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STEREOSELECTIVE SYNTHESIS OF VINYLSILANES FROM ALKYNYLSILANES BY REDUCTIVE ALKYLATION VIA HYDROBORATION, TRANSMETALLATION AND CARBODEMETALLATION

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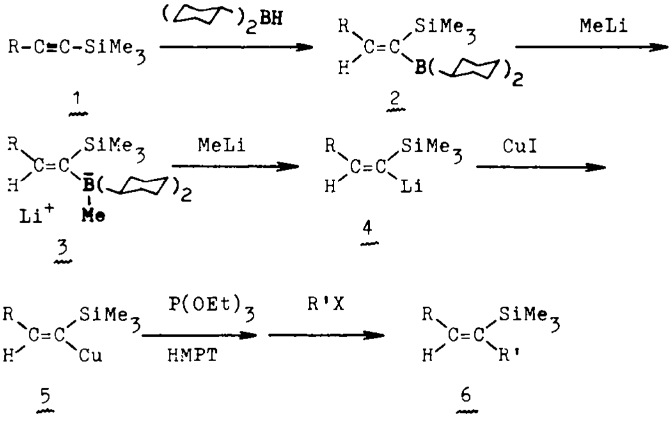
Abstract—Hydroboration of 1-trimethylsilyl-1-alkynes with dicyclohexylborane gives 1-trimethylsilylvinylboranes regio- and stereoselectively whose successive treatment with methyllithium, cuprous iodide and alkyl halides affords (*Z*)-1,2-dialkylvinylsilanes in high yields. Functionalized 1-trimethylsilyl-1-alkynes give analogous results. Successive treatment of the intermediary 1-trimethylsilylvinylboranes with methyllithium and methyl iodide gives 2-trimethylsilyl-2(*Z*)-alkenes. Allyl halides give 4-trimethylsilyl-1,4(*Z*)-alkadienes analogously.

Organosilicon compounds have attracted much attention as versatile reagents for organic synthesis,[1] for example, vinylsilanes have been shown to be useful precursors for carbonyl compounds,[2] vinyl halides[3] and olefins[4] of predictable stereochemistry. In spite of increasing attention to vinylsilanes as novel nucleophile, few examples have been reported for the useful stereoselective synthesis of vinylsilanes.[5] Prompted by the report on reductive methylation of 1-trimethylsilyl-1-alkynes via hydralumination,[6] we describe herein a novel and generally applicable procedure for the preparation of 1,2-dialkylvinylsilanes with fixed geometry which is based on regioselective *cis*-hydroboration of 1-trimethylsilyl-1-alkynes to vinylboranes and the following transmetallation and carbodemetallation under strict retention of configuration.[7]

Hydroboration of 1-trimethylsilyl-1-octyne (**1**, R = Hex) with excess dicyclohexylborane in tetrahydrofuran afforded a vinylborane[a] whose PMR (δ 5.48 ppm, t, J = 7 Hz, olefinic proton) indicated regio- and stereoselective reaction furnishing **2** as the sole product. Successive treatment of the reaction mixture with methyllithium[b] and then with cuprous iodide afforded an organocopper, to which 1-trimethylsilyl-1(*E*)-octenylcopper structure[8] would reasonably be assigned on the basis of the characteristic brown colour of the reaction mixture and the analysis of carbodemetallation products (*vide infra*). The mixture was treated with an alkyl halide in the presence of triethyl phosphite and hexamethylphosphoric triamide to afford a 1,2-dialkylvinylsilane with fixed geometry in excellent yield. Carbodemetallation with an alkyl iodide gave better results in yield and stereoselectivity as compared with an alkyl bromide.[c] The reactivity towards tosylate, homoallylic iodide, and alkyl bromide indicated that the above described organocopper was more reactive than the simple vinylcopper.[9] Table 1 shows the chemical yields and



Scheme 1.

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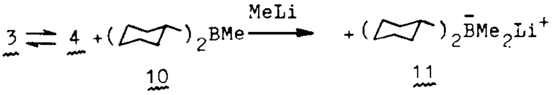
[a] Hydroboration of 1-trimethylsilyl-1-hexyne (**1**, R = Bu) was reported to give 1-trimethylsilyl-1(*Z*)-hexene (**6**, R = Bu, R' = H) after protonolysis with AcOH.[3] Regioselectivity of hydroboration and the structure of the intermediary boron compounds have not been mentioned.

[b] We assume that the borate **3** is in equilibrium with vinyllithium **4** and methyldicyclohexylborane **10**. Further addition of MeLi should complete the formation of **4** accompanying lithium dimethyldicyclohexylborate **11**. The vinyllithium **4** is responsible for alkylation giving the vinylsilane **6**. This reaction appears to be the first example of the direct transformation of vinylboranes to the corresponding vinyllithium compounds.



[c] Relative reactivity of EtI and EtBr towards **5** (R = Hex) under various reaction conditions was investigated. Details are shown in Table 2.

Table 1. Stereoselective synthesis of 1,2-dialkylvinylsilanes (**6a–s**)

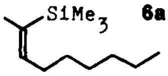
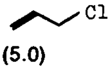
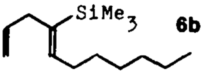
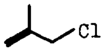
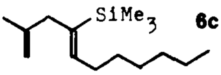
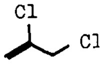
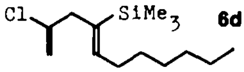
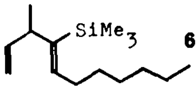
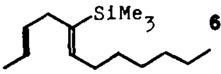
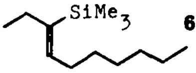
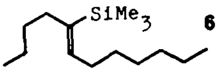
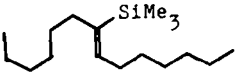
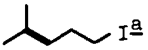
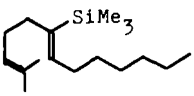
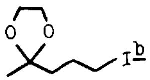
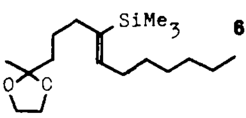
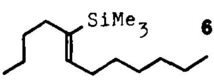
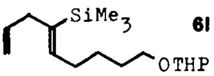
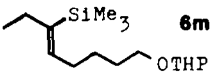
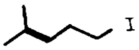
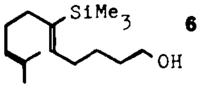
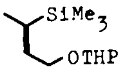
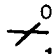
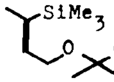
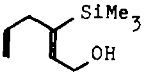
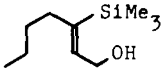
$RC\equiv CSiMe_3$ R (mmol)	R'X (mmol)	Method	Product (major isomer)		Yield (%)[d]	Isomer[i] purity (Z%)
n-C_6H_{13} **1a** (2.0)	CH_3I (10.0)	B		**6a l**	94(99)[e]	> 99
(3.0)	 (5.0)	B		**6b l**	93(91)[f]	> 99
(3.0)	 (5.0)	B		**6c l**	87	> 99
(3.0)	 (5.0)	B		**6d l**	71[g]	> 99
(3.0)	 (5.0)	B		**6e**	66	> 99
				**6f**	20	
(3.0)	C_2H_5I (4.5)	Cu		**6g**	89	98
(3.0)	n-C_4H_9I (4.5)	Cu		**6h**	81	97
(3.0)	n-$C_6H_{13}I$ (5.0)	Cu		**6i**	80[g]	97
(3.0)	 (3.6)	Cu		**6j**	27(29)[e]	94
(3.0)	 (4.5)	Cu		**6k**	46	90
(3.0)	n-C_4H_9OTs[c] (5.0)	Cu		**6h**	75	97
$—(CH_2)_4OTHP$ (1.05)	 (1.7)	B		**6l**	81	99[k]
(3.14)	C_2H_5I (4.5)	Cu		**6m**	85	98[k]
(3.0)	 (3.6)	Cu		**6n**	31[h]	94[k]
$—CH_2OTHP$ (3.0)	CH_3I (10.0)	B		**6p**	42[g](84)[f]	99[k]

Table 1 (*Contd*)

$RC{\equiv}CSiMe_3$ R (mmol)	R'X (mmol)	Method	Product (major isomer)		Yield (%)	Isomer[f] purity (Z%)
$-CH_2O$  **1d** (3.0)	CH_3I (10.0)	B		**6q**	80	99[k]
(3.0)	(4.5)	B		**6r**	59[j]	99[k]
(3.0)	$n\text{-}C_4H_9I$ (4.5)	Cu		**6s**	41[h]	85[k]

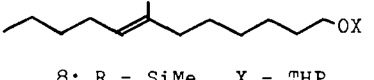
[a] J. P. McCormick and S. L. Barton, *J. Chem. Soc., Chem. Commun.* 303 (1975); [b] J. A. Findlay, Can. Pat. 939,369. [*Chem. Abstr.* **81**, 25105y (1974)]; E. A. Obol'nikova, M. Ts. Yanotovskii and G. I. Samokhvalov. *Zh. Obshch. Khim.* **34**, 1499 (1964). [*Chem. Abstr.* **61**, 5696b (1964)]. [c] Trimethyl phosphite was used in the place of triethyl phosphite. [d] Isolated yield after column chromatography unless otherwise stated. [e] Determined by GLC using an internal standard. [f] Via borate, see footnote *b*. [g] Isolated by column chromatography followed by distillation. [h] After isolation of the protected alcohol by column chromatography (silica gel or basic alumina), the alcohol was obtained by methanolysis followed by distillation. [i] After removal of the protecting group, the alcohol was purified by column chromatography. [j] Analysis by GLC. [k] GLC analysis of the corresponding trimethylsilyl ether. [l] This compound was prepared in Ref. 6*b*.

geometrical purity data of the resulting vinylsilanes. Functionalized R'X involving masked carbonyl moieties such as C=CCl and acetal reacted smoothly to give the expected products.

Vinyllithium derivatives (**4**) reacted with methyl iodide and allyl halides in excellent yields stereoselectively (Method B) although low reactivity was observed with ethyl iodide (as indicated by 10% yield of **6**). Similarly to the reported synthesis of vinylsilanes from alanates,[6] the borate **3** was able to react with methyl iodide and allyl chloride. Results are included in Table 1.

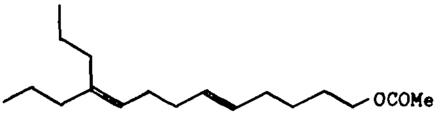
The above described procedures, coupled with the facile exchange of trimethylsilyl into hydrogen,[4] provide means of stereoselective synthesis of olefins from 1-alkynes under reductive alkylation and are novel addition to the synthetic reactions with organoboron compounds.[10]

The utility of the reaction sequence is illustrated by the following simple synthesis of sex pheromone of the false codling moth (*Argyroploce leucotreta*),[11] 7(*E*)-dodecenyl acetate (**9**) and that of the pink bollworm moth (*Pectinophora gossypiella*),[12] 10-propyl-5(*E*),9-tridecadienyl acetate (propylure) (**10**).



8: R = $SiMe_3$, X = THP

9: R = H, X = COMe



10

Treatment of vinylcopper **5** (R = Bu), prepared from 1-trimethylsilyl-1-hexyne (**1**, R = Bu), with 1 - iodo - 6 - (2 - tetrahydropyranyloxy)hexane[d] afforded vinylsilane **8** in 72% yield. Desilylation with iodine[4b,c] followed by acetylation gave the pheromone **9** (*E*:*Z* 9:1) in 82% yield. Analogously, propylure was prepared from 6 - (2 - tetrahydropyranyloxy) - 1 - trimethylsilyl - 1 - hexyne (**1b**, R = $-(CH_2)_4OTHP$) and 1 - bromo - 4 - propyl - 3 - heptene[14] in 22% overall yield (*E ca.* 80%).

EXPERIMENTAL

Gas chromatography was performed on a Shimadzu GC-4BPT with 3 m × 3 mm glass column packed with 20% HVSG and 20% PEG 20M on Chromosorb W-AW (80–100 mesh). PMR spectra were obtained on a Jeol JNM-PMX-60 and a Varian Associates EM-360 using TMS as an internal standard, mass spectra on a Hitachi RMU-6L with a chamber voltage of 70 eV, and IR on a Shimadzu IR-27G grating spectrometer. Bath temp on distillation refers to an oven temp of a "Kugelrohr" bulb-to-bulb distillation apparatus. Elemental analyses were carried out at the Elemental Analyses Centre of Kyoto University.

Starting materials

6 - (2 - Tetrahydropyranyloxy) - 1 - trimethylsilyl - 1 - hexyne (**1b**). To a stirred soln of EtMgBr (30 mmol) in THF (20 ml) was added 6 - (2 - tetrahydropyranyloxy) - 1 - hexyne[4c] (5.00 g, 27.4 mmol) at room temp and the mixture was further stirred for 1 hr and heated under reflux for 15 min. Treatment with Me_3SiCl and workup (aq. NH_4Cl) followed by distillation afforded the silylacetylene **1b** (6.24 g, 90% yield), b.p. 100–110°/0.2 mm. IR (neat): 2180, 1249, 1138, 1120, 1034, 840, 760 cm^{-1}; PMR (CCl_4): δ 0.13 (s, 9H), 1.2–1.9 (m, 10H), 2.19 (m, 2H), 3.1–4.0 (m, 4H), 4.46 (broad s, 1H); MS: *m/e* (rel. %) 254 (M^+, 0.2), 239 (0.4), 181 (2), 93 (14), 85 (100), 75 (30), 73 (45). (Found: C, 66.13; H, 10.55. Calc. for $C_{14}H_{26}O_2Si$: C, 66.09; H, 10.30%).

3 - (2 - Tetrahydropyranyloxy) - 1 - trimethylsilyl - 1 - propyne (**1c**). The tetrahydropyranyl ether[5d] was obtained from 3 - trimethylsilyl - 2 - propyn - 1 - ol[15] and 2,3-dihydropyran in 92% yield, b.p. 90–92°/5 mm.

3 - (1 - Methoxy - 1 - methylethoxy) - 1 - trimethylsilyl - 1 - propyne (**1d**). To a mixture of 3 - trimethylsilyl - 2 - propyn - 1 - ol[15] (3.84 g, 30.0 mmol) and methyl isopropenyl ether[16] (4.4 g, 60 mmol), two drops of $POCl_3$ was added at 0° and the whole set

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[d] Prepared from 6-iodo-1-hexanol[13] and 2,3-dihydropyran.

aside at room temp. for 1 hr.[17] The mixture was treated with triethylamine (3 drops), diluted with ether, and washed with water. The organic layer was dried (K_2CO_3) and concentrated *in vacuo*. Distillation afforded **1d** (5.53 g, 92% yield), b.p. 82–85°/7 mm. IR (neat): 2190, 1249, 1210, 1183, 1150, 1074, 1047, 843, 760 cm^{-1}; PMR (CCl_4): δ 0.16 (s, 9H), 1.29 (s, 6H), 3.13 (s, 3H), 3.95 (s, 2H); m/e (rel. %) 185 (M-15, 3), 113 (60), 111 (20), 85 (78), 83 (27), 75 (27), 73 (31), 61 (25). This acetal was too labile to be isolated in a pure form and did not give correct analysis. The sample was kept stable at −20° for a few months.

Preparation of 1,2-*dialkylvinylsilanes*

General procedure, Method B. To a well-stirred suspension of dicyclohexylborane (6.0 mmol) in THF, prepared from 6.0 mmol (5.6 ml of 1.08 M soln of BH_3 in THF) of borane and 0.98 g (12.0 mmol) of cyclohexene in 4.0 ml of THF at 0° for 1 hr, was added 1 - trimethylsilyl - 1 - alkyne (3.0 mmol) under argon atmosphere. After stirring at room temp. for 5 hr, the remaining dicyclohexylborane was quenched with 1-butene (*ca.* 6 mmol). The mixture was treated with 9.0 mmol (equimolar to the used borane and additional one equiv to **1**) of MeLi at 0°, stirred for 20 min at 0°, and finally treated with organic halide (1.2–5.0 equiv). After stirring at room temp. for 14 hr, the mixture was diluted with ether, treated with 2 ml of 3N NaOH and 4 ml of 30% H_2O_2 at 0°, and the whole was stirred for 1 hr at room temp. The products were taken up in ether and the ether extracts were washed, dried and concentrated *in vacuo*. The resulting oil was purified by column chromatography, which was performed on silica gel column (hexane or hexane–ether as eluent) unless otherwise specified.

Method Cu. To the soln of 1 - trimethylsilyl - vinyllithium reagent, prepared from a vinylborane as described in Method B, was added cuprous iodide (0.57 g, 3.0 mmol) at −30° and the whole was stirred for 5 min. The resulting dark brown mixture was treated with triethyl phosphite (0.60 g, 3.6 mmol), hexamethylphosphoric triamide (HMPT) (3.0 ml), and finally with alkyl halide (1.2–1.67 equiv) at −30°.[9] The mixture was allowed to warm to room temp. overnight and treated with 4 ml of 3N NaOH and 8 ml of 30% H_2O_2 at 0°. After stirring at room temp. for 1 hr, the products were extracted with ether. The combined ethereal extracts were washed (aq. NH_4Cl and brine), dried (K_2CO_3), and concentrated *in vacuo*. The residual material was purified by column chromatography, which was performed on silica gel column (hexane or hexane–ether as eluent) unless otherwise stated.

4-*Trimethylsilyl*-1,4(Z)-*undecadiene* (6b)

An alternate procedure via borate **3**. The vinylborane **2** (R = Hex), prepared from 1 - trimethylsilyl - 1 - octyne (3.0 mmol), was converted to **3** (R = Hex) by treatment with MeLi (6.0 mmol, equimolar to used borane) at room temp. for 20 min. The resulting mixture was treated with allyl chloride (5.0 mmol) to afford **6b** (0.61 g, 91% yield).

3 - *Methyl* - 4 - *trimethylsilyl* - 1,4(Z) - *undecadiene* (6e) *and* 5 - *trimethylsilyl*-2(E),5(Z)-*dodecadiene* (6f)

Alkylation of **4** (R = Hex) with 1-chloro-2(*E*)-butene gave a mixture of **6e** and **6f**, b.p. 120–125° (bath temp.)/2 mm. GLC (HVSG column at 190°) of the mixture revealed that the ratio **6e**/**6f** was 77:23. The ratio **6e**/**6f** was dependent upon alkylation conditions: 20 hr at 0°, 87% yield, **6e**/**6f** 89:11. The mixture gave correct analysis. (Found: C, 75.32; H, 12.67. Calc. for $C_{15}H_{30}Si$: C, 75.54; H, 12.68%). Each component was separated by preparative GLC, whose spectral data are given below.

3 - *Methyl* - 4 - *trimethylsilyl* - 1,4(Z) - *undecadiene*, IR (neat): 3100, 1634, 1613, 1251, 995, 956, 907, 834, 756, 687 cm^{-1}; PMR (CCl_4): δ 0.13 (s, 9H), 0.88 (t, J = 6 Hz, 3H), 1.06 (d, J = 7 Hz, 3H), 1.1–1.5 (m, 8H), 1.9–2.3 (m, 2H), 2.6–3.2 (m, 1H), 4.6–5.1 (m, 2H), 5.4–6.0 (m, 2H, C(2)$\underline{H}$ and C(5)$\underline{H}$); MS: m/e (rel. %) 238 (M^+, 5), 223 (2), 164 (12), 74 (8), 73 (100), 59 (12).

5 - *Trimethylsilyl* - 2(E),5(Z) - *dodecadiene*, IR (neat): 1613, 1250, 970, 835, 757, 691 cm^{-1}; PMR (CCl_4): δ 0.11 (s, 9H), 0.90 (t, J = 6 Hz, 3H), 1.1–1.6 (m, 8H), 1.6–1.8 (m, 3H, allylic methyl), 1.9–2.3 (m, 2H), 2.6–2.8 (m, 2H), 5.3–5.5 (m, 2H, olefinic proton), 5.88 (broad t, J = 7 Hz, 1H); MS: m/e (rel. %) 238 (M^+, 2), 223 (1), 164 (14), 74 (10), 73 (100), 59 (15).

3-*Trimethylsilyl*-3(Z)-*decene* (**6g**), b.p. 95–100° (bath temp.)/2 mm; IR (neat): 1613, 1245, 835, 755 cm^{-1}; PMR (CCl_4): δ 0.12 (s, 9H), 0.87 (t, J = 6 Hz, 3H), 0.92 (t, J = 7 Hz, 3H), 1.1–1.5 (m, 8H), 1.6–2.3 (m, 4H), 5.84 (t-t, J = 1, 7 Hz, 1H); MS: m/e (rel. %) 212 (M^+, 1), 197 (17), 138 (12), 99 (11), 87 (12), 73 (100), 59 (33). (Found: C, 73.54; H, 13.48. Calc. for $C_{13}H_{28}Si$: C, 73.50; H, 13.28%).

Yield and isomer ratio were dependent upon alkylation conditions. These results are summarized in Table 2. Reaction conditions of entry 1 gave the best result and was, therefore, applied as a general procedure designated as Method Cu.

5-*Trimethylsilyl*-5(Z)-*dodecene* (**6h**), b.p. 125–130° (bath temp.)/2 mm; IR (neat): 1610, 1245, 834, 755 cm^{-1}; PMR (CCl_4): δ 0.12 (s, 9H), 0.88 (t, J = 6 Hz, 6H), 1.1–1.7 (m, 12H), 1.8–2.3 (m, 4H), 5.83 (broad t, J = 7 Hz, 1H); MS: m/e (rel. %) 240 (M^+, 1), 225 (13), 166 (15), 74 (10), 73 (100), 59 (25). (Found: C, 74.62; H, 13.22. Calc. for $C_{15}H_{32}Si$: C, 74.91; H, 13.41%).

Butyl p-toluenesulfonate (1.7 equiv to **1**) was efficient alkylating agent of Method Cu in the presence of trimethyl phosphite (1.2 equiv to **1**) as a ligand (Table 1). In contrast, unmodified Method Cu gave less satisfactory result (39% yield, Z:E 83:17).

7-*Trimethylsilyl*-7(Z)-*tetradecene* (**6i**), b.p. 120–125° (bath temp.)/0.08 mm. IR (neat): 1611, 1244, 833, 754 cm^{-1}; PMR (CCl_4): δ 0.12 (s, 9H), 0.88 (t, J = 6 Hz, 6H), 1.1–1.7 (m, 16H), 1.8–2.3 (m, 4H), 5.84 (broad t, J = 7 Hz, 1H, olefinic proton); MS: m/e (rel. %) 268 (M^+, 0.1), 253 (5), 194 (8), 96 (12), 73 (100), 59 (20). (Found: C, 76.13; H, 13.37. Calc. for $C_{17}H_{36}Si$: C, 76.03; H, 13.51%).

PMR spectra of authentic E isomer[4b] showed the olefinic proton at δ 5.60 (CCl_4, t, J = 6.5 Hz).

2 - *Methyl* - 6 - *trimethylsilyl* - 2,6(Z) - *tridecadiene* (**6j**), b.p. 105–110° (bath temp.)/0.07 mm; IR (neat): 1612, 1249, 834, 756 cm^{-1}; PMR (CCl_4): δ 0.13 (s, 9H), 0.90 (t, J = 6 Hz, 3H), 1.1–1.5 (m, 8H), 1.62 (broad d, J = 5 Hz, 6H), 1.8–2.3 (m, 6H), 5.03 (broad s, 1H), 5.88 (t, J = 7 Hz, 1H); MS: m/e (rel. %) 266 (M^+, 1), 251 (1), 192 (4), 73 (100), 59 (38). (Found: C, 76.64; H, 13.03. Calc. for $C_{17}H_{34}Si$: C, 76.61; H, 12.86%).

2 - *Methyl* - 2 - (4 - *trimethylsilyl* - 4(Z) - *undecenyl*) - 1,3 -

Table 2. Yields and isomer ratios

	EtX (equiv to **1a**)	$(EtO)_3P$ (equiv to **1a**)	Isomer Ratio $\underline{Z}$: $\underline{E}$	Yield (%) **6g** + $\underline{E}$ isomer
1	EtI (1.5)	1.2	98:2	89
2	EtI (1.5)	1.0	95:5	85
3	EtI (2.0)	3.0	>99	40
4	EtBr (1.5)	1.2	95:5	85
5	EtBr (1.5)	1.0	88:12	85

dioxolane (**6k**), b.p. 135–140° (bath temp.)/0.07 mm. IR (neat): 1612, 1242, 1061, 834, 755 cm^{-1}; PMR (CCl_4): δ 0.12 (s, 9H), 0.89 (t, J = 6 Hz, 3H), 1.0–1.7 (m, 15H), 1.8–2.3 (m, 4H), 3.82 (s, 4H), 5.88 (broad t, J = 7 Hz, 1H); MS: *m/e* (rel. %) 312 (M^+, 1), 297 (1), 210 (7), 140 (35), 87 (58), 75 (20), 73 (100), 59 (21). (Found: C, 68.93; H, 11.62. Calc. for $C_{18}H_{36}O_2Si$: C, 69.17; H, 11.61%).

9 - (2 - *Tetrahydropyranyloxy*) - 4 - *trimethylsilyl* - 1,4(Z) - *nonadiene* (**6l**), b.p. 135–140° (bath temp.)/0.1 mm: IR (neat): 3080, 1638, 1612, 1248, 1135, 1120, 1077, 1033, 835, 758 cm^{-1}; PMR (CCl_4): δ 0.14 (s, 9H), 1.2–1.8 (m, 10H), 2.0–2.4 (m, 2H), 2.77 (broad d, J = 6 Hz, 2H), 3.1–4.0 (m, 4H), 4.48 (broad s, 1H), 4.7–5.1 (m, 2H), 5.4–6.1 (m, 2H); MS: *m/e* (rel. %) 296 (M^+, 0.1), 85 (100), 75 (18), 73 (44). The corresponding alcohol was obtained by exposure of the vinylsilane **6l** (0.61 g, 2.1 mmol) to MeOH soln of *p*-toluenesulfonic acid (30 ml of a 5 mM soln) at room temp. for 2 hr and by final distillation (0.39 g, 88% yield), b.p. 120–125° (bath temp.)/2 mm; IR (neat): 3330, 3080, 1638, 1614, 1247, 1063, 913, 838, 761 cm^{-1}; PMR ($CDCl_3$): δ 0.14 (s, 9H), 1.2–1.8 (m, 4H), 1.8–2.4 (m, 3H, C(4)$\underline{H}$ and O$\underline{H}$), 2.80 (broad d, J = 6 Hz, 2H), 3.63 (t, J = 6 Hz, 2H), 4.7–5.2 (m, 2H), 5.4–6.2 (m, 2H, C(8)$\underline{H}$ and C(5)$\underline{H}$); MS of trimethylsilyl ether: *m/e* (rel. %) 284 (M^+, 0.2), 269 (0.1), 202 (3), 147 (30), 75 (19), 73 (100), 59 (14). The corresponding acetate was submitted to the elemental analysis. (Found: C, 65.87; H, 10.40. Calc. for $C_{14}H_{26}O_2Si$: C, 66.09; H, 10.30%).

8 - (2 - *Tetrahydropyranyloxy*) - 3 - *trimethylsilyl* - 3(Z) - *octene* (**6m**), b.p. 125–130° (bath temp.)/0.1 mm; IR (neat): 1612, 1246, 1135, 1120, 1077, 1034, 837, 757 cm^{-1}; PMR (CCl_4): δ 0.13 (s, 9H), 0.95 (t, J = 7 Hz, 3H), 1.1–1.7 (m, 10H), 1.8–2.3 (m, 4H), 3.0–4.0 (m, 4H), 4.49 (broad s, 1H), 5.89 (broad t, J = 7 Hz, 1H); MS: *m/e* (rel. %) 185 (1), 85 (100), 75 (31), 73 (45). Methanolysis of **6m**, followed by column chromatography (silica gel, hexane–ether 3:1), afforded the corresponding alcohol (89% yield), b.p. 110–115° (bath temp.)/2 mm. IR (neat): 3310, 1614, 1245, 1060, 835, 757 cm^{-1}; PMR (CCl_4): δ 0.13 (s, 9H), 0.95 (t, J = 7 Hz, 3H), 1.2–1.8 (m, 4H), 1.8–2.3 (m, 4H), 3.63 (t, J = 6 Hz, 2H), 5.92 (broad t, J = 7 Hz, 1H); MS of trimethylsilyl ether: *m/e* (rel. %) 243 (M-29, 1), 147 (48), 75 (24), 73 (100), 59 (17). The corresponding acetate was submitted to the elemental analysis. (Found: C, 64.55; H, 10.82. Calc. for $C_{13}H_{26}O_2Si$: C, 64.41; H, 10.81%).

10 - *Methyl* - 6 - *trimethylsilyl* - 5(Z),9 - *undecadien* - 1 - *ol* (**6n**). The resulting tetrahydropyranyl ether was dissolved in methanoic *p*-toluene–sulfonic acid (5 mM soln, 35 ml). After 2 hr at room temp., column chromatography (silica gel, hexane–ethyl acetate 6:1) of the resulting oil followed by bulb-to-bulb distillation gave **6n** (0.24 g, 31% yield), b.p. 135–140° (bath temp.)/0.07 mm. IR (neat): 3330, 1613, 1243, 1057, 836, 757 cm^{-1}; PMR ($CDCl_3$): δ 0.13 (s, 9H), 1.2–1.8 (m, 11H, two methylenes, two allylic methyls, and O$\underline{H}$), 1.8–2.3 (m, 6H, allylic methylenes), 3.64 (t, J = 6 Hz, 2H), 5.12 (broad s, C(9)$\underline{H}$), 5.96 (t, J = 7 Hz, C(5)$\underline{H}$); MS of trimethylsilyl ether: *m/e* (rel. %) 326 (M^+, 0.4), 252 (1), 147 (16), 75 (23), 73 (100). (Found: C, 70.69; H, 11.94. Calc. for $C_{15}H_{30}OSi$: C, 70.79; H, 11.88%).

4 - (2 - *Tetrahydropyranyloxy*) - 2 - *trimethylsilyl* - 2(Z) - *butene* (**6p**), PMR spectrum of the resulting vinylborane **2** prepared from **1c** showed an olefinic proton as a triplet (CCl_4, δ 5.26 ppm). Methylation (Method B) gave **6p**, b.p. 110–115° (bath temp.)/5 mm; IR (neat): 1618, 1244, 1115, 1015, 834, 752, 688 cm^{-1}; PMR (CCl_4): δ 0.14 (s, 9H), 1.1–1.7 (m, 6H), 1.78 (broad s, 3H), 3.1–4.2 (m, 4H), 4.51 (broad s, 1H), 6.01 (q-t, J = 2, 7 Hz, 1H); MS: *m/e* (rel. %) 226 (M^+, 0.1), 213 (1), 127 (9), 99 (10), 85 (100), 75 (13), 73 (38), 67 (12), 57 (15). Methanolysis of **6p** (0.58 g, 2.5 mmol) as described in the preparation of **6l** followed by preparative TLC (silica gel, hexane–ethyl acetate 9:1) afforded the corresponding alcohol[5d,19] (0.30 g, 83% yield), b.p. 115–120° (bath temp.)/16 mm (lit.[19] 45–47°/2 mm). IR (neat): 3320, 1619, 1244, 1065, 999, 837, 757 cm^{-1}; PMR (CCl_4): δ 0.14 (s, 9H), 1.76 (broad s, 3H), 2.83 (broad s, 1H, O$\underline{H}$), 3.98 (d, J = 7 Hz, 2H), 6.02 (q-t, J = 2, 7 Hz, 1H); MS: *m/e* (rel. %) 144 (M^+, 1), 129 (26), 87 (10), 75 (100), 73 (65).

An alternate procedure as described in the preparation of **6b** gave better result. Methylation of the borate **3** (R = $-CH_2OTHP$) at room temp for 14 hr afforded **6p**.

4 - (1 - *Methoxy* - 1 - *methylethoxy*) - 2 - *trimethylsilyl* - 2(Z) - *butene* (**6q**), PMR analysis of the vinylborane **2** (R = $-CH_2OCMe_2OMe$) prepared from **1d** exhibited a single olefinic proton at δ 5.60 ppm (CCl_4, t, J = 6 Hz). Methylation (Method B) and oxidative workup followed by column chromatography (Woelm basic alumina, activity II, hexane–ether 15:1) to afford **6q** as an unstable oil. IR (neat): 1614, 1244, 1208, 1150, 1074, 1053, 1035, 839, 768 cm^{-1}; PMR (CCl_4): δ 0.12 (s, 9H), 1.24 (s, 6H), 1.77 (broad s, 3H), 3.10 (s, 3H), 3.86 (d, J = 7 Hz, 2H), 6.00 (q-t, J = 2, 7 Hz, 1H); MS: *m/e* (rel. %) 184 (1), 169 (5), 143 (8), 99 (12), 85 (15), 75 (37), 73 (100), 59 (16). Methanolysis of **6q** (5 mM *p*-toluenesulfonic acid in MeOH, room temp., 1 hr) gave the corresponding alcohol, whose retention time on GLC and spectral data were identical with the alcohol prepared from **6p**.

3-*Trimethylsilyl*-2(Z),5-*hexadien*-1-*ol* (**6r**). Oxidative workup followed by column chromatography (Woelm basic alumina, activity II, hexane : ether 15:1) gave the crude vinylsilane. After removal of the protecting group as above, column chromatography (silica gel, hexane–ethyl acetate 10:1) afforded **6r**, b.p. 95–100° (bath temp.)/2 mm. IR (neat): 3300, 3075, 1636, 1614, 1246, 1001, 912, 838, 758 cm^{-1}; PMR ($CDCl_3$): δ 0.16 (s, 9H), 1.46 (broad s, 1H), 2.84 (broad d, J = 6 Hz, 2H), 4.22 (d, J = 7 Hz, 2H), 4.7–5.2 (m, 2H), 5.4–6.3 (m, 2H, C(5)$\underline{H}$ and C(2)$\underline{H}$); MS: *m/e* (rel. %) 170 (M^+, 1), 153 (3), 79 (28), 75 (100), 73 (65), 59 (7). (Found: C, 63.54; H, 10.69. Calc. for $C_9H_{18}OSi$: C, 63.47; H, 10.65%).

3-*Trimethylsilyl*-2(Z)-*hepten*-1-*ol* (**6s**). The acetal was purified by column chromatography (Woelm basic alumina, activity II, hexane : ether 15:1). Removal of the protecting group as above and bulb-to-bulb distillation afforded **6s**, b.p. 105–110° (bath temp.)/2 mm. IR (neat): 3300, 1617, 1247, 1010, 835, 758 cm^{-1}; PMR (CCl_4): δ 0.14 (s, 9H), 0.91 (t, J = 6 Hz, 3H), 1.1–1.5 (m, 4H), 1.8–2.3 (m, 2H), 3.40 (broad s, 1H, O$\underline{H}$), 4.08 (d, J = 7 Hz, 2H), 6.04 (t, J = 7 Hz, 1H); MS: *m/e* (rel. %) 171 (M-15, 3), 143 (7), 129 (6), 81 (13), 75 (100), 73 (66), 67 (15), 54 (29). Preparative TLC or GLC did not give any analytically pure sample.

Synthesis of 7(E)-*dodecenyl acetate* (9)

By Method Cu. Alkylation of **5** (R = Bu), prepared from 1 - trimethylsilyl - 1 - hexyne (0.46 g, 3.0 mmol), with 1 - iodo - 6 - (2 - tetrahydropyranyloxy)hexane (1.40 g, 4.5 mmol) gave, after column chromatography (silica gel, hexane–ether 5:1), the crude **8** (0.87 g, 72% yield, *E*:*Z* 9:91 by GLC analysis of the corresponding trimethylsilyl ether). The vinylsilane obtained was used without further purification. The mixture of the crude vinylsilane (0.21 g, 0.62 mmol) and catalytic iodine dissolved in benzene (2 ml) was heated at reflux for 2 hr. After dilution with ether, the organic layer was washed (10% $Na_2S_2O_3$, brine), dried ($MgSO_4$) and concentrated *in vacuo*. The oil was dissolved in MeOH containing *p*-toluenesulfonic acid (5 mM, 5 ml) and the mixture set aside for 2 hr. After quenching with pyridine (2 drops) and concentration *in vacuo*, the residue was passed through a short silica gel column (hexane–ether 2:1 as eluent). The crude alcohol was treated with pyridine and Ac_2O (3 ml of 1:1 mixture) at room temp. overnight. Distillation afforded **9** (0.11 g, 82% yield from **8**, *E*:*Z* = 9:1[c]), b.p. 125–130° (bath temp.)/5 mm. IR (neat): 1740, 1232, 1038, 970 cm^{-1}; PMR (CCl_4): δ 0.90 (t, J = 6 Hz, 3H), 1.1–1.8 (m, 12H), 1.8–2.3 (m, 7H, allylic methylenes and $COCH_3$ at δ 1.97), 4.00 (t, J = 6 Hz, 2H), 5.2–5.5 (m, 2H); MS: *m/e* (rel. %) 226 (M^+, 0.1), 166 (3), 96 (15), 95 (15), 82 (28), 81 (30), 68 (28), 67 (62), 61 (10), 55 (90), 54 (56), 43 (100).[11]

Synthesis of 10-*propyl*-5(E),9-*tridecadienyl acetate* (10)

By Method Cu. The crude vinylsilane was obtained from **1b** (0.76 g, 3.0 mmol) and 1-bromo-4-propyl-3-heptene **14** (1.07 g, 4.9 mmol in 26% yield after column chromatography (silica gel, hexane–ether 9:1). Treatment with iodine followed by acetylation as above gave **10** in 83% yield. TLC and GLC analysis did not give any information on isomeric purity. The isomeric ratio was estimated by the comparison of the intensity at λ_{max} 970 cm^{-1} with that of authentic materials[4c,18] to be *ca* 80% E.

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[c] GLC analysis by capillary column (BDS, 45 ml) at 150°.

spectra of propylure. They also wish to thank the Ministry of Education, Japan, for a Grant-in-Aid (911506, 011010, 110309).

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