ORGANIC
LETTERS

2003
Vol. 5, No. 2
225−227

gem-Silylborylation of an *sp* Carbon: Novel Synthesis of 1-Boryl-1-silylallenes

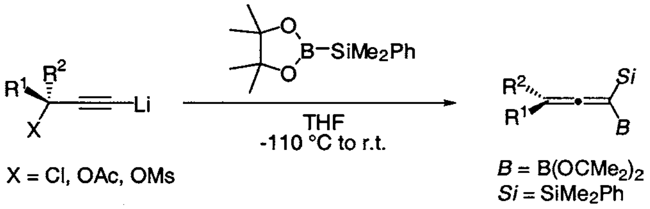
Masaki Shimizu,* Takuya Kurahashi, Hirotaka Kitagawa, and Tamejiro Hiyama

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan

shimizu@npc05.kuic.kyoto-u.ac.jp

Received November 27, 2002

ABSTRACT



Novel synthesis of 1-boryl-1-silylallenes involving *gem*-silylborylation of 3-chloro- or 3-alkoxyalkyn-1-yllithiums with (dimethylphenylsilyl)(pinacolato)borane has been established. The reaction proceeds via 1,2-migration of the silyl group from the negatively charged boron atom of an intermediary borate complex to the terminal acetylenic carbon and is accelerated by the addition of chlorotrimethylsilane in the case that methanesulfonyloxy is employed as a leaving group. Furthermore, axially enantioenriched products could be prepared from mesylates of optically active propargylic alcohols.

Since *gem*-diorganometallics are versatile reagents in organic synthesis,[1] facile synthesis of those dimetalated compounds is of great significance. Especially, reactions in which two metals are introduced simultaneously into an organic molecule by utilizing an interelement compound are straightforward and highly efficient for the purpose. From this point of view, we have developed a novel and efficient method for the preparation of 1-boryl-1-silyl-1-alkenes and 1-boryl-1-silyl-2-alkenes via *gem*-silylborylation of alkylidene-type carbenoids and α-chloroallyllithiums with silylboranes, respectively.[2] These reactions proceed through formation of an ate complex from a lithium carbenoid and a silylborane, followed by 1,2-migration of the silyl group from a negatively charged boron to the carbenoid carbon. To further extend the scope of *gem*-silylborylation utilizing silylboranes, we turned our attention to *gem*-silylborylation of an *sp* carbon in terminal acetylenes, leading to allenyl organodimetallics.[3] We report herein that treatment of 3-chloro- or 3-alkoxy-1-alkyne **1** (X = Cl or OR′) with a base generates the corresponding alkynyllithium **2**, which reacts with (dimethylphenylsilyl)(pinacolato)borane (**3**) to produce 1-boryl-1-silylallenes **5** in moderate to good yields (Scheme 1).[4,5] This method allows us to prepare enantioenriched allenes **5** by using optically active 3-mesyloxy-1-alkynes **1** (X = OMs).

---

[1] Reviews on *gem*-diorganometallics: (a) Marek, I.; Normant, J.-F. *Chem. Rev.* **1996**, *96*, 3241−3267. (b) Marek, I. *Chem. Rev.* **2000**, *100*, 2887−2900. (c) Matsubara, S.; Oshima, K.; Utimoto, K. *J. Organomet. Chem.* **2001**, *617−618*, 39. (d) Marek, I.; Normant, J. F. In *Organozinc Reagents−A Practical Approach*; Knochel, P., Jones, P., Eds.; Oxford University Press: Oxford, 1999; pp 119−137. (e) Normant, J. F. *Acc. Chem. Res.* **2001**, *34*, 640−644.

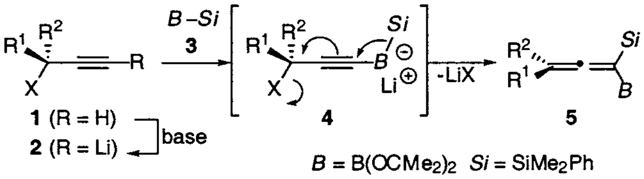
[2] (a) Hata, T.; Kitagawa, H.; Masai, H.; Kurahashi, T.; Shimizu, M.; Hiyama, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 790−792. (b) Shimizu, M.; Kitagawa, H.; Kurahashi, T.; Hiyama, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 4283−4286. (c) Kurahashi, T.; Kitagawa, H.; Masai, H.; Hata, T.; Shimizu, M.; Hiyama, T. *Tetrahedron* **2002**, *58*, 6381−6395. See also: (d) Shimizu, M.; Kurahashi, T.; Hiyama, T. *Yuki Gosei Kagaku Kyokai Shi* **2001**, *59*, 1062−1069. (e) Shimizu, M.; Kurahashi, T.; Hiyama, T. *Synlett* **2001**, 1006−1008.

[3] Reviews of allenyl organometallics: (a) Yamamoto, H. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 2, pp 81−98. (b) Masse, C. E.; Panek, J. S. *Chem. Rev.* **1995**, *95*, 1293−1316. (c) Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31−47. (d) Marshall, J. A. *Chem. Rev.* **2000**, *100*, 3163−3185.

[4] Preparations and reactions of 1-boryl-1-silylallenes: (a) Haruta, R.; Ishiguro, M.; Furuta, K.; Mori, A.; Ikeda, N.; Yamamoto, H. *Chem. Lett.* **1982**, 1093−1096. (b) Wang, K. K.; Nikam, S. S.; Ho, C. D. *J. Org. Chem.* **1983**, *48*, 5376−5377. (c) Yamamoto, Y.; Ito, W.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1984**, 1004−1005. (d) Furuta, K.; Ishiguro, M.; Haruta, R.; Ikeda, N.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2768−2776. (e) Nikam, S. S.; Wang, K. K. *J. Org. Chem.* **1985**, *50*, 2193−2195. (f) Yamamoto, Y.; Maruyama, K.; Komatsu, T.; Ito, W. *J. Org. Chem.* **1986**, *51*, 886−891. (g) Wang, K. K.; Wang, Z.; Gu, Y. G. *Tetrahedron Lett.* **1993**, *34*, 8391−8394.

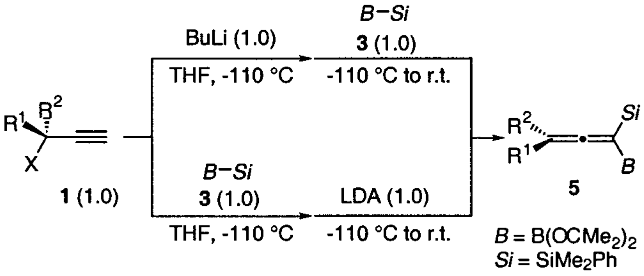
10.1021/ol027367o CCC: $25.00

Scheme 1. Novel Synthesis of 1-Boryl-1-silylallenes via *gem*-Silylborylation of an Acetylenic Carbon



Treatment of **1** with BuLi in THF at −110 °C was followed by the addition of **3** at −110 °C, while **1** was deprotonated in the presence of **3** at −110 °C when lithium diisopropylamide (LDA) was employed as a base (Scheme 2).[6] In both cases, the resulting solution was allowed to warm to room temperature before quenching with saturated aqueous NH_4Cl solution.

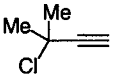
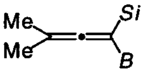
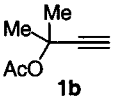
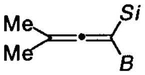
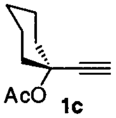
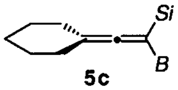
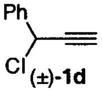
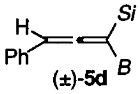
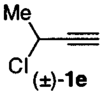
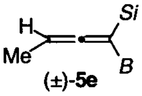
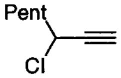
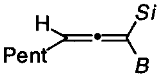
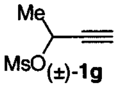
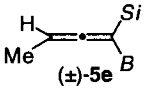
Scheme 2. Reaction Procedure for the Preparation of **5**



Workup and purification by column chromatography on silica gel afforded **5** in moderate to good yields.[7] The results are summarized in Table 1. Alkynyllithium **2a** prepared from 3-chloro-3-methyl-1-butyne (**1a**) with BuLi reacted with **3** to give **5a** in 70% yield (entry 1). The yield of **5a** was slightly increased by changing the leaving group from chlorine to OAc (entry 2). Deprotonation of **1c** with BuLi and subsequent treatment with **3** gave allenylidenecyclohexane **5c** in 53% yield (entry 3). Silylborylation of racemic α-monosubstituted propargylic chlorides **1d**−**f** using BuLi gave 3-substituted allenes **5d**−**f** in moderate to good yields (entries 5, 7, and 9). In the case of **1c**−**e**, better yields were obtained when LDA was used instead of BuLi (entries 4, 6, and 8).

Additionally, a mesyloxy group was found to be a good leaving group for the present transformation. *gem*-Silylborylation of (±)-**1g** proceeded via deprotonation with BuLi or LDA, giving rise to (±)-**5e** in 51% or 57% yield, respectively (entries 10 and 11). Noteworthy is that the addition of chlorotrimethylsilane to the reaction mixture starting from **1g** accelerated the *gem*-silylborylation and enhanced the yield of **5f** to 75% (entry 12). In this case, the reaction went to completion below −78 °C, whereas without chlorotrimethylsilane it was essential to warm to room temperature to consume **3**. Chlorotrimethylsilane is considered to play the role of a Lewis acid for promoting elimination of a mesyloxy group (Figure 1). In all cases, no isomerization of **5** to propargylboranes was observed.[8]

Table 1. *gem*-Silylborylation of **1**[a]

Entry	1	base	5	Yield/%[b]
1	 **1a**	BuLi	 **5a**	70
2	 **1b**	BuLi	 **5a**	77
3	 **1c**	BuLi	 **5c**	53
4		LDA		60
5	 (±)-**1d**	BuLi	 (±)-**5d**	41
6		LDA		52[c]
7	 (±)-**1e**	BuLi	 (±)-**5e**	50
8		LDA		58
9[d]	 (±)-**1f**	BuLi	 (±)-**5f**	83
10	 (±)-**1g**	BuLi	 (±)-**5e**	51
11		LDA		57
12[e]		LDA		75

[a] To a solution of **1** (0.50 mmol) in THF (3 mL) was added BuLi (0.50 mmol) at −110 °C. After stirring for 2 min, the reaction mixture was treated with **3** (0.50 mmol) and allowed to warm to room temperature before quenching with saturated aqueous NH_4Cl (1 mL). [b] Isolated yields after column chromatography on silica gel. [c] Purified by GPC. [d] Pent = n-C_5H_{11} [e] Chlorotrimethylsilane (0.55 mmol) was added to the reaction mixture at −110 °C after the addition of **3**.

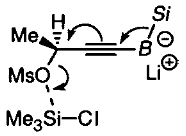


Figure 1. Acceleration of *gem*-silylborylation by Me_3SiCl.

---

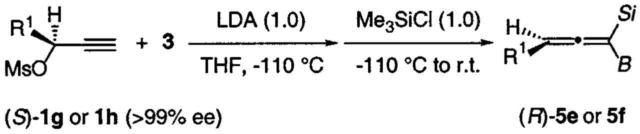
(5) Pioneering studies on the preparation of allenylboranes from propargylic chlorides or acetates and organoboranes: (a) Leung, T.; Zweifel, G. *J. Am. Chem. Soc.* **1974**, *96*, 5620−5621. (b) Midland, M. M. *J. Org. Chem.* **1977**, *42*, 2650−2651. Preparation of allenylzinc reagents via 1,2-migration of a carbonaceous substituent in alkynylzincates was reported. (c) Harada, T.; Katsuhira, T.; Osada, A.; Iwazaki, K.; Maejima, K.; Oku, A. *J. Am. Chem. Soc.* **1996**, *118*, 11377−11390.

(6) Treatment of **1** with LDA followed by the addition of **3** resulted in no production of **5** at all; the reason is not clear at present.

(7) Alkylidene-type carbenoids reacted smoothly with in situ generated (trimethylsilyl)(pinacolato)borane to give the corresponding 1-boryl-1-trimethylsilyl-1-alkenes in good yields (ref 2c), whereas silylborylation of **2** with the trimethylsilylborane failed.

To explore the possibility of asymmetric synthesis of 1-boryl-1-silylallenes, we next carried out the *gem*-silylborylation of optically active mesylates (*S*)-**1g** and (*S*)-**1h**.[9] After several experiments,[10] we found that treatment of (*S*)-**1g** or (*S*)-**1h** with LDA in THF at −110 °C in the presence of **3** followed by addition of chlorotrimethylsilane gave (*R*)-**5e** or (*R*)-**5f** in 75% or 67% yield with >74% ee (vide infra) or 70% ee (Scheme 3).[11] The fact that central *S* chirality transferred into axial *R* chirality can be reasonably explained by assuming that 1,2-migration of the silyl group with elimination of a mesyloxy group proceeds in anti S_N2' fashion as exemplified in Figure 1. These results are the first demonstration of asymmetric *gem*-silylborylation of organolithium reagents.

Scheme 3. Preparation of Axially Enantioenriched *gem*-Silylborylallenes **5**

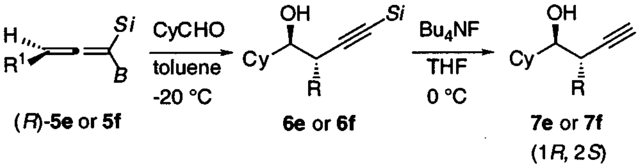


1	R^1	5	Yield/%	$[\alpha]_D^{25}$	% ee
1g	Me	**5e**	75	-11.44 (*c* 3.20, $CHCl_3$)	>74[a]
1h	Pent	**5f**	67	-9.78 (*c* 3.22, $CHCl_3$)	70[b]

[a] Estimated after transformation of **5e** into known compound **7e** (vide infra). [b]Determined by HPLC analysis using Daicel AD column.

Absolute configurations of **5e** and **5f** were deduced by chemical transformation to known alcohols **7e** and **7f** (Scheme 4). Thus, **5e** or **5f** reacted with cyclohexanecarbaldehyde in toluene at −20 °C to yield with high *anti* diastereoselectivity **6e** or **6f**, which was desilylated to give **7e** or **7f**, respectively. Since the negative sign of specific rotations (−1.78 (*c* 0.93, $CHCl_3$) for **7e**; −3.21 (*c* 1.37, $CHCl_3$) for **7f**) is attributed to the (1*R*,2*S*)-enantiomer, absolute configurations of **5e** and **5f** are assigned *R*.[12] No loss of optical purity in the reaction of (*R*)-**5e** indicates that this propargylation is perfectly stereospecific. Hence, the ee of **5e** was estimated to be >74% as shown in Scheme 3.

Scheme 4. Stereochemical Assignment of (*R*)-**5e** and -**5f**[a,b]



5	R^1	6	Yield/%	7	Yield/%
5e	Me	**6e**	92 (*anti* : *syn* = 93 : 7)	**7e**	72 (74% ee)[c]
5f	Pent	**6f**	67 (*anti* : *syn* = 89 : 11)	**7f**	82 (70% ee)[c]

[a] A toluene solution (2 mL) of **5** (0.30 mmol) and cyclohexanecarbaldehyde (0.45 mmol) was stirred at −20 °C for 24 h before quenching with water (10 mL). [b]To a solution of **6** (0.25 mmol) in THF (2 mL) was added a 1 M THF solution of Bu_4NF (0.25 mmol). The resulting solution was stirred at 0 °C for 6 h. [c]Determined by GC analysis using Chiral-DEX CB column.

In summary, we have demonstrated that 1-boryl-1-silylallenes can be efficiently synthesized from readily available 3-chloro- or 3-alkoxyalkyn-1-yllithiums with silylborane in moderate to good yields. In addition, the present method is applicable to the preparation of enantioenriched 1-boryl-1-silylallenes. Studies on synthetic application of the *gem*-dimetalated allenes are in progress.

Acknowledgment. This work was supported by Grants-in-Aid for COE Research on Elements Science, no. 12CE2005, and for Young Scientists (B), no. 14750678, from Ministry of Education, Culture, Sports, Science, and Technology, Japan. Japan Society for the Promotion of Science (JSPS) is highly acknowledged for the financial support to T.K. as a predoctoral research student.

Supporting Information Available: Detailed descriptions of experimental procedures and spectral data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OL027367O

---

(8) Zweifel, G.; Backlund, S. J.; Leung, T. *J. Am. Chem. Soc.* **1978**, *100*, 5561−5562.

(9) Examples of axially optically active allenylmetallic compounds. Allenylboranes: (a) Matsumoto, Y.; Naito, M.; Uozumi, Y.; Hayashi, T. *J. Chem. Soc., Chem. Commun.* **1993**, 1468−1469. Allenylsilanes: (b) Buckle, M. J. C.; Fleming, I. *Tetrahedron Lett.* **1993**, *34*, 2383−2386. (c) Marshall, J. A.; Maxson, K. *J. Org. Chem.* **2000**, *65*, 630−633. (d) Shepard, M. S.; Carreira, E. M. *J. Am. Chem. Soc.* **1997**, *119*, 2597−2605. (e) Marshall, J. A.; Adams, N. D. *J. Org. Chem.* **1997**, *62*, 8976−8977. (f) Han, J. W.; Tokunaga, N.; Hayashi, T. *J. Am. Chem. Soc.* **2001**, *123*, 12915−12916. α-Silylallenyltitaniums: (g) Okamoto, S.; An, D. K.; Sato, F. *Tetrahedron Lett.* **1998**, *39*, 4551−4554. (h) Song, Y.; Okamoto, S.; Sato, F. *Org. Lett.* **2001**, *3*, 3543−3545. Allenylzincs: (i) Marshall, J. A.; Adams, N. D. *J. Org. Chem.* **1999**, *64*, 5201−5204. Preparation of enantioenriched allenylzinc reagents by kinetic resolution of the racemates is reported. (j) Poisson, J.-F.; Normant, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 4639−4640. Allenylindiums, -bismuths, and -tins: (k) Marshall, J. A.; Grant, C. M. *J. Org. Chem.* **1999**, *64*, 8214−8219.

(10) Reaction of (*S*)-**1g** and **3** with Me_3SiCl in Et_2O resulted in the production of (*R*)-**5e** in 64% yield with 60% ee, and (*R*)-**5e** formed in THF without the addition of Me_3SiCl in 51% yield with 70% ee.

(11) With monitoring of the specific rotation of **5e** in solution such as THF, toluene, or CH_2Cl_2 with time, no racemization of **5e** was confirmed.

(12) Propargylation of aldehydes with allenylboranes is assumed to proceed via six-membered cyclic transition states. For example: Haruta, R.; Ishiguro, M.; Ikeda, N.; Yamamoto, H. *J. Am. Chem. Soc.* **1982**, *104*, 7667−7669.