Selective Formation of Propargylsilanes and Allenylsilanes and Their Reactions with Aldehydes for the Preparation of Homopropargylic and Allenic Alcohols

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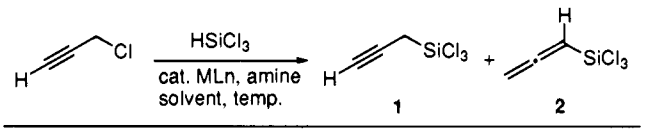
Acetylene and allene compounds and their chemistry have attracted much attention during the past two decades.[1] Regioselective reactions of propargyl and allenyl organometallics provide a potentially useful route for the synthesis of these compounds; however, these organometallics often exist as an equilibrium mixture,[1a] and few examples for the selective synthesis of these unstable intermediates are known.[2,3] In this paper, we report the selective formation of propargyltrichlorosilanes and allenyltrichlorosilanes from propargylic halides. Their regioselective reactions with aldehydes for the synthesis of homopropargylic and allenic alcohols are also described.

Although conventional methods for the preparation of propargyl- and allenylorganometallics are usually based on the reactions of metals with propargylic and allenic halides, our protocol depends on the reactions of propargylic halides with trichlorosilane. It has been reported that propargyl chloride reacts with trichlorosilane in the presence of triethylamine under thermal conditions (THF, 60 °C, 12 h) to give a mixture of propargyltrichlorosilane (**1**) and allenyltrichlorosilane (**2**).[4] We also found that isomerization between **1** and **2** occurred during distillation (from **1**/**2** = 6:1 to **1**/**2** = 1:2, bp = 96−109 °C). To direct the course of the reaction by kinetic control, we examined some transition metal salts for activation of propargyl chloride. After trials of several metal salts, it was found that **1** was selectively obtained in the presence of a Cu(I) salt, while **2** was produced preferentially in the presence of a Ni(II) salt. We also found that solvents and temperature influenced the ratio and, finally, that **1**[5] and **2**[6] were obtained in high selectivities under the respective conditions shown in Table 1.

Table 1. Selective Formation of **1** and **2**

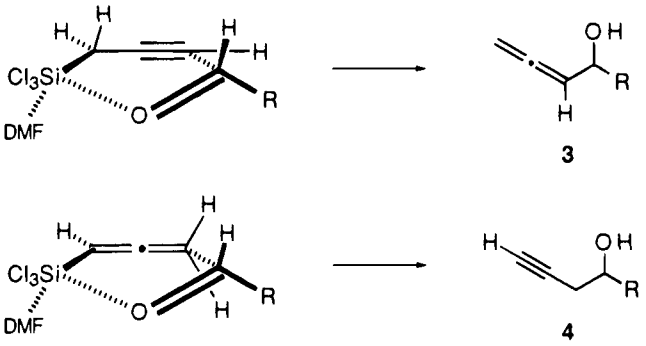


1 **2**

MLn	amine	solvent	temp/°C (time/h)	**1**:**2**
−	Et_3N	THF	60 (12)	mixture[a]
CuCl	Et_3N	THF	23 (12)	6:1
CuCl	$^iPr_2NEt$	Et_2O	23 (12)	7:1
NiL_2[b]	$^iPr_2NEt$	Et_2O	23 (12)	1:4
NiL_2[b]	$^iPr_2NEt$	Et_2O	35 (12)	1:6
CuCl	$^iPr_2NEt$	Et_2O/C_2H_5CN (10:1)	23 (12)	15:1
NiL_2[c]	pempidine[d]	THF	66 (5)	<1:>30

[a] See ref 3. [b] LH = $PhC(O)CH_2C(O)Ph$. [c] LH = $CH_3C(O)CH_2C(O)OEt$. [d] 1,2,2,6,6-Pentamethylpiperidine.

Scheme 1. Selective Synthesis of **3** from **1** and **4** from **2**



Next, the reactions of **1** or **2** with aldehydes for the synthesis of homopropargylic and allenic alcohols were examined. We have recently demonstrated that allyltrichlorosilanes regioselectively react with aldehydes in *N,N*-dimethylformamide (DMF) without catalysis to afford the corresponding homoallylic alcohols in high yields.[7] In these reactions, DMF coordinates to the silicon atom of the allyltrichlorosilanes to form hypervalent silicates,[8] which in turn react with aldehydes smoothly. Assuming that the same kind of intermediate could be formed, we examined the reactions of **1** and **2** with aldehydes in DMF at 0 °C. These reactions proceeded smoothly in high regioselectivities as expected. While allenic alcohols **3** were produced

(1) (a) Yamamoto, H. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 2, p 81. (b) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*; Wiley: New York, 1984. (c) Moreau, J.-L. In *The Chemistry of Ketenes, Allenes and Related Compounds*; Patai, S., Ed.; Wiley: New York, 1980; p 363. (d) Klein, J. In *The Chemistry of the Carbon-Carbon Triple Bond*; Patai, S., Ed.; Wiley: New York, 1978; p 343.

(2) Although some excellent work has been reported in this field, the selectivity depends on substrates and metals used. For example, allenyl organometallics **7** ("unsubstituted" allenyl organometallics) are generated preferentially in most cases, and there has been no example for the selective preparation of propargyl organometallics **8**, as far as we know. (a) Zhang, L.-J.; Mo, X.-S; Huang, Y.-Z. *J. Organomet. Chem.* **1994**, *471*, 77. (b) Suzuki, M.; Morita, Y.; Noyori, R. *J. Org. Chem.* **1990**, *55*, 441. (c) Ishiguro, M.; Ikeda, N.; Yamamoto, H. *Ibid.* **1982**, *47*, 2225. (d) Daniels, R. G.; Paquette, L. A. *Tetrahedron Lett.* **1981**, *22*, 1579.

7 **8**

(3) It has already been reported that propargyltrimethylsilanes and allenyltrimethylsilanes have been prepared from different materials, respectively. These silanes are rather stable and react with some electrophiles by the aid of some promoters such as Lewis acids. Cf.: (a) Becker, D. A.; Danheiser, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 389. (b) Danheiser, R. L.; Carini, D. J.; Kwasigroch, C. A. *J. Org. Chem.* **1986**, *51*, 3870. (c) Calas, R. *J. Organomet. Chem.* **1980**, *200*, 11.

(4) Mironov, V. F.; Kalinina, L. N.; Gar, T. K. *Zh. Obshch. Khim.* **1971**, *41*, 878; *Chem. Abstr.* **1971**, *75*, 76907v.

(5) **1**: ^1H NMR ($CDCl_3$) δ 2.42 (d, 2H, *J* = 3.0 Hz), 2.10 (t, 1H, *J* = 3.0 Hz); ^{13}C NMR ($CDCl_3$) δ 109.2, 71.3, 15.4.

(6) **2**: ^1H NMR ($CDCl_3$) δ 5.35 (t, 1H, *J* = 5.9 Hz), 4.92 (d, 2H, *J* = 5.9 Hz); ^{13}C NMR ($CDCl_3$) δ 216.4, 84.4, 74.1.

(7) (a) Kobayashi, S.; Nishio, K. *Tetrahedron Lett.* **1993**, *34*, 3453. (b) Kobayashi, S.; Nishio, K. *J. Org. Chem.* **1994**, *59*, 6620.

(8) For hypervalent silicates, cf.: (a) Kira, M.; Sato, K.; Sakurai, H. *J. Am. Chem. Soc.* **1988**, *110*, 4599. (b) Hosomi, A.; Kohra, S.; Ogata, K.; Yanagi, T.; Tominaga, Y. *J. Org. Chem.* **1990**, *55*, 2415. (c) Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Reye, C. *J. Organomet. Chem.* **1987**, *328*, C17.

(9) A typical experimental procedure is described for the reaction of propargyl chloride with 3-phenylpropionaldehyde. Synthesis of allenic alcohols **3**: To a CuCl (0.02 mmol) suspension in Et_2O/C_2H_5CN (10:1, 0.25 mL) were added at room temperature diisopropylethylamine (0.66 mmol) in Et_2O/C_2H_5CN (10:1, 0.5 mL) and then a mixture of propargyl chloride (0.6 mmol) and trichlorosilane (0.6 mmol) in Et_2O/C_2H_5CN (10:1, 0.5 mL). The mixture was stirred for 10 h at this temperature, and then DMF (2 mL) was added. After the mixture was cooled to 0 °C, 3-phenylpropionaldehyde (0.5 mmol) in DMF (1 mL) was added and the mixture was further stirred for 12 h at 0 °C. Cold 1 mol dm^{-3} hydrochloric acid was added to quench the reaction, and the aqueous layer was extracted with Et_2O. The organic material was dried, evaporated, and then purified by column chromatography (silica gel, hexane/ethyl acetate = 6:1) to afford **3** (R = $Ph(CH_2)_2$) in a 77% yield (**3**/**4** = >30:1). Synthesis of homopropargylic alcohols **4**: To a NiL_2 (LH = ethyl acetoacetate, 0.02 mmol) suspension in THF (0.25 mL) were added at room temperature 1,2,2,6,6-pentamethylpiperidine (0.66 mmol) in THF (0.5 mL) and a mixture of propargyl chloride (0.6 mmol) and trichlorosilane (0.6 mmol) in THF (0.5 mL). The mixture was stirred for 5 h under reflux, and then DMF (2 mL) was added at room temperature. After the mixture was cooled to 0 °C, 3-phenylpropionaldehyde (0.5 mmol) in DMF (1 mL) was added and the mixture was further stirred for 12 h at 0 °C. Cold 1 mol dm^{-3} hydrochloric acid was added to quench the reaction, and the aqueous layer was extracted with Et_2O. The organic material was dried, evaporated, and then purified by column chromatography (silica gel, hexane/ethyl acetate = 6:1) to afford **4** (R = $Ph(CH_2)_2$) in an 80% yield (**4**/**3** = >30:1).

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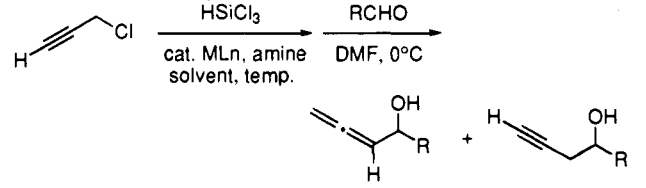
Table 2. Selective Synthesis of **3** and **4**



3 **4**

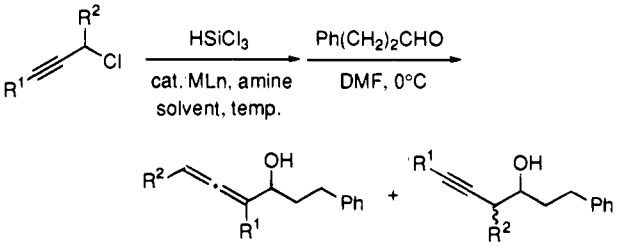
MLn	amine[a]	solvent	temp (°C)	RCHO	yield (%)	**3**:**4**[b]
CuCl	A	Et_2O	23	$Ph(CH_2)_2CHO$	82	7:1
CuCl	A	C_2H_5CN	23	$Ph(CH_2)_2CHO$	40[e]	10:1
CuCl	B	C_2H_5CN	23	$Ph(CH_2)_2CHO$	44[e]	19:1
CuCl	A	Et_2O/C_2H_5CN (4:1)	23	$Ph(CH_2)_2CHO$	71	>30:1
CuCl	A	Et_2O/C_2H_5CN (7:1)	23	PhCHO	60	10:1
CuCl	A	Et_2O/C_2H_5CN (10:1)	23	$CH_3(CH_2)_7CHO$	77	>30:1
NiL_2[c]	A	Et_2O	23	$Ph(CH_2)_2CHO$	69	1:4
NiL_2[d]	A	THF	66	$Ph(CH_2)_2CHO$	58	<1:>30
NiL_2[c]	B	THF	66	$Ph(CH_2)_2CHO$	70	1:24
NiL_2[d]	B	THF	66	$Ph(CH_2)_2CHO$	80	<1:>30
NiL_2[c]	B	THF	66	PhCHO	79	<1:>30
NiL_2[c]	B	THF	66	$CH_3(CH_2)_7CHO$	76	1:10

[a] A, diisopropylethylamine; B, 1,2,2,6,6-pentamethylpiperidine. [b] Determined by ^1H NMR analysis. [c] LH = $PhC(O)CH_2C(O)Ph$. [d] LH = $CH_3C(O)CH_2C(O)OEt$. [e] Moderate yields may be due to the slow first step (chlorosilane-producing reaction) in C_2H_5CN.

from **1**, homopropargylic alcohols **4** were obtained from **2**, both with high selectivities. The regioselectivities are rationalized by the approach of the silanes and aldehydes shown in Scheme 1. Moreover, it was found that one-pot reactions from propargyl chlorides also proceeded smoothly to afford allenic alcohols **3** or homopropargylic alcohols **4** with high selectivities (Table 2).[9]

Steric effects influenced the formation of substituted propargyltrichlorosilanes and allenyltrichlorosilanes in some cases (Table 3). 1-Chloro-2-butyne or 1-chloro-3-phenyl-2-propyne reacted with trichlorosilane in the presence of CuCl and diisopropylethylamine to form propargyltrichlorosilanes exclusively, which in turn reacted with aldehydes in DMF at 0 °C to afford allenic alcohols in high yields. The silylation reaction proceeded sluggishly when the nickel catalyst was used. On the other hand, the corresponding allenyltrichlorosilane was generated from 3-chloro-1-butyne regardless of the transition metal salt used (the copper(I) or nickel(II) salt), and this reacted with aldehydes regioselectively to give homopropargylic alcohols in high yields.

Table 3. Selective Synthesis of **5** and **6**



5 **6**

R^1	R^2	MLn	amine[a]	solvent	temp (°C)	yield (%)	**5**:**6**[b]
Me	H	CuCl	A	Et_2O	23	94	>30:1
Me	H	NiL_2[c]	B	THF	66	11	1:12
Ph	H	CuCl	A	Et_2O	23	84	>30:1
H	Me	CuCl	A	Et_2O/C_2H_5CN (10:1)	23	88	<1:>30[d]
H	Me	NiL_2[c]	B	THF	66	84	<1:>30[d]

[a] A, diisopropylethylamine; B, 1,2,2,6,6-pentamethylpiperidine. [b] Determined by ^1H NMR analysis. [c] LH = $CH_3C(O)CH_2C(O)OEt$. [d] *Syn*: *anti* = 7:1.

In summary, a new method for the selective formation of propargyltrichlorosilanes and allenyltrichlorosilanes from the same intermediates (propargyl halides) has been developed. Propargyltrichlorosilanes and allenyltrichlorosilanes thus prepared react with aldehydes in DMF at 0 °C to afford homopropargylic alcohols and allenic alcohols, respectively, and we have achieved a one-pot synthesis of allenic and homopropargylic alcohols in high yields with high selectivities.

Supplementary Material Available: Experimental procedures and ^1H and ^{13}C NMR spectral data (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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