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

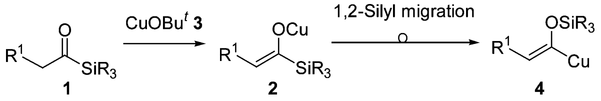
Akira Tsubouchi,* Kotaro Onishi, and Takeshi Takeda*

Department of Applied Chemistry, Graduate School of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

Received August 14, 2006; E-mail: takeda-t@cc.tuat.ac.jp

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$^{sp^2}$-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.

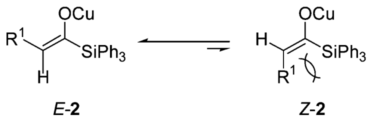
Scheme 1



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.

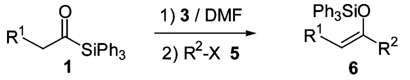
The stereoselective formation of (*Z*)-**6a** is attributable to the exclusive formation of the thermodynamically more stable (*E*)-copper enolate **2a** relative to the (*Z*)-isomer, which is destabilized by steric repulsion between the triphenylsilyl group and the β-alkyl group R^1 (Scheme 2). Subsequent 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**.

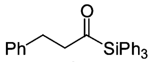
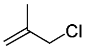
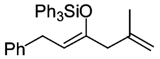
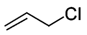
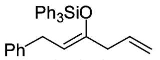
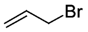
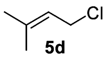
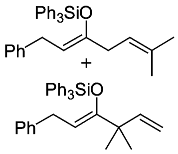
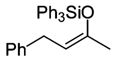
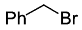
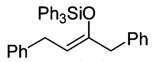
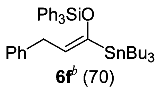
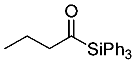
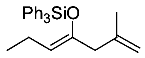
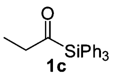
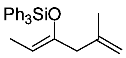
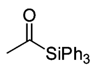
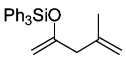
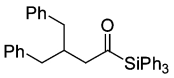
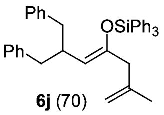
Scheme 2



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

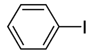
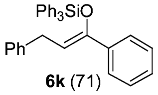
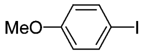
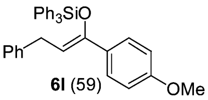
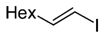
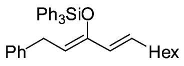
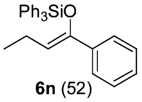
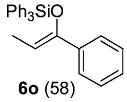
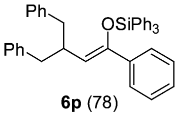


entry	acylsilane	halide	product (yield^a / %)
1	 **1a**	 **5a**	 **6a** (63)
2	**1a**	 **5b**	 **6b** (67)
3	**1a**	 **5c**	**6b** (61)
4	**1a**	 **5d**	 **6c** (66%; α : γ = 85 : 15)
5	**1a**	MeI **5e**	 **6d** (65)
6	**1a**	 **5f**	 **6e** (63)
7	**1a**	Bu$_3$SnCl **5g**	 **6f**^{b} (70)
8	 **1b**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

10.1021/ja0658822 CCC: $33.50

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.

Acknowledgment. This work was carried out under the 21st Century COE program of “Future Nanomaterial” in Tokyo University of Agriculture & Technology.

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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(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.

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(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).

JA0658822