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Stereoselective Preparation of 1-Siloxy-1-alkenylcopper Species by 1,2-C^{sp2}-to-O Silyl Migration of Acylsilanes

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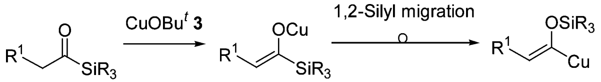
The Brook-type rearrangement of silicon from sp^3 carbon to oxygen has attracted much attention as a route to highly reactive organometallic species from organosilicon compounds.[1] In contrast, there has been limited synthetic application of the silyl migration from sp^2 carbon to oxygen,[2] though it is potentially an attractive method for the generation of synthetically useful alkenylmetal species. Recently we have investigated copper(I) alkoxide-promoted 1,3-[3] and 1,4-silyl migrations[4] from sp^2 carbon using β- and γ-silylallylic alcohols which include an alkenylsilane substructure. We also found that the 1,4-silyl migration of β-silyl-α,β-unsaturated ketones proceeds via their copper enolates.[4c] These findings prompted us to develop a new route to functionalized alkenylcopper species (Scheme 1). Our approach involves the transformation of acylsilanes **1** to their copper enolates **2** with copper(I) *tert*-butoxide **3**. If the enolates **2** undergo the 1,2-C^{sp2}-to-O (enolate) silyl migration, the alkenylcopper species **4** possessing an enol silyl ether substructure would be formed. Here we describe the preparation of **4** from acyltriphenylsilanes **1** and stereoselective preparation of (*Z*)-enol silyl ethers by their reaction with organic halides.

Scheme 1

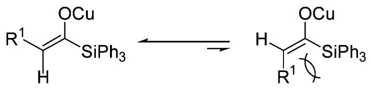


1 **2** **4**

The acyltriphenylsilane **1a** was treated with 1 equiv of the copper alkoxide **3**[5] in DMF for 10 min at 25 °C and then with methallyl chloride **5a** (2 equiv) to give stereochemically pure (*Z*)-enol silyl ether **6a** in 36% yield. The yield of **6a** was increased by use of 2 equiv of **3** (Table 1, entry 1).[6] DMF is crucial for the reaction; when the reaction was carried out in THF, only the *C*-allylation product of the enolate **2a** was obtained in 41% yield.

The stereoselective formation of (*Z*)-**6a** is attributable to the exclusive formation of the thermodynamically more stable (*E*)-copper enolate **2a** relative to the (*Z*)-isomer, which is destabilized by steric repulsion between the triphenylsilyl group and the β-alkyl group R^1 (Scheme 2). Subsequent 1,2-silyl migration of the enolate **2a** with retention of the configuration of double bond and the reaction of the resulting alkenylcopper species with **5a** afford (*Z*)-**6a**.

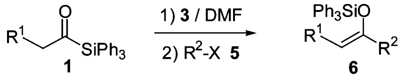
Scheme 2



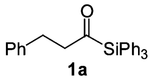
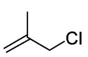
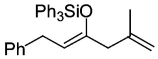
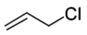
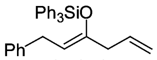
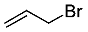
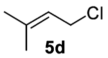
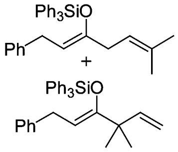
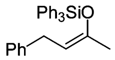
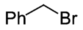
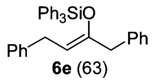
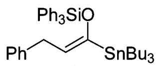
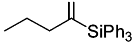
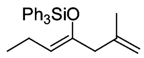
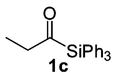
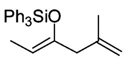
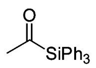
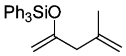
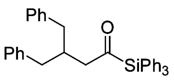
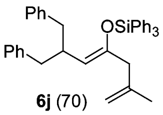
E-**2** *Z*-**2**

The formation of the copper enolates by the treatment of acylsilanes **1** with **3** and the subsequent silylmigration is in contrast to the modes of the reaction of **1** with alkali metal alkoxides. When

Table 1. Formation of (*Z*)-Enol Silyl Ethers by Copper(I) *tert*-Butoxide-Promoted Reaction of Acylsilanes with Organic Halides



1 **6**

entry	acylsilane	halide	product (yield^a / %)
1	 **1a**	 **5a**	 **6a** (63)
2	**1a**	 **5b**	 **6b** (67)
3	**1a**	 **5c**	**6b** (61)
4	**1a**	 **5d**	 **6c** (66%; α : γ = 85 : 15)
5	**1a**	MeI **5e**	 **6d** (65)
6	**1a**	 **5f**	 **6e** (63)
7	**1a**	Bu$_3$SnCl **5g**	 **6f**^{b} (70)
8	 **1b**	**5a**	 **6g** (60)
9	 **1c**	**5a**	 **6h** (61)
10	 **1d**	**5a**	 **6i** (37)
11	 **1e**	**5a**	 **6j** (70)

[a] Isolated yield. The sterochemistry of **6** was determined by NOE experiment, unless othwise noted. [b] The sterochemistry was determined based on the $^3J_{\mathrm{Sn-H}}$ coupling constant (24.1 Hz) across the double bond (see ref 9e).

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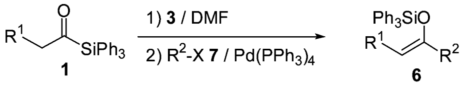
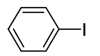
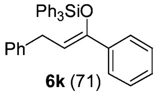
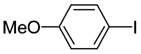
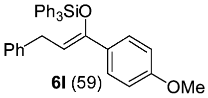
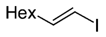
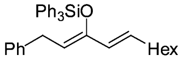
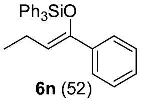
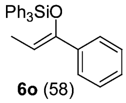
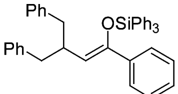
Table 2. Palladium(0)-Catalyzed Cross-Coupling of Alkenylcopper Species with Aryl and Alkenyl Iodides



entry	acylsilane	halide	product (yield^{a} / %)
1	**1a**	 **7a**	 **6k** (71)
2	**1a**	 **7b**	 **6l** (59)
3	**1a**	 **7c**	 **6m** (65)
4	**1b**	**7a**	 **6n** (52)
5	**1c**	**7a**	 **6o** (58)
6	**1e**	**7a**	 **6p** (78)

[a] Isolated yield.

potassium *tert*-butoxide was used instead of **3** for the reaction of **1a**, 1,3-diphenyl-1-propanol was formed in 48% yield via formation of a pentacoordinate silicate by nucleophilic attack of the alkoxide on silicon atom, followed by phenyl migration from the silicate to a carbonyl carbon. A similar reaction of acetyltriphenylsilane with sodium alkoxide has been reported by Brook et al.[7] Nuleophilic addition of potassium *tert*-butoxide to the carbonyl group of a certain acetylsilane followed by the 1,2-silyl migration has also appeared.[8]

The reactions of several acylsilanes **1b**−**e** with allylic halides **5** were performed under the similar reaction conditions and the (*Z*)-α-allylated enol silyl ethers **6b**, **6c**, and **6g**−**j** were obtained stereoselectively. The reaction of **1a** with prenyl chloride **5d** produced a mixture of the formal S_N2 and S_N2' products **6c** in which the former predominated (entry 4). The alkenylcopper species **4** also reacted with methyl iodide **5e** and benzyl bromide **5f** to produce the corresponding (*Z*)-enol silyl ethers **6d** and **6e** in good yields (entries 5 and 6). Chlorotributylstannane **5g** is also reactive toward the alkenylcopper species **4**, and the alkenylstannane **6f** was obtained in 70% yield (entry 7).

The above process has been extended to palladium catalyzed cross coupling with aryl and alkenyl iodides **7**. The acylsilanes **1** were treated with **3** (2 equiv) in the presence of a catalytic amount (3 mol %) of $Pd(PPh_3)_4$ in DMF for 30 min at 25 °C and then with aryl and alkenyl iodides **7** (Table 2). In all cases, the cross-coupling proceeded to form the enol silyl ethers **6** as single isomers in good yields. The stereochemistry of **6l** and **6m** was determined to be *Z* by NOE experiment. The other products were also expected to have *Z* configuration.

The Brook-type rearrangement-based preparations of enol silyl ethers from acylsilanes have been investigated.[9] Their typical strategy involves 1,2-addition of carbon nucleophiles bearing a leaving group, 1,2-C^{sp3}-to-O silyl migration, and β-elimination.[10] In contrast, the present reaction provides the reactive 1-siloxy-1-alkenylcopper species by the 1,2-silyl migration from the carbonyl carbon to the carbonyl oxygen. The alkenylcopper species are applicable to the subsequent carbon−carbon bond formation to produce the synthetically useful enole silyl ethers stereoselectively.

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Supporting Information Available: Typical experimental procedures and characterization of all products in the paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) (a) Taguchi, H.; Ghoroku, K.; Tadaki, M.; Tsubouchi, A.; Takeda, T. *Org. Lett.* **2001**, *3*, 3811. (b) Taguchi, H.; Ghoroku, K.; Tadaki, M.; Tsubouchi, A.; Takeda, T. *J. Org. Chem.* **2002**, *67*, 8450. (c) Taguchi, H.; Miyashita, H.; Tsubouchi, A.; Takeda, T. *Chem. Commun*. **2002**, 2218. (d) Taguchi, H.; Tsubouchi, A.; Takeda, T. *Tetrahedron Lett.* **2003**, *44*, 5205. (e) Taguchi, H.; Takami, K.; Tsubouchi, A.; Takeda, T. *Tetrahedron Lett.* **2004**, *45*, 429.

(5) Tsuda, T.; Hashimoto, T.; Saegusa, T. *J. Am. Chem. Soc.* **1972**, *94*, 658.

(6) When the trimethylsilyl analogue of **1a** was employed for the reaction, the *C*-allylation product of its enolate **2a** was obtained in 47% yield as a major product without the formation of the TMS analogue of **6a**.

(7) Brook, A. G.; Schwartz, N. V. *J. Org. Chem*. **1962**, *27*, 2311.

(8) Brook, A. G.; Vandersar, T. J. D.; Limburg, W. *Can. J. Chem.* **1978**, *56*, 2758.

(9) For example, see (a) Brook, A. G.; Limburg, W. W.; MacRae, D. M.; Fieldhouse, S. A. *J. Am. Chem. Soc.* **1967**, *89*, 704. (b) Brook, A. G.; Fieldhouse, S. A. *J. Organomet. Chem.* **1967**, *10*, 235. (c) Kato, M.; Mori, A.; Oshino, H.; Enda, J.; Kobayashi, K.; Kuwajima, I. *J. Am. Chem. Soc.* **1984**, *106*, 1773. (d) Enda, J.; Kuwajima, I. *J. Am. Chem. Soc.* **1985**, *107*, 5495. (e) Reich, H. J.; Holtan, R. C.; Bolm, C. *J. Am. Chem. Soc.* **1990**, *112*, 5609. (f) Jin, F.; Jiang, B.; Xu, Y. *Tetrahedron Lett.* **1992**, *33*, 1221. (g) Jin, F.; Xu, Y.; Huang, W. *J. Chem. Soc., Perkin Trans. 1* **1993**, 795. (h) Nakajima, T.; Segi, M.; Sugimoto, F.; Hioki, R.; Yokota, S.; Miyashita, K. *Tetrahedron* **1993**, *49*, 8343. (i) Takeda, K.; Nakajima, A.; Takeda, M.; Okamoto, Y.; Sato, T.; Yoshii, E.; Koizumi, T.; Shiro, M. *J. Am. Chem. Soc.* **1998**, *120*, 4947. (j) Berber, H.; Brigaud, T.; Lefebvre, O.; Plantier-Royon, R.; Portella, C. *Chem.*−*Eur. J.* **2001**, 7. (k) Ngo, S. C.; Chung, W. J.; Lim, D. S.; Higashiya, S.; Welch, J. T. *J. Fluorine Chem.* **2002**, *117*, 207.

(10) Alternative strategies have also appeared, for example the reaction of the acylsilanes having an α-leaving group with the carbon nucleophiles (see ref 9e); 1,2-addition of 1-alkenyl Grignard reagents to acylsilane; 1,2-silyl migration of the resulting α-silylallylic alkoxides; and reaction of nucleophiles at *γ*-position of α-siloxyallylic anions (see ref 9c and 9d).

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