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General and Functional Group-Tolerable Approach to Allenylsilanes by Rhodium-Catalyzed Coupling between Propargylic Carbonates and a Silylboronate

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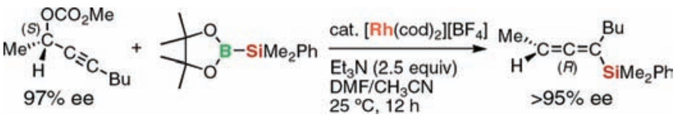
ABSTRACT

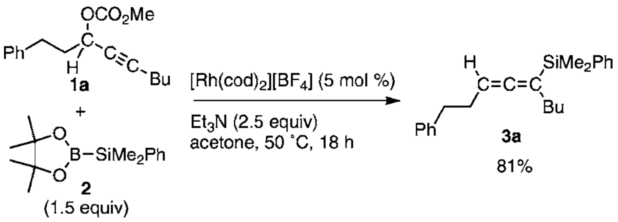


The Rh-catalyzed coupling reaction between propargylic carbonates and a silylboronate afforded allenylsilanes with different substitution patterns in high yields. The reaction tolerates a variety of functional groups in propargylic carbonates. The reaction of an optically active propargylic carbonate proceeded with excellent chirality transfer with 1,3-*anti* stereochemistry to give an axially chiral allenylsilane.

Allenylsilanes are useful organometallic reagents in organic synthesis because of their applicability toward various transformations.[1] In particular, the addition to carbonyl compounds offers a general approach to homopropargylic alcohols. Among a number of routes to allenylsilanes, the S_N2' displacement strategies, the substitution of γ-silyl-substituted propargylic alcohol derivatives with organocopper reagents,[2] or silylation of propargylic alcohol derivatives with silylcuprate reagents[3] are most straightforward. However, these methods often encounter problems of functional group compatibility because the organocopper reagents must be prepared from basic organometallic reagents such as Grignard or organolithium reagents, and the silylcuprate reagents are also strongly basic.

Herein, we report rhodium-catalyzed coupling between propargylic carbonates and a silylboronate as a general synthetic approach toward the preparation of allenylsilanes.[4−6] This reaction tolerated various functional groups in propargylic carbonates and afforded functionalized alle-

Scheme 1. Rh(I)-Catalyzed Coupling between Propargylic Carbonate **1a** and Silylboronate **2**



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[1] For reviews on allenylmetals, see: (a) Marshall, J. A.; Gung, B. W.; Grachan, M. L. *Modern Allene Chemistry*; Krause, N., Hashmi, A. S. K., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 2, pp 493−592. (b) Krause, N.; Hoffmann-Roder, A. *Tetrahedron* **2004**, *60*, 11671–11694. (c) Brummond, K. M.; DeForrest, J. E. *Synthesis* **2007**, 795–818. (d) Marshall, J. A. *J. Org. Chem.* **2007**, *72*, 8153–8166. (e) Masse, C. E.; Panek, J. S. *Chem. Rev.* **1995**, *95*, 1293–1316.

[2] For S_N2' substitutions of γ-silyl-substituted propargylic alcohol derivatives with organocopper reagents, see: (a) Danheiser, R. L.; Stoner, E. J.; Koyama, H.; Yamashita, D. S.; Klade, C. A. *J. Am. Chem. Soc.* **1989**, *111*, 4407–4413. (b) Westmijze, H.; Vermeer, P. *Synthesis* **1979**, 390–392.

[3] For silylations of propargylic alcohol derivatives with silylcuprate reagents, see: (a) Fleming, I.; Terret, N. K. *J. Organomet. Chem.* **1984**, *264*, 99–118. (b) Fleming, I.; Terret, N. K. *Tetrahedron Lett.* **1983**, *24*, 4153–4156. (c) Fleming, I.; Waterson, D. *J. Chem Soc., Perkin Trans. 1* **1984**, 1809–1813. (d) Marshall, J. A.; Maxson, K. *J. Org. Chem.* **2000**, *65*, 630–633.

10.1021/ol902339a

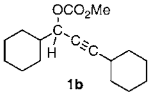
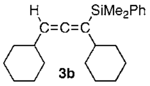
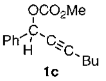
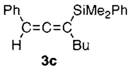
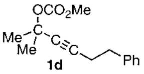
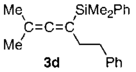
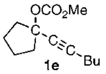
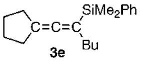
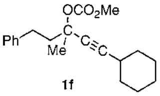
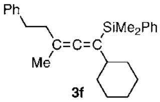
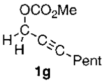
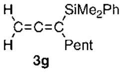
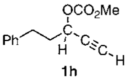
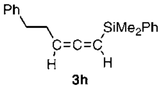
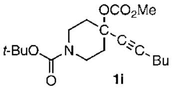
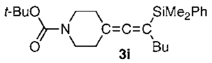
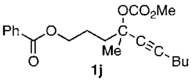
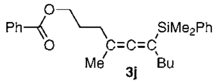
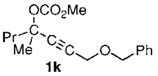
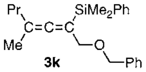
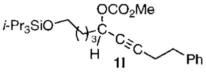
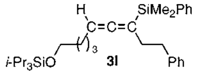
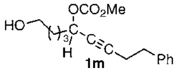
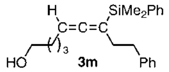
nylsilanes that are difficult to prepare by other methods. The reaction of an optically active propargylic carbonate took place with excellent point-to-axial chirality transfer with *anti* stereochemistry to give an axially chiral allenylsilane.

The reaction of propargylic carbonate **1a** with $PhMe_2SiB(pin)$[7] (**2**) (1.5 equiv) in the presence of $[Rh(cod)_2][BF_4]$ (5 mol %) and Et_3N (2.5 equiv) in acetone at 50 °C (18 h) gave allenylsilane **3a** in 81% yield (Scheme 1). The allenylsilane **3a** is a formal S_N2' product, assuming silyl anion $PhMe_2Si^-$ as a nucleophile. No S_N2 product was observed. Notably, the rhodium-catalyzed coupling could be performed even under air without affecting the product yield.

Several observations regarding the optimum reaction conditions are to be noted. Although the catalytic reaction proceeded without Et_3N, the yield was significantly reduced (31% yield). A neutral Rh complex $[RhCl(cod)]_2$ was less effective (17% yield) than the cationic $[Rh(cod)_2][BF_4]$. The use of other silylboron reagents[7] such as $FMe_2SiB(pin)$, $(i\text{-PrO})Me_2SiB(pin)$, and $(Et_2N)Me_2SiB(pin)$ instead of **2** resulted in no reaction under otherwise identical conditions. DMF was as effective as acetone as a solvent (76% yield). DME, THF, toluene, hexane, and 1,4-dioxane were also useful, while the rate of conversion of **1a** was slightly decreased (62%, 58%, 56%, 51%, and 49%, respectively). CH_3CN and 1,2-dichloroethane were even less effective (26% and 10%).

The rhodium-catalyzed reaction could be applied to the synthesis of the allenylsilanes with different substitution patterns (Table 1). The secondary propargylic carbonate **1b** bearing bulky cyclohexyl groups at both the α- and γ-positions underwent the coupling efficiently (entry 1). The secondary benzyl alcohol derivative **1c** with a phenyl group at the α-position was also silylated efficiently, giving the conjugated allenylsilane **3c** (entry 2). The tertiary propargylic carbonates **1d** and **1e** were converted into the corresponding fully substituted allenylsilanes **3d** and **3e**, respectively (entries 3 and 4). Furthermore, the tertiary propargylic carbonate **1f** bearing a bulky cyclohexyl group at the γ-position was also efficiently coupled with **2**, giving sterically more congested allenylsilane **3f** (entry 5). On the other hand, the reaction of the primary propargylic carbonate **1g** with no α-substituent resulted in a low conversion and a poor yield (17%) (entry 6). The reaction of terminal alkyne **1h** resulted in the complex mixtures (entry 7).

Table 1. Synthesis of Various Allenylsilanes[a]

entry	carbonate	product	time (h)	yield (%)[b]
1	 **1b**	 **3b**	12	91
2	 **1c**	 **3c**	24	80
3	 **1d**	 **3d**	12	92
4	 **1e**	 **3e**	12	80
5	 **1f**	 **3f**	12	97
6	 **1g**	 **3g**	48	17
7	 **1h**	 **3h**	24	0
8	 **1i**	 **3i**	12	96
9	 **1j**	 **3j**	12	92
10	 **1k**	 **3k**	12	85
11[c]	 **1l**	 **3l**	48	81
12[c]	 **1m**	 **3m**	18	93

[a] Conditions: $[Rh(cod)_2][BF_4]$ (5 mol %), Et_3N (0.5 mmol), $PhMe_2SiB(pin)$ (**2**) (0.3 mmol), **1** (0.2 mmol), acetone (1.0 mL), 50 °C. [b] Isolated yield. [c] $[Rh(cod)_2][BF_4]$ (10 mol %), Et_3N (0.5 mmol), $PhMe_2SiB(pin)$ (**2**) (0.3 mmol), **1** (0.2 mmol), acetone (1.0 mL), 50 °C.

The rhodium-catalyzed reaction was capable of affording a variety of functionalized allenylsilanes (Table 1). Functional groups such as carbamates and esters were tolerated in the propargylic carbonates (entries 8 and 9). The propargylic carbonate (**1k**) having a benzyloxy group at the opposite propargylic position underwent the reaction smoothly (entry 10). The substrate with the triisopropylsiloxy group **1l** was less reactive but led to completion with 10 mol % catalyst loading (entry 11). The free hydroxyl group in substrate **1m** did not inhibit the reaction, giving the corresponding hydroxy allenylsilane **3m** in 93% yield (entry 12). The neutral nature of the silylboronate reagent and the rhodium complex seems to contribute to the remarkable functional group tolerance of this catalytic reaction.

The reaction of an optically active propargylic carbonate (*S*)-**1n** (97% ee, 0.2 mmol) and **2** (0.3 mmol) was carried

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(4) For other approaches to allenylsilanes, see: (a) Kobayashi, S.; Nishio, K. *J. Am. Chem. Soc.* **1995**, *117*, 6392–6393. (b) Han, J. W.; Tokunaga, N.; Hayashi, T. *J. Am. Chem. Soc.* **2001**, *123*, 12915–12916. (c) Suginome, M.; Matsumoto, A.; Ito, Y. *J. Org. Chem.* **1996**, *61*, 4884–4885. (d) Brawn, R. A.; Panek, J. S. *Org. Lett.* **2007**, *9*, 2689–2692. See also ref.1a

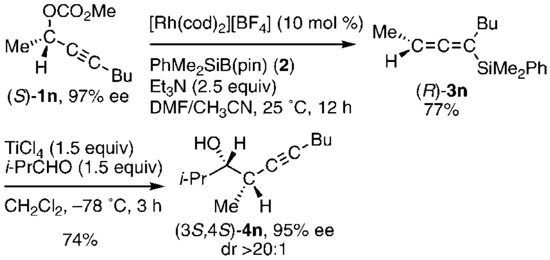
(5) For the synthesis of allenylboronates by the Cu-catalyzed substitution of propargylic carbonates with bis(pinacolato)diboron, see: Ito, H.; Sasaki, Y.; Sawamura, M. *J. Am. Chem. Soc.* **2008**, *130*, 15774–15775.

(6) For the synthesis of allenes by Cu-catalyzed reduction of propargylic carbonates with hydrosilanes, see: Zhong, C.; Sasaki, Y.; Ito, H.; Sawamura, M. *Chem. Commun.* **2009**, 5850–5852.

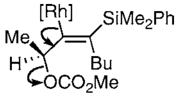
(7) For the preparation and reactivities of silylboronate reagents, see: (a) Suginome, M.; Matsuda, T.; Ito, Y. *Organometallics* **2000**, *19*, 4647–4649. (b) Ohmura, T.; Masuda, K.; Furukawa, H.; Suginome, M. *Organometallics* **2007**, *26*, 1291–1294. (c) Ohmura, T.; Suginome, M. *Bull. Chem. Soc. Jpn.* **2009**, *82*, 29–49.

out in the presence of [Rh(cod)$_2$][BF$_4$] (10 mol %) and Et$_3$N (0.5 mmol) in DMF/CH$_3$CN (100:1, 1.0 mL)[8] at 25 °C (Scheme 2). The allenylsilane **3n** was isolated in 77% yield. The subsequent TiCl$_4$-mediated addition of **3n** to isobutyraldehyde afforded homopropargylic alcohol (3*S*,4*S*)-**4n** (95% ee) with only slightly decreased enantiomeric purity.[4c] The diastereomer ratio (*syn*/*anti*, dr) with respect to the consecutive chiral centers was >20:1. The excellent *syn*-selectivity suggests that the addition of the allenylsilane **3n** to the aldehyde proceeded through an acyclic antiperiplanar transition state.[1e,9] On the basis of the established 1,3-*anti* stereochemical pathway on the Lewis acid-mediated addition of allenylsilanes to aldehydes,[1e] the absolute configuration of the axially chiral allenyl silane **3n** was deduced to *R*. Therefore, it was revealed that the point-to-axial chirality transfer in the Rh-catalyzed coupling proceeded with an *anti*-stereochemistry.

Scheme 2. Synthesis and Lewis Acid Addition of an Axially Chiral Allenylsilane (*R*)-**3n**



While it is not clear how silylboronate **2** reacts with a Rh complex,[10] the stereochemical outcome of the present rhodium-catalyzed reaction suggests that the reaction pathway may involve regioselective *cis*-1,2-addition of a silylrhodium species across the C−C triple bond of **1** to form an alkenylrhodium intermediate (**A**) and that the addition reaction be followed by *anti*-*β*-elimination to give allenylsilane **3** (Figure 1).[11,12]



A

Figure 1. Proposed *anti*-*β*-elimination from an alkenylrhodium intermediate.

In summary, the Rh-catalyzed coupling reaction between propargylic carbonates and a silylboronate is a general and functional group tolerable approach to allenylsilanes. The excellent point-to-axial chirality transfer with *anti*-stereochemistry was demonstrated in the preparation of an axially chiral allenylsilane from an optically active propargylic carbonate.

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Supporting Information Available: Experimental procedures and NMR spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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[8] The Rh-catalyzed reactions with DMF and CH$_3$CN, instead of DMF/CH$_3$CN (100:1), afforded **3n** with 93% ee (89% yield) and 97% ee (43% yield), respectively. These results suggest that the coordination of CH$_3$CN may have played a beneficial role in terms of the efficiency of the chirality transfer.

[9] (a) Danheiser, R. L.; Carini, D. J. *J. Org. Chem.* **1980**, *45*, 3925–3927. (b) Danheiser, R. L.; Carini, D. J.; Kwasigroch, C. A. *J. Org. Chem.* **1986**, *51*, 3870–3878. See also ref.3d

[10] For the Rh-catalyzed conjugate addition to α,*β*-unsaturated carbonyl compounds with PhMe$_2$SiB(pin), see: (a) Walter, C.; Auer, G.; Oestreich, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 5675–5677. (b) Walter, C.; Oestreich, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 3818–3820. (c) Walter, C.; Fröhlich, R.; Oestreich, M. *Tetrahedron* **2009**, *65*, 5513–5520.

[11] For the Rh-catalyzed substitutions of propargylic derivatives with arylboronic acid, see: (a) Murakami, M.; Igawa, H. *Helv. Chim. Acta* **2002**, *85*, 4182–4188. (b) Miura, T.; Shimada, M.; Ku, S.-Y.; Tamai, T.; Murakami, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 7101–7103.

[12] Similar mechanisms have been proposed for the Cu(I)-catalyzed reactions of allylic carbonates with bis(pinacolato)diboron. See: (a) Ito, H.; Kawakami, C.; Sawamura, M. *J. Am. Chem. Soc.* **2005**, *127*, 16034–16035. (b) Ito, H.; Ito, S.; Sasaki, Y.; Matsuura, K.; Sawamura, M. *J. Am. Chem. Soc.* **2007**, *129*, 14856–14857. (c) Ito, H.; Kosaka, Y.; Nonoyama, K.; Sasaki, Y.; Sawamura, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 7424–7427.