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Lewis Acid-Catalyzed *trans*-Carbosilylation of Simple Alkynes

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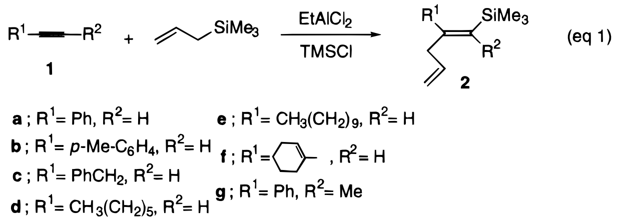
Since the first carbometallation discovered by Ziegler and Bähr in 1927,[1] a number of additions of organometallics to carbon−carbon multiple bonds have been reported.[2] Unfortunately, however, carbosilylation still remained unexploited due to the lack of a method for activation of carbon−silicon bonds.[3,4] We wish to report that allylsilylation of simple unactivated acetylenes **1** is catalyzed dramatically by Lewis acids such as $EtAlCl_2$ or $AlCl_3$ to give the corresponding *trans*-allylsilylated alkynes **2** in good to high yields (eq 1). The allylmetalation of activated alkynes, such as alkynyl ketones (Michael acceptor) and alkynols (functional group substituted alkynes), and/or the intramolecular allylmetalation proceed smoothly with various other allylmetals than allylsilanes.[2,5] However, allylmetalation of simple unactivated alkynes **1** is not easy, and only a limited number of allylmetals are available for this purpose.[2,6] Accordingly, it was rather surprising for us to discover that the allylsilylation of **1** proceeded so smoothly in the presence of Lewis acids (eq 1).



The results are summarized in Table 1. The reaction of phenylacetylene **1a** with allyltrimethylsilane catalyzed by $EtAlCl_2$ in the presence of 20 equiv of TMSCl gave the *trans*-carbosilylation product **2a** regio- and stereoselectively in 93% yield (Table 1, entry 1). Neither the stereoisomer of **2a** (*cis* addition product) nor the regioisomer of **2a** was produced.[7] The reaction of 4-ethynyltoluene (**1b**) gave **2b** in 95% yield (Table 1, entry 2), whereas the addition to 3-phenyl-1-propyne (**1c**) afforded **2c** in 57% yield along with the unsilylated product **3c** as a byproduct (Table 1, entry 3). Very trace amounts of unsilylated products were also detected in ^1H NMR spectra of the crude products in entries 1 and 2 (Table 1). The reactions of 1-octyne (**1d**) and 1-dodecyne (**1e**) gave **2d** and **2e**, respectively, in high yields (Table 1, entries 4 and 5). The *trans*-allylsilylation of the enyne **1f** and internal acetylene **1g** also proceed smoothly to give the corresponding alkenylsilanes **2f** and **2g**, respectively, in high yields (Table 1, entries 6 and 7). The use of other Lewis acids, such as $AlCl_3$, $AlBr_3$, and $HfCl_4$, in the reaction of 1-octyne (**1d**) gave the allylsilylation product **2d** in around 60% yield, but the use of $EtAlCl_2$ afforded the best result with respect to the yield of **2**. The *trans*-carbosilylation was unambiguously determined by the stereochemistry of the allylation product **2g**; irradiation of methyl protons attached to double bond of **2g** enhanced the signal of both methylene protons of the allylic position (5.7% NOE) and a vinyl proton at C-5 position (1.4% NOE), whereas irradiation of protons of TMS group did not enhance the signal of those protons at all.

Table 1. $EtAlCl_2$-Catalyzed Carbosilylation of Acetylenes with Allyltrimethylsilane

entry	1	R^1	R^2	2	product yield[a] (%)
1	**1a**	Ph	H	**2a**	93
2	**1b**	p-$CH_3C_6H_4$	H	**2b**	95
3	**1c**	$PhCH_2$	H	**2c**	57[b,c]
4	**1d**	$CH_3(CH_2)_5$	H	**2d**	90[b]
5	**1e**	$CH_3(CH_2)_9$	H	**2e**	85[b,d]
6	**1f**	1-cyclohexenyl	H	**2f**	73[b,e]
7	**1g**	Ph	Me	**2g**	88

[a] Isolated yield, except for where otherwise indicated. [b] Yield determined by ^1H NMR using *p*-xylene as an internal standard. [c] $PhCH_2(CH_2{=}CHCH_2)C{=}CH_2$ (**3c**) was produced in 13% yield. [d] $CH_3(CH2)_9(CH_2{=}CHCH_2)C{=}CH_2$ (**3d**) was produced in 5% yield. [e] 1-(1,4-Penadien-2-yl)cyclohexene (**3f**) was produced in 5% yield.

Preparation of **2b** from **1b** is representative. To a mixture of allyltrimethylsilane (0.19 mL, 1.2 mmol) and TMSCl (2.54 mL, 20 mmol) was added $EtAlCl_2$ (0.52 mL, 0.96 M in hexane, 0.5 mmol) at −47 °C. 4-Ethynyltoluene (**1b**) (0.13 mL, 1.0 mmol) was added, and the reaction mixture was stirred for 2 h at −47 °C. Diethylamine (2.0 mL, 19.4 mmol) was added, and the mixture was allowed to warm to 0 °C. Excess aqueous $NaHCO_3$ was added.

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(1) Ziegler, K.; Bähr, K. *Chem. Ber.* **1928**, *61*, 253.

(2) For reviews, see: (a) Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841 (organo-Li, Mg, Zn, B, Al, and Cu compounds). (b) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 38 (stoichiometric organo-Li, Mg, Zn, and catalytic Ni, Pd, Pt compounds). (c) Negishi, E. *Pure Appl. Chem.* **1981**, *53*, 2333 (organo-Al/Ti and Al/Zr system). (d) Knochel, P. *Comprehensive Organometallic Chemistry II*; Able, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1995; Vol. 11, p 159 (organo-Li, Mg, Zn, B, Al, Cu, Hg/Pd, Ni, Mn compounds). (e) Knochel, P. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 4, p 865. (f) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207 (organo-Li, Mg, Zn, B, Al compounds).

(3) The net carbosilylation from the three-component coupling reaction was reported. (a) Chatani, N.; Amishiro, N.; Murai, S. *J. Am. Chem. Soc.* **1991**, *113*, 7778. (b) Obora, Y.; Tsuji, Y.; Kawamura, T. *J. Am. Chem. Soc.* **1995**, *117*, 9814.

(4) For direct C−Si bond cleavages within a transition metal coordination sphere, see: (a) Lin, W.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* **1993**, *115*, 3022. (b) Horton, A. D.; Orpen, A. G. *Organometallics* **1992**, *11*, 1193. (c) Chang, L. S.; Johnson, M. P.; Fink, M. J. *Organometallics* **1991**, *10*, 1219 and references cited therein.

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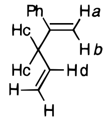
(6) (a) Takai, K.; Yamada, M.; Odaka, H.; Utimoto, K.; Fujii, T.; Furukawa, I. *Chem. Lett.* **1995**, 315 (allyl-Ta). (b) Takahashi, T.; Kotora, M.; Kasai, K.; Suzuki, N. *Tetrahedron Lett.* **1994**, *35*, 5685 (allyl-Zr). (c) Chatani, N.; Amishiro, N.; Morii, T.; Yamashita, T.; Murai, S. *J. Org. Chem.* **1995**, *60*, 1834 (allyl-Zn). (d) Molander, G. A. *J. Org. Chem.* **1983**, *48*, 5409 (allyl-Zn). (e) Miller, J. A.; Negishi, E. *Tetrahedron Lett.* **1984**, *25*, 5863 (allyl-Al). (f) Negishi, E.; Miller, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6761 (allyl-Zn). (g) Eishi, J. J.; Boleslawski, M. P. *J. Organomet. Chem.* **1987**, *334*, C1 (allyl-Ti). (h) Yeon, S. H.; Han, J. S.; Hong, E.; Do, Y.; Jung, I. N. *J. Organomet. Chem.* **1995**, *499*, 159 (allyl-Si).

(7) Jung and co-workers reported *cis*-allylsilylation of phenylacetylene (ref 6h). However, their stereochemical assignment of 2-phenyl-1,4-pentadiene is wrong: A proton that appeared at 5.12 ppm was assigned as Ha and that at 5.42 ppm as Hb. NOE experiments revealed that the Ha proton appears at 5.42 ppm and the Hb proton appears at 5.12 ppm. NOEs were observed at aromatic protons when a proton at 5.42 ppm was irradiated, and those were observed at Hc and Hd protons when a proton at 5.12 ppm was irradiated.



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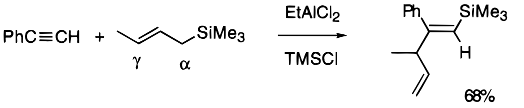
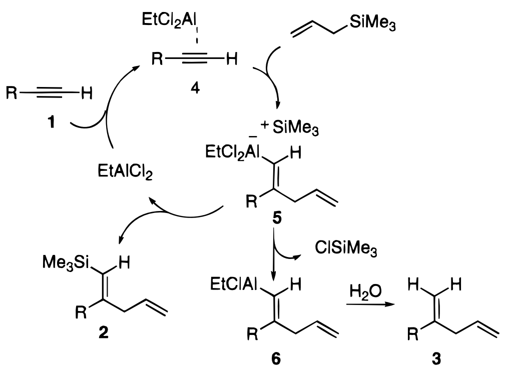
Extraction with ether, drying with anhyd Na_2SO_4, concentration, and purification with silica gel column chromatography using hexane as eluent gave **2b** in 93% yield. The use of 1 equiv of $EtAlCl_2$ gave a similar result, but the reaction using 0.1 equiv of $EtAlCl_2$ afforded **2b** in lower yield.

The present carbosilylation method is applicable to crotyltrimethylsilane. The reaction of 1.0 equiv of phenylacetylene with 1.2 equiv of crotyltrimethylsilane in the presence of 0.5 equiv of $EtAlCl_2$ and 20 equiv of TMSCl gave 3-methyl-2-phenyl-1-(trimethylsilyl)-1,4-pentadiene in 68% yield (eq 2). Trans-addition was confirmed by determining the stereochemistry of the products using NOE experiments. Only the γ-addition product was produced, and the α-addition product was not detected.



(eq 2)

Scheme 1



A plausible mechanism for the $EtAlCl_2$-catalyzed *trans*-allylsilylation is shown in Scheme 1, although it is highly speculative. The coordination of $EtAlCl_2$ to **1** would produce the π-complex **4**. Allyltrimethylsilane would attack the electron-deficient triple bond from the side opposite to $EtAlCl_2$ to produce the aluminum ate complex **5** stereoselectively. The coupling between the alkenyl and silyl group of the ate complex would afford **2** and $EtAlCl_2$, which again would work as a coordinating agent to **1**. On the other hand, the coupling between the chloro and silyl group would produce Me_3SiCl and the alkenylaluminum derivative **6**, which would afford the minor byproduct **3** upon hydrolysis. Excess amounts of TMSCl are needed to drive the equilibrium over in favor of replacing the aluminum with the silicon. Actually, the reaction of 1-octyne in the presence of 0.5 equiv of $EtAlCl_2$ and 1 equiv of TMSCl gave a 31:69 mixture of **2d** and **3d** in 30% yield, and the reaction using 0.5 equiv of $EtAlCl_2$ in the absence of TMSCl afforded a 5:95 mixture of **2d** and **3d** in 20% yield. The low yield in the absence of TMSCl supports the proposed mechanism (Scheme 1), since regeneration of $EtAlCl_2$ is diminished due to the side reaction leading to **6**. Furthermore, the addition order of TMSCl was important; the chemical yield of **2** decreased dramatically when TMSCl was added after the addition of an acetylene (see the above procedure). When the reaction of **1a** using 0.5 equiv of $EtAlCl_2$ was carried out in the absence of TMSCl and quenched with D_2O, the deuterated alkene (*Z*)-Ph(CH_2=$CHCH_2$)C=CHD was obtained in 20% yield, clearly indicating that an alkenylaluminum intermediate was involved.[8]

Although further investigation is needed to settle this unprecedented Lewis acid-catalyzed allylsilylation,[9] the procedure is useful for the stereocontrolled synthesis of alkenylsilanes.

Supporting Information Available: Characterization data for reaction products (10 pages).

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[8] Negishi reported that allylaluminums add to unactivated acetylenes in a *cis*-manner in the presence of Zr-catalyst (ref 6e). The present addition proceeds in *trans*-manner. Accordingly, it seems that the allylaluminum species is not involved as a reactive intermediate.

[9] For $ZrCl_4$-catalyzed hydrostannylation, see: Asao, N.; Liu, J.; Sudoh, T.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1995**, 2405.