

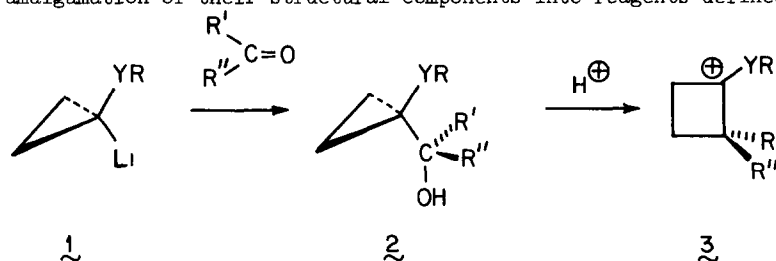
SILICON IN ORGANIC SYNTHESIS. 13. The 1-TRIMETHYLSILYLCYCLOPROPYL ANION AND ITS FORMAL EQUIVALENT¹

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Summary: Reaction of lithio 1-trimethylsilylcyclopropane or its formal equivalent [$\text{CH}_2 = \text{C}(\text{Li})\text{SiMe}_3$, CH_2I_2 , EtZnI] with carbonyl compounds leads to carbinols which dehydrate without rearrangement. Other attempts to induce ring expansion of the silicon substituted three-membered ring by ionic pathways are reported.

Because of their unique chemical properties, heteroatom stabilized organometallics and functionalized cyclopropanes have independently evolved to become highly useful instruments in organic synthesis. The versatility of both classes of intermediates has been recently amplified by amalgamation of their structural components into reagents defined by formula 1.

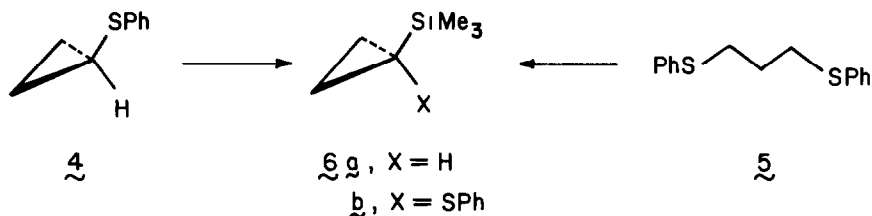


1, YR = SPh; 2, YR = OCH₃; 3, YR = SeCH₃, SePh; 4, YR = Si(CH₃)₃

Methods for the preparation of 1-lithiocyclopropyl phenyl sulfide (1a), methyl ether (1b), and alkyl/aryl selenide (1c) have been developed in the Trost,³ Cohen,⁴ and Krief⁵ laboratories, respectively. The adducts of all three anions with carbonyl compounds, i.e., 2a-c, are subject to ring expansion under acidic conditions and deliver cyclobutanes, cyclobutenes, and cyclobutanones from rearranged carbocations 3.

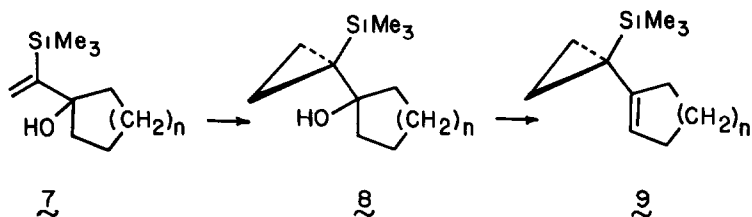
Despite the current widespread upsurge of interest in organosilicon chemistry, surprisingly little attention has been paid to the chemistry of silylcyclopropanes.⁶ The chemical versatility of carbinols 2a-c provided us with the incentive to develop syntheses of 1d and 1e. Herein and in the accompanying paper,⁷ we point out the boundaries of our present knowledge in this area.

Quite unlike 4, trimethylsilylcyclopropane (6a)⁸ does not undergo deprotonation at its α cyclopropyl site⁹ under a variety of conditions, including prolonged exposure to *sec*-BuLi and TMEDA in THF solution.¹⁰ On the other hand, reductive lithiation¹¹ of 6b with lithium naphthalenide in THF at -78°C nicely overcomes the lack of proton acidity in 6a

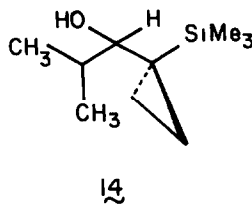
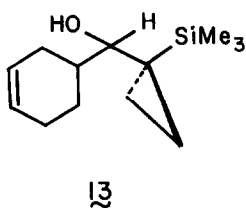
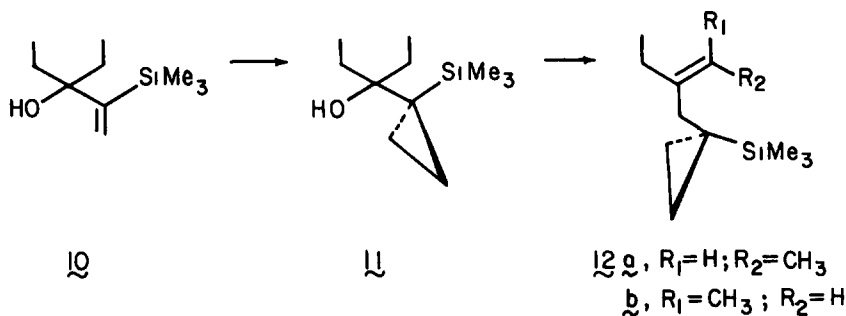


and delivers the silylated anion 1d. Disubstituted cyclopropane 6b can be readily prepared in large quantities either by deprotonation of 4³ followed by addition of chlorotrimethylsilane (88%) or, more conveniently, by sequential treatment of 5 with 2 equivs of *n*-butyllithium¹² and Me_3SiCl (85%).

The addition of 1d to carbonyl compounds proceeds uneventfully, although chromatographic separation of the resulting carbinols from naphthalene proved necessary.¹³ Some dehydration to 9 and 12 (not encountered with the secondary derivatives 13 and 14) was observed during the latter operation. Chiefly to bypass the need for chromatography, an alternative route



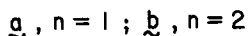
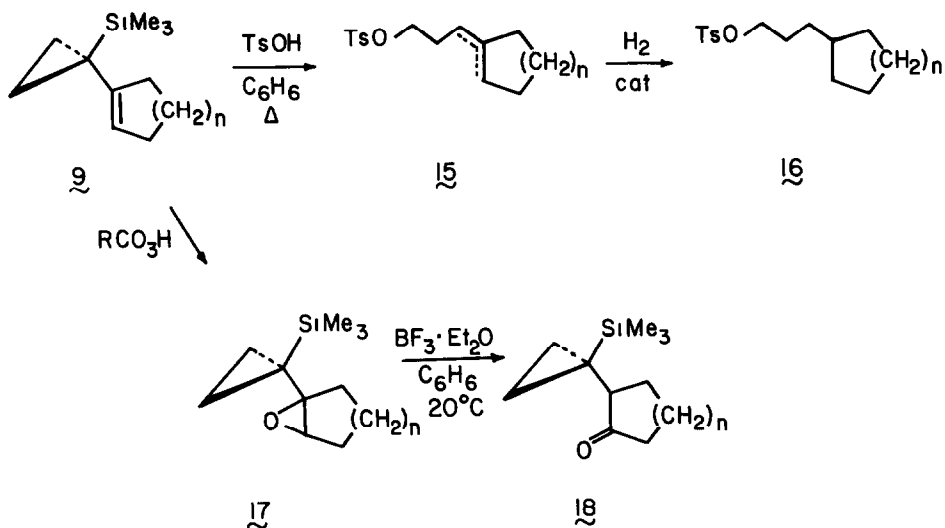
a, $n=1$; b, $n=2$



involving addition of α -lithiovinyltrimethylsilane to various ketones and aldehydes was concurrently examined.¹⁴ The product alcohols (7, 10, etc) underwent smooth cyclopropanation ($\text{C}_2\text{H}_5\text{ZnI}$, CH_2I_2 , 25°C ; NH_4Cl , H_2O)¹⁵ to again provide 8 and 11. Dehydration of the highly reactive tertiary carbinols without rearrangement was also encountered to some extent in

these experiments.

The latter approach is currently preferred because of higher degrees of reproducibility and greater ease of purification. Routinely the carbinols have been directly dehydrated with catalytic amounts of *p*-toluenesulfonic acid in benzene at 20°C. The overall yields of vinylcyclopropanes¹⁸ from carbonyl precursors fall in the range of 52-75%. No evidence was found for the occurrence of ring expansion processes under these conditions. In the case of 11, an *ca* 1:1 mixture of *Z* [12a; ¹H NMR (δ, CDCl₃) 1.75 (dt, *J* = 7 and 1 Hz, 3H), 1.08 (t, *J* = 7 Hz, 3H)] and *E* [12b, ¹H NMR (δ, CDCl₃) 1.66 (d, *J* = 6 Hz, 3H) and 1.08 (t, *J* = 7 Hz, 3H)] isomers was formed. Their separation was achieved by VPC, the individual



structural assignments rest convincingly upon their thermal behavior.⁷

When 9a was heated at the reflux temperature with 1 equiv of *p*-TsOH in benzene for 30 min, an 87% yield of isomerically pure cyclopentylidene tosylate 15a (exocyclic double bond only) was isolated. The cyclohexenyl analogue (9b) behaved comparably, except that a mixture of exo- and endocyclic isomers (15b) was formed.¹⁷ Structural confirmation was achieved by catalytic hydrogenation to 16 and direct comparison with authentic samples. Although several mechanisms can be advanced to account for the 9 \rightarrow 15 transformations, cyclopropane ring expansion is not one of them.

Equally informative was the response of epoxides 17a and 17b to the action of boron trifluoride etherate in benzene solution (20°C, 2-4 hr). Although cyclopropylcarbanyl cations presumably again intervene here, isomerization to 18a (100%) and 18b takes decided precedence. Accordingly, the energetic costs of positioning a positive charge α to silicon¹⁸ as in 3d are not outweighed by the imminent possibilities for strain relief.¹⁹

References and Notes

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- (19) We thank the National Science Foundation and the National Institutes of Health for their financial support of this research.

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