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Synthesis of Cyclopropylsilanols by the Simmons-Smith Reaction of Alkenylsilanols and Lithium Alkenylsilanolates

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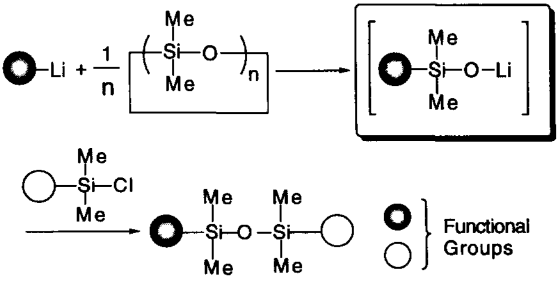
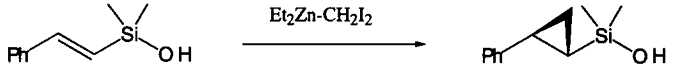
Abstract: *Alkenylsilanols and the corresponding lithium silanolates prepared in situ by the reaction of cyclic siloxanes with alkenyllithiums are transformed to the corresponding cyclopropylsilanols under the Simmons-Smith reaction conditions. The obtained cyclopropylsilanols are further converted into the corresponding cyclopropanols by the Tamao oxidation.* Copyright © 1996 Elsevier Science Ltd

We have recently demonstrated that the cleavage of cyclic siloxanes with organolithium reagents provides us with a practical way to introduce various polymerizable functionalities onto the siloxane segment. Subsequent reaction with functionalized chlorosilanes furnishes a variety of unsymmetrical mono- and di-functionalized siloxanes as shown in Scheme 1.[1] The siloxane monomers can be converted into various siloxanes involving polymeric materials, whose siloxane units are incorporated into the polymer backbone and/or the side-chain. Consequently, the polymers prepared in this manner open the way to speciality polymers such as side-chain liquid crystalline polymers and selective gas permeable membranes.[2]



Scheme 1

Noteworthy, furthermore, is that the lithium silanolates are formed as the intermediates during the procedure. Isolation of the silanolates or the corresponding silanols has been considered to be difficult and, thus, these compounds have scarcely been studied in organic synthesis.[3] We thus focused on the synthetic utilization of the silanolates or the silanols. Since alkenylsilanols are the silicon analogs of allylic alcohols, we envisaged that the olefinic group of alkenylsilanols might be modified in a manner similar to allylic alcohols.[4] Furthermore, transformation of the silicon moiety to various functional groups would also be possible. On the basis that the Simmons-Smith cyclopropanation of the olefin of an allylic alcohol is accelerated by the neighboring hydroxy group,[5] we expected a similar rate enhancement of the cyclopropanation of alkenylsilanols. We herein wish to report the Simmons-Smith reaction of alkenylsilanols and the subsequent transformation to cyclopropanols.

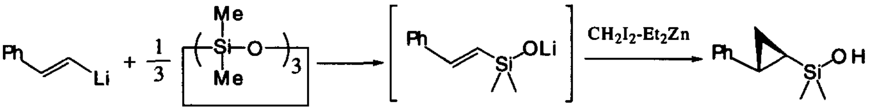


1a **2a**

The reaction of an alkenylsilanol **1a**[1] was examined using diethylzinc (1.0 mol) and diiodomethane (2.0 mol). Among several solvents examined, diethyl ether, dichloromethane and hexane were found to be suitable. THF and DMF, on the other hand, were not appropriate solvents to effect the cyclopropanation. As observed in the Simmons-Smith reaction of allylic alcohols, the hydroxy group on silicon also enhanced the reaction. Indeed, it is noted alkoxysilane (**1b**), disiloxane (**1c**) and vinyltrimethylsilane,[6] lacking a hydroxy group, did not undergo the cyclopropanation under similar conditions. Although Charette reported that the addition of a Lewis acid accelerated the cyclopropanation of allylic alcohols,[7] such effect was not observed in the cyclopropanation of the alkenylsilanols.

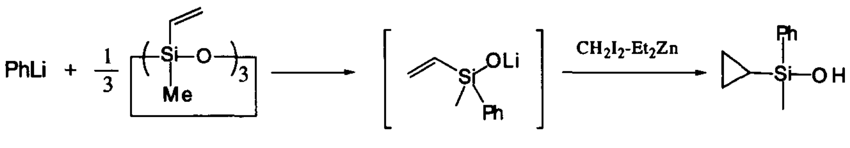
Alkenylsilanols having various substituents were similarly prepared by the reaction of the corresponding alkenyllithium with hexamethylcyclotrisiloxane (D$_3$) and subjected to the Simmons-Smith cyclopropanation to yield the corresponding cyclopropylsilanols in moderate to good yields. Results are summarized in Table 1.

It should be pointed out that the lithium silanolate also underwent the cyclopropanation. Thus, the cyclopropanation as well as the preparation of alkenylsilanols could be effected in one-pot. The reaction of **3** with 1/3 molar D$_3$ in diethyl ether furnished the corresponding silanolate which, without isolation, was successively treated with diiodomethane (3.0 mol) and diethylzinc (2.0 mol) to give the corresponding cyclopropane **2a** in 70% yield.



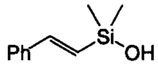
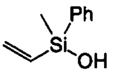
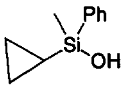
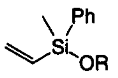
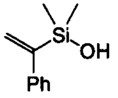
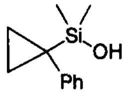
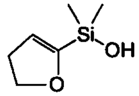
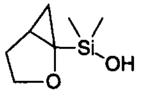
3 **2a** (70%)

Lithium methyl(phenyl)vinylsilanolate obtained by the reaction of $[CH_2=CHSi(Me)\text{-}O]_3$ with phenyllithium also underwent the cyclopropanation by treatment of $CH_2I_2\text{-}Et_2Zn$ to give **4** in 52% yield.



4 (52%)

Table 1. Cyclopropanation of alkenylsilanols and their ethers[a]

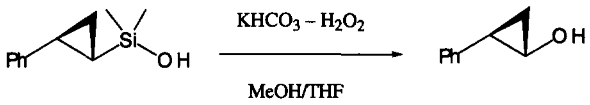
Substrate	Product	Time (h)	Yield(%)[b]
		6	70
		6	60
	—		
1b $(R=CH_2CH_2Ph)$		12	trace
1c $(R=SiMe_2Ph)$		24	0
		6	35
		2	63

a) All the reactions were carried out at room temperature in diethyl ether under an argon atmosphere.

b) Isolated yields are given. The low yields are probably due to the difficulty of isolation. Most of the reactions proceeded quantitatively.

The cyclopropylsilanols, thus obtained, were transformed to cyclopropanols by the Tamao oxidation.[8] For example, silanol **2a** was converted to the corresponding alcohol **5** in 48% yield. Studies on other transformations of the cyclopropylsilanols are in progress in our laboratories.[9]

In summary, alkenylsilanols are transformed to cyclopropylsilanols by the Simmons-Smith cyclopropanation using diethylzinc and diiodomethane. As in the case of allylic alcohols, the silanol functionality was found to enhance the rate of cyclopropanation compared with that of alkenyltrialkylsilane or alkoxydialkylsilane. Lithium alkenylsilanolates also undergo the Simmons-Smith cyclopropanation. Accordingly, one-pot preparation of cyclopropylsilanols from cyclic trisiloxane and alkenyllithiums is established.



2a **5** (48%)

References and notes

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6 The Simmons-Smith reaction of vinyltrimethylsilane using Et_2Zn/CH_2I_2 is reported to proceed at higher temperatures. See ref 5a.

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9 So far, attempts at protodesilylation with some fluoride reagents have been unsuccessful.

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