

## Communications to the Editor

## The Sila-Wittig Rearrangement

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The [2,3]-Wittig rearrangement of  $\alpha$ -alkoxy carbanions has been extensively studied because the rearrangement offers useful methodologies for regio- and stereoselective C–C bond formation (Scheme 1).<sup>1,2</sup> Recently, the aza-[2,3]-Wittig rearrangement of  $\alpha$ -amino carbanions has been also studied due to its potential utility.<sup>3</sup> In contrast to these carbanions, little attention has been paid to the analogs of other group 14 elements. On the basis of our recent studies of the  $\alpha$ -heteroatom-substituted silyl anions,<sup>4</sup> we now report the first examples of silicon analogs to the [2,3]-Wittig rearrangements, that is, [2,3]-sila-Wittig and aza-sila-Wittig rearrangements, which involve intramolecular migration of an allyl group from an oxygen or nitrogen to silicon in [(allyloxy)silyl]lithium or [(allylamino)silyl]lithium (Scheme 1). The term “sila-Wittig” rearrangement is used to differentiate the present reaction from the “silyl-Wittig” rearrangement (reversed Brook rearrangement).<sup>5</sup>

A typical example is shown in Scheme 2. [(Allyloxy)silyl]stannane **1**, a precursor of [(allyloxy)silyl]lithium **2**, was readily prepared from (chlorosilyl)stannane **3** and tertiary allyl<sup>6</sup> alcohol **4**. A solution of **1** in THF was treated with *n*-butyllithium (2.0 equiv) at  $-78$  °C for 3 h. The reaction mixture was stirred at room temperature for 2 h, and the reaction was quenched with  $\text{Me}_3\text{SiCl}$  to give the rearrangement product, allylsilanate-containing disiloxane **5**, in 68% isolated yield. No [1,2]-rearrangement product was detected. The intermediate [(allyloxy)silyl]lithium **2** could be trapped with  $\text{Me}_3\text{SiCl}$  at  $-78$  °C to afford the corresponding disilane **6** in 51% yield, together with the rearrangement product **5** in 21% yield.<sup>7,8</sup> Thus, **2** undergoes the [2,3]-sila-Wittig rearrangement to form lithium allylsilanolate

(1) For reviews, see: (a) Marshall, J. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Pattenden, G., Eds.; Pergamon Press: Oxford, 1991; Vol. 3, pp 975–1014. (b) Nakai, T.; Mikami, K. *Chem. Rev.* **1986**, *86*, 885. (c) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 563.

(2) For recent reports, see: (a) Tomooka, K.; Keong, P.-H.; Nakai, T. *Tetrahedron Lett.* **1995**, *36*, 2789. (b) Katritzky, A. R.; Wu, H.; Xie, L. *J. Org. Chem.* **1996**, *61*, 4035.

(3) (a) Durst, T.; Elzen, R. V. D.; LeBelle, M. *J. Am. Chem. Soc.* **1972**, *94*, 9261. (b) Broka, C.; Shen, T. *J. Am. Chem. Soc.* **1989**, *111*, 2981. (c) Coldham, I. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1275. (d) Ahman, J.; Somfai, P. *J. Am. Chem. Soc.* **1994**, *116*, 9781. (e) Ahman, J.; Somfai, P. *Tetrahedron Lett.* **1995**, *36*, 303. (f) Anderson, J. C.; Siddons, D. C.; Smith, S. C.; Swarbrick, M. E. *J. Chem. Soc., Chem. Commun.* **1995**, 1835. (g) Coldham, I.; Collis, A. J.; Mould, R. J.; Rathmell, R. E. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2739. (h) Gawley, R. E.; Zhang, Q.; Campagna, S. *J. Am. Chem. Soc.* **1995**, *117*, 11817. (i) Anderson, J. C.; Siddons, D. C.; Smith, S. C.; Swarbrick, M. E. *J. Org. Chem.* **1996**, *61*, 4820.

(4) For a review, see: (a) Tamao, K.; Kawachi, A. *Adv. Organomet. Chem.* **1995**, *38*, 1. (b) Tamao, K.; Kawachi, A.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 3989. (c) Tamao, K.; Kawachi, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 818. (d) Tamao, K.; Kawachi, A. *Organometallics* **1995**, *14*, 3108.

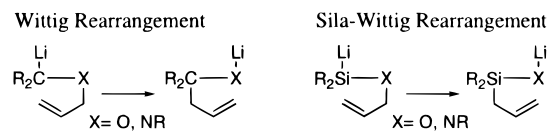
(5) For a review on rearrangements involving silicon, see: (a) Brook, A. G.; Bassindale, A. R. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; pp 149–227. (b) Wright, A.; West, R. *J. Am. Chem. Soc.* **1974**, *96*, 3214, 3222, 3227.

(6) The term “tertiary allyl” means that the allylic carbon is tertiary. The terms *primary* and *secondary* are used in a similar way in this paper.

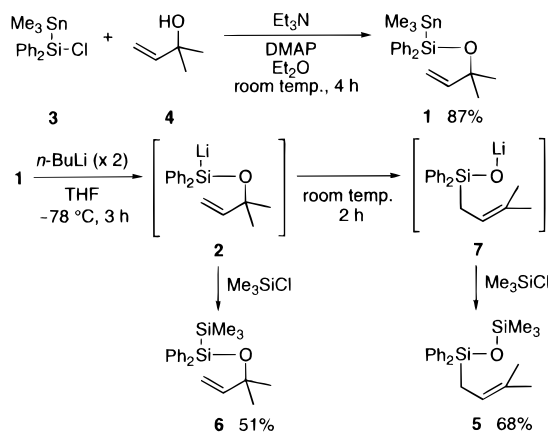
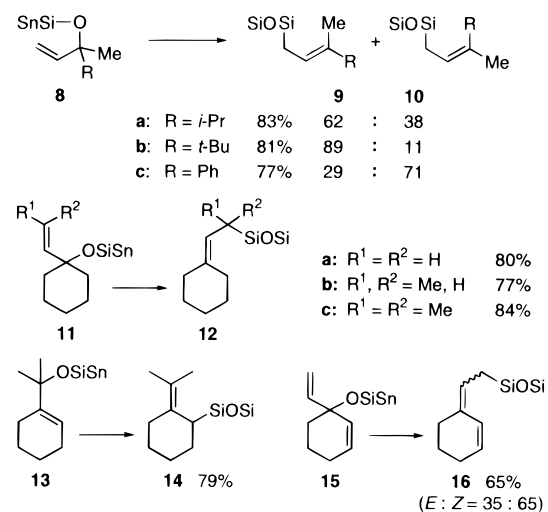
(7) For a formation of silylcuprates from silylstannanes by treatment with higher order cuprates, see: Lipshutz, B. H.; Reuter, D. C.; Ellsworth, E. L. *J. Org. Chem.* **1989**, *54*, 4975.

(8) The intramolecular fashion of the rearrangement was confirmed by a crossover experiment; see the Supporting Information.

## Scheme 1



## Scheme 2

Scheme 3<sup>a</sup>

<sup>a</sup> For clarity,  $-\text{SiPh}_2\text{SnMe}_3$  and  $-\text{SiPh}_2\text{OSiMe}_3$  groups are abbreviated to  $-\text{SiSn}$  and  $-\text{SiOSi}$ , respectively.

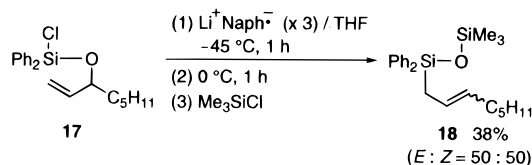
**7** quantitatively at room temperature and to some extent even at  $-78$  °C.<sup>9</sup> Furthermore, the rearrangement of **2** was greatly enhanced by a crown ether. Treatment of **2** with 12-crown-4 afforded only **5** in 55% yield even at  $-78$  °C within 1 h.<sup>10</sup>

Some other representative results are summarized in Scheme 3, where the starting materials were prepared from **3** and the corresponding allylic alcohols in 58–87% yields, as previously stated. Three points deserve comment. (1) An olefinic stereo-

(9) The rearrangements are considered to be thermodynamically favorable: the enthalpy for the reaction,  $(\text{CH}_2=\text{CH}-\text{CH}_2\text{O}-)\text{Ph}_2\text{Si}-\text{Li} \rightarrow \text{Li}-\text{O}-\text{Ph}_2\text{Si}(-\text{CH}_2-\text{CH}=\text{CH}_2)$ , was estimated to be about  $-40$  kcal/mol by PM3 calculations, SPARTAN Version 4.0.

(10) A similar solvent effect has been well documented in the Wittig rearrangements of carbanions. (a) Wittig, G.; Stahnecker, E. *Liebigs Ann. Chem.* **1957**, *605*, 69. (b) Mikami, K.; Kasuga, T.; Fujimoto, K.; Nakai, T. *Tetrahedron Lett.* **1986**, *26*, 4185. See also ref 3i.

## Scheme 4

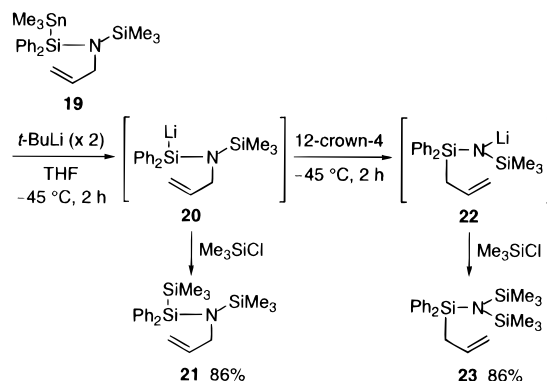


selection<sup>11</sup> has been investigated on **8** involving a chiral *tertiary* allylic carbon center. The rearranged allylsilanes preferentially had *E*-olefin moieties (**9**) with an increase in the bulkiness of the allylic alkyl substituent (**8a** and **8b**), but the reversed *Z*-selectivity (**10**) was observed in the phenyl case (**8c**).<sup>12</sup> Whereas the *E*-selectivity is similar to the general tendencies observed for the [2,3]-Wittig rearrangement,<sup>1,11</sup> the *Z*-selectivity implies a mechanistic complexity in the present silicon version, which must be clarified by further studies. (2) In addition to the rearrangement from *tertiary* allyloxy to *primary* allylsilanes (abbreviated as *tert-to-prim*) (all examples mentioned above and **11a**), *tert-to-sec* (**11b**), and *tert-to-tert* (**11c**) rearrangements proceeded smoothly to give **12b** and **12c**, respectively. (3) Exocyclic (allyloxy)silane **13** was converted into endocyclic allylsilane **14**. Further noted is the regioselectivity observed in **15** which exclusively underwent migration to the exocyclic olefin with the endocyclic olefin intact (**16**).

The present method, however, is applicable only to *tertiary* allyloxy derivatives. Some attempted transmetalations of [*prim*-(allyloxy)silyl]- and [*sec*-(allyloxy)silyl]stannanes were unsuccessful. However, this limitation has been partly overcome by a reductive lithiation method,<sup>3b,4d</sup> as shown in Scheme 4. (*sec*-Allyloxy)silyl chloride **17** was treated with lithium naphthalenide (3.0 equiv) in THF at  $-45\text{ }^{\circ}\text{C}$  for 1 h, followed by being stirred at  $0\text{ }^{\circ}\text{C}$  for 1 h and trapped with  $\text{Me}_3\text{SiCl}$ , to afford the rearrangement product **18** in 38% yield as a mixture of olefinic stereoisomers.

We turned our attention to silicon analogs to the aza-Wittig rearrangements<sup>3</sup> in which the oxygen atom is replaced by a nitrogen atom. An acyclic [(allylamino)silyl]lithium also undergoes an aza-sila-Wittig rearrangement, as shown in Scheme 5. Transmetalation of [(allylamino)silyl]stannane **19**<sup>13</sup> with *tert*-butyllithium (2.0 equiv) was complete at  $-45\text{ }^{\circ}\text{C}$  in 2 h, as indicated by trapping the silyllithium **20** with  $\text{Me}_3\text{SiCl}$  to give the corresponding disilane **21** in 86% yield. The transmetalation did not occur at  $-78\text{ }^{\circ}\text{C}$ . When 12-crown-4 was added,

## Scheme 5



silyllithium **20** smoothly underwent the rearrangement at  $-45\text{ }^{\circ}\text{C}$  to form lithium (allylsilyl)amide **22**, which was trapped with  $\text{Me}_3\text{SiCl}$  to give the corresponding allylsilane **23** in 86% yield.<sup>9</sup> In the absence of the crown ether, **20** underwent the rearrangement in only 10% yield even after warming to  $-20\text{ }^{\circ}\text{C}$ , and at higher temperatures, a complex mixture resulted.<sup>10</sup>

It is noteworthy that the sila-Wittig rearrangements offer a novel route from allyl alcohols or allylamines to sila-functionalized allylsilanes in a regiocontrolled fashion.<sup>14</sup> Although a large number of synthetic methods for allylsilanes have been reported, those for sila-functionalized allylsilanes are limited.<sup>14a</sup> One synthetic utility of the silicon functionality was demonstrated by conversion of the allylsilane<sup>15</sup> into the corresponding allyl alcohol by  $\text{H}_2\text{O}_2$  oxidation.<sup>16</sup> Thus, the overall result corresponds to a novel 1,3-skeletal transformation of the allyl alcohols. Our current study aims at the scope and limitations, synthetic applications, and reaction mechanism of the rearrangements.

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**Supporting Information Available:** Experimental details (19 pages). See any current masthead page for ordering and Internet access instructions.

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(14) For reviews on syntheses of allylsilanes, see: (a) Sarkar, T. K. *Synthesis* **1990**, 969, 1101. (b) Fleming, I.; Dunogues, J.; Smithers, R. *Org. React.* **1989**, 37, 57. For the syntheses from allyl alcohols, see: (c) Hwu, J. R.; Lin, L. C.; Liaw, B. R. *J. Am. Chem. Soc.* **1988**, 110, 7252. (d) Sugimoto, M.; Matsumoto, A.; Ito, Y. *J. Am. Chem. Soc.* **1996**, 118, 3061.

(15) The silanol and not the disiloxane should be used for oxidation;<sup>16</sup> the former can be obtained by trapping the lithium allylsilanolate with water instead of  $\text{Me}_3\text{SiCl}$ .

(16) (a) Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, 2, 1694. (b) Tamao, K.; Kawachi, A.; Tanaka, Y.; Ohtani, H.; Ito, Y. *Tetrahedron* **1996**, 52, 5765. (c) Fleming, I. *Chemtracts, Org. Chem.* **1996**, 9, 1. (d) Jones, G.; Landais, Y. *Tetrahedron* **1996**, 37, 7599. (e) Tamao, K. In *Advances in Silicon Chemistry*; Larson, G., Ed.; JAI Press: Greenwich, CT, 1996; Vol. 3, pp 1–62 (in press).

(11) (a) Still, W. C.; Mitra, A. *J. Am. Chem. Soc.* **1978**, 100, 1927. (b) Wu, Y.-D.; Houk, K. N.; Marshall, A. *J. Org. Chem.* **1990**, 55, 1421. (c) Hoffmann, R.; Brückner, R. *Angew. Chem., Int. Ed. Engl.* **1992**, 31, 647. (d) Verner, E. J.; Cohen, T. *J. Am. Chem. Soc.* **1992**, 114, 375. (e) Mikami, K.; Uchida, T.; Hirano, T.; Wu, Y.-D.; Houk, K. N. *Tetrahedron* **1994**, 50, 5917.

(12) The selectivity was determined by  $^1\text{H}$  NMR analysis of the isomeric mixtures, and the stereochemistry was assigned by NOE experiments; see the supporting information.

(13) [(Allylamino)silyl]stannane **19** was prepared by reaction of **3** with the corresponding lithium amide.