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Allylsilylation of Carbon−Carbon and Carbon−Oxygen Unsaturated Bonds *via* a Radical Process[1]

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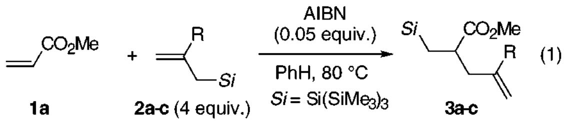
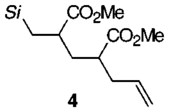
The carbometalation of alkenes and alkynes is a powerful and selective method for the construction of carbon−carbon and carbon−metal bonds,[2] in particular, *via* an ionic process. Previously, we have reported a novel type of allylmetalation in which allylstannanes bearing an electron-withdrawing group at the β-position react with alkenes and alkynes via a radical process.[3] Although radical-based allylation with allylstannanes has been extensively studied as a useful method of both carbon−carbon bond formation and introduction of an easily convertible functionality,[4] the use of tin-based reagents is not always convenient because of the inherent toxicity of organotin compounds.[5] In this context, Chatgilialoglu and Curran *et al.* have recently reported that allyltris(trimethylsilyl)silanes are more environmentally benign radical allylated agents.[6] Therefore, we attempted to utilize these silicon-based reagents instead of allylstannanes for homolytic allylmetalation.[7] We now describe our preliminary results on the allylsilylation of carbon−carbon and carbon−oxygen unsaturated bonds with allyltris(trimethylsilyl)silanes.[8]

First, the reactions of methyl acrylate (**1a**) with the allyltris(trimethylsilyl)silanes **2a**−**c** were examined (eq 1).



allylsilane	time	product (% yield)
2a (R = H)	4 h	**3a** (19) + **4** (30)
2b (R = COOMe)	40 min	**3b** (90)
2c (R = CN)	3 h	**3c** (65)



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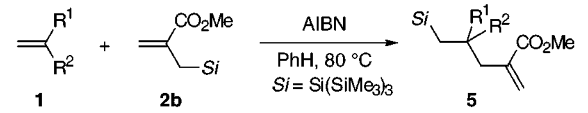
Treatment of **1a** with 4 equiv of **2a** in the presence of AIBN (0.05 equiv) at 80 °C gave the allylsilylated product **3a** in 19% yield along with a diastereomeric mixture of the diester **4**, which consisted of two molecules of **1a** and one molecule of **2a**. Introduction of an electron-withdrawing group at the β-position of **2a** significantly increased the allylsilylation of **1a**. Thus, the reaction of the β-substituted allyltris(trimethylsilyl)silanes **2b** (R = CO_2Me) and **2c** (R = CN) afforded **3b** and **3c** in 90% and 65% yields, respectively, without the 2:1 adducts such as **4**. A similar substituent effect was observed in our previous work on the homolytic allylstannylation of **1a**.[3b]

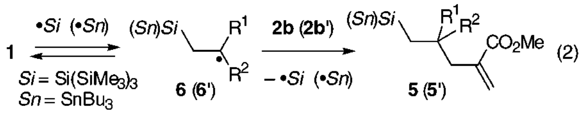
Table 1. Allylsilylation of Terminal Alkenes with 2b[a]



entry	alkene R¹	alkene R²	time/h	product (% yield)[b]
1	CN	H	4	**5a** (83)
2	CO_2Me	Me	3	**5b** (78)
3	Ph	H	3	**5c** (91)
4	n-C_8H_{17}	H	24	**5d** (44)
5	OBu	H	3	**5e** (58)
6	SPh	H	1.5	**5d** (55)

[a] All reactions were performed with a substrate (0.50 mmol), **2b** (2.0 mmol), and AIBN (0.025 mmol) in benzene (2.5 mL) at 80 °C. [b] Isolated yield.

As shown in Table 1, a variety of terminal alkenes including electron-deficient and electron-rich alkenes readily underwent the allylsilylation with **2b** to give the adducts **5** in moderate to good yields. This result is in sharp contrast to that observed in the homolytic allylstannylation, where the corresponding allylstannane **2b′** ($CH_2{=}C(CO_2Me)CH_2$-$SnBu_3$) hardly reacted with an electron-rich alkene such as 1-decene.[3b] This distinction is probably because the intermediary β-stannylalkyl radical **6′** rapidly reverts to alkene and stannyl radical before intermolecular addition to **2b′**, while the elimination of the silyl radical from the β-silylalkyl radical **6** is slow enough for the allylation with **2b** (eq 2).[9]



Internal alkenes bearing one electron-withdrawing group such as methyl crotonate and ethyl cinnamate underwent no allylsilylation with **2b**. However, dimethyl maleate (**7**) and dimethyl fumarate (**8**), highly electron-deficient alkenes, were good acceptors of **2b**, and their allylsilylation formed the erythro isomer **9**, exclusively (eq 3). The reactions of maleic anhydride (**11a**) and methyl maleic anhydride (**11b**) with **2b** proceeded with a trans addition to afford only adducts **12a** and **12b**, respectively (eq 4). The trans adduct **12a** could be converted to **10** by treatment with MeOH and K_2CO_3−MeI, which confirmed that **10** was a threo isomer. The reversal of diastereoselectivity in acyclic and cyclic systems can be rationalized by considering conformations (**A** and **B**) of intermediary radicals similar to those reported by Giese et al.[10] The allylations of the radicals **A** and **B**

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[1] Studies on Organosilicon Chemistry. 142.

[2] For reviews see: (a) Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841. (b) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 38. (c) Negishi, E. *Pure Appl. Chem.* **1981**, *53*, 2333. (d) Knochel, P. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1995; Vol. 11, p 159. (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.

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[7] For studies on chemical properties of silyl radicals see: Chatgilialoglu, C. *Chem. Rev.* **1995**, *95*, 1229.

[8] For studies on the ionic allylsilylation see: (a) Yoshikawa, E.; Gevorgyan, V.; Asao, N.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 6781. (b) Yeon, S. H.; Han, J. S.; Hong, E.; Do, Y.; Jung, I. N. *J. Organomet. Chem.* **1995**, *499*, 159. (c) Yeon, S. H.; Lee, B. W.; Yoo, B. R.; Suk, M.-Y.; Jung, I. N. *Organometallics* **1995**, *14*, 2361.

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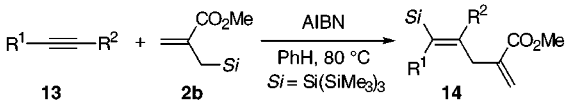
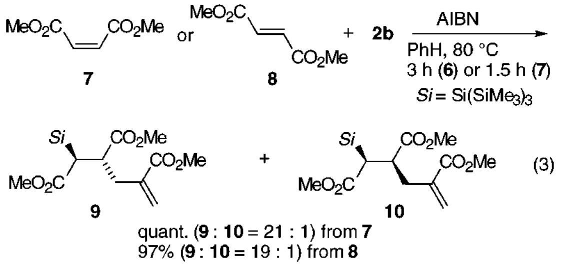
Table 2. Allylsilylation of Alkynes with 2b[a]

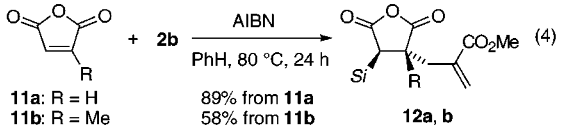


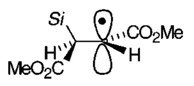
entry	alkyne R^1	alkyne R^2	time/h	product (% yield)[b]
1	H	CO_2Et	1.5	**14a** (71)
2	H	Ph	1.5	**14b** (80)
3	H	n-$C_{10}H_{21}$	10	**14c** (64)
4	H	$(CH_2)_2OH$	4	**14d** (57)
5	MeO_2C	Ph	8	**14e** (16) (9)[c]

[a,b] See footnotes a and b in Table 1. [c] The yield of adduct **15**.

with **2b** proceed at the opposite side of the bulky silyl group to give **9** and **12**, respectively.







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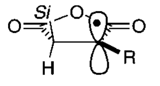
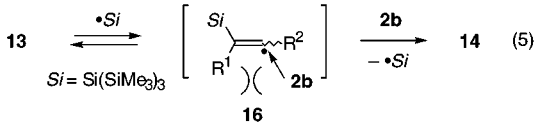
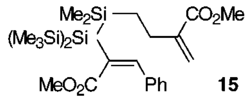


B

Various alkynes also underwent the allylsilylation with **2b** (Table 2). The reactions of terminal alkynes gave the trans adducts **14** in moderate to good yields (entries 1−4). The complete regio- and stereocontrol of the allylsilylation can be explained by the following mechanism (eq 5): to minimize the steric repulsion in the reaction course, (1) tris(trimethylsilyl)silyl radical adds to the terminal carbon of **13** and (2) the intermediary vinyl radical **16** is allylated at the opposite side to the silyl group.[3a,11]



Internal alkynes, even those bearing an electron-withdrawing group, exhibited much lower reactivity toward **2b** than terminal alkynes. For example, the reaction of methyl 3-phenyl-2-propynoate (**13e**) resulted in 16% yield of the allylsilylation product **14e** (entry 5).[12] The rearranged adduct **15** was also formed as a byproduct by the reaction involving 1,5-hydrogen transfer of the radical intermediate **16**.[13] In contrast to this result, it has been reported that



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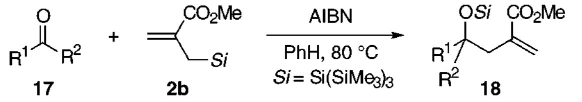
homolytic hydrosilylation of ethyl 3-phenyl-2-propynoate with tris(trimethylsilyl)silane smoothly proceeds under similar reaction conditions.[14] Accordingly, the low reactivity of **13e** is probably due to the sterically impeded addition of the intermediary radical **16** to **2b**.

Table 3. Allylsilylation of Aldehydes and Ketones with 2b[a]



entry	carbonyl compound R^1	carbonyl compound R^2	time/h	product (% yield)[b]
1	Ph	H	8	**18a** (81)
2	p-$MeOC_6H_4$	H	8 (12)[c]	**18b** (23) (45)[c]
3	p-NCC_6H_4	H	8 (12)[c]	**18c** (49) (78)[c]
4	Ph	Me	24	**18d** (21)
5	$Ph(CH_2)_2$	H	24	**18e** (7)
6	$(CH_2)_5$		8	**18f** (0)

[a,b] See footnotes a and b in Table 1. [c] Reaction time and isolated yield when the reaction was performed with intermittent addition of AIBN (0.025 mmol × 6, every 2 h).

Moreover, we attempted the allylsilylation of a carbon−oxygen double bond with **2b**. Treatment of benzaldehyde (**17a**) with **2b** in the presence of AIBN gave the homoallyl silyl ether **18a** in 81% yield. In the absence of AIBN, no adduct was obtained. It is well-established that allylsilanes react with various carbonyl compounds in the presence of Lewis acids or a fluoride ion to afford allylation products (Hosomi−Sakurai reaction).[15] However, allylation of a carbonyl carbon *via* a radical process is unprecedented, to the best of our knowledge.[16,17] To investigate the scope and limitations of the present methods, several aldehydes and ketones were subjected to the reaction with **2b** (Table 3). These results revealed that benzaldehyde was the most reactive among the examined carbonyl compounds. The use of other aromatic aldehydes led to lower yields of **18**, which could be improved by intermittent addition of AIBN. Aliphatic aldehydes and ketones hardly reacted with **3b**.

In conclusion, we have demonstrated that, in the presence of a radical initiator, **2b** reacts with a wide range of alkenes and alkynes to provide allylsilylation products with high levels of regio- and stereoselectivity, sometimes in high yields,[18] and this homolytic reaction is applicable to a new method of carbonyl allylation. Now we are further studying the synthetic utility of the present homolytic allylsilylation.

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Supporting Information Available: Experimental procedures and spectral data for the products (8 pages).

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(12) In contrast, the reaction of **13e** with **2b′** gave the allylstannylation product in 84% yield with the same regio- and stereocontrol.

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(15) Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200.

(16) We also found that AIBN promoted allylation of benzaldehyde with β-cyano-substituted allylstannane ($CH_2{=}C(CN)CH_2SnBu_3$) to afford a homoallyl alcohol after destannylation of the crude product (unpublished result).

(17) The reactivity of silyl radicals toward carbonyl compounds is well-known as described in ref 7.

(18) Functionalized substrates are not used in the Lewis acid-mediated allylsilylations (ref 8).