[11] a) J. M. Thomas, R. Raja, G. Sankar, R. G. Bell, *Nature* **1999**, *398*, 227–230; b) A. Clearfield, *Chem. Rev.* **1988**, *88*, 125–148; c) Y. F. Shen, R. P. Zerger, R. N. DeGuzman, S. L. Suib, L. McCurdy, D. I. Potter, C. L. O'Young, *Science* **1993**, *260*, 511–515; d) Z. R. Tian, W. Tong, J. Y. Wang, N. G. Duan, V. V. Krishnam, S. L. Suib, *Science* **1997**, *276*, 926–930.

[12] C. L. O'Young, R. A. Sawicki, S. L. Suib, *Microporous Mater.* **1997**, *11*, 1–8.

[13] Although we did not experience any incidents during the alcohol oxidation studies using our catalyst, adequate precautions need to be taken against explosion hazards associated with toluene–oxygen vapors at the high reaction temperature. This is so because the lower limit of flammability of toluene is a meager 1.2% by volume in air.

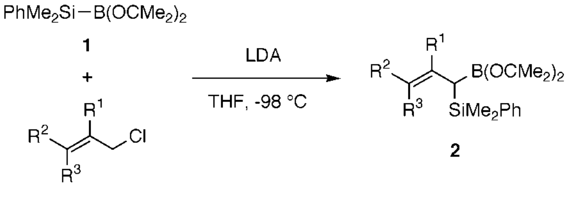
[14] R. A. Sheldon, M. Wallau, I. W. C. E. Arends, U. Schuchardt, *Acc. Chem. Res.* **1998**, *31*, 485–493.

1-Silyl-1-boryl-2-alkenes: Reagents for Stereodivergent Allylation Leading to 4-Oxy-(*E*)-1-alkenylboronates and 4-Oxy-(*Z*)-1-alkenylsilanes[**]

Masaki Shimizu,* Hirotaka Kitagawa,
Takuya Kurahashi, and Tamejiro Hiyama*

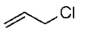
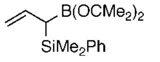
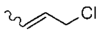
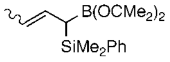
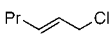
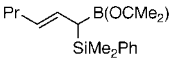
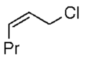
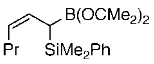
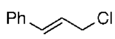
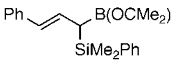
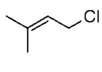
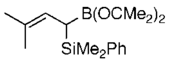
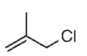
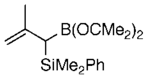
Allylmetal reagents have been widely used in organic synthesis.[1] In addition, allylic boranes[2] and silanes[3] are highly versatile owing to their wide availability, high stability, and low toxicity as well as excellent chemo-, regio-, and stereoselectivities. In sharp contrast, little attention has been paid to 1-silyl-1-boryl-2-alkenes, though such reagents can be regarded as a hybrid of allylic boranes and silanes and are attractive for the construction of stereochemically complex molecules.[4] Yamamoto, Yatagai, and Maruyama prepared α-trimethylsilyl-substituted crotyl-9-BBN (9-BBN = 9-borabicyclo[3.3.1]nonane) by deprotonation of crotyl-9-BBN followed by silylation with chlorotrimethylsilane.[5] Similar boronates were synthesized by Tsai and Matteson by the homologation of alkenylboronates with [chloro(trimethylsilyl)methyl]lithium.[6] Both reagents were found to allylate aldehydes[7] in a manner similar to allylic boranes. Although this methodology is effective for acyclic stereocontrol, allylation with allylic silanes and stereospecificity in boron-selective allylation remained to be explored. Herein we describe the novel stereocontrolled synthesis of 1-silyl-1-boryl-2-alkenes by *gem*-silylborylation of α-chloroallyllithiums and dual stereospecific allylation of aldehydes with silicon or boron functionality of the *gem*-silylboryl reagents.

Recently, the novel *gem*-silylborylation reaction of 1-halo-1-lithio-1-alkenes with (dimethylphenylsilyl)(pinacolato)borane (**1**) was disclosed[8] and is considered to proceed via borate formation followed by 1,2-migration of a silyl group from an ate-type boron to a carbenoid carbon. We envisaged that the title *gem*-silylboryl reagents **2** might be prepared readily by the *gem*-silylborylation with **1** of vinyl-substituted carbenoids [Eq. (1)].[9, 10] Thus, we treated **1**[11] with α-chloroallyllithiums generated in situ from allylic chlorides and lithium diisopropylamide (LDA) in THF at −98 °C. The results are summarized in Table 1. Allyl chloride was converted into **2a** in 82% yield (Entry 1). Substituted allylic chlorides were also *gem*-silylborylated smoothly in good yields irrespective of the substitution pattern (Entries 2–7). No trace of γ-silyl-α-boration by 1,4-migration of a silyl group was observed. Noteworthy is that the olefinic configuration was perfectly retained in compounds **2** (Entries 3–5): stereochemically pure allylic chlorides gave single stereoisomers of **2**.



(1)

Table 1. Synthesis of 1-silyl-1-boryl-2-alkenes from allylic chlorides.[a]

Entry	Allylic chloride	Product	Yield [%][b]
1		 **2a**	82
2	 [c]	 **2b**	86[d]
3	 [e]	 **2c**	75[e]
4	 [f]	 **2d**	79[f]
5	 [e]	 **2e**	75[e]
6		 **2f**	72
7		 **2g**	73

[a] allylic chloride (1.0 mol), **1** (1.1 mol), LDA (1.0 mol), THF, −98 °C, 10 min then warmed to room temperature. [b] Isolated yields are given. [c] *E*/*Z* = 85:15. [d] *E*/*Z* = 83:17. [e] *E*/*Z* = >99:<1. [f] *E*/*Z* = <1:>99.

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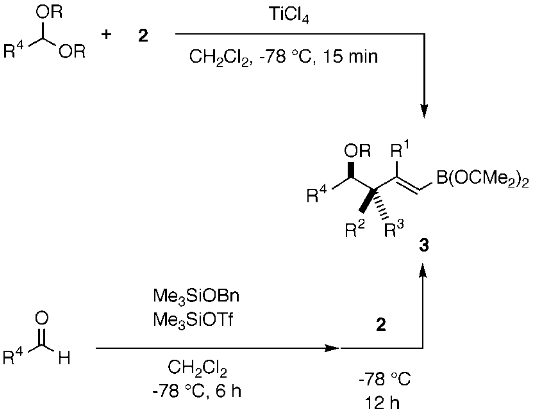
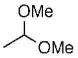
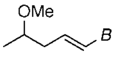
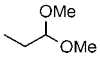
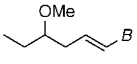
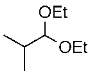
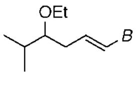
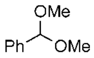
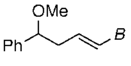
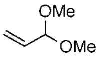
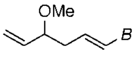
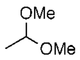
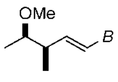
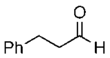
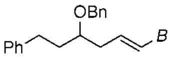
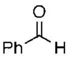
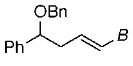
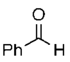
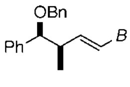
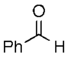
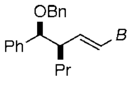
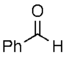
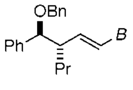
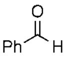
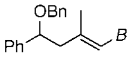
We next scrutinized the allylation of **2** taking advantage of allylic silane functionality. After many attempts,[12] we found that compounds **2** allylated acetals in the presence of titanium tetrachloride (Scheme 1).[13, 14] The results are summarized in Table 2. Aliphatic, aromatic, and α,β-unsaturated acetals reacted with **2** to produce alkenylboronates **3a–f** in good yields with high (*E*)-selectivity (Entries 1–6). Moreover, reagents **2** were shown to allylate an oxonium ion in situ generated from an aldehyde, Me_3SiOBn, and Me_3SiOTf, to give the corresponding (*E*)-benzyl ether **3g–l** stereoselectively (Entries 7–12).[15] High (*E*)-selectivity of **3** is observed irrespective of the olefinic geometry of **2** (Entries 6, 9, 10, and 11).[16] Markedly, allylation by 1-silyl-(*E*)- and (*Z*)-2-hexenyl boronates **2c** and **2d** proceeded stereospecifically with high (*E*, *erythro*) and (*E*, *threo*) selectivities, respectively (Entries 10 and 11).[17] These results are the first demonstration of silicon-selective allylation over boron in **2**.



Scheme 1. Allylation of acetals or aldehydes as allylic silanes. Bn = benzyl, OTf = trifluoromethanesulfonate.

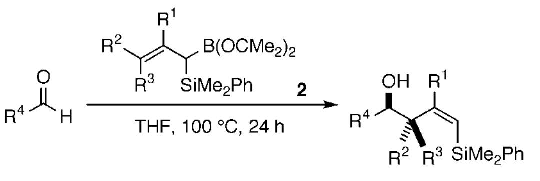
Table 2. Allylation of acetals or aldehydes with **2** as an allylic silane.[a]

Entry	2	Electrophile	Product	Yield [%][b]	Isomer ratio[c]
1	**2a**		 **3a**	78 (3)[d]	94:6[e]
2	**2a**		 **3b**	77	95:5[e]
3	**2a**		 **3c**	85	–[f]
4	**2a**		 **3d**	69	97:3[e]
5	**2a**		 **3e**	62	>95:<5[e]
6	**2b**[g]		 **3f**	81	73:24:3[h]
7	**2a**		 **3g**	85	>95:<5[e]
8	**2a**		 **3h**	88 (73)[i]	>95:<5[e]
9	**2b**[g]		 **3i**	81	84:16[j]
10	**2c**		 **3j**	83	95:5[j]
11	**2d**		 **3k**	94	9:91[j]
12	**2g**		 **3l**	70	>95:<5[e]

[a] For acetals: **2** (1.0 mol), acetal (2.0 mol), $TiCl_4$ (1.5 mol), CH_2Cl_2, −78 °C, 15 min. For aldehydes: aldehyde (1.0 mol), Me_3SiOBn (1.3 mol), Me_3SiOTf (1.0 mol), CH_2Cl_2, −78 °C, 6 h, then **2** (1.0 mol), −78 °C, 12 h; $B = B(OCMe_2)_2$. [b] Isolated yields are given. [c] Determined by ^1H NMR of a crude product mixture. [d] (*E*)-**3a**: 78% yield; (*Z*)-**3a**: 3% yield. [e] Ratios of *E*/*Z*. [f] The ratio was not determined. [g] *E*/*Z* Mixture of **2b** was used (*E*/*Z* = 83:17). [h] Ratio of (*E*, *erythro*):(*E*, *threo*):others. [i] 88%: Me_3SiOTf (1.0 mol); 73%: Me_3SiOTf (0.1 mol). [j] Ratio of (*E*, *erythro*):(*E*, *threo*).

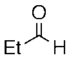
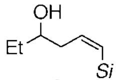
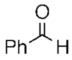
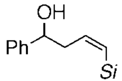
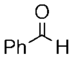
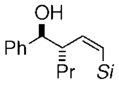
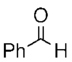
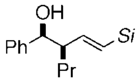
Allylation of aldehydes with allylic borane reagents **2a**, **2c**, and **2d** was also studied [Eq. (2)]. Some of results are summarized in Table 3. Both aliphatic and aromatic aldehydes were allylated by **2a** upon heating at 100 °C in the absence of any additive to yield the corresponding alkenylsilanes **4a** and **4b** in moderate to good yields with high *Z*-selectivity (Entries 1 and 2). Comparing with the results of pinacol α-trimethylsilyl allylboronate,[6] the selectivity slightly increased because of the bulkier dimethylphenylsilyl group. Stereochemically pure (*E*)-2-hexenyl boronate **2c** reacted with benzaldehyde to give **4c** in a (*E*, *threo*)/(*Z*, *threo*) ratio of 7:93 (Entry 3), whereas (*E*, *erythro*) isomer **4d** was produced by using **2d** with 94% selectivity (Entry 4). The stereospecific outcome is in accord with chairlike six-membered transition states.[5, 6]

Further synthetic elaboration of the allylated products with the aid of the remaining inorganic functional group and deprotection of benzyl group in **3** are illustrated in Scheme 2. Suzuki–Miyaura coupling[18] of **3d** with iodobenzene gave (*E*)-homoallylic ether **5**, while methoxyethoxymethylation of **4c** with methoxyethoxymethyl chloride (MEMCl) followed by acetal-vinylsilane cyclization mediated by titanium tetra-

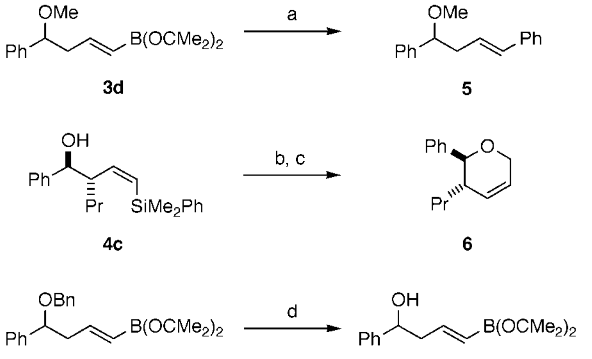


(2)

Table 3. Allylation of aldehydes with **2** as an allylic borane.[a]

Entry	2	Aldehyde	Product	Yield [%][b]	Isomer ratio[c]
1	**2a**		 **4a**	74 (17)	15:85[d]
2	**2a**		 **4b**	89 (0)	9:91[d]
3	**2c**		 **4c**	87 (10)	7: 93[e]
4[f]	**2d**		 **4d**	46 (20)	94:6[g]

[a] **2** (1.0 mol), aldehyde (1.1 mol), THF, 100 °C, 24 h. *Si* = $SiMe_2Ph$. [b] Isolated yields are given. The values in parentheses are recovery of **2**. [c] Determined by ^1H NMR. [d] Ratio of *E*/*Z*. [e] Ratio of (*E*, *threo*):(*Z*, *threo*). [f] Benzaldehyde (3 molar equivalents) was treated at 65 °C for 45 h. [g] Ratio of (*E*, *erythro*):(*Z*, *threo*).



Scheme 2. Synthetic applications of allylated products **3d**, **3h**, and **4c**. a) PhI (1.1 mol), $[Pd(PPh_3)_4]$ (4.9 mol %), aq. KOH (3.0 mol), dioxane, 100 °C, 86 % yield; b) NaH (5.1 mol), MEMCl (6.1 mol), THF, RT, 55 % yield; c) $TiCl_4$ (3.0 mol), CH_2Cl_2, −78 °C, 82 % yield; d) Me_3SiI (1.3 mol), CH_2Cl_2, RT, 73 % yield.

chloride gave *trans*-6-phenyl-5-propyl-5,6-dihydro-2*H*-pyran (**6**).[19] Debenzylation of **3h** was carried out in good yield by treatment with Me_3SiI with retention of the (*E*)-alkenylboryl moiety.[20]

In summary, we have demonstrated that *gem*-silylborylation of stereochemically defined α-chloroallyllithiums with silylborane **1** constitutes a new method for the stereocontrolled synthesis of 1-silyl-1-boryl-2-alkenes **2**. Furthermore, stereospecific allylation of aldehydes with **2** was achieved with either the silicon- or boron-functionality, and was demonstrated that under appropriate conditions the corresponding adducts are readily converted into substituted (*E*)- or (*Z*)-homoallylic alcohols.

Experimental Section

Full experimental details and analytical data can be found in the Supporting Information.

2a, *gem*-silylborylation of allyl chloride: A solution of LDA (3.3 mmol) in THF (8 mL) was added to a solution of allyl chloride (0.26 mL, 3.2 mmol) and (dimethylphenylsilyl)(pinacolato)borane (**1**) (0.92 g, 3.5 mmol) in THF (20 mL) at −98 °C. The reaction mixture was stirred for 10 min at −98 °C and then allowed to gradually warm to room temperature. The solution was stirred overnight followed by quenching with saturated aq. NH_4Cl solution. The aqueous layer was extracted with diethyl ether (20 mL). The organic layer was dried over anhydrous $MgSO_4$, and concentrated in vacuo to give the crude product. Purification by column chromatography on silica gel (hexane/ethyl acetate = 9/1) afforded **2a** as a colorless oil (0.79 g, 82 % yield); TLC: $R_f = 0.45$ (hexane/ethyl acetate = 9/1); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.34$ (s, 3H), 0.35 (s, 3H), 1.13 (s, 6H), 1.16 (s, 6H), 1.79 (d, J = 10.5 Hz, 1H), 4.74 (ddd, J = 16.8, 2.2, 0.6 Hz, 1H), 4.78 (dd, J = 10.5, 2.2 Hz, 1H), 5.85 (ddd, J = 16.8, 10.5, 10.5 Hz, 1H), 7.28–7.38 (m, 3H), 7.48–7.60 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -3.2, -3.2$, 24.7, 24.8, 82.8, 112.2, 127.4, 128.8, 133.9, 135.3, 138.0; IR (neat): $\tilde{\nu} = 2985$, 1623, 1374, 1339, 1318, 1145, 839 cm^{-1}; MS (EI, 70 eV): m/z 303 (M^++1, 1), 302 (M^+, 5), 301 (M^+ − 1, 1), 284 (M^+ − Me, 6), 245 (28), 235 (M^+ − Ph, 13), 202 (32), 187 (32), 160 (49), 135 ($PhMe_2Si^+$, 100); elemental analysis (%) calcd for $C_{17}H_{27}BO_2Si$: C 67.55, H 9.00; found: C 67.29, H 8.92.

Allylation of acetaldehyde dimethylacetal with **2a**: A solution of $TiCl_4$ in CH_2Cl_2 (1.0 M, 0.82 mL, 0.82 mmol) was added to a solution of **2a** (0.17 g, 0.55 mmol) and acetaldehyde dimethylacetal (116 µL, 1.10 mmol) in CH_2Cl_2 (6 mL) at −78 °C. The solution was stirred for 15 min at −78 °C before quenching with water (0.50 mL) at −78 °C. The mixture was warmed to room temperature, dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated to give a crude product consisting of *E*/*Z* = 94:6 as revealed by ^1H NMR spectra. Purification by silica gel column chromatography (hexane/ethyl acetate = 2/1) afforded (*E*)-**3a** (97 mg, 78 % yield) and (*Z*)-**3a** (4.1 mg, 3 % yield). (*E*)-**3a**: colorless oil; thin layer chromatography (TLC): $R_f = 0.53$ (hexane/ethyl acetate = 2/1); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.15$ (d, J = 6.0 Hz, 3H), 1.27 (s, 3H), 2.27 (ddd, J = 14.4, 6.6, 1.5 Hz, 1H), 2.44 (ddd, J = 14.4, 6.6, 1.5 Hz, 1H), 3.32 (s, 3H), 3.42 (m, J = 6.0 Hz, 1H), 5.50 (dt, J = 18.1, 1.5 Hz, 1H), 6.60 (dt, J = 18.1, 6.6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 19.1$, 24.8, 42.6, 56.0, 75.9, 83.1, 150.3. IR (neat): $\tilde{\nu} = 2980$, 2935, 1640, 1362, 1321, 1146, 998, 972, 852 cm^{-1}. MS (EI, 70 eV): m/z 225 (M^+ − 1, 0.6), 211 (M^+ − Me, 17), 111 (9), 101 (8.0), 95 (8), 59 (100); elemental analysis (%) calcd for $C_{12}H_{23}BO_3$: C 63.74, H 10.25; found: C 63.62, H 10.41.

Allylation of benzaldehyde with **2a**: A solution of **2a** (0.13 g, 0.42 mmol) and benzaldehyde (47 µL, 0.46 mmol) in THF (4 mL) was stirred at 100 °C (oil bath) for 24 h. The reaction mixture was cooled to room temperature, and then ethanolamine (42 µL) was added to the mixture at room temperature. The resulting milky suspension was stirred for 30 min. Filtration of the insoluble material followed by concentration of the filtrate gave a crude product. Purification by silica gel column chromatography (hexane/ethyl acetate = 4/1) gave **4b** as a colorless oil (0.11 g, 89 % yield, *E*/*Z* = 9:91); TLC: $R_f = 0.31$ (hexane/ethyl acetate = 4/1); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.38$ (s, 6H), 1.77 (brs, 1H), 2.35–2.65 (m, 2H), 4.64 (dd, J = 7.4, 5.6 Hz, 1H), 5.85 (dt, J = 13.9, 1.3 Hz, 1H), 6.46 (dt, J = 13.9, 7.4 Hz, 1H), 7.16–7.42 (m, 8H), 7.48–7.58 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -1.0$, 1.0, 43.0, 73.6, 125.7, 127.4, 127.8, 128.3, 128.9, 130.6, 133.7, 139.3, 143.8, 145.6. IR (neat): $\tilde{\nu}$3400 (br), 3070, 3035, 2965, 2900, 1608, 1428, 1250, 1114, 1053, 822 cm^{-1}; MS (EI, 70 eV): m/z 283 (M^+ + 1, 0.3), 282 (M^+, 0.5), 281 (M^+ − 1, 2), 264 (M^+ − H_2O, 13), 249 (M^+ − H_2O − Me, 16), 241 (34), 173 (52), 145 (36), 135 ($PhMe_2Si^+$, 91), 121 (47), 107 ($PhCHOH^+$, 100); elemental analysis (%) calcd for $C_{18}H_{22}OSi$: C 76.54, H 7.85; found: C 76.82, H 7.88.

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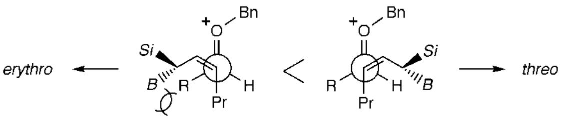

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Organoclay Derivatives in the Synthesis of Macrocycles

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Dimitrios Petridis*

The synthesis of macrocyclic systems is profoundly hindered by reactions of participating components that lead to the formation of mainly oligomeric or polymeric compounds. To overcome this deficiency, template-assisted methods based on metal coordination, electron-donor interactions, hydrogen bonding, and electrostatic interactions have been successfully developed.[1] In these reactions the templating agent plays the essential role of assembling and organizing the participating molecules in a way that makes possible a desirable reaction pathway that would not occur in its absence.[2]

Another potential approach to effectively assemble and organize compounds into well-defined supramolecular arrays

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