

1984

# The synthesis of carbacyclic silanes via organosilicon reactive intermediates

Michael J. Vuper  
Iowa State University

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THE SYNTHESIS OF CARBACYCLIC SILANES VIA ORGANOSILICON  
REACTIVE INTERMEDIATES

*Iowa State University*

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The synthesis of carbacyclic silanes via  
organosilicon reactive intermediates

by

Michael J. Vuper

A Dissertation Submitted to the  
Graduate Faculty in Partial Fulfillment of the  
Requirements for the Degree of  
DOCTOR OF PHILOSOPHY

Department: Chemistry  
Major: Organic Chemistry

Approved:

Signature was redacted for privacy.

~~In Charge of Major Work~~

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~~For the Major Department~~

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~~For the Graduate College~~

Iowa State Univeristy  
Ames, Iowa

1984

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v

DEDICATION

To my parents, who have shown me  
the way.

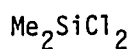
## NOMENCLATURE

The nomenclature used throughout this manuscript will be briefly outlined.

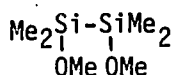
All carbon systems will be named following IUPAC conventions. Simple organosilicon compounds will be named as derivatives of silane ( $\text{SiH}_4$ ), while cyclic systems will be named as analogs of the corresponding carbocyclic systems.

Compounds containing silicon-carbon double bonds will be named as analogs of the corresponding unsaturated carbon systems. The term silene shall apply to the general class of compounds containing a silicon-carbon double bond. Silabenzene shall denote a cyclohexatriene ring system in which one carbon atom has been replaced by silicon. Substituents will be numbered with the silicon atom designated as one. Divalent silicon species will be named as derivatives of silylene ( $\text{H}_2\text{Si:}$ )

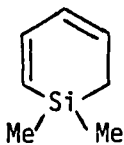
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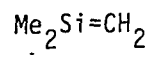
Dimethyldichlorosilane



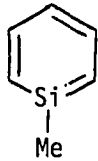
1,1,2,2-tetramethyl-1,2-dimethoxydisilane



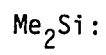
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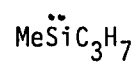
2-methyl-2-silapropene



1-methyl-1-silacyclohexa-1,3,5-  
triene  
1-methyl-1-silabenzene



Dimethylsilylene

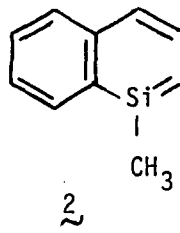
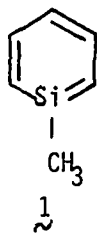


Methylpropylsilylene

## INTRODUCTION

Recent history has witnessed the generation of silabenzene (1-8) and compounds containing an isolable silicon-carbon (p-p)  $\pi$  bond (9).

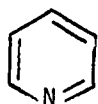
This thesis is concerned with the utilization of divalent silicon species (silylenes) (10) and (p-p)  $\pi$  silicon-carbon bonds (silenes) (11) to generate molecules which are of theoretical interest, such as 1 and 2. These molecules have proved themselves to be difficultly accessible by more common means.



## HISTORICAL

The unusual properties of benzene have intrigued chemists for years. The investigation of these properties has produced the theory of aromaticity (12). Hückel's rule (13) predicts that any monocyclic compound with all atoms  $sp^2$  hybridized and containing  $(4n + 2)$   $\pi$ -electrons will be aromatic. The search for examples and exceptions to this rule has been a fruitful area in organic chemistry (12).

For many years, heterocyclic compounds were considered to be aromatic if (i) a carbon atom is replaced by a heteroatom which contributes one electron to the  $\pi$ -system; or (ii) a carbon-carbon double bond unit is replaced by a heteroatom which contributes two  $\pi$ -electrons to the  $\pi$ -system. Examples of (i) and (ii) are pyridine, 3 and pyrrole, 4.



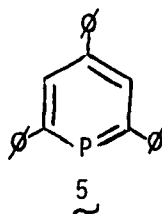
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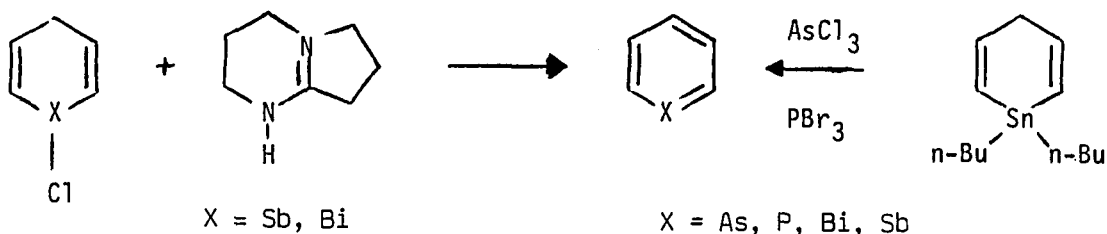
For a long period of time, aromatic heterocycles of type (i) were limited to pyridines since (p-p)  $\pi$ -bonded elements (other than C, O, N) in aromatic arrays were thought to be non-existent (14).

In 1966, Märkl (15) reported the synthesis of the stable 2,4,6-triphenyl-1-phosphabenzene, 5, the first example of a  $(3p-2p)$   $\pi$ -bonded phosphorus in an aromatic system. Since Märkl's pioneering



efforts, all of the Group V heterobenzenes have been synthesized (16-23). Scheme 1 shows the routes employed for the synthesis of these compounds. A review by Jutzi (16) discusses this work in greater detail.

Scheme 1



Even though the Group V heterobenzenes were known, the Group IV heterobenzenes remained elusive. This is surprising because these atoms are considered isovalent with carbon. Although all the Group IV elements form four  $\sigma$ -bonds from  $sp^3$  overlap, only carbon readily forms (p-p)  $\pi$ -multiply bonded compounds.

As one goal is the generation of sila-aromatic compounds ((p-p)  $\pi$ -bonded silicon) and subsequent study of their chemistry, a discussion of (p-p)  $\pi$ -bonded silicon in aromatic systems is warranted. This discussion will include theoretical considerations, methods of generation and chemical behavior, and spectroscopic properties of silabenzene. Emphasis will be placed on developments since 1977 as earlier work has been reviewed (24,25,26).

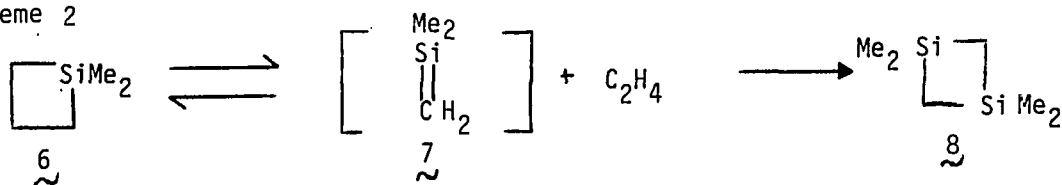
## Theoretical Considerations

The lack of (p-p)  $\pi$ -bonded compounds involving non-second row elements led to the advancement of two theories accounting for the non-existence of these compounds. The conclusion reached by Pitzer (27) was that repulsion between inner shell electrons and bonding electrons was responsible for the lack of heavy atom (p-p)  $\pi$ -bonding. This causes improper p-orbital overlap and prevents effective  $\pi$ -bond formation. The molecular orbital calculations performed by Mulliken (28) indicated that (p-p)  $\pi$ -bonding was unimportant in other than second row elements. This was attributed to the greater stability of  $\sigma$ -bonds relative to  $\pi$ -bonds (29).

It would follow from this line of reasoning that silicon would preferentially form four  $\sigma$ -bonds in polymeric structures rather than  $\pi$ -bonds. The validity of this theory was demonstrated by the numerous attempts (30-34) to generate silenes which resulted in the formation of dimeric or polymeric material.

In 1966, Nametkin et al. (35,36) presented strong evidence for the formation of 2-methyl-2-silapropene 7 in the gas phase pyrolysis of 1,1-dimethylsilacyclobutane, 6, Scheme 2. The search for a stable silene

Scheme 2

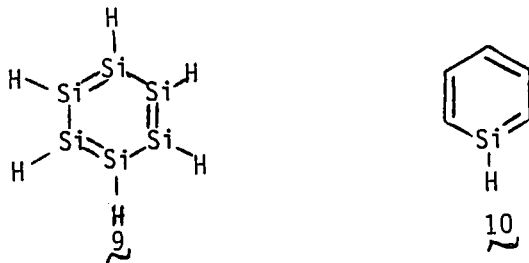




became secondary to obtaining evidence for silene intermediacy.

Nametkin's results precipitated much theoretical work on the nature of (p-p)  $\pi$ -bonded silicon (37-44).

The conclusions reached in these studies followed the same trends. The Si=C (p-p)  $\pi$ -bond would have a lower  $\pi$ -bond energy than a normal olefin, the Si=C bond would be polarized, almost ylide-like, with carbon bearing the negative charge and silicon bearing the positive charge. Silenes would also be highly reactive, which fits a polarized bonding picture. Only Dewar (43), and Dewar et al. (44) addressed the question of aromatic silanes and he predicted that hexasilabenzene, 9, and silabenzene, 10, would have aromatic stabilization similar to benzene itself.



In 1978, Schlegel et al. (45) discussed the structure of silabenzene based on ab initio calculations. The results included geometries and bond lengths for both a ground state singlet and triplet silabenzene. It was concluded that only small changes in bond angles (relative to benzene) were necessary to accommodate the larger silicon atom. The C=C bond lengths were essentially the same as in benzene and the decrease in Si=C bond distance was on the same order as the C=C bonds in benzene; i.e.

$\text{Si}-\text{C} < \text{Si}=\text{C} < \text{Si}=\text{C}$ . In triplet silabenzene, the bond lengths increase somewhat, but the molecule is predicted to be planar. This contrasts with the predicted triplet state for silaethylene which is thought to be twisted.

The molecular orbital (MO) energies for silabenzene are compared to those of benzene in Figure 1.

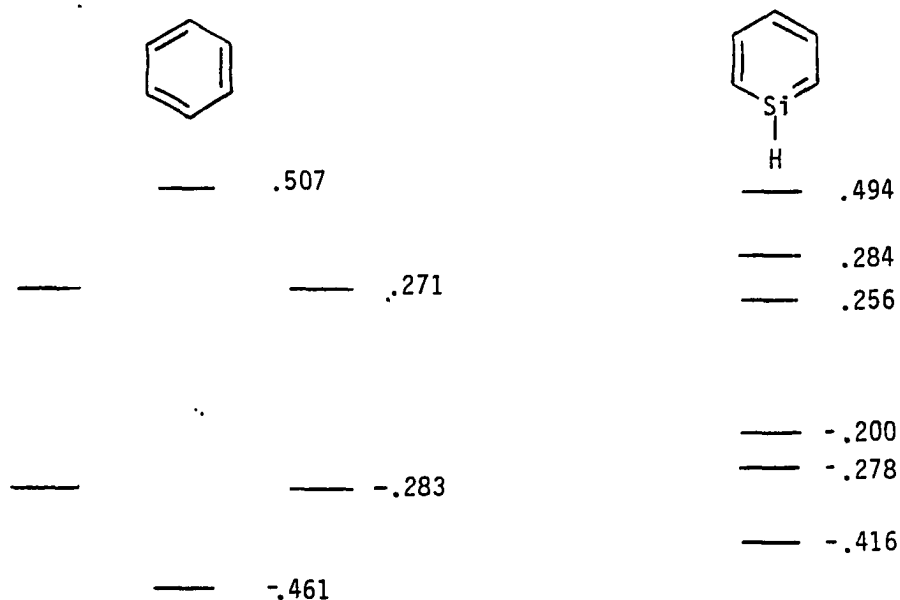


Figure 1. MO energies of benzene vs. silabenzene

Table 1. Mulliken population analysis of silabenzene

	SiH	C <sub>1</sub> H	C <sub>2</sub> H	C <sub>3</sub> H
$\sigma$	13.59	6.17	6.04	5.97
$\pi$	0.82	1.09	0.96	1.09

It can be seen in Figure 1 that silabenzene has no degenerate MO's. Furthermore, the highest occupied molecular orbital (HOMO) in silabenzene has a greater energy than the HOMO for benzene, suggesting that silabenzene would have less resonance energy stabilization.

The coefficients of the filled MO's indicate benzene-like  $\pi$ -delocalization. Table 1 shows the Mulliken population analysis (charge distribution) for silabenzene. The smaller  $\pi$  charge on silicon corresponds to an increase in  $\pi$  charge on the ortho and para carbons. The  $\sigma$  charge distribution indicates a much more highly polarized character in the Si—C bond. This effect may be exaggerated by deficiencies in the Mulliken population analysis (45). It may be concluded from these data that the elusive nature of silabenzene results from a high degree of reactivity rather than a low level of aromaticity.

The resonance energy calculated for benzene in this study was in fair agreement with experimental values. The resonance energy of silabenzene was concluded to be ca. 2/3 that of benzene.

In a later study, Blustin (46) predicted silabenzene to be a highly polarized molecule with a dipole moment of 2.85 D. The Si $\equiv$ C bond has a calculated dipole moment of 2.87 D which is in accordance with other calculations (27-41).

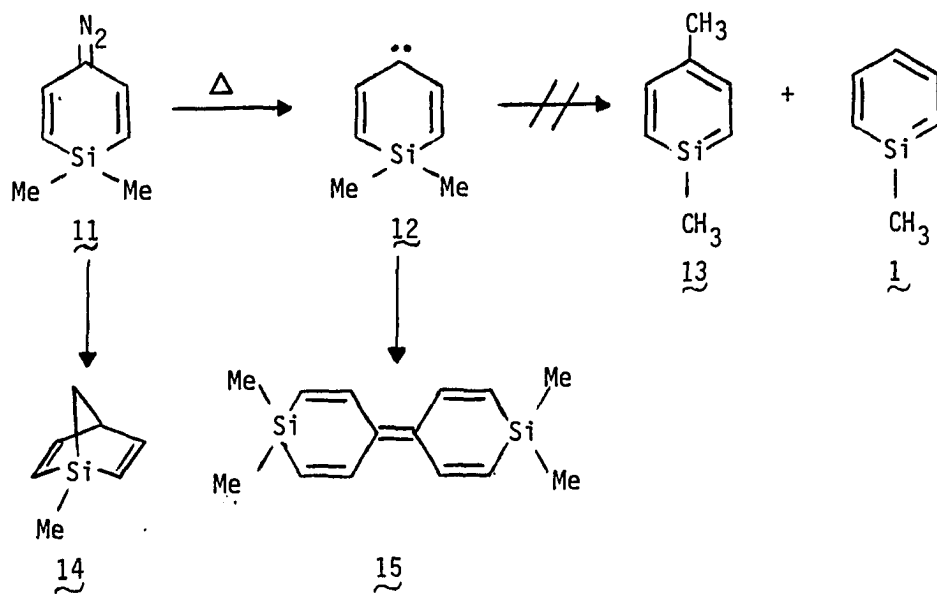
Blustin opposes the concept that silabenzene is a thermodynamically stable compound saying that the resonance energy gained in forming silabenzene would not be sufficient to offset the energy required to break

the weakest Si-element bond. In short, there is a thermodynamic barrier to silabenzene formation. This clearly contrasts the position of Dewar (43) and Schlegel et al. (45).

#### Methods of Generation and Chemical Behavior of Silabenzenes

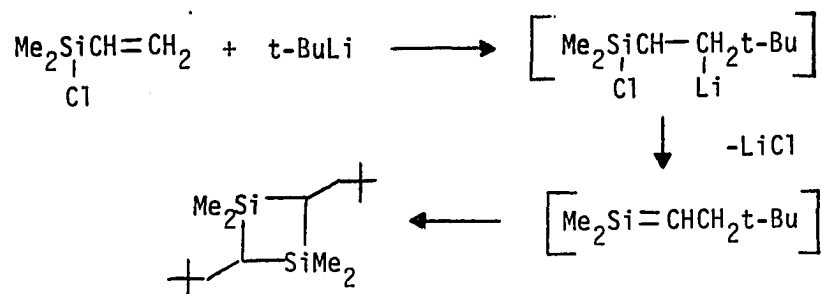
Prior to 1977, attempts to form sila-aromatic compounds had met with repeated failure (16). Barton and Banasiak (47) attempted silabenzene generation from rearrangement of carbene 12, shown in Scheme 3. The major product from pyrolysis of diazo compound 11 was the carbene dimer, 15. Photolysis of 11 in perfluoro-n-hexane through a quartz filter gave 14 in low yield. Mercury photo-sensitized decomposition of 11 in the gas phase gave similar results.

Scheme 3.



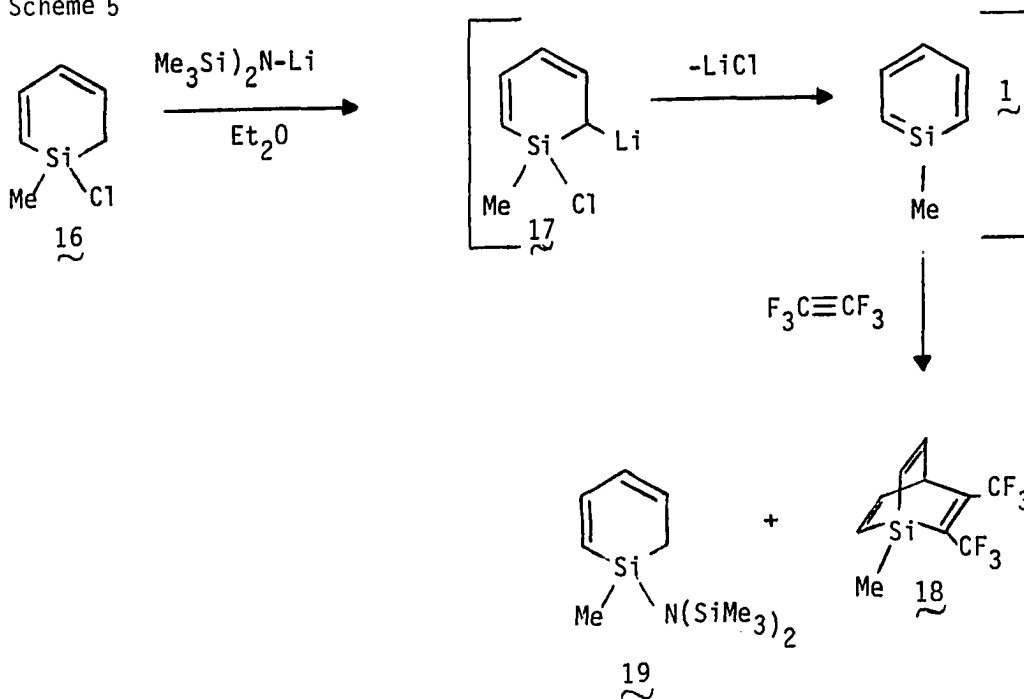
At this time, Jones and Lim (48) reported that addition of *t*-butyllithium to vinyldimethylchlorosilane led to products presumably arising from a silene intermediate (Scheme 4). A modification of this reaction

Scheme 4



was used in the apparent generation and trapping of the first silabenzene, (2) as outlined in Scheme 5. Carbanionic attack on the acetylene,

Scheme 5



followed by intramolecular displacement of chloride could not be ruled out. Anion 17 was not trapped with excess methyl iodide or trimethylchlorosilane. This result favors the intermediacy of 1-methyl-1-silabenzene, 1.

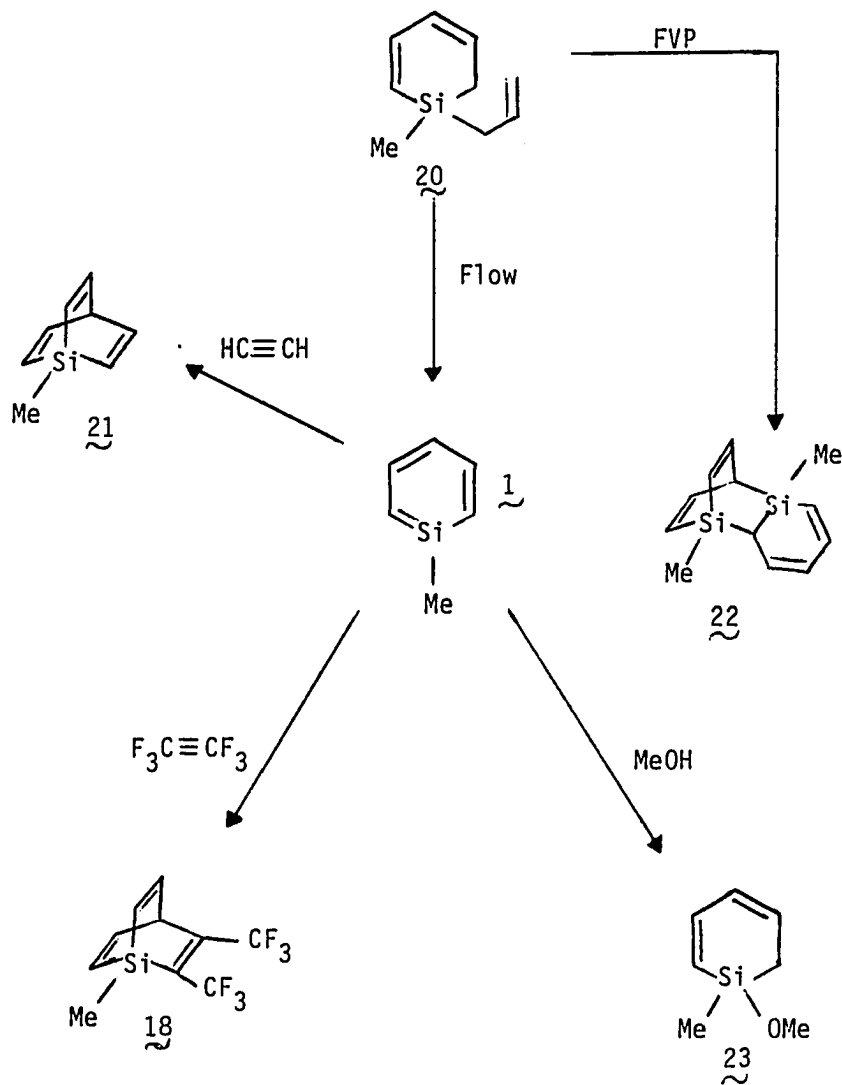
The first unambiguous silabenzene generation was accomplished by Barton and Burns (3). The formation of the desired 1-silatoluene 1 relied on the retro-ene elimination of propene from 1-methyl-1-allyl-1-silacyclohexa-2,4-diene, 20. The use of the retro-ene reaction had been introduced by Block and Revel (49) to form silacyclobutenes from the pyrolysis of di-allylsilanes. The observations of Barton and Burns (3), Bock et al. (4a), and Chapman et al. (4b) are summarized in Scheme 6.

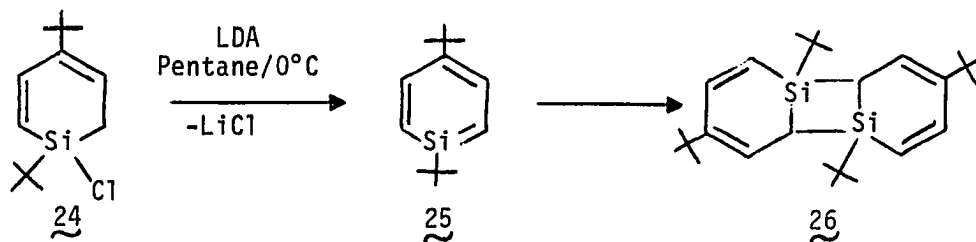
Silatoluene 1 reacts as a Diels-Alder diene with acetylenes to form the 1-sila [2.2.2] octatriene system. Under flash vacuum pyrolysis (FVP) conditions, the 1-silatoluene undergoes self [4 + 2] cycloaddition with one Si=C bond functioning as the dienophile. No [2 + 2] dimers were seen.

The adduct formed from 1 and MeOD arose from 1,2 addition across the Si=C bond. Only one deuterium atom was incorporated at the methylene position. This result demonstrates the susceptibility of the Si=C (p-p)  $\pi$ -bond to nucleophilic attack.

Shortly after the appearance of Barton's work, Márkl (7) generated 1,4-di-t-butyl-1-silabenzene, 25, via the route shown below. The [2 + 2] dimer, 26, was the sole product from this reaction (aside from

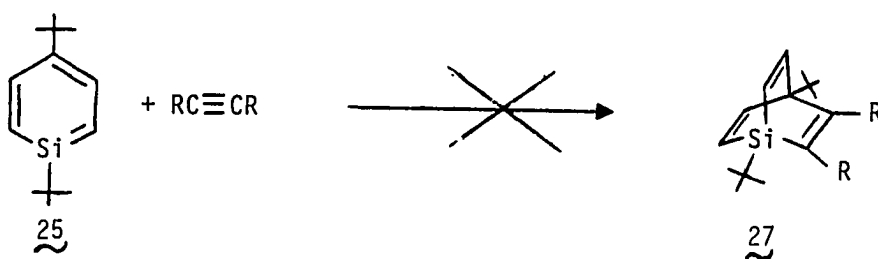
Scheme 6





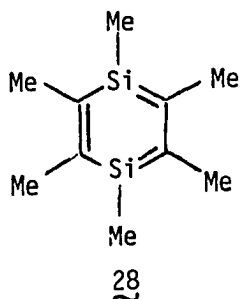
LiCl). The dimer is a solid with a melting point of 204°C. No silylamine is formed with **24** as opposed to **16** and this is attributed to the steric bulk of the t-butyl group.

**25** reacts with 1,3-dienes under these same conditions to give high yields of the [4 + 2] cycloadducts. When the dienes are present in large excess, dimerization (**25** → **26**) is completely suppressed. However, **25** is not intercepted by acetylenes to give 1-t-butyl-1-silabicyclo[2.2.2]octatrienes. Märkl speculates that steric hindrance could be preventing this reaction.

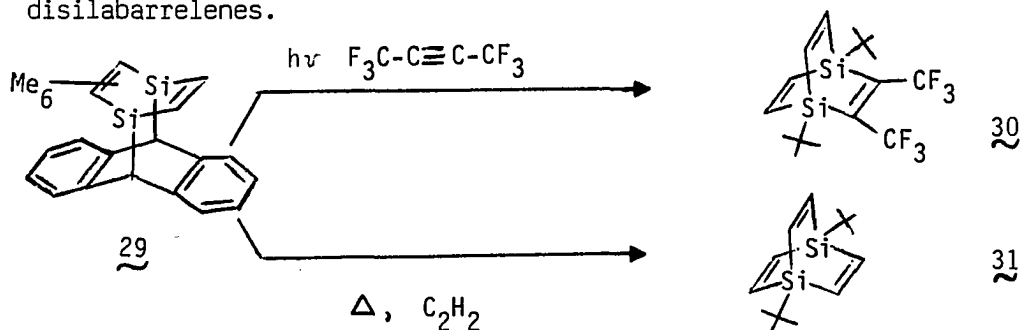




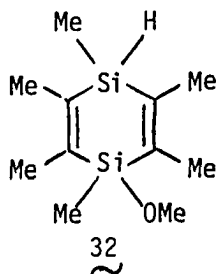
Rich and West (8) have recently described the synthesis of 1,4-disilabenzene, 28, the first such polysilaaromatic compound. 28 arises



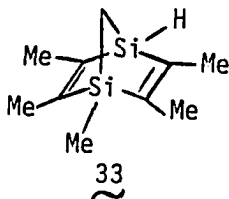
from photolysis (254 nm) of a THF solution of the precursor 29, or from nitrogen flow pyrolysis of 29 at 600°C with concurrent formation of anthracene. The use of acetylenes as traps gives the corresponding disilabarrelenes.



Methanol trapping gives a sole adduct which arises from 1,4-addition to give a 1:1 mixture of cis and trans 32.



FVP of 29 at 700°C ( $5 \times 10^{-5}$  Torr) gave anthracene and a minor product in 8% yield. The minor product was identified as 1,2,3,5,6-pentamethyl-1,4-disilabicyclo [2.2.1] hepta-2,5-diene, 33. Some mechanistic possibilities for the formation of 33 are shown in Scheme 7.

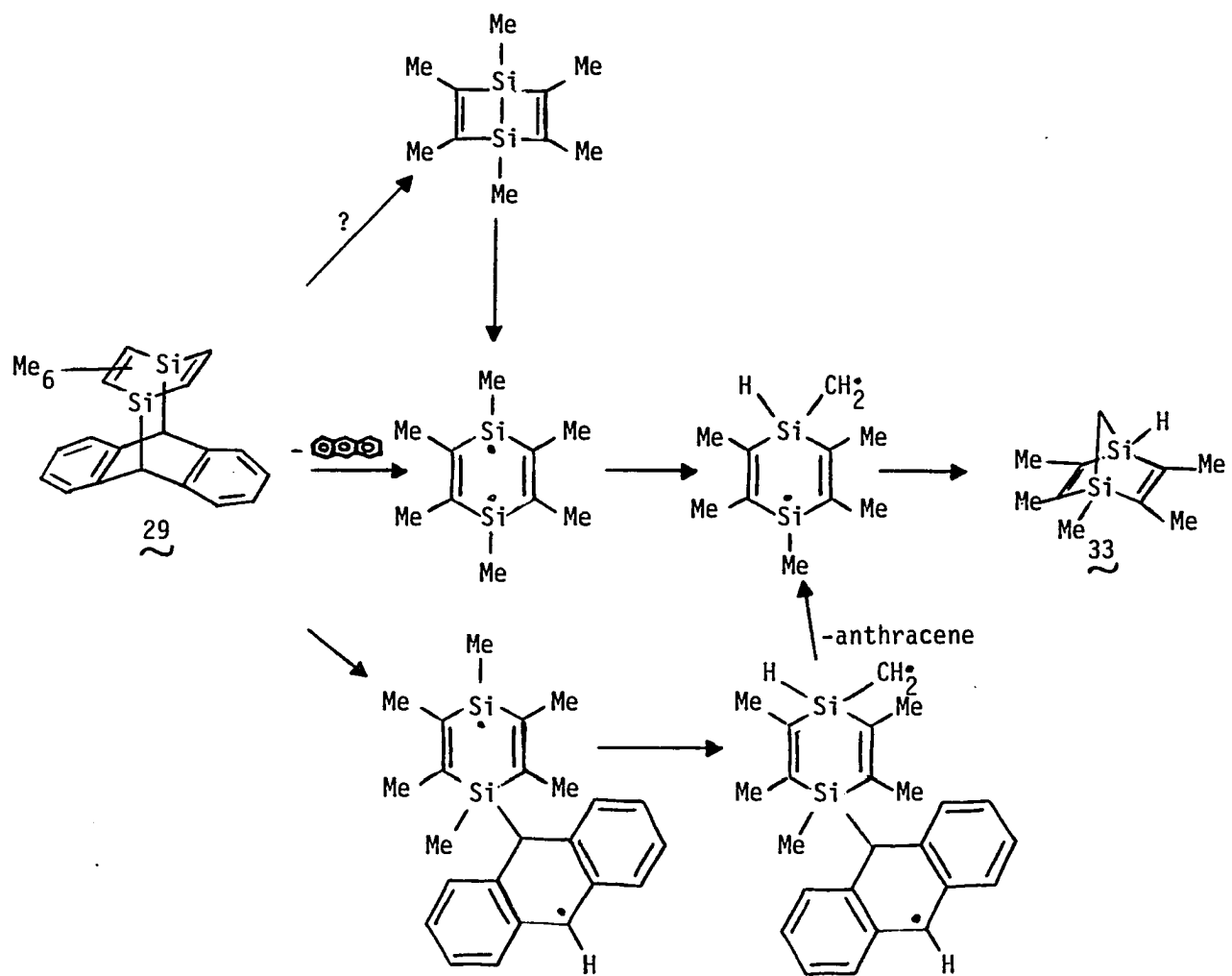


#### Spectroscopic Properties

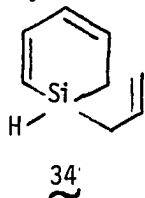
From quantum chemical calculations (5), silabenzene was predicted to be thermodynamically stable and have a singlet ground state (45). The first two ionization energies ( $IE_1$ ,  $IE_2$ ) were predicted to be 8.2 eV and 9.2 eV respectively (5).

The photoelectron spectrum (PES) of 1-silatoluene was obtained by flash vacuum pyrolysis of 20 and isolation of the pyrolysate on an Argon matrix. The spectrum of this pyrolysate showed two new bands at 7.7 eV and 9.1 eV (4) which were assigned the first and second ionization energies of 1-silatoluene. The perturbation due to the methyl group lowers  $IE_1$  by .4 eV, so the observed value of 7.7 eV matches with prediction well (5). The PES, along with the later published IR and UV spectra (6) demonstrated that silabenzene does exist.

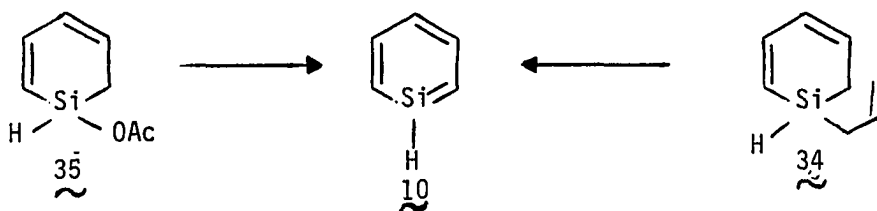
Scheme 7



Concurrent with the silatoluene research, silabenzene itself was being studied spectroscopically on argon matrices (6). Flash-vacuum pyrolysis of 34 followed by PES of the pyrolysate gave IEs of 8.0, 9.3, and 11.3 eV respectively. These values matched well with predicted



IEs of 8.2, 9.2, and 11.5 eV. FVP of 34 or 35, along with maxtix isolation, allowed the UV and IR spectra of 10 to be measured. The

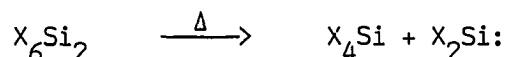


UV showed absorbances at 212, 272, and 320 nm which fit the bathochromic shifts observed for other donor substituted heterobenzenes. The IR had new bands at 418, 566, 598, 886, 1353, 1526, and 2217  $\text{cm}^{-1}$ . The bands in each type of spectrum disappeared upon continued irradiation or thawing of the matrix. The authors postulated (but never proved) that the silabenzene was converted to sila-Dewarbenzene.

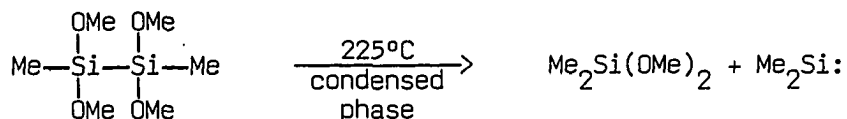
Silabenzene has evolved from a compound of purely theoretical interest to one whose existence is no longer questionable, yet whose isolation remains elusive.

## Thermal Generation of Silylenes (Divalent Silicon)

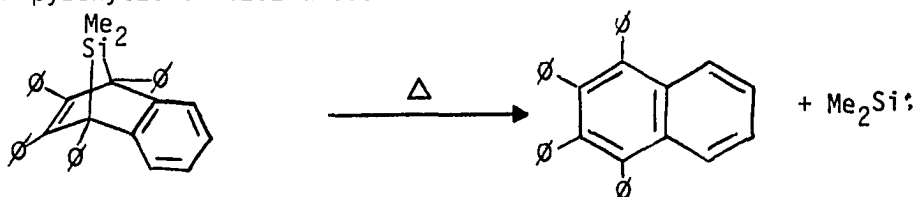
The thermal decomposition of hexahalodisilanes was first reported by Friedel and Ladenburg (50). Years later, Atwell and Weyenberg (51)



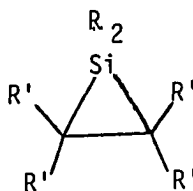
found that thermolysis of alkoxydisilanes gave rise to silylenes (divalent silicon). Both these methods provided much milder routes to silylenes than those used previously (52-55).



7-Silanorbornadienes were first shown by Gilman et al. (56) to extrude silylenes. The synthetic difficulties encountered in 7-silanorbornadiene syntheses make these less attractive routes to silylenes than pyrolysis of disilanes.



By far, the mildest thermal silylene generators are the silacyclopropanes or silaranes (57-60). When  $R = R' = \text{Me}$ , dimethylsilylene can



be trapped at temperatures below 80°C. Silarenes are synthesized with difficulty and are sensitive to air and water.

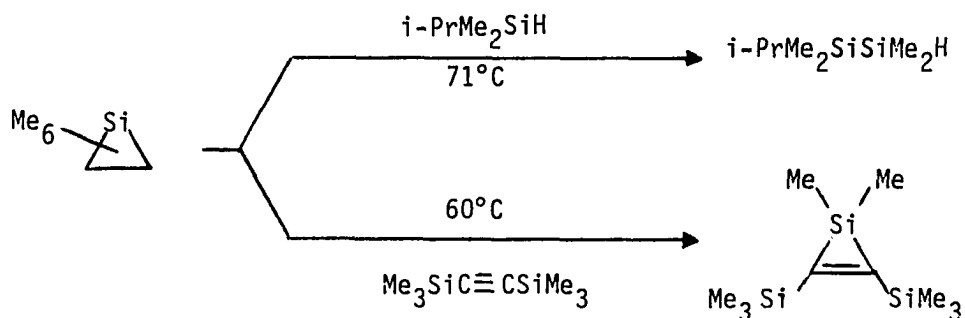


Table 2 shows some methods of thermal silylene generation.

#### Photochemical Silylene Generation

The photochemical decomposition of polysilanes to give silylenes has been known for over a decade and has been recently reviewed (61). Table 3 shows some polysilanes which have been used in these studies.

Although the silarene, 36, was found to photochemically give dimethylsilylene, silarenes are not good sources of silylenes as they react with silylene traps (ketones, olefins, and dienes) to give ring expanded products (62).

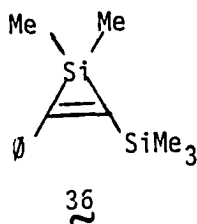


Table 2. Thermal silylene generation

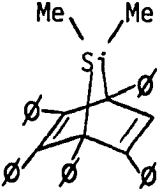
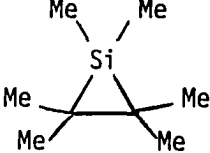
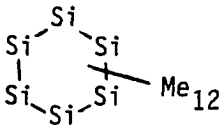
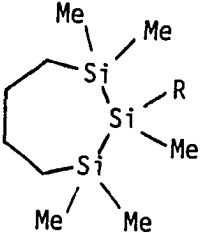
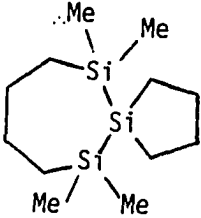
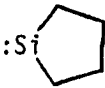
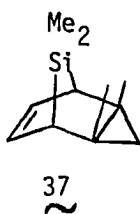
Precursor	Temperature liquid phase (gas phase)	Silylene	Reference
$\begin{array}{c} \text{Me}_2\text{Si}-\text{SiMe}_2 \\   \quad   \\ \text{OMe} \text{ OMe} \end{array}$	185(400)	$:\text{Si} \begin{array}{l} \text{OMe} \\ \text{Me} \end{array}$	63-66
$\text{Me}_3\text{Si})_2\text{SiMe(OMe)}$	350	$:\text{Si} \begin{array}{l} \text{Me} \\ \text{SiMe}_3 \end{array}$	67
$\text{Cl}_3\text{Si}-\text{SiCl}_3$	(600)	$:\text{SiCl}_2$	68,69
	(300)	$:\text{Si} \begin{array}{l} \text{Me} \\ \text{Me} \end{array}$	56,70
	80	$:\text{Si} \begin{array}{l} \text{Me} \\ \text{Me} \end{array}$	57-60

Table 3. Photochemical silylene generation

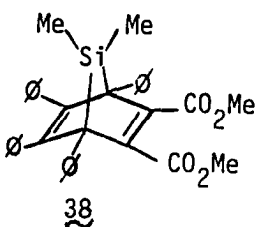
Polysilane	Silylene	Reference
$\text{Me}_3\text{Si}-\text{Si}-\text{SiR}$ $\text{R}=\text{Me}, \text{Ph}$	$\text{:Si} \begin{matrix} \text{R} \\ \text{SiMe}_3 \end{matrix}$	61
	$\text{:SiMe}_2$	61
$\text{Me}_3\text{Si}-\left[ \begin{matrix} \text{Me} \\   \\ \text{Si} \\   \\ \text{Me} \end{matrix} \right]_n-\text{SiMe}_3$ $n=1-6$	$\text{:SiMe}_2$	61
	$\text{:Si} \begin{matrix} \text{R} \\ \text{Me} \end{matrix}$	71
		71



The 8-silatricyclo-[3.2.1.0]-oct-6-ene, 37, will also give a silylene when photolyzed, but yields of trapped products are small (72).



Finally, the 7-silanorbornadiene, 38, gave an 88% yield of tetraphenyl phthalate when photolyzed, but no silylene trapping was reported (73).



### Reactions of silylenes

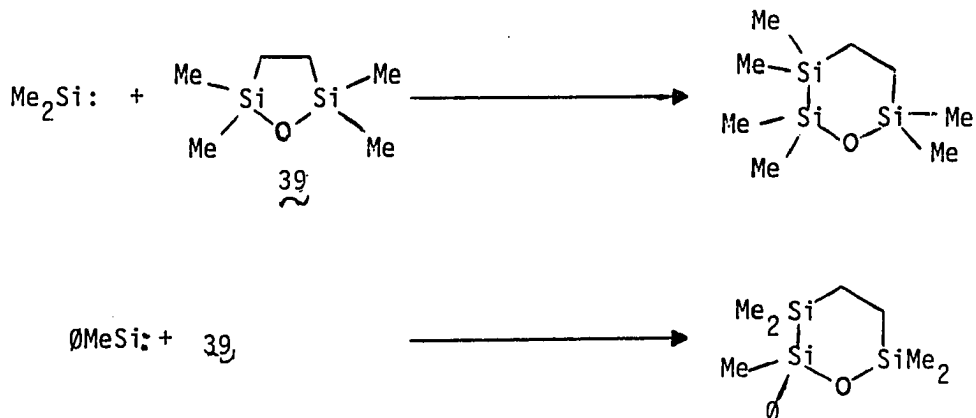
The reactions of silylenes may be divided into (a) insertion reactions, (b) addition reactions, (c) abstractions, (d) dimerizations and (e) rearrangements. The first four types of silylene reactions are depicted in Scheme 8. Only a brief summary of the work will be presented because recent comprehensive reviews exist (74).

The insertion of silylenes into the Si—Si bonds of 1,2-disilacyclobutenes is well-known, (75) but this sort of reactivity seems limited to strained Si—Si bonds.

Not all silylenes show the same reactivity towards the same reagent. Dimethylsilylene will react with hexamethylcyclotrisiloxane to give a ring-expanded product, but methylphenylsilylene does not (76). Both

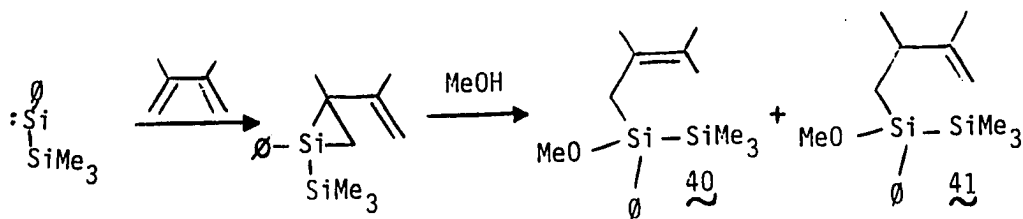


silylenes give ring expanded adducts with cyclic disiloxane 39. These results demonstrate that a delicate balance of factors govern silylene reactions; although the picture remains unclear as to the nature of these factors.

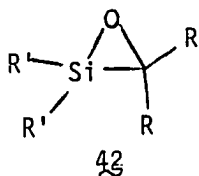


Photochemically generated silylenes add stereospecifically to olefins (77). The stereochemistry of addition of thermally generated silylenes to olefins is not known because the reaction conditions preclude the observation of the 1,2-addition product.

Silylenes generated photochemically are thought to add to dienes in a 1,2-fashion and then rearrange to silacyclopentenes. Trapping of the 1,2-adduct with methanol when trimethylsilylphenylsilylene was reacted with 2,3-dimethylbutadiene, gave methoxysilanes 40 and 41.



The addition of silylenes to carbonyl compounds is pictured as 1,2-addition to form an oxasilirane, 42, followed by rearrangement via diradicals (78). The thermal lability of 42 precludes its trapping,



(in pyrolyses), but with photochemically generated silylenes, dimers of 42, as well as carbonyl addition products, are isolated (78).

Thermally generated silylenes react with acetylenes to give 1,4-disila-2,5-cyclohexadienes (74), whereas photolysis of silylenes and acetylenes gives silacyclopropenes (79). The actual mechanism of 1,4-disila-2,5-cyclohexadiene formation is still questionable.

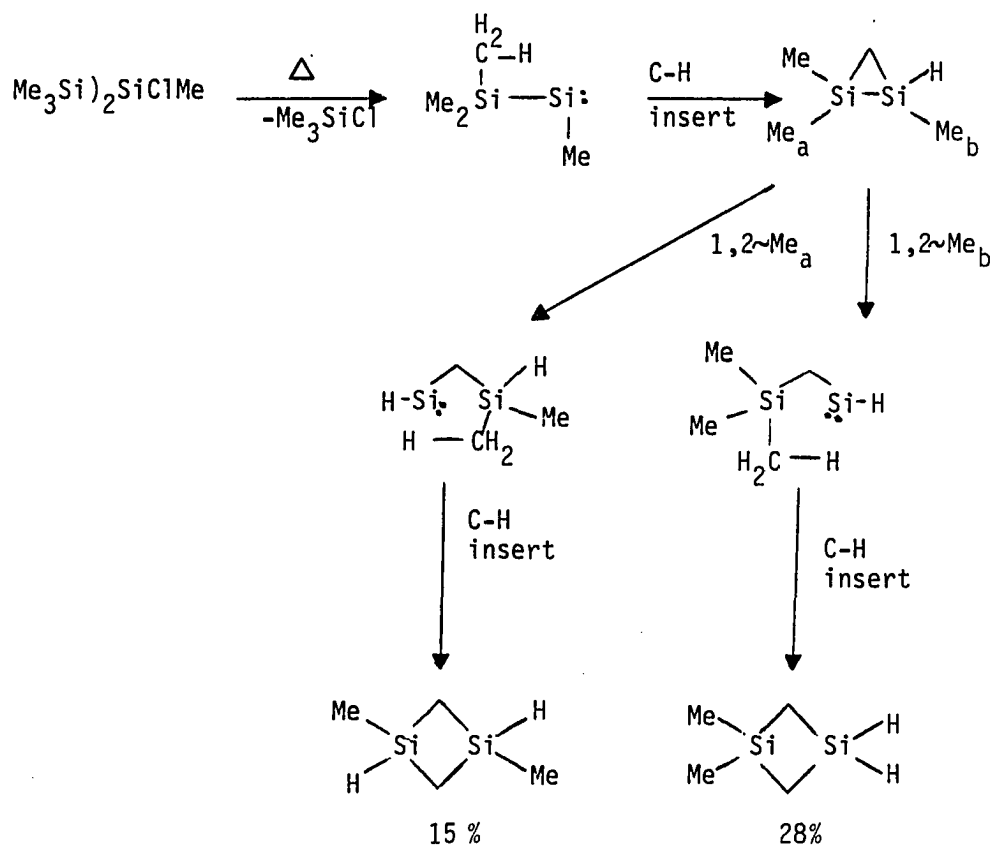
#### Silylene rearrangements

The rearrangement of methyltrimethylsilylsilylene in the gas phase has given rise to some novel chemistry (80). Barton proposed the mechanism in Scheme 9 to account for the 1,3-disilacyclobutanes found in the pyrolysis of 2-chloro-heptamethyltrisilane.

The unique step in Barton's mechanism is the formation of a disilacyclopropane via intramolecular C-H insertion by a silylene. This was the first example of silylene insertion into a C-H bond and the first proposed silylene to silylene rearrangement. Carbene-carbene rearrangements are known, but these occur by a different mechanism (81).

Generation of tetramethyldisilene in the gas phase gave the same 1,3-disilacyclobutanes as methyltrimethylsilylsilylene, prompting Barton's suggestion that the disilene rearranges to methyltrimethyl-

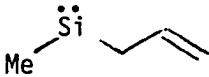
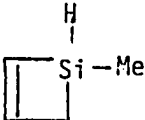
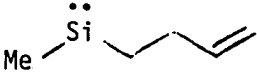
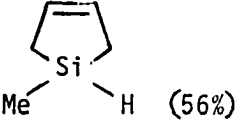
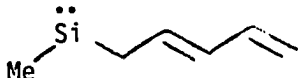
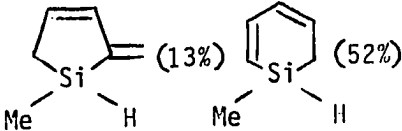
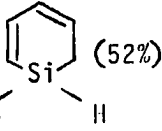
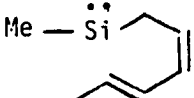
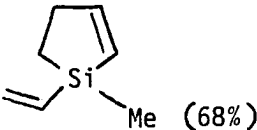
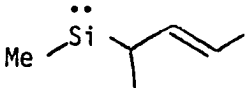
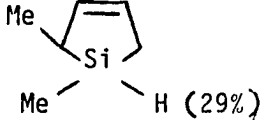
Scheme 9



silylsilylene via 1,2-methyl shift. Co-pyrolysis of the disilene or the silylene with  $\text{Me}_3\text{SiH}$  gave the same products. This strongly favors Barton's suggestion that the silylene and disilene are both on the same energy surface.

Alkenylsilylenes will undergo intramolecular trapping in two ways. They can either add to a  $\pi$ -bond, or they can insert into suitably located allylic C-H bonds (82). Table 4 shows some of the results.

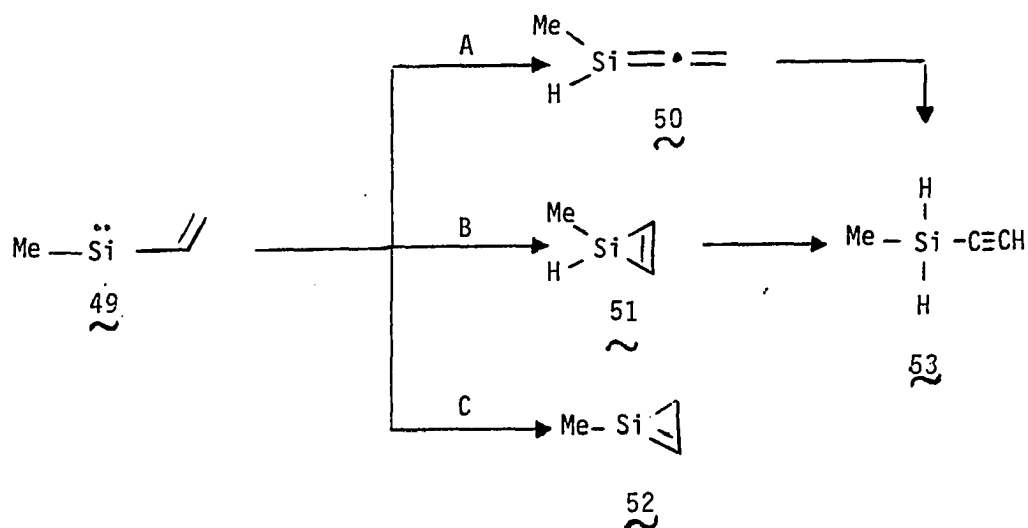
Table 4. Intramolecular cyclizations of alkenylsilylenes

Alkenylsilylene	Product(s)	Reference
		82
	 (56%)	82
	 (13%)  (52%)	82
	 (68%)	82
	 (29%)	82

For the butenylmethylsilylene, the silacyclopentene product has the double bond in the wrong position if simple  $\pi$ -addition of the silylene had occurred. Scheme 10 shows the mechanistic rationale.

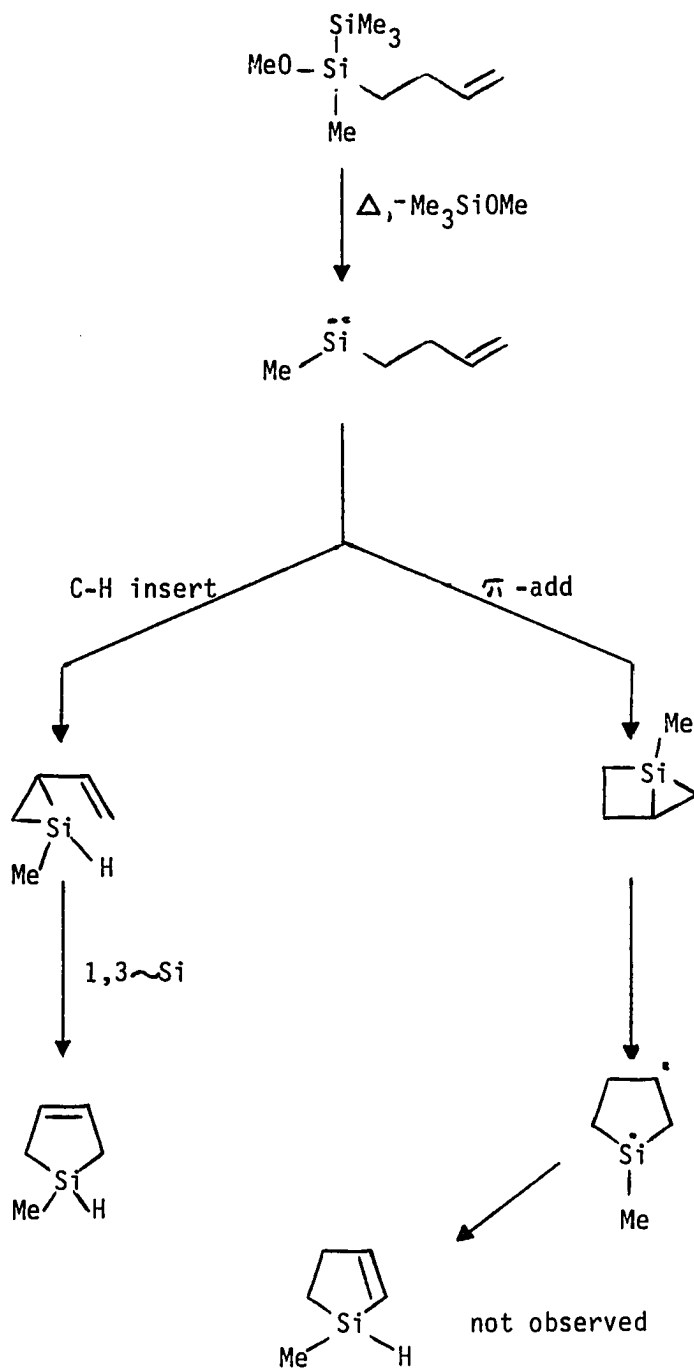
Results from Barton and co-workers show that methylcyclopropylsilylene, 44, may ring expand to a 1-methyl-1-silacyclobut-1-ene 46 which ring opens to give a 2-silabutadiene 47. Evidence for such a rearrangement was obtained from FVP of 43 which gave a 42% yield of cis and trans 48 (83) (see Scheme 11).

The rearrangement of methylvinylsilylene to methylethynylsilane can be accounted for by the three pathways shown below (84). Paths



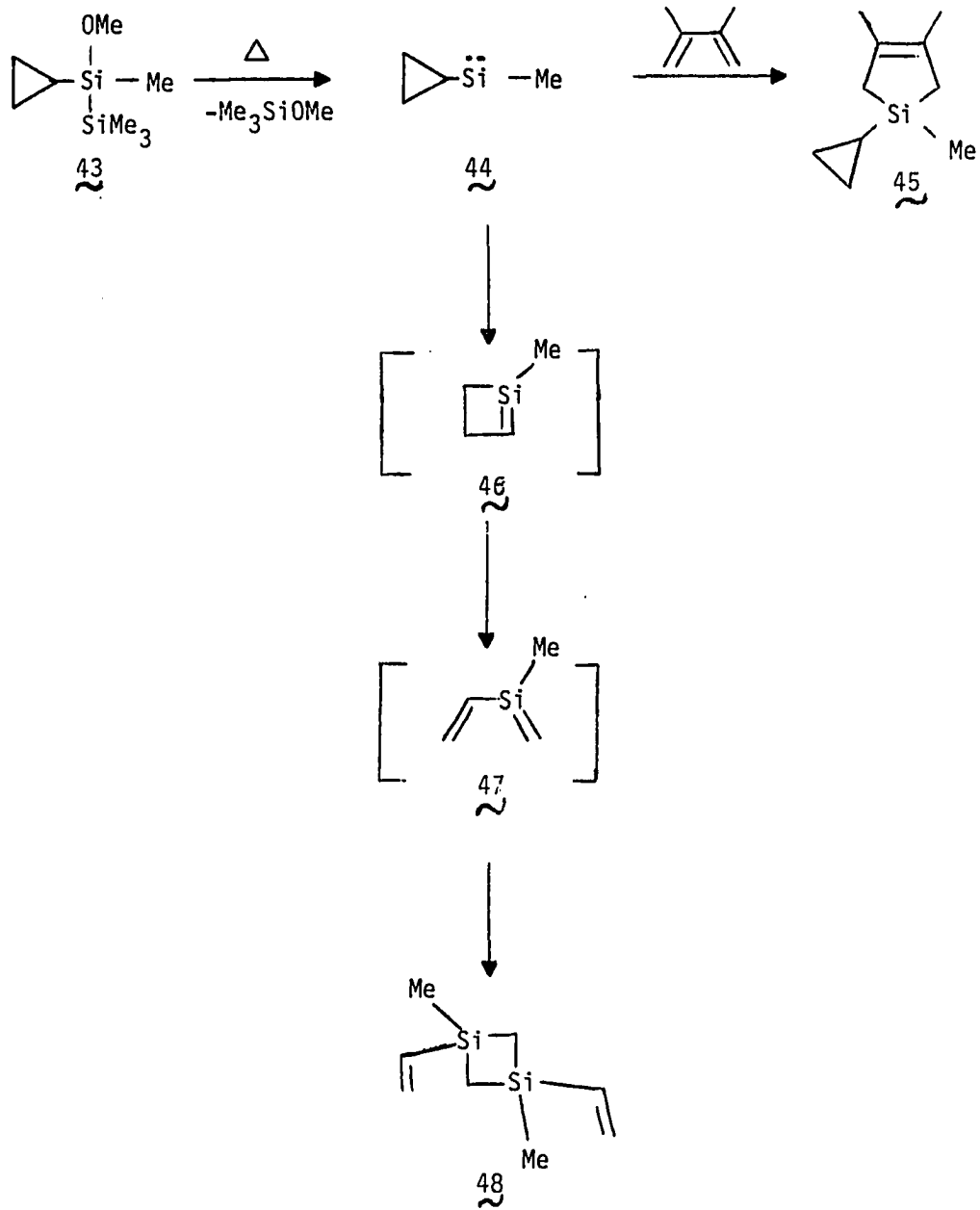
A and B involve silylene insertion into vinyl C-H bonds. This type of insertion has not been observed but the possibility cannot be dismissed out of hand because definitive labelling studies have yet to be done. The formation of 52 is thought by Gordon and Koob (85) to be contra-thermodynamic. Ab initio calculations have shown 52 to be ca. 36 Kcal/mole higher in energy than silylene 49, silarene 51 or silaallene 50.

Scheme 10





Scheme 11



To probe for the possible existence of a 1-silacyclopropene, Barton made trimethylsilylvinylsilylene by pyrolysis of 2-vinyl-2-methoxyhexamethyltrisilane. The 1-trimethylsilyl-1-silacyclopropene could then be diverted from path C by the known (80) silylsilene to silylene rearrangement, thus forming a silacyclopropanylidene. The results of FVP and flow pyrolysis (with 2,3-dimethylbutadiene) are given in Scheme 12.

These results apparently favor the formation of a 1-silacyclopropene, but do not rigorously exclude another mechanism. The preceding has been a very brief description of silylene rearrangements. No comment has been made on the controversy surrounding the interconversion of silenes and silylenes because it is not germane to this work.

#### Silenes: Silicon-Carbon (p-p) $\pi$ -Bonds

The search for methods of silene generation and the study of silene chemistry has provided an enormous volume of work. This amply reviewed field (1, 11, 20, 21, 24, 25, 86, 87, 88) would not benefit from yet another review, so an overview of the most general methods of silene generation and common reactions of silenes will be presented with limited commentary. Table 5 shows some common methods of silene generation.

Scheme 12

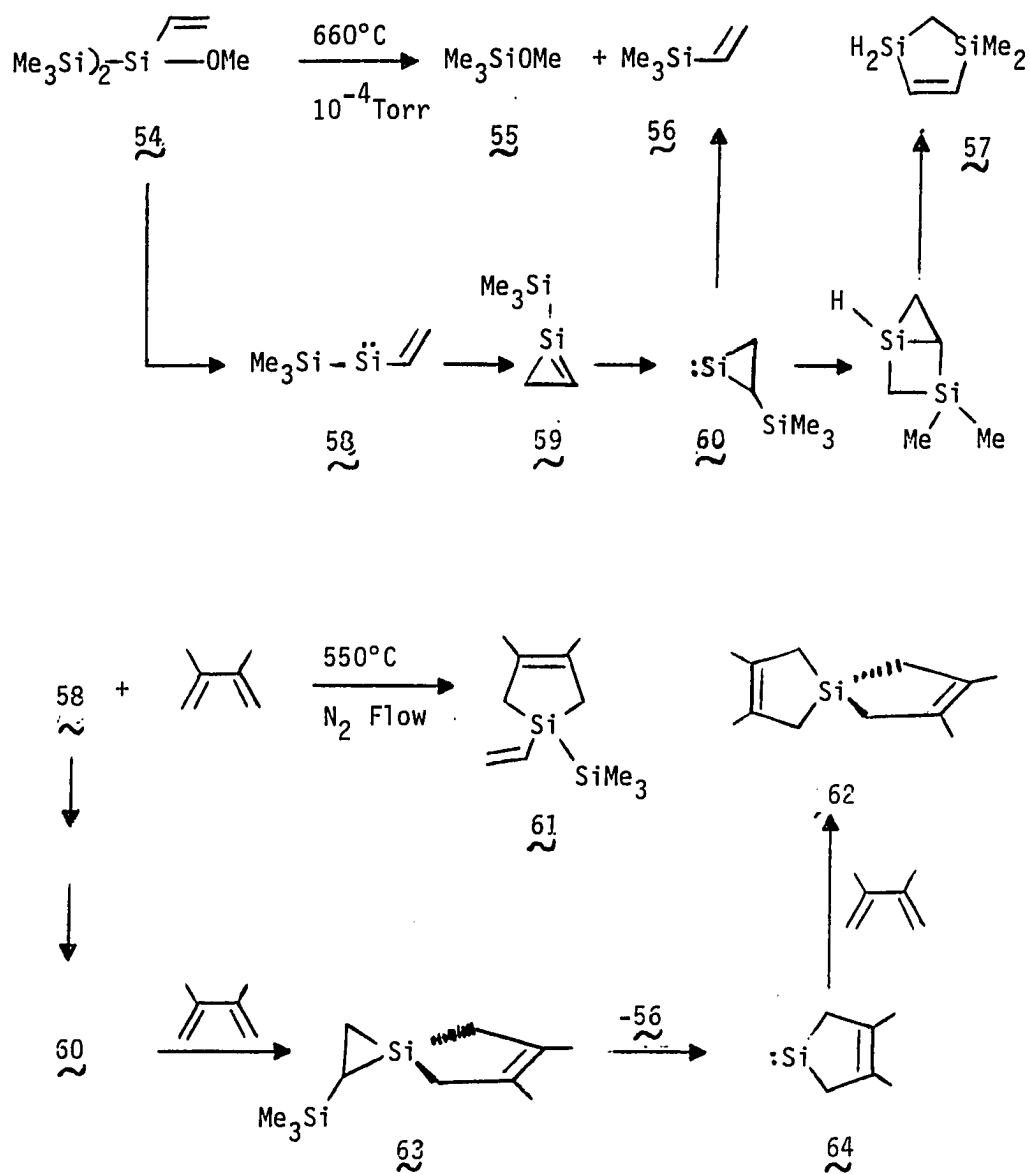


Table 5. Silene generation

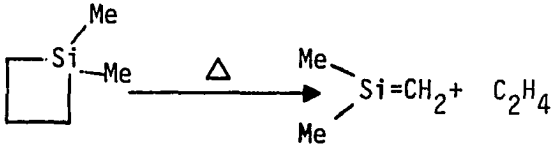
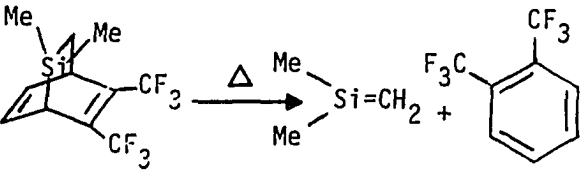
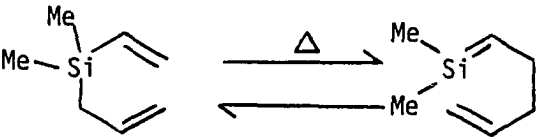
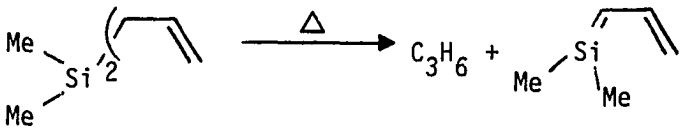
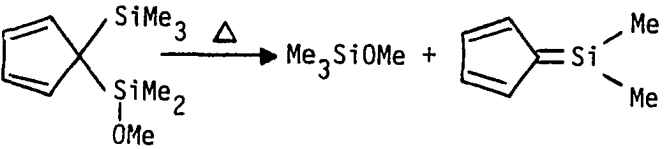
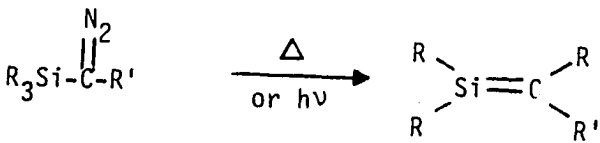
Precursor	Silene	Ref.
		39
		87
		90
		49
		91
		92

Table 5. (continued)

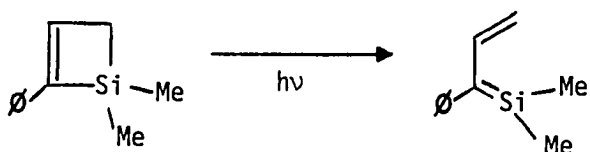
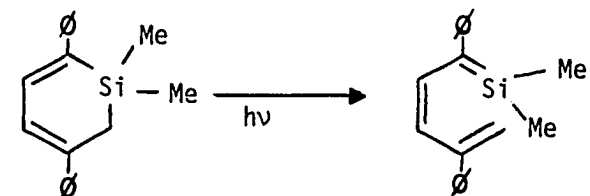
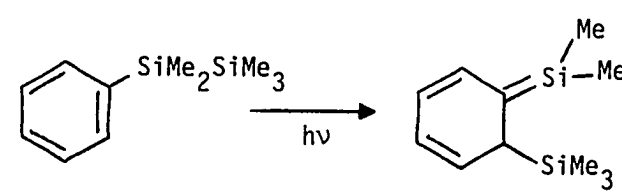
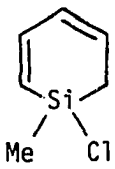
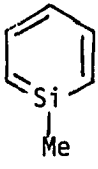
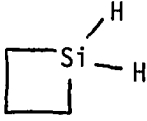
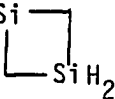
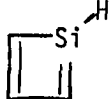
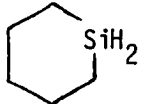
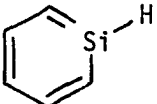
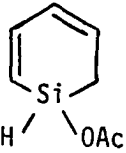
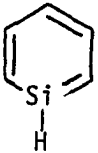
Precursor	Silene	Ref.
$R_3Si-SiR'_2-C(=O)R''$	$\xrightarrow[\text{or } h\nu]{\Delta} \begin{array}{c} R' \\ \diagdown \\ Si=C \\ \diagup \\ R' \end{array} \begin{array}{c} OSiR_3 \\ \diagdown \\ C \\ \diagup \\ R'' \end{array}$	93,94
	95	
	96	
$R_3Si-SiR'_2-CH=CH_2$	$\xrightarrow{h\nu} \begin{array}{c} R' \\ \diagdown \\ Si=C \\ \diagup \\ R' \end{array} \begin{array}{c} R'' \\ \diagdown \\ C \\ \diagup \\ CH_2SiR_3 \end{array}$	97a,b
	98	
$\begin{array}{c} Me_2Si-CH=CH_2 \\   \\ Cl \end{array}$	$\xrightarrow[-LiCl]{t-BuLi} \begin{array}{c} Me_2Si=C \\ \diagup \\ H \end{array}^+$	48

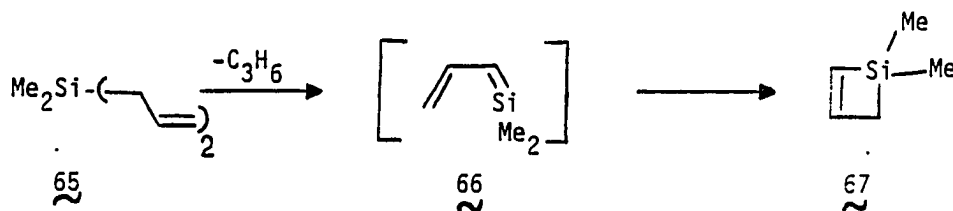
Table 5. (continued)

Precursor	Silene	Ref.
	$\xrightarrow[\text{-LiCl}]{\text{Me}_3\text{Si})}_2\text{NLi}$ 	2
	$\xrightarrow{\text{Pd}(110)} \text{H}_2\text{Si}$  + 	99
	$\xrightarrow{\text{Pd}(110)}$ 	99
	$\xrightarrow[\text{-HOAc}]{\Delta}$ 	6

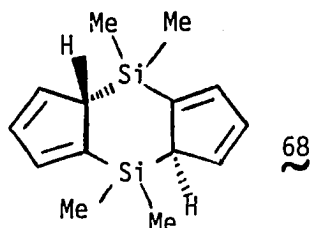
The thermal decomposition of silacyclobutanes was the earliest method found for silene generation (39b). Kinetic studies have shown this decomposition to be unimolecular and possessing kinetic parameters nearly equal to those for the thermolysis of 1,1-dimethylcyclobutane (25). This is a reversible reaction (100) whose mechanism is a topic of current debate.

Slutsky and Kwart (90) showed that allylvinylsilanes undergo reversible Cope rearrangement to give silenes. This interesting observation has not been further employed in silene generation.

Searching for a facile synthesis of silacyclobutenes, Block and Revell (49) discovered that diallylsilanes will eliminate propene via retro-ene reactions to initially form 1-sila-1,3-butadienes which then undergo [2 + 2] electrocyclicization to form the desired silacyclobutene.

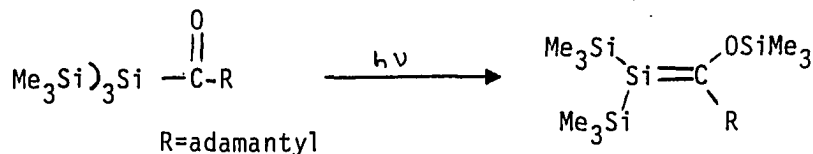


This retro-ene elimination has been used by Barton and Burns to synthesize 1-silatoluene, (4) the first C-unsubstituted silole, (101) and 6,6-dimethyl-6-silafulvene (91). The silafulvene was also generated from the pyrolysis of 1-trimethylsilyl-1-dimethylmethoxysilylcyclopentadiene. The product from either method was the silafulvene dimer, 68. The latter route was the first demonstration of a  $\beta$ -elimination of an alkoxy silane to form a silene, although such a reaction had been postulated by Rutherford and Seidewitz in 1975 (87).



$\alpha$ -Silyl diazo compounds produce silenes either photochemically or thermally by alkyl (or aryl) migration from silicon to the carbenic center (93). Methyl migration predominates over phenyl or benzyl migration (24).

The 1,3-migration of  $R_3Si-$  groups in acyl polysilanes was first used by Brook in 1979 to form Si-C (p-p)  $\pi$ -bonds. This work has culminated in the first stable  $\pi$ -bonded silicon compound (9).



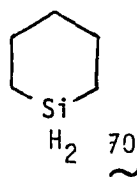
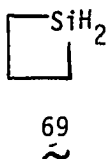
This molecule was twisted about the central Si-C axis by  $14.6^\circ$ ; meaning that the maximum deviation from planarity would be .01 to .03 Å. This fact is cited by Brook as evidence that the silicon atom is truly  $sp^2$  hybridized and that there is no significant reduction in the (p-p)  $\pi$  overlap between the silicon and the carbon. The twisting most likely results from relief of steric strain.

Brook states that the Si=C bond is not as polarized as was previously thought. A polarized bond would allow rotation about the Si-C axis which would make the trialkylsilyl groups equivalent in the



$^1\text{H}$  NMR spectrum. The NMR data show distinct resonances for each trialkylsilyl group, supporting Brook's claim. Definitive conclusions about Si-C (p-p)  $\pi$ -bonds must await further results.

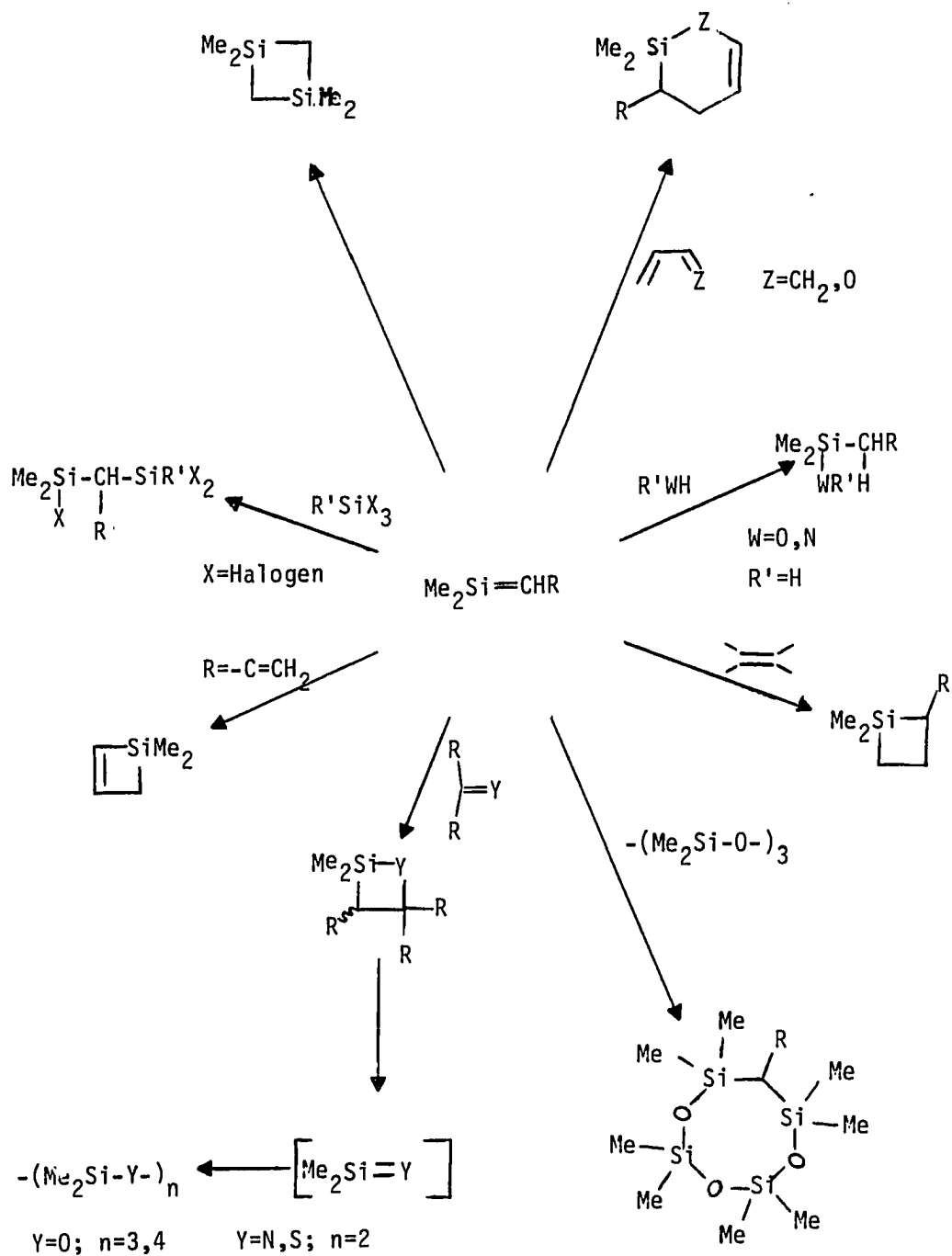
The remaining methods of silene generation are well-documented (95-98) and deserve no additional comment. Recently, Gentle and Muetterties (99) raised the titilating prospect of generating silenes in a very unique fashion. Silacycles, such as 69 and 70 can be chemisorbed



on a Pd [110] surface at  $-135^\circ\text{C}$ , under ultrahigh vacuum. As the surface is allowed to warm up, silacyclobutadiene and silabenzene are desorbed. These compounds were identified by mass spectral analysis only. Future work may give trapping evidence.

Scheme 13 shows the reactions silenes undergo in trapping experiments or synthetic work.

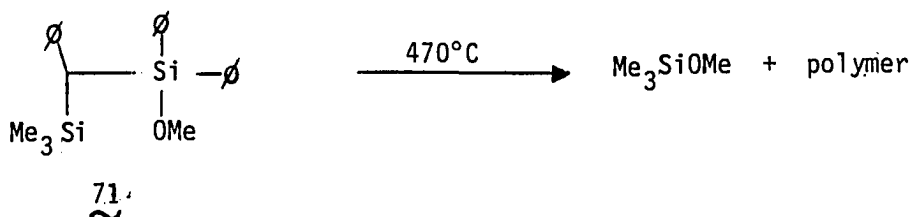
Scheme 13



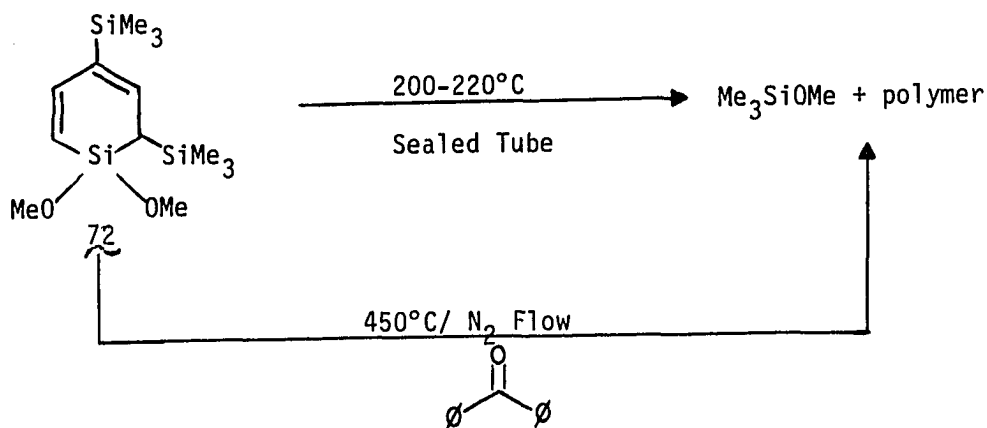
## RESULTS AND DISCUSSION

Synthesis and Pyrolysis of 4-Trimethylsilyl-1-methoxy-  
1-methyl-1-silacyclohexa-2,5-diene

Although appropriately  $\beta$ -substituted organosilanes are known to decompose to olefins and substituted silanes, Rutherford and Seidewand (87) failed to obtain evidence for generation of a silicon-carbon (p-p)  $\pi$ -bond via  $\beta$ -elimination of trimethylmethoxysilane from benzyldiphenylmethoxysilane 71. The products were trimethylmethoxysilane and unidentified high molecular weight material.

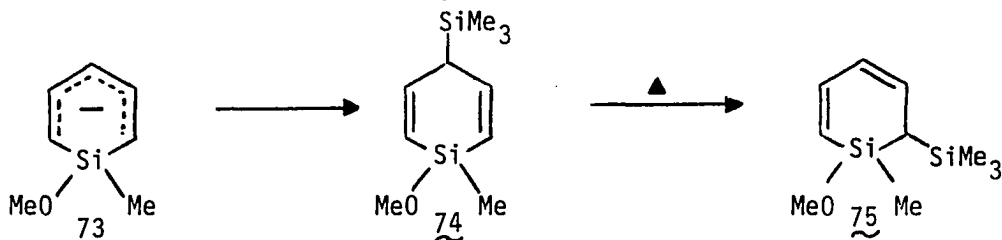


Banasiak employed this reaction in attempting to generate a 1-silabenzene (24). Several pyrolyses of the precursor, 72, gave trimethylmethoxysilane as the sole identifiable product. The silabenzene may have been formed, but it was not trapped under the conditions used.

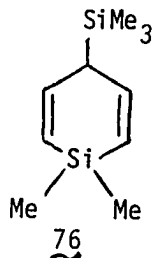


Barton et al. have demonstrated that the  $\beta$ -elimination of trimethylmethoxysilane can be used in Si-C (p-p)  $\pi$ -bond formation (91). They have also shown that silabenzene may be trapped by MeOH(D), acetylenes, or itself (3). An alternative synthesis of silabenzene was designed to make use of these facts and coupled with the known ability of silicon to undergo thermally-induced 1,3-migrations (90).

Kinetic quenching of the anion, 73, should produce silylated 74. From 74 the 1,3-migration of the 4-trimethylsilyl group to form 75, followed by a  $\beta$ -elimination of Me<sub>3</sub>SiOMe should give 1.



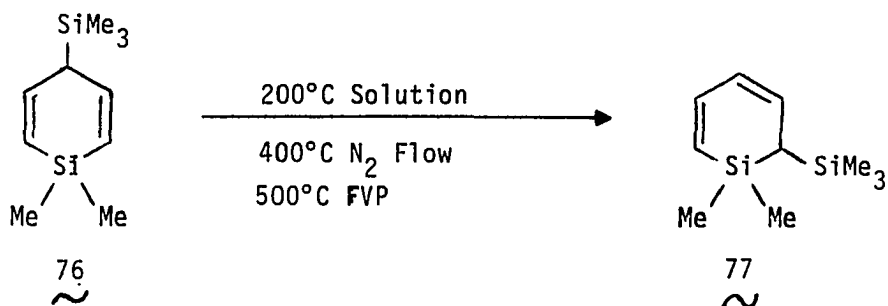
There have been no examples of a 1,3 silyl shift on a silacyclohexadienyl ring system, so the known 76 (24) was heated in a sealed, degassed NMR tube (D-6 benzene solution) and the reaction progress monitored by NMR.



After 6 hours at 200°C, all signals due to 76 were virtually gone. The methine proton resonating at  $\delta$  2.68 (d of t) had been replaced by a doublet at  $\delta$  1.4, reflecting the change in environment from diallylic to  $\alpha$ -silylallylic for this proton. The clean olefinic absorptions for

symmetrical 76 at  $\delta$  5.82 and  $\delta$  6.75, (both d of d), were replaced by complex multiplets centered at  $\delta$  5.9 and  $\delta$  6.9.

Vertical flow pyrolysis (450°C, N<sub>2</sub> flow) and vacuum pyrolysis (500°C, 10<sup>-4</sup> Torr) of 76 also afforded 77. It appears as though 76 is cleanly rearranged to 77.

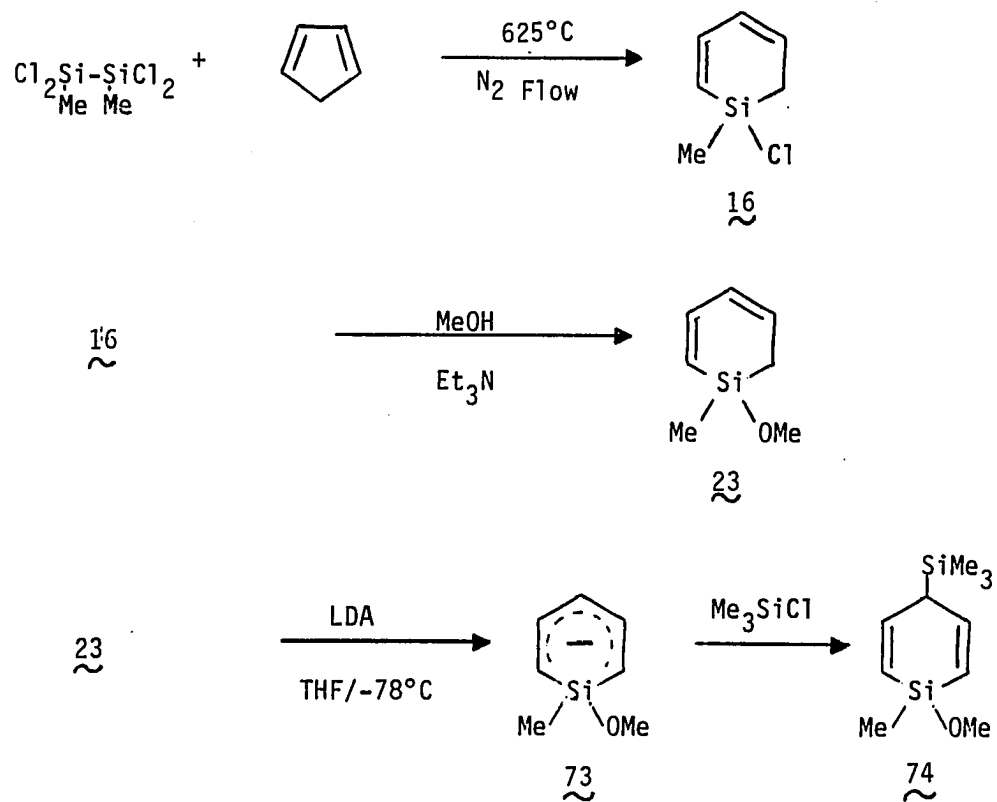


The synthesis of precursor 74 is shown in Scheme 14. The addition of methylchlorosilylene to cyclopentadiene produced methylchlorosilacyclohexadiene, 16, in approximately 25-30% yield (2). The conversion of 16 to the methoxy compound, 23 was carried out in a yield of 90% by treatment with MeOH/Et<sub>3</sub>N in ether. 23 was metalated by lithium diisopropylamide (LDA) in tetrahydrofuran (THF) at -78°C. Quenching the anion 73 with Me<sub>3</sub>SiCl gave 74 as a colorless oil (55-60% yield) after flash chromatography followed by distillation.

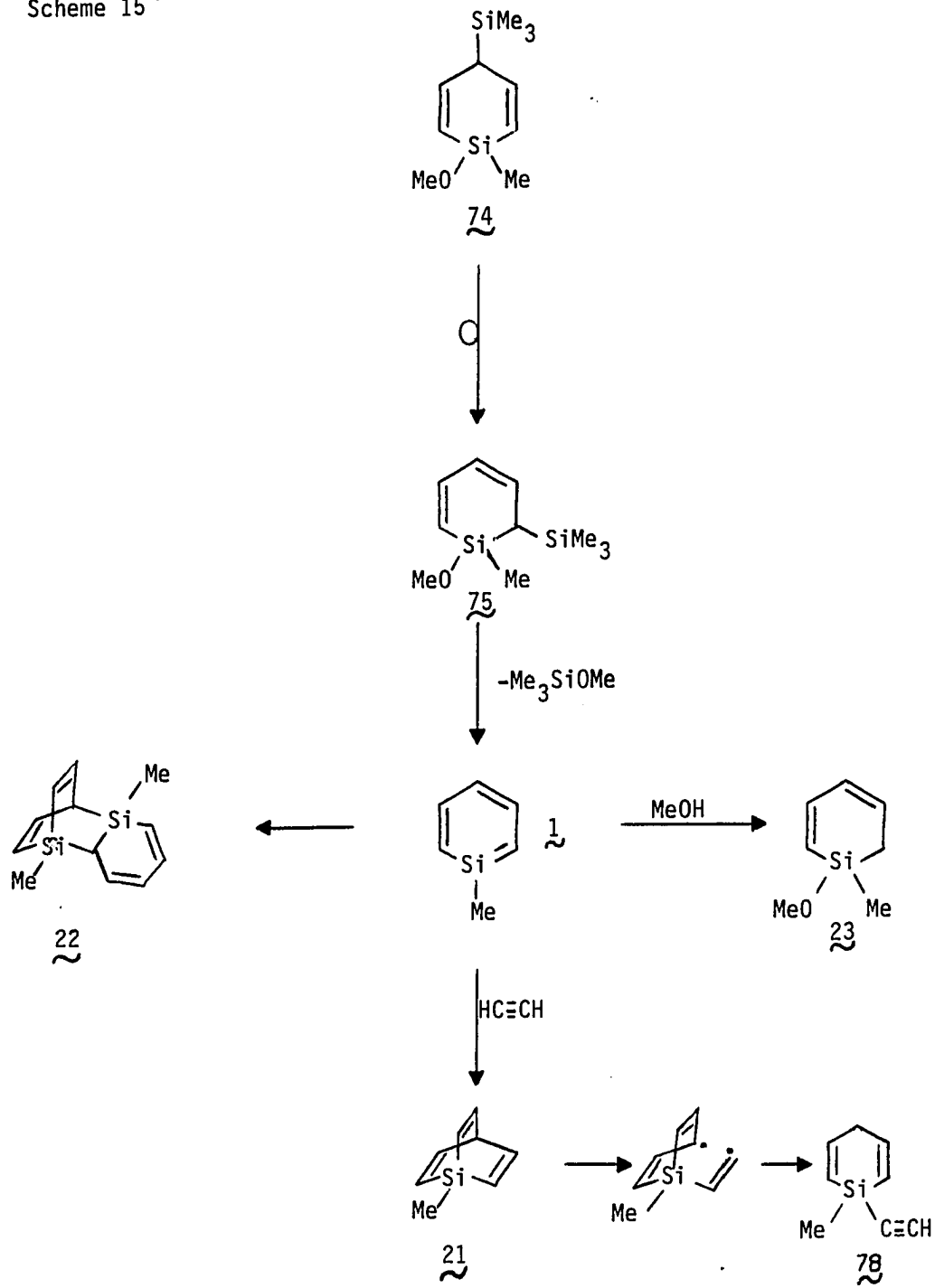
When a degassed solution of 74 in diphenyl ether was heated at 150°C for 10 hours, essentially all of 74 had rearranged to 75, which was isolated by preparative gas chromatography (GC).

FVP of 74 (660°C, 2 × 10<sup>-4</sup> Torr) through a 1 ft. horizontal, quartz tube packed with quartz chips gave a light yellow colored liquid which represented a 46% mass recovery. See Scheme 15.

Scheme 14



Scheme 15



Preparative GC allowed the isolation of the silatoluene dimer, 22, in 14% yield. Structural proof was based on a comparison of the  $^1\text{H}$  NMR and mass spectra of authentic 22 prepared from FVP of 20 (5).

Further trapping of silatoluene was accomplished by flow co-pyrolysis ( $\text{N}_2$ ) of 74 with a 10-fold molar excess of MeOH in a vertical tube furnace. Mass recovery (including MeOH) amounted to 61%. The amount of 23 formed was 51% based on reacted 74. It is possible that the conversion of 74 to 23 is simply a desilylative methanolysis followed by isomerization. While 1 generated from 20 has been trapped with MeOD, this sort of trapping experiment would not remove any mechanistic ambiguities.

Better evidence for silatoluene intermediacy was found in the flow co-pyrolysis of 74 with acetylene as carrier gas and reactant. The pyrolysate was a mixture of  $\text{Me}_3\text{SiOMe}$ , unreacted 74, and the adduct, 1-methyl-1-silabicyclo[2.2.2] octatriene, 21, formed in 28.5% yield. The  $^1\text{H}$  NMR and mass spectrum of 21 were identical to the 1-methylsilabarrelene, 21, prepared from 20 (3,4). A minor product, 78, was also isolated by preparative GC and identified by  $^1\text{H}$  NMR, mass spectrum, and IR spectrum. The origin of this product is uncertain, but it may arise via a radical process.

While the 1,3-silyl shift on a silacyclohexadienyl ring system had been shown to occur, another important point in this synthesis should be discussed. The expected  $\beta$ -elimination of  $\text{Me}_3\text{SiOMe}$  from 75 would depend on the stereochemistry of 75 since a syn relationship of the  $\text{Me}_3\text{Si}$ - and  $\text{MeO}$ - is required for a concerted reaction. Thus, the stereochemistry of



74 would ultimately control silatoluene formation. 74 is formed by kinetic quenching of anion 73 and the ring silicon is two carbons removed from the site of attack. Therefore, little stereochemical preference was expected. However, the NMR spectra of 74 clearly revealed it to be a single diastereomer. Based on the formation of much  $\text{Me}_3\text{SiOMe}$  from the pyrolyses of 74, it was presumed that the  $\text{Me}_3\text{Si-}$  and  $\text{MeO-}$  groups were indeed syn. The methoxyl oxygen may interact with the incoming silicon and direct it to the same side of the ring.

The generation of 1-silatoluene was realized via an unprecedented rearrangement-elimination sequence as evidenced by trapping experiments using acetylene and methanol. The rearrangement step was verified by monitoring the reaction progress by NMR.

#### Thermochemistry and Photochemistry of Silabarrelene

The facile synthesis of 1-methyl-1-silabicyclo [2.2.2] octatriene, 21 (silabarrelene), from co-pyrolysis of 74 with acetylene made possible the further study of this unique silacycle.

Photolysis of 2,3-perfluoromethyl-1-methyl-1-silabarrelene, 18, in benzene through quartz gave a complex mixture of products which were isomeric with the starting material. The structures of these isomers were never elucidated (24).

In the original studies on barrelene photoconversion to semi-bullvalene, barrelene was irradiated with Vycor filtered light in isopentane solution, using acetone as a sensitizer (102). These

photolyses were generally carried out to 30 - 45% conversion (irradiation time ~ 40-80 minutes).

Attempting to reproduce these conditions, a 2% (by weight) solution of silabarrelene 21 was photolyzed in cyclohexane through a quartz NMR tube. Prior to irradiation, argon was bubbled through the solution for 20 minutes. The light source was a quartz-jacketed, 450 W, Hanovia medium pressure Hg lamp. After approximately 1 hour irradiation time, a white, fluffy precipitate had formed. This precipitate was not soluble in acetone,  $\text{CHCl}_3$  or  $\text{CCl}_4$ . This result was obtained with or without acetone sensitization.

To prevent this decomposition, the photolysis was carried out as before, with a Pyrex NMR tube replacing the quartz, thereby decreasing the amount of light available. Thus, a 1 - 2% silabarrelene solution in cyclohexane was irradiated as before, using acetone as a sensitizer. After 20 minutes, a change was observed in the olefinic region of the  $^1\text{H}$  NMR spectrum. After 40 minutes, all the starting material olefinic signals had disappeared and had been replaced by a new set of signals. (See figure 2.)

By GC there was a single component (besides the solvent) in the reaction mixture. This compound had a retention time similar to that of the starting material. This compound was isolated by preparative GC and identified as 1-methyl-1-silatricyclo [3.3.0.0] octa-2,6-diene, 79, on the basis of  $^1\text{H}$  NMR and mass spectral data. This is the first example of a silasemibullvalene.

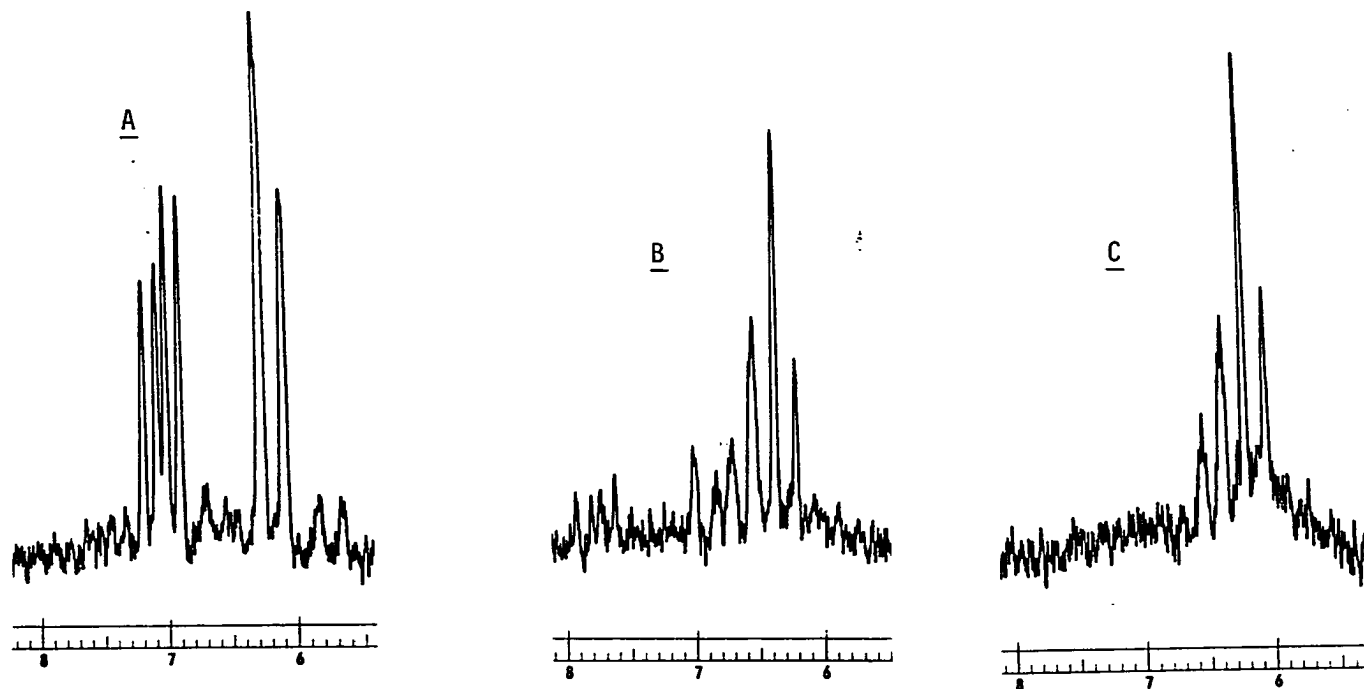


Figure 2. NMR spectra depicting the photoisomerization of 1-silabarrelene to silasemibullvalene. A is silabarrelene, B is the mixture after 20 minutes, C is the olefinic region of silasemibullvalene, <sup>79</sup>

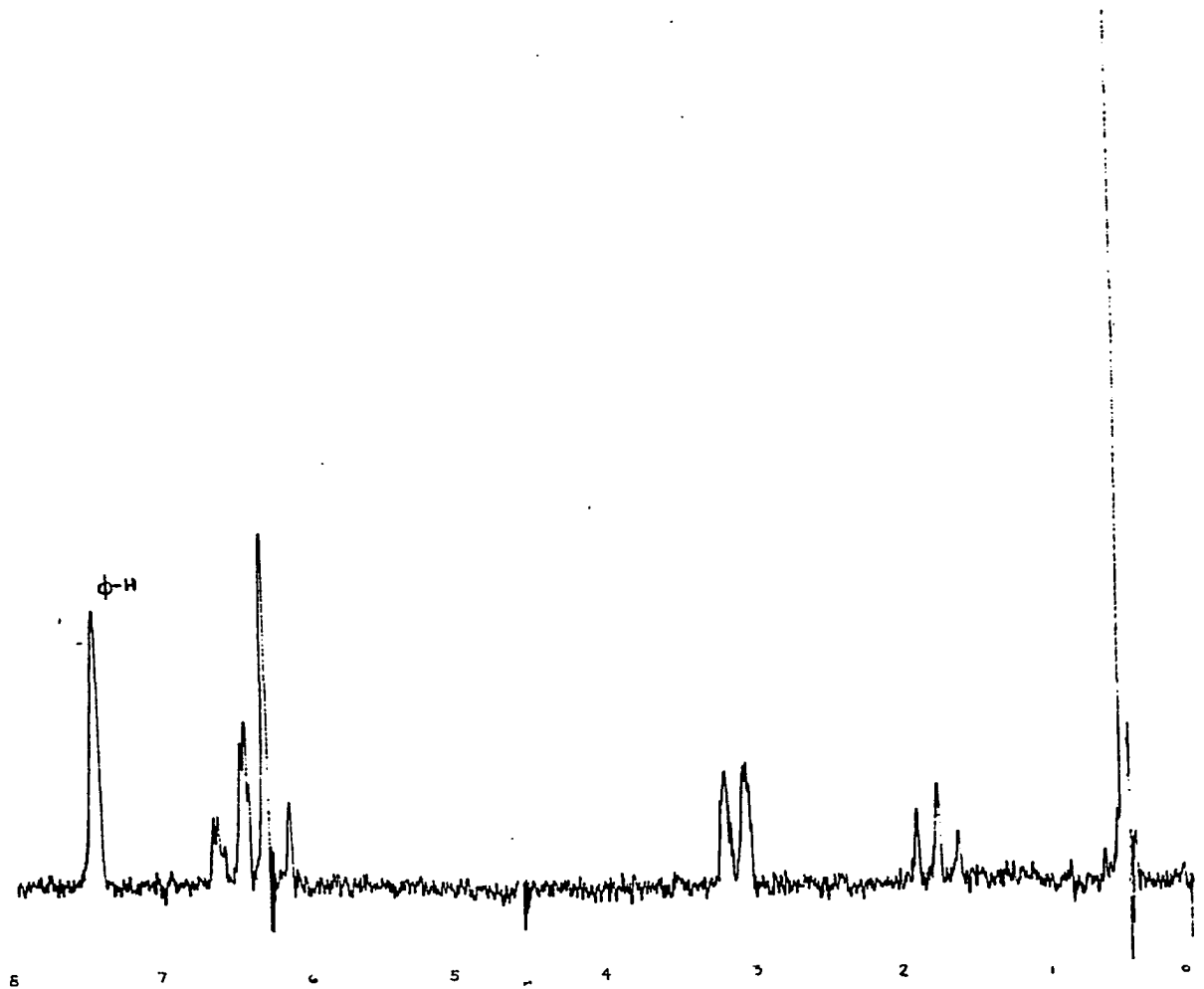
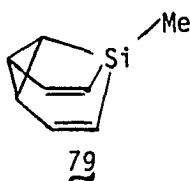
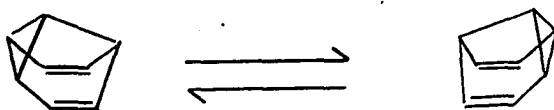


Figure 3.  $^1\text{H}$  NMR of silasemibullvalene in D-6 benzene



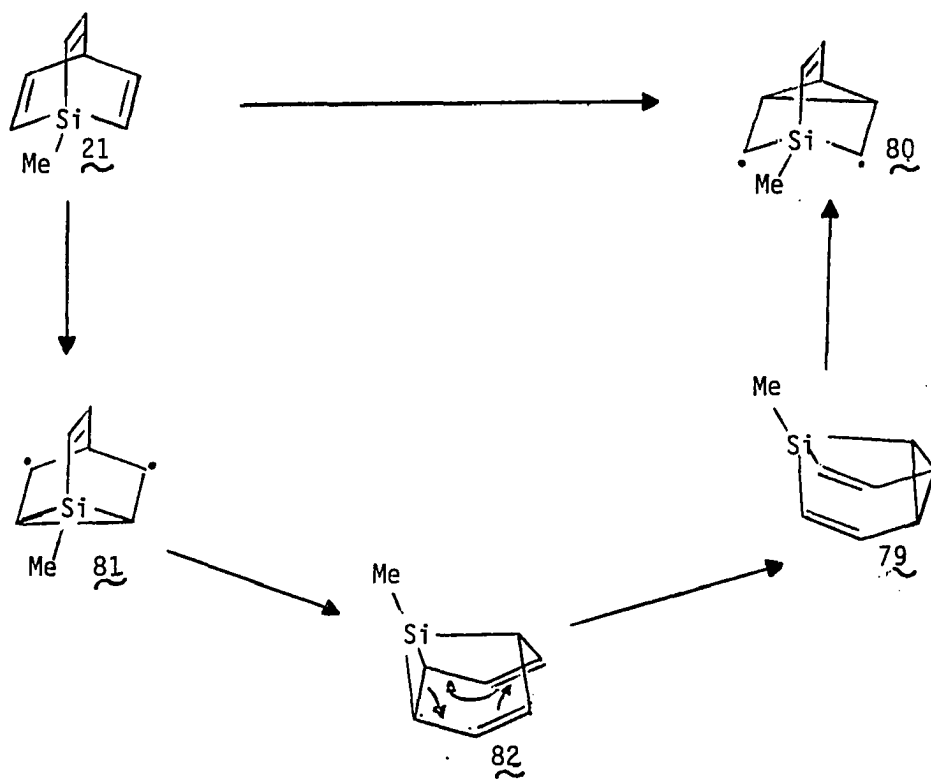
As in the rearrangement of barrelene itself, a di- $\pi$ -methane process is invoked (102). Due to the loss of symmetry in silabarrelene, there are two possible diradical intermediates, 80 and 81. 80 is presumably favored because of the considerable strain in the silacyclopropyl ring (103). However, formation of 82, followed by rapid Cope rearrangement to 79, cannot be excluded. (See Scheme 16.)

It is at this point where the chemistry of silabarrelene and silasemibullvalene diverge from the all-carbon systems. Semibullvalene undergoes degenerate Cope rearrangement at  $-150^{\circ}\text{C}$  with a small (4.8 Kcal/mole) activation energy (104).

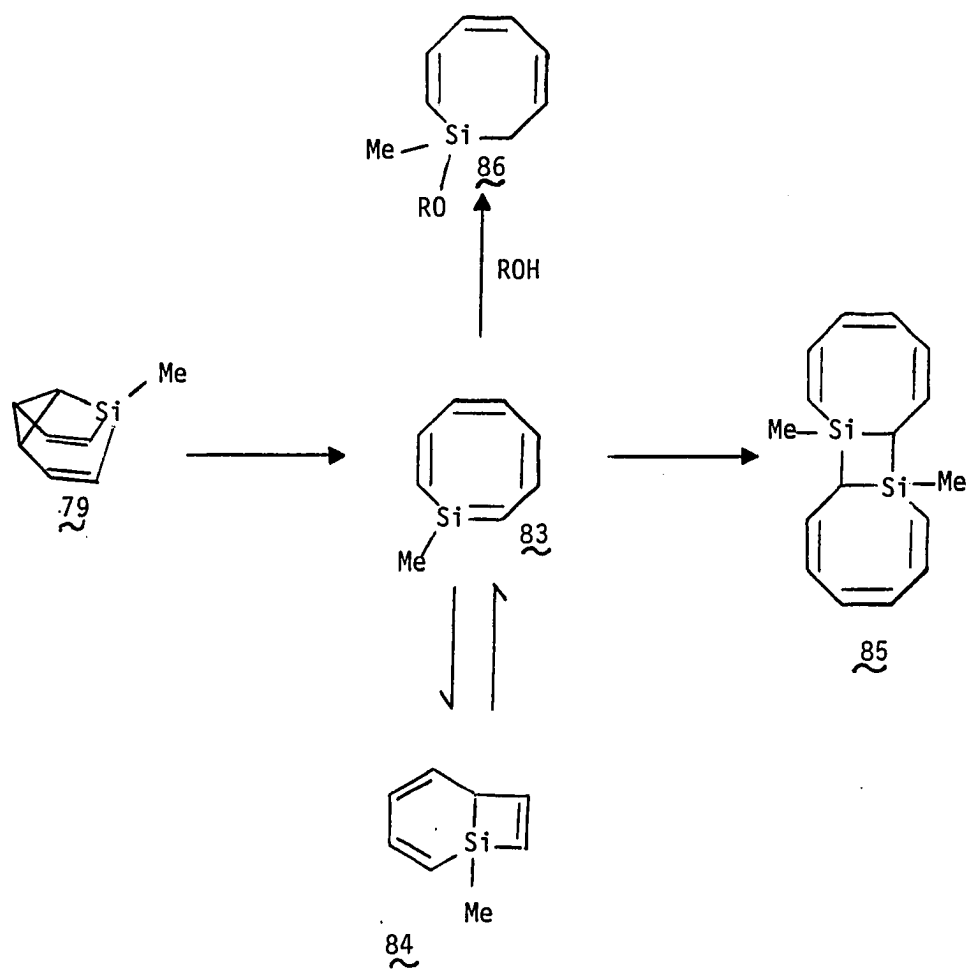


To test the possibility of an 79  $\rightleftharpoons$  82 equilibrium, 79 was freeze-thaw degassed and sealed under vacuum in an NMR tube with D-8 toluene. This was heated in the probe of an NMR spectrometer and spectra were recorded at  $100^{\circ}$ ,  $110^{\circ}$ ,  $120^{\circ}$ , and  $150^{\circ}\text{C}$ . There was never a visible change in the  $^1\text{H}$  NMR spectrum, even after several hours at  $150^{\circ}\text{C}$ . It appears that 79 is locked into that conformation because of the strain involved in forming a silacyclopropyl ring.

Scheme 16

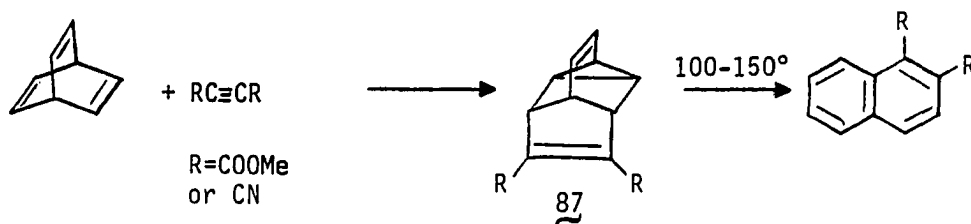


Semibullvalene can be photoisomerized to cyclooctatetraene (102). It was hoped that photolysis of 79 (or 21) would give silacyclooctatetraene, 83, or an isomer thereof, 84. Formation of dimer 85 or an adduct with alcohol, 86, would also provide evidence for a silacyclooctatetraene.



When silabarrelene was photolyzed in methanol through a quartz filter, unreacted 21 was recovered after 2 hours irradiation. Longer irradiation times led to a complex mixture of products. Silasemi-bullvalene was photolyzed through quartz in cyclohexane solution, using acetone sensitization. The reaction progress was followed by NMR and was stopped when the olefinic signals of 79 had virtually disappeared. Gas chromatography mass spectrometry (GCMS) showed the reaction mixture to contain 4 compounds (one of which was unreacted 79). The major peak had  $m/e = 150$ , but it contained no silicon. The mixture would not separate under preparative GC conditions. A single peak comprised of all 4 products was isolated. The  $^1\text{H}$  NMR revealed minute olefinic and silicon methyl signals (from 79) and four singlets at  $\delta$  3.7, 2.6, 2.1, and 1.5 in a ratio of 3:2:2.3:1. This material was not identified.

Zimmerman et al. (105a) and Krispan et al. (105b) reported that barrelene underwent a homo Diels-Alder reaction with dimethylacetylene dicarboxylate (DMADC) or dicyanoacetylene to give adducts 87.

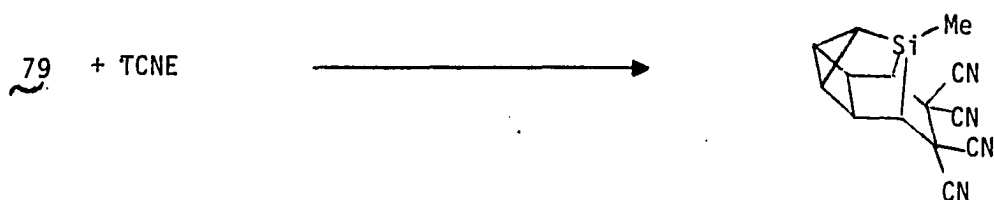




Were silabarrelene to undergo the same reactions, a dihydro-silanaphthalene with silicon at the ring juncture would be formed, providing entry into another highly sought ring system, 9-methyl-9-siladihydronaphthalene.

A solution of silabarrelene, DMADC, and D-6 benzene was degassed and sealed in an NMR tube under vacuum. This mixture was heated for over 10 hours at 150°C, but no change in the NMR was seen.

Two attempts were made at inducing 79 to undergo a homo Diels-Alder reaction. In these reactions, tetracyanoethylene (TCNE) was used as the



dienophile. Both reactions were run in septum-sealed NMR tubes and the solutions had been purged with argon for 10 minutes before the addition of the TCNE.

The first reaction was run in D-6 benzene at 60°C. After 1 hour, there was some solid formed in the tube and the NMR showed that the starting material had disappeared. GCMS showed the presence of TCNE and one compound with  $m/e = 112$ , but the  $m + 1$  (7.5%) and  $m + 2$  (.093%) did not indicate the presence of silicon in this molecule.

The solution was centrifuged down and the liquid pipetted off. The remaining liquid was evaporated in a nitrogen stream. The brown-red solid was taken up in D-6 acetone and the NMR taken. Except for the D-5

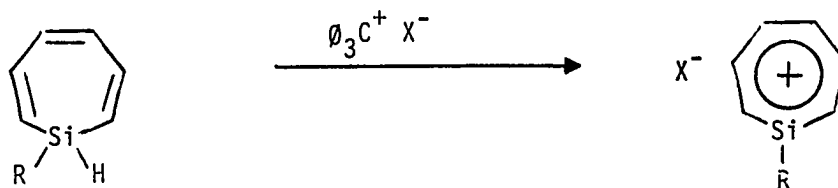
acetone signal at  $\delta$  2.05, the only other signal was a singlet at  $\delta$  2.85. As no silicon methyls were present, this solid was not investigated.

The reaction in D-8 toluene was kept at room temperature for 32 hours. Line broadening was the only change observed by NMR. Again, a solid was formed and it was removed by filtration. An NMR in D-6 acetone revealed a singlet at  $\delta$  2.84 (in relation to the D-5 acetone impurity at  $\delta$  2.05). The filtrate was analyzed by GCMS and it contained only solvent and 79.

Silabarrelene, 21, was shown to be quantitatively rearranged to silasemibullvalene, 79, when photolyzed through Pyrex using acetone as a sensitizer. Silasemibullvalene does not behave like semibullvalene under pyrolytic or photolytic conditions. It does not undergo a Cope rearrangement, nor does it rearrange to a ring expanded isomer. Silabarrelene does not react with Diels-Alder dienophiles as does barrelene. These results would support the idea that 21 and 79 do not react as their all-carbon analogues, although the experiments performed to date are by no means exhaustive.

#### Attempted Synthesis of a Silicon-functionalized Silacycloheptatriene

The search for a non-annulated, non-substituted, functionalized silacycloheptatriene (silepin) has not been rewarding (106,107). One goal of this search is the ultimate formation of a silylenium cation via hydride abstraction from the silepin precursor. If this reaction



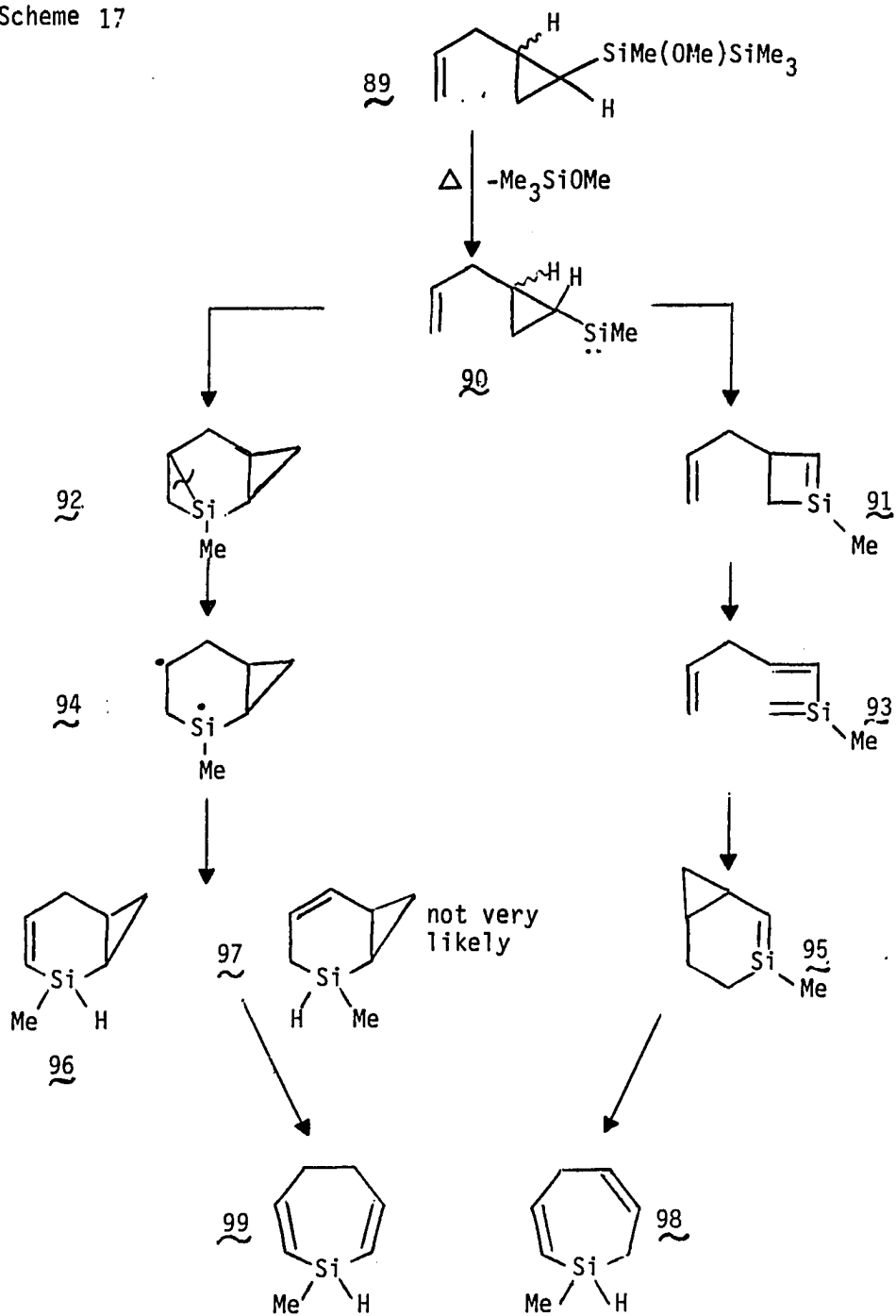
were to occur, it would offer the dual rewards of generating a silylenium cation and an aromatic silicon-containing species under mild conditions. The failure of more straightforward chemistry, coupled with the successful syntheses of 21 and 88 via organosilicon reactive inter-



mediates, would prompt us to apply similar methodology towards solving this problem.

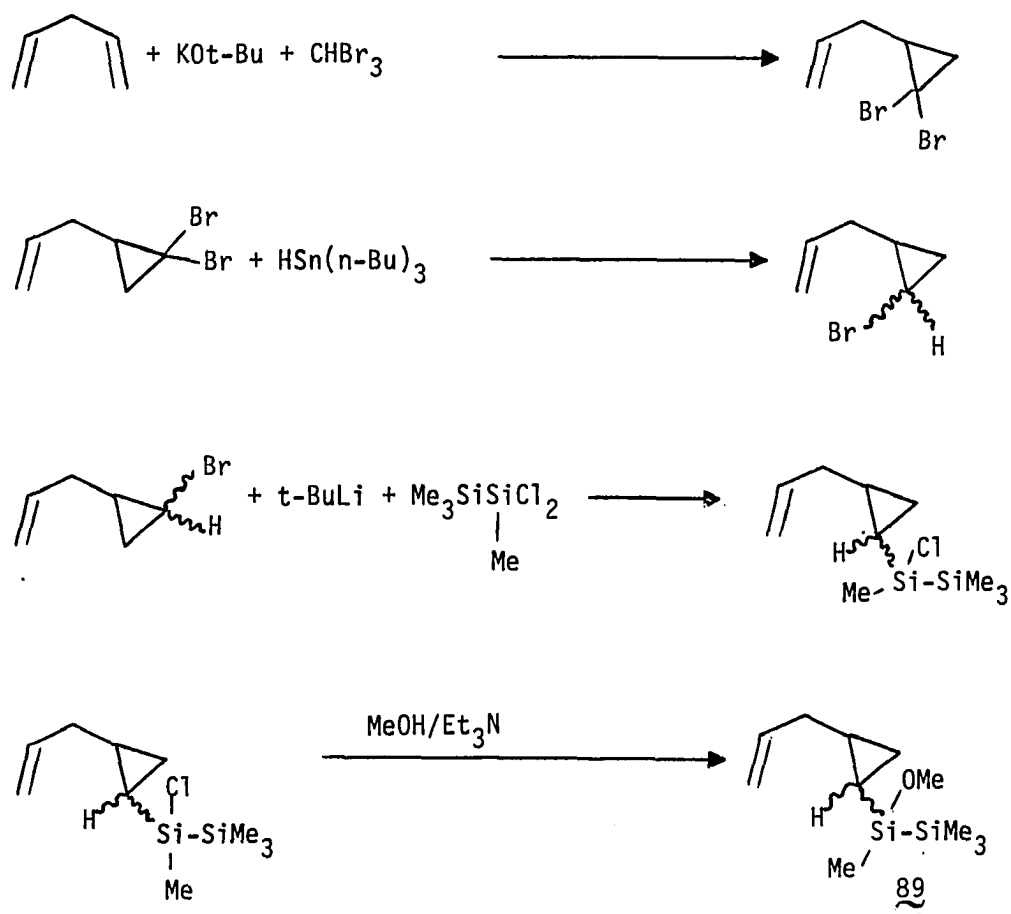
Of the two routes envisioned, the first attempted to take advantage of the known intramolecular addition-rearrangement of alkenylsilylenes and cyclopropylsilylenes to form unsaturated silacycles (82,84). Two mechanisms giving rise to a silepin precursor are shown in Scheme 17. Both pathways have literature precedent, (82,84) but no preference is indicated for one over the other.

Scheme 17



The silacycloheptadienes, 98, 99, could presumably be transformed to silepins by known methods (86,108). The synthesis of the desired silylene precursor, 89, is shown in Scheme 18.

Scheme 18



Prohibitive cost of 1,4-pentadiene necessitated its synthesis. The procedure followed was that of Benson and McKusick (109). The pentadiene was cyclopropanated with dibromocarbene generated from

bromoform and potassium tert-butoxide (110). The dibromocyclopropane was reduced with tri-n-butyltinhydride according to the method of Seyferth (110). This gave an approximately 1:1 mixture of the stereoisomeric monobromides which were purified by percolating the reaction mixture through silica gel, followed by vacuum distillation. The isomers were separable by GC, but the mixture was used in subsequent reactions. Following the instructions of Wender and Filosa, (111) the monobromides were metalated with tert-butyllithium at low temperature. Addition of the resultant organolithium reagent to 1,1-dichlorotetramethyldisilane at  $-78^{\circ}\text{C}$  was followed by warming to room temperature and quenching with MeOH and  $\text{Et}_3\text{N}$ . The cis- and trans-1-methoxy-1-(2-propenyl)cyclopropyl-disilanes were purified by GC.

FVP of 89 through a horizontal, quartz-packed tube at  $650^{\circ}\text{C}$  ( $10^{-4}$  Torr) gave a plethora of products ( $> 23$ ). The GCMS of the pyrolysate showed unreacted starting material to be the major component. Some trimethylmethoxysilane was formed as well as hexamethyldisiloxane. Also present were eight compounds with  $m/e = 124$  (loss of  $\text{Me}_3\text{SiOMe}$ ). Attempts at separation via GC failed because these elimination products appeared as two broad peaks under preparative conditions.

FVP was attempted at lower temperatures in the hope that milder conditions would lead to a cleaner reaction. Pyrolysis at either  $550^{\circ}$  or  $600^{\circ}\text{C}$  gave back only unreacted starting material. Nitrogen flow pyrolysis with 2,3-dimethyl butadiene at  $450^{\circ}\text{C}$  or  $525^{\circ}\text{C}$  also gave only starting material. Since the addition-rearrangement sequence desired

was not occurring smoothly, if at all, a precursor more amenable to clean silepin formation was sought.

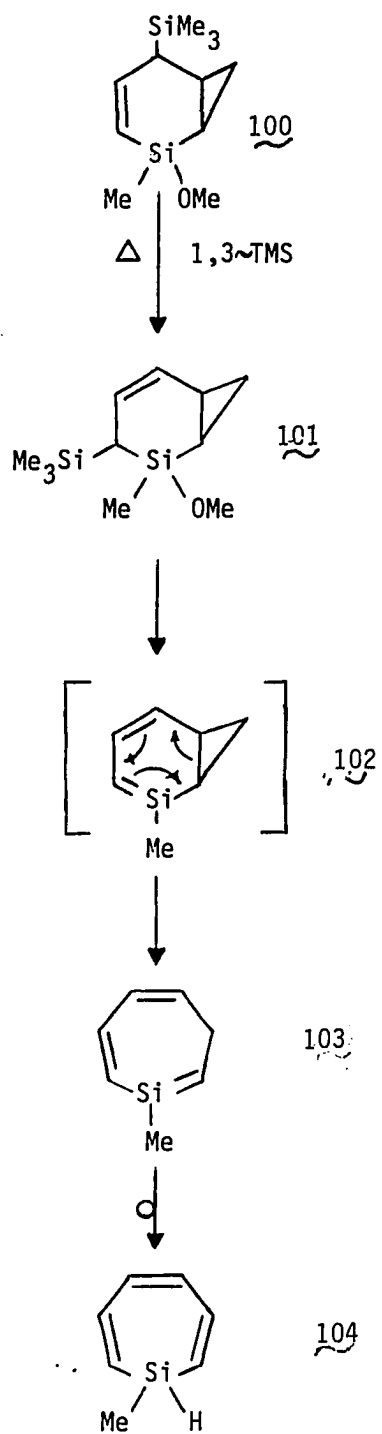
The known conversion of 74 to 1 via 75 raised the possibility of using 100 as a silepin precursor. If the chemistry of 100 could be extrapolated to that of 74, the 1,3-trimethylsilyl migration, forming 101, followed by elimination of  $\text{Me}_3\text{SiOMe}$ , would give the silanorcaradiene, 102, which should then give a silepin as shown in Scheme 19.

The synthesis of 100 was not straightforward as it was known (112) that previous attempts at cyclopropanating 74 using typical Simmons-Smith reaction conditions led to decomposition of starting material. Likewise, the use of strong bases and haloforms to give dihalocyclopropanes was avoided as this method presented problems such as nucleophilic attack on silicon and loss of the -OMe moiety (113).

In 1981, Kropp et al. (114) introduced a mild, non-basic cyclopropanation procedure involving the photolysis of  $\text{CH}_2\text{I}_2$  in the presence of various olefins. When performed in the presence of a  $\text{Na}_2\text{S}_2\text{O}_3/\text{NaHCO}_3$  solution (to scavenge  $\text{I}^-$  and HI), this procedure gave quite high yields of cyclopropanated products. Even substrates which were inert to Simmons-Smith conditions gave moderate yields of cyclopropanation products.

The initial attempt at cyclopropanating 74 under these conditions (hv, 4.5 hours) gave back unreacted starting material and just a trace of a product which had the correct m/e for 100 by GCMS. A second attempt utilized a much longer reaction time (12 hours). Vapor phase

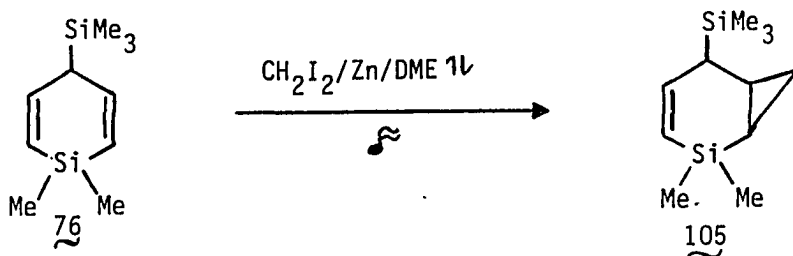
Scheme 19



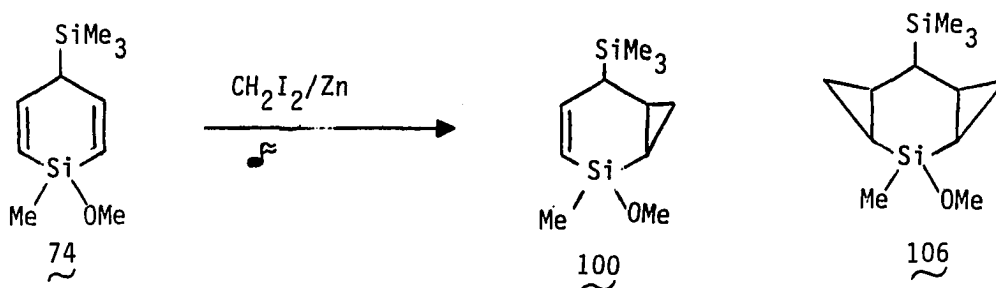


chromatography showed that 100 was present in about a 2:1 ratio with 74. However, this apparent success was marred by a low (< 30%) mass recovery. There was a viscous, orange-brown coating on the walls of the reaction vessel which could account for the poor yield. Although a product of the correct mass was formed, the material loss predicated the search for a better route to 100.

Repic and Vogt (115) reported that olefins could be cyclopropanated very efficiently using zinc metal, methylene iodide, and ultrasound. Yields were markedly better than those obtained using Simmons-Smith procedures. This method appeared to be compatible with the sensitive Si-OMe functionality. A test run involving 76 (10 mmoles) and 40 mmoles each of  $\text{CH}_2\text{I}_2$  and Zn in refluxing 1,2-dimethoxyethane (DME) in an ultrasound bath gave a mixture of 76 (75%) and 105 (25%) after 4 hours (yields were GC yields).



When 74 (10 mmoles) was reacted under the same conditions, GC analysis after four hours showed no 74 remaining, but two peaks of longer retention time than 74 were found. These products were isolated by preparative GC. The first peak (~ 25%) was the sought after 100 and was identified by  $^1\text{H}$  NMR and GCMS. The second peak (~ 75%) was identified by  $^1\text{H}$  NMR and GCMS as the bis-cyclopropanated product, 106.



The formation of 106 was surprising, but not wholly unpredictable as excess  $\text{CH}_2\text{I}_2$  and Zn were employed. The reaction was repeated on the same scale using equimolar amounts of 74,  $\text{CH}_2\text{I}_2$ , and Zn. After workup, only 74 and 100 could be found in the mixture. This seemed to be the most efficient route to 100 as unreacted 74 could be recycled and no unwanted 106 was formed.

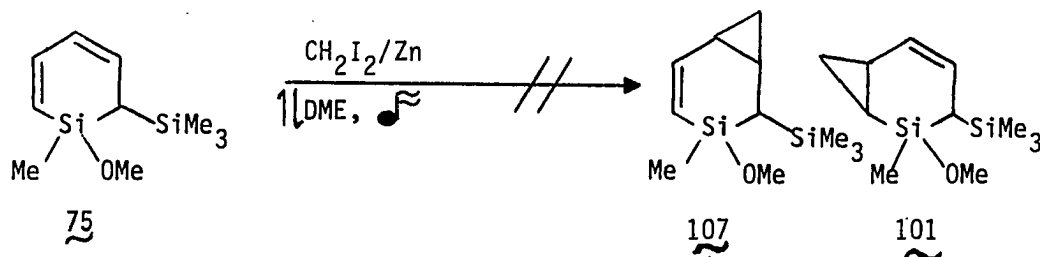
FVP ( $500^\circ\text{C}$ ,  $10^{-5}$  Torr) of 100 gave back only unreacted 100 with a 70% mass recovery. Increasing the temperature to  $650^\circ\text{C}$  produced a complex (> 20 products) pyrolysate with a total mass recovery of only 50%. The pyrolysate was mainly compounds with m/e of 226. Lowering the temperature to  $600^\circ\text{C}$  gave a less complex mixture (60% mass recovery) but it contained 14 compounds with the same molecular weight as the starting material. These compounds were not separable by preparative GC as they appeared as four broad, overlapping humps. In each of the last two pyrolyses, some  $\text{Me}_3\text{SiOMe}$  was observed by GCMS, along with eight compounds whose m/e corresponded to a dimer of the elimination product, but these were very minor constituents of the pyrolysates. The earlier promise of 100 as a silepin precursor was lost as it apparently did everything except what it was expected to do.

The bis-cyclopropanated silane, 106, proved equally reluctant to eliminate  $\text{Me}_3\text{SiOMe}$  via a homo-1,3-trimethylsilyl shift. Flow co-pyrolysis ( $450^\circ\text{C}$ ,  $\text{N}_2$ ) with excess  $\text{MeOH}$  gave back 106 untouched. FVP ( $700^\circ$  or  $600^\circ\text{C}$ ,  $10^{-4}$  Torr) of 106, followed by GCMS analysis, showed the presence of at least 10 isomers of the starting material. These isomers could not be resolved under preparative GC conditions.

It is not immediately apparent why the rearrangement-elimination sequence observed for 74 does not work with 100. The  $^{13}\text{C}$  spectrum of 100 shows it to be a single isomer. By analogy to 74, the structure of 100 is presumed to be that with the  $-\text{OMe}$ ,  $\text{Me}_3\text{Si}-$ , and methylene of the cyclopropyl all syn. There is precedence (116) for syn-cyclopropanation with allylic or homoallylic ethers and this would explain the stereospecificity observed. Credence then would be lent to the supposition of all-syn stereochemistry.

This stereospecificity is synthetically fortunate, but it also explains the problems encountered when 100 or 106 is pyrolyzed. Because of their syn orientation, the bulky trimethylsilyl group and the methylene of the cyclopropane must interact unfavorably with one another during the course of the trimethylsilyl migration. It is this interaction which prevents the desired shift. With 106, the trimethylsilyl group cannot undergo a homo-1,3-shift because the silicon is oriented anti to the cyclopropyl bond with which it must interact and antarafacial 1,3 migrations are geometrically prohibited. Therefore, it is believed that cyclopropyl bond homolysis, leading to 1,3-diradicals and their subsequent chemistry dominates the thermolyses of 100 and 106.

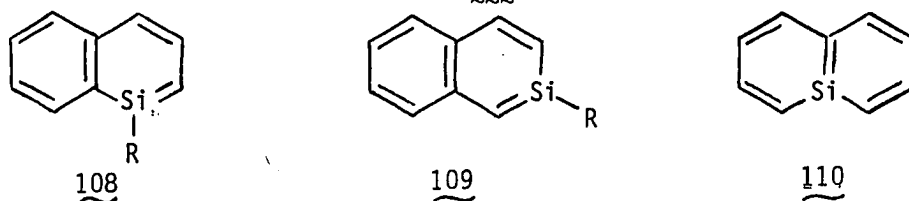
Since the 1,3-silyl migration was prevented in 100, 74 was rearranged to 75 prior to attempted cyclopropanation. Under the conditions previously employed, 75 failed to give 101 or its isomer, 107. Longer reaction times, higher temperatures, and excess  $\text{CH}_2\text{I}_2$  and Zn could not bring about the desired transformation. Therefore,



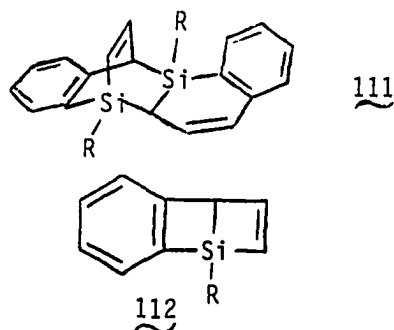
the question regarding the generation of a silanorcaradiene and its ultimate fate cannot be answered at this time.

#### Attempted Synthesis of 1- and 2-Silanaphthalene

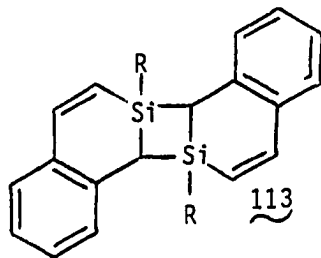
The successful  $\beta$ -elimination of  $\text{Me}_3\text{SiOMe}$  to make 1-silatoluene suggested its application to the synthesis of higher homologues of silatoluene, silanaphthalene in particular. Three isomeric silanaphthalenes are possible (108-110) and differences in their chemistry would be expected. The 1-silanaphthalene, 108, could be expected to react as



1-silatoluene, 1, under FVP conditions to give [4 + 2] dimers such as 111. It could possibly behave as a 1-silabutadiene and give a benzo-sila-Dewar benzene 112 via [2 + 2] electrocyclization. The 2-silanaphthalene would

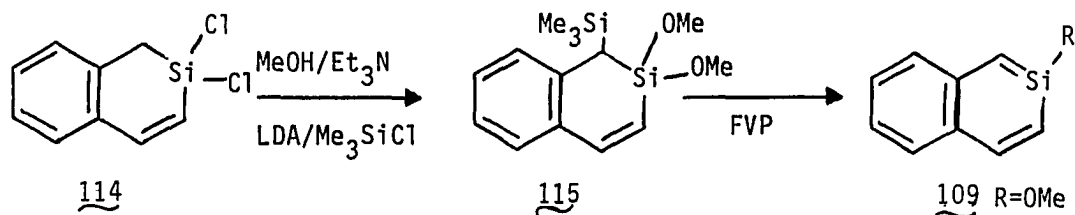


be expected to dimerize (under FVP) to give a head-to-tail dimer such as 113.

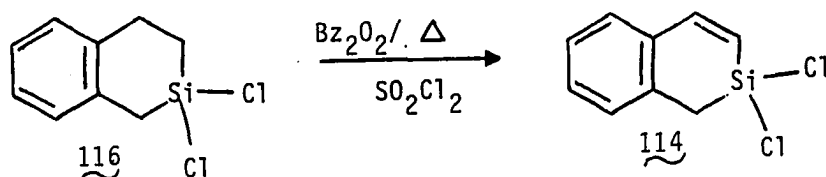


The 9-silanaphthalene, 110, may prove the most intriguing of the three because aromaticity must be disrupted in two rings for the Si--C (p-p)  $\pi$ -bond to react. This may present a sufficiently large energy barrier to allow isolation and characterization of 110. When this research began, a single route into the ring skeleton of 110 was known (7). Routes into 108 and 109 were better known and work began with these systems.

Chernyshev et al. (117) reported the synthesis of 2,2-dichloro-2-sila-1,2-dihydronaphthalene, 114, in 1975. Methoxylation of 114, followed by anion formation and quenching with  $\text{Me}_3\text{SiCl}$ , would give trimethyl silylated 115. Pyrolytic elimination of  $\text{Me}_3\text{SiOMe}$  would give 109 (R = -OMe).



Thus, benzylmagnesium chloride was coupled with vinyltrichlorosilane to give benzylvinylidichlorosilane (118). This was cyclized (117) ( $\text{AlCl}_3$ , refluxing heptane) to give the 2,2-dichloro-2-silatetrahydronaphthalene, 116. Refluxing 116 with sulfuryl chloride and benzoyl peroxide was reported to give a 23% yield of 114 (117). Repeated attempts at duplicating this work were unsuccessful.



When the dimethoxy derivative of 116 was subjected to a bromination - dehydrobromination procedure (2 equivalents NBS, then  $\text{Et}_3\text{N}$  or DBU), the results were disappointingly uniform. After solvent removal, there was a viscous, orange-red mass which would solidify upon standing or darken and solidify when distillation was attempted.

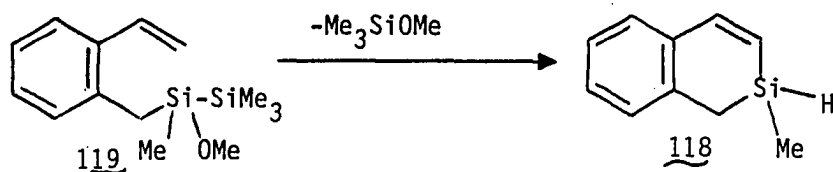
The inability to elaborate the 2-silatetrahydronaphthalenes initiated a search for alternative solutions. One possibility was the cyclization of  $\alpha$ -(bromovinyl)benzylidichlorosilane, 117, followed by dehydrobromination.

117 was synthesized by coupling benzylmagnesium chloride and  $\alpha$ -(bromo-vinyl)trichlorosilane (119). The cyclization of 117 was attempted using



$\text{AlCl}_3$  in refluxing heptane,  $\text{HCl(g)}$  and  $\text{AlCl}_3$  in refluxing heptane, and  $\text{BF}_3$  in benzene at room temperature. Variation of reaction times or the amount of catalyst used had no effect on the reaction. In all cases, the starting material was recovered untouched.

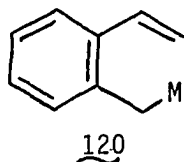
It was next planned to use the intramolecular cyclization of silylenes (82) to form 2-methyl-2-siladihydronaphthalene, 118. Pyrolysis of 119 followed by silylene addition to the styryl  $\pi$ -bond and subsequent rearrangement could give 118. 118 could presumably be transformed into



2-silanaphthalene by first converting the silyl hydride into the methoxy compound. This methoxy compound could be trimethylsilylated at the 1-position. Pyrolysis would then generate 109 ( $\text{R} = \text{Me}$ ) via  $\beta$ -elimination of  $\text{Me}_3\text{SiOMe}$ .

Key to the synthesis of 119 was the coupling of the organometallic reagent, 120 (a or b), (derived from metalation of *o*-(bromomethyl)

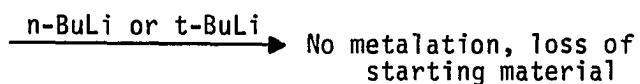
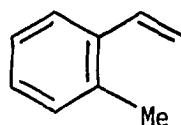
styrene, 121) with 1,1-dichlorotetramethyldisilane. The synthesis of o-(bromomethyl)styrene, 121, is shown in Scheme 20 (120,121).



a) M=MgBr  
b) M=Li

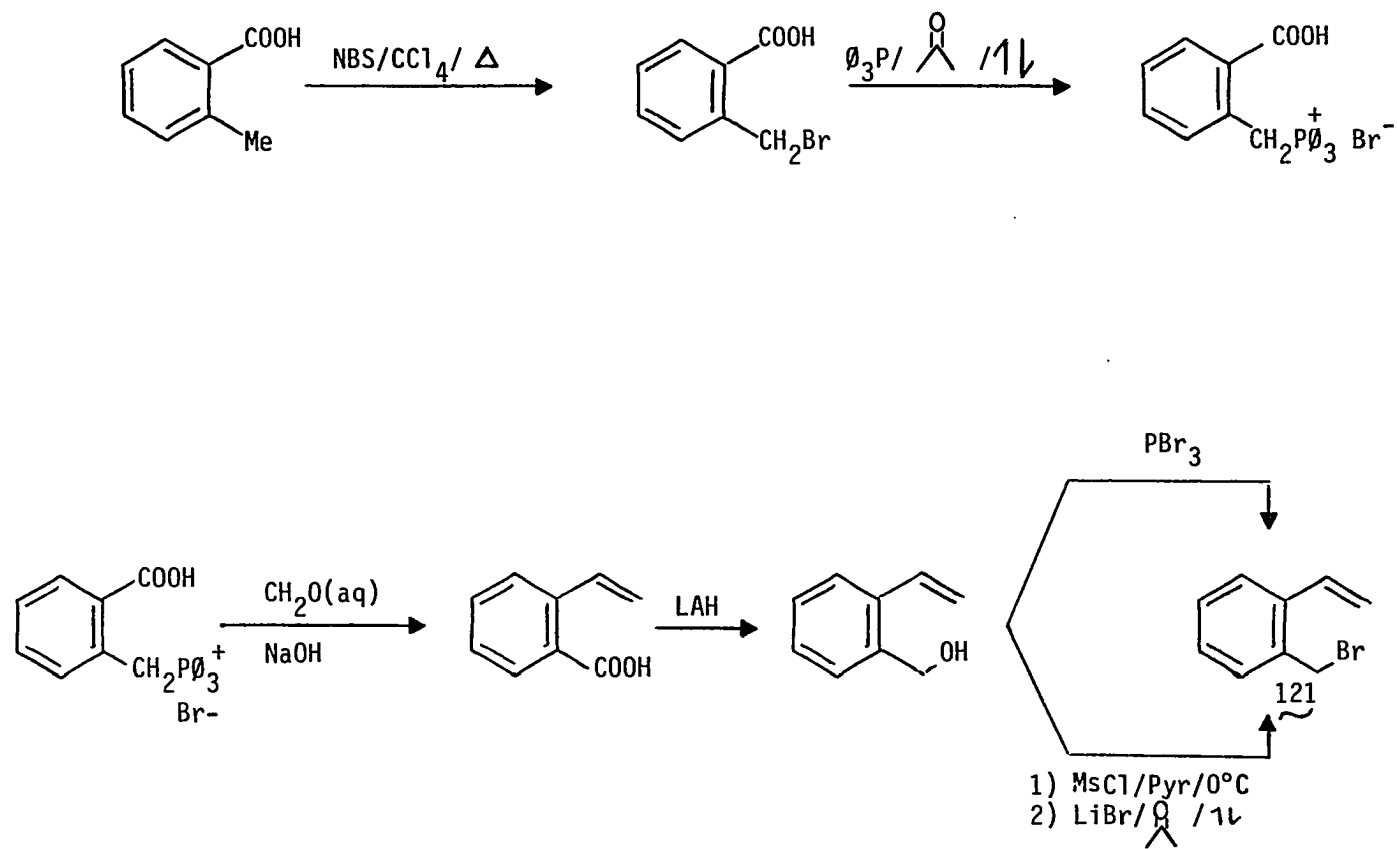
When an ether solution of 121 was added to a suspension of magnesium in ether at room temperature, no reaction was observed (i.e. the ether did not reflux, the Mg did not disappear, the solution remained clear, etc.). Addition of 1,2-dibromoethane caused a momentary reflux of the ether, but this rapidly subsided. The addition of  $\text{Me}_3\text{SiCl}$  also had no apparent effect. When 121 was refluxed with Mg (with or without  $\text{Me}_3\text{SiCl}$ ), the solution would turn orange-red and a viscous red material would accumulate on the bottom of the reaction vessel. Aqueous workup (dilute HCl/ice) gave no evidence of Grignard formation. There was no o-methylstyrene nor 121.

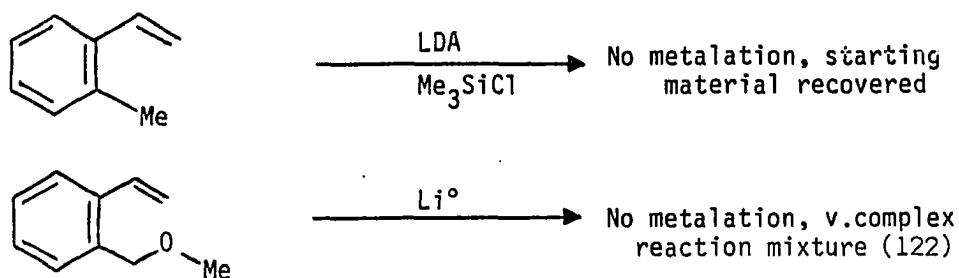
Lithium-halogen exchange was attempted at  $-78^\circ\text{C}$  using t-butyl-lithium. Again, various conditions offered no success. The usual result was a complex mixture which contained no vinyl protons in the NMR. Other attempts at forming 120b are shown in the following equations.





Scheme 20





Gilman and Marrs' synthesis of 122 offered a route to a functionalized 1-silatetrahydronaphthalene (123). It was hoped that this species, with only one benzylic position, would be readily converted to a 1-sila-1,2-dihydronaphthalene. The immediate target molecule was 1-methoxy-1-methyl-1-silatetrahydronaphthalene, 123. Its synthesis is depicted in Scheme 21.

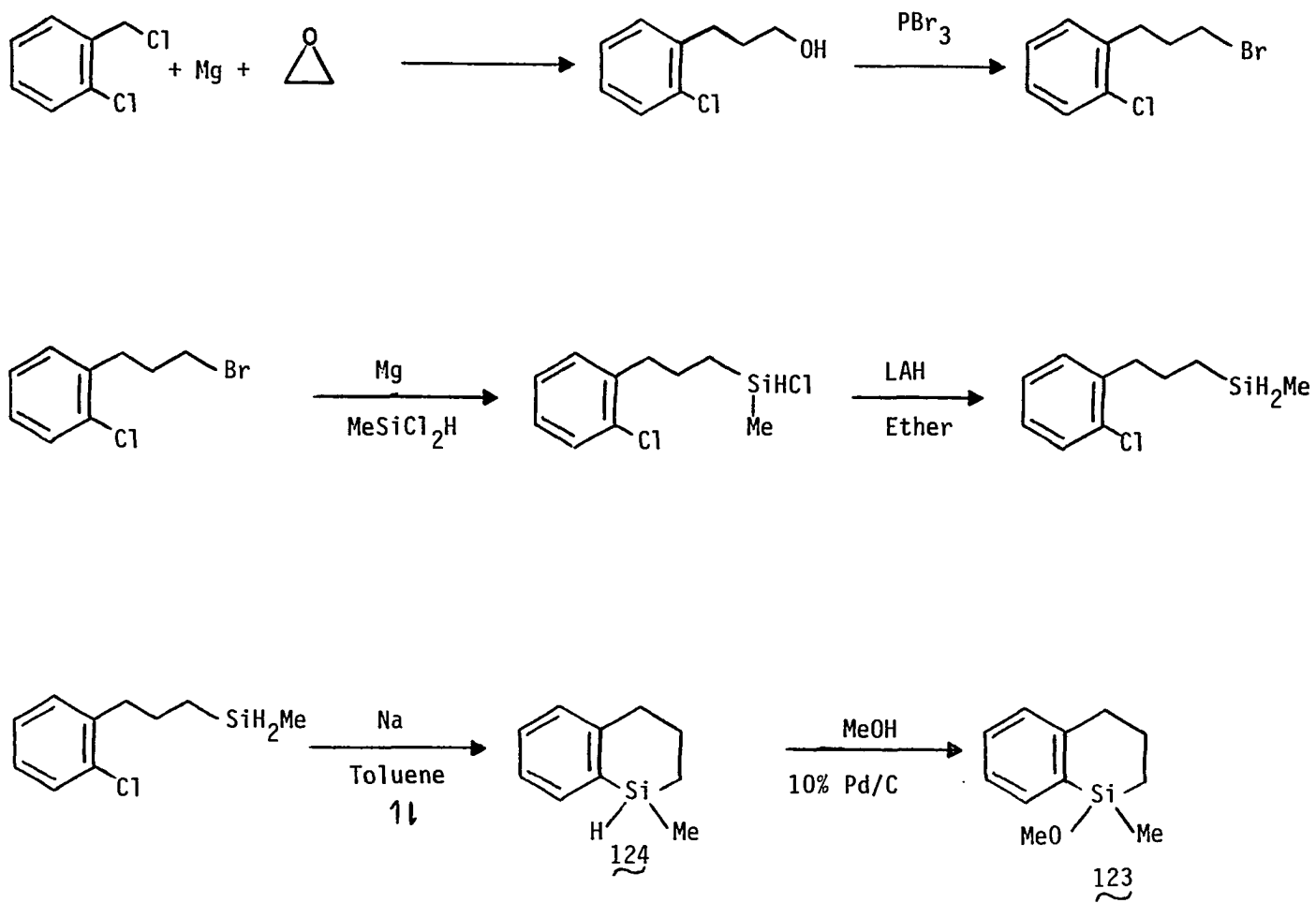


Introduction of the double bond in the saturated ring via bromination-dehydrobromination gave a mixture of compounds which was not amenable to separation by preparative GC or distillation. Similar problems plagued Corey et al. in their efforts to synthesize a benzannulated silepin with functionality at silicon (107).

A final attempt at producing the double bond in the saturated ring involved the synthesis of benzoate ester 125. Pyrolytic elimination of benzoic acid would give 126.

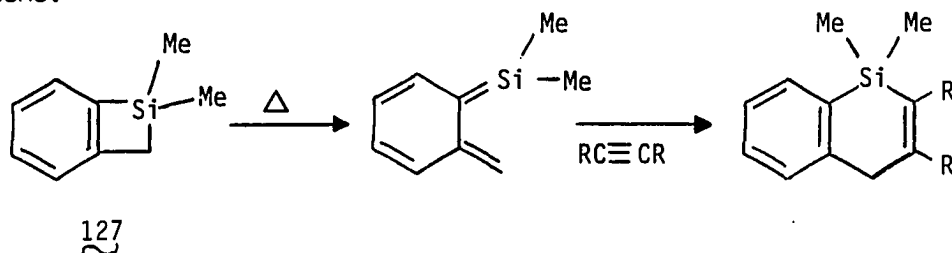


Scheme 21

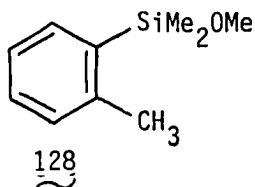


Treatment of 123 with tert-butylperoxybenzoate in the presence of CuBr (124) gave a light blue solution which showed no methoxyl signals in the NMR. Again, the reaction mixture appeared quite complex. No analysis was attempted. The failure of these routes to produce a silanaphthalene precursor warranted a change in strategy.

When heated with acetylenes, 3,4-disilacyclobutenes give 1,4-disilacyclohexa-2,5-dienes (125). Benzocyclobutenes have been used as o-quinodimethane precursors in the synthesis of polycyclic systems (126). From these came the idea of using benzosilacyclobutene, 127, to form a dihydrosilanaphthalene via Diels-Alder reaction with an acetylene.



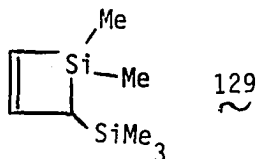
Thermally, 127 polymerizes at temperatures as low as 80°-100°C or even lower if the polymerization is catalyzed (e.g. the addition of BuLi) (127,128). Eaborn has shown that 127 is susceptible to attack by MeOH at room temperature to give the ring-opened 128 (129).



Initially, the procedures of Barton and Kilgour were used (125). 127 was placed in a thick-walled glass tube with 2 equivalents of 2-butyne. The tube was freeze-thaw degassed and sealed under vacuum. After heating in a Kugelrohr oven at 200°C for 20 hours, little liquid remained and a yellowish solid had formed. The solid was insoluble in CCl<sub>4</sub>, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and acetone. Use of 1-phenylpropyne under the same conditions gave a white solid which was also insoluble in CCl<sub>4</sub>, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and acetone. Diluting the latter reaction with benzene (making a 0.1 M solution of 127) and lowering the temperature to 100°C did not prevent the formation of the white solid.

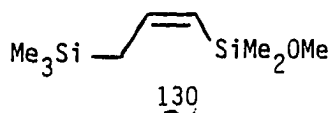
Flow co-pyrolyses of 127 using acetylene as the carrier gas also proved unsuccessful. At 400-500°C, only unreacted 127 was found; whereas at 600°C there was just a trace of 127 and much benzene. The reluctance of 127 to do any of the chemistry desired of it (or the failure to trap it) was unexpected. The question was raised whether this behavior was characteristic of all silacyclobutenes or if it was particular to benzosilacyclobutenes.

3,3-Dimethyl-4-trimethylsilyl-3-silacyclobutene, 129, was selected for the experiments involving silacyclobutenes because of its accessibility (130).



Co-pyrolysis of 129 and MeOH (10 equivalents) in a vertical quartz tube (N<sub>2</sub>, 450°C) gave a single product which resulted from ring opening.

Based on the results of Eaborn et al. with 127 (129), the structure of this ring-opened compound was assigned as (Z)-(1-dimethylmethoxysilyl)-3-trimethylsilylpropene, 130. Indeed, mixing 129 and MeOH at room temperature produced 130 almost immediately. This silacycle apparently suffers nucleophilic ring opening like 127. Pyrolysis of 129 with a variety of acetylenes, under static (sealed tube, 150-200°C) or nitrogen flow conditions (450-550°C) gave back unreacted starting material. Hence, there is no evidence for the formation of a 1-sila-1,3-butadiene in the pyrolysis of 129.

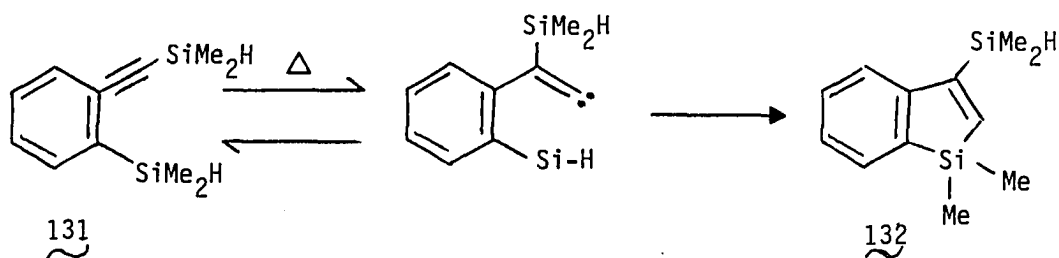


Sakurai and Takafumi reported in 1975 that silacyclobutanes would react with acetylenes in the presence of Pd catalysts to give 1-silacyclohex-2-enes (131). With unsymmetrical acetylenes, a single isomer was formed. Sakurai attributed this reactivity to the relief of strain in the silacyclobutane ring. It was reasoned that 127, being benzannulated, would be more strained and hence react with equal or greater facility under these conditions.

When equimolar amounts of 127 and dimethylacetylene dicarboxylate (DMADC) were refluxed in benzene, over 10% Pd on carbon, a new compound was formed (by GCMS and  $^1\text{H}$  NMR). The mass ( $m/e = 290$ ) of this compound indicated that addition had taken place. The compound was not isolated. This success was quickly overshadowed by the failure to obtain any addition products when other acetylenes were tried. Use of phenyl-

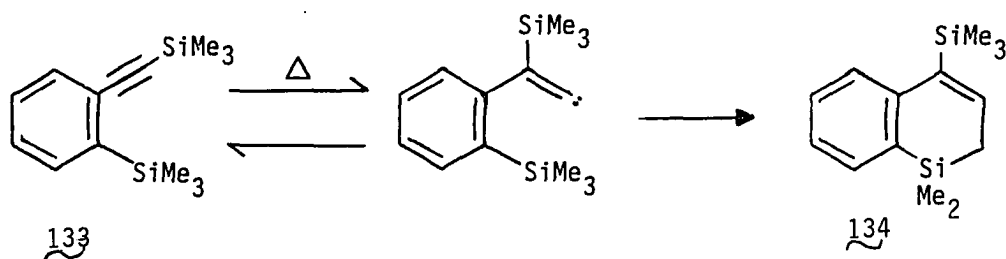
acetylene under the same conditions gave back only 127 and a compound whose *m/e* indicated that it was a dimer (of some sort) of 127. In the reaction with acetylene itself, the white, insoluble, polymeric material found in earlier experiments was formed.

Groh's observation that dimethylsilyl(*o*-dimethylsilyl)phenylacetylene, 131, cyclizes to the silaindene, 132, upon FVP rekindled hope for a completed silanaphthalene synthesis (132). The alkylidene



carbene intermediate presumably arises from a 1,2 silyl shift. A similar shift for hydrogen has been suggested by Brown to explain the results from the pyrolysis of several aryl acetylenes (133).

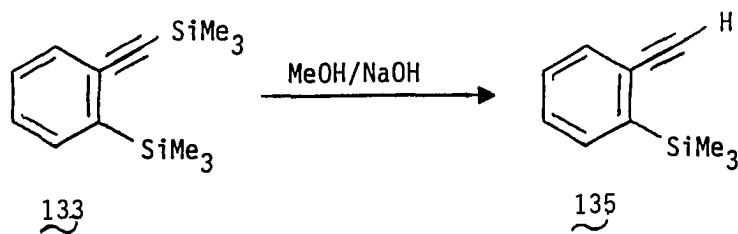
Trimethylsilyl(*o*-trimethylsilyl)phenylacetylene, 133, was the chosen precursor. It was hoped that the 1,2-silyl shift would give the alkylidene carbene which would then insert into a C-H bond of the *o*-trimethylsilyl group to give the dihydrosilanaphthalene, 134.



Acetylene 133 was prepared from phenylacetylene and trimethylchlorosilane by the procedure of Hommes and co-workers (134). This was isolated as a colorless liquid after distillation. FVP ( $10^{-3}$  Torr) of 133 was carried out at 700, 750, and 800°C. In each case, only unreacted 133 was recovered. Increasing the temperature merely increased the decomposition of 133 as evidenced by decreased mass recoveries.

One explanation for this disheartening result is that the 133 - to - alkylidene carbene interconversion occurs too rapidly for the C—H insertion to compete. Because silicon is known to migrate considerably faster than hydrogen in cyclopentadienyl systems (135), the same behavior was suspected here. It seemed reasonable to assume that the lifetime of the carbene could be increased if the silicon were replaced by a hydrogen.

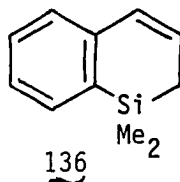
Thus, (o-trimethylsilyl)phenylacetylene, 135, was prepared nearly quantitatively by treating a 1.0 M solution of 133 in MeOH with 4.0 equivalents of NaOH for  $\frac{1}{2}$  hour at room temperature.



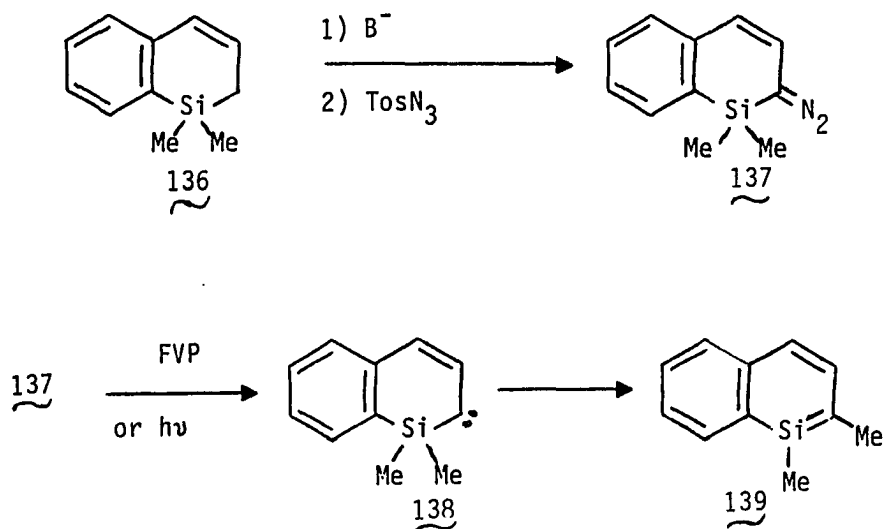
FVP of 135 was carried out as with 133. In the 600-800°C range, only 135 was recovered. At 850°C, the pyrolysate consisted of six peaks in the GC. By GCMS, these compounds were all isomeric with 135. The



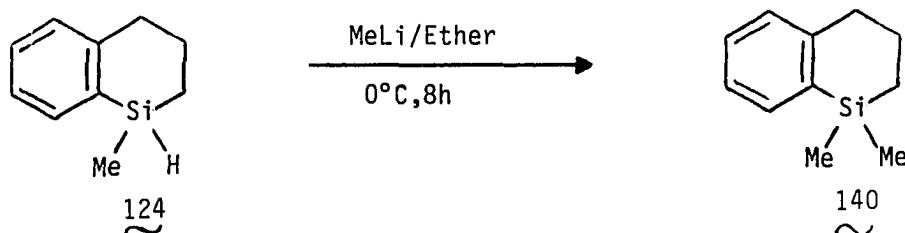
major component was 135, but the second largest peak proved to be the cyclized product, 1,1-dimethyl-1-sila-1,2-dihydronaphthalene, 136. The



structure of 136 was confirmed by  $^1\text{H}$ ,  $^{13}\text{C}$ , and mass spectra. 136 was formed in 18% yield based on recovered starting material. Although this result was gratifying, the tedious separation of minute quantities of 136 by preparative GC gave cause to search for a cleaner route to 136. It was hoped that 136 could be converted to the  $\alpha$ -silyldiazo compound, 137, which would give the carbene, 138, upon loss (thermally or photochemically) of  $\text{N}_2$ . Carbene 138 should then form 1,2-dimethyl-1-sila-naphthalene, 139, in accordance with literature precedent (93).



Thus, 1-methyl-1-silatetrahydronaphthalene, 124, could be converted to 1,1-dimethyl-1-silatetrahydronaphthalene 140 in 88% yield by reaction with MeLi in ether. Bromination of 140 was carried out with 1.0 equivalent



of NBS in  $\text{CCl}_4$ . Filtration of the succinimide and solvent removal gave a light, yellow-orange residue which was taken up in ether. An ether solution of 1.25 equivalents DBU was added dropwise at room temperature. After complete addition, the mixture was refluxed 6 hours, cooled, filtered, and the ether removed in vacuo. The red-brown residue was chromatographed on silica gel using Skelly "B" as the eluent. The dihydro-silanaphthalene, 136, eluted first along with an unknown impurity. Further purification of 136 (>95%) was achieved by vacuum distillation in a micro-distillation apparatus. Spectral data ( $^1\text{H}$ ,  $^{13}\text{C}$ , GCMS) for synthetic 136 was identical to 136 isolated from FVP of 135.

Deprotonation of 136 was achieved using n-BuLi in THF at  $0^\circ\text{C}$  for 1 hour. Addition of this dark, brick-red anion to a  $-78^\circ\text{C}$  THF solution of tosyl azide followed by slow warming to room temperature (12 hours), gave a chocolate brown mixture. This was poured into pentane and washed six times with distilled  $\text{H}_2\text{O}$ . After drying and solvent removal, the orange-red residue was distilled under vacuum using a micro-distillation apparatus. A dark red liquid was collected over the range of  $55\text{--}65^\circ\text{C}$  (pot temp.). By NMR, this liquid was a mixture of 136 and the 2- and

4-diazosiladihydronaphthalenes. IR showed a strong band at  $2030\text{ cm}^{-1}$  which closely matches the band at  $2020\text{ cm}^{-1}$  reported for the diazo compound 11 (24). Attempted purification of this mixture by column chromatography gave only 136. This indicated that the diazo compounds formed in this reaction were more prone to decomposition than was 11. Because of this, the mixture of 136 and the diazo compounds was pyrolyzed in the hope that intramolecular reactions would predominate under FVP conditions.

FVP of the mixture ( $600^\circ\text{C}$ ,  $2 \times 10^{-5}$  Torr) gave only 136 in the liquid  $\text{N}_2$  trap. There was considerable deposition of an orange-red material on the walls of the pyrolysis tube before and after the hot zone. The tube was cooled and this material was rinsed out with  $\text{CDCl}_3$ . GCMS showed two extremely small peaks with  $m/e = 344$ . These could either be carbene dimers or silanaphthalene dimers, but their small amounts prevented isolation. A 300 MHz  $^1\text{H}$  NMR was equally uninformative as only broad humps in the 7.20 - 7.5 and 0.5 to 0 regions were found. When the solvent was removed, the orange-red residue had the consistency of a thick paste.

Generation of a silanaphthalene has been attempted by a variety of methods, none of which were successful. The most promising of these, involving a diazo compound, resulted in a disappointing breakdown to high molecular weight materials. While there is little doubt that a silanaphthalene will eventually be made, the requisite precursor remains to be synthesized.

## CONCLUSION

The generation of silabenzene was realized via an unprecedented rearrangement-elimination sequence on a silacyclohexadienyl ring system. This route allowed the synthesis of 1-methyl-1-silabicyclo-[2.2.2]-octatriene (1-silabarrelene) and the study of its chemistry.

The 1-silabarrelene rearranges quantitatively to the unique silacycle, 1-methyl-1-silatricyclo [3.3.0.0] octa-2,6-diene, the first silasemibullvalene. Unlike its all-carbon analog, silasemibullvalene does not undergo degenerate Cope rearrangement.

The attempted synthesis of a functionalized silacycloheptatriene from a rearrangement-elimination route involving a trimethylsilylsilanorcarene was unsuccessful. This was the result of an unanticipated (but preceded) directive effect of a methoxyl substituent on the stereochemistry of the cyclopropanation step. Conditions were found where one could conveniently cyclopropanate a functionalized silacyclohexadiene ring system.

The synthesis of a silanaphthalene was attempted based on the successful  $\beta$ -elimination of  $\text{Me}_3\text{SiOMe}$  to form silabenzene, but the required precursor could not be synthesized. The synthesis of several benzannulated silacyclohexenes and silacyclohexadienes provided some new insights into the chemical manipulations of these ring systems. The diazo transfer reaction on 1,1-dimethyl-1-sila-2,3-benzocyclohexa-2,4-diene gave a mixture of diazo compounds (along with starting material) which gave no evidence of silanaphthalene formation when pyrolyzed.

The search for routes into silepins and other silaaromatic compounds, while not fruitful here, should continue as the potential for intriguing chemistry in these systems is great.

## EXPERIMENTAL

## Instrumentation

Routine proton NMR spectra were recorded either on a Varian model EM-360, Hitachi R20-B, or a Nicolet 1280 (300 MHz) spectrometer.

Decoupling experiments were performed either on the EM-360 or on the Nicolet 1280. All chemical shifts were reported as parts per million ( $\delta$  scale) using either tetramethylsilane, chloroform, or benzene as internal standards.

$^{13}\text{C}$  spectra were recorded either on a JEOL FX-90Q or a Nicolet 1280 spectrometer.

Variable temperature NMR experiments were performed on the JEOL FX-90Q spectrometer.

Infrared (IR) spectra were recorded on either a Beckman Acculab 2 or a Beckman 4250 infrared spectrophotometer. All bands are reported in reciprocal centimeters ( $\text{cm}^{-1}$ ).

Routine gas chromatographic analyses were done on one of the following instruments: Varian 1720, Varian 920, ( $\frac{1}{4}$  inch diameter columns), Fisher-Victoreen Series 4400 (1/8 inch column) and a Hewlett-Packard 5790A GC equipped with a polymethylsilicone capillary column. Preparative GC was performed on the Varian 1720 or 920 GCs, using  $\frac{1}{4}$  inch copper columns (5 foot to 12 foot length, SE 30 liquid phase). Pure 136 was obtained by preparative GC on an 8 foot X  $\frac{1}{4}$  inch 12% SE-30 packed glass column. This was used because the acetylenic precursor, 135, reacted with copper columns.

Gas chromatographic mass spectra (GCMS) were recorded on a Finnegan Model 4230. Mass spectrometric exact mass measurements were obtained on a MS-902 mass spectrometer.

### Procedures and Results

#### Standard procedures for flow pyrolysis

A vertical quartz tube (17 mm X 60 cm) was packed with quartz chips, and nitrogen (or acetylene, when used as a trap) was passed through the tube. A cold trap (cooled with either liquid nitrogen, dry ice/iPr-OH, or icewater) was used to collect the pyrolysate. Samples to be pyrolyzed, either neat or as solutions, were dripped into the heated tube and allowed to collect in the cold trap.

#### Procedure for flash vacuum pyrolysis (FVP)

A horizontal quartz tube, (17 mm X 60 cm) packed with quartz chips was used. One end was attached to a flask containing the material to be pyrolyzed; the other end was connected to a liquid nitrogen-cooled cold trap. The material in the flask was freeze-thaw degassed for three cycles using the roughing pump. After the final cycle, the sample was refrozen and the entire system opened to the diffusion-pump vacuum. After the ultimate vacuum had been obtained, the sample was allowed to thaw and distill through the hot tube and was collected in the cold trap.

Synthesis of 1-methoxy-1-methyl-1-silacyclohexadiene, 23

The 1-methyl-1-methoxysilacyclohexadiene, 23, was prepared from the 1-chloro-1-methyl-1-silacyclohexadiene, 16, obtained from co-pyrolysis (625°C, N<sub>2</sub> flow) of a mixture of 1,1,2,2-tetrachloro-1,2-dimethyldisilane, (containing some 1,1,2-trichloro-1,2,2-trimethyldisilane) and cyclopentadiene (4). A 1.0 M solution of 16 in ether was added to an ether solution (~1.0 M) of MeOH and Et<sub>3</sub>N at 0°C under N<sub>2</sub>. The mixture was stirred by a mechanical stirrer for 2 h. The solids were filtered and the solvent was removed in vacuo. Yield 91%: <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 0.18 (s, 3 H), 1.48 (m, 2 H), 3.30 (s, 3 H), 5.83 (m, 3 H), 6.8 (d of m, 1 H); GCMS (% relative intensity) 140 (24), 125 (53), 108 (26), 95 (29), 75 (57), 59 (48).

Synthesis of 4-trimethylsilyl-1-methyl-1-methoxy-1-silacyclohexa-2,5-diene 74

Into a dry, 100 mL flask equipped with a magnetic stirring bar was placed 4.0 grams (28.6 mmol) of the 1-methoxysilacyclohexadiene, 23, and 30 mL of dry THF. This solution was cooled to -78°C. Lithium diisopropylamide (28.6 mmol) in THF was added slowly via canula. This caused the solution to turn brick red. This mixture was stirred at -78°C for 1 h and then quenched by adding it (via canula) to neat Me<sub>3</sub>SiCl at -78°C and allowing the mixture to warm up overnight. The reaction mixture was filtered through Celite and the solvent removed in vacuo. This left a yellow-orange oil which was purified by flash chromatography (5% EtOAc/hexane) or by percolation through a dry pad of silica gel



using hexane eluent, followed by vacuum distillation (70°C, 40 Torr). This gives a colorless to slightly yellow oil in 58-65% yield:  $^1\text{H}$  NMR ( $\text{CCl}_4$ )  $\delta$  0.0 (s, 9 H), 0.13 (s, 3 H), 2.91 (m, 1 H), 3.31 (s, 3 H), 5.61 (d of d, 2 H,  $J = 14.5$  Hz and 4.5 Hz), 6.81 (d of d, 2 H,  $J = 14.5$  Hz and 4.5 Hz); Exact mass calculated for  $\text{C}_{10}\text{H}_{20}\text{Si}_2\text{O}$  212.1053, measured 212.1048; GCMS (% relative intensity) 212 (17), 197 (16.8), 124 (15), 108 (54), 73 (100), 59 (48).

#### Flash vacuum pyrolysis of 74

The FVP of 74 was carried out at 600°C,  $2 \times 10^{-4}$  Torr. The pyrolysate was 95 mg of a light yellow liquid which represents a 46% mass recovery. By GCMS there was considerable  $\text{Me}_3\text{SiOMe}$  and some of the sila-toluene dimer. The dimer was isolated in 14% yield by gas chromatography (8 ft.  $\times$   $\frac{1}{4}$  inch 10% SE-30 on Chromasorb W, Varian-Aerograph 1720 GC). The NMR and mass spectra were superimposable with those of the authentic material made from 20 (3).

#### Copyrolysis of 74 and acetylene

A vertical pyrolysis tube was heated to 450°C under  $\text{N}_2$  flow for  $\frac{1}{2}$  h. The tube was then purged for 15-20 minutes with a mixture of nitrogen and acetylene (which was purified by first bubbling through concentrated  $\text{H}_2\text{SO}_4$ , then by passage through alumina). Finally, the tube was purged with pure acetylene at a flow rate of 30 mL/minute for 15 minutes. Into the hot tube was dripped 0.567 g 74, and the pyrolysate was collected in a -78°C cold trap. The pyrolysate consisted

of 74 (~1 mg) and the adduct, 21, 1-methyl-1-silabicyclo[2.2.2]-octatriene. The mass recovery was 50% with the yield of 21 being 28.5%, based on reacted 74. The NMR and mass spectra of 21 were identical to those of authentic 21 derived from copyrolysis of 20 and acetylene (3).  
Synthesis 4-trimethylsilyl-1,1-dimethyl-1-silacyclohexa-2,5-diene 76

The procedures of Banasiak (24) were used with the exception that lithium diisopropylamide (LDA) was the metalating agent. After preparative GC, 76 was isolated as a colorless liquid. NMR (D-6 benzene)  $\delta$  0.0 (s, 9 H), .23 (s, 6 H), 2.68 (apparent t, 1 H), 5.83 (d of d, 2 H, J = 15 Hz, J = 1.5 Hz), 6.75 (d of d, 2 H, J = 15 Hz, J = 5 Hz).

Sealed tube thermolysis of 76

A solution of 76 (50 mg) in D-6 benzene was freeze-thaw degassed, then sealed under vacuum. The reaction was monitored by NMR spectroscopy. After 6 h at 200°C all signals due to 76 had been replaced by those of 77 NMR: (CCl<sub>4</sub>)  $\delta$  0.15 (two peaks, 15 H), 1.4 (d, 1 H, J = 7 Hz), 5.9 (m, 3 H), 6.9 (m, 1 H); GCMS (% relative intensity) 196 (6), 181 (2), 108 (74), 73 (100).

Flow pyrolysis of 76

Into a vertical pyrolysis tube at 450°C were dripped 50 mg of 76. N<sub>2</sub> flow was 30 mL/minute and the pyrolysate was collected in a liquid nitrogen-cooled trap. By NMR, only 77 was present. There were no traces of 76.

### Sealed tube thermolysis of 74

In an NMR tube containing 0.2 mL diphenyl ether was placed 0.1622 g 74. The tube was freeze-thaw degassed 4 times, and then sealed under vacuum. The tube was heated to 150°C and progress monitored by NMR. After 10 h, all of 74 had rearranged to 75. 75 was isolated by GC. NMR: (CCl<sub>4</sub>) δ 0.0 (s, 9 H), .18 (s, 3 H), 1.4 (d, 1 H, J = 6 Hz), 3.2 (s, 3 H), 5.9 (m, 3 H), 6.9 (m, 1 H). The mass spectrum of 75 was identical to that of 74.

### Photolysis of 1-methyl-1-silabicyclo[2.2.2]octatriene, 21, in cyclohexane

In a Pyrex NMR tube were mixed 21 (10 mg), acetone (12 mg), and cyclohexane (500 mg, distilled from Na). The tube was sealed with a rubber septum and deoxygenated by bubbling argon through the solution for 20 minutes. The tube was then attached to a quartz jacket and irradiated with a 450 W Hanovia medium pressure Hg lamp. The reaction was stopped every 15 minutes and checked by NMR. After ½ h, all the olefinic resonances due to 21 had been replaced by a new set of olefinic signals. The reaction mixture was separated by gas chromatography (4 ft. X ¼ inch, 12% SE-30 on Chromasorb W, 125°C Varian Model 920 GC). The first two peaks were acetone and cyclohexane. The last peak was identified as 1-methyl-1-silatricyclo[3.3.0.0]octa-2,6-diene, 79, formed in quantitative yield. <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 0.4 (s, 3 H), 1.68 (t, 1 H, J = 9 Hz), 3.07 (br. d of d, 2 H, J = 9 Hz, J = 2 Hz), 5.82 (d, 2 H, J = 9 Hz), 6.02 (d of d, 2 H, J = 9 Hz, J = 2 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>)

$\delta$  141.64, 132.16, 43.37, 28.03, and -5.55 ppm. GCMS (% relative intensity) 134 (26), 119 (100), 108 (57), 93 (82), 67 (24), and 53 (34).

Photolysis of 1-methyl-1-silabicyclo[2.2.2]octatriene in pentane

To 500 mL dry pentane (distilled from LAH) was added 10 mg of 21 in a quartz NMR tube sealed with a septum. The solution was deoxygenated by bubbling argon through it for 20 minutes. The tube was attached to a quartz-jacketed 450 W Hanovia medium pressure Hg lamp and irradiated for  $\frac{1}{2}$  h. After this time, there was a white, fluffy solid which was filtered off. This solid was not soluble in  $\text{CHCl}_3$ , acetone, or  $\text{CCl}_4$ . The filtrate showed no evidence of starting material. When this photolysis was repeated using acetone (12 mg) as a sensitizer, the same result was obtained.

Photolysis of 21 in MeOH

To an NMR tube containing 300 mg MeOH were added 13 mg 21. This was deoxygenated with argon for 20 minutes prior to photolysis. The tube was attached to a quartz-jacketed 450 W Hanovia medium pressure Hg lamp and irradiated for 2 h. Progress was monitored by NMR and by the end of 2 h all of the starting material remained. Continued irradiation (10 h) gave a complex mixture (> 20 components) by GC.

Sensitized photolysis of 79

To a septum-sealed quartz NMR tube were added 79, (12.9 mg), acetone (16.1 mg) and cyclohexane (.4 mL). Argon was passed through the mixture for 30 minutes and the solution was irradiated with a 450 W Hanovia medium pressure Hg lamp. At one hour intervals, an aliquot was

removed and its NMR spectrum recorded. The photolysis was stopped when the olefinic signals of the starting material were no longer observable (ca. 4 h). By GCMS there were four components. The largest of these had  $m/e$  of 150, but contained no silicon. The second largest peak was 79. The remaining peaks had  $m/e = 126$  and 173 but did not appear to contain silicon.

Reaction of 79 with tetracyanoethylene in D-6 benzene

In an NMR tube with 14 mg TCNE and 0.5 mL D-6 benzene was placed 6 mg 79. Argon was bubbled through the solution (which had changed to yellow with the TCNE addition) and the mixture was heated to 60°C. After 1 h, the mixture was checked by NMR and all that was found were some broad humps in the 7.2 - 6.0 region. There was a solid which was soluble in D-6 acetone. This solid had a singlet at  $\delta$  2.85; but as it contained no Si-Me peaks, it was not characterized.

Reaction of 79 with TCNE in D-8 toluene

To 0.5 mL D-8 toluene was added 10 mg 79. To this were added 12 mg TCNE. Addition of the TCNE caused the solution to turn yellow, then orange. (By NMR there had been no apparent reaction.) After 2 h at 25°C, a solid began to form. The NMR showed some changes such as another singlet in the Si-Me region and some new olefinic peaks. The reaction progressed without further change in the NMR spectrum, but with the formation of more solid. After 32 h, the tube was opened, the solid filtered and a GCMS obtained of the filtrate. This proved to be solvent and starting material. The NMR spectrum in D-6 acetone showed a sharp

singlet at  $\delta$  3.0 and very little else. Because there were no Si-Me absorptions this material was not analyzed further.

Reaction of  $\underline{21}$  with dimethylacetylenedicarboxylate (DMADC)

Into a septum-sealed NMR tube were placed  $\underline{21}$  (10 mg), DMADC (13 mg) and .45 mL D-6 benzene. Argon was passed through the solution for 20 minutes and the tube heated to 80°C. There was no change in the NMR after 3 h at 80°C or 10 h at 100°C. The mixture was transferred to a thick-walled glass tube, degassed by freeze-thaw, sealed, and heated to 150°C. After 10 h, the tube was opened and an NMR taken. Again, there was no observable change in the NMR, only starting material and trap were present.

Synthesis of 1,4-pentadiene

The procedure of Benson and McKusick (109) was followed starting from 1,5-pentanediol. The diacetate was formed in 96% yield and was pyrolyzed (625°C, N<sub>2</sub> flow) to give a 60-65% yield of 1,4-pentadiene (Bpt. 25-27°C). The NMR of the pentadiene thus formed matched well with that of an authentic sample.

Synthesis of 1,1-dibromo-2-propenylcyclopropane

The procedure of Seyferth (110) was followed and the product was formed in 40% yield after distillation (15 Torr, 75-80°C). <sup>1</sup>H NMR: (CCl<sub>4</sub>)  $\delta$  1.1 (m, 1 H), 1.7 (br. d, 2 H), 2.2 (apparent t, 2 H), 5.1 (multiplet, t, 2 H), 5.75 (m, 1 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  135.2, 116.2, 36.4, 30.3, 28.6, and 28.25 ppm. GCMS (% relative intensity) 201 (5), 199 (10), 197 (5), 161 (3), 119 (5), 107 (5), 79 (35), 54 (100). Exact

mass (no parent seen, but  $M-C_3H_5$  strong) calculated for  $C_3H_3Br_2$  198.8581, measured 198.8582. IR (neat) 3050, 2950, 1650, 1440, 1150, 930, 650  $cm^{-1}$ .

Synthesis of *cis* and *trans* 1-bromo-2-propenylcyclopropane

The procedure of Seyferth (110) was used. Tri-*n*-butyltinhydride (5.09 mmol) was added to 5.09 mmol of the dibromide, with an icewater bath to insure that the temperature would not exceed 40°C. After the addition was complete, the mixture was stirred for 1 h at 25°C. The crude reaction mixture was percolated through silica gel using Skelly "B" as eluent. This gave a mixture of the isomeric monobromides and some tributyltinbromide. The monobromides were distilled out as a 1:1 mixture (51-54°C, 48 Torr) in 56% yield.  $^1H$  NMR: ( $CCl_4$ ) *cis*-monobromide  $\delta$  .95 (m, 2 H), 1.70 (apparent t, 1 H), 2.2 (apparent t, 2 H), 3.0 (m, 1 H), 5.05 (m, 2 H), 5.85 (m, 1 H). *Trans*-monobromide:  $\delta$  1.0 (m, 2 H), 1.70 (apparent t, 1 H), 2.0 (apparent t, 2 H), 2.50 (m, 1 H), 5.0 (m, 2 H), 5.60 (m, 1 H). Isomer assignment was based on the observations of Landgrebe and Becker (136) that the proton on the halogen-bearing carbon has a .48 ppm downfield shift if it is *cis* to an alkyl group on the 2-carbon. GCMS (% relative intensity) 162 (1), 160 (1), 121 (4.4), 119 (4.5), 81 (59), 79 (100), 54 (70). Exact mass calculated for  $C_6H_9Br$ : 159.9887, measured 159.9891.

Synthesis of *cis* and *trans* 1-(2-propenylcyclopropyl-1-methoxy-1,2,2,2-tetramethyldisilane, 89

To a dry, 1 neck 25 mL flask equipped with a stirring bar and sealed with a septum were added .51 g (3.19 mmol) of a mixture of *cis* and *trans* 1-bromo-2-propenylcyclopropane and 6.5 mL ether under  $N_2$ . This

was cooled to  $-78^{\circ}\text{C}$  and then  $t\text{-BuLi}$  (4.2 mmol) was added dropwise over 5 minutes. This mixture was stirred at  $-78^{\circ}\text{C}$  for 1 h then added via canula to a  $-78^{\circ}\text{C}$  solution of 1,1-dichlorotetramethyldisilane (3.98 mmol) in 12 mL ether and stirred overnight. This was added to 8.0 mmoles each of MeOH and  $\text{Et}_3\text{N}$  in 15 mL ether and stirred at room temperature for 3 h. The salts were filtered, and the solvent removed in vacuo giving 1.0 g (~30%) of a clear, slightly yellow liquid which by GCMS contained the desired product along with traces of volatile impurities (solvent,  $\text{Et}_3\text{N}$ ). (Mixture of cis and trans 89) NMR ( $\text{CCl}_4$ )  $\delta$  0.1 (overlapped peaks, 14 H, silicon methyl and cyclopropyl Hs) .90 (m, 2 H, cyclopropyl  $-\text{CH}_2-$ ), 2.0 (apparent t, 2 H, allylic  $-\text{CH}_2-$ ), 3.4 (s, 3 H), 5.0 (m, 2 H), 5.7 (m, 1 H).  $^{13}\text{C}$  NMR ( $\text{DCCl}_3$ )  $\delta$  138.82, 137.84, 114.82, 114.28, 51.49, 39.63, 36.43, 16.28, 14.71, 8.75, 8.53, 8.42, 8.32, 3.66, 2.68, -1.49, -1.98. GCMS (% relative intensity) trans isomer 228 (1), 213 (2), 147 (9), 133 (100), 123 (24), 117 (12), 89 (26), 75 (57), 73 (44), 59 (63), cis isomer 228 (.11), 213 (2), 174 (3), 155 (17), 133 (12), 123 (24), 97 (20), 96 (79), 89 (43), 75 (100), 73 (59), 59 (82).  
Flash-vacuum pyrolysis of 89

Through a horizontal quartz tube at  $650^{\circ}\text{C}$  ( $2 \times 10^{-4}$  Torr) were distilled 100 mg of 89. There was 100 mg of pyrolysate recovered which by GCMS proved to be a complex mixture of over 20 products. Under preparative GC conditions (15 ft. x  $\frac{1}{4}$  inch 15% SE-30 on Chromasorb W,  $150^{\circ}\text{C}$ , Varian 920 GC) could only be resolved into 6 peaks.

Pyrolysis at lower temperatures ( $600^{\circ}\text{C}$ ,  $550^{\circ}\text{C}$ ) gave back unreacted starting material.



Flow pyrolysis of 89 with 2,3-dimethylbutadiene

A mixture of 127 mg 89 and 0.63 mL 2,3-dimethylbutadiene was dripped into a vertical pyrolysis tube at 450°C, N<sub>2</sub> flow. The pyrolysate was collected in a liquid nitrogen-cooled trap. By GCMS, it contained the trap and unreacted 89. Another pyrolysis at 550°C using the same trap gave the same result.

Photochemical cyclopropanation of 74

The procedure of Kropp et al. was used (114). A solution of 74 (0.106 g), 0.402 g CH<sub>2</sub>I<sub>2</sub>, and 10 mL 1,2-dichloroethane was mixed with 3 mL of an aqueous solution which was 10% each in sodium thiosulfate and sodium bicarbonate.

The reaction was carried out in a 50 mL 3-neck flask which was equipped with a nitrogen inlet, a condenser, and a magnetic stirring bar. Irradiation was accomplished with a 250 W G.E. sunlamp. After 4.5 h irradiation time, the reaction was worked up by separating the layers, drying the organic phase, and removing the solvent in vacuo. GC (4 ft. x 1/8 inch 12% SE-30 on Chrom W, 150°C, Varian Series 920 GC) showed the presence of solvent, CH<sub>2</sub>I<sub>2</sub>, and starting material. No peaks with longer retention times were found.

The reaction was repeated using 0.5 mmol 74, 1.5 mmol CH<sub>2</sub>I<sub>2</sub> in 10 mL 1,2-dichloroethane and 3 mL buffer solution. This time a 450 W Hanovia medium pressure Hg lamp was used. The reaction was monitored by periodically withdrawing aliquots and checking them by GC (8 ft. x 1/8 inch 10% OV-101 on Chrom W, 100°C-250°C at 10°C/min, Fisher Series 4400

GC). After 5 h, a small peak of longer retention time than 74 was found (as well as 74 itself) which continued to increase as photolysis time increased. After 12 h, no further increase in this new peak was observed. GC indicated only 74 and this new peak. The reaction vessel was coated with an orange-brown gel-like substance. Workup was as before and the sample was submitted for GCMS. GCMS of new peak (% relative intensity): 226 (1.9), 211 (3.3), 160 (1.9), 145 (2.3), 133 (20), 122 (46), 107 (9), 89 (53), 73 (100), 59 (66). The mass recovery, however, was quite poor as less than 30% of the silicon containing material was recovered.

Ultrasonically initiated cyclopropanation of 74

In a dry, 3-neck 50 mL flask equipped with an overhead stirrer, a condenser, and a nitrogen inlet was placed 2.50 g (38.4 mmol) granulated zinc metal and 20 mL 1,2-dimethoxyethane (DME). This was lowered into a Bransonic B-32 150 W bath-type ultrasonicator and sonicated for 2 h under N<sub>2</sub>. The zinc turned into a fine, grey-black powder after this treatment. The DME was then brought to reflux by lowering a coil of copper tubing into the bath and passing steam through it. The stirrer was started and 74 (9.6 mmol) was added, followed by 38.4 mmol CH<sub>2</sub>I<sub>2</sub>. There was an induction period of ~5 minutes whereupon the reaction became quite exothermic. This exothermicity subsided and the mixture was refluxed for 3.5 h, then cooled to 25°C and allowed to settle. The liquids were pipetted away from the solids, and the solids were rinsed twice with pentane. The pentane rinses were mixed with the DME and the

solvents removed in vacuo. This gave 2.69 g of a yellow oil which contained 2 major peaks. The products were separated by GC on a Varian Series 1720 gas chromatograph (16 ft. X  $\frac{1}{4}$  inch 20% SE-30 on Chrom W, 200°C). By NMR and GCMS, the compounds were the monocyclopropanated product, 100, (~25%) and the biscyclopropanated 106 (~75%).

$^1\text{H}$  NMR for 100 ( $\text{CDCl}_3$ )  $\delta$  0.125 (s, 9 H), 0.35 (s, 3 H), 0.85 (m, 3 H), 1.65 (s, 1 H), 2.17 (d, 1 H,  $J = 5$  Hz), 3.52 (s, 3 H), 5.39 (d of t, 1 H,  $J = 14$  Hz,  $J = 2$  Hz), 6.51 (d of d, 1 H,  $J = 14$  Hz,  $J = 2$  Hz).

$^{13}\text{C}$  ( $\text{CDCl}_3$ )  $\delta$  149.92, 118.02, 50.59, 33.56, 10.59, 5.98, 0.29, -2.35, and -2.74.

100 GCMS (% relative intensity) 226 (3.1), 211 (5.0), 163 (4.3), 138 (3.2), 133 (21.3), 122 (49.4), 121 (17.2), 89 (62), 73 (100), 59 (59.8). Exact mass calculated for  $\text{C}_{11}\text{H}_{22}\text{OSi}_2$  226.12093, measured 226.12099.

For 106, NMR ( $\text{CDCl}_3$ )  $\delta$  0.18 (overlapped peaks, 14 H), 0.45 (s, 3 H), 1.00 (apparent d of d, 4 H), 3.4 (s, 3 H).  $^{13}\text{C}$  ( $\text{CDCl}_3$ )  $\delta$  34.20, 17.36, 13.63, -2.14, -2.41, -3.06, -3.17. GCMS (% relative intensity) 240 (.28), 225 (1.4), 174 (2.7), 166 (5.0), 136 (21), 124 (8), 108 (21), 101 (48), 89 (28), 73 (100), 59 (54). Exact mass calculated for  $\text{C}_{12}\text{H}_{24}\text{OSi}_2$  240.13658, measured 240.13718. It should be noted that the formation of only 100 can be assured by running the reaction using equimolar amounts of 74 and  $\text{CH}_2\text{I}_2$ . The reaction mixture then contains unreacted 74 and 100 as the sole cyclopropanated product.

#### Flash vacuum pyrolysis of 100

FVP of 100 was carried out at 500°C,  $1 \times 10^{-5}$  Torr. The pyrolysate was collected in a liquid nitrogen-cooled trap. The mass recovery was

70%. By NMR, the pyrolysate was unreacted 100. When 85 mg 100 was pyrolyzed at 650°C,  $10^{-5}$  Torr, the mass recovery was only 50% and the pyrolysate was a complex mixture. At 600°C, 112 mg of 100 were pyrolyzed to give the same complex mixture as with pyrolysis at 650°C and a mass recovery of 60%. The last 2 pyrolysates were submitted for GCMS and consisted mainly of isomers of 100 (ca. 14 peaks). These components did not separate under preparative GC conditions.

#### Sealed tube thermolysis of 100

To 0.40 mL D-6 benzene in an NMR tube was added 20 mg 100. This solution was freeze-thaw degassed and sealed under vacuum. The tube was heated to 160°C and the reaction monitored by NMR. After 12 h at 160°C, there was no change in the NMR spectrum. The temperature was raised to 195°C and the reaction continued. After 12 h at 195°C, the NMR remained unchanged.

#### Flow copyrolysis of 106 and MeOH

A mixture of 106 (128 mg) and MeOH (171 mg) was pyrolyzed at 450°C using  $N_2$  flow. The pyrolysate was collected in a liquid nitrogen-cooled trap. The mass recovery was 53% (158 mg). The pyrolysate showed only MeOH and 106, based on GCMS.

#### Flash-vacuum pyrolysis of 106

FVP of 106 was carried out at 700°C,  $10^{-4}$  Torr. There was a 70% mass recovery. By GCMS, there was a complex mixture (~20 peaks) of which the majority were isomers of the starting material. Pyrolysis at 600°C

(167 mg) gave an 84% mass recovery, but an equally complex pyrolysate. These mixtures could only be resolved on capillary GC columns and no further attempt at isolation of individual peaks was made.

Attempted cyclopropanation of 2-trimethylsilyl-1-methyl-1-methoxy-1-sila-  
cyclohexa-2,4-diene, 75

In a dry, 3-neck, 50 mL flask equipped with an overhead stirrer, nitrogen inlet, and condenser were placed 1.44 g (22.1 mmol) of granulated zinc metal and 20 mL DME. The zinc was sonicated in a Bransonic B-32 150 W bath-type sonicator for 2 h. The DME was brought to reflux using steam passed through coiled copper tubing. 75 (1.56 g, 7.36 mmol) was added rapidly followed by 5.91 g (22.1 mmol)  $\text{CH}_2\text{I}_2$ . An exothermic reaction ensued and this mixture was stirred and refluxed for 4 h. The workup was the same as with 74. GCMS indicated only starting material. A repeat of this reaction on the same scale, but using an 8 h reaction time, afforded the same result.

Synthesis of 2,2-dichloro-2-silatetrahydronaphthalene, 116

Benzylmagnesium chloride was coupled to vinyltrichlorosilane according to the method of Corriu et al. (118). This gave a 54% yield of benzylvinylchlorosilane (B. pt. 100-110°C/0.35 Torr, lit., B. pt. 113-116°C/14 Torr) (118). The benzylvinylchlorosilane was cyclized according to the method of Chernyshev et al (117). This gave a 67% yield of 116 (B. pt. 123-130°C/4 Torr, lit. 91-92°C/1 Torr) (117).

Attempted synthesis of 114

Into a 100 mL 3 neck round-bottom flask was placed 90 mmol 116 along with 30.2 mmol  $\text{SO}_2\text{Cl}_2$  and 0.073 g benzoylperoxide. This mixture was heated to 75°C under  $\text{N}_2$  for 4 h. It was then cooled and 30.2 mmol  $\text{SO}_2\text{Cl}_2$  and 0.073 g benzoylperoxide added. The mixture was again heated at 75°C for 3 h, cooled, another portion each of  $\text{SO}_2\text{Cl}_2$  and the peroxide were added, and the mixture heated to 75°C for 9 h. Vacuum distillation (1 Torr) gave mostly unreacted 116 and a trace of a monochlorinated product. There was no 114 detected either by  $^1\text{H}$  NMR or GCMS. This result was obtained all 6 times it was tried.

Attempted bromination - dehydrobromination of 2,2-dimethoxy-2-silatetrahydronaphthalene

The silyl methoxy compound (25.5 mmol) was mixed with 51 mmol N-bromosuccinimide (NBS), 2.6 mmol benzoylperoxide and 55 mL  $\text{CCl}_4$ . This mixture was refluxed until all the succinimide was floating on the  $\text{CCl}_4$ . This mixture was filtered and the solvent distilled off. There were 8.75 g of a viscous, red-orange material isolated. Approximately  $\frac{1}{4}$  of this material was reacted with what was calculated to be 1 equivalent of DBU in 20 mL  $\text{CH}_2\text{Cl}_2$ . This was stirred overnight at room temperature. Removal of the solvent gave a viscous mass which became solid upon standing. The portion of the "brominated" product which had not been treated with DBU had also solidified.

When this reaction was repeated and a vacuum distillation attempted (to remove any product as quickly as possible), the material in the pot turned dark brown and rapidly solidified.

Synthesis of ( $\alpha$ -bromo)vinylbenzylchlorosilane, 117

( $\alpha$ -Bromo)vinyltrichlorosilane was prepared in two steps, 24% overall yield from vinyl trichlorosilane according to the method of Agree and Hilling (119). The ( $\alpha$ -bromo)vinyltrichlorosilane (44 mmol) was reacted with the benzylmagnesium chloride made from 44 mmol benzyl chloride and 55 mmol Mg in the same manner as vinyltrichlorosilane. Filtration, solvent removal, and vacuum distillation (125-130°C, 0.5-1.0 Torr) gave 117 in 46% yield.  $^1\text{H}$  NMR ( $\text{CCl}_4$ )  $\delta$  2.80 (s, 2 H), 6.55 (d, 1 H,  $J = 2$  Hz), 6.65 (d, 1 H,  $J = 2$  Hz), 7.2 (s, 5 H).

Attempted cyclization of 117 using  $\text{AlCl}_3$

To 1.0 mL heptane was added 6.7 mmol 117. This was added dropwise to 0.98 mmol  $\text{AlCl}_3$  in 6.0 mL refluxing heptane. This mixture was refluxed 8 h and checked by NMR. No cyclization had taken place. Refluxing for 8 h more did not affect the starting material.

Attempted cyclization of 117 using  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  in benzene

To 1.0 mL benzene was added 4.75 mmol 117. The  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (4.75 mmol) was added slowly at room temperature. (The solution turned slightly red-orange.) After 3 h at room temperature, the benzene was removed by distillation. A  $^1\text{H}$  NMR of the residue indicated some benzene, but mainly unreacted 117. Running this reaction overnight did not cause cyclization.

Attempted cyclization of 117 using  $\text{AlCl}_3$  and HCl

To 0.75 mL heptane was added 4.81 mmol 117 and this was added dropwise an HCl(g)-saturated heptane solution containing 0.35 mmol  $\text{AlCl}_3$ . The addition took place at room temperature and then the mixture was heated to reflux.

After refluxing for 16 h, the mixture was cooled to 0°C, 0.045 g Et<sub>3</sub>N were added, the mixture was filtered, and the heptane removed by distillation. NMR analysis showed unreacted 117.

Synthesis of o-(bromomethyl)styrene, 121

O-(bromomethyl)benzoic acid was prepared by the method of Tulleen (120) in 77% yield from o-toluic acid. <sup>1</sup>H NMR (CDCl<sub>2</sub>): δ 5.0 (s, 2 H), 7.5 (broad singlet, 3 H), 8.0 (multiplet, 1 H). The Wittig salt of this acid was prepared in 66% yield from o-(bromomethyl)benzoic acid and triphenyl phosphine in refluxing acetone. O-styrylbenzoic acid was prepared in 82% yield following the procedure of Broos et al. (121). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.6 (apparent t, actually overlapped d of d, 2 H), 8.2-7.3 (multiplet, 5 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 172.9, 140.6, 136.1, 133.1, 131.4, 127.6, 127.3, 116.8.

This acid was reduced by adding it (in ether solution) dropwise to a slurry of LAH (1.25 equivalent) in ether at a rate sufficient to maintain a gentle reflux. After completed addition, the mixture was stirred another 15 minutes, then hydrolyzed by dropwise addition to a 10-fold excess of H<sub>2</sub>O. The aluminum salts were destroyed by the slow addition of 10% H<sub>2</sub>SO<sub>4</sub>. The layers were separated and the aqueous phase extracted twice with ether. The collected ether washings were neutralized with 5% aq. NaHCO<sub>3</sub>, washed 3 times with H<sub>2</sub>O and dried over MgSO<sub>4</sub>. Solvent removal left a light yellow oil which was a single compound by GC. This material was not purified further. <sup>1</sup>H NMR (CCl<sub>4</sub>): δ 3.4 (br. s, 1 H, exchanges W/D<sub>2</sub>O), 4.6 (s, 2 H), 5.4 (d of d, 1 H, J = 10 Hz, J = 2 Hz), 5.65 (d of d, 1 H, J = 18 Hz, J = 2 Hz), 7.5-6.9 (multiplet, 5 H).



GCMS (% relative intensity) m/e 134 (79.8), 133 (84.0), 116 (13.5), 115 (40.0), 106 (10.0), 105 (100.0), 91 (47.0), 77 (46.0).

Dropwise addition of 1.57 mmol  $\text{PBr}_3$  to 3.5 mmol of the alcohol at  $0^\circ\text{C}$ , warming to room temperature, and stirring overnight gave a reddish solution which was percolated through silica gel using Skelly "B" as the eluent. Solvent removal gave 1.36 mmol of the bromocompound, 121. Similarly, the alcohol (20.72 mmol) was added to 104 mL  $\text{CH}_2\text{Cl}_2$  and 31.1 mmol  $\text{Et}_3\text{N}$ , then cooled to  $0^\circ\text{C}$ . Methanesulfonylchloride (22.8 mmol) was added dropwise and this mixture was stirred for 2 h at  $0^\circ\text{C}$ . The solvent and excess  $\text{Et}_3\text{N}$  were removed on a Rotovap. The crude mesylate was added to 40 mL acetone (dried over  $\text{K}_2\text{CO}_3$ ) and 4.12 g LiBr. This mixture was refluxed overnight in the dark. Filtration and solvent removal gave a 69% yield of the crude bromide (122).  $^1\text{H NMR}$  ( $\text{CCl}_4$ )  $\delta$  4.5 (s, 2 H), 5.5 (overlapped d of d, 2 H), 7.5-6.9 (multiplet, 5 H).

Attempted Grignard reaction of 121

To 10 mL ether was added 9.2 mmol 121 and this solution was added dropwise to 11.0 mmol Mg in 10 mL ether. Several additions of 1,2-dibromoethane (to catalyze Grignard formation) failed to initiate the reaction. The application of heat caused the formation of a gelatinous, bright red substance. Decanting the solution from this gummy mess and removing the ether gave an orange residue which had no vinyl protons in the NMR. When this reaction was repeated using twice as much solvent, the results were the same. The inclusion of  $\text{Me}_3\text{SiCl}$  in the reaction had no effect.

Attempted lithiation of 121 by lithium-halogen exchange

To 9.0 mL dry ether was added 3.1 mmol 121 and this was cooled to  $-78^{\circ}\text{C}$  under  $\text{N}_2$ .  $t\text{-BuLi}$  (3.68 mmol in pentane) was added dropwise and the mixture was stirred 1.5 h. The reaction was quenched with 5.0 mmol  $\text{Me}_3\text{SiCl}$  and the mixture was warmed to room temperature. Aqueous workup, followed by drying ( $\text{MgSO}_4$ ) and solvent removal revealed a complex mixture in which there were no vinyl protons in the NMR.

Synthesis of 1-methoxy-1-methyl-1-silatetrahydronaphthalene, 123

The 3-(*o*-chlorophenyl)-1-bromopropane was prepared according to Gilman and Marrs' instructions (123). The Grignard reagent prepared from 55 mmol of the bromide and 76.52 mmol Mg was added dropwise to a 0.30 M ether solution of  $\text{MeSiHCl}_2$  at  $0^{\circ}\text{C}$ . The mixture was stirred overnight and allowed to come to room temperature. This mixture was filtered and the ether removed by distillation. Vacuum distillation ( $125^{\circ}\text{C}/5$  Torr) gave a 49% yield of the silylated compound. The 3-(*o*-chlorophenyl)propylmethylchlorosilane was reduced to the dihydrido silane with 1.0 equivalent LAH in ether at  $0^{\circ}\text{C}$ . Addition of  $\text{H}_2\text{O}$ , followed by 10%  $\text{H}_2\text{SO}_4$ , separation of layers,  $\text{H}_2\text{O}$  washing of the organic phase, and drying ( $\text{MgSO}_4$ ) gave a colorless oil which was >95% pure (by GC) and was used without further purification.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  0.2 (t, 3 H), 0.9 (m, 2 H), 1.79 (m, 2 H), 2.8 (overlapped triplets, 2 H), 3.8 (septet, 2 H), 7.5-7.2 (m, 4 H's). IR (neat)  $3080\text{ cm}^{-1}$ ,  $3020\text{ cm}^{-1}$ ,  $2925\text{ cm}^{-1}$ ,  $2860\text{ cm}^{-1}$ ,  $2120\text{ cm}^{-1}$ ,  $1575\text{ cm}^{-1}$ ,  $1470\text{ cm}^{-1}$ ,  $1440\text{ cm}^{-1}$ . GCMS (% relative intensity) 198 (1.29), 197 (2.7), 170 (11.0), 163 (7.0), 155 (17.0), 125 (21.0),

117 (13.0), 115 (21.0), 91 (39.0), 90 (68.0), 73 (100.0).  $^{13}\text{C}$  ( $\text{CDCl}_3$ )  $\delta$  139.9, 134.0, 130.5, 129.5, 127.2, 126.7, 36.7, 25.6, 10.5, and -8.5 ppm. According to Gilman's instructions, 11.88 mmol of the dihydrido-silane in 14 mL dry toluene were added over a 90 minute period to 27.76 mmol molten sodium in 14 mL refluxing toluene (123). The addition rate was controlled by a syringe drive with variable speed. After the addition was complete, the mixture was refluxed 5 h more, then cooled. The supernatant liquid was pipetted away from the purplish solids and hydrolyzed with 10%  $\text{H}_2\text{SO}_4$  and ice. The layers were separated and the aqueous phase extracted twice with ether. The collected organic phases were washed with  $\text{H}_2\text{O}$ , brine, and dried over  $\text{MgSO}_4$ . Solvent removal and vacuum distillation (87-91°C/8 Torr) gave a clear, colorless fraction which amounted to a 40-50% yield (average of several runs) of 123.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  0.42 (d, 3 H), 0.9 (m, 1 H), 1.21 (m, 1 H), 2.1 (m, 2 H), 2.85 (triplet, 2 H), 4.48 (apparent quartet, 1 H), 7.6-7.2 (m, 4 H).  $^{13}\text{C}$  ( $\text{CDCl}_3$ )  $\delta$  148.8, 135.0, 132.1, 129.1, 128.7, 125.4, 35.1, 22.3, 9.7, -3.9 ppm. Exact mass for  $\text{C}_{10}\text{H}_{14}\text{Si}$  measured 162.08658, calculated 162.08648.

The methylhydridosilatetrahydronaphthalene (10.17 mmol) was added dropwise to 11.20 mmol MeOH in 15 mL ether containing a catalytic amount of 10% Pd on C in a 25 mL flask sealed with a septum. Hydrogen evolution was immediate. Gas continued to evolve for ~2 h. When the gas evolution stopped, the mixture was filtered and the volatiles removed on a Rotovap. This left a colorless liquid which was pure by GC. This was 123 based on the  $^1\text{H}$ ,  $^{13}\text{C}$ , GCMS and IR data.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.4 (s, 3 H),

0.9 (m, 1 H), 1.2 (m, 1 H), 2.1 (apparent t, 2 H), 2.8 (m, 2 H), 3.5 (s, 3 H), 7.6-7.2 (m, 4 H).  $^{13}\text{C}$  ( $\text{CDCl}_3$ )  $\delta$  149.4, 134.0, 129.7, 128.6, 125.5, 50.8, 35.3, 22.8, 12.5, and -2.2 ppm. IR (neat): 3070, 2925, 1600, 1440, 1255, 1190, 1080, 815, 790, 740  $\text{cm}^{-1}$ . GCMS (% relative intensity) 192 (29.5), 177 (100.0), 149 (30.0), 147 (33.0), 145 (58.0), 119 (29.0), 59 (73.0).

Attempted bromination-dehydrobromination of  $\underline{\underline{123}}$

To a 25 mL, 1 neck flask with a nitrogen inlet, condenser, and magnetic stirring bar were added 4.3 mmol  $\underline{\underline{123}}$ , 4.34 mmol NBS, a catalytic amount of azobisisobutyronitrile (AIBN) and 5.0 mL  $\text{CCl}_4$ . This was heated to reflux under  $\text{N}_2$ . When the bromination was finished, this mixture was filtered and added to 50 mL pentane containing 0.4343 g  $\text{Et}_3\text{N}$  and stirred overnight at room temperature. The mixture was filtered and the solvent removed. This left a viscous, red-orange residue which (by GC) had at least 13 components. Attempted GC prep failed as only a broad, unresolvable hump came off the column. A second attempt using excess  $\text{Et}_3\text{N}$  gave a dark red residue which turned brown and solid while standing. Use of DBU in ether, followed by chromatography on silicic acid, gave the disiloxane of the siladihydronaphthalene.

Attempted synthesis of 4-benzoyloxy-1-methoxy-1-methyl-1-silatetrahydro-naphthalene,  $\underline{\underline{125}}$

In a 10 mL flask equipped with a condenser, magnetic stirring bar, and  $\text{N}_2$  inlet were mixed 4.34 mmol  $\underline{\underline{123}}$ , 4.46 mmol t-butylperoxybenzoate, and 12.4 mg CuBr. This mixture was heated to 85-90°C for 3 h

whereupon the solution turned a brilliant turquoise. The mixture was cooled, filtered, and an NMR taken. The NMR showed broad peaks, but no methoxyl signals. The mixture was not investigated further.

#### Synthesis of benzosilacyclobutene, 127

This compound was synthesized by the method of Gilman (123) in 25-28% yield. NMR ( $\text{CCl}_4$ )  $\delta$  0.5 (s, 6 H), 2.1 (s, 2 H), 7.2 (br. singlet, 4 H).

#### Sealed tube thermolyses of 127 with acetylenes

To 0.22 g 2-butyne was added 1.0 mmol 127 in a thick-walled glass tube. The tube was freeze-thaw degassed for 3 cycles, then sealed under dynamic vacuum. The tube was heated at 225°C in a Kugelrohr oven for 24 h, then cooled, and opened. After excess butyne had evaporated, there was left a yellowish solid which did not dissolve in  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$  or acetone. This material was not identified, but it could be the polymer from Si- $\text{CH}_2$  bond fission (127, 128).

When the reaction was repeated using 1-phenylpropyne, a white solid formed which was also insoluble in  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , and acetone. Dilution of this reaction mixture with benzene (making the solution 0.1 M in 127 and 1-phenylpropyne) and employing a lower temperature (100°C) did not prevent the formation of this white material.

#### Flow pyrolyses of 127 and acetylene

Into a vertical quartz tube packed with quartz chips at 400°C was dripped 250 mg 127, using acetylene as a carrier gas and reactant. The flow rate was 25-30 mL per minute. The pyrolysate was collected in a

liquid N<sub>2</sub> trap and was shown (by NMR) to be unreacted 127. This reaction was repeated at 500°C with the same result. At 600°C, very little 127 was recovered and the major product was benzene.

Synthesis of 3,3-dimethyl-4-trimethylsilyl-3-silacyclobutene, 129

This silacycle was prepared by the method of Barton and Burns (129) in a yield of 60% from its linear precursor. <sup>1</sup>H NMR matched well with that reported in the literature (130).

Flow co-pyrolysis of 129 and MeOH

A mixture of 129 (170 mg) and 320 mg MeOH was dripped into a vertical quartz tube under N<sub>2</sub> flow (30 mL per minute). The pyrolysate was collected in a liquid N<sub>2</sub> trap and represented a 52% mass recovery (including MeOH). The major peak (aside from MeOH) was GC prepped. <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 0.0 (s, 9 H), 0.1 (s, 6 H), 1.65 (d, 2 H), 3.35 (s, 3 H), 6.0-5.2 (m, 2 H). This was assigned the structure 130 based on similar work of Eaborn with 127. Mixing 129 with excess MeOH in ether at room temperature produced the same product after ~5 minutes of mixing.

Synthesis of trimethylsilyl(o-trimethylsilyl)phenylacetylene, 133

The procedure of Hommes and co-workers was employed to make this compound in ~70% yield (134). <sup>1</sup>H NMR (CCl<sub>4</sub>) δ .38 (s, 9 H), .51 (s, 9 H), 7.2 (m, 4 H).

FVP of 133

These pyrolyses were all conducted the same way, save for the temperature differences. At 700°C, 85% of the mass was recovered. The mass recoveries for subsequent pyrolyses decreased each time the

temperature was raised, reaching a minimum of 70% when the pyrolysis was conducted at 800°C. In each case, the NMR and GC showed the pyrolysates to be unreacted 133.

Synthesis of (o-trimethylsilyl)phenylacetylene, 135

To 16.26 mmol NaOH in 40 mL MeOH at room temperature was added 4.06 mmol 133. The reaction was monitored by GC. All of the 133 had disappeared in  $\frac{1}{2}$  h. The product purified by GC.  $^1\text{H}$  NMR ( $\text{CCl}_4$ )  $\delta$  0.37 (s, 9 H), 3.02 (s, 1 H), 7.2 (m, 4 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  133.94, 133.40, 128.70, 128.00, 80.20, 75.65, -0.95. Exact mass calculated for  $\text{C}_{11}\text{H}_{14}\text{Si}$  174.08648, measured 174.08657.

FVP of 135

Three FVPs of 135 were performed. The first, at 800°C, .05 Torr gave back mostly 135 and some 136 (along with other products). At 850°C, .05 Torr, there was a 71% mass recovery and 136 was formed in 18% yield, based on reacted 135. At 900°C ( $1.8 \times 10^{-5}$  Torr, 86% mass recovery), there was comparatively more 136, but there were also more products than with previous pyrolyses. Preparative GC on an 8 ft. X  $\frac{1}{4}$  inch, 12% SE-30 glass column gave pure 136. 136  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.4 (s, 6 H), 1.6 (d of d, 2 H,  $J = 5$  Hz,  $J = 2$  Hz), 6.05 (apparent quintet, overlapped d of t, 1 H,  $J = 10$  Hz,  $J = 2$  Hz), 6.37 (d, 1 H,  $J = 10$  Hz), 7.5-7.05 (m, 4 H).  $^{13}\text{C}$  ( $\text{CDCl}_3$ )  $\delta$  141.96, 133.48, 132.85, 130.69, 129.67, 128.02, 126.92, 126.50, 13.30, -2.24 ppm. IR (neat): 3080, 3040, 2980, 2920, 2880, 1635, 1595, 1465, 1440, 1400, 1260, 1250, 1135, 850, 785  $\text{cm}^{-1}$ . Exact mass calculated for  $\text{C}_{11}\text{H}_{14}\text{Si}$  174.08648, measured 174.08616.

Synthesis of 136 from 1-methyl-1-hydrido-1-silatetrahydronaphthalene, 124

The methylhydridosilatetrahydronaphthalene (5.55 mmol) was added to 10 mL ether and cooled to 0°C under N<sub>2</sub>. MeLi (5.55 mmol) was added dropwise and the mixture stirred overnight and allowed to warm to ambient. The mixture was poured onto ice, the layers separated, and the aqueous phase extracted 3X with ether. The collected organic layers were washed with H<sub>2</sub>O, brine, dried over MgSO<sub>4</sub>, and the solvent removed in vacuo. This gave an 88% yield of 140.

To 26 mL CCl<sub>4</sub>, 16 mmol NBS, and a trace of benzoyl peroxide was added 16 mmol 140. This mixture was refluxed until all the NBS had been converted to succinimide. The mixture was filtered and the CCl<sub>4</sub> removed in vacuo. The residue was added to 75 mL ether in a 250 mL flask with a condenser, pressure equalizing addition funnel, magnetic stirring bar, and N<sub>2</sub> inlet.

An ether solution (75 mL) of 1.25 equivalents of DBU (calculated for quantitative bromination) was added dropwise over a ½ h period. The mixture was refluxed 6 h, cooled, filtered, and the solvent removed in vacuo. The orange-brown residue was chromatographed on silica gel, using Skelly "B" as the eluent. This gave 136 as a yellowish liquid which was distilled (55°C, 0.3 Torr) to give a 68% yield of 136 as a colorless liquid. In all spectral characteristics this was identical to 136 obtained from FVP of 135.

Reaction of the anion of 136 with tosyl azide

To 5.0 mL THF was added 2.87 mmol 136 and this was cooled to 0°C. n-BuLi (1.0 equivalents) was added dropwise. The anion so formed was a



dark brick-red. The anion was allowed to stir at 0°C for 1 h, then it was added dropwise to 3.37 mmol tosyl azide in 5 mL THF at -78°C. This mixture was stirred and allowed to warm to room temperature over a 12 h period. This mixture was poured into 150 mL pentane and washed 6 X 100 mL H<sub>2</sub>O, dried (MgSO<sub>4</sub>), and the solvent removed in vacuo. This left a reddish-brown oil which was vacuum distilled (55-70°C, .3 Torr) to give a mixture of 136 and the two isomeric diazo compounds. (Ratio of diazo compounds to 136 is ~2:1 with the 4-diazo isomer predominant.)

#### FVP of the 2- and 4-diazosiladihydronaphthalenes

The preceding mixture (55.3 mg) was pyrolyzed at 600°C,  $2 \times 10^{-5}$  Torr. The only material collecting in the cold trap was 136. There was copious deposition of an orange material on the walls of the tube. This was rinsed out with CDCl<sub>3</sub> and an NMR taken. There were broad, nondescript humps at  $\delta$  7.2-7.5 and 0.5 to 0 ppm. GCMS did show two compounds with m/e = 344, but the amounts of these compounds were extremely minute and hence they were not isolated.

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