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Metal-Catalyzed Rearrangement of Homoallylic Ethers to Silylmethyl Allylic Silanes in the Presence of a Di-*tert*-butylsilylene Source

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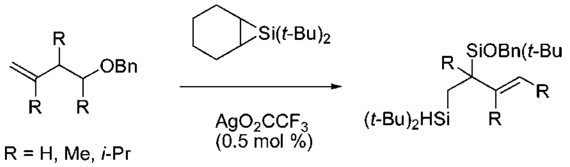
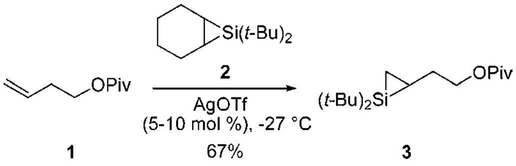
ABSTRACT



In examining the scope of the di-*tert*-butylsilylene transfer to *gem*-disubstituted alkenes to form silacyclopropanes, we discovered an unprecedented reaction of homoallylic ethers. When silylene transfer was performed at room temperature or above, two di-*tert*-butylsilylene units were incorporated into the molecule, and complete rearrangement of the carbon backbone occurred. This report describes the scope of this unique reaction as well as the mechanistic studies conducted that led to a proposed mechanism.

Studies of silylenes[1−3] and metal−silylene complexes[4] have emerged as important areas of organosilicon chemistry. Among the reactions of silylenes, some have exhibited unexpected reactivity, including rearrangements.[5] Our laboratory has been interested in applying the reactions of silylenes to organic synthesis. We have shown that metal-catalyzed di-*tert*-butylsilylene transfer reactions to alkenes and alkynes are efficient methods for the synthesis of silacyclopropanes and silacyclopropenes.[6−8] For example, silacyclopropanes can be formed from homoallylic esters at low temperature in good yield (Scheme 1).[7]

Scheme 1. Di-*tert*-butylsilylene Transfer to Alkenes



In examining the scope of the transformation shown in Scheme 1, we discovered an unprecedented reaction of homoallylic ethers. When silylene transfer was performed at room temperature or above, two di-*tert*-butylsilylene units were incorporated into the molecule and complete rearrangement of the carbon backbone occurred (Scheme 2).[9] While allylic ethers are known to undergo sigmatropic rearrange-

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(1) Gehrhus, B.; Lappert, M. F. *J. Organomet. Chem.* **2001**, *617−618*, 209−223.

(2) Hill, N. J.; West, R. *J. Organomet. Chem.* **2004**, *689*, 4165−4183.

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(9) The reaction of **4** with only 1 equiv of silacylopropane **2** yielded 50% of **6** and recovered starting material.

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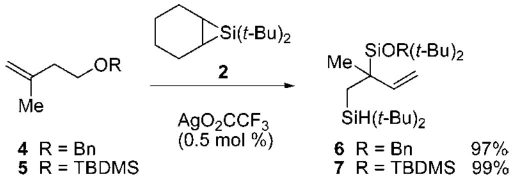
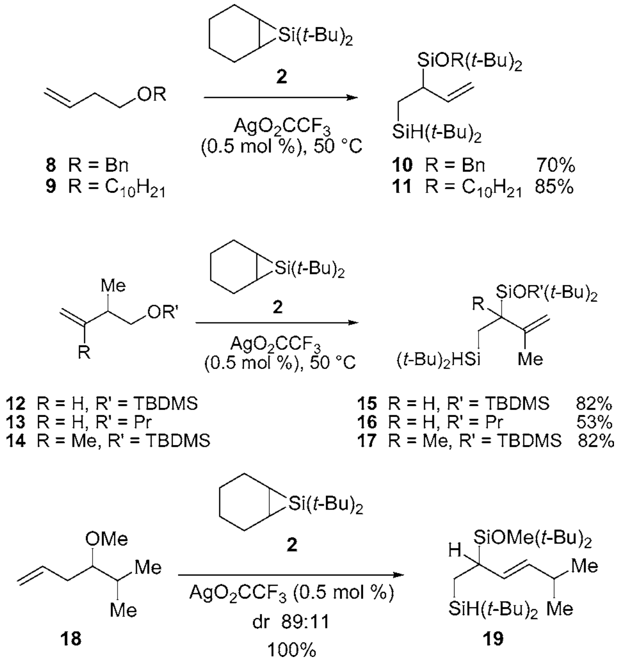
Scheme 2. Rearrangement of Homoallylic Ethers



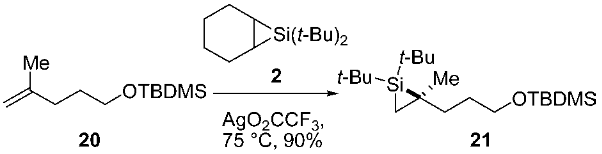
ments in the presence of silylenes,[10−13] rearrangements of homoallylic ethers have not been reported. We felt that this transformation merited further study because silylmethyl allylic silanes have been used in the synthesis of natural products,[14,15] but their syntheses have proven to be difficult.[16]

The rearrangement of alcohol derivatives is general for a variety of substrates. In addition to *gem*-disubstituted homoallylic ethers, monosubstituted homoallylic ethers rearranged, although higher temperatures were required (50 °C, Scheme 3). Homoallylic pivaloate esters, which form silacyclopropanes at low temperature (Scheme 1), rearranged at room temperature. Substitution at the allylic position was also tolerated.[17] *β*-Substituted silylmethyl allylic silanes can be constructed from homoallylic ethers with substitution at the homoallylic position. The rearrangement appears to be specific to homoallylic ethers and esters: di-*tert*-butylsilylene transfer to bishomoallylic ethers provided only the silacyclopropane (Scheme 4).

Scheme 3. Generality of the Rearrangement

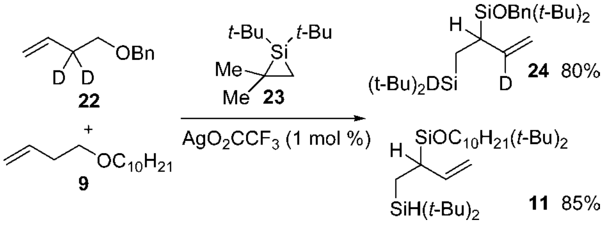


Scheme 4. Silacyclopropanation of Bishomoallylic Ethers



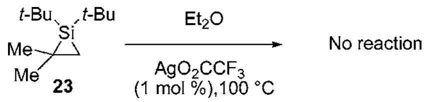
Because this reactivity of silylenes has not been observed, experiments were designed to probe its mechanism. A deuterium labeling/crossover experiment established the connectivity of the rearrangement and demonstrated that it is intramolecular. Subjecting a mixture of d_2-homoallylic benzyl ether **22** and homoallylic decyl ether **9** to the reaction conditions resulted in no crossover products (Scheme 5).[18,19]

Scheme 5. Deuterium Labeling/Crossover Experiment



Examination of the ^1H and ^2H NMR spectra of allylic silane **24** revealed the fate of the deuterium atoms as well as the reorganization of the carbon backbone. One of the deuterium atoms migrated to the terminal silicon atom, and the alkene walked two atoms down the chain. To confirm that an intermolecular reaction does not take place, 2,2-dimethylsilacylcopropane **23** was subjected to AgO_2CCF_3 and diethyl ether. No reaction was observed, even at elevated temperatures (Scheme 6).

Scheme 6. Demonstration of Intramolecularity of Rearrangement



Silacyclopropanes appear to be intermediates along the reaction pathway. When isolated silacyclopropane **25** (prepared by thermal silylene transfer[20]) was subjected to AgO_2-

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(10) Tzeng, D.; Weber, W. P. *J. Org. Chem.* **1981**, *46*, 693−696.

(11) Tortorelli, V. J.; Jones, M., Jr. *J. Chem. Soc., Chem. Commun.* **1980**, 785−786.

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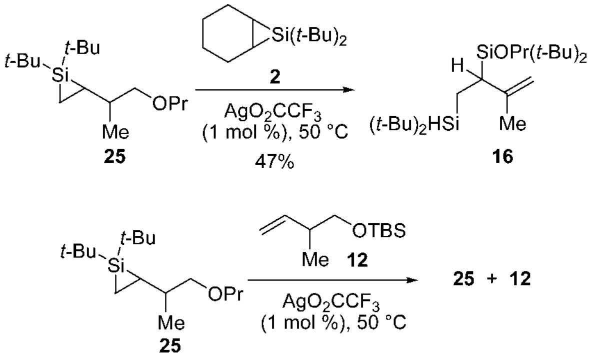
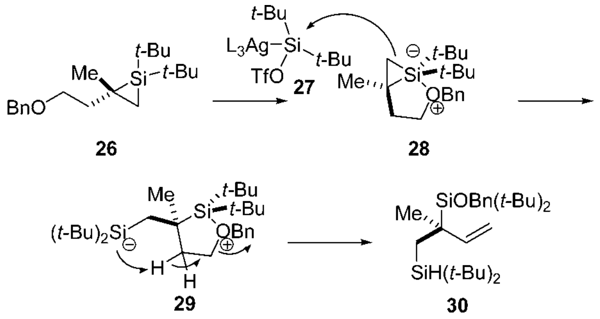
(17) X-ray crystallography confirmed the structure of **15**. See the Supporting Information for details.

CCF_3 and silacyclopropane **2**, rearrangement provided silylmethyl allylic silane **16** (Scheme 7).[21] Control experiments demonstrate that silacyclopropane **25** cannot liberate di-*tert*-butylsilylene to convert another molecule of **25** to allylic silane **16**. No reaction was observed when silacyclopropane **25** was treated with AgO_2CCF_3 in the absence of silacyclopropane **2**. In addition, silacyclopropane **25** does not transfer di-*tert*-butylsilylene to an exogenous alkene under these conditions.

Scheme 7. Silacyclopropanes as Intermediates along the Reaction Pathway



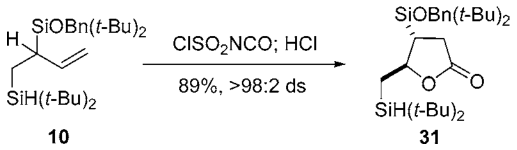
Scheme 8. Proposed Mechanism



The mechanism shown in Scheme 8 is consistent with our mechanistic experiments (Schemes 5−7). Upon formation of silacyclopropane **26**,[22] the ether oxygen atom can complex[23,24] to the Lewis acidic silicon atom.[25] The lengthened apical Si−C bond[25] of the resulting pentacoordinate siliconate becomes nucleophilic. Attack by electrophilic silver silylenoid complex **27** affords silyl anion **29**.[26,27] Intramolecular deprotonation and elimination then provides the silylmethyl allylic silane.

With this new, simple synthesis of silylmethyl allylic silanes, we felt it was important to show that these compounds would react as allylic silanes. Treatment of allylic silane **10** with *N*-chlorosulfonyl isocyanate provided lactone **31** in good yield and diastereoselectivity (Scheme 9).[15] Because the C−Si bonds can be oxidized to form C−O bonds,[28,29] these silylmethyl allylic silanes should find application in organic synthesis.

Scheme 9. Synthetic Utility of Rearrangement



In conclusion, homoallylic ethers undergo rearrangement when treated with a metal-salt catalyst and a di-*tert*-butylsilylene source to provide silylmethyl allylic silanes. Because the allylic silanes participate in annulation reactions, they should find utility in organic synthesis.

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Supporting Information Available: Experimental procedures; spectroscopic, analytical, and X-ray data for the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) ^1H NMR spectroscopic experiments show that **9** and **22** rearrange at comparable rates, indicating no significant kinetic isotope effect for the rearrangement.

(19) We have observed that the reactivity of silacyclopropane **23** is comparable to that of silacyclopropane **2**.

(20) Driver, T. G.; Woerpel, K. A. *J. Am. Chem. Soc.* **2003**, *125*, 10659−10663.

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