Pergamon

Tetrahedron Letters 41 (2000) 4499–4502

TETRAHEDRON
LETTERS

Lewis acid-catalyzed *trans*-carbosilylation of alkynes with propargyl- and allenyltrimethylsilanes

Eiji Yoshikawa, Masaki Kasahara, Naoki Asao and Yoshinori Yamamoto*

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

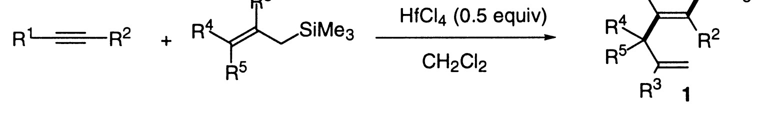
Received 10 March 2000; accepted 20 April 2000

Abstract

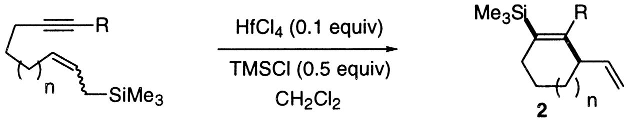
Lewis acid-catalyzed *trans*-carbosilylation of alkynes with propargyl- and allenyltrimethylsilanes produces the corresponding silylated 1,4-enynes and vinylallenes regio- and stereoselectively.

Keywords: Lewis acid; alkynes; carbosilylation; propargylsilanes.

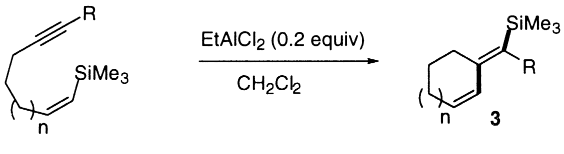
We recently reported the Lewis acid-catalyzed inter- and intramolecular *trans*-allylsilylation[1a–c] and intramolecular *trans*-vinylsilylation[2] of unactivated alkynes. The $HfCl_4$-catalyzed addition of allylic silanes to alkynes gave **1** in high yields, and the intramolecular version of the allylic silane–alkyne addition produced **2** in good to high yields (Eqs. (1) and (2)). Furthermore, the $EtAlCl_2$-catalyzed intramolecular reaction of alkenylsilanes bearing an alkynyl carbon tether afforded **3** in good yields (Eq. (3)).



(1)



(2)



(3)

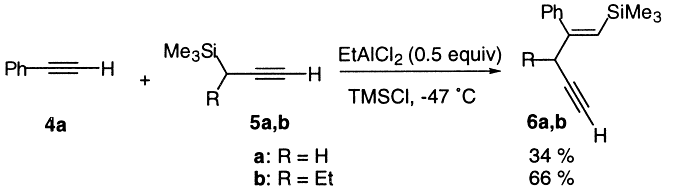
---

* Corresponding author. Tel: +81 22 217 6581; fax: +81 22 217 6784; e-mail: yoshi@yamamoto1.chem.tohoku.ac.jp

PII: S0040-4039(00)00650-X

It occurred to us that the use of propargyl- or allenylsilanes, instead of allylsilanes, would give the corresponding allenyl or propargyl addition products, respectively. A report about the carbometallation of alkynes with propargylmetals is available.[3] One of the reasons for the lack of investigation of the propargyl metallation is perhaps the fact that the selective synthesis of propargyl organometallics is not easy and is very often accompanied by the formation of allenyl organometallics due to facile equilibration between these two substrates.[4,5] Fortunately, however, propargyltrimethylsilanes can be easily prepared with good yields,[6] and they are, in general, air and moisture stable, while the corresponding magnesium, zinc, and aluminium derivatives are not stable.

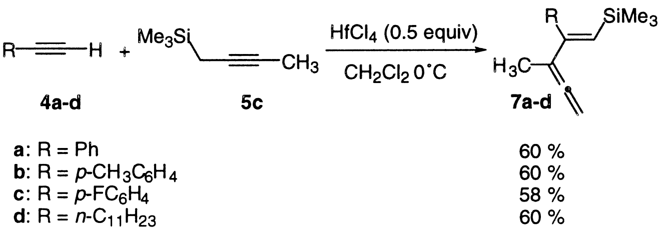
The $EtAlCl_2$-catalyzed carbosilylation of phenylacetylene **4a** with propargyltrimethylsilane **5a** afforded the 1,4-enyne **6a** in 34% yield along with many by-products (Eq. (4)).



(4)

Other Lewis acids, such as $HfCl_4$ and $ZrCl_4$, gave lower yields. It was thought that it would be difficult for Lewis acids to distinguish the three different triple bonds, that of propargyl-trimethylsilane **5a**, the starting alkyne **4a**, and the product **6a**. Therefore, we investigated the reaction of the substituted propargyltrimethylsilane **5b**; it was expected that the stereoelectronic difference between the three alkyne units of **4a**, **5b**, and **6b** must become more conspicuous than that between **4a**, **5a**, and **6a**. The propargylsilane **5b** was prepared from the reaction of the dilithiated 1-pentyne with chlorotrimethylsilane.[6e] The $EtAlCl_2$-catalyzed reaction of **5b** with **4a** produced the 1,4-enyne **6b** in 66% yield.

The reaction of the non-terminal propargyltrimethylsilane **5c** with **4a** gave a different type of product, the vinylallene **7a**, in 60% yield (Eq. (5)).

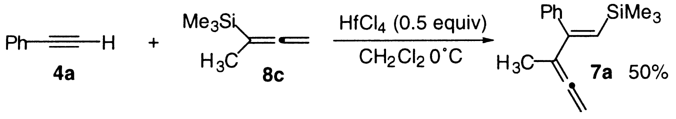


(5)

Other catalysts, such as $EtAlCl_2$–TMSCl and $AlCl_3$, also gave the vinylallene **7a** in lower yields. Other alkynes **4b**, **c**, and **d** reacted similarly to give the corresponding allenylsilylated products **7b,** **c**, and **d**, respectively, in good yields. The structures of **6a**, **b**, and **7a–d** were confirmed unambiguously by ^1H NMR, ^{13}C NMR, IR, and mass spectra.[7]

The $HfCl_4$-catalyzed carbosilylation of phenylacetylene **4a** with allenyltrimethylsilane **8c**, which was prepared from the reaction of the mesylate of 3-trimethylsilyl-2-propyn-1-ol with CH_3MgCl

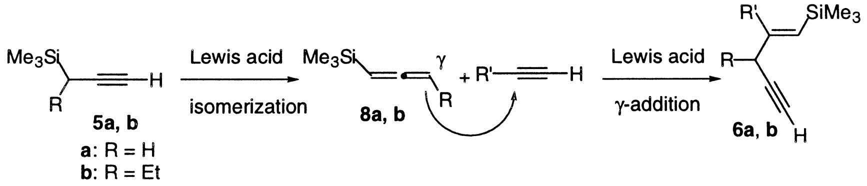
and CuBr–LiBr,[6f] gave the vinylallene **7a** in 50% yield (Eq. (6)). It should be noted that the reaction of **8c** and that of **5c** gave the same product **7a**.



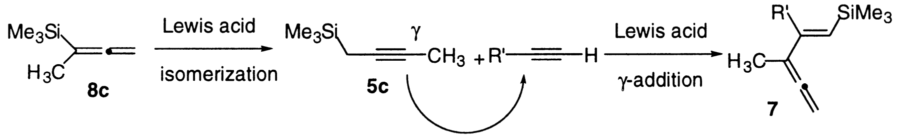
(6)

The isomerization of **5c** under the reaction conditions (HfCl$_4$, CH$_2$Cl$_2$, 0°C) did not take place, but **8c** isomerized under the reaction conditions to afford **5c**. On the other hand, the terminal propargyltrimethylsilane **5b** isomerized under the reaction conditions to afford the corresponding allenyltrimethylsilane **8b**.

The above complicated observations can be summarized and explained as follows: The terminal propargyltrimethylsilanes **5a** and **b** undergo isomerization in the presence of Lewis acids to give the corresponding allenyltrimethylsilanes **8a** and **b**, respectively. Then, the reaction of **8a** and **b** with alkynes give the corresponding *trans*-addition products, 1,4-enynes **6a** and **b**, respectively (Eq. (7)). On the other hand, the non-terminal propargyltrimethylsilane **5c** reacts with alkynes without isomerization to give vinylallenes **7** (Eq. (8)). It is clear that here γ-addition of the allenylsilanes **8a** and **b** and the propargylsilane **5c** to alkynes also takes place, as observed in the reaction of allylsilanes.[1a,b]

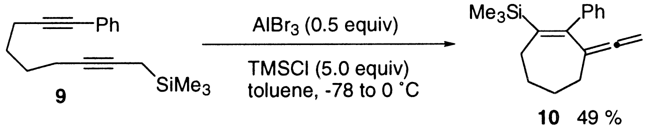


(7)



(8)

The intramolecular version of the propargylsilane–alkyne addition was investigated. The AlBr$_3$-catalyzed reaction of **9** gave the silylated cyclic vinylallene **10** in 49% yield (Eq. (9)).



(9)

We are now in a position to prepare effectively various types of silylated 1,4-enynes and vinylallenes regio- and stereoselectively in good yields via the Lewis acid-catalyzed carbosilylation of unactivated alkynes. The resulting silylated 1,4-enynes and vinylallenes[8] may be useful as building blocks in organic synthesis.

References

1. (a) Asao, N.; Yoshikawa, E.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 4874. (b) Yoshikawa, E.; Gevorgyan, V.; Asao, N.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 6781. (c) Imamura, K.; Yoshikawa, E.; Gevorgyan, V.; Yamamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 5339. (d) Yeon, S. H.; Han, J. S.; Hong, E.; Do, Y.; Jung, I. N. *J. Organomet. Chem.* **1995**, *499*, 159.
2. Asao, N.; Shimada, T.; Yamamoto, Y. *J. Am. Chem. Soc.* **1999**, *121*, 3797.
3. Bellasoued, Y.; Frangin; Gaudemar, M. *J. Organomet. Chem.* **1979**, *166*, 1.
4. Yamamoto, H. In *Comprehensive Organic Synthesis*; Trost, B. M, Ed.; Pergamon Press: Oxford, **1991**, *2*, 81.
5. Although some excellent works have been reported in this field, the selectivity depends on substrates and metals used. (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.
6. (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. *J. Organomet. Chem.* **1980**, *200*, 11. (d) Kobayashi, S.; Nishio, K. *J. Am. Chem. Soc.* **1995**, *117*, 6392. For synthesis of **5b**, see: (e) Brandama, L.; Verkruijsse, H. D. In *Synthesis of Alkynes, Allenes, and Cummlenes*; Elsevier: New York, 1981; p. 52. For synthesis of **8c**, see: (f) Danheiser, R. L.; Tsai, Y.-M.; Fink, D. M. *Org. Synth.* **1987**, *66*, 1.
7. Compound **6b**: ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.30–7.22 (m, 3H), 7.16–7.11 (m, 2H), 5.99 (s, 1H), 3.35–3.28 (m, 1H), 2.32–2.30 (m, 1H), 1.61–1.49 (m, 1H), 1.45–1.30 (m, 1H), 0.94 (t, $J=6.8$ Hz, 3H), –0.21 (s, 9H); ^{13}C NMR (68 MHz, CDCl$_3$) δ 156.0, 129.0, 128.6, 127.6, 127.2, 85.2, 72.7, 44.4, 26.6, 11.3, –0.1. IR (neat) 3309, 2964, 1612, 1595, 1490, 1440, 1248, 875, 704 cm^{-1}. Anal. calcd for $C_{16}H_{22}Si$: C, 79.27; H, 9.15. found: C, 79.15; H, 9.18. Compound **7a**: ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.31–7.24 (m, 3H), 7.14–7.09 (m, 2H), 5.74 (t, $J=1.3$ Hz, 1H), 4.53 (dq, $J=1.3$, 2.7 Hz, 2H), 1.98 (t, $J=2.7$ Hz, 3H), –0.18 (s, 9H); ^{13}C NMR (68 MHz, CDCl$_3$) δ 211.9, 154.3, 142.4, 129.2, 127.1, 127.0, 126.8, 104.4, 75.6, 16.9, 0.0. IR (neat) 2978, 1936, 1568, 1248, 850, 700 cm^{-1}. MS (EI) *m/z* 228 (M$^+$, 27.9), 213 (M$^+$–CH$_3$, 21.1), 73 (TMS, 100). HRMS calcd for $C_{15}H_{20}Si$: 228.1334; found: 228.1361. Compound **10**: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.24–7.21 (m, 3H), 7.10–7.08 (m, 2H), 4.42 (t, $J=2.5$ Hz, 2H), 2.46 (tt, $J=6.5$, 2.5 Hz, 2H), 2.42 (t, $J=6.0$ Hz, 2H), 1.83 (tt, $J=6.5$, 6.5 Hz, 2H), 1.74 (tt, $J=6.5$, 6.0 Hz, 2H), –0.23 (s, 9H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 149.1, 145.1, 141.4, 129.6, 127.3, 126.6, 109.0, 74.4, 31.6, 31.3, 27.9, 26.1, –0.4. IR (neat) 2930, 1932, 1442, 1248, 838, 758, 700 cm^{-1}. MS (EI) *m/z* 268 (M$^+$, 15.0), 73 (TMS, 100). HRMS calcd for $C_{18}H_{24}Si$: 268.1647; found: 268.1652.
8. Murakami, M.; Amii, H.; Itami, K.; Ito, Y. *Angew. Chem. Int., Ed. Engl.* **1995**, *34*, 1476.