Stereoselective Formation of Cyclopropylsilane through Intramolecular Rearrangement of [(Allyloxy)dimesitylsilyl]lithiums (SYNTHETIC ORGANIC CHEMISTRY-Synthetic Design)

Author(s)
Kawachi, Atsushi; Maeda, Hirofumi; Tamao, Kohei

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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 episulfonium and episelenonium ions.

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)diphenylsilyl]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 °C 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-
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 benzyl lithium moiety, resulting in the ring cleavage of the oxasilacyclobutane and the formation of the cyclopropane ring during the second step.

The stereoselective formation of (r-Si-trans, trans)-2 was followed as shown in Scheme 2, which includes the Newman 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 benzyllic 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 benzyllic 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 stereochernistry, inversion or retention, because the stereochemical courses of the benzyl lithium 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.

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

References


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.


4. The crystal includes one H2O molecule per 2. Crystal data for (r-Si-trans, trans)-2·H2O: C28H36O2Si; M = 432.68; Rigaku RAXIS-IV imaging plate area detector; crystal size 0.25 x 0.25 x 0.25 mm; monoclinic, space group P21/c (No. 14), Z = 4, a = 8.5408(6) Å, b = 17.948(2) Å, c = 15.996(2) Å, β = 93.875(7)º, V = 2446.3999 Å³, Dcalc = 1.175 g/cm³; T = 173 K; 2θmax = 55.1º. The structure analysis is based on 5108 reflections, 4443 observed (I>3.0σ(I)), and 281 parameters. R = 0.071, Rw = 0.083.

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