

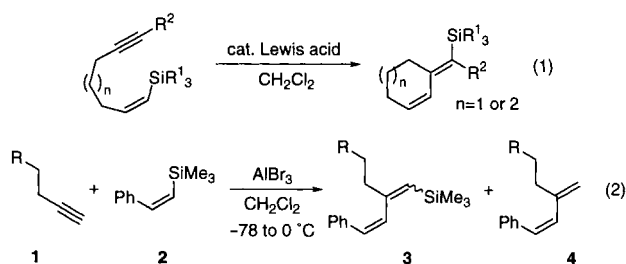
## Lewis Acid Mediated Intermolecular Vinylsilylation of Alkynes

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Intermolecular vinylsilylation of the alkynes **1b–c**, having an alkoxy group at the homopropargylic position, with the vinylsilane **2** proceeded in the presence of  $\text{AlBr}_3$  to give the corresponding dienylsilanes **3b–c** in moderate to good yields. In contrast, no product was obtained in the reaction of 1-octyne. The  $\text{AlBr}_3$  mediated vinylsilylation of the phenylacetylene **9c**, bearing methoxy group at the *ortho* position, also proceeded in good yield.

The carbometalation of a carbon–carbon multiple bond is one of the most fundamental and straightforward methodologies for the preparation of new organometallics.<sup>1</sup> Particularly, the carbometalation of alkynes is a practical method for the preparation of vinyl metals, which have great versatility as building blocks in organic synthesis. Despite the extensive investigation of the carbometalation reactions, there are very few reports on vinylmetalation of alkynes.<sup>2–5</sup> Recently, we communicated that the intramolecular *trans*-vinylsilylation of unactivated alkynes is catalyzed by certain Lewis acids to give the cyclic vinylsilanes in high yields (eq 1).<sup>6</sup> It was rather surprising for us to learn that the alkenyl-silicon bond is cleaved so easily in the presence of Lewis acids to lead to the vinylsilylation of alkynes, although it is an intramolecular reaction. Accordingly, the next question is whether the intermolecular vinylsilylation of alkynes takes place equally easily or not. In this paper, we wish to report that the intermolecular vinylsilylation of alkynes **1** with the phenyl-substituted vinylsilane **2** occurs rather easily in the presence of  $\text{AlBr}_3$  (eq 2).

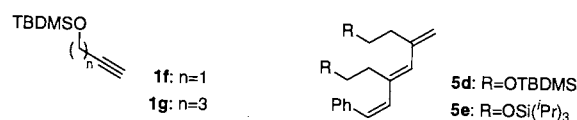


We examined the vinylsilylation reaction of various alkynes **1** with the phenyl-substituted vinylsilane **2** in the presence of  $\text{AlBr}_3$  (eq 2) and the results are summarized in Table 1. The initial attempt using 1-octyne **1a** and **2** resulted in failure; the adducts (**3a** and/or **4a**) were not obtained (entry 1). However, when we used the alkyne **1b**, bearing a benzyloxy group at the homopropargylic position, the reaction proceeded and the vinylsilylation product **3b** was obtained in 41% yield as a mixture of stereoisomers (*E:Z* = 73:27) together with a small amount of the desilylated product **4b** (entry 2). These results clearly show that the benzyloxy group plays a crucial role in the present reaction. The reaction of **1c** having an allyloxy group instead of a benzyloxy group also proceeded while the chemical yield of the vinylsilylation product **3c** slightly decreased (entry 3). On the other hand, no vinylsilylation products were obtained

**Table 1.**  $\text{AlBr}_3$ -mediated intermolecular vinylsilylation of alkyne<sup>a</sup>

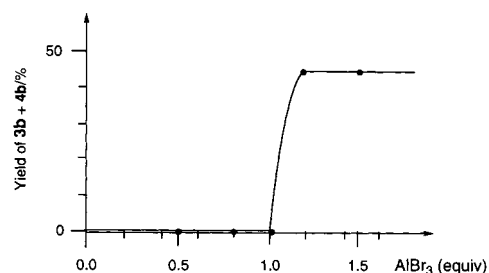
Entry	substrate <b>1</b> R	Yield/% <b>3</b>	Ratio ( <i>E:Z</i> )	Yield/% <b>4</b>
1	<b>1a</b> C <sub>4</sub> H <sub>9</sub>	<b>3a</b> 0	–	<b>4a</b> 0
2	<b>1b</b> OBn	<b>3b</b> 41	73:27	<b>4b</b> 4
3	<b>1c</b> OCH <sub>2</sub> CH=CH <sub>2</sub>	<b>3c</b> 33	82:18	<b>4c</b> 19
4 <sup>b</sup>	<b>1d</b> OTBDMS	<b>3d</b> 0	–	<b>4d</b> 42
5 <sup>c</sup>	<b>1e</b> OSi( <sup>i</sup> Pr) <sub>3</sub>	<b>3e</b> 0	–	<b>4e</b> 52

<sup>a</sup>The reaction was carried out in the presence of 1.2 equiv amounts of  $\text{AlBr}_3$  in  $\text{CH}_2\text{Cl}_2$  at  $-78$  to  $0$  °C. <sup>b</sup>Compound **5d** was obtained in 4% yield. <sup>c</sup>Compound **5e** was obtained in 10% yield.



in the reactions of **1d** and **1e** having silyloxy groups, but the corresponding desilylated products **4d** and **4e** were obtained in moderate yields, respectively (entries 4 and 5). In the reactions of **1d** and **1e**, small amounts of the double addition products **5d** and **5e** were also obtained. Interestingly, no reaction took place when we used 3-(*t*-butyldimethylsilyloxy)propyne **1f** or 5-(*t*-butyldimethylsilyloxy)pentyne **1g** as starting materials. It means that the position of the alkoxy group of alkyne compounds is very important to the present reaction.<sup>7</sup>

Previously, we reported that the intramolecular vinylsilylation proceeded in the presence of catalytic amounts of Lewis acid such as  $\text{EtAlCl}_2$ .<sup>6</sup> To investigate the influence of the amount of Lewis acid on the reaction progress, we carried out the reaction of **1b** with **2** in the presence of various amounts of  $\text{AlBr}_3$ . The combined yields of the vinylsilylation product **3b** and the desilylated product **4b** were plotted as functions of equivalents of added  $\text{AlBr}_3$  (Figure 1). Interestingly, while no product was obtained at all in the presence of 1.0 equiv or less than 1.0 equiv of  $\text{AlBr}_3$ , the reaction proceeded rapidly in the presence of 1.2 equiv of the Lewis acid. Furthermore, the combined chemical yield of **3b** and **4b** in the presence of 1.2 equiv of  $\text{AlBr}_3$  was almost same as that in the presence of 1.5 equiv of  $\text{AlBr}_3$ . Evans reported the stereoselective Diels–Alder reaction in

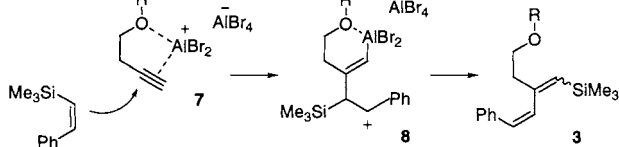
**Figure 1.** Variation of the combined yield of **3b** and **4b** in the  $\text{AlBr}_3$ -mediated vinylsilylation of **1b** with **2**.

the presence of  $\text{Me}_2\text{AlCl}$ . When the reaction was carried out with less than 1 equiv of  $\text{Me}_2\text{AlCl}$ , the stereoselectivities were modest. However, in the presence of an excess of the Lewis acid, not only the stereoselectivity but also the reactivity was dramatically improved. To account for the results, he proposed that a cationic aluminum Lewis acid might be produced and it would behave as a bidentate Lewis acid.<sup>8</sup> Most probably, here also a similar cationic aluminum species is generated and the  $\sigma$ - $\pi$  coordination of this species (see below) participates in the present reaction. It is presumed that, with 1 equiv or less than 1 equiv of  $\text{AlBr}_3$ , the coordination of the alkoxy group of **1** to  $\text{AlBr}_3$  leads to the ordinary complex **6**, in which the activation of alkyne by  $\text{AlBr}_3$  is not enough to induce the intermolecular vinylsilylation (Scheme 1). On the other hand, in the presence of an excess amount of  $\text{AlBr}_3$  (>1.0 equiv), **6** reacts further with  $\text{AlBr}_3$  to give **7** in which more positively charged  $\text{Al}^+\text{Br}_2$  can activate alkyne strongly through the  $\sigma$ - $\pi$  chelation.<sup>9</sup> Next, the  $\alpha$ -carbon of the vinylsilane **2** would attack the electron deficient triple bond from the side opposite to the Lewis acid to produce the zwitterionic intermediate **8** as shown in Scheme 2. The elimination of the silyl group and its transfer to the vinylaluminum moiety would form the product **3**.

#### Scheme 1.

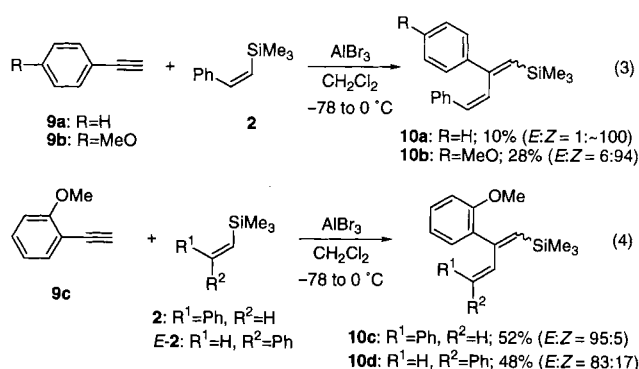


#### Scheme 2.



Previously, we reported the Lewis acid-catalyzed hydro- and carbometalation of unactivated alkynes.<sup>1d</sup> In all cases, the trans addition takes place exclusively in these reactions to give the corresponding *Z*-isomers as sole products. Probably, due to the coordination of the alkoxy group to alkenylaluminum, the present reaction would give *E*-isomers predominantly rather than *Z*-isomers. The desilylated product **4** might be produced by protonation of the vinylaluminum group when the reaction was quenched with  $\text{H}_2\text{O}$ . Particularly, in the reactions using silyloxy-substituted alkynes, the steric bulkiness of the silyloxy group might hamper the approach of the trimethylsilyl moiety, so that the vinylsilylation products would not be obtained. The geometry of the styrenyl part of **3** was *cis*; this observation is in good agreement with the results reported in the literature.<sup>10</sup>

Since the intermolecular vinylsilylation of alkynes having the alkoxy substituents at the homopropargyl position proceeded in moderate yields, we next examined the reaction of aromatic alkynes. While the reaction of phenylacetylene **9a** and *p*-methoxyphenylacetylene **9b** with **2** gave the corresponding vinylsilylation products **10a** and **10b** respectively, the chemical yields were low (eq 3). However, when we used the alkyne **9c**, bearing a methoxy group at the ortho position, the reaction proceeded much smoothly as we expected and the vinylsilylation product **10c** was obtained in 52% yield (eq 4). The reaction of **9c** with *E*-**2** also gave the corresponding vinylsilylation product **10d** in 48% yield (eq 4).



In conclusion, we have developed the first intermolecular vinylsilylation of aliphatic or aromatic alkynes bearing an alkoxy group at the homopropargylic position or at the ortho position, respectively, although the vinylsilane is limited to the phenyl-substituted one **2**. Perhaps, the carbocation stabilization by phenyl group, as shown in **8**, is also another important factor to induce the intermolecular vinylsilylation. Further studies to elucidate the mechanism of this reaction and to extend the scope of synthetic utility are in progress in our laboratory.

Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

#### References and Notes

- For reviews, see: a) "Lewis Acids in Organic Synthesis," ed. by H. Yamamoto, Wiley-VCH, Weinheim (2000), Vol. 1–2. b) I. Marek and J. F. Normant, in "Metal-catalyzed Cross-coupling Reactions," ed. by F. Diederich and P. J. Stang, Wiley-VCH, Weinheim (1998), p 271. c) P. Knochel, in "Comprehensive Organic Synthesis," ed. by B. M. Trost and I. Fleming, Pergamon Press, Oxford (1991), Vol. 4, p 865. d) N. Asao and Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, **73**, 1071 (2000).
- For Al, see: a) G. Wilke and H. Muller, *Chem Ber.*, **89**, 444 (1956). b) G. Wilke and H. Muller, *Justus Liebigs Ann. Chem.*, **618**, 267 (1958). c) J. J. Eisch and W. C. Kaska, *J. Am. Chem. Soc.*, **88**, 2213 (1966). d) G. Zweifel, J. T. Snow, and C. C. Whitney, *J. Am. Chem. Soc.*, **90**, 7139 (1968).
- For Cu, see: a) J. F. Normant and A. Alexakis, *Synthesis*, **1981**, 841. b) A. Alexakis and J. F. Normant, *Tetrahedron Lett.*, **23**, 5151 (1982). c) M. Furber, R. J. K. Taylor, and S. C. Burford, *Tetrahedron Lett.*, **26**, 3285 (1985). d) M. Furber, R. J. K. Taylor, and S. C. Burford, *J. Chem. Soc., Perkin Trans. 1*, **1986**, 1809.
- For Mg, see: H. G. Richey, Jr. and F. W. Von Rein, *J. Organomet. Chem.*, **20**, 32 (1969).
- For Zr, see: T. Takahashi, D. Y. Kondakov, Z. Xi, and N. Suzuki, *J. Am. Chem. Soc.*, **117**, 5871 (1995).
- N. Asao, T. Shimada, and Y. Yamamoto, *J. Am. Chem. Soc.*, **121**, 3797 (1999).
- While the reaction of **1e** with *Z*-pentyl-substituted vinylsilane instead of **2** was examined, the desired vinylsilylation product was not obtained and a complex mixture was produced.
- a) D. A. Evans, B. D. Allison, and M. G. Yang, *Tetrahedron Lett.*, **40**, 4457 (1999). b) D. A. Evans, K. T. Chapman, and J. Bisaha, *J. Am. Chem. Soc.*, **110**, 1238 (1988).
- a) N. Asao, T. Asano, T. Ohishi, and Y. Yamamoto, *J. Am. Chem. Soc.*, **122**, 4817 (2000). b) N. Asao, T. Shimada, and Y. Yamamoto, *Tetrahedron Lett.*, **41**, 9533 (2000). c) N. Asao, T. Ohishi, K. Sato, and Y. Yamamoto, *J. Am. Chem. Soc.*, **123**, 6931 (2001).
- It is well known that vinylsilanes react with electrophiles with retention of configuration, see: a) E. W. Colvin, "Silicon in Organic Synthesis," Butterworth, London (1981). b) W. P. Weber, "Silicon Reagents for Organic Chemistry," Springer Verlag, Berlin (1983). c) I. Fleming, J. Dunoguès, and R. Smithers, *Org. React. (N.Y.)*, **37**, 57 (1989).