon electronic effects.

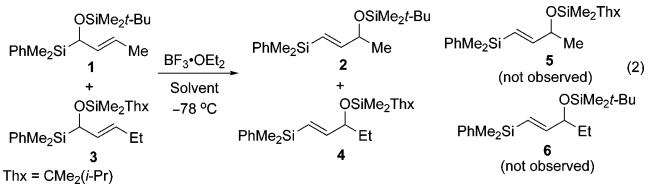
A study of α-silyloxy allylic silanes as nucleophilic partners in [3+2] annulations[1] led to the discovery of a rearrangement involving the α-silyloxy allylic silanes. Treating α-silyloxy allylic silane **1** with BF_3•OEt_2 resulted in the formation of silyloxy vinylic silane **2** in 84% yield (eq 1). A comparable



(1)

rearrangement involving α-acetoxy allylic silanes was previously reported with use of BF_3•OEt_2 catalysis at higher temperatures.[3] A direct comparison between the two substrates showed that the α-silyloxy allylic silanes were more reactive than α-acetoxy allylic silanes toward this rearrangement. This discovery was unexpected considering that the α-acetoxy allylic silane could rearrange by a concerted [3,3] sigmatropic process or through an ionization mechanism that proceeds through a less basic acetate counterion. To discover the origins of the increased reactivity of the α-silyloxy allylic silane, a detailed mechanistic study was undertaken.

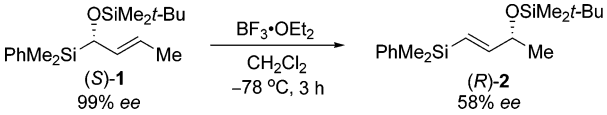
A crossover experiment between two distinct α-silyloxy allylic silanes demonstrated that the rearrangement was an intramolecular process. Treating a mixture of allylic silanes **1** and **3** with BF_3•OEt_2 afforded only vinylic silanes **2** and **4** (eq 2); crossover products **5** and **6** were not observed. The crossover



(2)

experiment was repeated in a variety of polar solvents, including 2-nitropropane, and at different concentrations (0.014 and 1.4 M) in CH_2Cl_2.[5] In all cases, increased solvation did not provide the crossover products, verifying that the transformation was an intramolecular rearrangement.

An asymmetric variant of the α-silyloxy allylic silane rearrangement established that the rearrangement proceeds via a contact ion pair. Treatment of enantioenriched allylic silane (*S*)-**1** with BF_3•OEt_2 afforded the vinylic silane (*R*)-**2** with a diminished enantiomeric excess (eq 3).[6] The absolute stereochemistry of the major enantiomer of the vinylic silane was deduced from the known deprotected alcohol.[7] The partial retention observed, coupled with a lack of crossover products, suggested an ionic mechanism was operating through a contact ion pair.



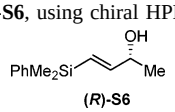
(3)

Control experiments provided additional support for the contact ion pair mechanism. To discount racemization occurring prior to the rearrangement, the stereochemistry scrambling experiment was repeated and stopped prior to completion (eq 4). Analysis of the recovered starting material revealed no loss of stereochemical information,[8] indicating that racemization was

(1) Romero, A.; Woerpel, K. A. *Org. Lett.* **2006**, *8*, 2127−2130.
(2) Perrone, S.; Knochel, P. *Org. Lett.* **2007**, *9*, 1041−1044.
(3) Panek, J. S.; Sparks, M. A. *J. Org. Chem.* **1990**, *55*, 5564−5566.
(4) Sakaguchi, K.; Higashino, M.; Ohfune, Y. *Tetrahedron* **2003**, *59*, 6647−6658.

(5) Rearrangements were carried out successfully in CH_2Cl_2 and 2-nitropropane. Other solvents such as toluene and propionitrile provided the rearrangement, but other products were also formed.

(6) Analysis of the isolated vinylic silane indicates that the partial chirality transfer occurred with retention of configuration. The analysis consisted of deprotection of the vinylic silane to afford the alcohol **S6** and comparing it to the known[7] alcohol (*R*)-**S6**, using chiral HPLC analysis.[7]



(*R*)-**S6**

(7) Smitrovich, J. H.; Woerpel, K. A. *J. Org. Chem.* **2000**, *65*, 1601−1614.

(8) Analysis was performed with the use of optical rotations because the allylic silanes could not be resolved by HPLC. Attempts to deprotect allylic silanes were unsuccessful due to a competing Brook rearrangement.

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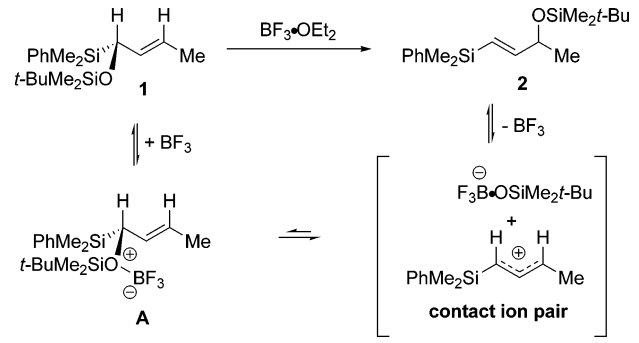
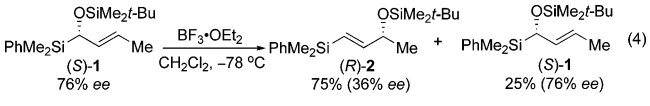
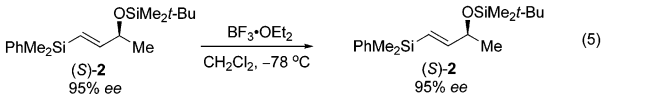
SCHEME 1. Proposed Mechanism for Allylic Rearrangement



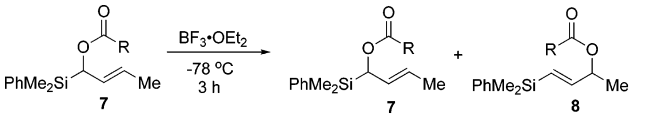
not occurring before the rearrangement. To discount the possibility of racemization occurring after the rearrangement, enantiomerically enriched vinylic silane (*S*)-**2** was subjected to the rearrangement conditions for 3 h (eq 5). The recovered vinylic silane revealed no loss of stereochemical information, so racemization does not occur after the rearrangement.





Both the crossover and the stereochemistry scrambling experiments suggest an intramolecular ionic mechanism consistent with a contact ion pair. According to these data, we propose the mechanism illustrated in Scheme 1. Complexation of the Lewis acid[9] would afford intermediate **A**. This intermediate can adopt a conformation that minimizes A^{1,3} strain[10] and allows for $\pi_{CC} \rightarrow \sigma^*_{CO}$ donation likely required for ionization.[11] Dissociation of the silyl ether from **A** affords a Lewis acid-complexed silanol and an allylic cation. Accessing the allylic cation through the lowest energy conformer **A** provides the (*E*)-allylic cation, which would lead to the (*E*)-olefin.[12] Recombination then affords the thermodynamically preferred vinylic silane (vide infra) with retention because the Lewis acid-complexed silanol recombines on the same face of the cation on which it is formed. This mechanism agrees with our experimental data and may also be used to explain the α-acetoxy rearrangement reported previously.[3]

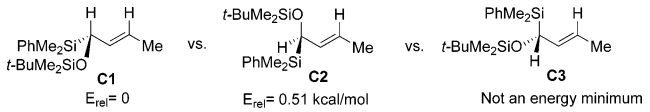
Steric effects were found to play a significant role in the rate of the reaction. Previous studies had demonstrated that α-acetoxy allylic silanes rearrange at 24 °C under BF_3•OEt_2 catalysis to afford α-acetoxy vinylic silanes.[3] Exposing α-acetoxy allylic silane **7a** to the rearrangement conditions yielded no rearrangement (eq 6). Treatment of the more sterically encumbered α-pivalyloxy allylic silane **7b** with BF_3•OEt_2 at −78 °C for 3 h afforded pivalyloxy vinylic silane **8b** in 20% yield (eq 7). These experiments support the hypothesis that steric interactions activate the α-silyloxy allylic silanes toward rearrangement.[13]



Steric and electronic preferences drive the Lewis acid-catalyzed rearrangement to the thermodynamically preferred α-silyloxy vinylic silane. Ab initio calculations illustrate a thermodynamic preference for recombination of the contact ion pair at the γ-position over the α-position.[14] This preference arises from alleviation of steric congestion.[15] Ab initio calculations also demonstrate a thermodynamic preference of vinylic silanes over allylic silanes.[16] These calculations are in good agreement with previous reports that attribute the stabilization of vinylic silanes to hyperconjugation of the $\pi_{CC} \rightarrow \sigma^*_{Si-C}$ orbitals.[17,18] The experimental data and ab initio calculations show that the driving force for this rearrangement is relief of steric interactions and hyperconjugation.

(9) For evidence supporting Lewis acid chelation of an OSiMe$_2$*t*-Bu group see: Chen, X.; Hortelano, E. R.; Eliel, E. L.; Frye, S. V. *J. Am. Chem. Soc*. **1992**, *114*, 1778−1784.

(10) Possible conformations **C1**−**C3** were calculated by using ab initio calculations performed at the HF/6-31G* level, using Macspartan (Wavefunction, Irvine, CA). Conformation **C1** was the lowest energy conformer by 0.51 kcal/mol relative to **C2**. Conformer **C3** was found to not be an energy minimum.

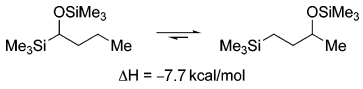


(11) The orbital overlap of $\pi_{CC} \rightarrow \sigma^*_{CO}$ is much better in **C1** than **C2** because the two orbitals are orthogonal to each other in **C2**.

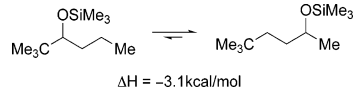
(12) The barrier to rotation of the allyl cation is estimated to be 36−38 kcal/mol: (a) Wiberg, K. B.; Breneman, C. M.; LePage, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 61−72. (b) Gobbi, A.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 9275−9286.

(13) Attempts to influence the rearrangement by varying the size of the silyl substituent were unsuccessful. Utilizing the Me$_3$Si-protected allylic silane led to the deprotected α-hydroxy allylic silane. Utilizing the *i*-Pr$_3$-Si-protected allylic silane, the rearrangement proceeded at the same rate, within experimental error, as the *t*-BuMe$_2$Si-protected allylic silane.

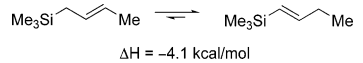
(14) The energetic difference between 1-trimethylsilyl-1-trimethylsilyloxybutane and 1-trimethylsilyl-3-trimethylsilyloxybutane was calculated using ab initio calculations performed at the HF/6-31G* level. 1-Trimethylsilyl-3-trimethylsilyloxybutane was lower in energy, presumably for steric reasons.



(15) To ensure the energy difference between 1-trimethylsilyl-1-trimethylsilyloxybutane and 1-trimethylsilyl-3-trimethylsilyloxybutane was due to steric and not electronic effects, ab initio calculations were performed for 2,2-dimethyl-3-trimethylsilyloxyhexane and 2,2-dimethyl-5-trimethylsilyloxyhexane at the HF/6-31G* level. The calculation showed the same preference for both the *tert*-butyl and Me$_3$Si groups, suggesting that this was indeed a steric phenomenon and not an electronic one.



(16) To determine if any stereoelectronic preference existed for the alkene, calculations were carried out between but-2-enyltrimethylsilane and but-1-enyltrimethylsilane. A preference was found for vinylic silanes over allylsilanes presumably due to hyperconjugation in the vinylic silane.[18] Ab initio calculations were performed at the HF/6-31G* level.



(17) (a) Bock, H.; Seidl, H. *J. Am. Chem. Soc.* **1968**, *90*, 5694−5700. (b) Mollére, P.; Bock, H.; Becker, G.; Fritz, G. *J. Organomet. Chem.* **1972**, *46*, 89−96. (c) Horn, M.; Murrell, J. N. *J. Organomet. Chem.* **1974**, *70*, 51−60.

(18) (a) Giordan, J. C.; Moore, J. H. *J. Am. Chem. Soc.* **1983**, *105*, 6541−6544. (b) Giordan, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 6544−6546.

The Lewis acid-catalyzed rearrangement of α-silyloxy allylic silanes to silyloxy vinylic silanes has been examined. The rearrangement proceeds through an ionic mechanism involving an ion pair. The formation of silyloxy vinylic silanes is thermodynamically favorable due to alleviation of the steric congestion between the two geminal silyl moieties of the α-silyloxy allylic silane and the stabilization of the vinylic silanes by hyperconjugation.

Experimental Section

Representative Procedure for the Isolation of α-Siloxy Allylic Silanes. To a solution of $PhMe_2SiCl$ (1.15 equiv) in THF (0.35 M) was added finely cut lithium wire (9.2 equiv). The suspension was stirred at 24 °C for 18 h. The resultant $PhMe_2SiLi$ solution was transferred by cannula to a clean flask and cooled to −78 °C. Crotonaldehyde (1.00 equiv) in THF (1.2 M) was then added dropwise. The solution was stirred for 20 min at −78 °C, and then the reaction mixture was added to saturated aqueous NH_4Cl. The resultant layers were separated and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with saturated aqueous NaCl. The resultant organic phase was dried over $MgSO_4$ and filtered. The filtrate was concentrated in vacuo to afford the α-hydroxy allylic silane as a yellow oil. The oil was then dissolved in anhydrous DMF (2 M) followed by the addition of TBDMSCl (1.05 equiv) and imidazole (2.05 equiv). The solution was allowed to stir at 23 °C for a minimum of 12 h. The reaction mixture was diluted with hexanes and the resultant solution was washed with saturated aqueous NH_4Cl. The layers were separated and the aqueous layer was extracted with hexanes. The combined organic layers were washed with saturated aqueous NaCl. The resultant organic phase was dried over $MgSO_4$ and filtered. The filtrate was concentrated in vacuo to afford the α-silyloxy allylic silane as a light yellow oil. Purification by flash chromatography (hexanes) afforded the α-silyloxy allylic silanes as colorless oils.

α-Silyloxy Allylic Silane 1: GC t_R 12.4 min (50 °C, 10 deg/min); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (m, 2H), 7.35 (m, 3H), 5.42 (m, 2H), 4.04 (dt, J = 6.1, 1.5 Hz, 1H), 1.66 (dt, J = 6.1, 1.3 Hz, 3H), 0.88 (s, 9H), 0.30 (s, 3H), 0.28 (s, 3H), −0.04 (s, 3H), −0.11 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.7, 134.6, 132.2, 129.2, 127.7, 122.2, 68.4, 26.1, 18.4, 18.0, −4.1, −5.0, −5.3, −5.6; IR (thin film) 2957, 1472, 1252, 1084 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{32}OSi_2Na$ $(M + Na)^+$ 343.1889, found 343.1888. Anal. Calcd for $C_{18}H_{32}OSi_2$: C, 67.43; H, 10.06. Found: C, 67.23; H, 10.21.

α-Silyloxy Allylic Silane 3: GC t_R 15.5 min (50 °C, 10 deg/min); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (m, 2H), 7.35 (m, 3H), 5.42 (m, 2H), 4.05 (m, 1H), 2.0 (m, 2H), 1.68 (septet, J = 6.9 Hz, 1H), 0.95 (t, J = 7.4 Hz, 3H), 0.90 (d, J = 6.8 Hz, 3H), 0.88 (d, J = 6.8 Hz, 3H), 0.83 (s, 3H), 0.82 (s, 3H), 0.38 (s, 3H), 0.32 (s, 3H), 0.01 (s, 3H), −0.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.7, 134.6, 130.3, 129.6, 129.2, 127.6, 68.5, 34.4, 25.7, 25.3, 20.7, 20.6, 18.9, 18.8, 14.4, −1.9, −3.1, −5.3, −5.6; IR (thin film) 2959, 1464, 1251, 1028 cm^{-1}. Anal. Calcd for $C_{21}H_{38}OSi_2$: C, 69.54; H, 10.56. Found: C, 69.65; H, 10.75.

Asymmetric Reduction with a Chiral Lithium Amide:[19] α-Silyloxy Allylic Silane (−)-1. The asymmetric reduction was performed according to the Takeda procedure.[19] To a cooled (−80 °C) solution of (1-oxo-2-butenyl)dimethylphenylsilane[20] (0.600 g, 2.94 mmol) in THF (20 mL) was added chiral lithium amide dropwise [the chiral lithium amide was freshly prepared by treating (*S*)-*N*-(2,2-dimethylpropyl)-1-phenyl-2-(4-methylpiperazinyl)ethylamine (1.02 g, 3.52 mmol) with *n*-butylithium (1.4 mL, 3.5 mmol, 2.5 M solution in hexanes)]. The mixture was stirred for 30 min at −80 °C then diluted with acetic acid (0.11 g, 1.9 mmol) in THF (2 mL). The resultant solution was poured into half-saturated aqueous NH_4Cl (50 mL) and extracted with Et_2O (3 × 50 mL). The combined organic phases were washed with saturated aqueous NaCl (75 mL), dried over Na_2SO_4, and concentrated in vacuo to afford a bright yellow oil. Purification by flash chromatography (97:3 hexanes/EtOAc to 80:20 hexanes/EtOAc) afforded α-hydroxy allylic silane (0.325 g, 54%) as a slightly yellow oil. The α-hydroxy allylic silane was isolated in ≥99% ee by chiral HPLC (Chiralcel OD-H column, 99:1 hexanes/IPA, 1 mL/min, 254 nm). The oil was dissolved in DMF (1.0 mL) and TBDMSCl (0.250 g, 1.66 mmol) and imidazole (0.221 g, 3.24 mmol) were added. The reaction mixture was stirred for 12 h, at which point hexanes (10 mL) was added and the resultant solution was washed with saturated aqueous NH_4Cl (10 mL). The layers were separated and the aqueous layer was re-extracted with hexanes (3 × 8 mL). The combined organic layers were washed with saturated aqueous NaCl (10 mL). The resultant organic phase was dried over $MgSO_4$ and filtered. The filtrate was concentrated in vacuo to afford the α-silyloxy allylic silane as a light yellow oil. Purification by flash chromatography (hexanes) afforded (−)-**1** as a colorless oil (0.080 g, 16%). The product was identical with (±)-**1** by ^{1}H NMR and ^{13}C NMR spectroscopic analysis (vide supra): $[\alpha]^{20}_D$ −35.0 (*c* 1.03, $CHCl_3$).

Asymmetric Reduction with a Chiral Borane:[4] α-Siloxy Allylic Silane (−)-1. To a cooled (−78 °C) solution of (+)-DIP-Cl (3.14 g, 9.79 mmol) in anhydrous THF (10 mL) was added a solution of (1-oxo-2-butenyl)dimethylphenylsilane[20] (0.800 g, 3.92 mmol) in anhydrous THF (10 mL). The resultant solution was then allowed to warm to 23 °C. After the solution was stirred for 52 h at 23 °C, diethanolamine (2.31 g, 22.0 mmol) was added. The resultant suspension was stirred for 14 h at 23 °C. Diethyl ether (100 mL) was added, and the solution was filtered. The filtrate was dried over $MgSO_4$ and filtered again. The filtrate was concentrated in vacuo to afford the α-hydroxy allylic silane as a light yellow oil. Purification by flash chromatography (hexanes to 90:10 hexanes:EtOAc) afforded α-hydroxy allylic silane (0.350 g, 44%) as a light yellow oil. The α-hydroxy allylic silane was isolated in 76% ee by chiral HPLC (Chiralcel OD-H column, 99:1 hexanes/IPA, 1 mL/min, 254 nm). The α-hydroxy allylic silane (0.165 g, 0.804 mmol) was dissolved in DMF (0.8 mL), and TBDMSCl (0.182 g, 1.21 mmol) and imidazole (0.138 g, 2.01 mmol) were added. The solution was stirred at 23 °C for 36 h. The reaction mixture was diluted with hexanes (15 mL) and the resultant solution was washed with saturated aqueous NH_4Cl (15 mL). The layers were separated and the aqueous layer was extracted with hexanes (3 × 10 mL). The combined organic layers were washed with saturated aqueous NaCl (15 mL). The resultant organic phase was dried over $MgSO_4$ and filtered. The filtrate was concentrated in vacuo to afford the α-siloxy allylic silane as a light yellow oil. Purification by flash chromatography (hexanes) afforded (−)-**1** as a colorless oil (0.160 g, 63%). The product was identical with (±)-**1** by ^{1}H NMR and ^{13}C NMR spectroscopic analysis (vide supra): $[\alpha]^{23}_D$ −25.1 (*c* 1.00, $CHCl_3$).

Representative Procedure for α-Silyloxy Allylic Silane Rearrangement. To a cooled solution (−78 °C) of α-silyloxy allylic silane in methylene chloride (0.1 M) was added $BF_3{\cdot}OEt_2$ (1.1 equiv). After 3 h at −78 °C an aqueous solution of $NaHCO_3$ was added. The resultant layers were separated and the aqueous layer was re-extracted with EtOAc. The combined organic layers were washed with saturated aqueous NaCl, dried over $MgSO_4$, and filtered. The filtrate was concentrated in vacuo to afford the silyloxy vinylic silane as a light yellow oil. Vinylic silanes were purified by silica gel chromatography (2% EtOAc/98% hexanes).

Silyloxy vinylic silane 2: GC t_R 12.8 min (50 °C, 10 deg/min); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (m, 2H), 7.37 (m, 3H), 6.15 (dd, J = 18.6, 4.4 Hz, 1H), 5.95 (d, J = 18.6 Hz, 1H), 4.35 (m, 1H), 1.23 (d, J = 6.4 Hz, 3H), 0.92 (s, 9H), 0.35 (s, 6H), 0.07 (s,

(19) Takeda, K.; Ohnishi, Y.; Koizumi, T. *Org. Lett.* **1999**, *1*, 237−239.

(20) Danheiser, R. L.; Fink, D. M.; Okano, K.; Tsai, Y.-M.; Szczepanski, S. W. *J. Org. Chem.* **1985**, *50*, 5393−5396.

6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.5, 139.3, 134.2, 129.3, 128.1, 124.9, 71.5, 26.3, 24.3, 18.7, −2.2, −2.3, −4.3, −4.4; IR (thin film) 2956, 2857, 1620, 1250 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{32}OSi_2Na$ $(M + Na)^+$ 343.1889, found 343.1886.

Silyloxy vinylic silane 4: GC t_R 13.7 min (50 °C, 10 deg/min); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (m, 2H), 7.37 (m, 3H), 6.05 (dd, J = 18.7, 5.6 Hz, 1H), 5.89 (dd, J = 18.7, 1.0 Hz, 1H), 4.09 (m, 1H), 1.68 (septet, J = 6.8 Hz, 1H), 1.50 (m, 2H), 0.89 (d, J = 6.8 Hz, 6H), 0.86 (m, 3H), 0.84 (s, 6H), 0.34 (s, 6H), 0.09 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.6, 139.2, 134.1, 129.1, 127.9, 126.3, 77.0, 34.4, 30.8, 25.3, 20.6, 18.9, 9.9, −2.0, −2.2, −2.3, −2.5; IR (thin film) 2959, 1250, 831 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{21}H_{38}OSi_2Na$ $(M + Na)^+$ 385.2359, found 385.2360. Anal. Calcd for $C_{18}H_{32}OSi_2$: C, 69.54; H, 10.56. Found: C, 69.32; H, 10.40.

Crossover Rearrangement. To a cooled solution (−78 °C) of α-silyloxy allylic silane **1** (0.177 g, 0.551 mmol) and α-silyloxy allylic silane **3** (0.200 g, 0.551 mmol) in 4 mL of solvent was added $BF_3{\cdot}OEt_2$ (0.162 g, 1.14 mmol). After 3 h at −78 °C, an aqueous solution of $NaHCO_3$ (15 mL) was added. The resultant layers were separated and the aqueous layer was extracted with 3 × 5 mL of hexanes. The combined organic layers were washed with saturated aqueous NaCl (15 mL), dried over $MgSO_4$, and filtered. GC analysis revealed the formation of vinylic silanes **2** and **4** exclusively.

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Supporting Information Available: Full experimental details, spectral data, and characterization for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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