Chemical Reviews

Silyl-Substituted Cyclopropanes as Versatile Synthetic Reagents

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I. Introduction

Three-membered carbocyclic rings hold a particularly prominent position for theoretical, mechanistic, and synthetic chemists alike. Because a cyclopropyl unit possesses "double bond character" and consequently resembles most closely a vinyl substituent, interesting and useful electronic interactions are often brought into play. The high level of strain that is simultaneously present lends itself to chemical reactivity not otherwise attainable. Accordingly, it comes as no surprise that cyclopropanes have served extensively as probes of chemical reactivity, as substrates for varied theoretical analyses, and as utilitarian synthons in organic synthesis.

In recent years, there has occurred a widespread upsurge of interest in the application of organosilicon reagents to new synthetic transformations.[1] This activity has undoubtedly stimulated interest in the use of silylcyclopropanes not only as novel reagents in their own right,[2] but also as important new tools for molecular construction. Although the parent system 1 was
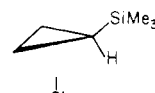
first prepared in 1962,[3] the subsequent decade was witness only to the intermittent development of alternative approaches to simple silicon-substituted three-membered rings. More recently, however, an increasing number of original publications devoted to the preparation, application, and mechanistic understanding of silyl-substituted cyclopropanes has appeared. A rather diverse range of chemistry has already surfaced. It is the intent of this review to define the boundaries of our present knowledge of this area. The emphasis will be heavily synthetic rather than mechanistic. The aim is to alert synthetic organic chemists to the recognized properties of this class of molecules and thereby to promote their utilization as intermediates in future synthetic undertakings.

## II. Synthetic Protocols

A. Cyclopropylsilanes

One of the historically most revered and extensively studied methods of silylcyclopropane construction involves the insertion of Me₃SiCH: or its equivalent into a carbon–carbon double bond. Two methods have proven to be especially convenient and in some respects complementary. The first involves use of (trimethylsilyl)diazomethane (2), a relatively stable (bp 95 °C at 760 torr)[4] and commercially available[5] reagent. Although this substance was originally available via one of several multistep syntheses,[4-7] two abbreviated alternatives have recently become available that allow the convenient preparation of multigram quantities. Barton and Hoekman have reported that metallation of (chloromethyl)trimethylsilane and condensation of the resulting anion with tosyl azide produces 2 in 38% yield.[8]

Leo A. Paquette was born in Worcester, MA, on July 15, 1934. He received the B.S. degree magna cum laude from Holy Cross College in 1956 and was awarded the Ph.D. in Organic Chemistry by the Massachusetts Institute of Technology in 1959. After serving as a Research Associate at The Upjohn Company from 1959 to 1963, he joined the faculty of the Ohio State University as Assistant Professor and from 1969 to 1981 has been Professor of Chemistry there. Since 1981, he has held the title Kimberly Professor of Chemistry.

Dr. Paquette has been a Visiting Professor at Michigan State University (1968), the University of Iowa (1970), the University of Colorado (1974), the University of California at Santa Barbara (1975), the University of Groningen (1975), Texas A&M University (1979), Northwestern University (1981), and the University of Heidelberg (1984). He has served in an advisory capacity on the Chemistry Division Advisory Committee of the National Science Foundation and the Medicinal Chemistry B Study Section of the National Institutes of Health, and as a member of the editorial boards of the *Journal of Organic Chemistry*, *Mechanisms of Reactions of Sulfur Compounds*, and *Chemical Reviews*. During 1984, he served as chairman of the Columbus Section of the American Chemical Society. Currently, he is a member of the editorial boards of *Organic Reactions*, *Organic Syntheses*, *Synthetic Communications*, and *Current Abstracts of Chemistry and Index Chemicus*. Other current activities include membership on the Board on Chemical Sciences and Technology of the National Research Council and on the Medicinal Chemistry Study Section of the NIH.

In 1965, Professor Paquette was named a Fellow of the Alfred P. Sloan Foundation. On several occasions, he has been honored by the Americal Chemical Society: Morley Medalist of the Cleveland Section in 1971, recipient of the Columbus Section Award in 1979, and the national Award for Creative Work in Synthetic Organic Chemistry in 1984. He was the holder of a Guggenheim Fellowship during the 1976–77 academic year and was elected to the National Academy of Sciences in 1983. In 1980, The Ohio State University awarded him its prestigious Senior Research Award, and in 1984, he was presented an honorary degree by his alma mater. He has been the Chairman of the Gordon Conference on Heterocyclic Compounds (1969) and a Plenary Lecturer at numerous conferences in the U.S. and abroad. He is the author of 630 research papers in organic chemistry and has more than 40 patents to his credit.
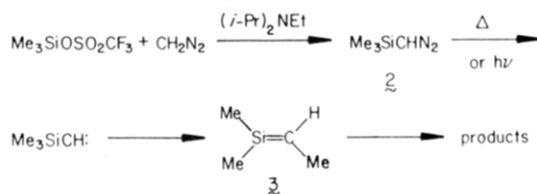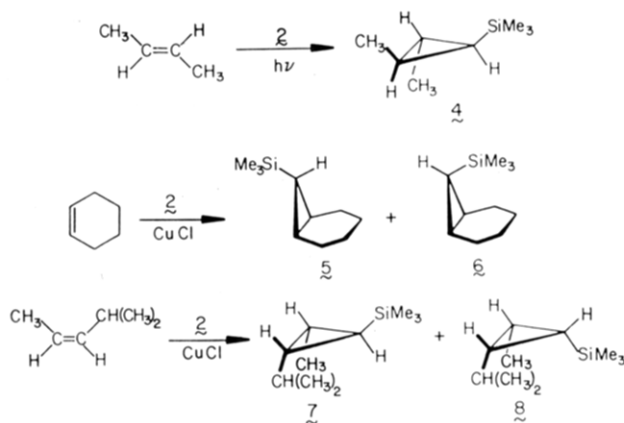

More expedient still is Martin's procedure involving mixing of equimolar amounts of trimethylsilyl triflate and diazomethane in the presence of diisopropyl-ethylamine. The quantity of redistilled **2** isolated amounts to 74%.[9]

When **2** is thermolyzed in the gas phase or photolyzed in solution, conversion to (trimethylsilyl)carbene occurs. Methyl migration ensues to give 2-methyl-2-sila-2-

butene (**3**) and products thereof.[10–12] Hazeldine and his co-workers have demonstrated that if the photolysis of **2** is performed in an alkene medium, the carbene can be intercepted.[13] As is illustrated for *trans*-2-butene (1:3 molar ratio), **4** could be isolated in 23% yield. The stereospecific addition was taken as evidence for formation of the carbene in its singlet state during the photochemical decomposition.

More convenient is the cuprous chloride-induced denitrogenation of **2**.[6] Under such conditions, cyclohexene is converted to a 13:1 mixture of **5** and **6**, and *cis*-4-methyl-2-pentene is similarly transformed into **7** and **8** (3.4:1) without loss of stereochemistry. A pref-


erence for formation of the less sterically hindered cyclopropane is invariably found. A drawback to this methodology is the operation of competitive dimerization of the carbene to *cis*- and *trans*-1,2-bis(trimethylsilyl)ethylenes. In those instances where the products are of low molecular weight, these contaminants can prove difficultly separable. This complication is not encountered in the Olofson method.

The useful process developed by the Penn State group involves deprotonation of chloromethyltrimethylsilane with lithium 2,2,6,6-tetramethylpiperidide in hexane solution.[14] The second stage of the 1,1-elimination reaction is completed by heating at the reflux temperature, the liberated singlet carbene or carbenoid then inserting stereospecifically into the olefin present as it is generated (see **9** and **10**). Only trace amounts of the disilylethylenes are produced under these conditions.

A direct and detailed comparison of the two silyl carbene trapping procedures has been made by Daniels and Paquette.[15] Their work has revealed that the anionic approach generally gives 5–10% higher yields of the desired cyclopropanes. One limitation of this methodology did, however, surface. Whereas treatment of 1,4-dihydronaphthalene with (chloromethyl)trimethylsilane and lithium 2,2,6,6-tetramethylpiperidide resulted in formation of a mixture of allylic C–H insertion products, direct conversion to **11** was achieved uneventfully by means of the Seyferth method.

The cuprous chloride catalyzed addition of (trimethylsilyl)diazomethane to 1,3-cyclohexadiene and to cyclobutene has been reported to give **12**[16] and a 4:1 mixture of **13** and **14**, respectively.[17]

The action of sodium or potassium vapor on $Me_3SiCHCl_2$ is reputed to produce the same carbene.[18] Although this chemistry was not applied in a synthetic context, an interesting and useful intramolecular variant
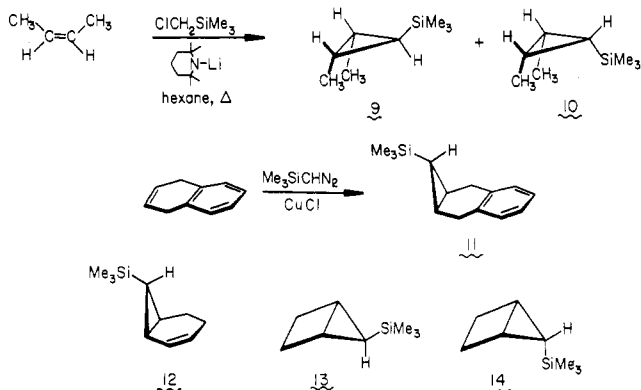
has recently made its appearance. Thus, exposure of **15a** to methyllithium in ether at 20–35 °C has been
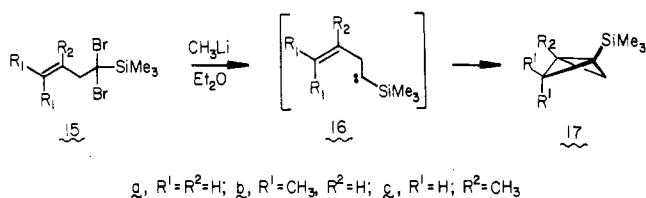
found to give bicyclobutane **17a** in 47% yield. The higher homologues **17b** (53%) and **17c** (48%) were analogously prepared.[19] Thus, trapping of the reactive center in **16** by the proximate double bond is relative efficient.

Simmons–Smith cyclopropanation of vinylsilanes constitutes an entirely practical synthesis of cyclopropylsilanes.[3,20-25] The method is tolerant of as many as three alkoxy groups on silicon. Subsequent exchange reactions can result in acquisition of potentially serviceable intermediates. The **18** → **20** transposition is
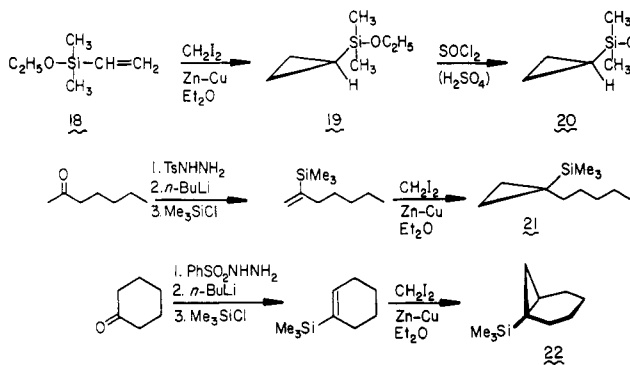
illustrative.[21] Futhermore, when this procedure is implemented subsequent to a ketone arenesulfonyl-hydrazone → vinylsilane transformation,[26-28] a wide variety of 1,1- and 1,2-dialkylated products such as **21** and **22** can be obtained.[15]
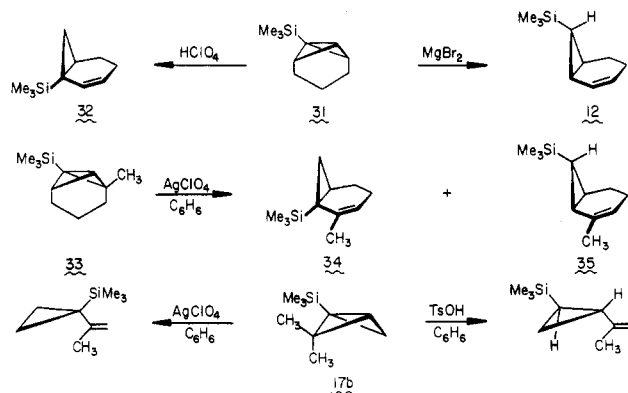
In a related context, Mironov and co-workers have demonstrated that the irradiation of diiodomethane in trimethylvinylsilane can also lead to 1, although the yield (11%) is unimpressive.[21]

Another useful entry to cyclopropyl silanes entails treatment of cyclopropyllithium reagents with chloro-trimethylsilane and related electrophiles.[29,30] As concerns cyclopropyllithiums, one is dependent upon initial halogen–metal exchange within the bromide precursor. However, when the acidity of the relevant protons is increased, the requisite anions are available by direct deprotonation. The behavior of methylenecyclopropane
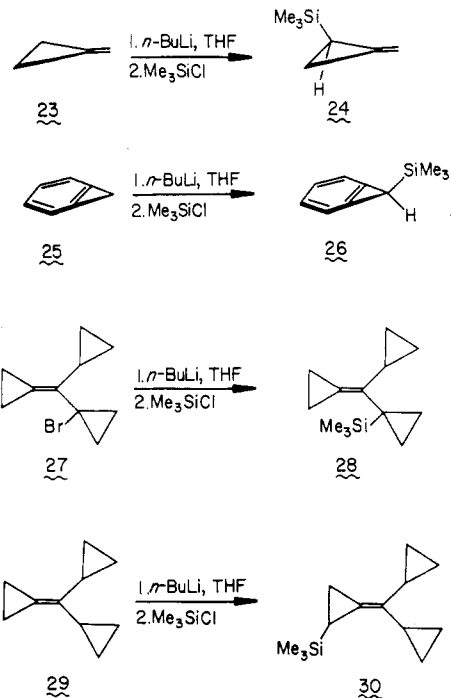
(23)[31] and cyclopropabenzene **(25)**[32,33] nicely illustrates this more direct functionalization scheme. A Russian group has demonstrated how these two processes can take on complementary aspects. Thus, silylation of the lithium reagent derived from bromide **27** leads to **28**.[34] In contrast, direct metalation of the parent hydrocarbon **(29)** results instead in regioselective deprotonation of the unsaturated three-membered ring and delivers ultimately the isomeric allyl silane **30**.[35]

Rearrangement reactions are also recognized to offer useful synthetic advantages. A case in point is the response of **31**, obtained by silylation of 1-lithio-

tricyclo[4.1.0.0^{2,7}]heptane, to acidic reagents of various type. Exposure to catalytic quantities of 70% perchloric acid in benzene, for example, leads instantaneously to **32**. With p-toluenesulfonic acid, a mixture of **12** and **32** is formed.[16] In contrast, ethereal magnesium bromide promotes isomerization only to **12**. When an additional methyl substituent is present as in **33**, a catalytic quantity of silver perchloratte in benzene promotes conversion to a 9:1 mixture of **34** and **35**.[16] Bicyclobutane **17b** behaves comparably.[19]

Addition of freshly sublimed aluminum chloride (10 mol %) to solutions of (chloromethyl)vinylsilanes in dichloromethane at room temperature often results in rearrangement to cyclopropylchlorosilanes.[36,37] Subsequent methylation with CH$_3$MgBr delivers cyclo-

propylsilanes such as 36–38. The product distributions
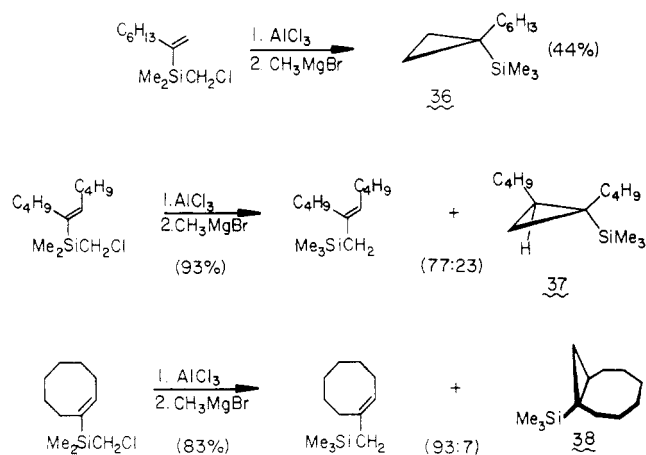
appear to be determined by the relative stabilities of the α- and β-silyl carbocation intermediates.

Sakurai has recently demonstrated that irradiation of molecules such as 39 and 40 can result in photoinduced 1,2-silyl migration and formation of structurally unusual silylcyclopropane structures.[38]
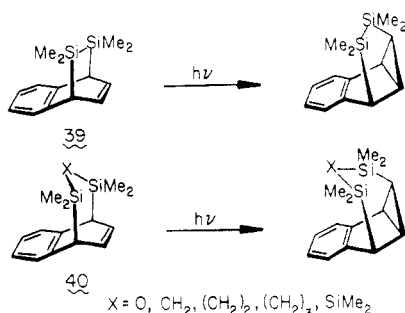
## B. 1,1-Bis(silylated) Cyclopropanes

A simple, general, and efficient route to *gem*-disilylcyclopropanes[39] consists of reacting dichlorocyclopropanes with lithium metal and chlorotrimethylsilane in tetrahydrofuran solution.[40–42] The substitution of potassium 1-(dimethylamino)naphthalenide is substantially less effective in producing 41 cleanly.[43] Also
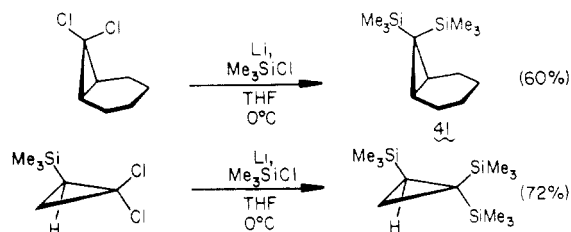
somewhat less satisfactory from the preparative viewpoint is the combination of 1,1-dibromocyclopropanes with chlorotrimethylsilane and magnesium metal, since monosilylated cyclopropanes and silylated ring-opened products are formed concurrently.[44] The eventual product distribution appears to be controlled by the extent and site of alkyl substitution.
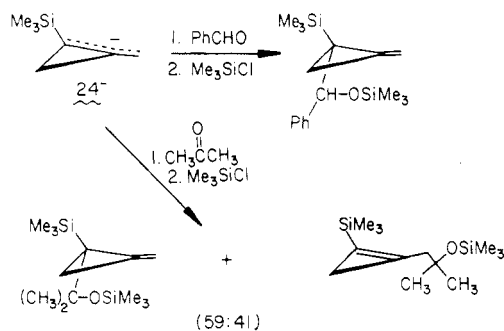
The facility with which silicon stabilizes an α-anion can offer ready synthetic entry to this class of compounds. To illustrate, quenching of the anion derived from 42 with 1 equiv of chlorotrimethylsilane delivers 44 and not 43.[33] Since unreacted 42 is recovered from this reaction, it would seem that 43 is deprotonated immediately upon its formation by the anion of 42.

Although 42⁻ offers no opportunity for assessing the regioselectivity of electrophilic capture in these highly strained systems, the anion 24 does. With *n*-butyllithium as the base, 24⁻ proceeds to give 45 and 46 in an 88:12 ratio (74% yield) alongside the trisilyl derivative 47 (13%).[31] For comparison, alkylation of 24⁻
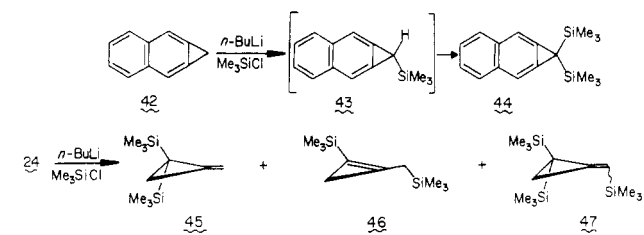

with various halides results only in formation of α-silylated products related to 45. These results differ somewhat from the known reactivity of allylsilane anions where γ-alkylation predominates, likely because of the greater ring strain associated with cyclopropenes as compared to methylenecyclopropanes. That some 46 results at all is probably due to steric factors arising from geminal disilylation that inhibits this anion from reacting exclusively with chlorotrimethylsilane at the α-position.

In contrast, 24⁻ reacts with benzaldehyde and with acetone in the manner illustrated.[31] An electron-

transfer mechanism[45] has been invoked to rationalize these findings. Although this may be accurate, additional research is required to fully comprehend the scope of such processes and the underlying cause for exclusive coupling of the benzaldehyde radical anion and the radical cation of 24⁻ at the γ-position.[46]

Fleming and Floyd have uncovered an example of a bis(silylated) cyclopropane-forming reaction that constitutes a formal homo-Peterson reaction (the only known example). Where tris(trimethylsilyl)lithium is
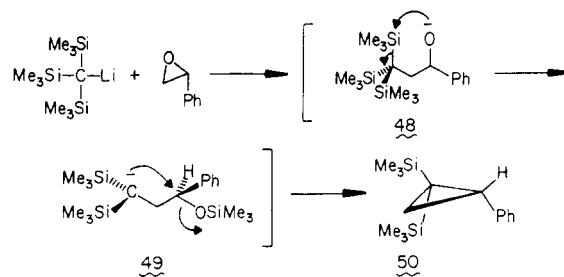

allowed to condense with styrene oxide, alkoxide 48 is produced. A 1,4-silyl shift presumably ensues to generate carbanion 46, cyclization of which by intramolecular displacement of trimethylsilyl oxide anion leads to 50.[47] This process appears not to be general, seem-

ingly because the final step is feasible only at a secondary benzylic site.

## C. Functionalized 1-(Trimethylsilyl)cyclopropanes

A reagent that attracted early attention is the silicon-substituted organomermercurial $(Me_3SiCCl_2)_2Hg$, heating of which in hot (120 °C) bromobenzene for 6 days results in slow thermal decomposition to (trimethylsilyl)chlorocarbene.[48] In the presence of cyclohexene, the single adduct **51** is formed in 24% yield. If
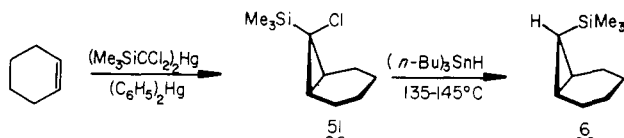
a molar equivalent of diphenylmercury is also added, the yield of **51** increases to 62%. These conditions have been successfully applied to cyclooctene (73%) and to allyltrimethylsilane. However, the Me_3SiCCl adduct of 2,3-dimethyl-2-pentene proved insufficiently stable to the rather drastic reaction conditions to survive. Tri-n-butyltin hydride reduction of **51** leads chiefly to **6**, the minor product of direct Me_3SiCH: insertion.

Analogously, $(Me_3SiCBr_2)_2Hg$ reacts with cyclohexene at 95 °C in the presence of diphenylmercury to give 7-bromo-7-trimethylsilylnorcarane in 36% yield. However, $(Me_3SiCHBr)_2Hg$ is too stable, even at 160 °C, to serve as a divalent carbon transfer agent.[48]

Schöllkopf and co-workers have made the interesting discovery that mercury bis(diazoethylacetate) (**52**) is capable of smooth reaction with bis(trimethylsilyl)-sulfide to give (trimethylsilyl)diazoethyl acetate (**53**, 82%).[49] As expected, **53** is characterized by unusual
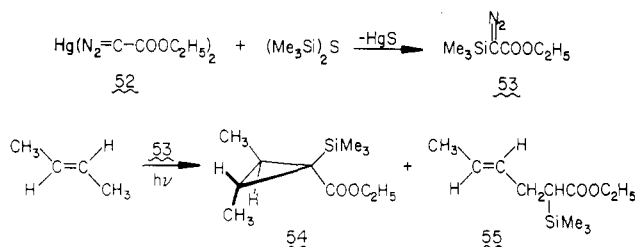
thermostability and undergoes [3 + 2] cycloaddition to dimethyl fumarate more slowly than does ethyl diazoacetate. On the other hand, **53** readily decomposes when photochemically irradiated. The resulting carbene adds with ca. 95% cis stereoselectivity to olefins to give 1-trimethylsilyl-1-ethoxycarbonylcyclopropanes such as **54** (41%). The concurrent formation of side products of type **55** signals that this reactive intermediate also inserts easily into C–H bonds.

The chemical versatility of cyclopropylcarbinols has provided considerable incentive for the development of routes to silylated analogues. Quite unlike cyclopropyl phenyl sulfide, which undergoes ready deprotonation at its α-cyclopropyl site under a variety of conditions,[50] 1 is inert to strong bases[51] including prolonged exposure to sec-butyllithium and TMEDA in tetrahydrofuran solution.[52] Consequently, a comparably direct route to the 1-(trimethylsilyl)cyclopropyl anion is not available. However, because (α-bromovinyl)trimethylsilane can be conveniently prepared in large quantities[53] and readily coaxed into halogen–metal exchange with tert-butyl-

lithium in ether at −78 °C,[54] the first synthetic entry made use of organometallic **56**.[52,55,56] Its addition to
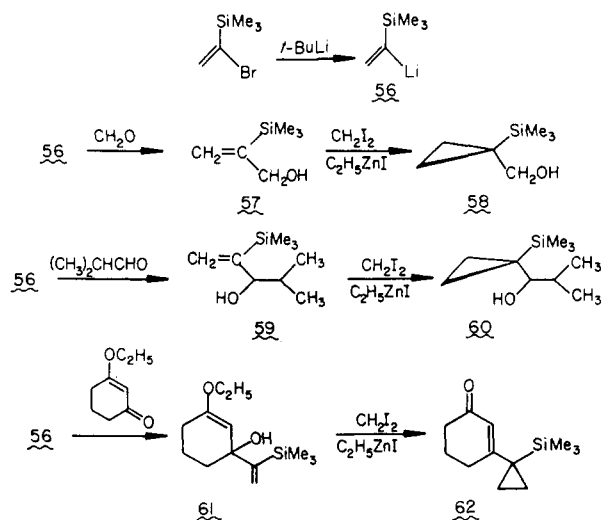

carbonyl compounds and epoxides proceeds uneventfully. Products such as **57**, **59**, and **61** undergo Simmons–Smith cyclopropanation best when the modified form of this procedure that utilizes ethylzinc iodide[57] is applied.

The lack of proton acidity in 1 can also be readily overcome by reductive lithiation[8] of **65** with lithium naphthalenide[52,55] or 1-dimethylaminonaphthalenide (LDMAN).[55,59] The bifunctional cyclopropane **65** is available in large quantities either by deprotonation of **63** followed by addition of chlorotrimethylsilane (88%)
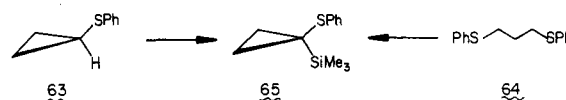

or, more conveniently, by sequential treatment of **64** with 2 equiv of n-butyllithium[60] and Me_3SiCl (85%).

This methodology can be extended to include reductive lithiation of cyclopropanone dithioketals, which are now routinely available by one of the several newer versatile procedures developed by Cohen's group.[61] An example of such a procedure is the reaction of the sulfur-stabilized conjugate base of **66** with **67** to produce
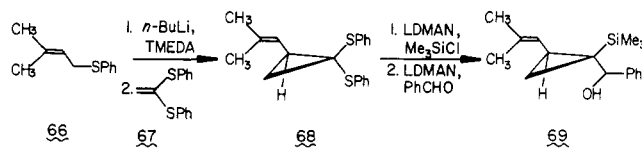

the vinylcyclopropanone dithioketal **68**. The conversion to **69** is then effected as described above.[62]

Very recently, (1-lithiocyclopropyl)trimethylsilanes have been prepared by bromine–lithium[55,63] and selenium–lithium exchange reactions.[64] The preparation of 1,1-dibromocyclopropane from ethylene has been described,[65] but autoclave conditions and an expensive dibromocarbene source must be utilized.[66] These unattractive requirements can be bypassed by making recourse instead to the readily available **70**.[67] Hunsdiecker degradation provides **71**, a low melting solid that undergoes routine lithiation to give **72**.[55] Similarly, Krief has shown that **73** is capable of efficient selenium–metal exchange and silylation to give **74**.[64] This substance can, in its own right, be transformed into the lithio derivative **72**.
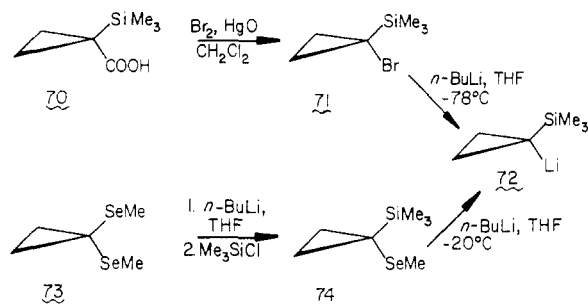
More highly substituted 1,1-dibromocyclopropanes such as 75,[68] 76,[63a] and 78[63b] can similarly be transformed via silyl bromides to 1-(trimethylsilyl)cyclopropyllithium reagents. Whereas 76 experiences exo
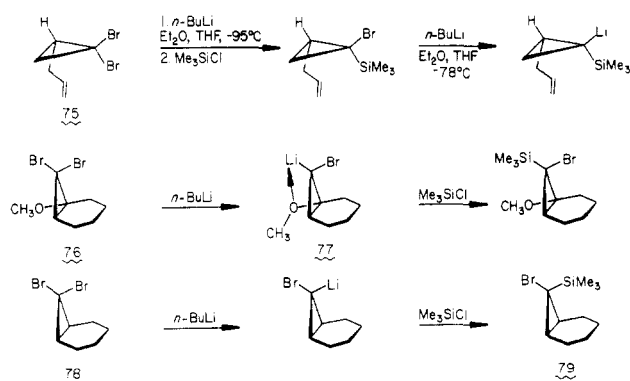
silylation as a direct consequence of coordination within carbenoid 77, the more normal stereochemical outcome is formation of the *endo*-trimethylsilyl product (e.g. 79). This is because the more sterically congested bromine atom in the dibromocyclopropane is usually the more reactive, with lithiation and electrophilic capture occurring with retention of configuration.[69]

Since reductive lithiation of 1-phenylthio-1-(trimethylsilyl)cyclopropanes produces 1-lithio-1-(trimethylsilyl)cyclopropanes, additional methods for directly preparing starting materials of this type provide greater accessibility to these important organometallics. Weber and Neuenschwander have made the unusual and unexplained observation that silylation of the anion of 80 leads chiefly (25%) to 81' instead of 81 (18%).[70] More synthetically useful are two complementary procedures recently developed by Cohen and co-workers.[71] The first of these involves nucleophilic addition of sulfur-stabilized anions to 82,[72] obtained simply by deprotonation–silylation of phenyl vinyl sulfide.[73] The anions so generated (e.g., 83) undergo spontaneous cyclization. The formation of 84–87 illustrates the power of the technique. Alternatively, if the anion (88)[74] of (phenylthio)(trimethylsilyl)methane[75] is allowed to condense with an epoxide, a trans alkoxide results. Without isolation, formation of the benzenesulfonate is carried out and intramolecular S$_N$2 displacement is achieved by exposure to *sec*-butyllithium (2 equiv) in TMEDA at 0 °C.[76] The yields of cyclopropane product such as 89 are 59–69%.[71]

Additional functionalized 1-(trimethylsilyl)cyclopropanes have been obtained by deprotonation–silylation[56] of phosphonium salt 90,[77] flash vacuum pyrolysis
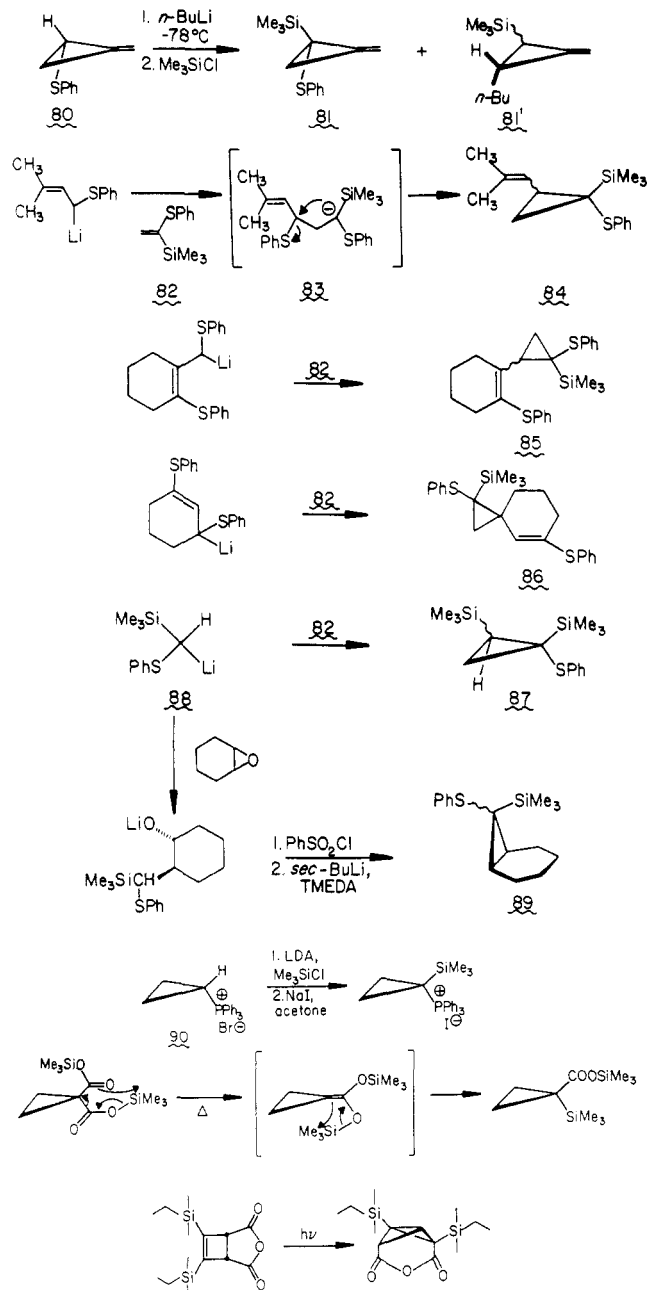
of bis(trimethylsilyl) cyclopropane-1,1-dicarboxylate,[78] and irradiation of silylated cyclobutenedicarboxylic anhydrides.[79]

D. Functionalized 2-(Trimethylsilyl)cyclopropanes

Entries 2 and 3 in Table I indicate that under comparable steric conditions vinylsilanes are somewhat more reactive toward dihalocarbenes than their hydrocarbon analogues. It is not clear that Si is more electron-withdrawing than carbon when attached to a carbon atom with a developing positive charge. Silicon is more electropositive than carbon and should be able to donate electrons better to a positive charge. It is unlikely that silicon stabilizes π bonds significantly better than carbon because this would require utilization of d orbitals which are thought not to be involved.

From a preparative point of view, the success of dichlorocarbene capture is highly reagent-dependent. While the chloroform–potassium *tert*-butoxide combi-

TABLE I. Relative Rates of Dihalocarbene Additions to Vinylsilanes[65,80]

| olefin	PhHgCCl₂Br, 80 °C	CHCl₃, KO-t-Bu, −30 °C	Me₃SnCF₃, NaI, 80 °C
1-heptene	1.00	1.00	1.00
C₂H₅(CH₃)₂CCH=CH₂	0.043		0.12
C₂H₅(CH₃)₂SiCH=CH₂	0.069		0.26
(C₂H₅)₃SiCH=CH₂	0.048		0.15
(CH₃)₃SiCH=CH₂		0.047	

nation usually produces only small quantities of 2-trimethylsilylated 1,1-dichlorocyclopropanes,[80] moderate to good yields can be realized by thermal degradation of phenyl(bromodichloromethyl)mercury in benzene at 80 °C[65,81,82] or of (trichloromethyl)trichlorosilane at 250 °C.[83] Difluorocarbene, as generated by the Me₃SnCF₃–sodium iodide reagent pair in 1,2-dimethoxyethane at 80 °C is also rather efficiently trapped by this class of olefins.[84]

Because use of the mercurial agents on a large scale is unattractive and pyrolysis reactions at 250 °C are impractical, Miller's discovery of the feasibility of phase-transfer conditions for vinylsilane dichlorocyclopropanation is one of major importance.[85] Thus, submission of cis-1-(trimethylsilyl)hex-1-ene to a medium consisting of chloroform–50% sodium hydroxide–Cetrimide at 55 °C for 12 h delivers **91** in 80%
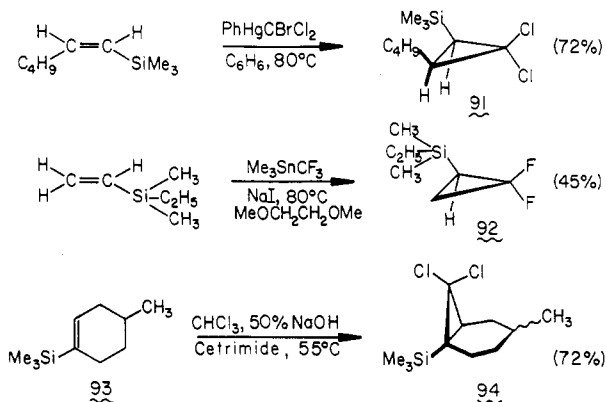

yield. With a trisubstituted vinylsilane such as **92**, a 72% yield of adduct is realized.[85]

The synthetic utility of lithium carbenoids derived from these molecules has been tested with respect to the synthesis of 5,6-dihydrocalicenes. The preparation of **95** is illustrative.[86]
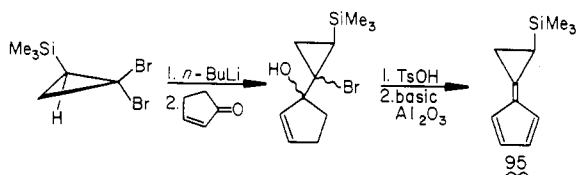
The (trimethylsilyl)sulfurane **96** has been shown to react with α,β-unsaturated ketones to silylcyclopropyl ketones.[87] The yields of product (e.g., **97** and **98**) are moderate. The arsonium ylide **99** behaves comparably toward chalcones.[88]

Slow addition of ethereal diazomethane to (trimethylsilyl)ketene[89] at −130 °C leads to (trimethylsilyl)cyclopropanone (**100**, 50% yield), accompanied by
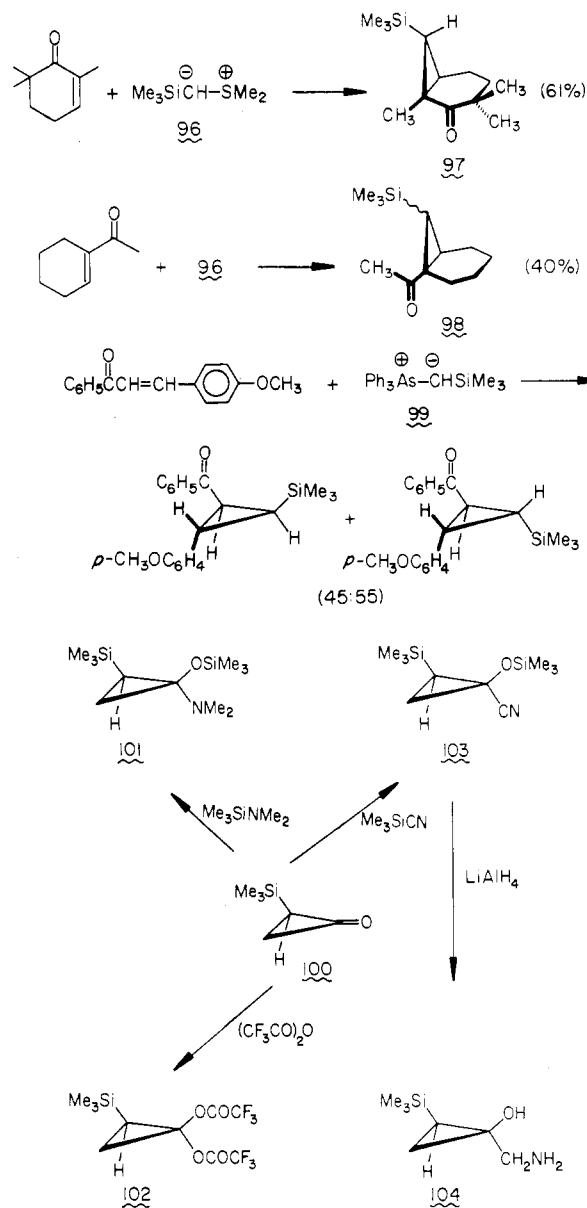

lesser amounts of 2- and 3-(trimethylsilyl)cyclobutanones.[90] Derivatives differently substituted about the silicon atom are also known.[91] Unlike cyclopropanone itself or its methyl derivative, which are stable only for a short time in solutions at low temperature,[92] the silylated cyclopropanones can be isolated by fractionation and stored at 5 °C without decomposition and polymerization for reasonably long periods of time. In stability, they compare closely to the very much less accessible 2,2- and trans-2,3-di-tert-butylcyclopropanones.[93] This last fact suggests that steric factors may contribute partially for the enhanced stability of these otherwise reactive compounds. Another parameter that merits consideration is the well-recognized ability of silicon to stabilize a β-carbocationic center.

Cyclopropanone **100** reacts practically instantaneously with alcohols and amines at −60 to −78 °C to give carbonyl addition products.[91] Isomerization to ring-opened compounds occurs upon heating. More powerful electrophiles such as bromine promote direct ring fission. Nonetheless, a group of reactions are known that occur with preservation of the three-membered ring. Several examples are given by 101–104.[91,94]

III. Functional Group Modifications with Preservation of the Silicon Substituent

The carbinols available from condensation of **72** with ketones undergo dehydration smoothly when treated with catalytic quantities of *p*-toluenesulfonic acid in benzene at 20 °C. The overall yields of vinylcyclopropanes such as **105** is 52–75%. No evidence for the
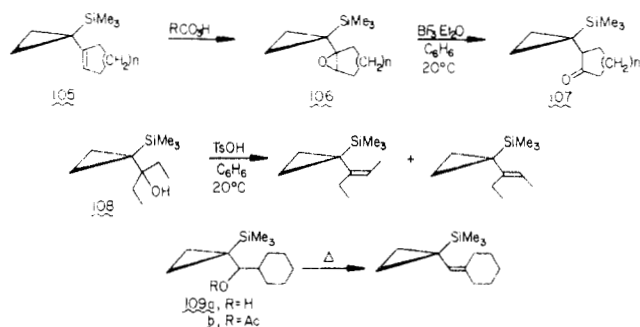
occurrence of ring expansion processes was found under these conditions.[53,55] In the case of **108**, an ca. 1:1 mixture of the *Z* and *E* isomers is formed; their separation can be simply effected by vapor phase chromatography.[53,55] When aldehyde condensation products (e.g., **109a**) are involved, dehydration is more problematical. This complication can readily be bypassed by formation of the acetate (**109b**) and subsequent thermal extrusion of acetic acid at elevated temperatures in the vapor phase.

The cuprate formed by reaction of 1-lithio-1-(trimethylsilyl)-2-benzyloxymethylcyclopropane with dibutylcopperlithium reacts with allyl bromide and acetyl chloride to produce the *cis*-allyl (77%) and *cis*-acetyl derivatives (52%), respectively. Consequently, versatile highly functionalized intermediates are available in this fashion.[63a]

Bifunctional aldehyde **110**, readily accessible by oxidation of **58** with manganese dioxide,[56] diisobutylaluminum hydride reduction of 1-(trimethylsilyl)-cyclopropyl nitrile,[56] or, less efficiently, by condensation of **72** with dimethylformamide,[64] has proven to be a very serviceable electrophilic reaction partner. Condensation with α-lithio selenides[95] at –78 °C proceeds in 80–90% yield to give adducts typified by **111**, whose elimination to **112** is conveniently achieved by exposure to an excess
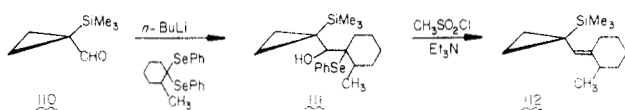
of methanesulfonyl chloride and triethylamine.[96] The process is fully regioselective and delivers only vinylcyclopropanes.

Lithiation of 1-(bromomethylene)cyclobutane followed by condensation with **110** delivers **113**.[97] As
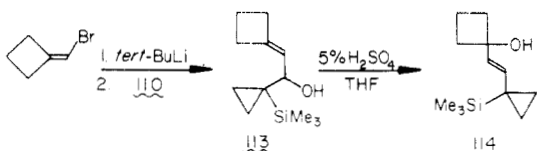
expected from thermodynamic considerations, clean rearrangement of **113** to the more stable isomeric cyclobutanol **114** occurs in the presence of 5% sulfuric

acid. No desilylation intravened during this isomerization.

While direct condensation of **110** with thiophenol or benzeneselenol proceeds to give the corresponding acetals **116a** and **116b** only with low efficiency, exchange reactions involving dimethyl acetal **115** proceed quantitatively.[56] Both **116a** and **116b** can be transformed into their nucleophilic lithium derivatives **117**.
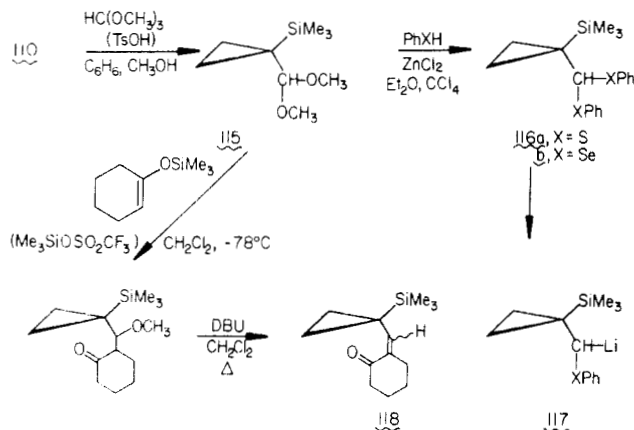

The dimethoxy derivative **115** also enters efficiently into crossed aldol condensations. Admixture with 1-(trimethylsiloxy)cyclohexene in the presence of 1–5 mol % trimethylsilyl trifluoromethanesulfonate followed by β-elimination of methanol with DBU in refluxing dichloromethane containing molecular sieves delivers the conjugated enone **118**.[56]

An additional interesting example of this chemistry is found in the preparation of **119**.[56]
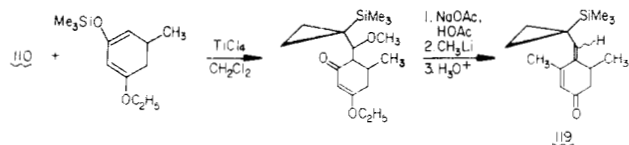

Reductive coupling of aldehyde **110** with zerovalent titanium affords the symmetric olefin **120** in 38% yield.[98] Köbrich and Merkel have described a synthesis of the cis isomer by Lindlar reduction of the corresponding acetylene.[99] An alternative higher yielding pathway to **120** consists in converting bromide **121** to sulfone **123** via sulfide **122**. Subsequent Ramberg–
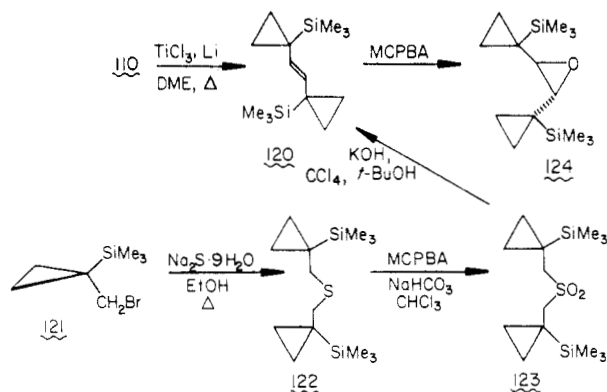

Backlund rearrangement of the α-chlorosulfone derived from **123** reproducibly afforded **120** in 53% yield.[98]

Unsymmetrical coupling of **110** to α,β-unsaturated ketones has also proven to be efficient. Thus, condensation with **125** in the presence of Ti(0) provides **126** as a single stereoisomer.[96,100]
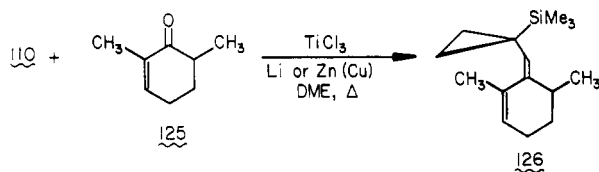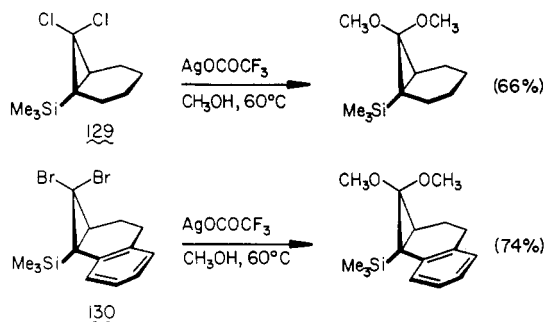
Despite the neopentyl nature of the halogen-substituted carbon in **121**, the substance enters readily into S_N2 displacement reactions.[56] That this bromide is a respectable electrophilic reagent can be seen in the following.
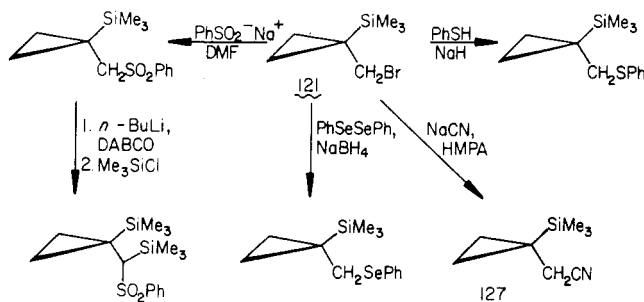
The functional group combination found in **127** has proven useful in the preparation of molecules such as **128**, which incorporates allylsilane and acrylonitrile moieties that work in electronic opposition.[56]
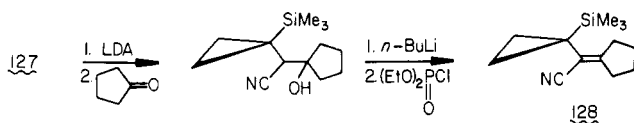
Generally, silver ion-assisted ionizations of *gem*-dihalocyclopropanes result in disrotatory ring cleavage with formation of an allyl cation whose geometry is dependent on the specific halogen that is abstracted.[101] In contrast, treatment of **129**, **130**, and related 1-(tri-


methylsilyl)-7,7-dihalobicyclo[4.1.0]heptanes with silver trifluoroacetate in methanol or ethanol at 0–60 °C gives the corresponding dialkyl acetals resulting from substitution of the intact carbocyclic framework.[102] This unusual chemical behavior is, however, restricted to norcarane derivatives.

IV. Reactions Involving Substitution of the Silicon Group

A. Electrophilic

A trimethylsilyl group so modifies the reactivity of an adjoining cyclopropane ring that certain electrophilic *substitution* reactions which leave the three-membered ring intact are also possible. For example, **1** has been shown to react with iodine monochloride,[103] acyl halides in the presence of aluminum trichloride,[22] and tri-

methylsilylchlorosulfonate[23] to give **131a–c**, respectively.
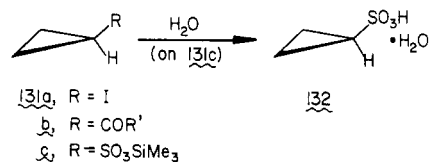
With 48% hydrobromic acid or 92% sulfuric acid, cyclopropane is produced,[21] presumably by a related pathway.

Treatment of **131c** with water eventuates in an exothermic reaction that liberates hexamethyldisiloxane and generates the previously elusive cyclopropanesulfonic acid (**132**).

B. Nucleophilic

Chan and Massuda have relied on the ability of 2-functionalized cyclopropylsilanes to undergo facile β-elimination as the basis for a general cyclopropene synthesis.[104] Upon treating substrates such as **133** and **129** with cesium fluoride in diglyme under nitrogen at 25–80 °C, the cyclopropenes **134** and **135** are formed.
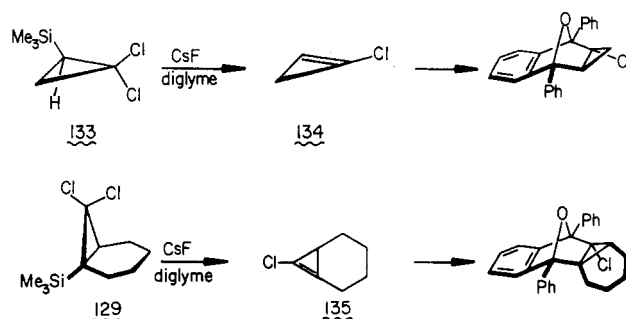

These highly reactive substances can be trapped in situ by suitable dienes such as 1,3-diphenylisobenzofuran.

Trihalide **136**, prepared from α-bromovinyltrimethylsilane,[105] is converted to **137** when exposed to tetra-*n*-butylammonium fluoride in tetrahydrofuran at –20 °C.[106] This cyclopropene reacts readily with cyclopentadiene (80–90%) and **138**; in the latter instance,
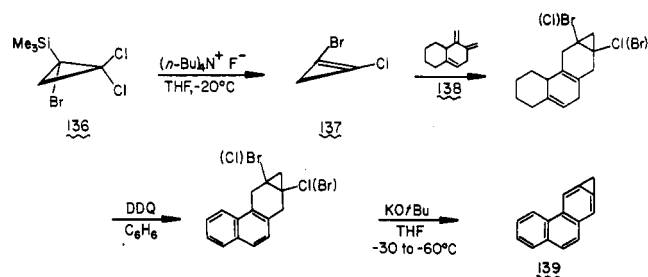

both regioisomers are formed. A convenient synthesis of 1*H*-cyclopropa[*b*]phenanthrene (**139**) has been developed therefrom.[106]

Epoxide **124** undergoes clean monodesilylation with oxirane cleavage when heated with tetra-*n*-butylammonium fluoride in tetrahydrofuran.[98] All attempts to apply Peterson olefination chemistry[107] to β-hydroxy silane **140** under acidic and basic conditions[108] returned unreacted starting material. However, dicyclopropylideneethane (**141**) could be arrived at by reaction instead with thionyl chloride. This reagent induced allylic rearrangement to deliver a chloride whose elimination to give the target diene proceeds in essentially quantitative yield.[98]
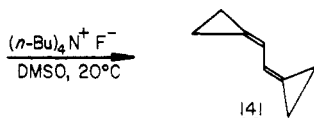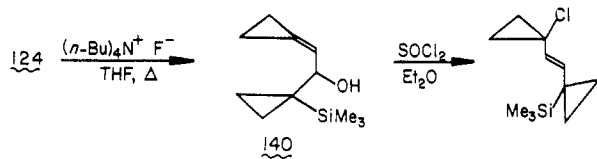
Heating **126** with anhydrous tetra-*n*-butylammonium fluoride and acetone in tetrahydrofuran solution at the reflux temperature generates pentadienyl anion **142**,
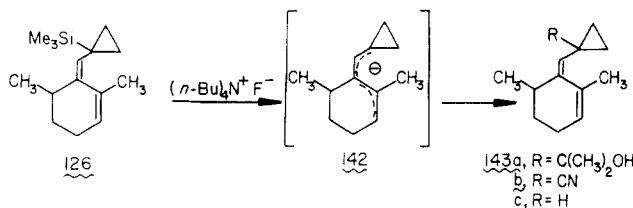
which enters into regioselective electrophile capture at the cyclopropyl carbon atom to give **143a** in order to avoid the development of methylenecyclopropene character.[96,100] With phenyl cyanate as the coreagent, **143b** (69%) and **143c** (20%) result.[96] The high regioselectivity of this new method for carbon–carbon bond formation has been utilized for gaining access to the spirocyclic sesquiterpenes α-vetispirene, hinesol, and β-vetivone.
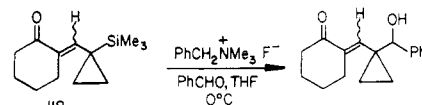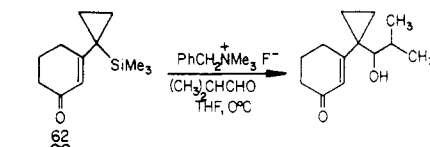
Despite the intrinsically greater acidity of protons attached to cyclopropane rings,[109] cyclopropanes carrying carbonyl, nitro, and sulfonyl groups exhibit markedly decreased equilibrium acidities relative to suitable acyclic models.[110] This is because proton abstraction is accompanied by formation of an exocyclic π bond with a sharp enhancement of ring strain and chemical reactivity. The consequences of these influences are dramatic. Thus, attempts to deprotonate ethyl cyclopropanecarboxylate[111,112] and nitrocyclopropane[112] lead to dimeric and trimeric self-condensation and disproportionation products. Near 50 °C, the dianion of cyclopropanecarboxylic acid[113] undergoes dimerization.[114] Nevertheless, simple electronegatively substituted cyclopropanes are now available for use as basic synthetic building blocks by making recourse to fluoride ion-induced desilylation of their α-(trimethylsilyl)-substituted congeners.[115] The behavior of **144** and **145** is exemplary. The condensation of ketone
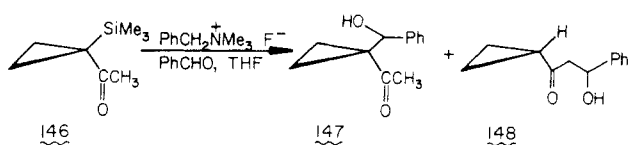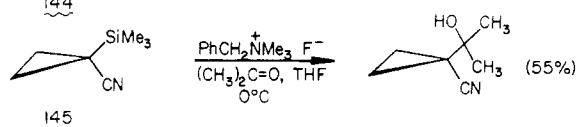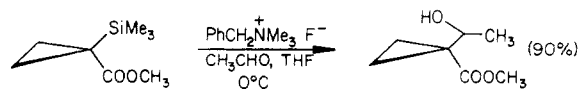
146 with aldehydes in the presence of benzyltri-

methylammonium fluoride delivers **147** and not **148** as the overwhelmingly favored product. Thus, proton transfer is not a serious side reaction during aldol condensation.[115]

The seviceable nature of this methodology is further reflected in the response of the more extended systems **62** and **118**.[115] Although the enolates obtained by de-


silylation of these substrates are certain to be less reactive due to enhanced charge delocalization, they enter usefully into aldol condensation with impressively high regioselectivity. The one restriction is that the electrophilic reagent be relatively inert toward direct reaction with F⁻ at 0 °C for short time periods.

V. Peterson Olefination Chemistry

This section concerns itself with the conversion of silylcyclopropane derivatives to alkylidene cyclopropanes. Earlier, the inability of **140** to undergo direct elimination with formation of **141** was discussed. Intermediate conversion to the rearranged chloride followed by treatment with fluoride ion did, however, proceed in the desired direction.[98] An analogous two-step sequence was employed by Misra to convert both diastereomers of **149** to the methylenecyclopropane analogues **150** of arachidonic acid.[68]
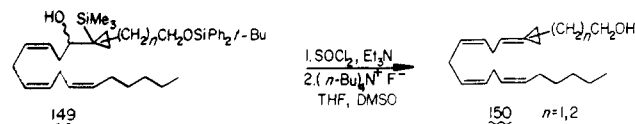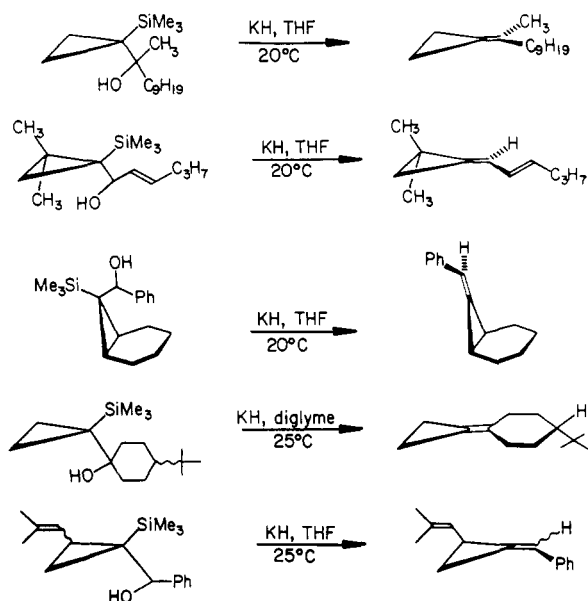

Direct olefin formation from β-hydroxy silanes of this type appears to be highly dependent upon the specific substrate structure and the conditions used. Like **140**, **151** has been recovered unchanged following exposure
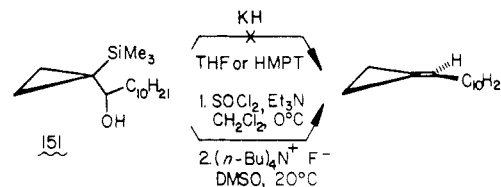
to potassium hydride in THF or HMPT at temperatures up to 60 °C.[64] However, the desired alkylidene cyclopropane is attainable if an intermediate activation step is implemented as before.

The Peterson olefination has proven to be facile and reliable in a number of other instances. It is necessary only to stir the β-hydroxy silane with KH in THF or diglyme at room temperature for 1–20 h. A selection of examples is illustrated below.[62,63b,64]

In some related chemistry, treatment of **44** with potassium *tert*-butoxide[116] and benzophenone or acetophenone in anhydrous tetrahydrofuran results in essentially quantitative conversion to the yellow, crys-

talline methylenecyclopropa[b]naphthalenes 152.[33]
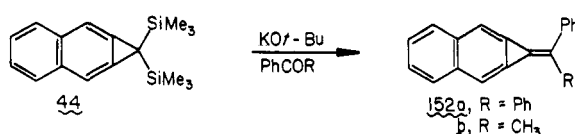
VI. Ring Cleavage Reactions

A. Acid-Promoted Processes

Although silylcyclopropanes show appreciable stability in the presence of a variety of chemical reagents, they do undergo facile ring opening when exposed to anhydrous hydrogen chloride in dichloromethane[15] or carbon tetrachloride[30] at temperatures as low as −78 °C. Bicyclic systems 5 and 153 (as well as their endo isomers) experience regiospecific peripheral bond cleavage, the capture of chloride ion occurring with net inversion of configuration. A corner-protonated cyclopropane intermediate has been invoked.[15] Further suggestion that carbocations were involved came from the response of 155, which was transformed into a 92:8 mixture of 156 and 157 under these conditions.
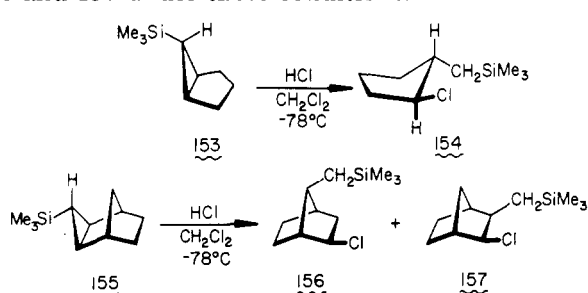
The conversion of 21 uniquely to 159 holds interest since it denotes that nucleophilic attack on an edge-protonated intermediate such as 158 can occur at the silicon-substituted carbon atom if the other option involves an incipient primary carbocation. The situation with 22 is somewhat more complex in that the combined formation of 160 and 161 suggests that initial edge protonation is followed by a 1,2 shift of the trimethylsilyl group.[15]

The response of 5, 6, and 153 to the BF₃·2HOAc reagent in carbon tetrachloride closely parallels, but is
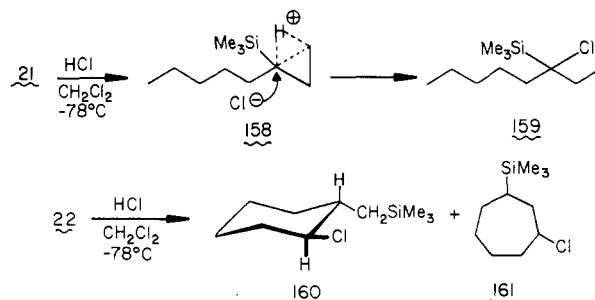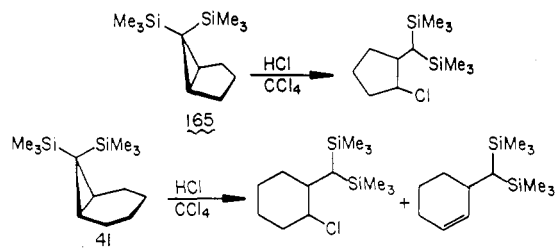
not identical with, the reaction pathway described above.[30] Replacement of HCl by TiCl₄ also leads to analogous results. However, because ring cleavage with the latter reagent leads directly to organotitanium reagents of type 162, hydrolysis with D₂O results in the efficient introduction of a deuterium label α to silicon (viz., 163).[15] The exclusive transannular pathway seen when 164 is similarly handled attests to electrophile-induced rupture of one of the flanking cyclopropane C–C bonds.
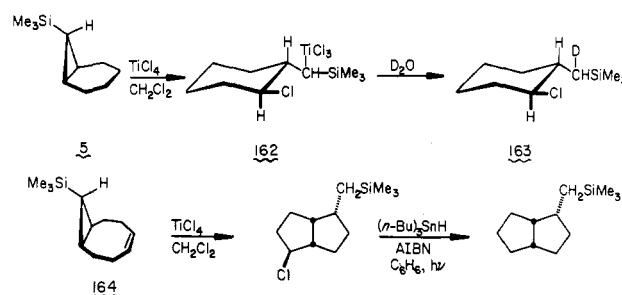
These findings allow an analogy to be drawn between silylcyclopropanes and vinylsilanes, in the sense that the electrophile most often becomes bonded to the silyl-substituted carbon atom in both situations, except where ring strain factors become too larger or, as in the case of 1 and 21, where C(2) and C(3) lack alkyl substituents.[117]

Bis(trimethylsilyl)bicyclo[n.1.0]alkanes also react with acids; substitution of one Me₃Si group and/or opening of the three-membered ring rapidly materialize.[41] Ring size (i.e., the value of n) plays a very important role in directing the course of the reactions, probably for steric reasons. Thus, 41 and 165 react with HCl in the manner illustrated. Under these conditions, the n = 6 system is unreactive.

Heating of 105 at the reflux temperature with p-toluenesulfonic acid in benzene resulted in desilylative ring cleavage. In the n = 1 example, pure cyclopentylidene tosylate 166a (exocyclic double bond only) was isolated. The cyclohexenyl analogue (n = 2) be-

haved comparably, except that a mixture of exo- and endocyclic isomers was formed. Clearly, cyclopropane ring expansion is not a viable mechanistic option.[52,55]
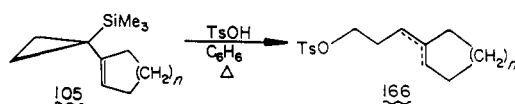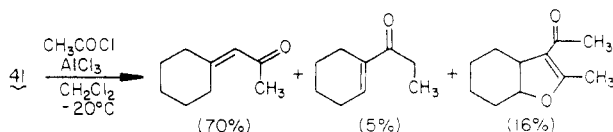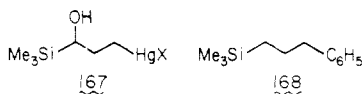
Complete desilylation similarly results when *gem*-disilylcyclopropanes are treated with 2 equiv of the CH₃COCl·AlCl₃ complex.[40] The response of 41 is more or less typical.


At a more prosaic level, mercuric salts in aqueous solution have been reported to act very slowly on 1 to give ring-opened products of type 167.[118] With aluminum chloride in benzene, 168 is formed rather inef-

ficiently (18%).[21] A remarkable feature of this pair of reactions is their contrasting regioselectivity. While 168 presumably results from cleavage in that direction that transiently positions the positive charge as remotely as possible from the trimethylsilyl group, 167 arises instead from a process that generates carbocation character α to silicon. The latter state of affairs is generally strongly destabilizing, a fact reflected in the relative rates of attack of HgX₂ on 1 which are substantially retarded relative to other substituted cyclopropanes.[118]

The parent silane 1 reacts with elemental bromine or Br₂–AlBr₃ to give mixtures of 169–171.[22] It is possible that 171 arises from initial substitution of Me₃Si by Br
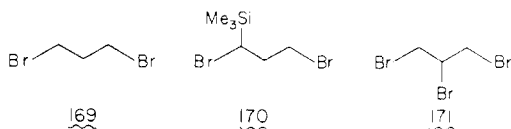
and subsequent brominative ring cleavage. The formation of 169 is thought to result from the liberation of hydrogen bromide, ensuing protodesilylation, and ultimate cyclopropane ring scission.

Claims exist that 1 is completely stable to iodine and is unreactive toward boiling 48% hydrobromic acid and 1 N sodium hydroxide solutions.[21,119]

## B. Solvolytic Behavior

Usually, a β-silicon atom, if properly aligned stereoselectronically, so strongly accelerates the departure of a leaving group that elimination results.[120] Exceptions to this general rule have been found in trimethylsilyl-substituted cyclopropane systems where elimination must necessarily generate a methylenecyclopropane product and introduce significant additional strain. The smooth, acid-catalyzed dehydration of 108 and related alcohols to give 1-(trimethylsilyl)cyclopropyl alkenes, the isomerization of allylic alcohol 113 under acidic conditions, the substitution reactions of acetal 115 in the presence of Lewis acids and of 129/130 in methanolic solutions of silver trifluoroacetate, and the boron trifluoride etherate promoted isomerization of 106 to 2-((1-trimethylsilyl)cyclopropyl)cycloalkanones (107) comprise a representative group of examples.

| compd	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_{rel}
172a	21.0	−17.0	27
173a	20.6	−18.1	25
174a	23.1	−10.0	45
cyclopropylcarbinyl trifluoroacetate	−	−	1

This behavior had led to a kinetic investigation of the impact of the trimethylsilyl group on the solvolysis of trifluoroacetates 172a–174a.[121] Table II summarizes
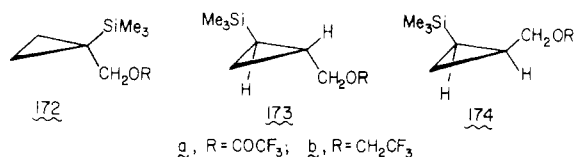

the good first-order kinetic data realized in 2,2,2-trifluoroethanol, a solvent employed to minimize the effect of external nucleophiles.[122] At 50 °C, 172a was cleanly converted (CaCO₃ as buffer) to a mixture of 172b (20%), 175a (20%), and 175b (60%). The solvolysis mixture from 173a consisted of 173b (70%), the 1,3-disubstituted cyclobutane 176 (20%), and a minor unidentified ester (<10%). For 174a, the major less volatile product is 177.[121]
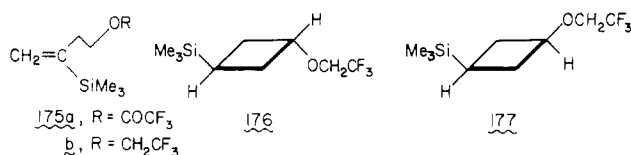
Significantly, the rate enhancements produced by positioning a Me₃Si group at C(1) and C(2) of cyclopropylcarbinyl trifluoroacetate are appreciable (25- to 45-fold), although not excessively large as in cyclohexyl systems.[123] Methyl substituent effects under comparable circumstances result in only 5- to 11-fold acceleration.[124] Thus, additional acceleration is attainable when a trimethylsilyl group is present, presumably as a direct result of through-bond contributions.

The solvolytic rearrangement of 178 in ethanol solution containing potassium carbonate proceeds with orbital symmetry assistance to give 179.[63a] On acidic
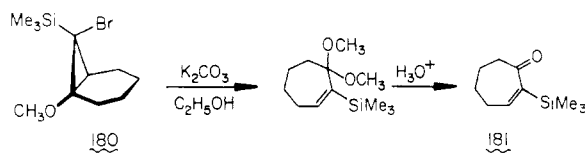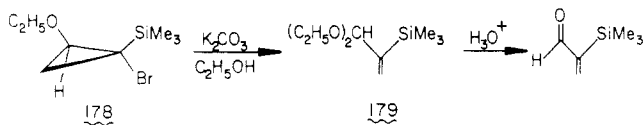
hydrolysis, this product leads conveniently to 2-(trimethylsilyl)acrolein. The norcarane derivative 180 behaves comparably to deliver 2-(trimethylsilyl)cycloheptenone (181).

Whereas 129, 130, and related bicyclo[4.1.0]heptanes undergo only substitution chemistry when treated with silver trifluoroacetate in methanol, ring expansion materializes in the case of 182 and 184. The later substrate gave 3-methoxycyclononyne (186) in 77%
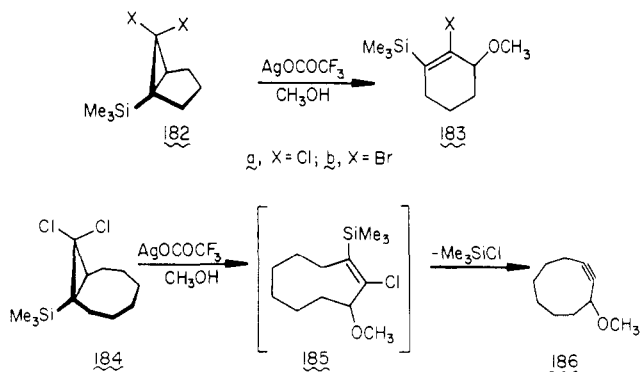
yield, which likely results from further elimination of chlorotrimethylsilane from **185**.[102]

Reduction of **187** with methanolic sodium borohydride delivers **188** as a cis/trans isomer mixture. These alcohols are transformed in acetic acid containing perchloric acid (5%) into the ring-expanded acetoxy silane **189**.[125] With peracetic acid, clean conversion to **190** is observed. Evidently, the first formed **189** experiences additional electrophilic attack at its double bond and desilylative ring openings. Tertiary alcohol **191**

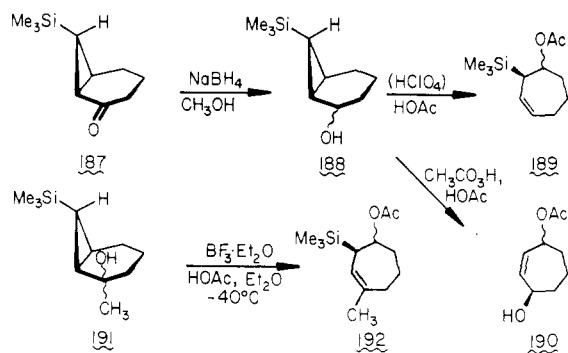afforded only complex product mixtures when subjected to the above conditions. However, the ring-expanded allylsilane **192** is formed efficiently in the presence of boron trifluoride etherate in ether–acetic acid solution at −40 °C.[125]

The cyclopropylcarbinol **151** experiences facile ring cleavage when reacted with phosphorus triiodide and triethylamine in dichloromethane at 0 °C.[126]
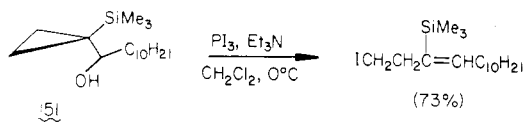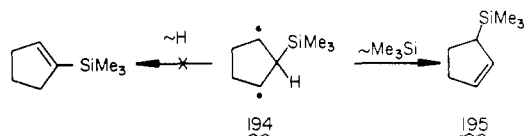

C. Thermal Isomerizations

It is widely recognized[127,128] that the thermal isomerization of cyclopropane and it monoalkyl derivatives leads to products arising from ring cleavage and subsequent nonregiospecific hydrogen migration. Where simple silylcyclopropanes such as **1**, **20**, and **193** are concerned, however, high yield conversion to allylsilanes is seen to result exclusively.[21,29]
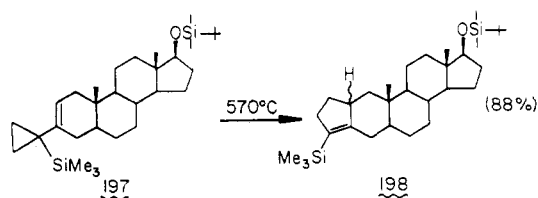
In his detailed kinetic investigation of the thermal behavior of *exo*- and *endo*-5-(trimethylsilyl)bicyclo-[2.1.0]pentanes, Ashe observed that **14** rearranges 60 times faster than **13** because of substantial ground state steric crowding in the endo derivative.[17] The bicyclic isomers are not interconverted at 195 °C, but give rise exclusively to 3-(trimethylsilyl)cyclopentene (**195**) upon
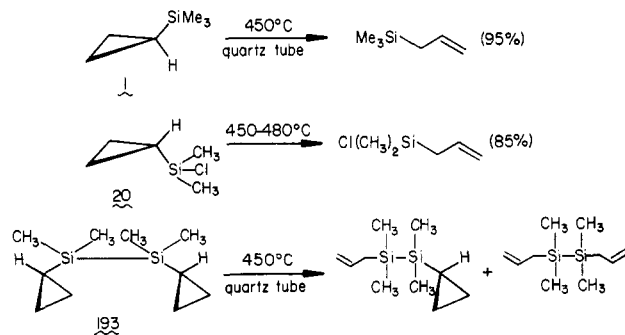
raising the temperature to 235 °C. Consequently, no evidence was found for hydrogen atom migration within the common biradical intermediate **194**. Furthermore, the 1,2-shift of Me₃Si must occur at least 10⁶ times faster than the movement of hydrogen.

The attachment of electronegative heteroatoms (O, N, etc.) at C(1) of a vinylcyclopropane exerts a powerful accelerating effect on the rate of thermal isomerization to the cyclopentene.[129] The electropositive character of a pendant silyl group has the opposite effect.[55,96,100,130] Nevertheless, the ring expansion of molecules such as **62**, **105**, **126**, and **197** is efficient at more elevated tem-

peratures. Since the product vinylsilanes are subject to the usual replacement of Me₃Si with various electrophiles, the overall process serves as a versatile cyclopentannulation technique for ketones. Additionally, this procedure delivers bicyclic vinylsilanes having the double bond invariably positioned at the more highly substituted site (see **196** and **198**). This regiochemistry is not attainable through application of the Shapiro reaction, while leads via kinetically controlled proton abstraction to the lesser substituted vinylsilane.[26–28] As a result, the methodologies are usefully complementary.
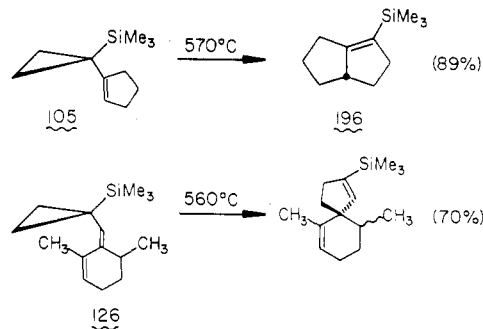
The influence of the trimethylsilyl group in these thermal rearrangements is again reflected in the response of **199** to heat. This first example of intramolecular vinyl cyclopropane competition delivers **200** as the exclusive product.[55,130] The end result indicates that the unsubstituted cyclopropane ring in **199** enters more
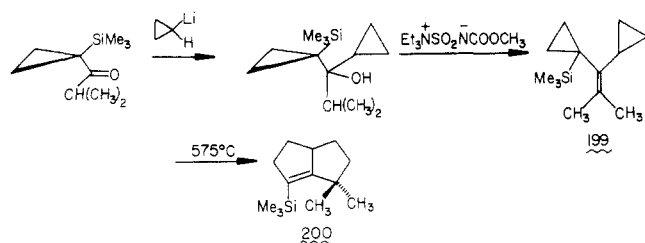
readily into the bond reorganization than does its trimethylsilyl-substituted counterpart.

VII. Configurational Properties of 1-(Trimethylsilyl)cyclopropyl Carbanions and Free Radicals

In an experimental study designed to probe the configurational stability of 1-(trimethylsilyl)cyclopropyl carbanions and free radicals, Paquette, Uchida, and Gallucci prepared the levorotatory carboxylic acid 201 by resolution via its *l*-cinchonidine salt.[131] The absolute configuration of this substance was shown to be *R* by transformation into (-)-(*R*)-202, a molecule alternatively prepared in unequivocal fashion by metalation and silylation of (-)-(*R*)-203.[132] Follo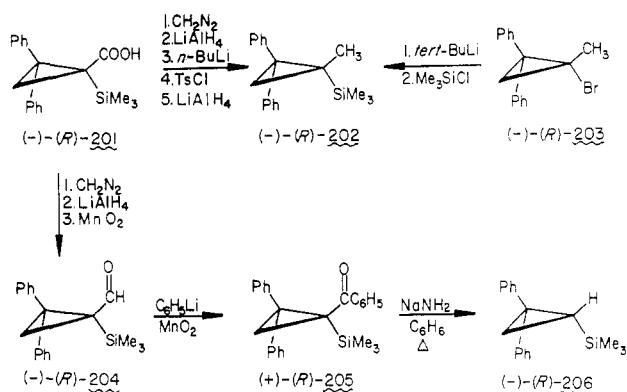wing conversion of (-)-(*R*)-201 to (-)-(*R*)-204, this aldehyde was condensed with phenyllithium and oxidized with manganese dioxide to give (+)-(*R*)-205. Cleavage of this optically active phenyl ketone under Haller–Bauer conditions led to (-)-(*R*)-206 with complete retention of stereochem-


istry. This conclusion was reached following the preparation of the optical antipodes of 207, X-ray analysis of the *l*-menthyl ester (208) of the dextrotatory enantiomer, and suitable conversion of (-)-207 to the identical levorotatory silane (-)-(*R*)-206.[131]
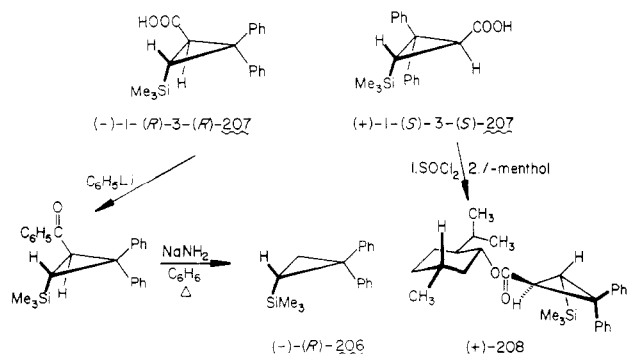
Since carbanions are known to intervene in Haller–Bauer cleavage reactions, the maintenance of full optical purity during the 205 → 206 conversion requires that

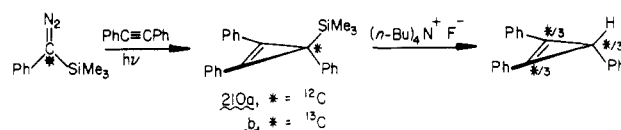a reasonable barrier to planarization exist in the reactive intermediate.

The situation is quite different when free radical species are involved. For example, various Hunsdiecker degradation conditions applied to (-)-(*R*)-201 invariably led to the isolation of racemic bromide.[131] One reason why a neighboring Me₃Si group may be unable to stabilize a pyramidal configuration under these circumstances is because of steric congestion involving a nearby phenyl substituent. To rule out this possibility, the ^{13}C-labeled compound 209 was prepared and
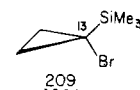
transformed into the free radical under conditions where ESR analysis was possible.[133] Whereas the spectrum showed $a^{13}C_\alpha = 40.0$ G, a^{H_β} (4 H) = 27.0 G, and $g = 2.0024$, no $a^{29}Si$ signal was observed and the a^H (SiMe₃) signal could not be resolved. Consequently, it is irrefutable that this free radical is essentially planar.

VIII. Silylated Cyclopropenes

To date, there has been very little work done in this area. The pair of isotopically labeled cyclopropenes 210a and 210b was prepared by photolysis of the cor-

responding labeled phenyl(trimethylsilyl)diazomethane in molten diphenylacetylene. When either substance was fluorodesilylated, the 1,2,3-triphenylcyclopropane obtained was labeled in close to the statistical ratio of 1:2. These findings indicate that pseudorotation in the derived cyclopropenyl anion must occur faster than protonation.[34]

The naturally occurring cyclopropenone 212 has been conveniently prepared by addition of dichlorocarbene to 211. The intermediate adduct is sufficiently reactive that hydrolysis occurs during workup to give rise to 212 in moderate yield.[135]
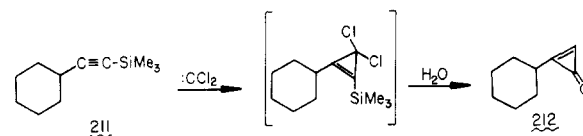
IX. Addendum

Section II. A. Whereas the addition of diazomethane to vinyltrimethylsilane at room temperature affords 3-(trimethylsilyl)-1-pyrazoline (213), (tri-

methylsilyl)diazomethane acts on ethylene at 55 °C to produce 1-(trimethylsilyl)-2-pyrazoline exclusively.[136] Thermal elimination of nitrogen from either heterocycle leads to cyclopropyltrimethylsilane (1, 35–48%), as well as allyltrimethylsilane and *E*- and *Z*-propenyltrimethylsilane.
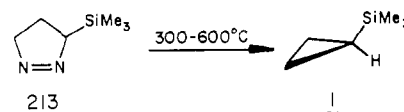
Metalation of methylenecyclopropane **214** with *n*-butyllithium and trapping of the resulting allyl anions with Me₃SiCl gives rise to a mixture of the syn and anti products **215** and **216**.[137]
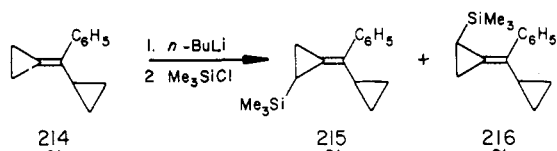
Section II. C. Cunico and Kuan have demonstrated the feasibility of preparing 1-(trimethylsilyl)cyclopropanol (**217**) by sequential silylation of the enolate
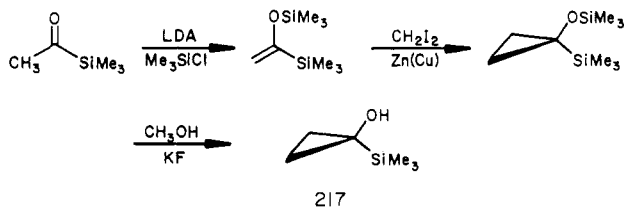
of acetyltrimethylsilane, modified Simmons–Smith cyclopropanation involving hot dioxane as solvent (no reaction otherwise), and finally transetherification in neat methanol containing potassium fluoride.[138]

Section II. D. Quite suprisingly, efforts to dehalogenate **218** with magnesium in acetonitrile gave a mixture of the four possible stereoisomeric β-keto acid chlorides **219**.[139] When the reducing agent was changed to zinc in boiling acetonitrile, there was produced instead a mixture of the four stereoisomeric dimers **220** and the pair of trimers **221** and **222** in a 2:1 ratio

(combined yield of 60%). The C_3 symmetry of **222** was easily recognized by ¹H NMR spectroscopy (one Me₃Si signal and only one ABM system).

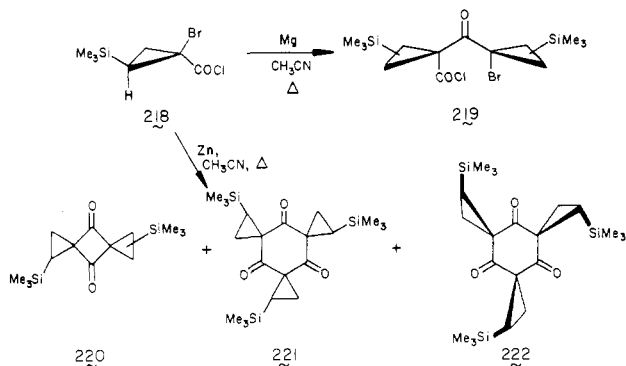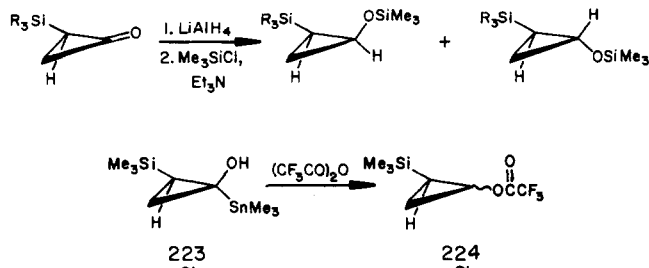**Section III.** 2-(Trialkylsilyl)cyclopropanones are reduced readily to their stereoisomeric cyclopropanols, which in turn undergo silylation without ring cleavage.[140] The more highly functionalized alcohol **223** reacts with trifluoroacetic anhydride with ejection of the tin substituent to give **224**.[140]

Osmium tetraoxide catalyzed dihydroxylation of **225** produces **226** whose oxidation under Swern conditions leads to the silyl substituted tropolone **227** with loss of hydrogen bromide.[141]
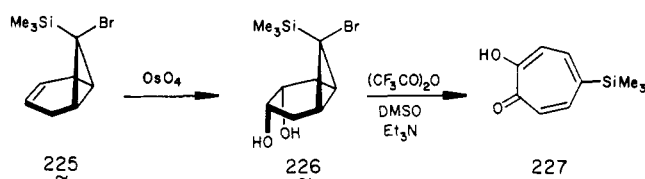
Section IV. A. Acetylation of endo- and exo-(trimethylsilyl)-substituted bicyclo[n.1.0]alkanes (**228**) has

228 (n = 3, 4, 6)
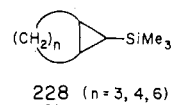
been studied using the CH₃COCl/AlCl₃ complex. The results demonstrate that the ultimate course of the reaction is dependent both upon ring size and substituent stereochemistry. Depending upon the structure of the reactant, either bicyclo or ethylenic ketones were formed in addition to chloro-substituted analogues.[142]

Section VI. A. When mixed with an equivalent amount of trifluoroacetic acid at 0 °C, cyclopropanol **217** is completely converted to **229** within 15 min. Bromination of its trimethylsilyl ether was also examined.[138]

Section VI. C. Upon flash vacuum photolysis at 625 °C, 1-(trimethylsiloxy)-1-(trimethylsilyl)cyclopropane
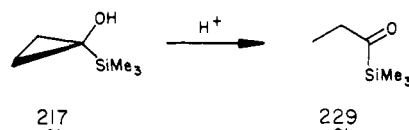
afforded mostly hexamethyldisiloxane and some *cis*- and *trans*-1-(trimethylsiloxy)-3-(trimethylsilyl)propene. The 1-ethoxy derivatives behaves analogously. In contrast, comparable treatment of the acetoxy compound (**230**) leads via a different mechanistic pathway to **231**.[143]
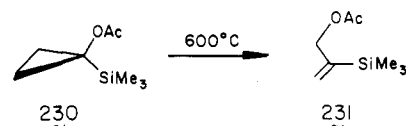
Section VII. Reductive debromination of 1-bromo-1-(trimethylsilyl)cyclopropane-1-¹³C produced the labeled radical, the EPR spectrum of which confirmed the species to be planar or nearly so.[144]

Section VIII. Cyclopropanation of bis(trimethylsilyl)acetylene with diazomalonic esters affords adducts such as **232**, which are desilylated to 2-cyclopropene-1,1-dicarboxylic esters by treatment with potassium fluoride/crown ether in acetonitrile.[145] Selective hydrolysis of the carbalkoxy groups can be realized with trimethylsilyl iodide.

Exposure of **232** to diazomethane for 1 week results in the formation of **233**, which when irradiated undergoes nitrogen extrusion to deliver the bicyclobutane **234**.[145]

232

233 234
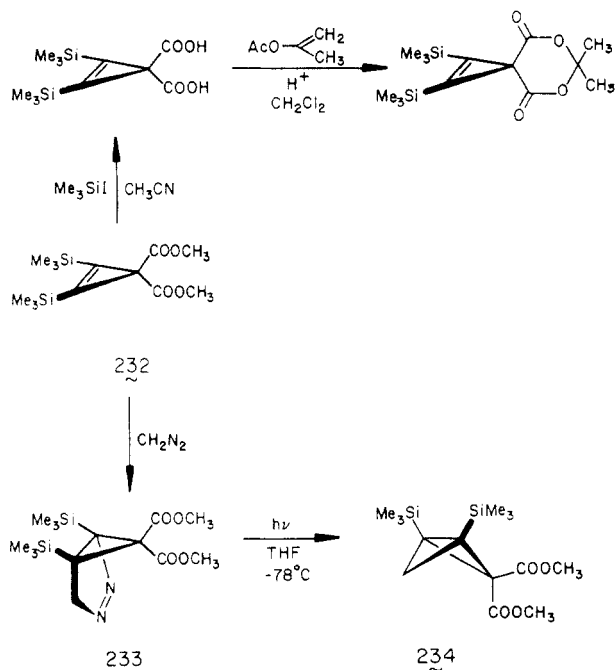
Treatment of *cis*-1-iodo-3-chloro-1-propene derivative **235**, available via trans addition of organometallic reagents to the trimethylsilylated propargyl alcohol followed by iodinolysis and chlorination, reacts with alkyllithiums at −78 °C to give the cyclopropene **236**

235 236

237 238 239
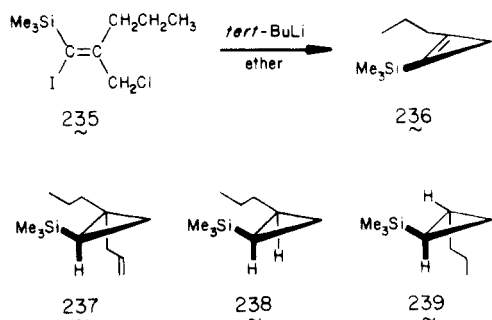
with high efficiency. The reaction of **236** with 2 equiv of allylzinc bromide provided **237** in 92% yield after protonolysis. On exposure of **236** to diisobutyl-aluminum hydride, conversion to **238** (> 98% isomeric purity) resulted. With lithium aluminum hydride as reducing agent, a 70:30 mixture of **238** and **239** was formed in 95% yield.[146]

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