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Lithium Dienolate Generation by α-Regioselective Reaction of (1-Silylallyl)lithiums with Carbon Monoxide

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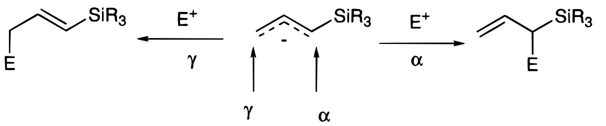
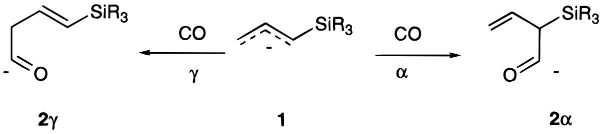
Summary: Lithium dienolates of α,β-unsaturated acylsilanes can be conveniently obtained by the reaction of (1-silylallyl)lithiums with carbon monoxide at ambient temperature. This reaction represents a rare example of α-selective C−C bond formation for an ambident 1-silylallyl anion, which may be rationalized by assuming an equilibration process.

The ambident character of allyllithium poses regiochemical problems with respect to α/γ selectivity associated with the reaction of such reagents with electrophiles. The case of (1-silylallyl)lithium is no exception (eq 1).



(1)

We previously reported that acyllithiums, generated from (1-silyl)alkyllithiums and carbon monoxide, can be efficiently converted to the lithium enolates of acylsilanes via an anionic 1,2-silicon shift.[1,2] For the related (1-silylallyl)lithium/CO system, if a similar reaction would take place, lithium dienolate would be the expected product. The success of such a reaction, however, depends upon the extent that CO addition is α-selective, since, of two possible acyllithiums **2**γ and **2**α, derived from **1** and CO (eq 2), only the latter can paticipate in a 1,2-silicon shift. We now report a unique procedure for lithium dienolates of α,β-unsaturated acylsilanes resulting from the reaction of (1-silylallyl)lithiums with CO, a reaction which proceeds via complete α-selective C−C bond formation.[3]



(2)

In contrast to the high reactivity of allylithium which absorbs an equimolar amount of CO within 2 h at −78 °C,[4] (1-silylallyl)lithium **1a** reacted more slowly with CO at this low temperature. When a THF−TMEDA solution of **1a** was exposed to CO at 15 °C, however, the smooth uptake of CO was observed over a period of 3.5 h.[5] Quenching the reaction mixture with trimethylchlorosilane afforded the silyl ether of acylsilane dienolate **3a** in 89% yield (*E*/*Z* = 96/4). This clearly shows that the acyllithium−lithium dienolate conversion proceeded by a 1,2-silicon shift via **2**α (eq 3). The reaction was clean, and neither product arising from γ-attack nor the product of an intermolecular reaction was detected by NMR spectra of the crude product.

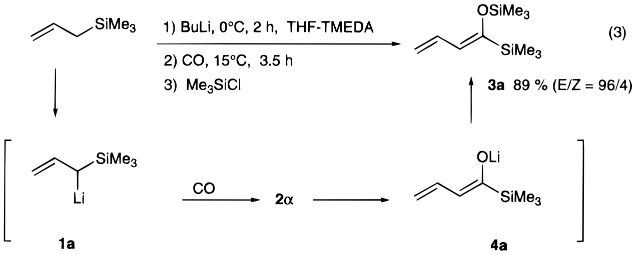


Table 1, which summarizes some results of the reaction of other (1-silylallyl)lithiums with CO, demonstrates the generality of this one carbon homologation protocol leading to lithium dienolates.[6] Dienolate formation took place in a stereoselective manner relative to the C1−C2 double bonds and gave *E* isomers predominantly or exclusively. This geometrical preference is similar to our previous observation with (1-silyl)-alkyllithium/CO systems.[1] Quenching of the reaction mixture by acidification gave α,β-unsaturated acylsilane (entry 3). When coupled with the subsequent desilylation procedure (TBAF, HCOOH−THF) reported by Zweifel and Miller,[8c] the reaction gave the corresponding

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[1] Murai, S.; Ryu, I.; Iriguchi, J.; Sonoda, N. *J. Am. Chem. Soc.* **1984**, *106*, 2440.

[2] For other intramolecular conversions of acyl- and aroyllithiums, see: (a) Ryu, I.; Hayama, Y.; Hirai, A.; Sonoda, N.; Orita, A.; Ohe, K.; Murai, S. *J. Am. Chem. Soc.* **1990**, *112*, 7061. (b) Orita, A.; Ohe, K.; Murai, S. *Organometallics* **1994**, *13*, 1533. (c) Orita, A.; Fukudome, M.; Ohe, K.; Murai, S. *J. Org. Chem.* **1994**, *59*, 477. (d) Kai, H.; Iwamoto, K.; Chatani, N.; Murai, S. *J. Am. Chem. Soc.* **1996**, *118*, 7634. (e) Smith, K.; Pritchard, G. J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 282. Also see intermolecular reactions: (f) Seyferth, D.; Hui, R. C.; Wang, W.-L. *J. Org. Chem.* **1993**, *58*, 5843 and references cited therein.

[3] For reviews, see: (a) Chan, T. H.; Wang, D. *Chem. Rev.* **1995**, *95*, 1279. (b) Panek, J. S. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, U.K., 1991; Vol. 1, Chapter 2.5. (c) Yamamoto, Y. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, U.K., 1991; Vol. 2, Chapter 1.2. Also see: (d) Schaunamn, E.; Krischning, A. *Tetrahedron Lett.* **1988**, *29*, 4281. (e) Horvath, R. F.; Chan, T. H. *J. Org. Chem.* **1989**, *54*, 317. (f) Blanco, F. J.; Cuadrado, F.; Gonzalez, A. M.; Pulido, F. J. *Synthesis* **1996**, 42.

[4] The reaction conducted in a THF solution afforded a mixture of more than 10 products which were incorporated by CO.

[5] The formation of the lithium dienolate **4a** was ascertained by ^{1}H NMR measurement: ^{1}H NMR (THF-d_8) δ 0.02 (s, 9H), 4.50 (dd, J = 12, 2 Hz, 1H), 4.70 (dd, J = 17, 2 Hz, 1H), 5.30 (d, J = 12 Hz, 1H), 5.80−6.10 (m, 1H). For an NMR study of 1-(silyl)allyllithium, see: Fraenkel, G.; Chow, A.; Winchester, W. R. *J. Am. Chem. Soc.* **1990**, *112*, 2582.

[6] Representative procedure for **3b**: To a solution of allyl(phenyl)-dimethylsilane (**1b**, 0.77 g (4.4 mmol)) in dry THF (10 mL) and TMEDA (2 mL) was added a hexane solution of *n*-BuLi (3.6 mL, 5.7 mmol) dropwise via a syringe at 0 °C, and then the solution was stirred for 2 h at 0 °C. After being warmed to 15 °C, the solution was degassed and then exposed to CO via a balloon. After 10 h, excess CO gas was evacuated and Ar gas was introduced. The solution was cooled to 0 °C, trimethylchlorosilane (0.57 mL, 4.5 mmol) was added, and the resulting solution was warmed to 15 °C and stirred for 1 h. After aqueous workup, drying over $MgSO_4$, and evaporation of the solvents, the residual oil was purified by bulb to bulb distillation yielding **3b** (0.914 g, 75%) as a clear oil.

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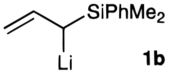
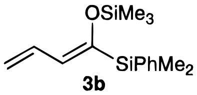
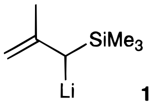
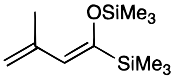
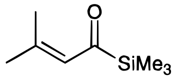
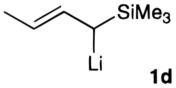
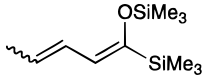
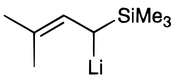
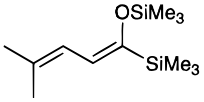
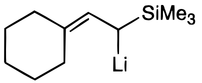
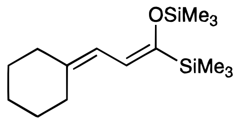
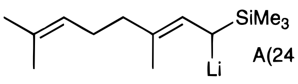
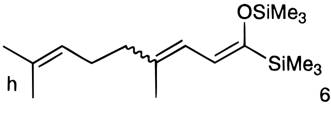
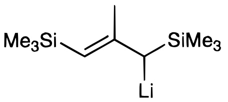
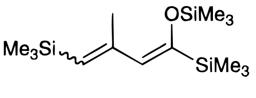
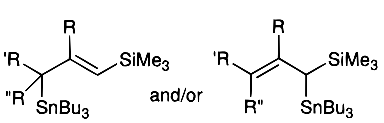
Table 1. Preparation of Lithium Dienolates from (1-Silylallyl)lithiums and CO[a]

entry	RR'C=CR"CHLiSiR'"$_3$, **1**	method for **1**[b]	conditions	product	yield (%)[c]	(E/Z)[d]
1	 **1b**	A(2 h)	15°C, 10 h	 **3b**	(75)93	(93/7)
2	 **1c**	A(15 h)	15°C, 3 h	 **3c**	71	(100/0)
3		A(15 h)	15°C, 3 h	 **6**	(65)	
4	 **1d**	A(24 h)	15°C, 2 h	 **3d**	72	(100/0, 50/50)
5		B[e](2 h)	15°C, 3 h		(71)86	(100/0, 50/50)
6	 **1e**	A(24 h)	15°C, 2 h	 **3e**	63	(100/0)
7		B[f](2 h)	15°C, 2.5 h		87	(100/0)
8	 **1f**	A(24 h)	15°C, 2 h	 **3f**	78	(100/0)
9		B[g](2 h)	15°C, 2 h		(63)85	(100/0)
10	 **1g**	A(24 h)	15°C, 2 h	 **3g**	64	(100/0, 70/30)
11	 **1h**	A(15 h)	25°C, 11 h	 **3h**	59	(100/0, 66/34)

[a] All reactions were carried out on 1−5 mmol scale using a CO balloon. Except for run 3 (proton quenching), lithium dienolates were quenched by Me$_3$SiCl. [b] Method A (H−Li exchange): allylsilanes, *n*-BuLi (1.2−1.3 equiv), THF−TMEDA (2 equiv) or TMEDA only (entries 4, 8, and 10), 0−25 °C , 2−24 h (indicates in parentheses). Method B (Sn−Li exchange): A mixture of α- and γ-silylated allyltins (**5**: R′R″(SnBu$_3$)CC(R)=CHSiMe$_3$ and/or R′R″C=C(R)CH(SnBu$_3$)SiMe$_3$, *n*-BuLi (1.1−1.3 equiv), THF, 0 °C, 2h. [c] GC yields. Isolated yields by column chromatography (entries 1, 3, and 9) or by distillation (entry 5) are in parentheses. [d] Determined by GC and/or NMR. [e] α/γ = 24:76. [f] α/γ = 100:0. [g] α/γ = 100:0.

α,β-unsaturated aldehyde in 75% yield.[7,8] Starting (1-silylallyl)lithiums are readily available from the corresponding allylsilanes by proton abstraction (*n*-BuLi/THF−TMEDA or TMEDA, method A), but the substituted allylsilanes **1c**−**h** required longer reaction times for the completion of proton abstraction. The inefficiency in this step appeared to influence the yields of **3**. Indeed, when more efficient Li−Sn exchange (*n*-BuLi/THF, method B) was employed to generate **1** with silyl-substituted allyltin compounds **5** (R′R″C(SnBu$_3$)CR=CHSiMe$_3$ and/or R′R″C=CRCH(SnBu$_3$)SiMe$_3$), the yields of **3** were significantly improved (entries 5, 7, and 9), thus demonstrating that the conversion of **1** to **4** is very efficient. It should be noted that, in contrast to the Me$_3$Si analog **1a**, the reaction of Me$_2$PhSi derivative **1b** with CO required a longer reaction time for completion (entry 1).[9]



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Complete α-regioselectivity observed for CO capture in this study seems rather exceptional, compared with previously reported results of the reaction of (1-silyl-

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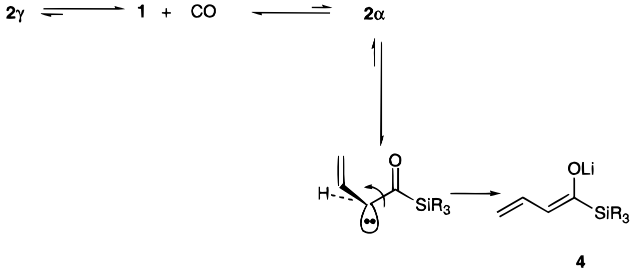
(7) The overall procedure provides a unique [3 + 1] protocol for the synthesis of α,β-unsaturated aldehydes.

(8) α,β-Unsaturated acylsilanes are potent synthetic intermediates; for examples, see: (a) Reich, H. J.; Olson, R. E.; Clark, M. C. *J. Am. Chem. Soc.* **1980**, *102*, 1423. (b) Reich, H. J.; Eisenhart, E. K. *J. Org. Chem.* **1984**, *49*, 5282. (c) Miller, J. A.; Zweifel, G. *J. Am. Chem. Soc.* **1981**, *103*, 6217. (d) Sato, T.; Arai, M.; Kuwajima, I. *J. Am. Chem. Soc.* **1977**, *99*, 5827. (e) Danheiser, R. L.; Fink, D. M.; Okana, K.; Tsai, Y.-M.; Szczepanski, S. W. *J. Org. Chem.* **1985**, *50*, 5393. (f) Nowick, J. S.; Danheiser, R. L. *J. Org. Chem.* **1989**, *54*, 2798. (g) For the use of **3a**, see: Ogoshi, S.; Ohe, K.; Chatani, N.; Kurosawa, H.; Kawasaki, Y.; Murai, S. *Organometallics* **1990**, *9*, 3021.

allyl)lithium with a variety of electrophiles.[3] The origin of the high α-regioselection is postulated to result from the nature of CO as a "modest electrophile" which allows an equilibrium among two regioisomeric acyllithiums **2**α and **2**γ and (1-silylallyl)lithium plus CO. Of the acyllithiums, only **2**α can undergo a 1,2-silicon shift to give the lithium dienolate **4**, thus shifting the equilibrium to the right (Scheme 1).[10]

(Bis(silyl)allyl)lithium **1h** reacted sluggishly with CO (entry 11). The apparent modest reactivity of **1h** toward CO may relate to its enhanced thermodynamic stability resulting from the additional silyl substituent. Preliminary semiempirical calculations using PM3 have shown that the ΔE value for the formation of the acyl anion from 1,3-bis(trimethylsilyl)allyl anion and CO is ca. 5.0 kcal/mol smaller than that from 1-(trimethylsilyl)allyl anion and CO, supporting this hypothesis.

Scheme 1



The data presented herein show that (1-silylallyl)lithiums undergo α-selective CO addition and subsequent 1,2-silicon shift to give lithium dienolates of acylsilanes in good yields. Although the use of CO for synthetic purposes is not very common in chemical laboratories, the operational simplicity of this one carbon homologation protocol for dienolate formation, together with the ready availability of starting allylsilanes, holds considerable promise in organic syntheses.

Acknowledgment. We thank Shin-Etsu Chemical Inc. for providing the chlorosilanes as a gift. This work was supported by a grant from the Ministry of Education, Science, and Culture of Japan.

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(9) Similarly, the reaction of the t-BuMe$_2$Si derivative was sluggish. This is due presumably to the steric effect associated with silyl migration. For recent examples of steric effects of substituents at silicon on anionic migration, see: Marumoto, S.; Kuwajima, I. *J. Am. Chem. Soc.* **1993**, *115*, 9021.

(10) We have confirmed that CO pressures (5−10 atm) can assist the reaction. Cf.: An equilibrium is suggested in the addition of organolithiums to isonitriles, isoelectronic compounds of CO. See: Niznik, G. E.; Morrison, W. H., III; Warborsky, H. M. *J. Org. Chem.* **1974**, *39*, 600. A reviewer pointed out that CO, considered as a "small electrophile," could react with a kinetic preference at the α-position. For an argument for regioselectivity based on steric factors associated with ethylene oxide, see ref 3d.