Stereospecific Cationic [1,2] Silyl Shift with Retention of Configuration at the Migrating Terminus

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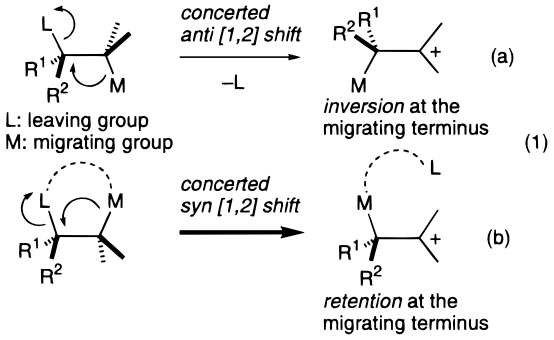
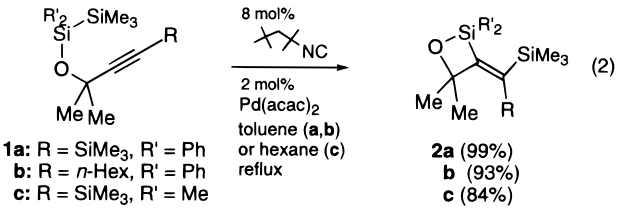
Nucleophilic [1,2] alkyl shift to cationic carbon center is a fundamental process in organic chemistry, being involved in such well-known reactions as Wagner−Meerwein and pinacol rearrangements.[1] From the mechanistic point of view, stereochemical investigation has been carried out to reveal that the cationic [1,2] shift generally proceeds with inversion or racemization at the migrating terminus.[1,2] It has been reported that the silyl group similarly migrates to an electron-deficient carbon center to provide useful synthetic methods of stereodefined organosilicon compounds.[3,4] In a manner similar to that of the alkyl shift, inversion at the migrating terminus (anti migration) was observed in the reactions of stereochemically defined organosilicon compounds.[3] In these cases, anti periplaner conformation of the leaving group and the migrating silyl group may be responsible for the observed anti migration (eq 1a). However, concerted, stereospecific syn



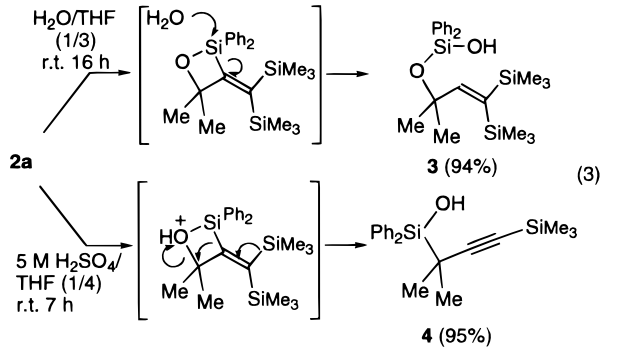
migration could be possible if the syn periplaner conformation is favorable due to structural reason, e.g., the leaving and the neighboring silicon groups are fixed syn in a cyclic system (eq 1b). In this paper, we disclose a highly stereospecific skeletal rearrangement involving the syn [1,2] silyl shift, which produces enantiomerically enriched propargylsilane and allylsilanes, in the reaction of oxasilacycloalkanes prepared by intramolecular bis-silylation of propargylic and allylic alcohols.[5]

In a previous paper, we demonstrated the palladium(0)-catalyzed intramolecular bis-silylation of secondary propargylic alcohols leading to the stereospecific synthesis of chiral allenylsilanes.[5b] Intermediary four-membered cyclic oxasiletanes were spectroscopically identified but were not isolable due to hydrolysis of the strained Si−O bond during chromatographic purification. However, the bis-silylation of *tertiary* alcohols provided stable four-membered cyclic oxasiletanes (eq 2). Tri-



methyl-2,2-diphenyldisilanyl ethers **1a**,**b** having an alkyl or a silyl group at the sp carbon reacted in the presence of the palladium catalyst under reflux in toluene to give the corresponding 4-exo cyclization products **2a** and **b** in high yields after column chromatography on silica gel. Pentamethyldisilanyl derivative **1c** also afforded **2c** at 75 °C in good yield.[6]

Stirring of **2a** in aqueous THF at room temperature resulted in the formation of protiodesilylation product **3** presumably via nucleophilic attack of water to the silicon in the four-membered ring followed by cleavage of the silicon−carbon bond (eq 3).



Simple hydrolysis at the Si−O bonds, which may usually take place for strained silyl ethers, was not observed at all. In sharp contrast, treatment of **2a** with acidic aqueous THF gave tertiary propargylsilanol **4** in high yield through [1,2] silyl migration in high yield without formation of **3**. It is presumed that silyl group in the ring migrates to the tertiary carbocation, which was generated by the carbon−oxygen bond cleavage with protonation, to form vinylic cation stabilized by the three β-silyl groups. The rearrangement reaction finishes with an elimination of the trimethylsilyl group.

The [1,2] silyl migration reaction of **2a** was more effectively catalyzed by catalytic amount of trimethylsilyl triflate (Me_3SiOTf)

(1) Hanson, J. R. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 3, pp 705−719. Rickborn, B. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 3, pp 721−732. For the stereochemical aspect, see: Kallmerten, J. In *Stereoselective Synthesis*; Helmchen, G., Ed.; Thieme Verlag: Stuttgart, Germany, 1996; Vol. 6, pp 3810−3832.

(2) A [1,2] alkyl shift with net retention of configuration at the migrating terminus was reported for the skeletal rearrangement of a rigid bicyclic system. For example, see: Uyehara, T.; Yamada, J.; Kato, T. *Tetrahedron Lett.* **1985**, *26*, 5069.

(3) For the [1,2] silyl shift to the cationic centers generated from sp^3 carbon, see: (a) Hudrlik, P. F.; Hudrlik, A. M.; Nagendrappa, G.; Yimenu, T.; Zellers, E.; Chin, E. *J. Am. Chem. Soc.* **1980**, *102*, 6896−6898. (b) Miura, K.; Hondo, T.; Saito, H.; Ito, H.; Hosomi, A. *J. Org. Chem.* **1997**, *62*, 8292−8293. (c) Ooi, T.; Kiba, T.; Maruoka, K. *Chem. Lett.* **1997**, 519−520. (d) Tanino, K.; Yoshitani, N.; Moriyama, F.; Kuwajima, I. *J. Org. Chem.* **1997**, *62*, 4206−4207.

(4) For examples of the reactions involving a similar cationic [1,2] silyl shift, see: (a) Danheiser, R. L.; Carini, D. J.; Basak, A. *J. Am. Chem. Soc.* **1981**, *103*, 1604−1606. (b) Danheiser, R. L.; Carini, D. J.; Fink, D. M.; Basak, A. *Tetrahedron* **1983**, *39*, 935−947. (c) Danheiser, R. L.; Kwasigroch, C. A.; Tsai, Y.-M. *J. Am. Chem. Soc.* **1985**, *107*, 7233−7235. (d) Danheiser, R. L.; Carini, D. J.; Kwasigroch, C. A. *J. Org. Chem.* **1986**, *51*, 3870−3878. (e) Knölker, H.-J.; Jones, P. G.; Pannek, J.-B. *Synlett* **1990**, 429. (f) Danheiser, R. L.; Dixon, B. R.; Gleason, R. W. *J. Org. Chem.* **1992**, *57*, 6094−6097. (g) Panek, J. S.; Beresis, R. *J. Org. Chem.* **1993**, *58*, 809−811. (h) Panek, J. S.; Jain, N. F. *J. Org. Chem.* **1993**, *58*, 2345−2348. (i) Yamazaki, S.; Tanaka, M.; Yamaguchi, A.; Yamabe, S. *J. Am. Chem. Soc.* **1994**, *116*, 2356−2365. (j) Brengel, G. P.; Rithner, C.; Meyers, A. I. *J. Org. Chem.* **1994**, *59*, 5144−5146. (k) Akiyama, T.; Ishikawa, K.; Ozaki, S. *Chem. Lett.* **1994**, 627−630.

(5) (a) Suginome, M.; Matsumoto, A.; Ito, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3061−3062. (b) Suginome, M.; Matsumoto, A.; Ito, Y. *J. Org. Chem.* **1996**, *61*, 4884−4885. (c) Suginome, M.; Iwanami, T.; Matsumoto, A.; Ito, Y. *Tetrahedron: Asymmetry* **1997**, *8*, 859−862.

(6) The reaction of **1c** under reflux in toluene resulted in the formation of a complex mixture.

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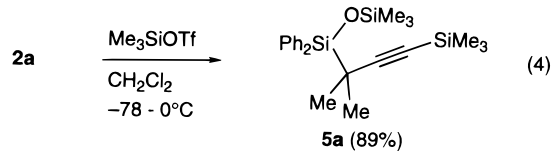
Table 1. Stereospecific Silyl Migration Producing Enantioenriched Propargylsilanes[a]

entry	6 (%ee (config))	Me_3SiOTf (equiv)	8 yield (%)[b]	8 %ee (config)[c]
1	**a** (97.2 (*R*))	1.5	70	97.0 (*R*)
2	**b** (92.8 (*S*))	1.5	67	89.7 (*S*)
3	**c** (95.3 (*S*))	1.5	70	94.4 (*S*)
4	**d** (93.2 (*S*))	0.2	89	90.9 (*S*)

[a] $Pd(acac)_2$ (2 mol %) and 1,1,3,3-tetramethylbutyl isocyanide (8 mol %) were used for the bis-silylation step (reflux in toluene for 1 h). The reaction mixtures were then treated with Me_3SiOTf at −78 °C. [b] Isolated yields for the two steps. [c] Determined by HPLC.

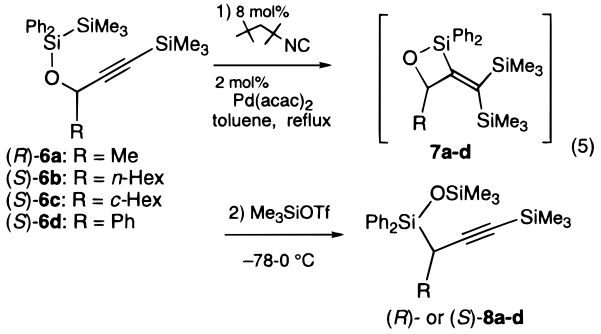
at −78 °C to give the corresponding propargylsilane **5a** with formation of a siloxane bond in high yield (eq 4). Me_3SiOTf



(4)

also catalyzed the rearrangement of **2b** and **c** to give the corresponding propargylic siloxanes in moderate yields (42 and 58%, respectively).

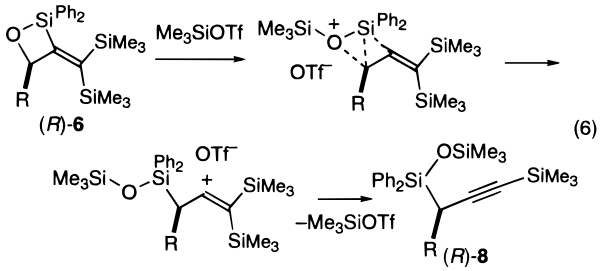
Next, the stereochemical course of the present rearrangement reaction was investigated with optically active secondary oxasiletanes **7a**−**d**, which were formed by the bis-silylation with the corresponding disilanyl ethers **6a**−**d** of optically active propargylic alcohols of 92.8−97.2% enantiomeric excess (ee) (eq 5).



(5)

As **7a**−**d** thus produced were not isolable, the reaction mixtures containing **7a**−**d** were treated with Me_3SiOTf at −78 to 0 °C. For alkyl derivatives **7a**−**c**, 1.5 equiv of Me_3SiOTf were required for the completion of the reaction to give rearranged propargylic siloxane **8a**−**c** (Table 1, entries 1−3). Noteworthy is that the rearrangement took place in high stereospecificity with retention of stereochemistry at the migrating termini.[7] In addition, phenyl-substituted **7d** also underwent the rearrangement in the presence of catalytic amount of Me_3SiOTf to give optically active **8d** with retention of configuration in good yield (entry 4).

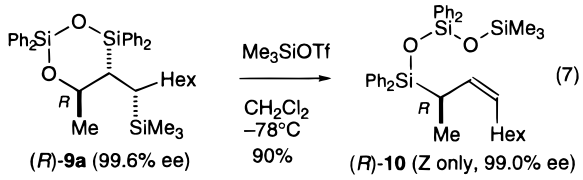
The stereochemical outcome indicates that the [1,2] silyl shift takes place in a concerted manner, i.e., the oxygen atom activated by Me_3SiOTf leaves from the secondary carbon atom with the concurrent growing of the vacant p orbital, which is stabilized by the α-Si−C bond (eq 6). The syn periplaner stabilization should be responsible for the stereospecific syn migration. Presumably, the two trimethylsilyl groups at the methylidene terminal assist the reaction effectively by pushing the migrating



(6)

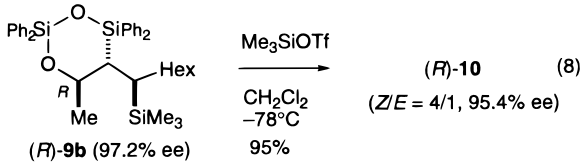
silyl group sterically as well as by stabilizing the resultant cation by the β-silicon effect, which leads to the elimination of the trimethylsilyl group to furnish the product **8**. The fact that the phenyl group, which may stabilize the generated cation and often result in racemization, did not affect the stereospecificity in the reaction of **7d** indicated that the concerted [1,2] silyl shift is a highly favorable process.

To our surprise, the stereospecific [1,2] silyl shift was observed not only for the four-membered rings but also for optically active six-membered disiladioxanes (*R*)-**9a**,**b**, which were readily prepared by intramolecular bis-silylation of optically active (*R*)-(*E*)- and (*R*)-(*Z*)-3-decen-2-ol, respectively.[5a,c] A treatment of (*R*)-**9a** (99.6% ee) with Me_3SiOTf at −78 °C immediately provided *cis*-allylsilane (*Z*)-**10** of >99.0% ee with (*R*) configuration in high yield (eq 7).[7] The (*R*)-configuration unambiguously manifested



(7)

that the [1,2] silyl shift also proceeded with retention of configuration at the migrating terminus. Furthermore, the highly selective formation of (*Z*) isomer indicated that the elimination of the Me_3Si group, following the migration reaction, took place exclusively from a conformation anti to the migrating silyl group. Similarly, nearly complete syn [1,2] silyl shift was observed for the reaction of its epimer (*R*)-**9b**, giving (*R*)-**10** in good yield (eq 8). In this case, however, the olefin geometry was found to be



(8)

4:1 (*Z*/*E*), suggesting that the syn elimination of the trimethylsilyl group proceeded predominantly. These results conclude that the highly stereospecific syn [1,2] silyl shift was followed by the nonstereospecific elimination of the Me_3Si group from the thermodynamically favorable conformations.

In summary, we described that the stereospecific cationic syn [1,2] silyl shift is able to occur with the retention of configuration of the stereochemistry at the migrating terminus through the syn periplanar conformation of the leaving and migrating silyl groups in cyclic system.

Supporting Information Available: Detailed experimental procedures, involving the determination of enantiomeric excesses and absolute configurations, and characterization of the new compounds (7 pages). See any current masthead page for ordering information and Web access instructions.

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(7) The enantiomeric excesses and absolute configurations of **8a**−**d** and **10** were determined by HPLC analyses after derivatization by hydrogenation of the carbon−carbon multiple bond with diimide and subsequent oxidation of the silicon−carbon bond with hydrogen peroxide. The slight loss of the enantiomeric excesses might be due to partial racemization during the diimide reduction ($TsNHNH_2$, Et_3N, dioxane reflux).[5c] For derivatization, see the Supporting Information.