ORGANIC LETTERS

2001
Vol. 3, No. 23
3811−3814

# Copper(I) *tert*-Butoxide-Promoted 1,4 C$^{sp^2}$-to-O Silyl Migration: Stereospecific Allylation of (*Z*)-$\gamma$-Trimethylsilyl Allylic Alcohols

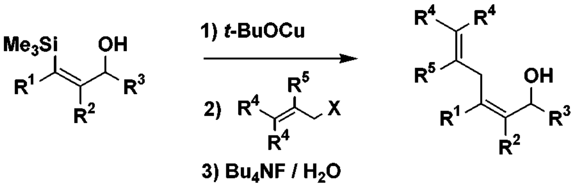
**Haruhiko Taguchi, Kazushi Ghoroku, Makoto Tadaki, Akira Tsubouchi, and Takeshi Takeda***

*Department of Applied Chemistry, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan*

*takeda-t@cc.tuat.ac.jp*

**Received October 1, 2001**

## ABSTRACT



**The cyclic silyl ethers, 2,2-dimethyl-1-oxa-2-sila-3-cyclopentenes, were produced by the treatment of (*Z*)-$\gamma$-trimethylsilyl allylic alcohols with a catalytic or stoichiometric amount of lithium *tert*-butoxide. On the other hand, successive treatment of the alcohols with copper(I) *tert*-butoxide and allylic halides followed by the tetrabutylammmonium fluoride assisted hydrolysis produced the allylation products, 2,5-alkadien-1-ols, with complete retention of configuration of the double bond.**

Transmetalation of organosilicon compound through the Brook-type rearrangement is an attractive approach to produce reactive organometallic species. Although 1,4 C$^{sp^3}$-to-O silyl migrations have been employed for the preparation of various carbanions,[1] 1,4 C$^{sp^2}$-to-O silyl migration has provided so far little synthetic significance. Spinazzé and Keay studied the 1,4 C$^{sp^2}$-to-O silyl migration of a furan system and suggested that a formal C-2 carbanion cannot be formed by the treatment of 2-(*tert*-butyldimethylsilyl)-3-(hydroxymethyl)furan with sodium hydride in DMF.[2] Kim and Magriotis reported that the treatment of 1-iodo-3-(trimethylsilyloxy)-1-propene derivatives with excess *tert*-butyllithium affords the 1,4 O-to-C$^{sp^2}$ silyl migration product exclusively, indicating that the preparation of vinylmetal species by 1,4 C$^{sp^2}$-to-O silyl migration of the lithium salts of $\gamma$-silyl allylic alcohols **1** is not feasible.[3] In contrast to this result, they also found the formation of the 1,4 C$^{sp^2}$-to-O silyl migration product, the trimethylsilyl ether of cinnamyl alcohol, by the treatment of (*Z*)-3-phenyl-3-(trimethylsilyl)-2-propen-1-ol **1d** with a catalytic amount of *tert*-butyllithium. It is suggested that the intermediate vinyllithium stabilized with the phenyl moiety would be produced partially in equilibrium, and the protonation of the vinyl-

---

[1] (a) Woodbury, R. P.; Rathke, M. W. *J. Org. Chem.* **1978**, *43*, 1947−1949. (b) Matsuda, I.; Murata, S.; Ishii, Y. *J. Chem. Soc., Perkin Trans. 1* **1979**, 26−30. (c) Isobe, M.; Kitamura, M.; Goto, T. *Tetrahedron Lett.* **1979**, 3465−3468. (d) Fleming, I.; Floyd, C. D. *J. Chem. Soc., Perkin Trans.* **1981**, 969−976. (e) Takeda, T.; Naito, S.; Ando, K.; Fujiwara, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 967−968. (f) Takeda, T.; Ando, K.; Fujiwara, T. *Chem. Lett.* **1983**, 1285−1288. (g) Brook, A. G.; Chrusciel, J. J. *Organometallics* **1984**, *3*, 1317−1381. (h) Isobe, M.; Ichikawa, Y.; Funabashi, Y.; Mio, S.; Goto, T. *Tetrahedron* **1986**, *42*, 2863−2872. (i) Tietze, L. F.; Geissler, H.; Gewert, J. A.; Jakobi, U. *Synlett* **1994**, 511−512. (j) Jankowski, P.; Raubo, P.; Wicha, J. *Synlett* **1994**, 985−992. (k) Shinokubo, H.; Miura, K.; Oshima, K.; Utimoto, K. *Tetrahedron* **1996**, *52*, 503−514. (l) Smith, A. B., III.; Boldi, A. M. *J. Am. Chem. Soc.* **1997**, *119*, 6925−6926. (m) Bräuer, N.; Michel, T.; Schaumann, E. *Tetrahedron* **1998**, *54*, 11481−11488. (n) Smith, A. B., III; Pitram, S. M. *Org. Lett.* **1999**, 1, 2001−2004. (o) Moser, W. H. *Tetrahedron* **2001**, *57*, 2065−2084.

[2] Spinazzé, P. G.; Keay, B. A. *Tetrahedron Lett.* **1989**, *30*, 1765−1768.

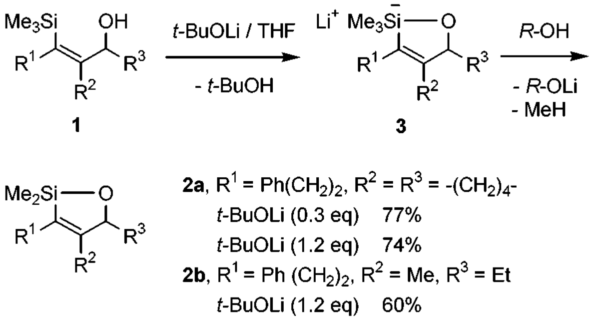
[3] Kim, K. D.; Magriotis, P. A. *Tetrahedron Lett.* **1990**, *31*, 6137−6140.

10.1021/ol016837w CCC: $20.00

lithium with the starting alcohol **1d** serves to displace the unfavorable equilibrium to the product formation.[4]

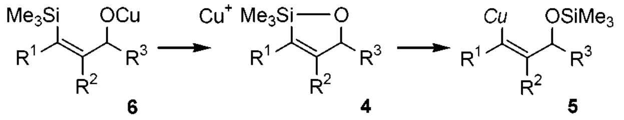
In connection with our continuous study on the preparation and reaction of group 14 vinylmetals,[5] we were intrigued with the 1,4 C$^{sp^2}$-to-O silyl migration of conformationally rigid $\gamma$-trimethylsilyl allylic alcohols **1a** and **1b**.[6] Unlike the reaction of cinnamyl alcohol derivative **1d** described above, the treatment of **1a** and **1b** with a stoichiometric or catalytic amount of lithium *tert*-butoxide at room temperature for 24 h gave the cyclic silyl ethers 1-oxa-2-silacyclopent-3-enes **2a** and **2b** as sole products (Scheme 1). These results, indeed, indicate the formation of intermediary pentavalent silicon anions **3**. Generally the alkenyl group is protonated preferentially to the alkyl group in hypervalent silicon compounds.[7] The unusual formation of silacycle **2** would be explained by the protonolysis of the methyl group *trans* to the donor atom in the pentacoordinate system **3**.[8] The similar activation of C$^{sp^3}$−Si bond by the intramolecular nucleophilic attack at silicon has been studied.[9] In marked contrast to the above results, the conformationally more flexible alcohols **1c** and **1e** were recovered unchanged when being treated with lithium *tert*-butoxide under similar conditions. This observation agrees with the result of the reaction of the (*Z*)-4-(triisopropylsilyl)-4-(trimethylsilyl)-3-propen-2-ol with a catalytic amount of methyllithium reported by Lautens and coworkers.[4]

**Scheme 1**



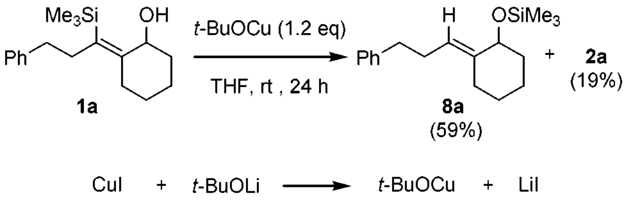
Recently, we found that the vinylsilanes bearing a 2-pyridylthio group at the carbon α to the trimethylsilyl group reacted with allylic halides in the presence of CuI−KF to produce the cross-coupling products.[5e] We tentatively assume that the reaction proceeds via transmetalation of silicon to copper assisted by the intramolecular coordination of nitrogen to silicon. Therefore it is anticipated that the hypercoordinated silicon compound **4** reacts with electrophiles at its C$^{sp^2}$-carbon via the formation of a Brook-type rearrangement product, the vinylcopper species **5** (Scheme 2). Then we investigated the preparation of copper(I) alkoxides of (*Z*)-$\gamma$-trimethylsilyl allylic alcohols **6** and their reaction with allylic halides **7**.

**Scheme 2**



As expected, the treatment of the cyclic alcohol **1a** with copper(I) *tert*-butoxide (1.5 equiv), prepared in situ by the reaction of copper(I) iodide with lithium *tert*-butoxide,[10] in THF at room temperature predominantly gave the 1,4 C$^{sp^2}$-to-O silyl migration product **8a**, and the formation of a small amount of the cyclic silyl ether **2a** was observed (Scheme 3).

**Scheme 3**



The successive treatment of **1a** with copper(I) *tert*-butoxide (1.5 equiv) and methallyl chloride **7a** (1.2 equiv) for 23 h at room temperature produced the trimethylsilyl ether of dienyl alcohol **9a** in 92% yield. The tetrabutylammmonium fluoride assisted hydrolysis of **9a** afforded the alcohol **10a** in 80% overall yield (Scheme 4).

Under similar reaction conditions, the coupling reactions of several (*Z*)-$\gamma$-trimethylsilyl allylic alcohols **1** including

---

(4) Lautens, M.; Delanghe, P. H. M.; Goh, J. B.; Zhang, C. H. *J. Org. Chem.* **1995**, *60*, 4213−4227.

(5) (a) Takeda, T.; Sugi, S.; Nakayama, A.; Suzuki, Y.; Fujiwara, T. *Chem. Lett.* **1992**, 819−822. (b) Takeda, T.; Kabasawa, Y.; Fujiwara, T. *Tetrahedron* **1995**, *51*, 2515−2524. (c) Takeda, T.; Matsunaga, K.; Kabasawa, Y.; Fujiwara, T. *Chem. Lett.* **1995**, 771−772. (d) Takeda, T.; Matsunaga, K.; Uruga, T.; Takakura, M.; Fujiwara, T. *Tetrahedron Lett.* **1997**, *38*, 2879−2882. (e) Takeda, T.; Uruga, T.; Gohroku, K.; Fujiwara, T. *Chem. Lett.* **1999**, 821−822.

(6) The following two methods were employed for the setereoselective preparation of (*Z*)-$\gamma$-trimethylsilyl allylic alcohols **1**. (*Z*)-$\beta$-Trimethylsilyl-α,$\beta$-unsaturated ketones were prepared by the tin(IV) chloride promoted reaction of α-trimethylsilyl thioacetals with enol trimethylsilyl ethers followed by the elimination of thiophenol similarly to the synthesis of (*Z*)-$\beta$-tributylstannyl-α,$\beta$-unsaturated ketones.[5a,b] The reduction of the silyl ketones with lithium aluminum hydride gave the secondary alcohols **1a**−**c**. The primary alcohols **1d**−**f** were prepared from acylsilanes. Their olefination using ethyl trimethylsilyl acetate (for **1d** and **1e**) or diethyl ethoxycarbonylmethylphosphonate (for **1f**) followed by DIBAH reduction gave the alcohols **1**. Fujiwara, T.; Sawabe, K.; Takeda, T. *Tetrahedron* **1997**, *53*, 8349−8370.

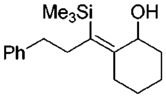
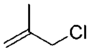
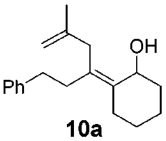
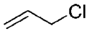
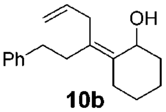
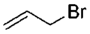
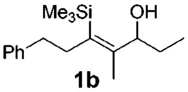
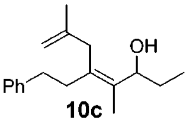
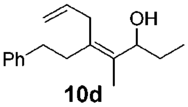
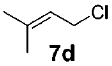
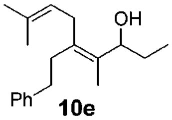
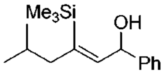
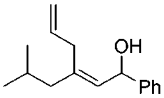
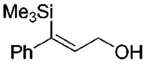
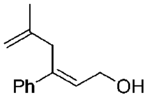
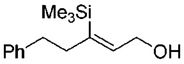
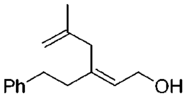
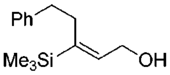
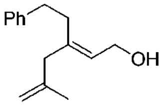
(7) Cella, J. A.; Cargioli, J. D.; Williams, E. A. *J. Organomet. Chem.* **1980**, *186*, 13−17.

(8) Similar reversal of selectivity in cleavage of mixed tetraorganotin compounds by halogens has been reported: Jousseaume, B.; Villeneuve, P. *J. Chem. Soc., Chem. Commun.*, **1987**, 513−514. Also see ref 5a.

(9) (a) Eaborn, C.; Mahmoud, F. M. S. *J. Organomet. Chem.* **1981**, *209*, 13−16. (b) Hudrlik, P. F.; Abdallah, Y. M.; Hudrlik, A. M. *Tetrahedron Lett.* **1992**, *33*, 6743−6746. (c) Hudrlik, P. F.; Abdallah, Y. M.; Hudrlik, A. M. *Tetrahedron Lett.* **1992**, *33*, 6747−6750.

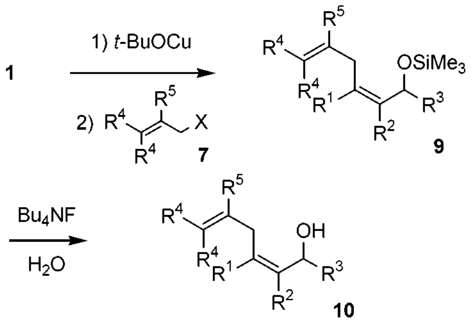
(10) Tsuda, T.; Hashimoto, T.; Saegusa, T. *J. Am. Chem. Soc.* **1972**, *94*, 658−659.

**Table 1.** Stereospecific Allylation Promoted by Copper(I) *tert*-Butoxide

| entry | γ-silyl allylic alcohol | allylic halide | solvent / time (h) | product (yield / %) | |
|---|---|---|---|---|---|
| **1** | <br>**1a** | <br>**7a** | **THF / 20** | <br>**10a** | **(80)** |
| **2**[a] | **1a** | **7a** | **DMF / 2** | **10a** | **(84)** |
| **3** | **1a** | <br>**7b** | **THF / 16** | <br>**10b** | **(88)** |
| **4** | **1a** | <br>**7c** | **THF / 16** | **10b** | **(89)** |
| **5** | <br>**1b** | **7a** | **THF / 21** | <br>**10c** | **(85)** |
| **6** | **1b** | **7b** | **THF / 14** | <br>**10d** | **(80)** |
| **7** | **1b** | <br>**7d** | **THF / 16** | <br>**10e** | **(66)** |
| **8**[a] | **1b** | **7d** | **DMF / 4** | **10e** | **(75)** |
| **9** | <br>**1c** | **7b** | **THF / 30** | <br>**10f** | **(51)** |
| **10**[a] | **1c** | **7b** | **DMF / 10** | **10f** | **(76)** |
| **11**[a] | <br>**1d** | **7a** | **DMF / 15** | <br>**10g** | **(74)** |
| **12** | <br>**1e** | **7a** | **THF / 20** | <br>**10h** | **(46)** |
| **13**[a] | **1e** | **7a** | **DMF / 12** | **10h** | **(73)** |
| **14**[a] | <br>**1f** | **7a** | **DMF / 12** | <br>**10i** | **(0)** |

[a] A 1.2 equiv portion of copper(I) *tert*-butoxide was used

**Scheme 4**



the conformationally flexible acyclic compounds with allylic chlorides **7** were performed, and the allylation products **10** were obtained with complete retention of configuration regardless of their conformational mobility (Table 1). In some cases, DMF was the solvent of choice (see entries 8, 10, and 13).

Contrary to the above results, the reaction of (*E*)-allylic alcohol **1f** with methallyl chloride **7a** was found to be messy, and the formation of the corresponding dienyl alcohol **10i** was not observed (entry 14). This result clearly shows that the formation of pentavalent silicate by intramolecular coordination is indispensable for the allylation.

In the past few years, copper(I) salt promoted self- and cross-coupling reactions of organosilicon compounds have become a subject of increasing research interest.[11] Organocopper compounds have been suggested to be active species of these reactions, and indeed, copper(I) acetylides were isolated as intermediates in a certain case.[11g] Although palladium-catalyzed cross-coupling reactions of functionalized alkenylsilanes and alkenylsilacyclobutanes with organic halides are employed for the preparation of various olefinic compounds,[12] the synthetic application of copper(I)-promoted reactions of alkenylsilanes is generally restricted because the silanes should have an electronegative ligand such as fluorine and are only applied to the preparation of symmetrical 1,3-dienes by homocoupling.[11a,d,e]

In summary, we have developed the copper(I) *tert*-butoxide-promoted 1,4 $C^{sp^2}$-to-O silyl migration of (*Z*)-$\gamma$-trimethylsilyl allylic alcohols. The intermediates of this migration react with allylic halides to afford the cross-coupling products, dienyl alcohols, with retention of configuration. It should be noted that this reaction provides a useful method for the preparation of reactive alkenylmetal species or their equivalents under mild conditions. Studies aimed at broadening the scope of this reaction and understanding its mechanism are currently in progress.

**Supporting Information Available:** Experimental procedures and characterization data for compounds **1a**–**f**, **2a**, **2b**, **9a**, and **10a**–**h**. This material is available free of charge via the Internet at http://pubs.acs.org.

OL016837W

---

(11) (a) Yosida, J.; Tamao, K.; Kakui, T.; Kumada, M. *Tetrahedron Lett.* **1979**, 1141–1144. (b) Urata, H.; Fuchikami, T. *Tetrahedron Lett.* **1991**, *32*, 91–94. (c) Lermontov, S. A.; Rakov, I. M.; Zefirov, N. S. *Tetrahedron Lett.* **1996**, 37, 4051–4054. (d) Kang, S.-K.; Kim, T.-H.; Pyun, S.-J. *J. Chem. Soc., Perkin Trans. 1* **1997**, 797–798. (e) Ikegashira, K.; Nishihara, Y.; Hirabayashi, K.; Mori, A.; Hiyama, T. *Chem. Commun.* **1997**, 1039–1040. (f) Ito, H.; Sensui, H.; Arimoto, K.; Miura, K.; Hosomi, A. *Chem. Lett.* **1997**, 639–640. (g) Ito, H.; Arimoto, K.; Sensui, H.; Hosomi, A. *Tetrahedron Lett.* **1997**, *38*, 3977–3980. (h) Nishihara, Y.; Ikegashira, K.; Mori, A.; Hiyama, T. *Tetrahedron Lett.* **1998**, *39*, 4075–4078.

(12) (a) Hatanaka, Y.; Hiyama, T. *Synlett* **1991**, 845–853. (b) Horn, K. A. *Chem. Rev.* **1995**, *95*, 1317–1350. (c) Suginome, H.; Kinugasa, H.; Ito, Y. *Tetrahedron Lett.* **1994**, 35, 8635–8638. (d) Denmark, S. E.; Choi, J. Y. *J. Am. Chem. Soc.* **1999**, 121, 5821–5822. (e) Denmark, S. E.; Yang, S.-M. *Org. Lett.* **2001**, 3, 1749–1752 and references therein.