Stereoselective Formation of Cyclopropylsilane through Intramolecular Rearrangement of [(Allyloxy)dimesitylsilyl]lithiums

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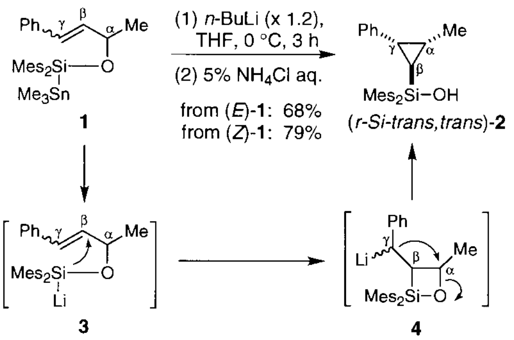
A [(*sec*-allyloxy)dimesitylsilyl]stannane bearing a phenyl group on the olefin part reacts with *n*-BuLi in THF to give a cyclopropylsilane as a single diastereomer, in contrast to the [2,3]-sila-Wittig rearrangement affording an allylsilane, previously observed for a substrate bearing an alkyl group on the olefin part. The striking substituent effect is revealed by ab initio calculations in terms of the regioselectivity in the reaction of silyllithiums with an olefin.

We previously reported the [2,3]-sila-Wittig rearrangement,[1] the silicon analogs to the [2,3]-Wittig rearrangement; the [(*tert*-allyloxy)diphenylsilyl]lithiums[2] generated from the corresponding silylstannane and *n*-BuLi underwent the [2,3]-rearrangement to afford the lithium allylsilanolates. This rearrangement offers a new methodology for the synthesis of allylsilanes from (allyloxy)silanes with the allylic transposition.[3] During the course of this study, we have now found that when a phenyl group is attached to the terminus of the olefin, the reaction mode of the rearrangement dramatically changes in such a way that a cyclopropylsilane is formed in a stereoselective manner, in contrast to the [2,3]-sila-Wittig rearrangement observed for substrates bearing alkyl group(s) on the olefin part.

(*E*)-[(*sec*-allyloxy)dimesitylsilyl]stannane[2,4] (*E*)-**1** bearing a phenyl group on the olefin[5] was treated with *n*-BuLi (1.2 mol amt.) in THF at 0 °C for 3 h, as shown in Scheme 1. The reaction was then quenched with a 5% aqueous solution of NH_4Cl. Purification of the reaction mixture by column chromatography on silica gel afforded the cyclopropylsilane **2** in 68% yield as a single diastereomer.[6] It was found that (*Z*)-**1** afforded the same diastereomer **2** in 79% yield. The relative configuration of **2** was determined by the X-ray diffraction analysis of the single crystals,[7] which were recrystallized from hexane, as shown in Figure 1. Referring to the silyl group, both the phenyl group and the methyl group are *trans*.[8] This product is thus properly designated as (*r-Si-trans, trans*)-**2**.



Scheme 1.

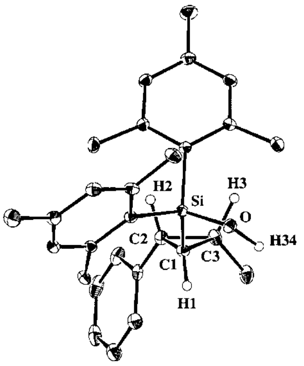
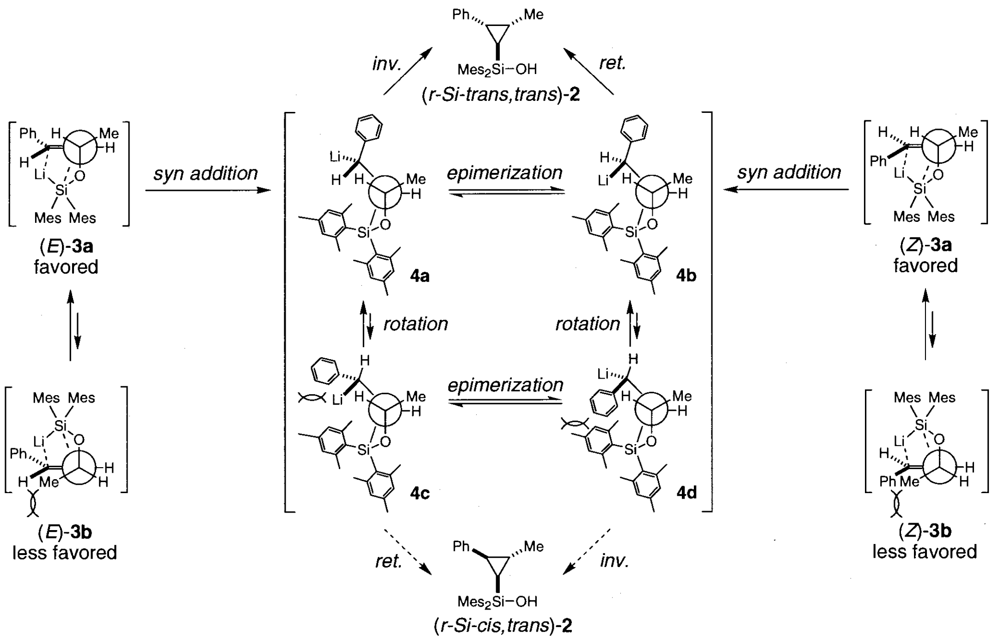


Figure 1. Crystal structure of (*r-Si-trans,trans*)-**2**•H_2O. The H_2O molecule and hydrogen atoms except for H1, H2, H3, and H34 are omitted for clarity.

The formation of the cyclopropylsilane may proceed in two steps (Scheme 1). Thus, the silyllithium **3** generated in situ undergoes intramolecular addition to the olefin on the β-carbon (C(β)) in the first step, and the resulting 1-oxa-2-sila-cyclobutane[9] **4** is so reactive due to the ring strain that it readily suffers a nucleophilic substitution on the α-carbon (C(α)) by the internal benzyllithium moiety, resulting in the ring cleavage of the oxasilacyclobutane and the formation of the cyclopropylsilane during the second step.[10,11]

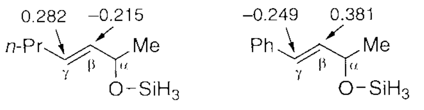
The Newmann projections of **3** and **4** along the C(α)–C(β) bond axis are shown in Scheme 2. Upon starting from (*E*)-**1**, the syn addition[12] of the silyllithium (*E*)-**3** to the olefin proceeds in the sterically less hindered conformer (*E*)-**3a** rather than (*E*)-**3b**, giving **4a**. The cyclization in **4a** with inversion of the configuration at the lithiated benzylic carbon provides (*r-Si-trans,trans*)-**2**.[10a] Alternatively, **4a** may undergo epimerization at the lithiated carbon to give **4b**, which now cyclizes with retention of the configuration at the lithiated carbon to also provide (*r-Si-trans,trans*)-**2**.[10b,c] In a similar manner, (*Z*)-**1** also provides the same (*r-Si-trans,trans*)-**2** as the single diastereomer via the common intermediates **4a** and/or **4b**. We cannot determine the reaction stereochemistry, inversion or retention, because the stereochemical courses of the benzyllithium derivatives are sensitive to several factors such as the nature of the leaving group.[13] Other rotamers **4c** and **4d** around the C(β)–C(γ) bond axis of **4a** and **4b**, respectively, would give (*r-Si-cis,trans*)-**2**, but these are less favored due to the steric repulsion between the phenyl group and the mesityl group(s).

The regioselectivity of the reaction of the silyllithium to the olefin, which determines the reaction mode, was rationalized by ab initio molecular orbital calculations (MP2/6-31G**//HF/3-21G) of the model compounds **5** and **6**.[14] As shown in Figure 2, the maximum of the molecular orbital coefficient in the LUMO appears on C(γ) in the alkyl-substituted compound **5**, indicating that the nucleophilic attack occurs at



Scheme 2.

this position, resulting in the sila-Wittig rearrangement. In contrast, the maximum of the molecular orbital coefficient in the LUMO appears on C(β) in the phenyl-substituted compound **6**, indicating that the nucleophilic attack occurs on C(β) in **3**, resulting in the cyclopropylsilane formation.[15]



5 **6**

Figure 2. Molecular orbital coefficients on LUMO of the model compounds **5** and **6**.

In summary we have determined the stereoselective formation of the cyclopropylsilane based on the intramolecular rearrangement of the [(allyloxy)silyl]lithiums. Further study is now in progress for the synthesis of optically active cyclopropanes based on this methodology.

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References and Notes

1 a) A. Kawachi, N. Doi, and K. Tamao, *J. Am. Chem. Soc.*, **119**, 233 (1997). b) A. Kawachi and K. Tamao, *Bull. Chem. Soc. Jpn.*, **70**, 945 (1997).

2 The term "*tert*-allyl" means that the allylic carbon is tertiary. The term "*sec*-allyl" is used in a similar way in this paper.

3 Recent allylsilane synthesis: e.g., a) M. Suginome, A. Matsumoto, and Y. Ito, *J. Am. Chem. Soc.*, **118**, 3061 (1996). b) J. H. Smitrovich and K. A. Woerpel, *J. Org. Chem.*, **65**, 1601 (2000).

4 The mesityl groups on the silicon are introduced to prevent the attack of *n*-BuLi on the silicon center.

5 The silylstannane **1** was prepared by the reaction of the (*E*)- and (*Z*)-4-phenyl-3-buten-2-ols and [(chloro)dimesitylsilyl]-trimethylstannane in THF in the presence of triethylamine and pyridine in a manner similar to the procedure reported in Ref. 1a.

6 Analytical data of (*r-Si-trans,trans*)-**2**: ^{1}H NMR (300 MHz, C_6D_6) δ 0.68 (dd, *J* = 7.1 and 7.1 Hz, 1H), 0.98 (d, *J* = 6.0 Hz, 3H), 1.32–1.41 (m, 1H), 1.49 (s, 1H), 2.15 (s, 3H), 2.16 (s, 3H), 2.41 (dd, *J* = 7.1 and 8.7 Hz, 1H), 2.50 (s, 6H), 2.52 (s, 6H), 6.76 (s, 2H), 6.78 (s, 2H), 7.08–7.17 (m, 5H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.27, 16.34, 18.44, 21.01, 23.78, 26.60, 125.62, 127.82, 129.06, 129.09, 132.20, 132.79, 138.90, 139.01, 139.48, 143.49, 143.68 (Although there should be 12 peaks of the sp^2 carbon, 11 peaks were observed). Anal. Calcd for $C_{28}H_{34}OSi$: C, 81.10; H, 8.26%. Found: C, 81.04; H, 8.49%.

7 The crystal includes one H_2O molecule per **2**. Crystal data for (*r-Si-trans,trans*)-**2**•H_2O: $C_{28}H_{36}O_2Si$; M = 432.68; Rigaku RAXIS-IV imaging plate area detector; crystal size 0.25 × 0.25 × 0.25 mm; monoclinic, space group $P2_1/c$ (No. 14), $Z = 4$, $a = 8.5408(6)$ Å, $b = 17.948(2)$ Å, $c = 15.996(2)$ Å, $\beta = 93.875(7)°$, $V = 2446.3999$ Å^3, $D_{calcd} = 1.175$ g/cm^3; $T = 173$ K; $2\theta_{max} = 55.1°$. The structure analysis is based on 5108 reflections, 4443 observed ($I > 3.00\sigma(I)$), and 281 parameters. $R = 0.071$, $R_w = 0.083$. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (No. CCDC-147730).

8 Nomenclature of cyclic compounds: E. L. Eliel and S. H. Wilen, in "Stereochemistry of Organic Compounds," John Wiley & Sons, Inc., New York (1994), Chap. 11.

9 Formation of oxasilacyclobutanes, e.g.: K. Tamao, Y. Nakagawa, and Y. Ito, *Organometallics*, **12**, 2297 (1993). See also Ref. 3a.

10 Cyclopropane synthesis by intramolecular cyclization of organolithium compounds: a) A. Krief and M. Hobe, *Tetrahedron Lett.*, **33**, 6529 (1992). b) D. Hoppe, M. Paetow, and F. Hintze, *Angew. Chem., Int. Ed. Engl.*, **32**, 394 (1993). c) S. Norsikian, I. Marek, J-F. Poisson, and J. F. Normant, *J. Org. Chem.*, **62**, 4898 (1997). d) D. Cheng, K. R. Knox, and T. Cohen, *J. Am. Chem. Soc.*, **122**, 412 (2000).

11 Reviews for cyclopropane synthesis: a) J. Salaün, *Chem. Rev.*, **89**, 1247 (1989). b) A. Pfaltz, *Acc. Chem. Res.*, **26**, 339 (1993). c) A. B. Charette and J-F. Marcoux, *Synlett*, **1195**, 1197.

12 A silylcuprate adds to allenes in a syn fashion: F. J. Blanco, P. Cuadrado, A. M. González, and F. J. Pulido, *Tetrahedron Lett.*, **35**, 8881 (1994).

13 R. E. Gawley, E. Low, Q. Zhang, and R. Harris, *J. Am. Chem. Soc.*, **122**, 3344 (2000), and references cited therein.

14 All calculations were performed with the Gaussian 94 program package.

15 The nature of the nucleophile, the silyllithium moiety, may be also an important factor for this reaction mode, considering that the carbon analog derived from cinnamyl methyl ether underwent the [2,3]-Wittig rearrangement: M. P. Doyle, V. Bagheri, and N. K. Harn, *Tetrahedron Lett.*, **29**, 5119 (1988).