Communications to the Editor

β-Borylallylsilanes as a New Tool for Convenient Synthesis of Alkenylboranes

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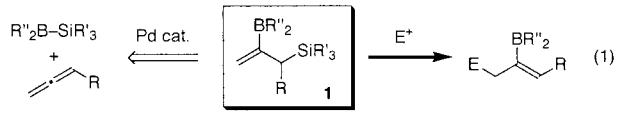
Allylsilane is one of the most useful building blocks for nucleophilic allylation in organic synthesis.[1] The usefulness of the allylsilanes, which are synthetically accessible with regio- and stereo-defined forms, arises from high regio- and stereoselectivities in the allylation reactions. Furthermore, stability of the allylsilanes, which is due to the covalent character of their silicon−carbon bond, may enable selective carbon−carbon bond-forming reactions with functional groups, which are not tolerable by means of anionic allylmetal reagents.

In our recent exploitation of the synthetic application of silylboranes,[2,3] we found that palladium-catalyzed silaboration of allenes proceeded in good yields to give *β*-borylallylsilanes **1** (eq 1).[4,5] Notably, the addition took place at the more substituted C═C

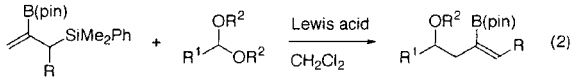


(1)

bond of terminal allenes in a highly regioselective manner with exclusive B−C bond formation at the central *sp* carbon of the allene. With these new organometallic compounds in our hands, our interest has been focused on its synthetic utilization.[6] Herein, we disclose new organometallic synthons (**1**), which promotes nucleophilic allylation in the presence of Lewis acid to lead to the formation of functionalized alkenylboranes,[7] including cyclic ones, whose synthesis is not trivial.

Initially, we examined the reactions of simple *β*-borylallylsilanes **1a-c** with acetals in the presence of Lewis acids (eq 2). These allylsilanes were readily prepared by silaboration of the corresponding allenes in good yield with high regioselectivity.[4] It was our pleasure to find that the reaction of **1a** with propionaldehyde diethyl acetal (**2a**) proceeded in the presence of TMSOTf, $AlCl_3$, and $TiCl_4$ (1.2 equiv each) to give boryl-substituted homoallyl ether **3aa** (Table 1, entries 1−3). In particular, $TiCl_4$ exhibited the highest activity for the reaction to give **3aa** in high yield at −78 °C for 3 h. The comparable yield

Table 1. Lewis Acid-Promoted Reactions of *β*-Borylallylsilanes with Acetals[a]

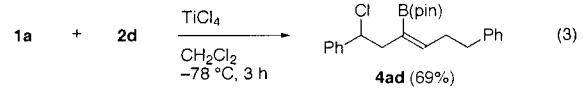


(2)

entry	allylsilane **1** (R)	acetal **2** (R^1, OR^2)	Lewis acid, temp/°C	product **3** (%yield[b])
1	**1a** (CH_2CH_2Ph)	**2a** (Et,OEt)	$TiCl_4$, −78	**3aa** (94)
2	**1a**	**2a**	$AlCl_3$, −20[c]	**3aa** (82)
3	**1a**	**2a**	TMSOTf, −20[c]	**3aa** (30)
4	**1a**	**2b** (Cy,OMe)	$TiCl_4$, −78	**3ab** (98)
5[d]	**1a**	 (**2c**)	$AlCl_3$, −20[c]	**3ac** (64)
6	**1a**	**2d** (Ph,OMe)	$AlCl_3$, −78	**3ad** (87)
7	**1b** (H)	**2a**	$TiCl_4$, −78	**3ba** (99)
8	**1c** (Cy)	**2a**	$TiCl_4$, −78	**3ca** (95)

[a] Allylsilane **1**, acetal **2** (1.2 equiv), and Lewis acid (1.2 equiv) were reacted in CH_2Cl_2 at −78 °C for 3 h unless otherwise noted. [b] Isolated yield. [c] The reaction was conducted at −78 °C for 0.5 h and −20 °C for 2.5 h. [d] 1.5 equiv of **2c** and $AlCl_3$ were used.

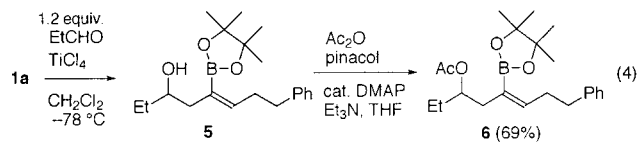
was attained with $AlCl_3$, although higher temperature (−20 °C) was required.[8] Under the reaction conditions using $TiCl_4$, reactions of **1a** with an acetal **2b** derived from α-branched aldehyde (entry 4) similarly gave the corresponding homoallyl ether **3ab** in an almost quantitative yield. In the reaction with 2-methoxytetrahydropyran (**2c**), $AlCl_3$ provided 2-substituted THP **3ac** in slightly higher yield than $TiCl_4$ (entry 5). Reaction of benzaldehyde dimethyl acetal (**2d**) with **1a** may deserve some comments. Use of $TiCl_4$ as a Lewis acid at −78 °C resulted in facile allylation followed by chloro-demethoxylation to give a homoallyl chloride **4ad** in 69% yield without formation of the expected homoallyl ether **3ad** (eq 3). However, the chloro-demethoxylation was



(3)

almost completely suppressed by alternative use of $AlCl_3$ at −78 °C, affording homoallylic ether **3ad** in good yield (entry 6). In the presence of $TiCl_4$, unsubstituted and cyclohexyl-substituted *β*-borylallylsilanes **1b** and **1c** also reacted with acetal **2a**, giving alkenylboranes **3** in high yields (entries 7 and 8). It is noteworthy that, in all the reactions, only (*E*)-alkenes **3** were obtained without being accompanied by any possible (*Z*)-isomers.

Reaction of **1a** with propionaldehyde also proceeded in the presence of $TiCl_4$ at −78 °C to form boryl-substituted homoallylic alcohol **5** selectively (eq 4). Attempts at isolation of **5** by column



(4)

chromatography, however, failed due to its partial conversion to a five-membered cyclic boronate through intramolecular B−O bond formation with loss of the pinacol group. An acetyl-protected

(1) (a) Fleming, I.; Dunogues, J.; Smithers, R. *Org. React.* **1989**, *37*, 57. (b) Panek, J. S. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, 1991; Vol. 1, p 579.

(2) (a) Suginome, M.; Ito, Y. *Chem. Rev.* **2000**, *100*, 3221. (b) Suginome, M.; Matsuda, T.; Ito, Y. *J. Am. Chem. Soc.* **2000**, *122*, 11015. (c) Suginome, M.; Fukuda, T.; Ito, Y. *Organometallics* **2000**, *19*, 719. (d) Suginome, M.; Nakamura, H.; Matsuda, T.; Ito, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4248.

(3) For the convenient preparation of silylboranes, see: Suginome, M.; Matsuda, T.; Ito, Y. *Organometallics* **2000**, *19*, 4647.

(4) (a) Suginome, M.; Ohmori, Y.; Ito, Y. *Synlett* **1999**, 1567. (b) Suginome, M.; Ohmori, Y.; Ito, Y. *J. Organomet. Chem.* **2000**, *611*, 403.

(5) For closely related synthesis of *β*-borylallylsilanes, see: Onozawa, S.-y.; Hatanaka, Y.; Tanaka, M. *Chem. Commun.* **1999**, 1863.

(6) For an example of the synthesis of *β*-borylallylsilane, see: Rivera, I.; Soderquist, J. A. *Tetrahedron Lett.* **1991**, *32*, 2311.

(7) For the synthetic utility of alkenylboranes, see: (a) Matteson, D. S. *Stereodirected Synthesis with Organoboranes*; Springer, Berlin, 1995. (b) Miyaura, N.; Suzuku, A. *Chem. Rev.* **1995**, *95*, 2457.

(8) No reaction took place in the presence of $AlCl_3$ or TMSOTf, at −78 °C.

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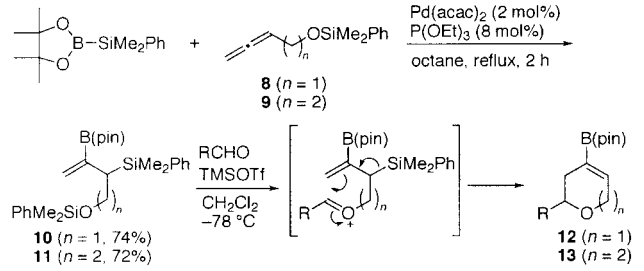
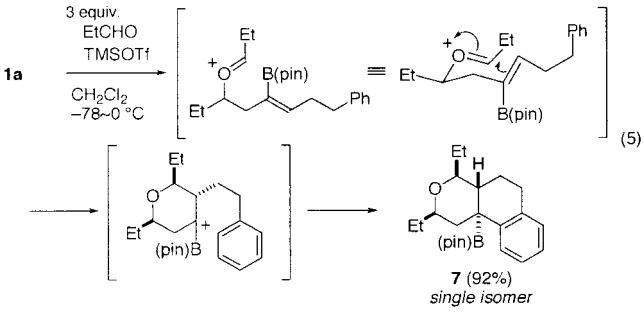
Scheme 1



homoallyl alcohol **6** was obtained in good yield on acetylation of the crude reaction mixture in the presence of pinacol. Unlike the $TiCl_4$-catalyzed reaction, TMSOTf-catalyzed reaction of **1a** with propionaldehyde afforded a cyclization product, in which two molecules of propionaldehyde were incorporated. A single-crystal X-ray analysis revealed a tricyclic structure **7**, which may be formed through Prins-type cyclization followed by intramolecular Friedel−Crafts reaction (eq 5). The formation of the



(5)

single stereoisomer **7** may suggest highly regio- and stereoselective cyclization via six-membered chairlike conformation as shown in eq 5.

We finally turned our attention to the reactions of β-boryl-allylsilanes bearing siloxyalkyl group, which may be applicable to the synthesis of cyclic alkenylboranes through an acetalization−cyclization sequence with aldehydes.[9] Allylsilanes **10** and **11**, which possessed a siloxyalkyl side chain (n = 1 and 2), were prepared by silaboration of siloxyalkyl-substituted allenes **8** and **9** and subjected to the reaction with aldehydes in the presence of TMSOTf at −78 °C (Scheme 1). In the reaction of **10** with primary and secondary alkyl aldehydes, 6-substituted 4-boryloxacyclohex-3-enes **12a** and **12b** were obtained in high yields (Table 2, entries 1 and 2). Pivalaldehyde and benzaldehyde afforded the corresponding cyclic alkenylboranes **12c** and **12d**, respectively, although concurrent elimination of the adjacent silyl and siloxy groups resulted in low yields of the desired products (entries 3 and 4).[10] The formation of seven-membered cyclic alkenylborane **13** starting from **11** was more effective than the six-membered ring formation. Thus, *prim*-, *sec*-, and *tert*-alkyl aldehydes as well as aromatic aldehyde afforded 2-substituted 4-boryloxacyclohept-4-enes **13a**−**d** in high yields (entries 6−9). Seven-membered cyclic ether **13e** bearing a benzyloxymethyl group was synthesized in high yield by reaction of **11** with benzyloxyacetaldehyde (entry 9).

Scheme 2

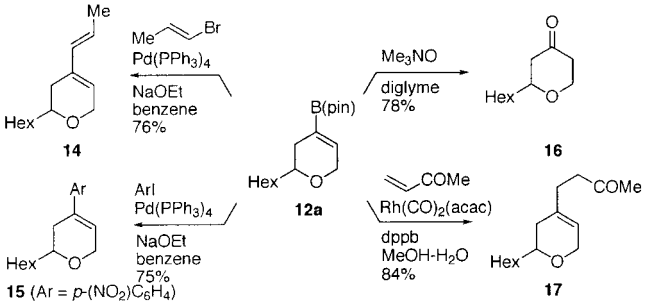


Table 2. TMSOTf-Promoted Cyclization of β-Borylallylsilanes **10** and **11** with Aldehydes[a]

entry	allylsilane	aldehyde (R)	product	% yield[b]
1	**10** (n = 1)	*n*-Hex	**12a**	89
2	**10**	Cy	**12b**	89
3	**10**	*t*-Bu	**12c**	50
4	**10**	Ph	**12d**	34
5	**11** (n = 2)	*n*-Hex	**13a**	87
6	**11**	Cy	**13b**	83
7[c]	**11**	*t*-Bu	**13c**	85
8	**11**	Ph	**13d**	94
9	**11**	$BnOCH_2$	**13e**	85

[a] For entries 1−4, allylsilane **10**, aldehyde (1.0 equiv), and TMSOTf (0.5 equiv) were reacted in CH_2Cl_2 at −78 °C for 1 h. For entries 5−9, **11**, aldehyde (1.1 equiv), and TMSOTf (1.1 equiv) were employed at −78 °C unless otherwise noted. [b] Isolated yield. [c] At −40 °C.

The new synthetic access to the cyclic alkenylboranes seems to be highly attractive, since their preparation has been less explored than that for acyclic counterparts.[11] Synthetic utility of the cyclic alkenylborane **12a** thus prepared was demonstrated by some transformations including oxidation, Suzuki−Miyaura coupling,[7b] and Rh-catalyzed conjugate addition[12] that led to the formation of useful synthetic intermediates **14**−**17** (Scheme 2).

In summary, we established the synthetic utility of β-boryl-allylsilanes as a convenient tool for the delivery of β-borylallyl groups through C−C bond formation. Although a similar delivery of the β-borylallyl group with a β-borylallylborane prepared by diboration of allenes was briefly documented,[13] the present approach may greatly expand the scope of the β-borylallylation chemistry. Further synthetic exploitation of more elaborated β-borylallylsilanes are now undertaken in this laboratory, directing toward stereoselective organic synthesis.

Supporting Information Available: Experimental procedures, characterization data for the new compounds, and details of a single-crystal X-ray analysis of **7** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0058381

(9) (a) Markó, I. E.; Mekhalfia, A. *Tetrahedron Lett.* **1992**, *33*, 1799. (b) Markó, I. E.; Bayston, D. J. *Tetrahedron Lett.* **1993**, *34*, 6595. (c) Markó, I. E.; Bayston, D. J. *Tetrahedron* **1994**, *50*, 7141. (d) Markó, I. E.; Bailey, M.; Murphy, F.; Declercq, J. P.; Tinant, B.; Feneau-Dupont, J.; Krief, A.; Dumont, W. *Synlett* **1995**, 123. (e) Mohr, P. *Tetrahedron Lett.* **1993**, *34*, 6251. (f) Oriyama, T.; Ishiwata, A.; Sano, T.; Matsuda, T.; Takahashi, M.; Koga, K. *Tetrahedron Lett.* **1995**, *36*, 5581. (g) Sano, T.; Oriyama, T. *Synlett* **1997**, 716. Asymmetric synthesis: (h) Suginome, M.; Iwanami, T.; Ito, Y. *J. Org. Chem.* **1998**, *63*, 6096. (i) Suginome, M.; Iwanami, T.; Ito, Y. *Chem. Commun.* **1999**, 2537. (j) Huang, H.; Panek, J. S. *J. Am. Chem. Soc.* **2000**, *122*, 9836.

(10) Buta-1,3-dien-2-ylpinacolborane, formed by the elimination reaction, was detected by ^{1}H NMR.

(11) For recent progress in the synthesis of cyclic alkenylboranes via Ru-catalyzed ring-closing metathesis, see: Renaud, J.; Ouellet, S. G. *J. Am. Chem. Soc.* **1998**, *120*, 7995.

(12) Sakai, M.; Hayashi, H.; Miyaura, N. *Organometallics* **1997**, *16*, 6, 4229.

(13) Ishiyama, T.; Kitano, T.; Miyaura, N. *Tetrahedron Lett.* **1998**, *39*, 2357.