New Synthesis of (*E*)-Allylsilanes with High Enantiopurity via Diastereoselective Intramolecular Bis-Silylation of Chiral Allylic Alcohols

Michinori Suginome, Akira Matsumoto, and Yoshihiko Ito*

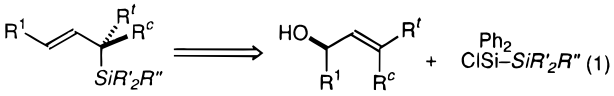
Department of Synthetic Chemistry and Biological Chemistry, Faculty of Engineering Kyoto University, Kyoto 606-01, Japan

Received December 19, 1995

Much interest has been focused on the development of new and versatile organosilicon reagents which may be utilized for organic synthesis. Allylsilanes are one of the convenient organosilicon reagents which have made possible some useful regio- and stereoselective allylations and [3 + 2] cyclizations.[1] Accordingly, the preparation of enantio-enriched allylsilanes is highly desirable. However, widely applicable synthetic methods for their preparation are still limited.[2−6]

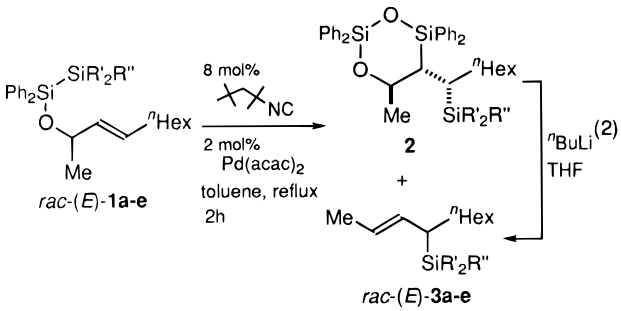
It was previously reported by us that intramolecular bis-silylation of carbon−carbon double bonds was achieved by the use of a palladium(*tert*-alkyl isocyanide) catalyst.[7] The bis-silylation reaction with various homoallyl alcohols proceeded with high regio- and diastereoselectivities, ultimately leading to the stereoselective synthesis of polyols via oxidative cleavage of the resultant silicon−carbon bonds.

Herein, we disclose a new synthesis of geometrically pure (*E*)-allylsilanes with high enantiopurity by the intramolecular bis-silylation with chiral (*E*)- or (*Z*)-allylic alcohols, which proceeds with extremely high diastereoselectivity. This highly enantioselective synthesis of allylsilanes involves stereospecific 1,3-transfer of chirality (eq 1).

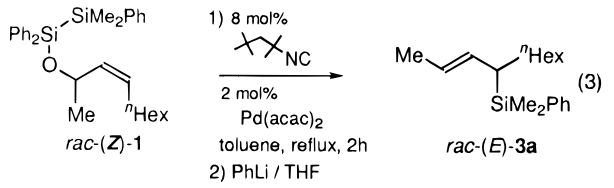


(1)

Disilanyl ether (*E*)-**1a**, which was prepared from the corresponding allylic alcohol and 1-chloro-2,2-dimethyl-1,1,2-triphenyldisilane, was heated for 2 h in the presence of $Pd(acac)_2$ (2 mol %) and 1,1,3,3-tetramethylbutyl isocyanide (8 mol %) under reflux in toluene (eq 2). The mixture of (*E*)-allylsilane **3a** (49%) and six-membered cyclic siloxane **2** (46%) thus produced was separated and isolated by column chromatography. Treatment of the latter (**2**) with *n*-butyllithium in THF at 0 °C led to the formation of **3a** in high yield. The transformation of **2** to **3a** may be rationalized by cleavage of the silicon−oxygen bonds of **2** followed by Peterson-type *syn*-elimination.[8] It is noted that the relative stereochemistry of the three consecutive stereogenic centers in **2** as well as the trans geometry of the carbon−carbon double bond in **3a** was completely controlled.



The palladium-catalyzed bis-silylation followed by treatment with *n*-butyllithium was carried out in one flask without isolation of **2** to afford allylsilane (*E*)-**3a** in 93% yield (Table 1, entry 1).[9] The one-pot syntheses of allylsilanes via the bis-silylation of disilanyl ethers **1b**−**e** bearing various terminal silyl groups are summarized in Table 1.[10] In the case of **1e** with the terminal triisopropylsilyl group, the bis-silylation reaction sluggishly proceeded under forced conditions (see Table 1) to give only allylsilane **3e** in moderate yield without formation of the corresponding cyclic siloxane **2** (entry 5). It should be noted that the (*E*)-allylsilane **3a** was obtained also from (*Z*)-**1a** in 83% yield according to the one-pot procedure with phenyllithium (eq 3).



As we proposed in an earlier paper,[7c] the intramolecular bis-silylation may involve a bis(organosilyl)palladium(II) complex **4**, which undergoes intramolecular insertion of the carbon−carbon double bond (eq 4). It is presumed that the insertion reaction proceeds through the "exo" complex, which is accompanied by less steric repulsion than the "endo" one.[11] Indeed, the high diastereofacial selection in the intramolecular bis-silylation led to the stereoselective formation of **2** and (*E*)-**3**. Probably, a four-membered *trans*-**5** initially formed under-

(1) For the stereochemical aspect of the reaction of chiral allylsilanes with electrophiles, see: (a) Hayashi, T.; Konishi, M.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4963−4965. (b) Hayashi, T.; Konishi, M.; Kumada, M. *J. Org. Chem.* **1983**, *48*, 281−282. (c) Masse, C. E.; Panek, J. S. *Chem. Rev.* **1995**, *95*, 1293−1326 and references therein.

(2) Asymmetric cross coupling of α-(silyl)alkyl Grignard reagents with alkenyl bromides in the presence of chiral ferrocenylphosphine−palladium complexes: (a) Hayashi, T; Konishi, M.; Ito, H.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4962−4963. (b) Hayashi, T.; Konishi, M.; Okamoto, Y.; Kabeta, K.; Kumada, M. *J. Org. Chem.* **1986**, *51*, 3772−3781.

(3) Wittig olefination of enantiomerically enriched α-silylaldehydes: Bhushan, V.; Lohray, B. B.; Enders, D. *Tetrahedron Lett.* **1993**, *34*, 5067−5070.

(4) Regioselective nucleophilic substitution of enantiomerically enriched allyl esters and carbamates with (organosilyl)cuprate reagents: (a) Fleming, I.; Thomas, A. P. *J. Chem. Soc., Chem. Commun.* **1986**, 1456−1457. (b) Fleming, I.; Higgins, D.; Lawrence, N. J.; Thomas, A. P. *J. Chem. Soc., Perkin Trans. 1* **1992**, 3331−3349.

(5) Claisen rearrangement of chiral allylic alcohol derivatives: (a) Mikami, K.; Maeda, T.; Kishi, N.; Nakai, T. *Tetrahedron Lett.* **1984**, *25*, 5151−5154. (b) Sparks, M. A.; Panek, J. S. *J. Org. Chem.* **1991**, *56*, 3431−3438.

(6) Other preparation of enantio-enriched allylic silanes. (a) Buckle, M. J. C.; Fleming, I.; Gil, S. *Tetrahedron Lett.* **1992**, *33*, 4479−4482. (b) Sarkar, T. K. *Synthesis* **1990**, 969−983, 1101−1111.

(7) (a) Murakami, M.; Andersson, P. G.; Suginome, M.; Ito, Y. *J. Am. Chem. Soc.* **1991**, *113*, 3987−3988. (b) Murakami, M.; Suginome, M.; Fujimoto, K.; Nakamura, H.; Andersson, P. G.; Ito, Y. *J. Am. Chem. Soc.* **1993**, *115*, 6487−6498. (c) Suginome, M.; Matsumoto, A.; Nagata, K.; Ito, Y. *J. Organomet. Chem.* **1995**, 499, C1−C3. (d) Suginome, M.; Yamamoto, Y.; Fujii, K.; Ito, Y. *J. Am. Chem. Soc.* **1995**, *117*, 9608−9609.

(8) Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780−784.

(9) Prior to the addition of *n*-BuLi (1.5 equiv) at 0 °C, toluene was replaced by THF.

(10) The requisite chlorodisilanes were readily prepared by the reaction of (diethylamino)diphenylsilyllithium with the corresponding triorganochlorosilanes followed by treatment with acetyl chloride. (a) Tamao, K.; Kawachi, A.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 3989−3990. (b) Tamao, K.; Kawachi, A.; Nakagawa, Y.; Ito, Y. *J. Organomet. Chem.* **1994**, *473*, 29−34.

(11) Tamao, K.; Nakajima, T.; Sumiya, R.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1986**, *108*, 6090−6093. (b) Tamao, K.; Nakagawa, Y.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 3712−3714.

(12) The formation of a trans four-membered ring was observed in the reaction of the related (2-methyl-3-butenyl)disilane, though the selectivity was not as high (84:16). See ref 7b.

(13) The disproportionation of siloxetane was described. (a) Barton, T. J. *Pure. Appl. Chem.* **1980**, *52*, 615−624. (b) Bachrach, S. M.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 1186−1190.

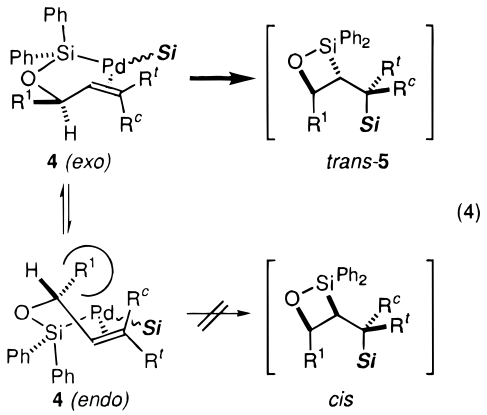
0002-7863/96/1518-3061$12.00/0

Table 1. One-Pot Synthesis of Racemic (*E*)-*sec*-Allylsilanes[a]

entry	*rac*-**1**	R″R′$_2$Si	*rac*-**3** (yield/%)[b]
1	(*E*)-**1a**	PhMe$_2$Si	(*E*)-**3a** (93)
2	(*E*)-**1b**	Me$_3$Si	(*E*)-**3b** (82)
3	(*E*)-**1c**	*t*-BuMe$_2$Si	(*E*)-**3c** (88)
4	(*E*)-**1d**	Et$_3$Si	(*E*)-**3d** (92)
5	(*E*)-**1e**	*i*-Pr$_3$Si	(*E*)-**3e** (55)

[a] Reagents and conditions for entries 1−4: (1) Pd(acac)$_2$ (2 mol %), 1,1,3,3-tetramethylbutyl isocyanide (8 mol %), toluene reflux 2 h; (2) *n*-BuLi (1.5 equiv), THF, 0 °C, 0.5 h. For entry 5: Pd(acac)$_2$ (3 mol %), 1-adamantyl isocyanide (45 mol %), xylene reflux 2 days. [b] Isolated yield.

went *syn*-elimination under the reaction conditions to give (*E*)-allylsilane **3** with Ph$_2$Si═O, which rapidly reacted, in turn, with *trans*-**5** to afford siloxane **2**.[12,13]



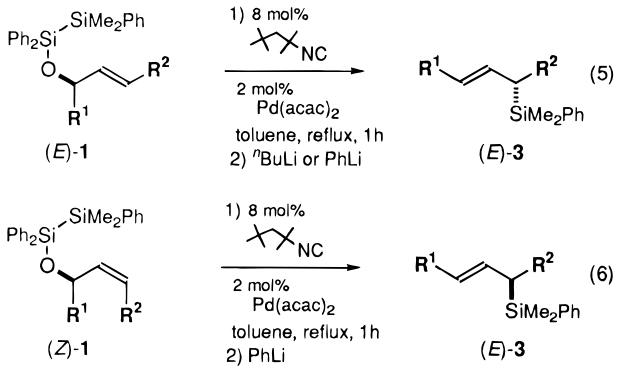
(4)

The highly selective formation of (*E*)-allylsilanes prompted us to use enantio-enriched allylic alcohols, which were readily available by asymmetric syntheses, e.g., Sharpless kinetic resolution.[14] The palladium-catalyzed reaction of (*R*)-(*E*)-**1a** (99.7% ee) gave (*E*)-**3a** with (*S*)-configuration (96.1% ee) together with **2**, which was subsequently treated with *n*-butyllithium to also give (*S*)-(*E*)-**3a** with 99.1% ee.[15] The mechanism proposed above is in accord with the observed chirality transfer during the transformation of the allylic alcohol to the corresponding (*E*)-allylsilane. Thus, (*S*)-(*E*)-**3a** with 97.3% overall ee was obtained from (*R*)-(*E*)-**1a** in 87% yield by a procedure similar to that used for the synthesis of racemic allylsilanes (eq 5; Table 2, entry 1).[16] The enantiomer, (*R*)-(*E*)-**3a**, was complementarily synthesized from the (*Z*)-isomer with the same absolute configuration (eq 6; entry 2). Reactions with some disilanyl ethers of highly enantio-enriched allylic alcohols (*E*)-**1f**−**h** successfully gave the corresponding allylsilanes (*E*)-**3f**−**h** with high enantiopurities in good yields. Thus, the diastereoselective bis-silylation offers a convenient synthetic access to (*E*)-allylsilanes with high enantiomeric purity. The present method has the advantages of being a general preparation for highly enantiomerically enriched allylsilanes with complete selectivity for the (*E*)-isomer and of having manipulative simplicity.

Table 2. Synthesis of Enantiomerically Enriched (*E*)-*sec*-Allylsilanes

entry	**1** (ee/%)	R^1	R^2	**3** (yield/%)[a]	ee/%[b]
1	(*R*)-(*E*)-**1a** (99.7)	Me	*n*-hex	(*S*)-**3a** (87)	97.3
2	(*R*)-(*Z*)-**1a** (96.0)	Me	*n*-hex	(*R*)-**3a** (84)	95.4
3	(*S*)-(*E*)-**1f** (>99.0)	Ph	*n*-hex	(*S*)-**3f** (95)	96.3
4	(*R*)-(*E*)-**1g** (99.8)	*c*-hex	*n*-hex	(*S*)-**3g** (96)	98.0
5	(*R*)-(*E*)-**1h** (98.2)	Me	Ph	(*R*)-**3h** (85)	94.8

[a] Isolated yield after treatment with *n*-BuLi (for entries 1, 3, and 4) or PhLi (for entries 2 and 5). [b] Determined by HPLC.



(5)

(6)

(14) (a) Martin, V. S.; Woodard, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 6237−6240. (b) Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765−5780.

(15) Enantiomeric excess was determined by HPLC analysis with a chiral stationary phase column. The column used is specified in the supporting information.

(16) For the synthesis of enantio-enriched allylsilanes, palladium catalyst was removed prior to the treatment with RLi by passing the mixture through a short column of Florisil.

Supporting Information Available: Detailed experimental procedures and characterization of the new compounds (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA954251X