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

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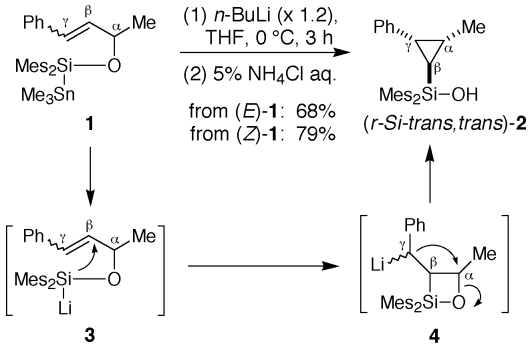
A [(*sec*-allyloxy)dimesitylsilyl]stannane having a phenyl group on the olefin part reacts with *n*-BuLi in THF to give a cyclopropylsilane as a single diastereomer, in contrast to the [2,3]-sila-Wittig rearrangement affording an allylsilane, previously observed for a substrate having an alkyl group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

keywords: silyllithiums / sila-Wittig rearrangement / cyclopropanation reaction / cyclopropylsilane

Previously we demonstrated 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 [(*tert*-allyloxy)diphenysilyl]stannane and *n*-BuLi underwent the [2,3]-rearrangement to afford the lithium allylsilanolates. During the course of this study, we have found that when a phenyl group is attached to the terminus of the olefin, the reaction mode of the rearrangement 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 having alkyl group(s) on the olefin part [2].

(*E*)-[(*sec*-allyloxy)dimesitylsilyl]stannane (*E*)-**1** having a phenyl group on the olefin was treated with *n*-BuLi (1.2 mol amt.) in THF at 0 ºC for 3 h, as shown in Scheme 1. The reaction was then quenched with a 5% aqueous solution of NH4Cl to afford the cyclopropylsilane **2** in 68% yield as a single diastereomer. 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 [4], as shown in Figure 1. Both the phenyl group and the methyl group are *trans* to the silyl group. This product is thus designated as (*r-Si-trans, trans*)-**2**.

The formation of the cyclopropylsilane can be rationalized as shown in Scheme 1. The silyllithium **3** generated in situ undergoes intramolecular addition to the olefin on the β-carbon (C(β)) in the initial step. The result-



Scheme 1.

SYNTHETIC ORGANIC CHEMISTRY — Synthetic Design —

Scope of research

(1) Synthesis, structural studies, and synthetic applications of organosilicon compounds, such as pentacoordinate silicon compounds, functionalized silyl anions, and functionalized oligosilanes. (2) Design and synthesis of novel π-conjugated polymers containing silacyclopentadiene (silole) rings, based on new cyclization reactions and carbon-carbon bond formations mediated by the main group and transition metals. (3) Chiral transformations and asymmetric synthesis via organosulfur and selenium compounds, especially via chiral episulfoniun and episelenonium ions.

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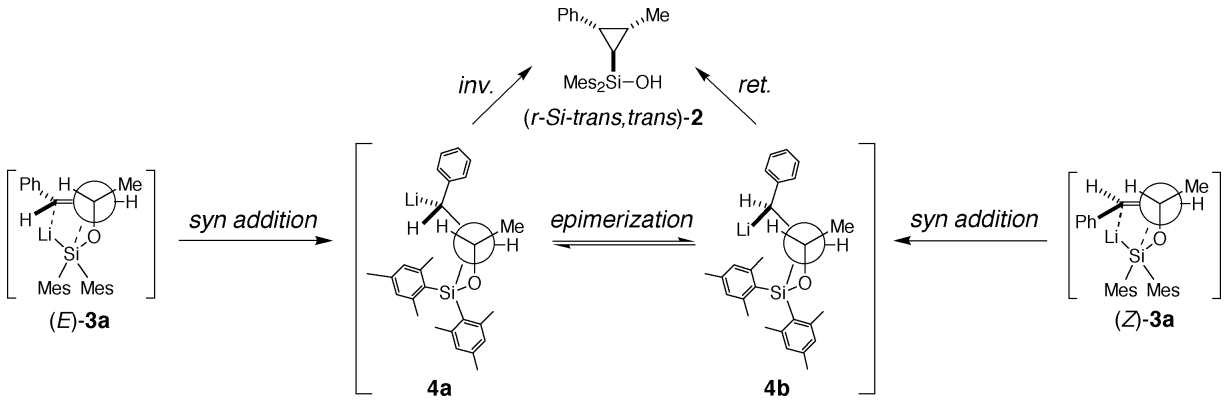


Scheme 2.

ing 1-oxa-2-sila-cyclobutane **4** is so reactive due to the ring strain that it readily suffers a nucleophilic substitution on the α-carbon (C(α)) by the benzyllithium moiety, resulting in the ring cleavage of the oxasilacyclobutane and the formation of the cyclopropane ring during the second step.

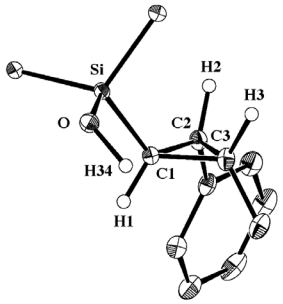
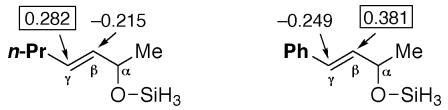


Figure 1. Crystal structure of (*r-Si-trans,trans*)-**2**•H_2O. The H_2O molecule and hydrogen atoms except for H1, H2, H3, and H34 are omitted for clarity.

The stereoselective formation of (*r-Si-trans, trans*)-**2** was followed as shown in Scheme 2, which includes the Newmann projections of **3** and **4** along the C(α)-C(β) bond axis. The silyllithium (*E*)-**3**, coming from (*E*)-**1**, favors the conformer (*E*)-**3a** to avoid the steric repulsion between the phenyl group and the mesityl group(s). The syn addition of (*E*)-**3a** to the olefin gives **4a**. The cyclization in **4a** with inversion of configuration at the lithiated benzylic carbon provides (*r-Si-trans,trans*)-**2**. Alternatively, **4a** may undergo epimerization at the lithiated carbon to give another epimer **4b**. The cyclization in **4b** with retention of configuration at the lithiated benzylic carbon also provides (*r-Si-trans,trans*)-**2**. In a similar manner, the conformer (*Z*)-**3a**, coming from (*Z*)-**1**, also provides the same (*r-Si-trans,trans*)-**2** as a 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.

The observed regioselectivity of the reaction of the silyllithium to the olefin was rationalized by ab initio molecular orbital calculations (MP2/6-31G**//HF/3-21G) of the model compounds **5** and **6**, as shown in Figure 2 [5]. The alkyl-substituted compound **5** exhibits the maximum of the molecular orbital coefficient in the LUMO on C(γ) and thus accepts the nucleophilic attack at this position, resulting in the sila-Wittig rearrangement. In contrast, the phenyl-substituted compound **6** exhibits the maximum of the molecular orbital coefficient in the LUMO on C(β) and thus accepts the nucleophilic attack on C(β), resulting in the cyclopropylsilane formation.



5 **6**

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

In summary we have demonstrated the stereoselective formation of the cyclopropylsilane based on the intramolecular rearrangement of the [(allyloxy)silyl]lithiums.

References

1. (a) Kawachi A, Doi N, and Tamao K, *J. Am. Chem. Soc.*, **119**, 233 (1997). (b) Kawachi A and Tamao K, *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. Kawachi A, Maeda H, Tamao K, *Chem. Lett.*, 1216 (2000).
4. 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 x 0.25 x 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. $R = 0.071$, $R_W = 0.083$.
5. All calculations were performed with the Gaussian 94 program package.