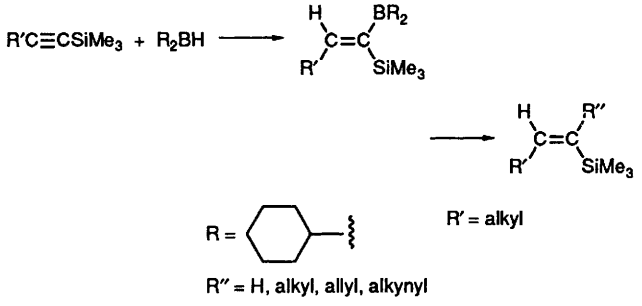
The Hydroboration of (Trimethylsilyl)ethyne with Dialkylboranes and its Application to the Syntheses of (*E*)-1-(Trimethylsilyl)alk-1-enes and 2-(Trimethylsilyl)alk-1-enes

Masayuki Hoshi, Yuzuru Masuda, and Akira Arase*
Department of Industrial Chemistry, Kitami Institute of Technology, Koen-cho Kitami 090, Japan

The reaction of (trimethylsilyl)ethyne **1** with a stoicheiometric amount of dialkylborane **2** proceeds to the monohydroboration stage, giving a mixture of regioisomers, (*E*)-[2-(trimethylsilyl)ethenyl]dialkylborane **3** and [1-(trimethylsilyl)ethenyl]dialkylborane **4**. In the hydroboration with bulky dialkylboranes, derived from internal alkenes, the former predominates. Successive treatment of the mixture with methyllithium and benzenesulphenyl chloride exclusively affords highly pure (*E*)-2-alkyl-1-(trimethylsilyl)ethene **6** whose alkyl group migrates from the boron atom, while in the hydroboration with less bulky dialkylboranes, derived from terminal alkenes, the latter predominates. Successive treatment of the mixture with aq. NaOH and iodine exclusively affords highly pure 2-(trimethylsilyl)alk-1-ene **7** whose alkyl group migrates from the boron atom.

Various useful syntheses have been developed using alkenylboranes as intermediates.[1] In the course of our study on the application of such syntheses to modified alkenylboranes which have functionality at a position very close to the alkenyl moiety,[2] we are interested in the chemistry of trimethylsilylated alkenylboranes. The trimethylsilylated alkenylborane having both a vinylborane moiety and a vinylsilane moiety in its molecule seems to be a potential intermediate.

The most convenient approach to the trimethylsilylated alkenylboranes may be monohydroboration of trimethylsilylated alkynes.[3,4] The monohydroboration of 1-(trimethylsilyl)alk-1-ynes with dicyclohexylborane has already been studied and a remarkably high regioselectivity of the orientation of the dicyclohexylboryl group to C-1 has been observed. The dicyclohexylboryl group of the resulting (*Z*)-[1-(trimethylsilyl)alk-1-enyl]dicyclohexylboranes is replaced by an alkyl,[3] allyl,[2c,3,5] or alkynyl[2c] group to afford the corresponding internal vinylsilane (Scheme 1). Similar trimethylsilylated alkenylboranes are also transformed into terminal (*Z*)-vinylsilanes by protonolysis of the boron–carbon bond.[4b,5]



Scheme 1.

Similar monohydroboration of (trimethylsilyl)ethyne **1**† seems to be of interest because the C-2 with no alkyl group substituent is relatively free from steric hindrance and thus the orientation of the hydroboration may be different from that of 1-(trimethylsilyl)alk-1-ynes. Further, since the hydroboration is expected to provide a new type of trimethylsilylated alkenylborane which has no alkyl group on C-2, there is a possibility that the trimethylsilylated alkenylborane may be used as the intermediate in a new synthesis of trimethylsilylated compounds.

We now report the hydroboration of compound **1** with some dialkylboranes and new stereoselective syntheses of monoalkylated vinylsilanes from the resulting trimethylsilylated alkenylboranes intermediates.

Results and Discussion

A stoicheiometric hydroboration of compound **1** with dicyclohexylborane **2a**, obtained by the reaction of BH_3 in tetrahydrofuran (THF) with two mol equiv. of cyclohexene, proceeded smoothly at 0 °C, and after 2 h no residual alkyne **1** and no residual hydride of compound **2a** was detected by GLC or by hydrolysis of the reaction mixture, respectively. These facts indicated that the hydroboration proceeds to the monohydroboration stage.

The ^1H NMR spectrum of the reaction mixture, obtained after the removal of THF, showed that the hydroboration had given two regioisomeric alkenylboranes. As one had a couple of *trans* alkenyl protons (d, *J* 22 Hz), and the other had a couple of geminal alkenyl protons, the products were assigned to be (*E*)-[2-(trimethylsilyl)ethenyl]dicyclohexylborane **3a** and [1-(trimethylsilyl)ethenyl]dicyclohexylborane **4a** respectively. The ratio of products **3a**:**4a** was estimated to be 67:33 from the peak areas of the respective alkenyl protons in the ^1H NMR spectrum. The above results show that dicyclohexylboryl group orients predominantly to the β-carbon atom, in contrast to the case of monohydroboration of 1-(trimethylsilyl)alk-1-ynes.

Similar results were obtained when bis-(1,2-dimethylpropyl)borane **2b** was employed as the hydroborating agent. Thus, monohydroboration gave a mixture of (*E*)-[2-(trimethylsilyl)ethenyl]bis-(1,2-dimethylpropyl)borane **3b** and [1-(trimethylsilyl)ethenyl]bis-(1,2-dimethylpropyl)borane **4b** in the ratio 75:25 (Scheme 2).

These results suggest that the ability of the trimethylsilyl group to orient the dialkylboryl group to the silylated carbon atom is appreciably inhibited by the steric hindrance between the trimethylsilyl group and the bulky dialkylboryl group.

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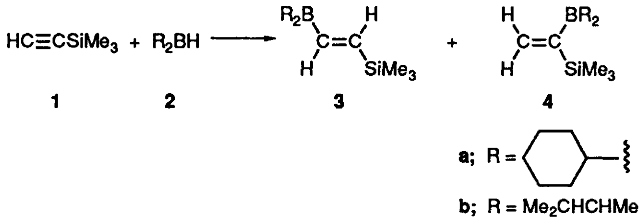
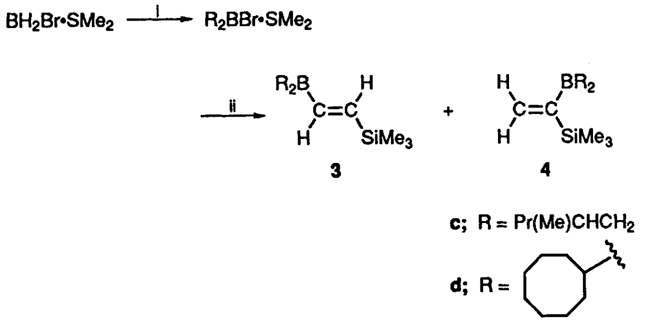
† Recently, Soderquist *et al.* studied the hydroboration of (trimethylsilyl)ethyne with 9-borabicyclo[3.3.1]nonane by means of ^1H NMR spectroscopy and found that the 9-borabicyclo[3.3.1]nonyl group oriented exclusively to the β-alkenyl carbon atom (J. A. Soderquist, J. C. Colberg, and L. D. Valle, *J. Am. Chem. Soc.*, 1989, **111**, 4873).



Scheme 2.

A similar hydroboration was examined by employing a less hindered dialkylborane, derived from 2-methylpent-1-ene or cyclooctene. It is difficult to obtain the dialkylborane cleanly by the reaction of BH_3 with such alkenes (1:2). Thus a modified hydroboration procedure was devised. The alkene was hydroborated with monobromoborane–dimethyl sulphide complex [$BH_2Br{\cdot}SMe_2$][6] and the resulting dialkylbromoborane was treated with an equimolar amount of diisobutylaluminium hydride (DIBAH) to give the desired dialkylborane (Scheme 3).



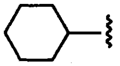
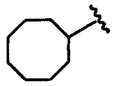
Scheme 3. *Reagents:* i, 2-methylpent-1-ene or cyclooctene; ii, **1**, DIBAH

Although sodium hydride,[7a] aluminium hydride,[7b] and lithium aluminium hydride[7c] may be used as the reducing agent for similar transformations of the boron–bromine bond to give the boron–hydrogen bond as above, DIBAH in hexane solution is also a convenient reducing agent in the present transformation.

A stoicheiometric hydroboration of the alkyne **1** with bis-(2-methylpentyl)borane **2c** was carried out in diethyl ether at 0 °C for 3 h and at room temperature for 2 h. The ^1H NMR spectrum of the hydroboration product, recorded after removal of the solvent, showed that the hydroboration had given a mixture of two regioisomeric compounds. As one had a couple of *trans* alkenyl protons (d, *J* 22 Hz), and the other had a couple of geminal alkenyl protons, they were assigned to be (*E*)-[2-(trimethylsilyl)ethenyl]bis-(2-methylpentyl)borane **3c** and [1-(trimethylsilyl)ethenyl]bis-(2-methylpentyl)borane **4c** respectively. The ratio of **3c**: **4c** was estimated to be 7:93 from the peak areas of the respective alkenyl protons. The above results showed that in the hydroboration the dialkylboryl group orients predominantly to the α-carbon atom, in contrast to the case for such bulky dialkylboranes as **2a** and **2b**. In the hydroboration of compound **1** with dicyclooctylborane **2d**, prepared in a similar manner to **2c**, however, the dicyclooctylboryl group attached predominantly to the β-alkenyl carbon atom.

Thus it appears that in the case of less bulky dialkylboranes, such as **2c**, the electrophilic boron atom can attach to the α-alkenyl carbon atom, while in the case of bulkier ones, such as **2a**, **2b** or **2d**, the steric hindrance between the trimethylsilyl group and the dialkylboryl group may counteract the electronic factor of the boron atom, leading to attachment to the β-alkenyl carbon atom.

Table 1. ^1H NMR spectral data of the alkenyl protons of (*E*)-[2-(trimethylsilyl)ethenyl]dialkylboranes **3** and [1-(trimethylsilyl)ethenyl]dialkylboranes **4**

	3	4	Ratio[a] 3:4
a; R = 	6.85 (d, *J* 22 Hz)[b] 7.00 (d, *J* 22 Hz)[b]	5.3–6.2 (m)	67:33
b; R = Me2CHCHMe[c]	6.78 (d, *J* 22 Hz)[b] 7.00 (d, *J* 22 Hz)[b] 6.87 (d, *J* 22 Hz)[b] 7.05 (d, *J* 22 Hz)[b]	5.5–5.9 (m)	75:25
c; R = Pr(Me)CHCH2	6.89 (d, *J* 22 Hz)[b] 7.05 (d, *J* 22 Hz)[b]	5.5–5.9 (m)	7:93
d; R = 	6.7–7.1 (m)	5.4–5.9 (m)	68:32

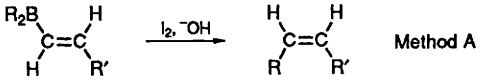
[a] Determined from the peak area of the alkenyl protons. [b] Unsymmetrical doublet. [c] A mixture of two diastereoisomers in the ratio *ca.* 4:3.

These ^1H NMR data are summarized in Table 1.

Although complete regioselectivity in the hydroboration was not achieved, it was found that the regioselectivity was dependent on the bulkiness of the dialkylborane. We turned our attention to the use of trimethylsilylated alkenylboranes as intermediates for the synthesis of vinyltrimethylsilanes. Vinyltrimethylsilanes are useful intermediates, on account of their potentiality to be converted into a wide variety of organic compounds by reactions with electrophiles.[8]

We made use of 1,2-migration reactions for the transformation of the trimethylsilylated alkenylboranes into vinyltrimethylsilanes. The migration of an alkyl group from the dialkylboryl group of (*E*)-[2-(trimethylsilyl)ethenyl]dialkylborane **3** or [1-(trimethylsilyl)ethenyl]dialkylborane **4** is expected to give monoalkylated ethenyltrimethylsilanes whose alkyl group is derived from the terminal or internal alkene.

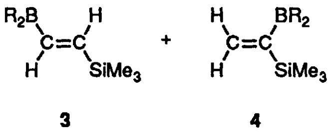
Zweifel *et al.* reported that treatment of alk-1-enyldialkylboranes with aq. NaOH and iodine resulted in transfer of an alkyl group from the boron atom to the α-alkenyl carbon atom to provide (*Z*)-alkenes.[9]



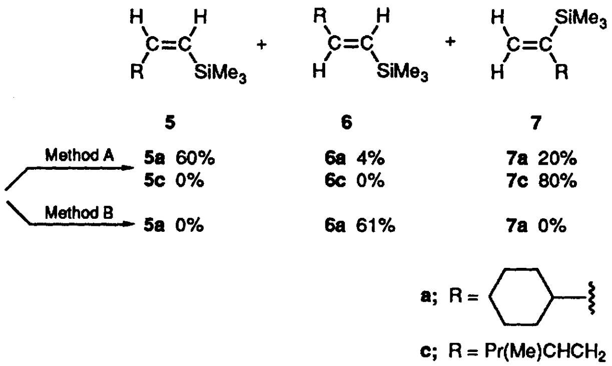
This transfer reaction (Method A in Scheme 4) was applied to the hydroboration mixture containing compounds **3a** and **4a** to give a mixture of three trimethylsilylated alk-1-enes. A couple of stereoisomers and a regioisomer, (*Z*)-2-cyclohexyl-1-(trimethylsilyl)ethene **5a**, (*E*)-2-cyclohexyl-1-(trimethylsilyl)ethene **6a**, and 1-cyclohexyl-1-(trimethylsilyl)ethene **7a** were produced in 63, 4 and 20% yield, respectively, based on starting amount of **1**. A similar mixture was produced when compound **2b** was used as the hydroborating agent.

However, application of the transfer reaction to the hydroboration mixture containing compounds **3c** and **4c**, obtained from the less bulky hydroborating agent, gave solely 4-methyl-2-(trimethylsilyl)hept-1-ene **7c** in 80% yield based on starting amount of **1**. Product **7c** must be derived from compound **4c** *via* the migration of the 2-methylpentyl group from the boron atom (Scheme 4). The reason why products derived from compound **3c** are not formed is obscure at present. Similarly, the corresponding 2-(trimethylsilyl)alk-1-ene **7** was provided when dihexylborane **2e** or bis-(2-phenylpropyl)borane **2f** was employed as the hydroborating agent.

These products were isolated from the reaction mixture by column chromatography. Thus, the above procedure provides a



3a : 4a = 67:33
3c : 4c = 7:93



Scheme 4.

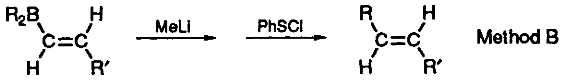
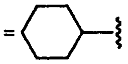
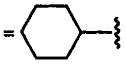
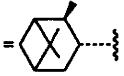


Table 2. Migration reaction of a mixture of an (*E*)-[2-(trimethylsilyl)ethenyl]dialkylborane **3** and a [1-(trimethylsilyl)ethenyl]dialkylborane **4** by methods A and B

2	Method	Yield of products(%)[a] **5**	 **6**	 **7**
a; R = 	A	63	4	20
b; R = $Me_2CHCHMe$	A	70	0	20
c; R = $Pr(Me)CHCH_2$	A	0	0	80 (75)[b]
e; R = Hexyl	A	0	0	45 (41)[b]
f; R = $Ph(Me)CHCH_2$	A	0	0	70 (67)[b]
a; R = 	B	0	61 (57)[b]	0
b; R = $Me_2CHCHMe$	B	0	60 (57)[b]	0
g; R = 	B	0	42 (39)[b]	0

[a] Determined by GLC and based on amount of alkyne **1** used. [b] Isolated yields after column chromatography.

synthetic method for compounds **7** whose alkyl group on the double bond is primary.

Previously, we have reported that treatment of alk-1-enyldialkylboranes with methyllithium and benzenesulphenyl chloride resulted in transfer of an alkyl group from the boron atom to the α-alkenyl carbon atom to provide (*E*)-alkenes in a very high stereoselective manner.[10] An application of this transfer reaction (Method B in Scheme 4) to the hydroboration mixture containing compounds **3a** and **4a** gave the *E*-alkene **6a**, in 61% yield based on starting amount of **1**, uncontaminated with its isomers **5a** and **7a**. Similarly, the corresponding highly pure (*E*)-2-alkyl-1-(trimethylsilyl)ethene **6** was provided when compound **2b** or bis(*trans*-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)borane **2g** was employed as the hydroborating agent.

As shown in Table 2, methods A and B provide two types of the isomerically pure (trimethylsilyl)alk-1-enes whose alkyl-group migrated from the boron atom to the alkenyl carbon atom. Thus compounds **7** are provided from the terminal alkene by method A, while compounds **6** are provided from the bulky internal alkene by method B.

1,2-Dialkylated vinylsilanes have been synthesized utilizing an alkene as the source of one of the alkyl groups on the double bond *via* a trialkylalkynylborate process,[11] while 1- or 2-monoalkylated vinylsilanes have been synthesized utilizing alkynes, ketones, or halogenoalkenes where the alkyl group of the products is the same one originally existing in the starting materials.[12] We note that the present study provides a new synthesis of highly pure monoalkylated vinylsilanes whose alkyl group is derived from an alkene.

Experimental

^1H 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_H- and δ_C-values relative to Me_4Si, with chloroform (δ_H 7.25 and δ_C 77.5) or dichloromethane (δ_H 5.28 and δ_C 54.0) as internal reference for the ^1H 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 operating at 20 eV. 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.

All reactions were carried out under argon. Alkenes and solvents employed in the reactions were used after purification by methods generally employed in similar organoborane chemistry.[13] (Trimethylsilyl)ethyne (Aldrich) was dried over Na_2SO_4, purified by distillation, and stored under argon. A 1.0 mol dm^{-3} solution of $BH_2Br{\cdot}SMe_2$ in dichloromethane, a 1.0 mol dm^{-3} solution of DIBAH in hexanes, and a 1.4 mol dm^{-3} solution of methyllithium in diethyl ether were obtained from Aldrich Chemicals. A solution of BH_3 in THF[14] and benzenesulphenyl chloride[15] were prepared by the literature methods.

General Procedure for the Synthesis of (E)-1-(*Trimethylsilyl*)-*alk*-1-*enes* **6**.—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, a dialkylborane **2** (10 mmol) was prepared by the hydroboration of a sterically hindered internal alkene (20 mmol) with BH_3 (10 mmol) in THF under conditions described in the literature.[1,13,14]

(Trimethylsilyl)ethyne **1** (0.98 g, 10 mmol) was added to the dialkylborane at −15 °C, and the reaction mixture was stirred for 2 h at 0 °C to complete the hydroboration. To the reaction mixture at 0 °C was added a solution of methyllithium (7.14 cm^3, 10 mmol) in diethyl ether, and the mixture was stirred for 30 min at the same temperature to form the corresponding ate-complex. Then, benzenesulphenyl chloride (1.45 g, 10 mmol) was added dropwise to the cooled solution (−78 °C), and the reaction mixture was stirred for 30 min at the same temperature. The solution was brought to 0 °C, stirred for an additional 30 min, and treated with water (10 cm^3). The mixture was extracted three times with diethyl ether. The combined extracts were washed with brine (in the analytical experiment GLC analyses were carried out at this point), dried over Na_2SO_4, and concentrated on a rotary evaporator under reduced pressure. The crude product was purified by column chromatography on silica gel (Wakogel Q-50, 60–200 mesh) (Wako), with pentane as eluent, to give the corresponding vinylsilane **6a**, **6b** and **6g**.

For (E)-2-*Cyclohexyl*-1-(*trimethylsilyl*)*ethene* **6a** (1.06 g, 57%) (Found: C, 72.2; H, 12.05. $C_{11}H_{22}Si$ requires C, 72.4; H, 12.15%); ν_{max}(neat)/cm^{-1}: 2920, 2850, 1610, 1445, 1245, 990, 865, 835, 765, 720 and 690; δ_H: 0.04 (9 H, s, Me_3Si), 0.70–2.10 (11 H, m, ring H), 5.56 (1 H, d, *J* 18.5 Hz, 1-H) and 5.98 (1 H, dd, *J* 18.5 and 5.8 Hz, 2-H); δ_C −0.80 (3 × Me), 26.36 (2 × CH_2), 26.56 (CH_2), 32.69 (2 × CH_2), 44.15 (CH), 126.44 (=CH) and 153.12 (=CH); *m*/*z* 182 (M^+, 7%), 167 (20), 139 (13), 108 (27), 85 (7), 73 (100) and 59 (23).

For (E)-3,4-*Dimethyl*-1-(*trimethylsilyl*)*pent*-1-*ene* **6b** (0.97 g, 57%) (Found: C, 70.6; H, 12.9. $C_{10}H_{22}Si$ requires C, 70.5; H, 13.0%); ν_{max}(neat)/cm^{-1}: 2950, 2860, 1610, 1450, 1380, 1360, 1245, 990, 865, 835, 750, 745 and 685; δ_H 0.03 (9 H, s, Me_3Si), 0.83 (6 H, br d, *J* 6.8 Hz, CH*Me*$_2$), 0.93 (3 H, d, *J* 6.8 Hz, CH*Me*), 1.40–1.65 (1 H, m, C*H*Me$_2$), 1.85–2.05 (1 H, m, C*H*Me), 5.54 (1 H, d, *J* 18.5 Hz, 1-H) and 5.90 (1 H, dd, *J* 18.5 and 6.8 Hz, 2-H); δ_C −0.72 (3 × Me), 16.80 (Me), 19.92 (Me), 20.21 (Me), 32.96 (CH), 46.77 (CH), 128.58 (=CH) and 151.76 (=CH); *m*/*z* 170 (M^+, 8%), 155 (22), 127 (6), 113 (10), 99 (20), 96 (9), 85 (13), 77 (100) and 59 (19).

For (E)-2-(trans-2,6,6-*Trimethylbicyclo*[3.1.1]*heptan*-3-*yl*)-1-*trimethylsilyl*)*ethene* **6g** (0.96 g, 39%) (Found: C, 76.4; H, 12.05. $C_{15}H_{28}Si$ requires C, 76.2; H, 11.9%); ν_{max}(neat)/cm^{-1}: 2950, 2890, 1610, 1465, 1445, 1380, 1345, 1310, 1245, 1145, 990, 870, 850, 835, 750, 730, 710 and 690; δ_H 0.04 (9 H, s, Me_3Si), 0.98 (3 H, d, *J* 6.8 Hz, CH*Me*), 1.02 (3 H, s, CMe), 1.19 (3 H, s, CMe), 1.40–2.60 (8 H, m, ring 1-, 2-, 3- and 5-H, and 4- and 7-H$_2$), 5.44 (1 H, d, *J* 18.5 Hz, 1-H) and 5.85 (1 H, dd, *J* 18.5 and 7.3 Hz, 2-H); δ_C −0.72 (3 × Me), 20.99 (Me), 23.20 (Me), 28.63 (Me), 34.44 (CH_2), 34.95 (CH_2), 39.16 (C), 41.98 (CH), 42.93 (CH), 45.09 (CH), 48.01 (CH), 126.75 (=CH) and 154.70 (=CH); *m*/*z* 236 (M^+, 1%), 221 (5), 181 (12), 109 (16), 107 (14), 95 (18), 83 (51), 73 (100) and 59 (12).

General Procedure for the Synthesis of 2-(*Trimethylsilyl*)*alk*-1-*enes* **7**.—The experiment set-up was the same as described in the synthesis of compounds **6**. The flask was cooled to 0 °C and charged with a solution of $BH_2Br{\cdot}SMe_2$ (10 cm^3, 10 mmol) in dichloromethane. To the stirred solution was added the terminal alkene (20 mmol), and the reaction mixture was stirred for 2 h at 25 °C to complete the hydroboration. After removal of dichloromethane and dimethyl sulphide under reduced pressure with a water aspirator, dry diethyl ether (40 cm^3) and dry dimethyl sulphide (2 cm^3) were added to the resulting dialkylbromoborane at 0 °C, and the solution was stirred for 30 min at the same temperature. (Trimethylsilyl)ethyne **1** (0.98 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. Aq. NaOH (6 mol dm^{-3}; 12 cm^3) and THF (20 cm^3) were added to the reaction mixture at −15 °C, followed by the dropwise addition of a solution of iodine (5.08 g, 20 mmol) in THF (20 cm^3). The reaction mixture was warmed to 0 °C, stirred for 30 min, and then oxidized by the successive addition of aq. NaOH (3 mol dm^{-3}; 5 cm^3) and H_2O_2 (30%; 5 cm^3) at the same temperature. After being stirred for 1 h at 0 °C, the mixture was extracted three times with diethyl ether. The combined extracts were washed with brine (in the analytical reaction GLC analyses were carried out at this point), dried over Na_2SO_4, and concentrated. The crude product was purified by column chromatography on silica gel (Wakogel Q-50), with pentane as eluent, to give the corresponding vinylsilane **7c**, **7e** and **7f**.

For 4-*Methyl*-2-(*trimethylsilyl*)*hept*-1-*ene* **7c** (1.38 g, 75%) (Found: C, 71.7; H, 13.15. $C_{11}H_{24}Si$ requires C, 71.6; H, 13.1%); ν_{max}(neat)/cm^{-1}: 3040, 2950, 2920, 2860, 1465, 1455, 1375, 1245, 925, 835 and 755; δ_H 0.07 (9 H, s, Me_3Si), 0.80 (3 H, d, *J* 6.8 Hz, CH*Me*), 0.87 (3 H, t, *J* 6.8 Hz, 7-H$_3$), 1.00–1.65 (5 H, m, 4-H and 5- and 6-H$_2$), 1.80–1.95 (1 H, m, =CCH*H*), 2.10–2.25 (1 H, m, =CC*H*H), 5.34 (1 H, d, *J* 3.4 Hz, =C*H*H) and 5.45–5.55 (1 H, m, =CH*H*); δ_C −0.89 (3 × Me), 14.67 (Me), 19.77 (Me), 20.48 (CH_2), 31.76 (CH), 39.65 (CH_2), 45.29 (CH_2), 125.63 (=CH_2) and 151.61 (=C); *m*/*z* 184 (M^+, 2%), 169 (8), 141 (4), 99 (20), 73 (100), 59 (16) and 43 (13).

For 2-(*Trimethylsilyl*)*oct*-1-*ene* **7e** (0.76 g, 41%) (Found: C, 71.7; H, 13.0. $C_{11}H_{24}Si$ requires C, 71.6; H, 13.1%); ν_{max}(neat)/cm^{-1}: 3040, 2950, 2920, 1460, 1450, 1245, 920, 850, 830 and 750; δ_H 0.07 (9 H, s, Me_3Si), 0.88 (3 H, t, *J* 6.8 Hz, 8-H$_3$), 1.00–1.60 (8 H, m, 4-, 5-, 6- and 7-H$_2$), 2.00–2.20 (2 H, m, 3-H$_2$), 5.29 (1 H, d, *J* 3.0 Hz, =C*H*H) and 5.50–5.60 (1 H, m, =CH*H*); δ_C −1.11 (3 × Me), 14.40 (Me), 22.96 (CH_2), 29.38 (CH_2), 29.53 (CH_2), 32.10 (CH_2), 36.48 (CH_2), 123.88 (=CH_2) and 152.93 (=C); *m*/*z* 184 (M^+, 1%), 169 (13), 113 (12), 99 (20), 73 (100) and 59 (26).

For 4-*Phenyl*-2-(*trimethylsilyl*)*pent*-1-*ene* **7f** (1.46 g, 67%) (Found: C, 77.1; H, 10.2. $C_{14}H_{22}Si$ requires C, 77.0; H, 10.15%); ν_{max}(neat)/cm^{-1}: 3020, 2950, 2910, 1595, 1490, 1445, 1400, 1370, 1245, 1010, 925, 845, 830, 755 and 695; δ_H 0.08 (9 H, s, Me_3Si), 1.20 (3 H, d, *J* 6.8 Hz, CH*Me*), 2.15–2.35 (1 H, m, C*H*Me), 2.40–2.60 (1 H, m, =CCH*H*), 2.75–2.95 (1 H, m, =CC*H*H), 5.35 (1 H, d, *J* 2.9 Hz, =C*H*H), 5.45–5.55 (1 H, m, =CH*H*) and 7.05–7.40 (5 H, m, Ph); δ_C −0.68 (3 × Me), 21.98 (Me), 39.25 (CH), 45.89 (CH_2), 126.39 (=CH), 126.65 (=CH_2), 127.53 (2 × =CH), 128.82 (2 × =CH), 148.28 (=C) and 150.86 (=C); *m*/*z* 218 (M^+, 5%), 204 (8), 144 (8), 135 (9), 105 (100) and 73 (17).

(Z)-1-(*Trimethylsilyl*)*alk*-1-*enes* **5**.—Cyclohexene was hydroborated with BH_3 in THF, followed by reaction of the alkyne **1** in the same manner as described in the general procedure for the synthesis of the *E*-alkenes **6**. The reaction mixture was treated as described in the general procedure for the synthesis of compound **7**. Compound **5a**, contaminated with a small amount of its isomer **7a**, was collected from the worked up reaction mixture by column chromatography on silica gel (Wakogel Q-50), with pentane as eluent. 2-Methylbut-2-ene was treated in a similar manner as described above. Compounds **5a** and **5b** were identified by the following spectral data.

For (*Z*)-2-cyclohexyl-1-(trimethylsilyl)ethene **5a**, ν_{max}(neat)/cm^{-1}: 2920, 2850, 1605, 1445, 1250, 890, 855, 835 and 760; δ_H 0.10 (9 H, s, Me_3Si), 0.80–2.25 (11 H, m, ring H), 5.35 (1 H, d, *J* 14.1 Hz, 1-H) and 6.10 (1 H, dd, *J* 14.1 and 10.2 Hz, 2-H); δ_C 0.65 (3 × Me), 26.10 (2 × CH_2), 26.24 (CH_2), 33.37 (2 × CH_2), 43.03 (CH), 126.85 (=CH) and 155.29 (=CH); *m*/*z* 182 (M^+, 8%), 167 (17), 139 (16), 108 (29), 85 (17), 73 (100) and 59 (22).

For (*Z*)-3,4-dimethyl-1-(trimethylsilyl)pent-1-ene **5b**, ν_{max}(neat)/cm^{-1}: 2960, 2870, 1605, 1455, 1380, 1365, 1250, 925, 880, 850, 835, 760 and 690; δ_H 0.09 (9 H, s, Me_3Si), 0.85 (3 H, d, *J* 6.3 Hz, CH*Me*), 0.87 (3 H, d, *J* 6.3 Hz, CH*Me*), 0.92 (3 H, d, *J* 6.8 Hz, CH*Me*), 1.30–1.55 (1 H, m, 4-H), 1.90–2.15 (1 H, m, 3-H), 5.40 (1 H, d, *J* 14.1 Hz, 1-H) and 6.12 (1 H, dd, *J* 14.1 and 10.2 Hz, 2-H); δ_C 0.80 (3 × Me), 18.68 (Me), 20.23 (Me), 20.75 (Me), 33.39 (CH), 44.44 (CH), 127.39 (=CH) and 154.41 (=CH); *m*/*z* 170 (M^+, 4%), 155 (14), 127 (6), 113 (10), 99 (20), 96 (10), 85 (12), 73 (100) and 59 (17).

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