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Lewis Acid-Catalyzed *trans*-Hydrosilylation of Alkynes

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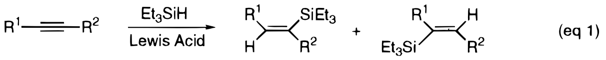
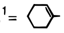
Hydrosilylation[1] of alkynes is one of the simplest and the most straightforward preparative methods for vinylsilanes, which have great versatility as building blocks in organic synthesis.[2] It is well known that the hydrosilylation of acetylenes is induced either by radical initiators[3] or by transition metal catalysts.[4] The radical induced procedure often provides a mixture of *trans*- and *cis*-hydrosilylation products. Although the transition metal-catalyzed reaction proceeds with high stereoselectivity via a *cis*-hydrosilylation pathway, it usually produces a mixture of two regioisomers (terminal and internal adducts) in the reaction with terminal alkynes. We wish to report that the hydrosilylation of alkynes **1** with trialkylsilanes is catalyzed dramatically by Lewis acids such as $AlCl_3$ and $EtAlCl_2$, leading to *cis*-alkenylsilanes **2** with very high regio- and stereoselectivities in good to high yields (eq 1).[5,6] Although most hydrometalations of alkynes proceed in a *cis*-manner, the Lewis acids catalyzed hydrosilylation proceeds in a *trans*-manner.[7]

Table 1. Lewis Acid-Catalyzed Hydrosilylation of Acetylenes with Et_3SiH[a]



1 **2** **3**

(eq 1)

1,2, and **3** **a** ; R^1=$CH_3(CH_2)_9$, R^2=H
b ; R^1=$PhCH_2$, R^2=H
c ; R^1=*tert*-C_4H_9, R^2=H
d ; R^1=Me_3Si, R^2=H
e ; R^1=  , R^2=H
f ; R^1=Ph, R^2=H
g ; R^1=$(i\text{-}Pr)_3SiO(CH_2)_2$, R^2=H
h ; R^1=$(i\text{-}Pr)_3SiO(CH_2)_4$, R^2=H
i ; R^1=$PhCH_2O(CH_2)_2$, R^2=H
j ; R^1=R^2=$CH_3(CH_2)_4$
k ; R^1=R^2=Ph
l ; R^1=Ph, R^2=CH_3
m ; R^1=Ph, R^2=C_2H_5

entry	Lewis acid (equiv)	1			yield (%)	
		R^1	R^2		**2**	**3**
1	$ZrCl_4$ (0.2)	$CH_3(CH_2)_9$	H	(**1a**)	trace	0
2	$HfCl_4$ (0.2)	$CH_3(CH_2)_9$	H	(**1a**)	28	0
3	$AlCl_3$ (0.2)	$CH_3(CH_2)_9$	H	(**1a**)	93	0
4	$EtAlCl_2$ (0.2)	$CH_3(CH_2)_9$	H	(**1a**)	95	0
5[b]	Et_2AlCl (0.2)	$CH_3(CH_2)_9$	H	(**1a**)	0	0
6[c]	$AlCl_3$ (0.2)	$CH_3(CH_2)_9$	H	(**1a**)	90	0
7	$AlCl_3$ (0.2)	$PhCH_2$	H	(**1b**)	85	0
8	$AlCl_3$ (0.2)	$t\text{-}C_4H_9$	H	(**1c**)	82	0
9	$AlCl_3$ (0.2)	Me_3Si	H	(**1d**)	89	0
10	$AlCl_3$ (0.2)	1-cyclohexenyl	H	(**1e**)	45	0
11[d]	$EtAlCl_2$ (1.0)	Ph	H	(**1f**)	61	0
12[e]	$EtAlCl_2$ (1.2)	$(i\text{-}Pr)_3SiO(CH_2)_2$	H	(**1g**)	86	0
13	$AlCl_3$ (1.2)	$(i\text{-}Pr)_3SiO(CH_2)_4$	H	(**1h**)	74	0
14	$EtAlCl_2$ (1.2)	$PhCH_2O(CH_2)_2$	H	(**1i**)	72	0
15	$AlCl_3$ (0.2)	$CH_3(CH_2)_4$	$CH_3(CH_2)_4$	(**1j**)	73	
16	$AlCl_3$ (0.2)	Ph	Ph	(**1k**)	66	
17	$AlCl_3$ (0.2)	Ph	CH_3	(**1l**)	76	10
18	$AlCl_3$ (0.2)	Ph	C_2H_5	(**1m**)	54	26

[a] Reactions were conducted in toluene at 0 °C under Ar unless otherwise noted. [b] The starting material **1a** was recovered quantitatively. [c] Reaction was carried out without any solvents. [d] **2f** was obtained in 40% yield, if 0.2 equiv of $AlCl_3$ was used as a catalyst. [e] Hexane was used as a solvent.

The results are summarized in Table 1. First, we examined the hydrosilylation of 1-dodecyne using triethylsilane with several different kinds of Lewis acids. Recently, we found that the hydrostannation of alkynes proceeds smoothly in the presence of Lewis acids, such as $ZrCl_4$ and $HfCl_4$, producing the corresponding alkenyltins with high regio- and *trans*-stereoselectivities in good yields.[8] However, $ZrCl_4$-catalyzed hydrosilylation gave only a trace amount of **2a** (entry 1). A slight improvement was made by using $HfCl_4$ as a catalyst, but the yield was still low (entry 2). Fortunately, however, the reaction in the presence of 0.2 equiv of $AlCl_3$ afforded the *trans*-hydrosilylation product **2a** in 93% yield (entry 3). Neither a stereoisomer of **2a** (*cis* addition product) nor a regioisomer (**3a**) was detected in the ^{1}H-NMR spectra of the crude reaction product. While $EtAlCl_2$ was also an efficient catalyst for the *trans*-hydrosilylation (entry 4), starting material **1a** was recovered quantitatively in the Et_2AlCl-catalyzed reaction (entry 5). It seems that the reaction did not proceed due to lower Lewis acidity of Et_2AlCl, compared to $AlCl_3$ and $EtAlCl_2$. The use of nonpolar solvents such as toluene or hexane was essential for obtaining high stereoselectivity and chemical yield. Unlike $EtAlCl_2$, $AlCl_3$ is not soluble in such solvents, and thus the $AlCl_3$-catalyzed hydrosilylation proceeds in a heterogeneous system. The $AlCl_3$-catalyzed hydrosilylation proceeded smoothly even without a solvent to give **2a** in 90% yield (entry 6).

The $AlCl_3$- or $EtAlCl_2$-catalyzed hydrosilylation was examined with several other alkynes. The reactions of 3-phenyl-1-propyne (**1b**), 3,3-dimethyl-1-butyne (**1c**) hav-

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[1] (a) Hiyama, T.; Kusumoto, T. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 8, p 763. (b) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983.

[2] (a) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic: London, 1988. (b) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer: Berlin, 1983. (c) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworth: London, 1981.

[3] (a) Selin, T. G.; West, R. *J. Am. Chem. Soc.* **1962**, *84*, 1860. (b) Benkeser, R. A.; Burrous, M. L.; Nelson, L. E.; Swisher, J. V. *J. Am. Chem. Soc.* **1961**, *83*, 4385.

[4] Transition metal complexes derived from Pt, Ir, Pd, Rh, Ru, Ni, Co, Fe, Re, and Mn metals have been used for hydrosilylation; see ref 1a.

[5] Although $AlCl_3$-catalyzed hydrosilylation of alkynes had been reported by Voronkov's group, detailed information on regio- and stereoselectivities and generality of the reaction are not available; see: (a) Voronkov, M. G.; Adamovich, S. N.; Pukhnarevich, V. B. *J. Gen. Chem. USSR (Engl. Transl.)* **1982**, *52*, 2058. (b) Voronkov, M. G.; Adamovich, S. N.; Sherstyannikova, L. V.; Pukhnarevich, V. B. *J. Gen. Chem. USSR (Engl. Transl.)* **1983**, *53*, 706. (c) W. Ger. Pat. 2, 804, 204 (1979); *Chem. Abstr.* **1979**, *91*, 193413x. (d) Br. Pat. 684, 597 (1953); *Chem. Abstr.* **1954**, 2761d. (e) U.S. Pat. 2, 555, 589 (1971); *Chem. Abstr.* **1951**, 8814.

[6] $AlCl_3$-catalyzed hydrosilylation of alkenes was reported; see: (a) Oertle, K.; Wetter, H. F. *Tetrahedron Lett.* **1985**, *26*, 5511. (b) Wetter, H. F.; Oertle, K. *Tetrahedron Lett.* **1985**, *26*, 5515. (c) Yamamoto, K.; Takemae, M. *Synlett* **1990**, 259.

[7] (a) Hydroboration, see: Smith, K.; Pelter, A.; Brown, H. C. *Borane Reagents*; Academic Press: London, 1988. Smith, K.; Pelter, A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 8, p 703. (b) Hydroalumination, see: Sato, F. *Janssen Chim. Acta* **1990**, *8*, 3. Eisch, J. J. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 8, p 733. (c) Hydromagnesation, see: Sato, F. *J. Organomet. Chem.* **1985**, *285*, 53. (d) Hydrostannation, see: Pereyre, M.; Quintard, J. -P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987. (e) Hydrozirconation, see: Labinger, J. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press, Oxford, **1991**, *8*, 667. (f) Hydrozincation, see: Gao, Y.; Harada, K.; Hata, T.; Urabe, H.; Sato, F. *J. Org. Chem.* **1995**, *60*, 290.

[8] Asao, N.; Liu, J.-X.; Sudoh, T.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1995**, 2405. Asao, N.; Liu, J-. X.; Sudoh, T.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 4568.

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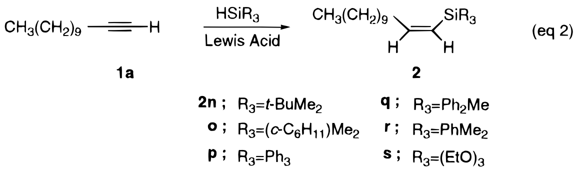
Table 2. Lewis Acid-Catalyzed Hydrosilylation of 1-Dodecyne 1a with R_3SiH



entry	Lewis acid (equiv)	R_3SiH		yield (%)
1	$AlCl_3$ (0.2)	t-$BuMe_2SiH$	(**2n**)	78
2	$AlCl_3$ (0.2)	$(c\text{-}C_6H_{11})Me_2SiH$	(**2o**)	73
3	$EtAlCl_2$(0.2)	Ph_3SiH	(**2p**)	40
4	$EtAlCl_2$(0.2)	Ph_2MeSiH	(**2q**)	45
5	$EtAlCl_2$ (0.2)	$PhMe_2SiH$	(**2r**)	60
6[a]	$AlCl_3$ (0.2)	$(EtO)_3SiH$	(**2s**)	0

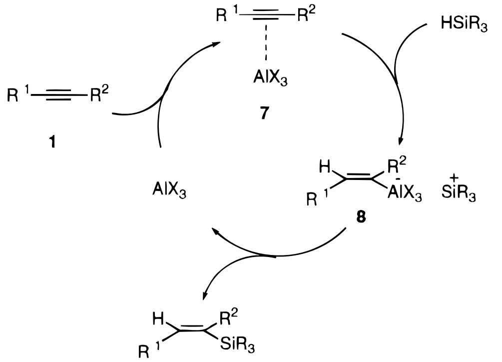
[a] The starting material **1a** was recovered quantitatively.

ing a bulky *tert*-butyl group, and (trimethylsilyl)acetylene (**1d**) proceeded smoothly to produce **2b**, **2c**, and **2d**, respectively, in high yields (entries 7−9), whereas the hydrosilylation of a conjugated enyne, 1-ethynyl-1-cyclohexene (**1e**), gave **2e** in moderate yield (entry 10). The reaction of phenylacetylene (**1f**) afforded **2f** in 61% yield when a stoichiometric amount of $EtAlCl_2$ was used (entry 11). The use of 0.2 equiv $AlCl_3$ as a catalyst gave **2f** in 40% yield. The hydrosilylation of alkynes bearing silyloxy and benzyloxy groups gave the corresponding *trans*-hydrosilylation products in good to high yields (entries 12−14). Very interestingly, the use of 1.2 equiv of Lewis acids was essential for obtaining good chemical yields (entries 12−14). Most probably, 1 equiv of Lewis acid would be needed to coordinate to an oxygen atom of the silyloxy or benzyloxy group, and the remaining 0.2 equiv of Lewis acid would act as a catalyst. The reaction of symmetrical internal acetylenes, such as 6-dodecyne (**1j**) and tolan (**1k**), also proceeded smoothly (entries 15 and 16), whereas the reaction of unsymmetrical acetylenes, such as 1-phenyl-1-propyne (**1l**) and 1-phenyl-1-butyne (**1m**), afforded a mixture of regioisomers, **2l** and **3l** and **2m** and **3m**, respectively (entries 17 and 18). The regioisomeric ratio depended on the steric bulk of the substituent R^2. The methyl substituent gave a ratio of 76:10, whereas the ethyl group afforded that of 54:26.

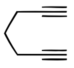
Next, we carried out the $AlCl_3$- or $EtAlCl_2$-catalyzed hydrosilylation of **1a** with various silanes, and the results are shown in Table 2. The reaction of *tert*-butyldimethylsilane and cyclohexyldimethlysilane proceeded smoothly to give the corresponding *trans*-hydrosilylation products **2n** and **2o**, respectively, in good yields (entries 1 and 2). The addition of phenyl-substituted silanes, such as triphenyl-, diphenylmethyl-, and phenyldimethylsilane, gave lower yields in comparison with that of alkyl-substituted silanes (entries 3−5 vs 1−2). The reaction of triethoxysilane did not proceed at all (entry 6). These results suggest that the silanes having an electron-donating substituent, such as alkyl groups, are more suitable to the Lewis acid-catalyzed hydrosilylation.

Preparation of **2a** from **1a** is representative. To a suspension of $AlCl_3$ (27 mg, 0.2 mmol) in toluene (1.0 mL) was added triethylsilane (0.19 mL, 1.2 mmol) at 0 °C under an Ar atmosphere. The mixture was stirred for 5 min, and then **1a** (0.21 mL, 1.0 mmol) was added. The mixture was stirred for 1 h at 0 °C, and excess amounts of triethylamine (0.2 mL, 1.5 mmol) were added. After addition of aqueous $NaHCO_3$ solution, the usual workup gave crude product, which was purified by silica gel column chromatography using hexane as an eluent to afford **2a** (263 mg, 0.93 mmol) in 93% yield.

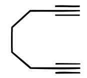
Scheme 1



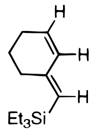
The Lewis acid-catalyzed hydrosilylation of diyne compounds was examined. Very interestingly, the $AlCl_3$ (0.2 equiv)-catalyzed hydrosilylation of 1,6-heptadiyne **4a** with 4 equiv of Et_3SiH gave the six-membered cyclization product **5** in 60% yield, whereas that of 1,7-octadiyne **4b** afforded bis-hydrosilylation product **6** in 47% yield. The assignment of the stereochemistry of **5** was made by NOE experiments (see the supporting information). No cyclization product was obtained from **4b** under various reaction conditions: for example, the use of less than 4 equiv of Et_3SiH gave a mixture of **6** and a monohydrosilylation product. The results are in marked contrast to the cyclization reaction of diyne compounds by Ni-catalyzed hydrosilylation.[9]



4a



4b



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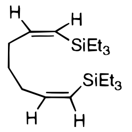

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A plausible mechanism for the $AlCl_3$- or $EtAlCl_2$-catalyzed *trans*-hydrosilylation is shown in Scheme 1, although it is speculative. The $AlCl_3$ or $EtAlCl_2$ (AlX_3) would coordinate to the acetylenic bond of **1** to produce complex **7**.[10] A hydride from R_3SiH would attack an electron-deficient triple bond from the side opposite to AlX_3 to produce an aluminum ate-complex **8**. The intermediate **8** would undergo coupling between the trialkylsilyl cation and the vinyl group with retention of geometry to give **2** and AlX_3. The above mechanism is very much related to the mechanism of Lewis acid-catalyzed hydrostannation,[8] allylstannation,[11a] and allylsilylation,[11b] developed recently in our laboratory.

Supporting Information Available: Full spectroscopic and analytical characterization for compounds **2a**,**b**,**d**,**e**,**g**−**r**, **3l**,**m**, **5**, and **6** (26 pages).

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[9] Tamao, K.; Kobayashi, K.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 6478.

[10] The addition order of reagent, substrate, and Lewis acid is important to obtain higher yields of the desired product. The order mentioned in the synthesis of **2a** is essential. If the acetylene **1a** was added to $AlCl_3$ prior to the addition of Et_3SiH, significant amounts of the trimerization product of **1a** (aromatic compounds) were obtained as a byproduct. Accordingly, it seems that coexistence of Et_3SiH is needed, when the coordination of $AlCl_3$ to the acetylene takes place, in order to capture instantaneously an activated triple bond.

[11] (a) Asao, N.; Matsukawa, Y.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1996**, 1513. (b) Asao, N.; Yoshikawa, E.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 4784.