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Control of Stereochemistry by σ-Participation of a Silyl Group. A Novel Method for Diastereoselective Polyol Synthesis

Keiji Tanino, Naoei Yoshitani,
Fumiko Moriyama, and Isao Kuwajima*

Department of Chemistry, Tokyo Institute of Technology, Meguro, Tokyo 152, Japan

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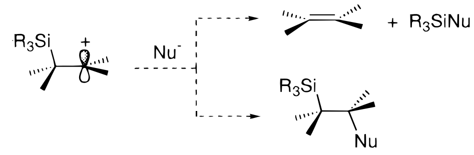
It is well documented that a silyl group significantly stabilizes a carbocation at the β-position by $\sigma-\pi$ orbital interaction,[1] and various synthetic reactions have been developed on the basis of this effect.[2] While these reactions usually proceed through desilylation of the β-silyl cationic intermediates to afford olefinic compounds, notable exceptions involving a nucleophilic attack on the cationic carbon rather than on silicon have recently been reported (Scheme 1).[3] Although the latter reaction path would constitute a new methodology for control of stereochemistry by neighboring-group participation, there are few examples demonstrating the stereochemical features in this type of reaction.[4]

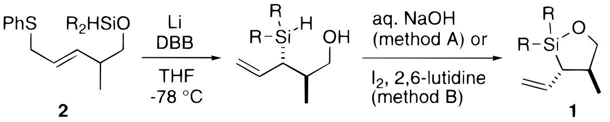
In order to induce stereoselective introduction of a nucleophile, allylsilane **1** with a 1-oxa-2-silacyclopentane skeleton[5] was designed as a precursor of a β-silyl cationic species. We envisioned that the cyclic structure would contribute to stabilizing the cationic intermediate as well as to fixing the conformation. Allylsilanes **1a**−**1c** were prepared as shown in Scheme 2.

Allyl sulfides **2** containing a dialkylsiloxy moiety were treated with lithium dispersion in the presence of a catalytic amount of 4,4′-di-*tert*-butylbiphenyl (DBB).[6] Intramolecular migration of the silyl group[7] took place regio- and stereoselectively to afford a hydroxyallylsilane. Cyclization reaction of the alcohol proceeded smoothly under the influence of aqueous NaOH or I_2/2,6-lutidine.

Scheme 1



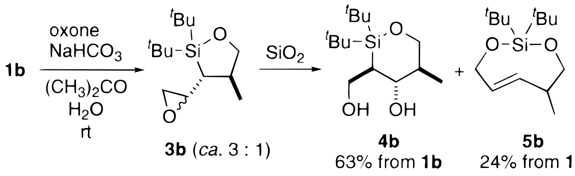
Scheme 2. Diastereoselective Synthesis of Cyclic Allylsilanes



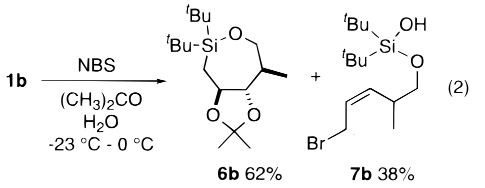
	R	method	yield from **2**	(*anti* : *syn*)
1a	^{i}Pr	A	87%	(<99 : >1)
1b	^{t}Bu	A	95%	(<99 : >1)
1c	2,4,6-$Me_3C_6H_2$	B	85%	(93 : 7)

First, the solvolysis reaction of epoxides[8] derived from allylsilanes **1** was planned to confirm the effect of $\sigma-\pi$ participation by silicon, which would promote regioselective substitution at the β-position with retention of the configuration. PM3 calculations[9] on allylsilane **1b** were performed to estimate diastereofacial selectivity of the epoxidation reaction (Figure 1). The results indicate that conformer C-2 is 1.3 kcal/mol more stable than C-1, and electrophiles are expected to attack the double bond of C-2 from the opposite side of the bulky *tert*-butyl group.

Although the oxidation reaction of **1a** with Oxone[10] in acetone gave a complex mixture, **1b** afforded the desired epoxide **3b** as a *ca.* 3:1 mixture of diastereomers. Surprisingly, treatment of the crude product with silica gel resulted in formation of six-membered silyl ether **4b** and eight-membered product **5b** (eq 1). Furthermore, seven-membered silyl ether **6b** along with allyl bromide **7b** were formed by reaction of **1b** with *N*-bromosuccinimide (NBS)[11] in acetone−water (eq 2). It should be noted that both of the ring expansion products **4b** and **6b** were obtained in diastereomerically pure form,[12] and the



(1)



(2)

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[1] (a) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496. (b) Lambert, J. B.; Wang, G.-t.; Finzel, R. B.; Teramura, D. H. *Ibid.* **1987**, *109*, 7838. (c) Lambert, J. B.; Chelius, E. C. *Ibid.* **1990**, *112*, 8120.

[2] (a) Colvin, E. *Silicon in Organic Synthesis*; Butterworths: London, 1981. (b) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983. (c) Colvin, E. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988. (d) Fleming, I.; Dunoguès, J.; Smithers R. *Org. React.* **1989**, *37*, 57.

[3] (a) Danheiser, R. L.; Dixon, B. R.; Gleason, R. W. *J. Org. Chem.* **1992**, *57*, 6094. (b) Danheiser, R. L.; Takahashi, T.; Bertok, B.; Dixon, B. R. *Tetrahedron Lett.* **1993**, *34*, 3845. (c) Knölker, H.-J.; Baum, G.; Graf, R. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1612. (d) Kiyooka, S.; Shiomi, Y.; Kira, H.; Kaneko, Y.; Tanimori, S. *J. Org. Chem.* **1994**, *59*, 1958. (e) Panek, J. S.; Jain, N. F. *Ibid.* **1994**, *59*, 2674. (f) Monti, H.; Audran, G.; Léandri, G.; Monti, J.-P. *Tetrahedron Lett.* **1994**, *35*, 3073. (g) Akiyama, T.; Ishikawa, K.; Ozaki, S. *Chem. Lett.* **1994**, 627. (h) Miura, K.; Okajima, S.; Hondo, T.; Hosomi, A. *Tetrahedron Lett.* **1995**, *36*, 1483. (i) Dussault, P. A.; Zope, U. *Ibid.* **1995**, *36*, 3655 and references cited therein.

[4] Although stereoselective annulation reactions[3] via intramolecular trapping of a β-silyl cationic intermediate have been reported, it should be noted that few examples are known for the intermolecular version. For example, see: (a) Hayashi, T.; Okamoto, Y.; Kabeta, K.; Hagihara, T.; Kumada, M. *J. Org. Chem.* **1984**, *49*, 4224. (b) Hayashi, T.; Matsumoto, Y.; Morikawa, I.; Ito, Y. *Tetrahedron: Asymmetry* **1990**, *1*, 151.

[5] (a) Tamao, K.; Nakajima, T.; Sumiya, R.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1986**, *108*, 6090. (b) Bodnar, P. M.; Palmer, W. S.; Shaw, J. T.; Smitrovich, J. H.; Sonnenberg, J. D.; Presley, A. L.; Woerpel, K. A. *J. Am. Chem. Soc.* **1995**, *117*, 10575. (c) Young, D. G. J.; Hale, M. R.; Hoveyda, A. H. *Tetrahedron Lett.* **1996**, *37*, 827.

[6] Freeman, P. K.; Hutchinson, L. L. *J. Org. Chem.* **1980**, *45*, 1924.

[7] (a) Marumoto, S.; Kuwajima, I. *J. Am. Chem. Soc.* **1993**, *115*, 9021. (b) Behrens, K.; Kneisel, B. O.; Noltemeyer, M.; Brückner, R. *Liebigs Ann.* **1995**, 385.

[8] (a) Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, *59*, 737. (b) Rosowsky, A. in *Heterocyclic Compounds with Three and Four-Membered Rings, Part I*; Weissberger, A., Ed.; Interscience Publishers: New York, 1964; Chapter I.

[9] (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209; (b) **1989**, *10*, 211.

[10] (a) Curci, R.; Fiorentino, M.; Troisi, L.; Edwards, J. O.; Pater, R. H. *J. Org. Chem.* **1980**, *45*, 4758. (b) Cicala, G.; Curci, R.; Fiorentino, M.; Laricchiuta, O. *Ibid.* **1982**, *47*, 2670.

[11] Guss, C. O.; Rosenthal, R. *J. Am. Chem. Soc.* **1955**, *77*, 2549.

[12] The stereochemistry of the products was determined by NOE experiments.

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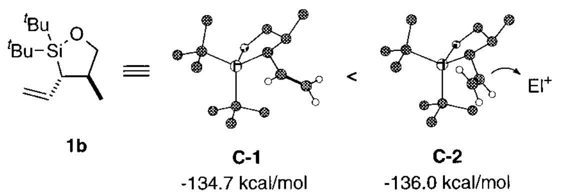
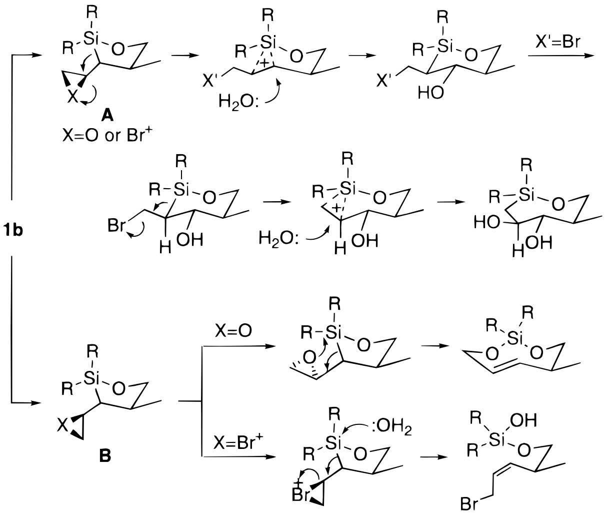


Figure 1. Conformational analysis of **1b** based on PM3 calculations.

Scheme 3. Proposed Reaction Mechanism of the Ring Expansion Reactions

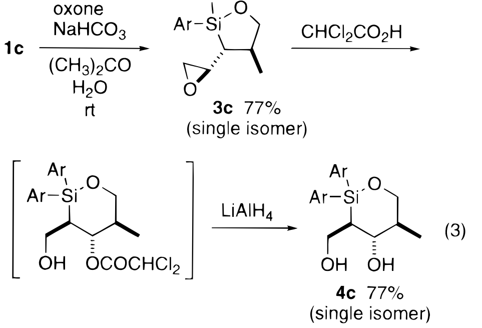


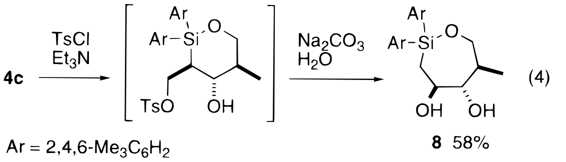
geometry of olefinic products **5b** and **7b** was controlled as *E* and *Z*, respectively.

The mechanism and stereochemistry of these reactions could be explained by assuming $\sigma-\pi$ orbital interaction by silicon as shown in Scheme 3. The major diastereomer (A) of both epoxide and the epibromonium ion intermediate, which was anticipated to arise from the stable conformer C-2 in Figure 1, undergoes cleavage of the three-membered ring to form a β-silyl cationic species. Because of the neighboring-group participation, a nucleophile should be introduced stereoselectively either at the β-position of X′ (OH or Br) directly or at the γ-position via rearrangement of silicon.[3a,b,d,f] The site selectivity observed here may be attributable to the greater stability of the six-membered ring than that of the five-membered ring.[13] In the reaction with NBS, the six-membered bromo alcohol seems to be labile and leads to a seven-membered diol through a similar ring expansion reaction involving participation by silicon. As the seven-membered ring is not energetically more favored than the six-membered ring, the site selectivity in this second hydroxylation step should be rationalized by the Markovnikov rule.

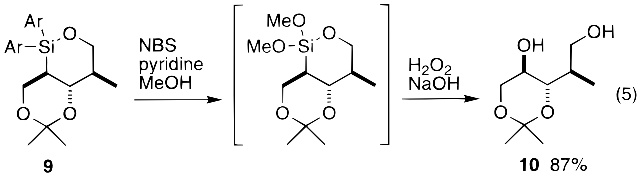
On the other hand, a similar ring expansion reaction of the minor diastereomer (B) would give a six-membered intermediate that is relatively unstable due to a hydroxymethyl or bromomethyl group on the axial position. Therefore, alkenes **5** and **7** were formed via intramolecular or intermolecular attack on silicon by oxygen followed by cleavage of the C–Si bond. It is noteworthy that the geometry of these olefinic products is completely consistent with that expected to arise from B.

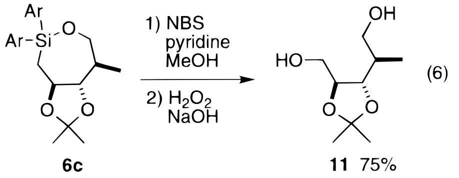
Next, a new method for stereoselective synthesis of polyols using these ring expansion reactions was developed. Since initial attempts for oxidative cleavage of the carbon–silicon bond[14] of **4b** or **6b** were unsuccessful, the analogous compounds with aromatic substituents on silicon were prepared as shown in eqs 3 and 4. Oxidation of allylsilane **1c** afforded epoxide **3c** as a single isomer, which underwent a ring expansion reaction under the influence of dichloroacetic acid. Seven-membered diol **8** was also prepared from diol **4c** through selective tosylation followed by hydrolysis.





Finally, treatment of the corresponding acetonides **9** and **6c** with NBS in methanol followed by aqueous alkaline H_2O_2 yielded the desired tetrol derivatives **10** and **11** in diastereomerically pure form.





In conclusion, a novel ring expansion reaction involving stereoselective introduction of a hydroxy group controlled by neighboring-group participation of silicon was accomplished. We are currently investigating ring expansion reactions of other cyclic allylsilanes and the application to stereoselective synthesis of polyols.

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Supporting Information Available: Experimental procedures and characterization data for **1**–**11** (6 pages).

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[13] Mundy, B. P. *Concepts of Organic Synthesis*; Marcel Dekker: New York, 1979; p 8.

[14] (a) Tamao, K.; Kakui, T.; Iwahara, T.; Kanatani, R.; Yoshida, J.; Kumada, M. *Tetrahedron* **1983**, *39*, 983. (b) Tamao, K. *J. Synth. Org. Chem.* **1988**, *46*, 861. (c) Tamao, K.; Hayashi, T.; Ito, Y. *Nihon Kagakukai Shi* **1990**, 509. (d) Colvin, E. W. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 7, p 641.