The Hydroboration of 3-Chloro-1-trimethylsilyl-1-propyne with Dialkylboranes and Its Application to the Syntheses of (*E*)-3-Trimethylsilyl-2-alkenes and 3-Trimethylsilyl-1-alkenes

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The reaction of 3-chloro-1-trimethylsilyl-1-propyne with a stoichiometric amount of dialkylborane proceeds to the monohydroboration stage, giving a mixture of regioisomers, (*Z*)-dialkyl(3-chloro-1-trimethylsilyl-1-propenyl)borane and (*Z*)-dialkyl[1-chloromethyl-2-(trimethylsilyl)vinyl]borane. The hydroboration mixture is protonolyzed with acetic acid to give (*Z*)-3-chloro-1-trimethylsilyl-1-propene in a quantitative yield. Treatment of the hydroboration mixture with aqueous sodium hydroxide gives a good yield of highly pure (*E*)-3-trimethylsilyl-2-alkene whose alkyl group migrates from the boron atom. On the other hand, successive treatment of the hydroboration mixture with methyllithium and acetic acid gives a good yield of 3-trimethylsilyl-1-alkene whose alkyl group migrates from the boron atom. The above procedures provide convenient syntheses of (*E*)-3-trimethylsilyl-2-alkenes and 3-trimethylsilyl-1-alkenes. It is proposed that both products are afforded through the corresponding allylboranes derived from (*Z*)-dialkyl(3-chloro-1-trimethylsilyl-1-propenyl)borane, respectively. Thus, the former is formed by hydrolysis of alkyl[1-alkyl-1-(trimethylsilyl)allyl]hydroxyborane, while the latter is formed by protonolysis of alkylmethyl[3-alkyl-3-(trimethylsilyl)allyl]borane.

Alkenylboranes are receiving much attention as versatile intermediates in organic synthesis.[1] Alkenylboranes having one or more functionalities in the neighborhood of the alkenyl moiety are expected to be potential intermediates. For example, 1-halo-1-alkenylboranes can be utilized for a variety of organic transformations.[2] In the course of our study on such alkenylboranes[3] we became interested in the hydroboration of 3-chloro-1-trimethylsilyl-1-propyne (**1**) whose hydroboration would provide doubly functionalized alkenylborane expected to be an interesting intermediate. We herein report the hydroboration of **1** with dialkylboranes (**2**) and its application to the synthesis of trimethylsilylated alkenes.[4]

Results and Discussion

A stoichiometric hydroboration of **1** with dicyclohexylborane (**2a**) was carried out in tetrahydrofuran (THF) at 0 °C. After 2 h of the reaction, no residual **1** and no residual hydride of **2a** was detected by GLC or by hydrolysis of the reaction mixture, respectively.

The ^{1}H NMR spectrum of the reaction mixture, obtained after removal of THF, included a triplet (J=7.8 Hz) and a singlet peak in the alkenyl proton region, and a doublet(J=7.8 Hz) and a singlet peak in the α-monosubstituted aliphatic proton region. On the other hand, treatment of the reaction mixture with acetic acid, a well known method for conversion of the carbon–boron bond of alkenylboranes into a carbon–hydrogen bond with retention of configuration, afforded (*Z*)-3-chloro-1-trimethylsilyl-1-propene (**5**) in a quantitative yield with high stereochemical purity.

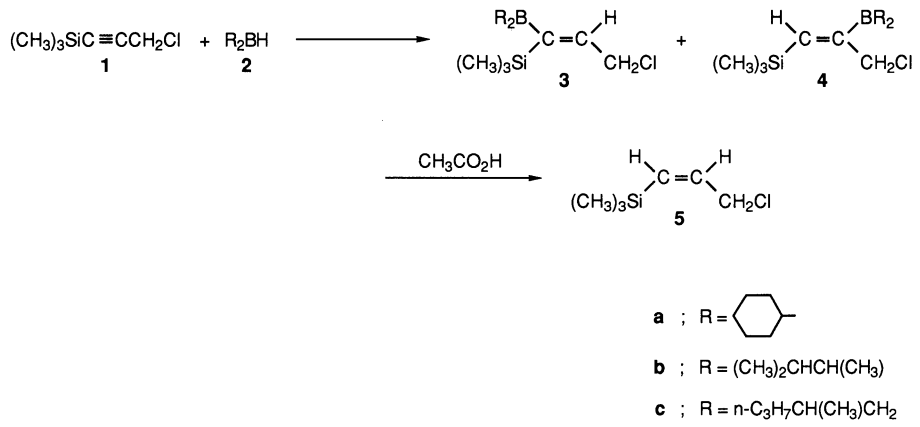
These results indicated that the hydroboration proceeded to the monohydroboration stage in a *cis*-addition manner. Thus two compounds in the hydroboration mixture were assigned to (*Z*)-(3-chloro-1-trimethylsilyl-1-propenyl)dicyclohexylborane (**3a**) and (*Z*)-[1-chloromethyl-2-(trimethylsilyl)vinyl]dicyclohexylborane (**4a**). The ratio of **4a**:**5a** was estimated to be 77:23 from the peak areas of the respective alkenyl and methylene protons in the ^{1}H NMR spectrum (Scheme 1).

A similar result was obtained in the case where bis(1,2-dimethylpropyl)borane was employed as the hydroborating agent, giving a mixture of (*Z*)-(3-chloro-1-trimethylsilyl-1-propenyl)bis(1,2-dimethylpropyl)borane (**3b**) and (*Z*)-[1-chloromethyl-2-(trimethylsilyl)vinyl]bis(1,2-dimethylpropyl)borane (**4b**) in the ratio 63:37. A similar hydroboration of **1** was examined by employing a less bulky dialkylborane prepared by hydroboration of less hindered alkene with monobromoborane–dimethyl sulfide complex [$BH_2Br{\cdot}S(CH_3)_2$][5] followed by treatment with diisobutylaluminium hydride (DIBAH).[6] Thus, hydroboration of **1** with bis(2-methylpentyl)borane (**2c**), derived from 2-methyl-1-pentene, was carried out in a mixture of diethyl ether and hexanes at 0 °C for 3 h, and then room temperature for 2 h, giving a mixture of (*Z*)-(3-chloro-1-trimethylsilyl-1-propenyl)bis(2-methylpentyl)borane (**3c**) and (*Z*)-[1-chloromethyl-2-(trimethylsilyl)vinyl]bis(2-methylpentyl)borane (**4c**) in the ratio 87:13 (Scheme 1).

Both of the above hydroboration mixtures were protonolyzed with acetic acid to give **5** in 100% and 90% yields (estimated by GLC). Thus, this hydroboration–protonolysis sequence provides an efficient preparative method for highly pure **5** which is a potentially useful synthon for trimethylsilylated compounds.

The results are shown in Table 1.

As **3** or **4** could not be isolated from the reaction mixture simply, we examined application of the major component **3** to organic synthesis without isolation and



Scheme 1.

Table 1. ^{1}H NMR Spectral Data of the Alkenyl Proton (**A**) and the Chloromethyl Protons (**B**) of (*Z*)-Dialkyl(3-chloro-1-trimethylsilyl-1-propenyl)boranes (**3**) and (*Z*)-Dialkyl[1-chloromethyl-2-(trimethylsilyl)vinyl]boranes (**4**), and Protonolysis of Mixture of **3** and **4** with Acetic Acid

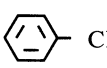
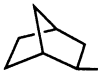
R of R_2BH (**2**)		**3** δ	**4** δ	Ratio/%[a] **3**:**4**	Yield of **5**/%[b]
	**A**	5.66 (t, J=7.8 Hz)	5.38 (s)	77:23	100
	B	4.11 (d, J=7.8 Hz)	4.34 (s)		
$(CH_3)_2CHCH(CH_3)$	**A**[c]	5.84 (t, J=7.8 Hz) 5.87 (t, J=7.8 Hz)	5.91 (s)	63:37	100
	B	4.15 (d, J=7.8 Hz)	4.34 (s)		
n-$C_3H_7CH(CH_3)CH_2$	**A**	5.94 (t, J=7.8 Hz)	6.19 (s)	87:13	90
	B	4.03 (d, J=7.8 Hz)	4.34 (s)		

a) Determined from the peak area of **A** and **B**. b) Determined by GLC and based on **1** employed. c) A mixture of two diastereoisomers.

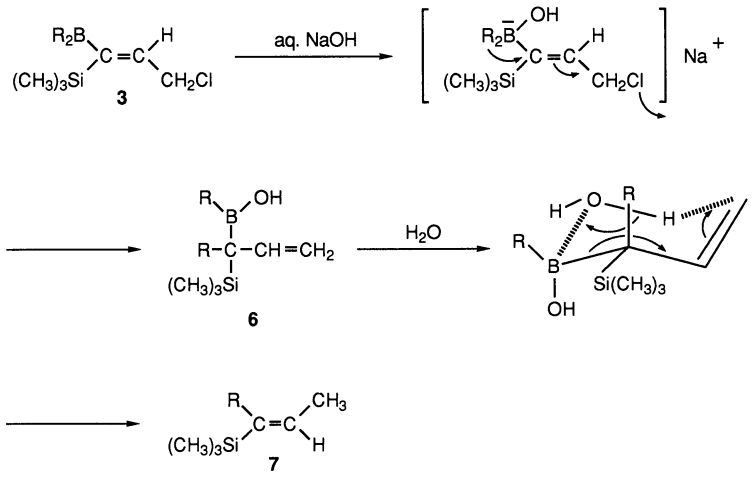
in a one-pot manner starting from the preparation of dialkylborane. As communicated previously,[4] treatment of the hydroboration mixture containing **3** and **4** with an excess amount of aqueous sodium hydroxide at 0 °C for 1 h[7] provided isomerically pure (*E*)-3-trimethylsilyl-2-alkenes (**7**) whose alkyl group was migrated from the boron atom of **3**. As appeared in Table 2, several types of dialkylboranes, derived from terminal, internal, and cyclic alkene, could be employed successfully.

The reaction is speculated to proceed in the following way. Thus, the reaction of **3** with aqueous sodium hydroxide results in a concomitant migration of an alkyl group from the boron atom to the α-alkenyl carbon atom and an elimination of the allylic chlorine atom via borate complex to give an allylic compound, alkyl[1-alkyl-1-(trimethylsilyl)allyl]hydroxyborane (**6**).[8] Allylborane **6** is then hydrolyzed rapidly to afford **7** through a cyclic transition state, where less hindered hydroxyl group on the boron atom occupies an axial position and the trimethylsilyl group occupies an equatorial position

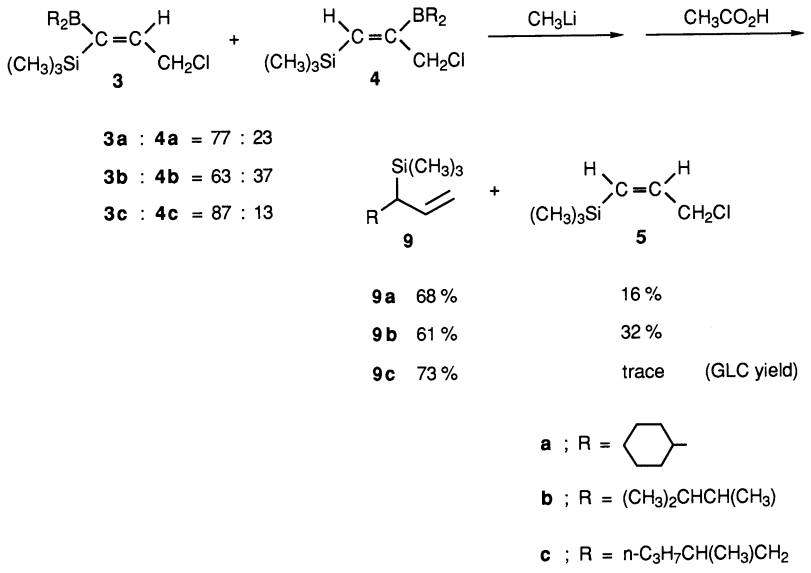
Table 2. Synthesis of (*E*)-3-Trimethylsilyl-2-alkenes (**7**) by Successive Reaction of 3-Chloro-1-trimethylsilyl-1-propyne (**1**) with Dialkylboranes (**2**) and Aqueous Sodium Hydroxide

R of R_2BH (**2**)		Yield of **7**/%[a]
	**a**	70
$(CH_3)_2CHCH(CH_3)$	**b**	31
n-$C_3H_7CH(CH_3)CH_2$[b]	**c**	69
n-C_6H_{13}[b]	**d**	57
 $CH(CH_3)CH_2$[b]	**e**	90
 [b]	**f**	73
 [b] (exo)-	**g**	60

a) Isolated yields and based on **1** employed. b) Prepared by hydridation of R_2BBr with DIBAH.



Scheme 2.



Scheme 3.

(Scheme 2).

A similar migration–elimination sequence occurs in the case of alkenylboranes having a chloromethyl group on the β-alkenyl carbon atom.[3d,9-11] On the other hand, alkenylboranes having a chloromethyl group on the α-alkenyl carbon atom result in a β-elimination on treatment with strong base.[3d,10,11] Thus it is probable that (trimethylsilyl)allene is formed from **4** concomitantly. However, no other product than **7** was found in all cases.

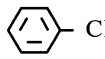
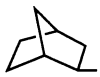
Allylic rearrangement occurs in allylborane system. In the case of α-substituted allylboranes, the boryl group tends to migrate to the less substituted carbon atom to form more thermodynamically stable isomers.[8] Thus **6** has a possibility to provide a more stable allylborane by the allylic rearrangement. However, the treatment with aqueous sodium hydroxide seems to cause immediate hydrolysis of **6** before the rearrangement.

Above speculation led us to expect that treatment of **3** with base in an aprotic solvent might provide a rearranged allylborane. Thus the hydroboration mixture containing **3a** and **4a** (77:23) was treated with an equimolar amount of methyllithium in diethyl ether at −78 °C for 0.5 h, and the reaction temperature was raised slowly to room temperature. Then the reaction mixture was protonolyzed with acetic acid to give 3-cyclohexyl-3-trimethylsilyl-1-propene (**9a**) in 68% yield (estimated by GLC) without the formation of **7a**. However, this protonolysis gave simultaneously the protonolysis product, **5**, in 16% yield (estimated by GLC) (Scheme 3). Compound **5** must be derived from **4a** which scarcely reacted with methyllithium. Compound **5** was removed

from the protonolyzed reaction mixture by washing with aqueous potassium carbonate. After work-up **9a** was isolated by column chromatography on silica gel in 62% yield based on **1**. A similar treatment of the hydroboration mixture containing **3b** and **4b** also gave a mixture of diastereoisomeric 4,5-dimethyl-3-trimethylsilyl-1-hexene (**9b**) correspondingly (Scheme 3).

Similarly, the corresponding 3-trimethylsilyl-1-alkene (**9**) was provided when less bulky dialkylborane was employed as the hydroborating agent. For example, successive treatment of the hydroboration mixture containing **3c** and **4c** with two equimolar amounts of methyllithium in the presence of hexamethylphosphoric triamide (HMPT), and then acetic acid gave diastereoisomeric 5-methyl-3-trimethylsilyl-1-octene (**9c**) in 73% yield (estimated by GLC) without the formation of **5** and **7c** (Scheme 3). These results are shown in Table 3. As appeared in Table 3, the alkyl group of **9** can be derived from terminal, internal, and cyclic alkene via dialkylborane.

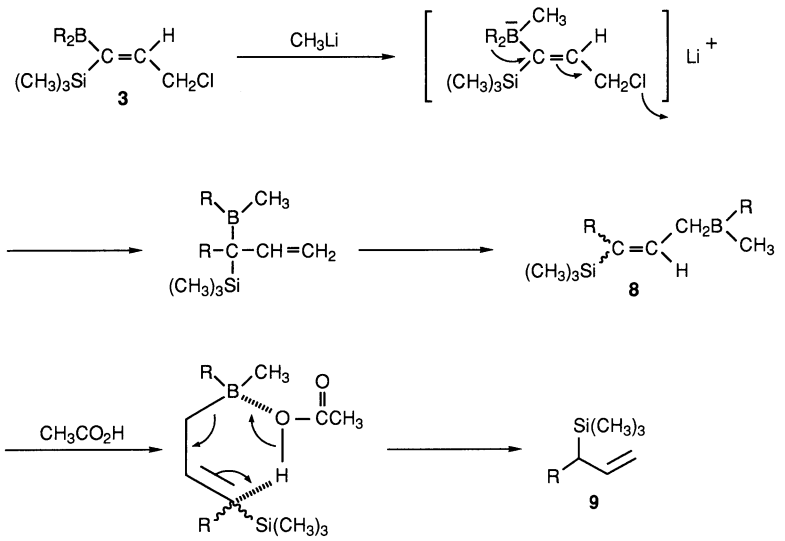
Table 3. Synthesis of 3-Trimethylsilyl-1-alkenes (**9**) by Successive Reaction of 3-Chloro-1-trimethylsilyl-1-propyne (**1**) with Dialkylboranes (**2**), Methyllithium, and Acetic Acid

R of R_2BH (**2**)		Yield of **9**/%[a]
	**a**	62
$(CH_3)_2CHCH(CH_3)$	**b**	56[b]
n-$C_3H_7CH(CH_3)CH_2$[c]	**c**	67[b]
n-C_6H_{13}[c]	**d**	58
 $CH(CH_3)CH_2$[c]	**e**	61[b]
 [c]	**f**	65
 [c] (exo)-	**g**	57[b]

a) Isolated yields and based on **1** employed. b) A mixture of two diastereoisomers. c) Prepared by hydridation of R_2BBr with DIBAH.

It is speculated that **9** is formed in the following way. Thus, the reaction of **3** with methyllithium results in a migration of an alkyl group from the boron atom to the adjacent carbon atom with a concomitant shift of the double bond and an elimination of chloride ion via borate complex. Allylborane, thus formed, then rearranges to a thermodynamically more stable isomer, alkyl[3-alkyl-3-(trimethylsilyl)allyl]methylborane (**8**), which is protonolyzed with acetic acid through a six-membered cyclic transition state to afford **9** (Scheme 4).

Both vinylsilanes[12] and allylsilanes[13] are useful intermediates in organic synthesis and a number of methods for their syntheses have been reported. There are some reports utilizing organoboranes and these methods are classified into two groups. One includes the hydroboration of trimethylsilylated alkynes with dialkylboranes[14] and the other includes the reaction of trialkylalkynylborates with halogenides.[15] In the former reactions, the dialkylboryl group is used merely as an intermediary substituent and thus the alkyl group is not included in the product molecule. In the latter reactions, one of three alkyl groups on the boron atom is introduced into the β-alkenyl carbon atom of the resulting vinylsilanes, not into the silylated carbon atom. In both of the present reactions, however, an alkyl group on the boron atom is introduced into the trimethylsilylated carbon atom. In all cases, (*E*)-3-trimethylsilyl-2-alkenes (**7**) are provided stereoselectively and 3-trimethylsilyl-1-alkenes (**9**) are provided regioselectively. The alkyl group of both products is derived from an alkene via hydroboration.



Scheme 4.

Experimental

Instruments. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL FX-200 (200 MHz) FT NMR spectrometer for $CDCl_3$ solutions. Chemical shifts are reported as δ-values relative to TMS, with chloroform (δ_H=7.25 and δ_c=77.5) or dichloromethane (δ_H=5.28 and δ_c=54.0) as internal standard for the ^{1}H and ^{13}C NMR spectra, respectively. IR spectra were recorded for liquid films inserted between NaCl plates in a Hitachi 285 spectrometer. Mass spectra were recorded with a Hitachi M-52 mass spectrometer. GLC analyses using the internal standard method were performed with a Hitachi 163 gas chromatograph equipped with a glass column (10% PEG-20M on Diasolid M, 2 m or 5% FFAP on Diasolid M, 1 m), a flame ionization detector, and a Shimadzu C-R3A Chromatopac digital integrator-recorder.

Materials. Alkenes and solvents in the reactions were used after purification by methods generally employed in similar organoborane chemistry.[16] 3-Chloro-1-trimethylsilyl-1-propyne was prepared by a method described in the literature.[17] A 1.0 mol cm^{-3} solution of $BH_2Br{\cdot}S(CH_3)_2$ in dichloromethane, a 1.0 mol cm^{-3} solution of DIBAH in hexanes, and a 1.4 mol cm^{-3} solution of methyllithium in diethyl ether were obtained from Aldrich Chemicals. A solution of BH_3 in THF was prepared by a method described in the literature.[18] HMPT was distilled under vacuum from calcium hydride, and stored over Molecular Sieves-4A.

Representative Procedure. Synthesis of (*Z*)-3-Chloro-1-trimethylsilyl-1-propene (5). A dry 100 cm^3 round-bottomed flask, equipped with a gas inlet for argon, a sample inlet with a serum cap, and a magnetic stirring bar, was flushed with argon. In the flask, dicyclohexylborane (**2a**) (10 mmol) was prepared by the hydroboration of cyclohexene (1.64 g, 20 mmol) with BH_3 (10 mmol) in THF at 0 °C for 2 h.

3-Chloro-1-trimethylsilyl-1-propyne (**1**) (1.47 g, 10 mmol) was added to **2a** at −15 °C, and the reaction mixture was stirred for 2 h at 0 °C to complete the hydroboration. To the reaction mixture was added acetic acid (10 cm^3) at 0 °C, and the solution was stirred for 4 h at room temperature. The mixture was treated with water, and extracted three times with pentane. The combined extracts were washed with brine, dried over anhydrous sodium sulfate, and concentrated on a rotary evaporator under reduced pressure. The crude product was purified by column chromatography on silica gel (Wakogel Q-50). Product **5** (1.34 g, 90% yield) was isolated with pentane as eluent.

Synthesis of (*E*)-1-Cyclohexyl-1-trimethylsilyl-1-propene (7a). The hydroboration of **1** (10 mmol) with **2a** (10 mmol) was carried out in the same manner as described in the synthesis of **5**. To the reaction mixture at 0 °C was added 3 mol cm^{-3} aqueous sodium hydroxide (10 cm^3), and the mixture was stirred for 1 h at the same temperature. Then, 30% hydrogen peroxide (5 cm^3) was added to the resulting mixture at 0 °C to decompose the residual boron compound. After stirring for 1 h at 0 °C, the mixture was extracted three times with diethyl ether. The combined extracts were washed with brine, dried over anhydrous sodium sulfate, and concentrated on a rotary evaporator under reduced pressure. The crude product was purified by column chromatography on silica gel (Wakogel Q-50). Product **7a** (1.37 g, 70% yield) was isolated with pentane as eluent.

Synthesis of (*E*)-5-Methyl-3-trimethylsilyl-2-octene (7c). The experimental set-up was the same as described in the synthesis of **5**. The flask was cooled to 0 °C and charged with a solution of $BH_2Br{\cdot}S(CH_3)_2$ (10 cm^3, 10 mmol) in dichloromethane. To the stirred solution was added 2-methyl-1-pentene (1.68 g, 20 mmol), and the reaction mixture was stirred for 2 h at 25 °C to complete the hydroboration. After removal of dichloromethane and dimethyl sulfide under reduced pressure with a water aspirator, dry diethyl ether (40 cm^3) and dry dimethyl sulfide (2 cm^3) were added to neat bis(2-methylpentyl)bromoborane at 0 °C, and the solution was stirred for 0.5 h at the same temperature. 3-Chloro-1-trimethylsilyl-1-propyne (**1**) (1.47 g, 10 mmol) was added to the cooled solution (−78 °C), followed by the slow addition of a solution of DIBAH (10 cm^3, 10 mmol) in hexanes. The reaction mixture was brought to 0 °C, stirred for 3 h at the same temperature and for an additional 2 h at room temperature to complete the hydroboration.

In an argon flushed 200 cm^3 round-bottomed flask with the same equipments as described above was placed 6 mol cm^{-3} aqueous sodium hydroxide (10 cm^3), THF (20 cm^3), and HMPT (10 cm^3), and then the flask was cooled to −15 °C. The above hydroboration mixture was transferred slowly to the 200 cm^3 flask using a double-ended needle, and the reaction mixture was stirred for 1 h at 0 °C. After the same work-up as described in the synthesis of **7a**, the crude product was purified by column chromatography on silica gel (Wakogel Q-50), with pentane as eluent, to give **7c** (1.37 g, 69% yield).

The Synthesis of 3-Cyclohexyl-3-trimethylsilyl-1-propene (9a). The hydroboration of **1** (10 mmol) with **2a** (10 mmol) was carried out as described in the synthesis of **5**. The hydroboration mixture was cooled to −78 °C. To the cooled solution was added dropwise a solution of methyllithium (7.14 cm^3, 10 mmol) in diethyl ether, and the mixture was stirred for 0.5 h at −78 °C. The solution was allowed to warm slowly to room temperature and stirred overnight. Acetic acid (10 cm^3) was added to the solution at 0 °C, and the reaction mixture was stirred for 1 h at room temperature. The mixture was treated with water, and extracted three times with pentane. The combined extracts were washed with aqueous potassium carbonate and with brine, dried over anhydrous sodium sulfate, and concentrated on a rotary evaporator under reduced pressure. The crude product was purified by column chromatography on silica gel (Wakogel Q-50). Product **9a** (1.22 g, 62% yield) was isolated with pentane as eluent.

Synthesis of 5-Methyl-3-trimethylsilyl-1-octene (9c). 2-Methyl-1-pentene was hydroborated with $BH_2Br{\cdot}S(CH_3)_2$ in dichloromethane, followed by treatment with DIBAH in hexanes in the presence of **1** in the same manner as described in the synthesis of **7c**. To the reaction mixture was added HMPT (5 cm^3) at 0 °C, and the solution was cooled to −78 °C immediately. The solution was treated as described in the synthesis of **9a**, except that two-fold amounts of methyllithium (14.28 cm^3, 20 mmol) were employed. The crude product was purified by column chromatography on silica gel (Wakogel Q-50), with pentane as eluent, to give **9c** (1.33 g, 67% yield).

The products were identified by following data.

(*Z*)-3-Chloro-1-trimethylsilyl-1-propene (5): ^{1}H NMR δ=0.16 (s, 9H), 4.08 (d, J=7.8 Hz, 2H), 5.78 (d, J=13.7 Hz, 1H), and 6.39 (dt, J=13.7 and 7.8 Hz, 1H); ^{13}C NMR δ=0.31 (CH_3–×3), 44.20 (–CH_2–), 135.36 (–CH=), and 142.52 (–CH=); IR 2950, 2920, 2845, 1600, 1450, 1250, 850, 835, and 770 cm^{-1}; MS

m/z 148 and 150 (M^+); Found: C, 48.65; H, 8.90%. Calcd for $C_6H_{13}ClSi$: C, 48.46; H, 8.81%.

(*E*)-1-Cyclohexyl-1-trimethylsilyl-1-propene (7a): ^1H NMR δ=0.08 (s, 9H), 0.9—2.0 (m, 10H), 1.69 (d, *J*=6.8 Hz, 3H), 2.3—2.7 (m, 1H), and 5.80 (q, *J*=6.8 Hz, 1H); ^{13}C NMR δ=1.22 (CH_3-×3), 14.86 (CH_3-), 26.56 (-CH_2-), 27.31 (-CH_2-×2), 32.91 (-CH_2-×2), 41.42 (>CH-), 133.93 (-CH=), and 147.55 (>C=); IR 3010, 2920, 2840, 1590, 1440, 1255, 1245, 955, 885, 845, 830, 750, and 675 cm^{-1}; MS *m/z* 196 (M^+); Found: C, 73.48; H, 12.38%. Calcd for $C_{12}H_{24}Si$: C, 73.38; H, 12.32%.

(*E*)-4,5-Dimethyl-3-trimethylsilyl-2-hexene (7b): ^1H NMR δ=0.14 (s, 9H), 0.79 (d, *J*=6.8 Hz, 3H), 0.83 (d, *J*=6.8 Hz, 3H), 0.90 (d, *J*=6.8 Hz, 3H), 1.5—1.7 (m, 1H), 1.76 (d, *J*=6.8 Hz, 3H), 1.8—2.1 (m, 1H), and 6.00 (q, *J*=6.8 Hz, 1H); ^{13}C NMR δ=0.93 (CH_3-×3), 17.57 (CH_3-), 18.13 (CH_3-), 19.10 (CH_3-), 22.43 (CH_3-), 32.60 (>CH-), 45.90 (>CH-), 134.52 (-CH=), and 145.46 (>C=); IR 2950, 1600, 1445, 1365, 1245, 1090, 890, 830, 750, and 675 cm^{-1}; MS *m/z* 184 (M^+); Found: C, 71.59; H, 13.30%. Calcd for $C_{11}H_{24}Si$: C, 71.65; H, 13.12%.

(*E*)-5-Methyl-3-trimethylsilyl-2-octene (7c): ^1H NMR δ=0.04 (s, 9H), 0.80 (d, *J*=6.4 Hz, 3H), 0.88 (t, *J*=6.4 Hz, 3H), 1.0—1.6 (m, 5H), 1.66 (d, *J*=6.4 Hz, 3H), 1.9—2.2 (m, 2H), and 5.92 (q, *J*=6.4 Hz, 1H); ^{13}C NMR δ=−0.41 (CH_3-×3), 14.70 (CH_3-), 15.16 (CH_3-), 19.78 (CH_3-), 20.70 (-CH_2-), 33.30 (>CH-), 37.27 (-CH_2-), 39.87 (-CH_2-), 135.22 (-CH=), and 141.55 (>C=); IR 2950, 2910, 2860, 1610, 1450, 1370, 1245, 1150, 1090, 1010, 955, 890, 830, 750, and 680 cm^{-1}; MS *m/z* 198 (M^+); Found: C, 72.75; H, 13.36%. Calcd for $C_{12}H_{26}Si$: C, 72.64; H, 13.21%.

(*E*)-3-Trimethylsilyl-2-nonene (7d): ^1H NMR δ=0.04 (s, 9H), 0.88 (t, *J*=6.4 Hz, 3H), 1.1—1.45 (m, 8H), 1.67 (d, *J*=6.4 Hz, 3H), 1.95—2.2 (m, 2H), and 5.83 (q, *J*=6.4 Hz, 1H); ^{13}C NMR δ=−0.09 (CH_3-×3), 14.40 (CH_3-), 14.53 (CH_3-), 22.99 (-CH_2-), 29.63 (-CH_2-), 30.04 (-CH_2-), 30.11 (-CH_2-), 32.09 (-CH_2-), 134.18 (-CH=), and 142.55 (>C=); IR 2950, 2920, 2850, 1610, 1460, 1370, 1295, 1245, 1145, 1015, 940, 830, 745, and 680 cm^{-1}; MS *m/z* 198(M^+); Found: C, 72.55; H, 13.31%. Calcd for $C_{12}H_{26}Si$: C, 72.64; H, 13.21%.

(*E*)-5-Methyl-5-phenyl-3-trimethylsilyl-2-pentene (7e): ^1H NMR δ=0.06 (s, 9H), 1.21 (d, *J*=6.8 Hz, 3H), 1.55 (d, *J*=6.8 Hz, 3H), 2.05—2.55 (m, 2H), 2.55—2.9 (m, 1H), 5.93 (q, *J*=6.8 Hz, 1H), and 7.0—7.45 (m, 5H); ^{13}C NMR δ=−0.12 (CH_3-×3), 15.37 (CH_3-), 21.38 (CH_3-), 39.16 (-CH_2-), 40.48 (>CH-), 126.44 (-CH=), 127.58 (-CH=×2), 128.80 (-CH=×2), 136.58 (-CH=), 140.87 (>C=), and 148.46 (>C=); IR 3025, 2950, 2910, 1605, 1490, 1445, 1370, 1245, 1135, 1010, 950, 890, 830, 750, and 695 cm^{-1}; MS *m/z* 232 (M^+); Found: C, 77.68; 10.32%. Calcd for $C_{15}H_{24}Si$: C, 77.51; H, 10.41%.

(*E*)-1-Cyclopentyl-1-trimethylsilyl-1-propene (7f): ^1H NMR δ=0.08 (s, 9H), 1.1—1.9 (m, 8H), 1.69 (d, *J*=6.8 Hz, 3H), 2.7—2.95 (m, 1H), and 5.85 (q, *J*=6.8 Hz, 1H); ^{13}C NMR δ=0.83 (CH_3-×3), 14.96 (CH_3-), 25.59 (-CH_2-×2), 32.67 (-CH_2-×2), 42.55 (>CH-), 134.76 (-CH=), and 145.39 (>C=); IR 2950, 2860, 1600, 1445, 1245, 1120, 1015, 935, 830, 750, and 680 cm^{-1}; MS *m/z* 182 (M^+); Found: C, 72.56; H, 12.25%. Calcd for $C_{11}H_{22}Si$: C, 72.44; H, 12.16%.

(*E*)-1-(*exo*-Bicyclo[2.2.1]heptan-2-yl)-1-trimethylsilyl-1-propene (7g): ^1H NMR δ=0.10 (s, 9H), 1.05—1.8 (m, 8H), 1.68 (d, *J*=6.8 Hz, 3H), 2.1—2.3 (m, 2H), 2.4—2.6 (m, 1H), and 5.84 (q, *J*=6.8 Hz, 1H); ^{13}C NMR δ=1.63 (CH_3-×3), 16.18 (CH_3-), 29.02 (-CH_2-), 31.36 (-CH_2-), 36.90 (>CH-), 37.36 (-CH_2-), 39.72 (-CH_2-), 42.57 (>CH-), 44.78 (>CH-), 135.61 (-CH=), and 148.21 (>C=); IR 2940, 2860, 1585, 1445, 1300, 1245, 1150, 1125, 1010, 960, 890, 870, 830, 750, and 675 cm^{-1}; MS *m/z* 208 (M^+); Found: C, 75.08; H, 11.73%. Calcd for $C_{13}H_{24}Si$: C, 74.92; H, 11.61%.

3-Cyclohexyl-3-trimethylsilyl-1-propene (9a): ^1H NMR δ=−0.01 (s, 9H), 0.8—2.0 (m, 12H), 4.78 (dd, *J*=16.6 and 2.4 Hz, 1H), 4.86 (dd, *J*=9.8 and 2.4 Hz, 1H), and 5.55—5.8 (m, 1H); ^{13}C NMR δ=−1.36 (CH_3-×3), 26.64 (-CH_2-), 27.15 (-CH_2-×2), 31.74 (-CH_2-), 34.42 (-CH_2-), 38.82 (>CH-), 42.98 (>CH-), 113.14 (CH_2=), and 138.68 (-CH=); IR 3070, 2920, 2840, 1615, 1440, 1405, 1340, 1245, 1150, 1100, 1065, 1045, 995, 965, 910, 890, 850, 830, 765, 745, 715, 680, and 635 cm^{-1}; MS *m/z* 198 (M^+).

4,5-Dimethyl-3-trimethylsilyl-1-hexene (9b) (ca. 1:1 diastereomeric mixture): ^1H NMR δ=−0.01 and 0.01 (2s, 9H), 0.67, 0.86, and 0.91 (3d, *J*=6.8 Hz), 0.79, 0.83, and 0.85 (3d, *J*=6.4 Hz), (9H), 1.3—1.65 (m, 2H), 1.7—1.9 (m, 1H), 4.76 and 4.81 (2dd, *J*=16.6 and 2.0 Hz, *J*=19.0 and 2.4 Hz, 1H), 4.85 and 4.87 (2dd, *J*=10.2 and 2.0 Hz, *J*=10.2 and 2.4 Hz, 1H), and 5.45—5.85 (m, 1H); ^{13}C NMR δ=−1.75 and −0.68 (CH_3-×3), 14.84, 14.87, 15.11, 20.17, 21.31, and 22.12 (3 CH_3-), 29.68, 33.18, 39.07, 39.21, 39.46, and 40.92 (3 >CH-), 112.48 and 113.09 (CH_2=), and 137.68 and 140.60 (-CH=); IR 3060, 2950, 2860, 1620, 1455, 1370, 1245, 1115, 1060, 995, 890, 830, 765, 735, 710, 675, and 635 cm^{-1}; MS *m/z* 184 (M^+); Found: C, 71.73; H, 13.20%. Calcd for $C_{11}H_{24}Si$: C, 71.65; H, 13.12%.

5-Methyl-3-trimethylsilyl-1-octene (9c) (ca. 1:1 diastereomeric mixture): ^1H NMR δ=−0.04 (s, 9H), 0.76 (d, *J*=6.8 Hz, 3H), 0.86 (t, *J*=6.8 Hz, 3H), 0.9—1.8 (m, 8H), 4.65—4.9 (m, 2H), and 5.4—5.7 (m, 1H); ^{13}C NMR δ=−3.09 and −3.01 (CH_3-×3), 14.72, 14.79, 18.59, and 20.00 (2 CH_3-), 19.00 and 20.53 (-CH_2-), 31.16, 31.40, 32.52, and 32.72 (2 >CH-), 35.86, 36.34, 37.51, and 40.87 (2 -CH_2-), 111.73 and 111.90 (CH_2=), and 140.62 and 140.96 (-CH=); IR 3060, 2950, 2910, 2850, 1620, 1420, 1370, 1245, 1135, 1060, 990, 925, 890, 855, 830, 770, 740, 715, 680, and 635 cm^{-1}; MS *m/z* 198 (M^+); Found: C, 72.70; H, 13.34%. Calcd for $C_{12}H_{26}Si$: C, 72.64; H, 13.21%.

3-Trimethylsilyl-1-nonene (9d): ^1H NMR δ=−0.04 (s, 9H), 0.87 (t, *J*=6.8 Hz, 3H), 0.9—1.8 (m, 11H), 4.79 (dd, *J*=17.1 and 1.5 Hz, 1H), 4.85 (dd, *J*=10.2 and 2.0 Hz, 1H), and 5.45—5.75 (m, 1H); ^{13}C NMR δ=−2.99 (CH_3-×3), 14.40 (CH_3-), 23.01 (-CH_2-), 28.73 (-CH_2-), 29.51 (-CH_2-), 29.65 (-CH_2-), 32.13 (-CH_2-), 35.25 (>CH-), 111.90 (CH_2=), and 140.82 (-CH=); IR 3060, 2960, 2920, 2850, 1625, 1460, 1370, 1245, 1130, 1070, 995, 890, 850, 830, 770, 745, 710, 680, and 635 cm^{-1}; MS *m/z* 198 (M^+).

5-Phenyl-3-trimethylsilyl-1-hexene (9e) (ca. 1:1 diastereomeric mixture): ^1H NMR δ=−0.09 and −0.02 (2s, 9H), 1.18 and 1.23 (2d, *J*=6.8 Hz, *J*=7.3 Hz, 3H), 1.4—1.85 (m, 3H), 2.65—2.95 (m, 1H), 4.65—5.0 (m, 2H), 5.5—5.75 (m, 1H), and 7.0—7.5 (m, 5H); ^{13}C NMR δ=−3.18 and −3.04 (CH_3-×3), 19.51 and 23.98 (CH_3-), 32.84 and 32.94 (>CH-), 37.12 and 37.92 (-CH_2-), 37.88 and 38.80 (>CH-), 112.58 (CH_2=), 126.03 (-CH=), 127.12 and 127.66 (-CH=×2), 128.51 and 128.61 (-CH=×2), 139.94 and 140.33 (-CH=), and 147.07 and 149.24 (>C=); IR 3060, 3020, 2950, 2900, 2850, 1620, 1595, 1490, 1445, 1400, 1370, 1245, 1120, 1085, 1045, 990, 930, 890, 855, 830, 775, 755, 715, 695, and 630 cm^{-1}; MS *m/z* 232 (M^+); Found: C, 77.41; H, 10.36%. Calcd for $C_{15}H_{24}Si$: C, 77.51; H, 10.41%.

3-Cyclopentyl-3-trimethylsilyl-1-propene (9f): ^1H NMR δ=−0.01 (s, 9H), 1.0—2.1 (m, 10H), 4.7—4.9 (m, 2H), and

5.5—5.8 (m, 1H); ^{13}C NMR δ=−1.60 (CH_3-×3), 25.29 (-CH_2-), 25.59 (-CH_2-), 32.15 (-CH_2-), 33.01 (-CH_2-), 40.67 (>CH-), 40.94 (>CH-), 112.65 (CH_2=), and 139.50 (>C=); IR 3060, 2950, 2860, 1620, 1445, 1405, 1340, 1245, 1110, 1055, 995, 945, 895, 855, 830, 770, 745, 720, 680, and 635 cm^{-1}; MS *m*/*z* 182 (M^+); Found: C, 72.59; H, 12.21%. Calcd for $C_{11}H_{22}Si$: C, 72.44; H, 12.16%.

3-(*exo*-Bicyclo[2.2.1]heptan-2-yl)-3-trimethylsilyl-1-propene (9g) (ca. 1:1 diastereomeric mixture): ^{1}H NMR δ=−0.02 and 0.00 (2s, 9H), 0.9—1.8 (m, 10H), 1.95—2.25 (m, 2H), 4.6—4.95 (m, 2H), and 5.4—5.7 (m, 1H); ^{13}C NMR δ=−1.41 and −1.31 (CH_3-×3), 29.12 (-CH_2-), 30.48, 30.77, 35.08, 35.95, 38.29, and 39.72 (3-CH_2-), 37.10 (>CH-), 40.16, 41.87, 41.96, 42.23, 42.42, and 42.50 (3>CH-), 112.11 and 112.65 (CH_2=), and 139.51 and 140.60 (-CH=); IR 3060, 2940, 2860, 1780, 1620, 1445, 1405, 1340, 1305, 1295, 1245, 1205, 1160, 1120, 1090, 995, 945, 920, 890, 850, 830, 775, 755, 740, 710, 680, and 635 cm^{-1}; MS *m*/*z* 208 (M^+); Found: C, 75.05; H, 11.68%. Calcd for $C_{13}H_{24}Si$: C, 74.92; H, 11.61%.

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