

1977

# Evidence for the generation and trapping of a silabenzene

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Iowa State University,  
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Evidence for the generation and  
trapping of a silabenzene

by

Dennis Stephen Banasiak

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

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Ames, Iowa

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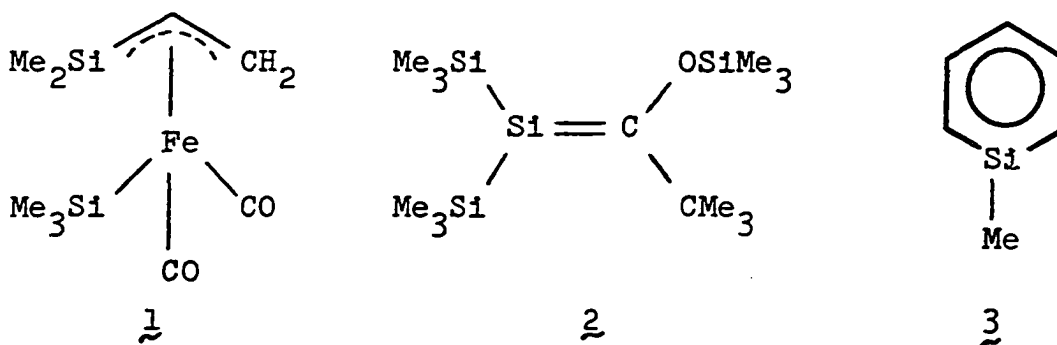
DEDICATION

To Diane

## INTRODUCTION

The existence of  $\pi$ -bonded silicon was virtually unsuspected prior to 1966. Early claims to multiple bonded silicon, near the turn of the century, were later disproved (1). Theoretical studies predicted that  $\pi$ -bonded silicon, unlike carbon, was not possible (2,3).

In 1966, this view rapidly changed with the report of Nametkin and co-workers, in which a species containing a silicon carbon double bond was claimed as an intermediate (4). This report caused renewed interest in the area. Since that report,  $\pi$ -bonded silicon has been implicated as reactive intermediates in numerous reactions (1). The search for a stable species was recently completed with the reports of Sakurai *et al.* (5), and Harris and Brooks (6). Sakurai



stabilized the  $\pi$ -bond by complexing it with iron, 1, while Harris and Brooks used steric interactions 2.

This thesis will be concerned with the synthesis of silabenzene 3, an alternate attempt to generate a stable silicon-carbon  $\pi$ -bond. It was hoped that by placing the bond in a potentially aromatic system, electronic interactions would stabilize the  $\pi$ -bond, and allow its isolation and study.

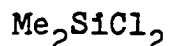


## NOMENCLATURE

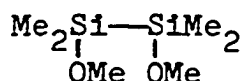
The nomenclature which will be used throughout this manuscript will now be briefly outlined.

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

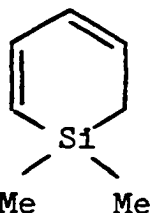
Examples:



dimethyldichlorosilane



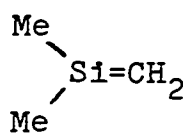
1,1,2,2-tetramethyl-1,2-dimethoxydisilane



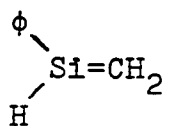
1,1-dimethyl-1-silacyclohexa-2,4-diene

All compounds containing silicon-carbon double bonds will be named as analogs of the corresponding unsaturated carbon systems. When referring to the general class of compounds containing the silicon-carbon double bond, the term silene shall be used. In the case of silabenzene, 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.

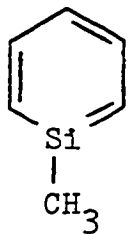
Examples:



2-methyl-2-silapropene



1-phenyl-1-silaethylene

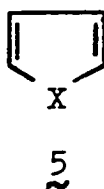


1-methyl-1-silacyclohexa-  
1,3,5-triene

1-methyl-1-silabenzene

## HISTORICAL

Since the discovery of benzene, its unusual properties have intrigued chemists. Extensive investigations of these properties produced the theory of aromaticity (7). Huckel's rule (8), instrumental in establishing the theory of aromaticity, predicts that any monocyclic, all  $sp^2$  hybridized, compound containing  $(4n+2)$   $\pi$  electrons will be aromatic. The search for both examples and exceptions to this rule has prompted an incredible amount of research in many areas of organic chemistry (7). Heterocyclic compounds, for example, are found to be aromatic if (i) a carbon atom in a carbocyclic aromatic compound is replaced by a heteroatom, which provides one electron to the  $\pi$  system; or (ii) a carbon-carbon double bond unit is replaced by a heteroatom, which provides two  $\pi$ -electrons to the  $\pi$ -system (9). Pyridine 4, ( $X=N$ ), and pyrrole 5, ( $X=NH$ ), are examples of (i) and (ii),



respectively. For a long period of time, aromatic heterocycles of type (i) were limited to examples of 4, ( $X=N$ ), since (p-p)  $\pi$  bonds between elements other than C,N,O, were thought to be nonexistent (10). Then, in 1966, Märkl



by dehydrohalogenation of the corresponding cyclohetero-halodiene (7). These compounds provide an excellent opportunity to determine information about aromatic heterocycles and multiple bonds as a function of increasing atomic number (14-19). A more complete discussion of these compounds can be found in a review by Jutzi (12).

It is quite remarkable, in view of the fact that all of the Group V heterobenzenes are known, that the Group IV heterobenzenes have remained elusive. This absence is even more surprising when one considers that carbon and the heavier Group IV elements are isovalent. All Group IV elements are known to readily form four single bonds due to  $sp^3$  orbital overlap. However, only carbon readily forms stable (p-p)  $\pi$ -multiple bonded compounds.

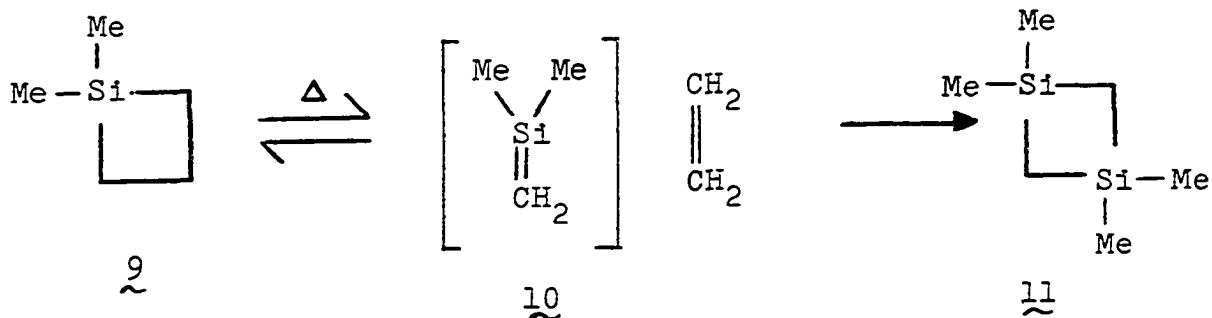
Since the ultimate goal of this thesis is the generation and study of a (p-p)  $\pi$  silicon carbon bond in an aromatic system, a discussion of the (p-p)  $\pi$  bonded silicon, as it is understood today, is warranted. The discussion will be divided into three categories: (1) theoretical considerations, (2) methods of generation, and (3) chemical behavior. Also, emphasis will be placed upon developments since early 1975; the earlier work has been extensively reviewed (1, 20-22).

## Theoretical Considerations

Failure of early attempts to generate compounds containing (p-p)  $\pi$ -bonds involving silicon and other heavier atoms (23-25) prompted the advancement of various theories to account for the nonexistence of these species.

Pitzer (2) concluded the absence of heavy atom (p-p)  $\pi$  bonding was due to a repulsion between inner shell electrons and bonding electrons. This would ultimately lead to a lack of proper p-orbital overlap necessary for effective  $\pi$ -bonding. Mulliken (3) carried out molecular orbital calculations and, although his results are somewhat ambiguous, they indicate (p-p)  $\pi$ -bonding as unimportant in other than second row elements. The unimportance was attributed to the greater stability of  $\sigma$ -bonds relative to  $\pi$ -bonds (28). Thus, by this reasoning, silicon would prefer to form 4  $\sigma$ -bonds in polymeric structures rather than  $\pi$ -bonds. Indeed, all previous (23-25) (and later (26-28)) attempts to prepare silenes had resulted in dimeric or polymeric material giving further credence to Mulliken's theory.

In 1966, Nametkin and co-workers (4,29) presented strong evidence for 2-methyl-2-silapropene 10 as a reactive intermediate in the flow pyrolysis of 1,1-dimethylsilacyclobutane 9 (Scheme 2). These reports precipitated a change in the concept of (p-p)  $\pi$ -bonding involving silicon.



No longer was the stable silene sought, but rather evidence for the intermediary of these species.

Jackson (30) estimated the  $\pi$ -bond energy for the silicon carbon bond at approximately 28 Kcal/mole, based on dissociation energies. He also pointed out that these weak  $\pi$ -bonds (about 1/2 energy of olefins), comment not on the instability of these species toward unimolecular decomposition, but rather on its very reactive behavior in bimolecular reactions with other molecules (30).

Walsh (31), improving upon Jackson's crude estimation, places the  $\pi$ -bond energy somewhere in the range of  $28 \leq D\pi(\text{Si}=\text{C}) < 46$  Kcal/mole. Walsh based his calculation on the kinetic data of Flowers and Gusel'nikov (32) (pyrolysis of 1,1-dimethylsilacyclobutane), and Davidson and Lambert (33) (pyrolysis of trimethylsilane).

Curtis (34) conducted Extended Hückel Molecular Orbital (EHMO) and Complete Neglect of Differential Overlap (CNDO) calculations on the carbon-carbon, carbon-silicon and

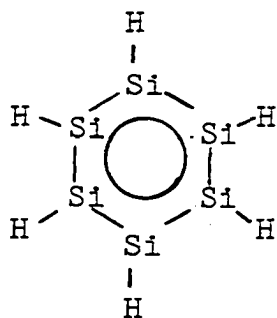
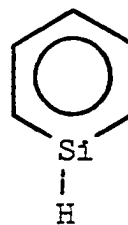
silicon-silicon  $\pi$ -bonds (34). These calculations indicate that the silene  $\pi$ -bond is exceedingly polar. Also, the relative weakness of this  $\pi$ -bond is attributed to energy mismatching of the carbon and silicon p-orbitals. The barrier to rotation about the  $\pi$  bond was predicted to increase in the order silaethylene ( $9 \frac{\text{Kcal}}{\text{mole}}$ ) < disilaethylene ( $34 \frac{\text{Kcal}}{\text{mole}}$ ) < ethylene ( $111 \frac{\text{Kcal}}{\text{mole}}$ ). Inclusion of d-orbital interactions were found to increase the strength of the  $\pi$ -bond while at the same time decreasing rotational barriers. These calculations also show the triplet state is the lowest energy excited state of twisted ethylene and disilaethylene. Conversely, the singlet state is calculated to be the lowest energy excited state of twisted silaethylene, which is consistent with a polar  $\pi$ -bond in planar silaethylene. The low barrier to rotation and polarity of the bond predict silenes to be highly reactive and that they should behave as ylides, that is, carbon being nucleophilic and silicon electrophilic.

The inherent stability of the silicon-carbon  $\pi$ -bond is further supported with CNDO/2 calculations by Damrauer and Williams (35). They agree with Curtis on a high degree of polar character for silenes. Further, they propose the polarity is the dominant factor in the reactivity of the species with itself and other polar compounds. They also note the polarity may be influenced by introduction of



fluorine substituents on silenes. Finally, they conclude that there are large d-orbital contributions in silene  $\pi$ -bonds.

MINDO/3 calculations for a number of unsaturated organo-silicon compounds are reported by Dewar and co-workers (36, 37). The  $\pi$ -bond strength of silaethylene is calculated to be 42.3 Kcal/mole with a barrier of rotation of ca. 40 Kcal/mole, values in close agreement with Curtis (34) and Walsh (31). Dewar also discusses aromatic silanes. Hexasila-benzene 12 and monosilabenzene 13 are predicted to have aromatic stabilization very similar to benzene itself. In

1213

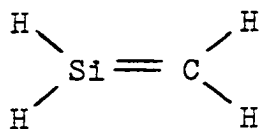
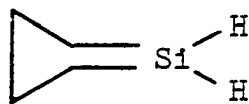
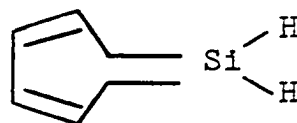
fact, he predicts the heat of dimerization of monosilabenzene, 13, should be no greater than that of olefin dimerization, leading to a conclusion that the silabenzene should be a stable species.

A theoretical infrared spectrum for silaethylene has been generated from Ab Initio Molecular Orbital calculations by Schlegel, Wolfe, and Mislow (38). The silicon carbon stretching frequency is predicted at  $1490\text{ cm}^{-1}$  in the parent silene.

Ab Initio calculations on the ground electronic state of silaethylene have been reported by Strausz and co-workers (39). The results predict the ground state of silaethylene to be a triplet, but the lowest singlet state lies only 1.4 Kcal/mole above it. Therefore, at room temperatures, both states should be populated, having an influence on the reactivity of silenes. The authors note that more sophisticated calculations could lead to a singlet ground state, but that the difference in energy between the triplet and singlet should still be small.

Strausz also predicts that in the triplet ground state, carbon is  $sp^2$  hybridized and the silicon is  $sp^3$  hybridized, leading to a nonplanar structure. Blustin (40), using a Floating Spherical Gaussian Orbital Model (FSGO), also predicts the silicon in silenes will prefer a tetrahedral environment ( $sp^3$ ) and the carbon trigonal ( $sp^2$ ).

Mollere and Hoffmann (41), using molecular orbital calculations, predict the overlap population of a silicon-carbon double bond can be increased by 11-12% over the parent compound 14 by making the  $\pi$ -bond exocyclic to a

141516

cyclopropane ring 15. A similar result for dimethylsilafulvene 16 was reported by Ustynyuk *et al.* (42) in which the CNDO/2 calculations indicate the planar system may be stable.

In summary, the theoretical view of silenes has changed from that of a nonexistent compound to one of a stable but highly reactive polarized species.

#### Methods of Silene Generation

With the realization that silenes are stable, but highly reactive, and that isolation would prove difficult, the area of unsaturated organosilicon chemistry has blossomed. Today, the reports of silenes are too numerous to discuss in any detail (4,5,6,29,33,43-110). Table 1 lists the various precursors from which silenes have been prepared.

The flow pyrolysis (510→700°C) of 1-silacyclobutanes is the most common method of generating silenes (4,29,32,43-64,68). This method has been used quite successfully in determining the behavior of the silicon-carbon double bond. The various aspects of these reactions have been discussed elsewhere (1,22).

Table 1. Reactions involving silenes

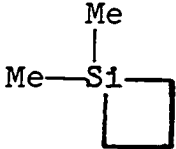
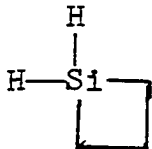
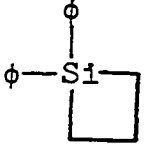
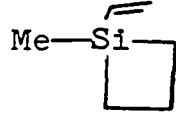
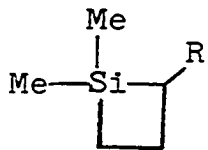
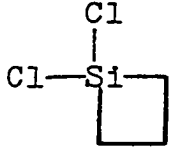
Silene Generator	Method of Generation	Silene	References
	$\Delta$ $h\nu$	$\text{Me}_2\text{Si} = \text{CH}_2$ $\text{Me}_2\text{Si} = \text{CH}_2$	4,29,32,43-55 80
	$\Delta$	$\text{H}_2\text{Si} = \text{CH}_2$	56
	$\Delta$ $h\nu$	$\phi_2\text{Si} = \text{CH}_2$	54,58,59 79
	$\Delta$	$\text{Me-Si} = \text{CH}_2$ $\text{CH} = \text{CH}_2$	57
	$\Delta$	$\text{Me}_2\text{Si} = \text{CH}(\text{R})$	60,61,62
$\text{R} = \text{Me}, \phi$		$\text{R} = \text{Me}, \phi$	
	$\Delta$	$\text{Cl}_2\text{Si} = \text{CH}_2$	4,29

Table 1. (Continued)

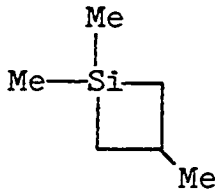
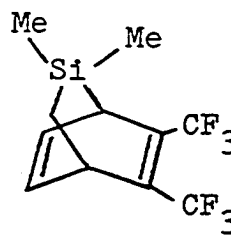
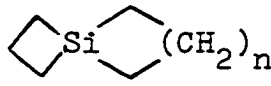
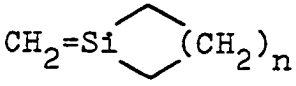
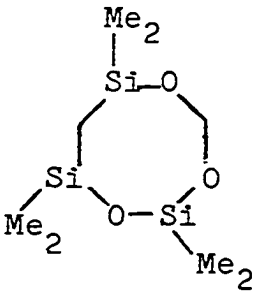
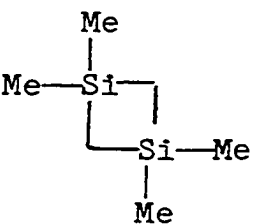
Silene Generator	Method of Generation	Silene	References
	$\Delta$	$\text{Me}_2\text{Si} = \text{CH}_2$	63,64
	$\Delta$ or hv	$\text{Me}_2\text{Si} = \text{CH}_2$	65,66,67
 $n = 1,2,3$	$\Delta$	 $n = 1,2,3$	56,68
	$\Delta$	$\text{Me}_2\text{Si} = \text{CH}_2$	69,70,71
	$\Delta$	$\text{Me}_2\text{Si} = \text{CH}_2$	60,70

Table 1. (Continued)

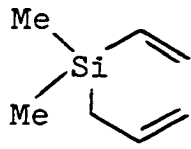
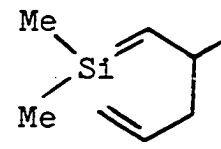
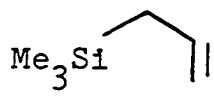
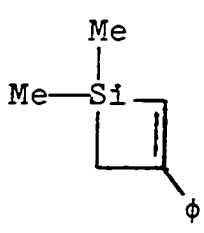
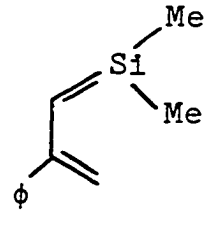
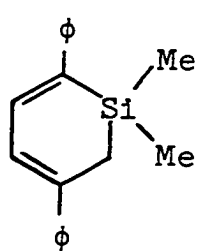
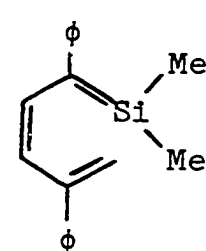
Silene Generator	Method of Generation	Silene	References
	$\Delta$		72
	$\Delta$	$\text{Me}_2\text{Si} = \text{CH}_2$	73,74
$\text{Me}_4\text{Si}$	$\Delta$	$\text{Me}_2\text{Si} = \text{CH}_2$	75,76
$\text{Me}_3\text{Si}-\text{SiMe}_3$	$\Delta$	$\text{Me}_2\text{Si} = \text{CH}_2$	77,78
	$h\nu$	$\text{Me}_2\text{Si} = \text{CH}_2$	89
	$h\nu$		81
	$h\nu$		82

Table 1. (Continued)

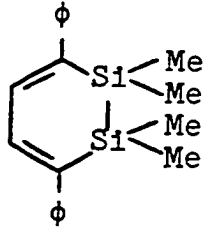
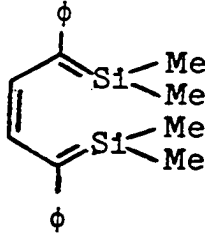
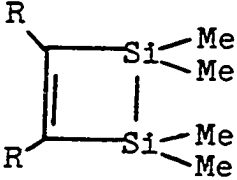
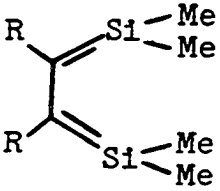
Silene Generator	Method of Generation	Silene	References
	hν		83
	Δ		84,85
R = Me, φ		R = Me, φ	
$(R_3Si)_3Si-C(=O)R'$	hν	$(R_3Si)_2Si=C(R')OSiR_3$	6,86
R = Me, R' = Me, φ, t			
Me <sub>3</sub> SiH	Δ	Me(R)Si = CH <sub>2</sub> R = H, Me	33
MeSiH <sub>3</sub>	vacuum hν	H <sub>2</sub> Si = CH <sub>2</sub>	87,88
Me <sub>3</sub> Si - CMe <sub>3</sub>	vacuum hν	Me <sub>2</sub> Si = CH <sub>2</sub>	89

Table 1. (Continued)

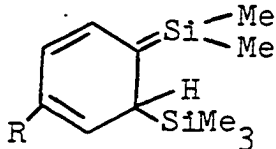
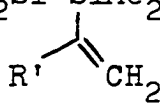
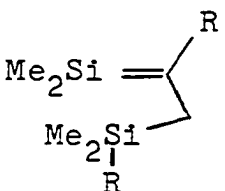
Silene Generator	Method of Generation	Silene	References
$\phi_3\text{Si} - \text{Si}\phi_2\text{Me}$	hv	$\phi_2\text{Si} = \text{CH}_2$	90
$\text{ArMe}_2\text{Si} - \text{SiMe}_3$	hv	 $\text{R} = \text{H}, \text{CH}_3$	91-95
Ar = $\phi$ , tolyl			
$\text{RMe}_2\text{Si} - \text{SiMe}_2$  $\text{R} = \phi, \text{Me}, \text{vinyl}$ $\text{R}' = \text{H}, \phi$	hv	 96-98	
$\text{Me}_3\text{Si} - \text{SiMe}_2 - \equiv - \phi$	hv	$(\text{Me}_3\text{Si})\phi\text{C} = \text{C} = \text{SiMe}_2$	99
$\text{Me}_3\text{Si} \overset{\text{N}_2}{\parallel} \text{CCO}_2\text{R}$	$\Delta$ or hv	$\text{Me}_2\text{Si} = \text{CMeCO}_2\text{R}$	100, 101
$\text{Me}_3\text{Si} \overset{\text{N}_2}{\parallel} \text{CR}$ $\text{R} = \text{H}, \phi$	$\Delta$ or hv	$\text{Me}_2\text{Si} = \text{CHR}$ $\text{R} = \text{H}, \phi$	102-105



Table 1. (Continued)

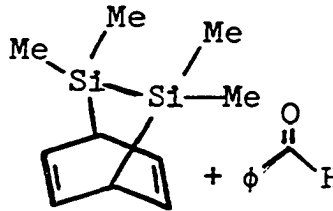
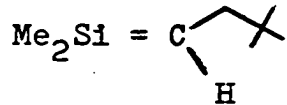
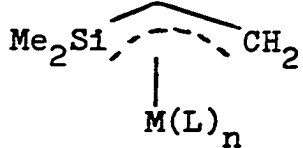
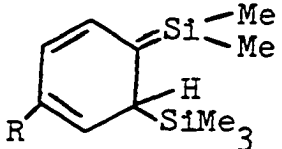
Silene Generator	Method of Generation	Silene	References
$\begin{array}{c} \text{Me}_2\text{Si}-\text{CH}_2\text{Cl} \\   \\ \text{Cl} \end{array}$	$\Delta$ , Na-K	$\text{Me}_2\text{Si} = \text{CH}_2$	106
$\text{Me}_3\text{Si}-\text{SiMe}_2\text{CH}_2\text{Cl}$	NaOEt	$\text{Me}_2\text{Si} = \text{CH}_2$	107
$\begin{array}{c} \text{Me}_2\text{HSiCH}_2\text{Br} \\ + \\ \phi_2\text{C} = \text{O} \end{array}$	Mg, $\text{Et}_2\text{O}$	$\text{Me}_2\text{Si} = \text{CH}_2$	108
	$\Delta$	$\text{Me}_2\text{Si} = \text{CH}\phi$	109
$\begin{array}{c} \text{O} \\    \\ \text{Me}_2\phi\text{Si}-\text{C}-\phi \end{array}$	$\Delta$	$\phi\text{MeSi} = \text{CH}_2$	110
$\begin{array}{c} \text{Me}_2\text{SiCH}=\text{CH}_2 \\   \\ \text{Cl} \end{array}$	$\underline{t}$ -BuLi		111,112
$\begin{array}{c} \text{Me}_3\text{Si}-\text{SiMe}_2 \\   \\ \text{CH}=\text{CH}_2 \end{array}$	$\text{Fe}_2(\text{CO})_9$ $\text{Pd}(\text{L})_n$		5,113

Table 1. (Continued)

Silene Generator	Method of Generation	Silene	References
$\begin{array}{c} \phi_2\text{Si} - \text{CH}\phi \\   \quad   \\ \text{OMe} \quad \text{OMe} \end{array}$	$\Delta$	$\phi_2\text{Si} = \text{CH}\phi$	114
$\begin{array}{c} \text{MeO}_2\text{C} \quad \text{OMe} \\ \diagdown \quad / \\ \text{C} = \text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{OSiMe}_3 \end{array}$	$\Delta$	$\text{Me}_2\text{Si} = \text{CH}_2$	115
$\begin{array}{c} \text{Me} \\   \\ (\text{Me}_3\text{SiOSi-CH}_2)_3\text{B} \\   \\ \text{Me} \end{array}$	$\Delta$ , NaOEt	$\text{Me}_2\text{Si} = \text{CH}_2$	116
$\begin{array}{c} \text{Me}_2\text{Si} - \text{C}(\text{SiMe}_3)_2 \\   \quad   \\ \text{OR} \quad \text{Br} \end{array}$	n-BuLi, $\Delta$	$\text{Me}_2\text{Si} = \text{C}(\text{SiMe}_3)_2$	117
R = Tos, phosphate			
$\text{ArMe}_2\text{Si} - \text{SiMe}_3$	hv		118
Ar = $\phi$ , tolyl		R = H, CH <sub>3</sub>	

+

The pyrolysis (400→500°C) of 7-silabicyclo[2,2,2]octadienes is another convenient route to silenes (65-67). However, both pyrolytic methods suffer from the higher temperatures required as many initial products are unstable to the reaction conditions. They decompose to secondary products which are sometimes difficult to identify and explain.

The generation of silenes at lower temperatures has been accomplished photolytically (6,33,78-83,86-98). Alicyclic aliphatic silanes undergo photochemical decompositions producing double bonded silicon intermediates (87,88,89). Thus, methyl silane, when irradiated at 147 nm, produces the parent silene 14 via a radical pathway (87,88). The authors refer to the species as a diradical rather than assigning the compound any olefinic character.

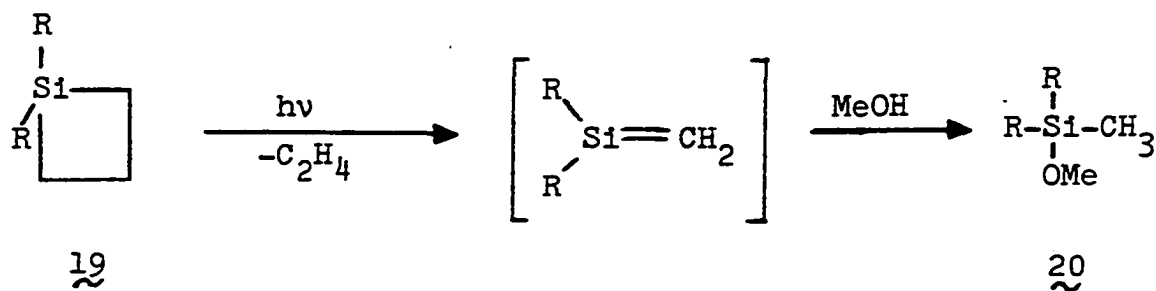
Boudjouk and Koob (89) studied the vacuum-ultraviolet photochemistry of hexamethyldisilane 17 and tert-butyltrimethylsilane 18. The reaction of hexamethyldisilane produces trimethylsilane as the most important stable fragmentation product (Scheme 3). Trimethylsilane is envisioned to occur via a four-centered transition state in which 2-methyl-2-silapropene 10 is also produced. The photolysis of tert-butyltrimethylsilane 18 provided an opportunity to study the probability of the production of silicon-carbon double bond relative to the formation of a carbon-carbon double bond (Scheme 4). Elimination of trimethylsilane would favor



carbon-carbon double formation (path a), while elimination of isobutane would favor silicon-carbon double bond formation (path b). The yield of isobutane was approximately twice that of trimethylsilane, strongly suggesting silicon-carbon double bond formation is important in this reaction. Radical sources of isobutane and trimethylsilane were eliminated by photolyzing in the presence of oxygen.

Silacyclobutanes, the work horse of the thermal generations, also yield silenes upon photolysis. Boudjouk and Sommer (79) photolyzed 1,1-diphenyl-1-silacyclobutane 19 ( $R = \phi$ ) in a cyclohexanemethanol solution and observed the formation of ethylene and the methanol trap of 1,1-diphenyl-1-silaethylene 20 ( $R = \phi$ ) (Scheme 5). They also carried out the reaction in methanol-1-D to show the reaction was not the result of a thermal reaction.

Scheme 5



Koob and co-workers (80) recently reported the vacuum photolysis of 1,1-dimethyl-1-silacyclobutane 19 (R = Me) (Scheme 5). Evidence for 2-methyl-2-silapropene was also reported as formation of the methanol adduct, methyltrimethylsilylether 20 (R = Me). In the absence of traps, only a very low yield of 1,3-disilacyclobutane, the dimer normally found in thermal reactions, is observed. The relative lack of silene dimers in the absence of traps seems to be characteristic of photochemically generated silenes and is, at present, unexplained.

Valkovich and Weber (81) found that 1,1-dimethyl-2-phenyl-1-silacyclobut-2-ene, when photolyzed in acetone, yields an 83% yield of 2,2,6,6-tetramethyl-1-oxa-3-phenyl-2-sila-3-cyclohexene. This product arises from initial ring opening to form the intermediate 1,1-dimethyl-2-phenyl-1-silabutadiene. It then reacts with acetone in an apparent Diels-Alder reaction.

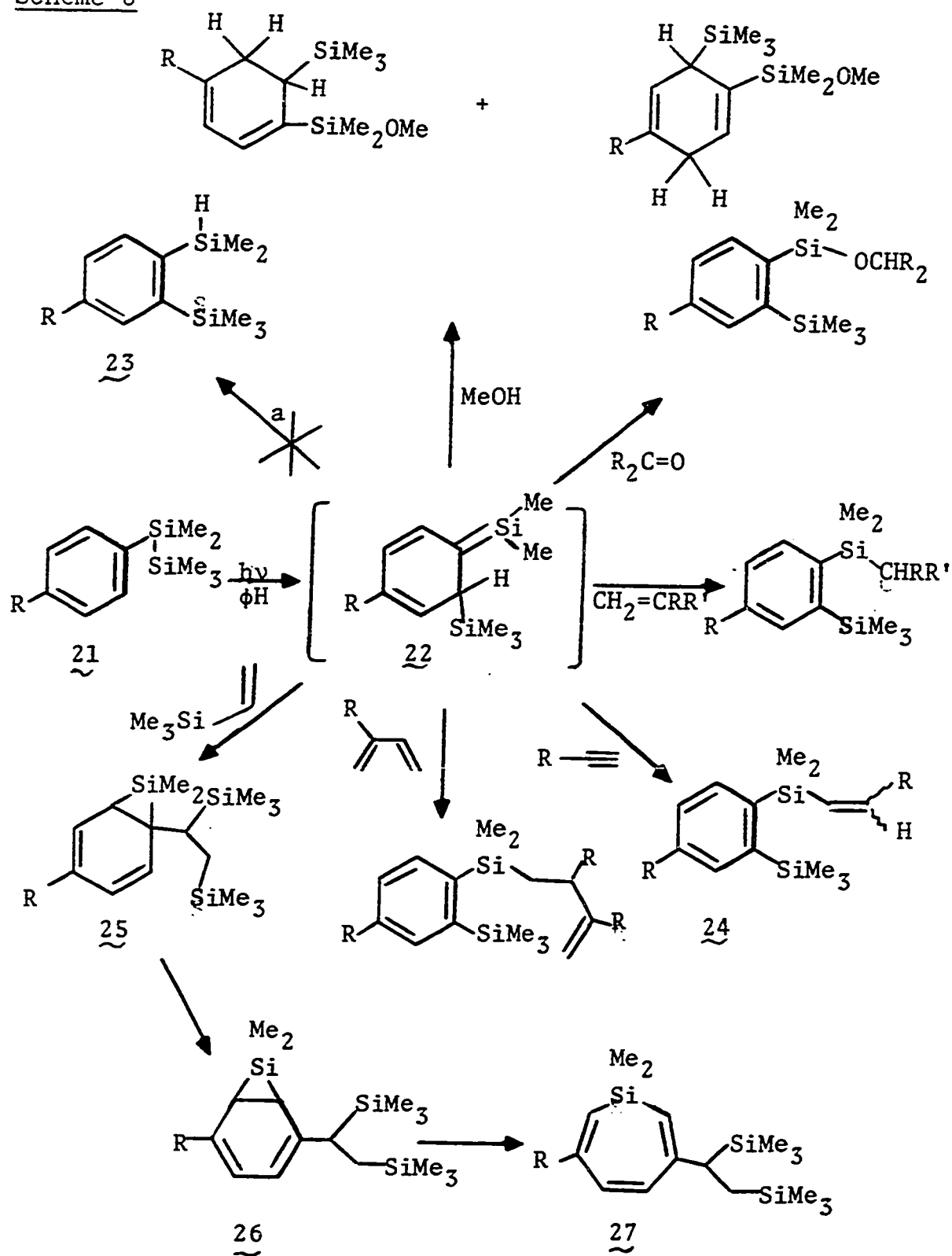
The photochemistry of 2,4-diphenyl-1,1-dimethyl-1-silacyclohexa-2,4-diene (82) and 3,5-diphenyl-1,1,2,2-tetramethyl-1,2-disilacyclohexa-3,5-diene (83) also involves ring opening to conjugated sila- and disilahexatrienes, respectively. This work is discussed in detail elsewhere (22).

The photochemical behavior of phenyl substituted disilanes has received considerable attention (83,90-99).

Boudjouk and co-workers (90) studied the photochemistry of pentaphenylmethyldisilane. This molecule undergoes a photochemically initiated dehydrosilylation yielding 1,1-diphenyl-1-silaethylene and triphenylsilane. The 1,1-diphenyl-1-silaethylene was trapped by methanol. A small amount of homolytic cleavage of the silicon-silicon bond, as evidenced by solvent trapping of the resultant radicals, also occurs.

Ishikawa and co-workers (91-95) have investigated the photochemical reactions of pentamethylarylsilanes 21. The initial step is photoisomerization of the pentamethylaryldisilane to the intermediate silene 22 via intramolecular transfer of a trimethylsilyl group to the benzene ring (Scheme 6). This intermediate is trapped by olefins (91,94), dienes (92), methanol (93), alkynes (95), and carbonyls. Isomerization of the intermediate 22 to the aromatized compound 23 via H-transfer prior to reaction with trap was considered. It was ruled out by the absence of all the products expected from the reaction of 23 with the traps. The authors believe the intermediate silene 22 reacts with the various traps through a radical mechanism. The adducts 24 occurring from the reaction with acetylenes are found to be mixtures of E and Z isomers. These isomers are said to arise from H-abstraction of intermediate vinylradicals. Photoisomerization of initial adducts was important, but could not totally account for the E-Z ratios, thus leading

Scheme 6



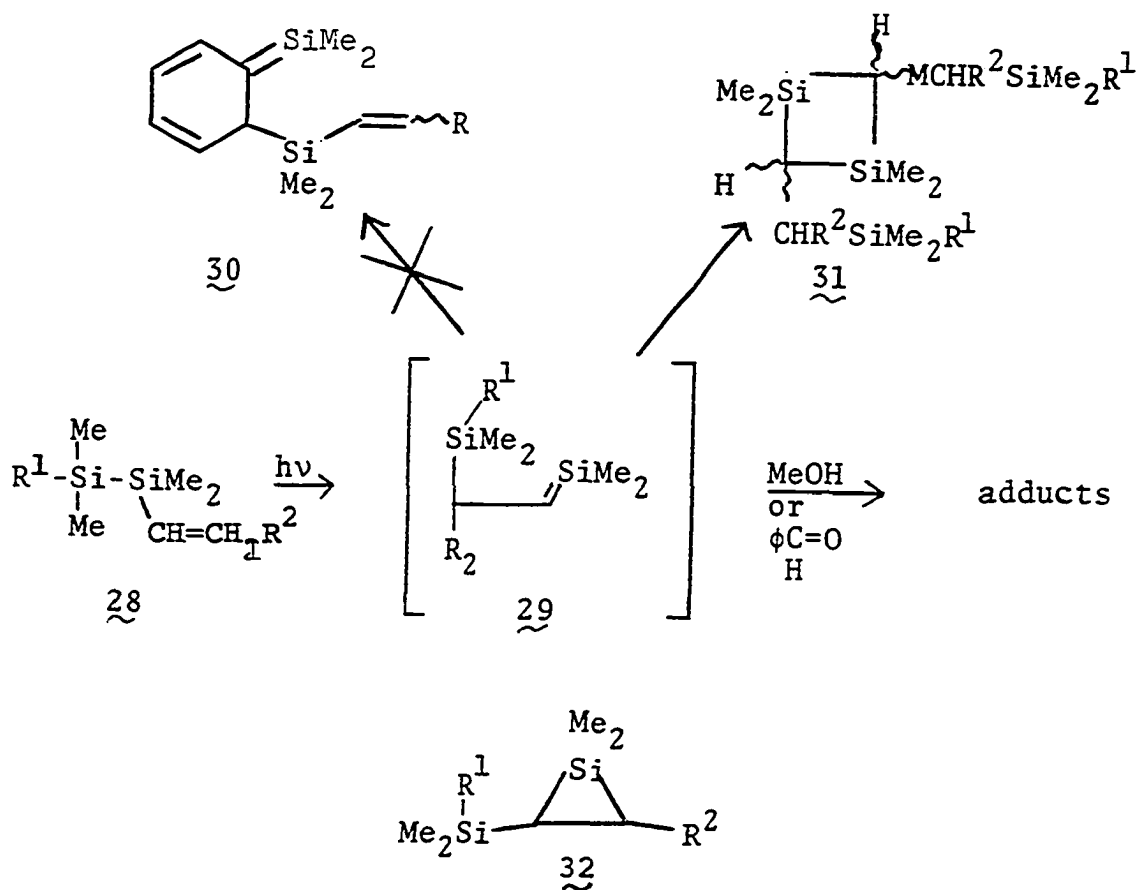


to the conclusion of initial formation of both isomers via intermediate vinyl radicals.

An interesting side light is the formation of silepin 27 in these reactions. The authors postulate silanorcaradiene intermediates 25 and 26 are involved.

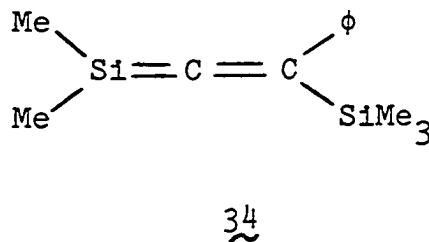
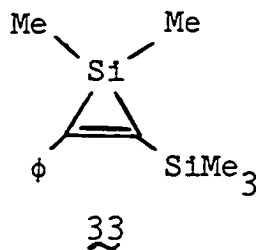
Vinyl disilanes 28 undergo similar reactions (96-98). The trimethylsilyl group is now transferred to the terminal end of the vinyl group instead of a benzene ring (Scheme 7). The silene 29 which results has been trapped with methanol

Scheme 7



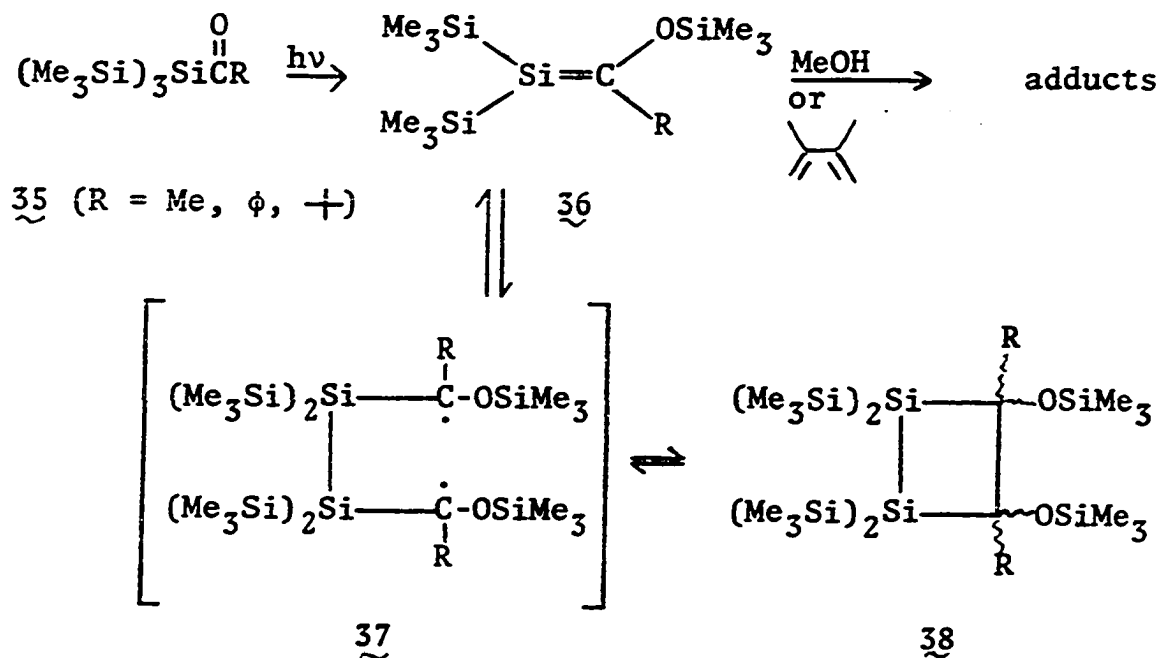
and benzaldehyde. A competition experiment was carried out using 1-phenyl-2-vinyl-1,1,2,2-tetramethyl-1,2-disilane 28 ( $R^1 = \phi$ ,  $R^2 = H$ ). No transfer of the trimethylsilyl group to the phenyl ring 30 was observed, indicating a greater tendency of migration towards vinyl. When no trap is added, the corresponding 1,3-disilacyclobutanes 31 are observed in 40% yield, a significant amount of dimer for a photochemical reaction. When  $\beta$ -styryldisilanes 28 ( $R^2 = \phi$ ) are photolyzed, silacyclopropanes 32 are observed rather than silenes. The authors (96) view the formation of silacyclopropanes as occurring via photochemically allowed intramolecular ( $\sigma+\pi$ ) process.

The photolysis of disilanes has now been extended to include alkynyl substituted disilanes (99). Thus, when phenylacetylenepentamethyldisilane is photolyzed, 1,1-dimethyl-2-trimethylsilyl-3-phenyl-1-silacyclopropene 33 and 1,1-dimethyl-3-trimethylsilyl-3-phenyl-1-sila-1,2-propadiene 34 are produced. This is the first example of a cumulated silene.



Brook and Harris (6,86) report acyldisilanes undergo a similar photochemical trimethylsilyl transfer reaction (Scheme 8). Thus, when tris-trimethylsilylacylsilanes 35 are photolyzed, sterically hindered silenes 36 are produced. These sterically hindered silenes are trapped with methanol and 2,3-dimethylbutadiene. The surprising feature is that in the absence of traps, the silenes dimerize in a head-to-head fashion, forming 1,2-disilacyclobutanes 38. This is

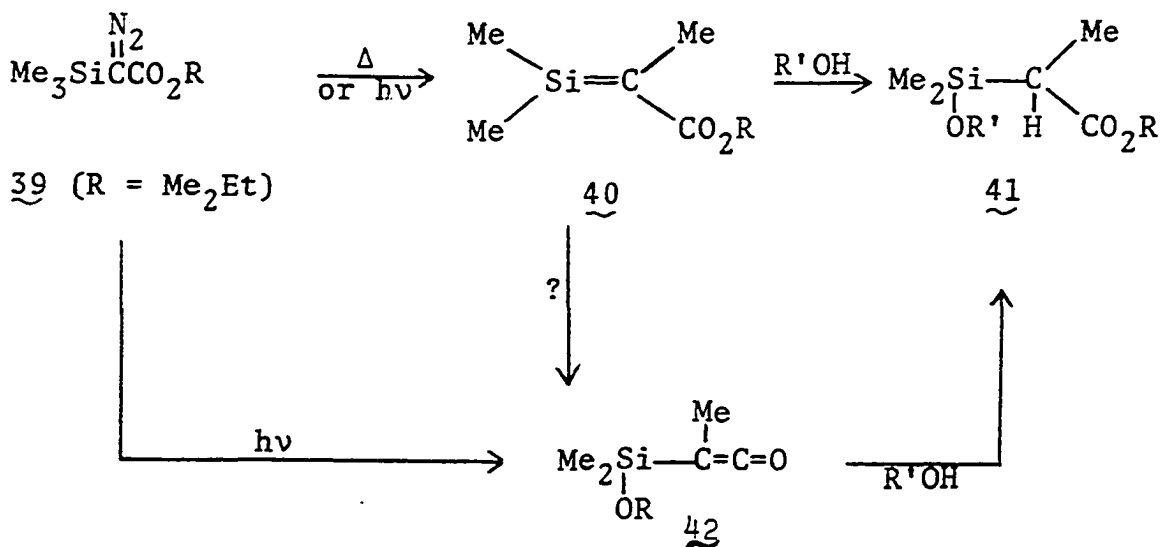
Scheme 8



the first example of head-to-head dimerization of silenes. All other cases, to date, lead to head-to-tail dimers. An equilibrium exists between the dimer 38 and the diradical 37 ( $R = \text{Me}, \phi$ ) at  $70^\circ\text{C}$  thermally, and  $0^\circ\text{C}$  photochemically. This equilibrium includes the silene 36 at  $25^\circ\text{C}$  when pivaloyltris(trimethylsilyl)silane 35 ( $R = t\text{-butyl}$ ) is used (6). The silicon-carbon double bond species 36 is favored at room temperature, while the dimer 38 is favored at lower temperatures. Thus, the t-butyl system, 36, represents the first stable free silene. Brook and Harris have obtained spectral data on this silene species (6).

The rearrangement of  $\alpha$ -silylcarbenes is yet another source of silenes. Ando and co-workers reported the photochemical (100) and thermal (101) decomposition of trimethylsilylcarboalkoxydiazomethanes 39 (Scheme 9). In the

Scheme 9



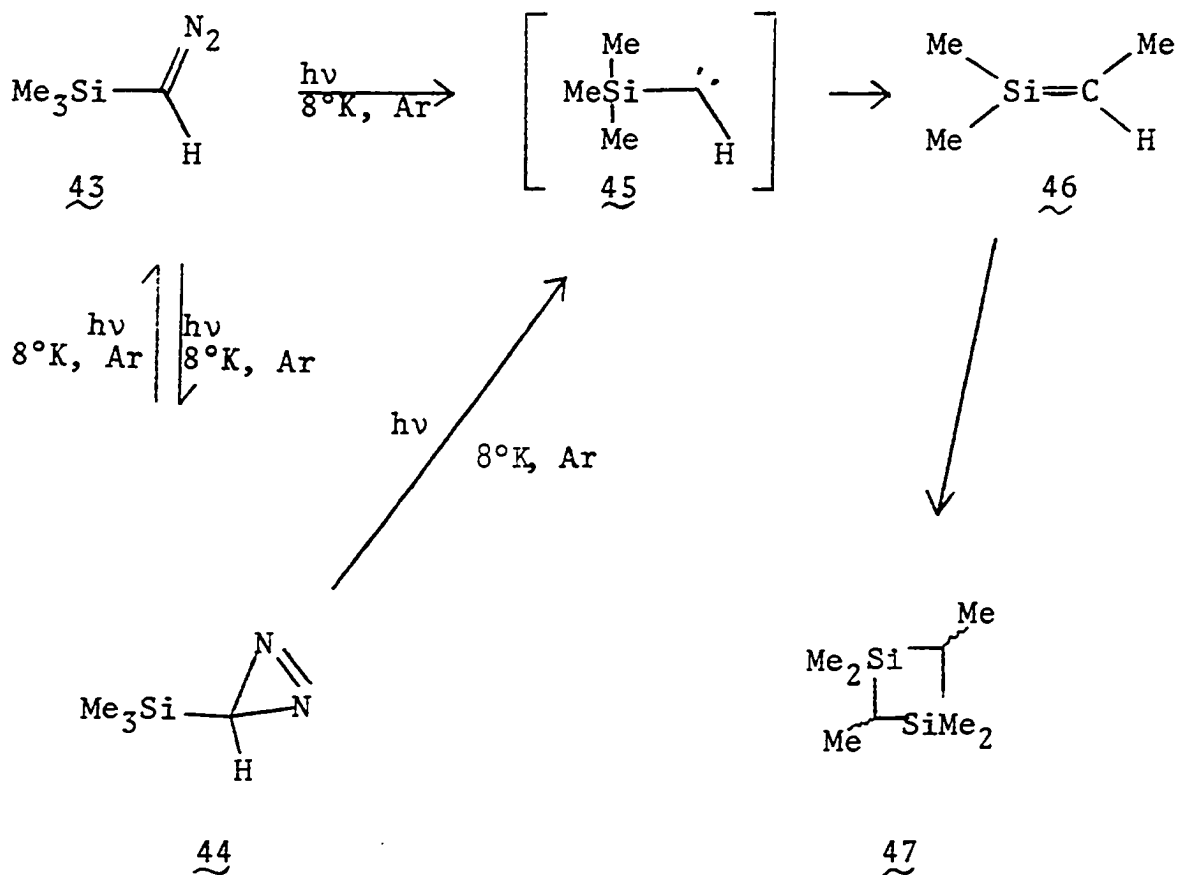
photochemical process, trimethylsilylcarboethoxydiazomethane 39 (R = Et) rearranges to 2-methyl-3-carboethoxy-2-silabut-2-ene 40 (R = Et). The silene was trapped by a series of alcohols 41, strongly indicating its presence in the reaction. The thermal process also produced the alcohol trapping products 41, but it was shown, in this case, R' and R are both derived from the added alcohol. The authors indicate the trapped product 41 arises from the ketene 42, which was shown to undergo both addition and exchange when exposed to alcohols. No definite mechanism was given for the origin of the ketene 42 although it may rise from the silene 40 (22).

Ando and co-workers (102) pyrolyzed phenyltrimethylsilyldiazomethane and observed its rearrangement to 2-methyl-3-phenyl-2-silabut-2-ene. The silene was trapped with acetone and 2,3-dimethylbutadiene.

Trimethylsilyldiazomethane 43 has also received much attention (103-105). Kreeger and Shechter (103) pyrolyzed trimethylsilyldiazomethane and isolated, in addition to carbene dimers, 1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutanes 47, the dimers of 2-methyl-2-silabut-2-ene 46. The silene was also trapped with isopropanol and benzaldehyde. Deuterium labeling experiments showed the silene resulted from a methyl shift rather than an intermediate silacyclopropane. Chapman and co-workers (104) and Chedekel and co-workers (105) studied the matrix isolated photochemistry

of trimethylsilyldiazomethane 43 (Scheme 10). The reaction was followed by infrared spectroscopy.

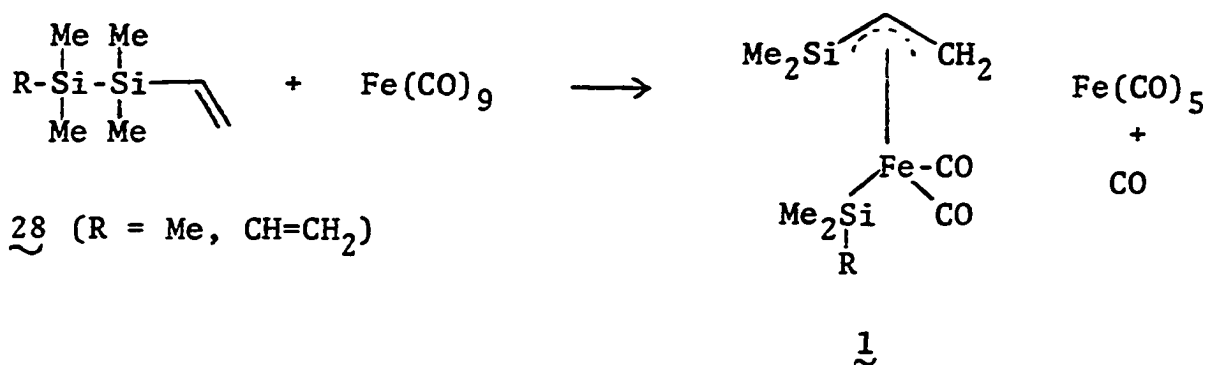
Scheme 10



They observed an initial equilibrium between the diazo compound 43 and the diazarene 44. Both decomposed to the carbene 45 upon further irradiation. The carbene rearranged to 2-methyl-2-silabut-2-ene 46 which upon warming above  $45^\circ\text{K}$  dimerized to the 1,3-disilacyclobutanes 47. No band was assigned in the observed IR for the silicon-carbon double bond.

The chemical generation of silenes has proved more difficult than thermal and photochemical generation. Early attempts were ambiguous (107,108,116), but three very interesting methods have recently been reported (5,111,112, 117). Sakurai and co-workers (5), utilizing the fact that transition metals can stabilize highly unstable molecules, reacted vinylpentamethyldisilane 28 with enneacarbonyldiiron and obtained a  $\eta^3$ -1-silapropenyl complex of iron 1 (Scheme 11). The  $\eta^3$ -1-silapropenyl complex 1 is the first example

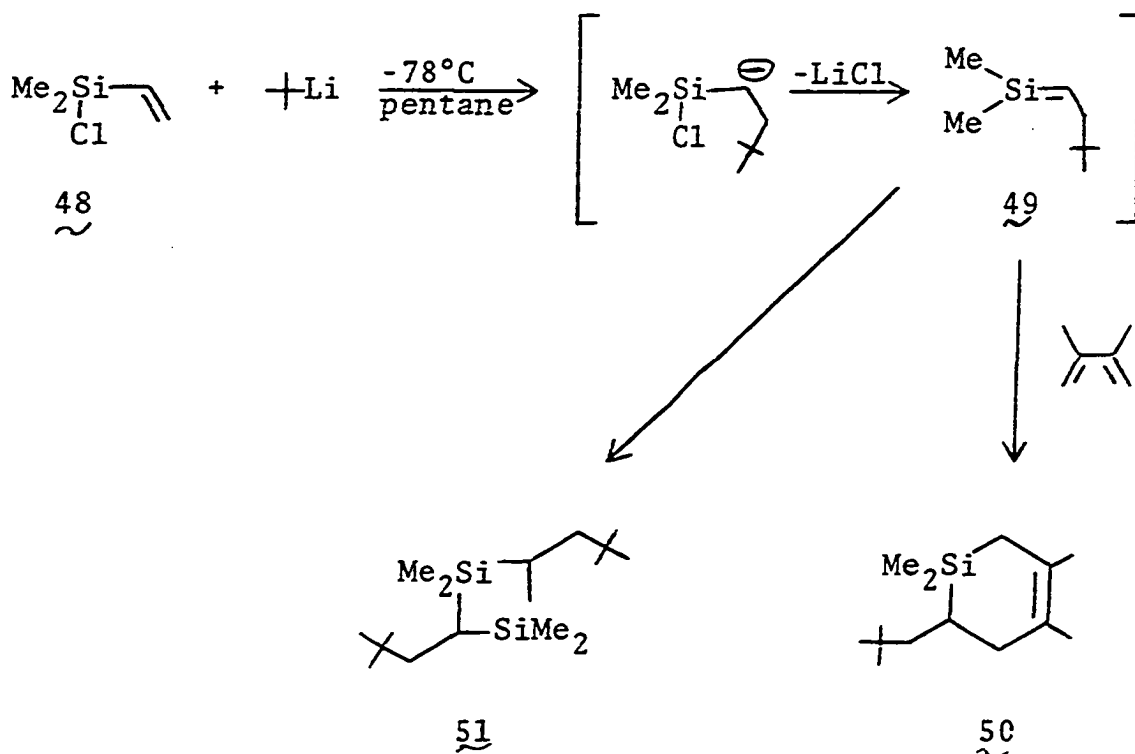
Scheme 11



of transition metal stabilized silene. The complex exhibits a band in the IR at  $1315 \text{ cm}^{-1}$ , which the authors assign to the frequency of the coordinated silicon-carbon double bond.

Jones and Lim (111,112) found t-butyllithium reacts with vinyl dimethylchlorosilane 48 at low temperatures ( $-78^{\circ}\text{C}$ ) in hydrocarbon solvents to produce 2,5,5-trimethyl-2-silahex-2-ene 49 (Scheme 12). The intermediacy of the silene 49

Scheme 12

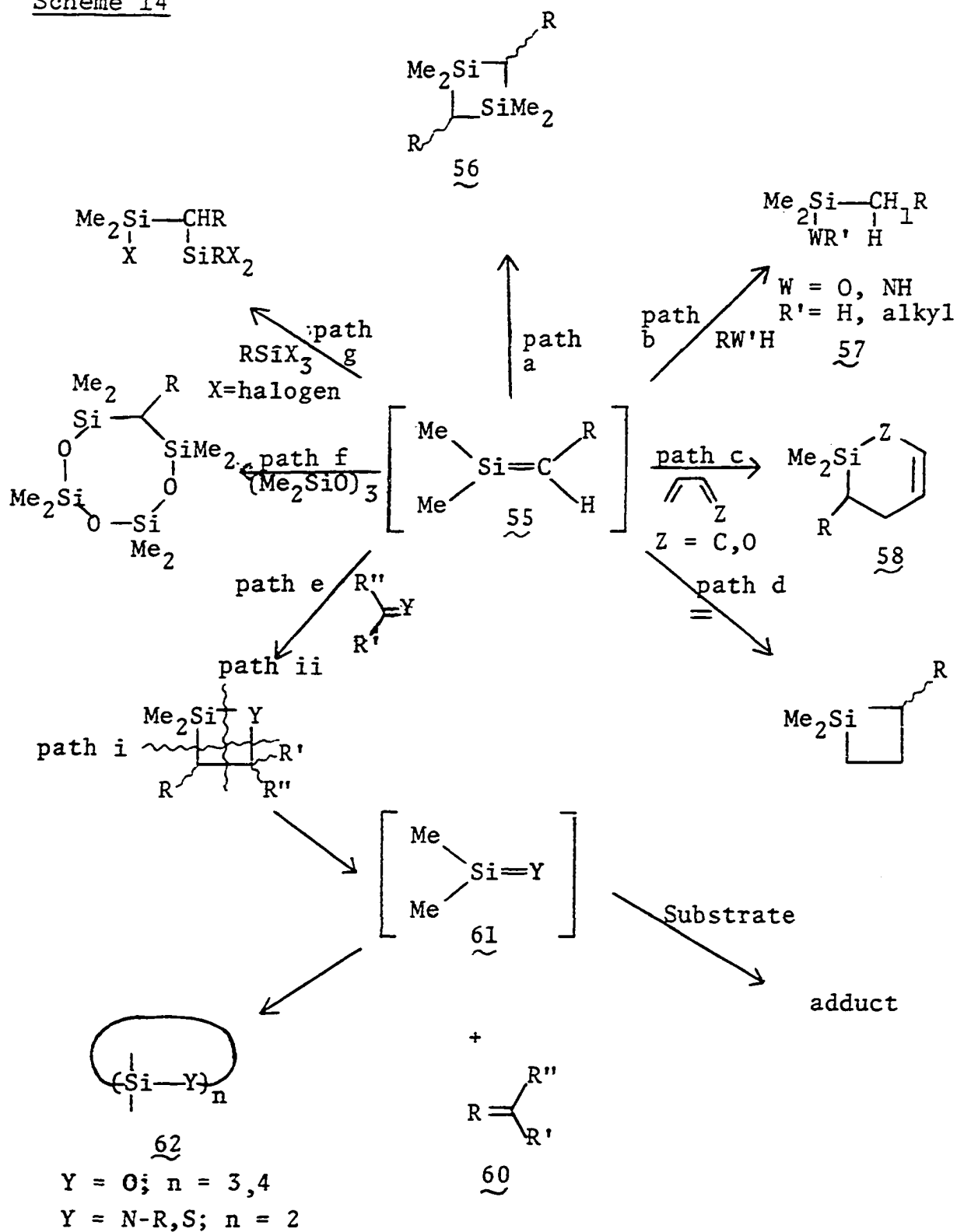


was shown by trapping with 2,3-dimethylbutadiene 50 and the formation of 1,3-disilacyclobutanes 51. The possibility that the dimer and trapped products resulted from an anionic mechanism was ruled out by conducting the experiments in the presence of a ten-fold excess of trimethylchlorosilane. No intermediate anions were detected.





Scheme 14



The first reported trap is the silene itself (4). Silicon-carbon double bonds readily dimerize in a head-to-tail fashion, forming 1,3-disilacyclobutanes 56 (path a), although some photochemically generated silenes form polymers instead of dimers (80,89,91). The only examples of head-to-head dimers 38 are found with Brook's sterically hindered silenes (6,86).

Alcohols, as well as water and amines, are very effective traps (path b) (1,50). They readily produce adducts 57 in which the oxygen or nitrogen attaches itself to the silicon, while the proton becomes attached to the carbon of the  $\pi$ -bond.

Silenes can also be trapped by a number of  $\pi$ -bonded species (1,43-56,58-62,65,66,81,84-86,91-100,111,112,117,118). Dienes (1) and dienones (59) add to silenes in a Diels-Alder fashion (path c). In the reaction with dienones, the possibility that the adduct 58 arises from addition to the carbonyl bond followed by ring expansion of the intermediate siloxetane cannot be eliminated (59).

While the "ene"-type reaction of alkenes, dienes, and alkynes with silenes generated photochemically from phenyl-disilanes is very efficient (Scheme 6), the (2+2) cycloaddition of alkenes to silenes is not a good reaction (path d).

$\pi$ -Bonded heteroatoms such as carbonyls (45,52,65), thiocarbonyls (54) and imines (49), all undergo addition to

silenes to initially form the corresponding four-membered ring 59 (path e). The four-membered rings are unstable and decompose (path i) to olefins 60 and the corresponding  $\pi$ -bonded heterosilene 61. The silanones 61 (Y = O), thiasilanones 61 (Y = S), and silaimines 61 (Y = N-R) are also quite reactive and afford dimers or cyclic polymers 62. There is only one example in which the four-membered ring 69 cleaves to form a silene and a ketone (110). In this example, the siloxetane 59 is formed directly from phenyldimethylsiloxylphenylcarbene. Decomposition of this siloxetane occurs by both paths i and ii.

It should be noted that often when the trapping ketone contains enolizable hydrogens, silyl enol ethers are formed rather than the siloxetanes. The silyl enol ethers are formed by reaction of the silene with the enol form of the ketone in a manner analogous to that of silenes and alcohols (50,65).

Cyclotrisiloxane, in the presence of silenes, undergoes a ring expansion (62) (path f). The silene inserts into a silicon-oxygen bond with the silicon of the silene forming a bond to the oxygen and the carbon to the silicon of the cyclotrisiloxane 63.

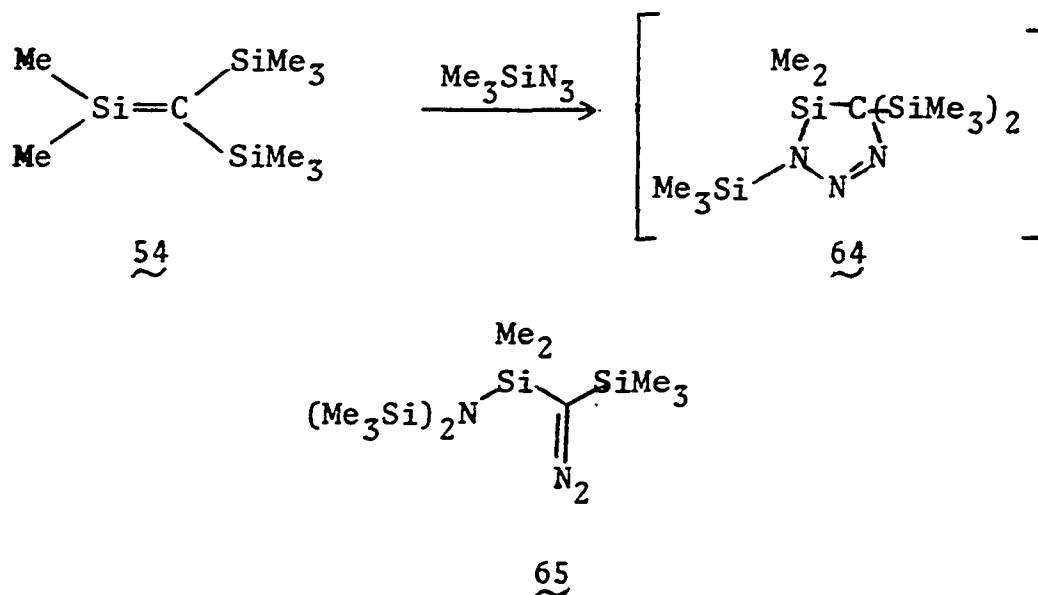
Bush and co-workers (51) have studied the reaction of silenes with halosilanes (path g). They report that the insertion of silenes into silicon halide bonds is controlled

by the polar character of the silicon-carbon  $\pi$ -bond, and also that the reaction does not proceed by a radical mechanism.

Silenes have also been trapped with nitriles (46). This reaction proceeds through a four-centered transition state to yield  $\alpha$ -silyl substituted acetonitriles.

The cycloaddition of silenes with azo compounds and azides has recently been reported (117). Azo compounds behave in a manner similar to imines, ultimately producing imines and cyclic dimers of the silicon-nitrogen double bond. The reaction with trimethylsilyl azide produces an intermediate triazole 64, which rearranges to a substituted bis-trimethyl silyl diazomethane 65 (Scheme 15).

Scheme 15



In summary, silenes have been trapped with a variety of compounds. The traps most accepted as proof of silene intermediacy are the silene itself, alcohols, and butadienes. The reactions with carbonyls, and other  $\pi$ -bonded heteroatoms are excellent sources of silicon-hetero  $\pi$ -bonds.

#### Previous Attempts to Prepare Silabenzene

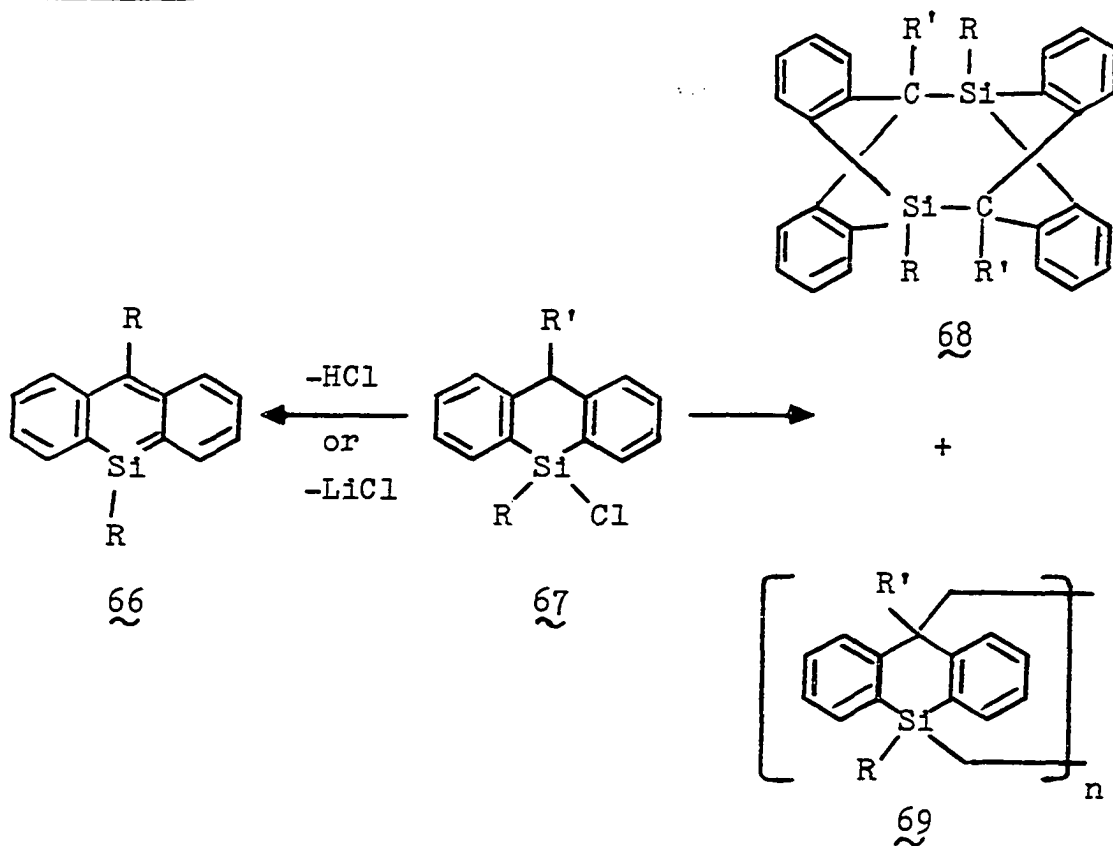
Although there is an abundance of research concerning the silicon-carbon  $\pi$ -bond, only a very small fraction has been directed toward the synthesis of a silabenzene. West (119) attempted the catalytic dehydrogenation of 1-silacyclohexane by passage over platinum and palladium. The silacyclohexane was recovered unchanged.

Urry (120) treated 50% ferrosilicon with silicon-tetrachloride vapor at 600°C to 1000°C. A white crystalline solid possessing the molecular formula  $\text{Si}_6\text{Cl}_6$  was obtained. Urry claimed that an aromatic nature is strongly indicated for this compound. No confirmation of this work has been obtained (1).

The base promoted elimination of hydrogen chloride from 9-chloro-9,10-dihydro-9-silaanthracenes 67 was attempted as a route to silanthracene (121,122,123). This seemed a logical attempt since the mass spectrum of 9-chloro-9,10-dihydro-9-silaanthracenes 66 showed a facile loss of HCl giving the desired silanthracene 67 (123,124). The chloro-dihydrosilaanthracenes were metalated with alkyl lithiums

with the hope elimination of lithium chloride would follow (Scheme 16). The necessary elimination fails to occur and

Scheme 16

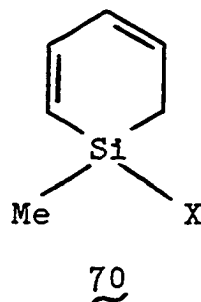
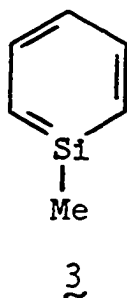


the reaction proceeds via intermolecular substitution leading to dimeric **68** and polymeric **69** products.

Lastly, Jutzi (12) reports the attempted elimination of hydrogen chloride from 1-chloro-1-silacyclohexa-2,4-dienes. Although the elimination of HCl is found to be quantitative, no silabenzene was detected. The other products of this reaction were not reported.

## RESULTS AND DISCUSSION

At the outset of this work, no stable silene was known. An investigation into the possibility that the stability of the silene moiety could be achieved by its generation as an essential part of an aromatic system was begun. Silabenzene 3, containing 2- $\pi$  bonds in conjugation with a silicon-carbon  $\pi$ -bond, could conceivably, through delocalization of these  $\pi$ -bonds, provide the desired stability. Precedence for increased stability of hetero  $\pi$ -bonds in aromatic compounds is found in many examples of the Group V heterobenzenes (12).



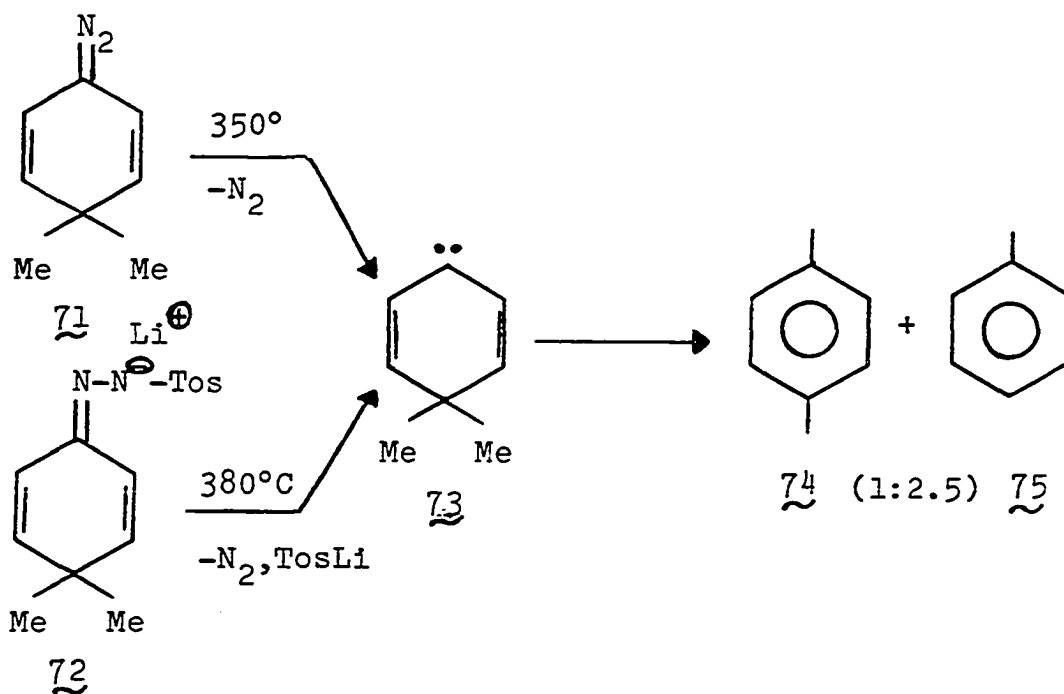
The silacyclohexadiene ring system 70 was chosen as a logical chemical synthon for silabenzene. The choice of the silacyclohexadiene ring system was in part due to its availability with a moderate variety of functionality, both on the ring and on silicon. This functionality could then be transformed to the desired potential precursors of silabenzene.



The Synthesis and Chemistry of  
4-Diazo-1,1-dimethyl-1-sila-cyclohexa-2,5-diene

The first attempt to obtain silabenzene was based upon the gas phase rearrangement of 4,4-dimethylcyclohexadienylidene 73 to para-xylene 74 and toluene 75 (125) (Scheme 17). Only the para isomer of xylene was obtained. The

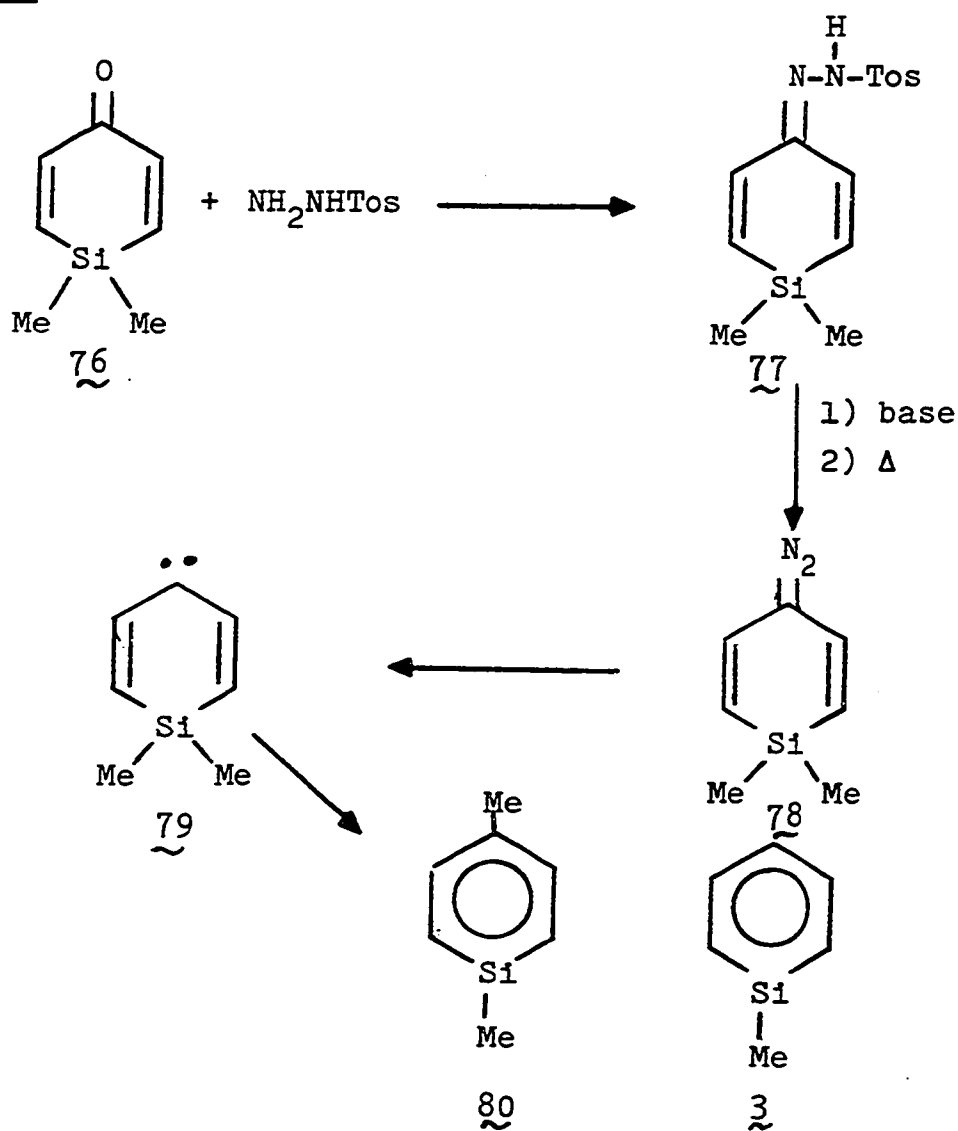
Scheme 17



rearrangement was accomplished by either decomposing the diazo compound 71 in a vertical flow pyrolysis or by the flash vacuum pyrolysis of the lithium salt of the tosylhydrazone of 4,4-dimethylcyclohexadienone 72.

It was hoped an analogous rearrangement would occur upon replacement of the 4-carbon of 1,1-dimethylcyclohexadienylidene 73 with silicon 79 (Scheme 18). The immediate precursor, 1,1-dimethyl-4-diazo-1-silacyclohexa-2,5-diene 78 was not known but the corresponding ketone 76 is a known compound (126,127).

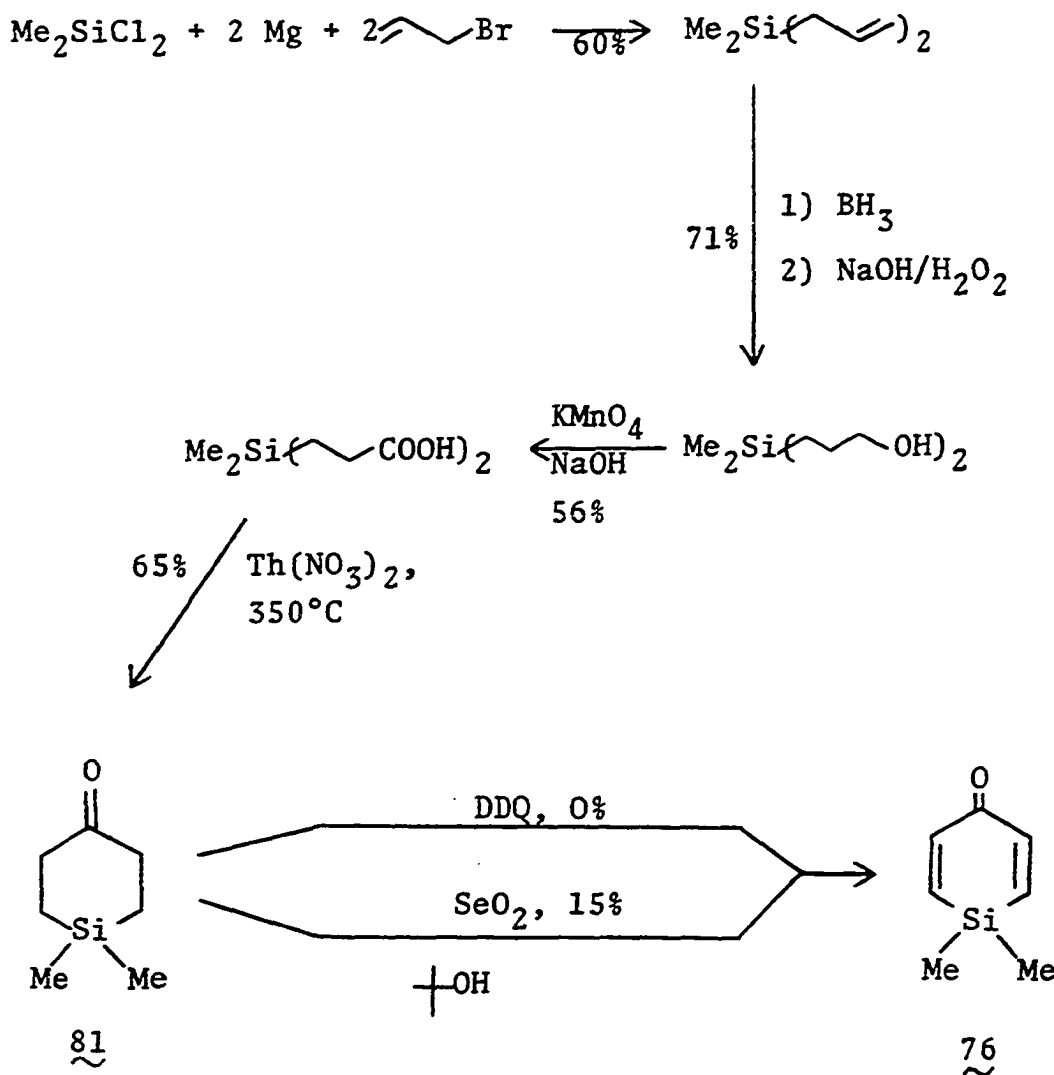
Scheme 18



Synthesis of 4-diazo-1,1-dimethyl-1-silacyclohexa-2,5-diene 78

The synthesis of 4,4-dimethyl-4-silacyclohexa-2,5-diene-1-one 76, was accomplished in five steps with an overall yield of 2-3%, following literature procedures (Scheme 19) (126-129)

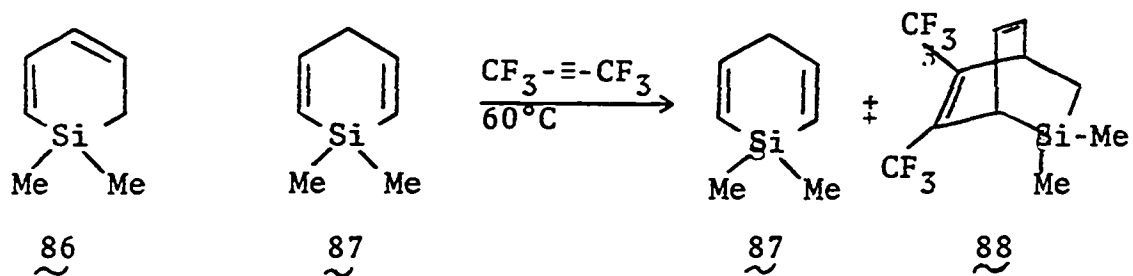
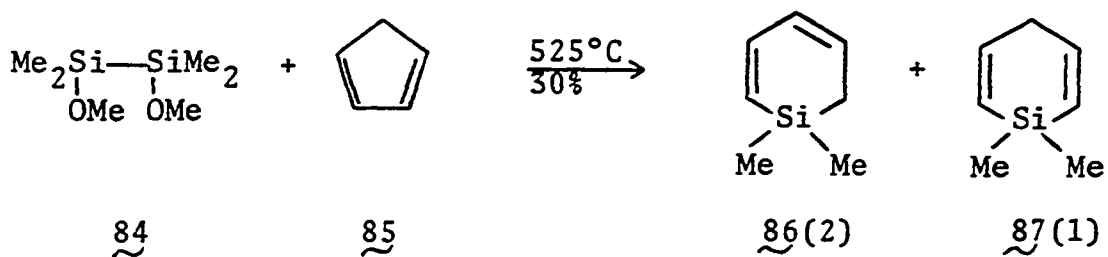
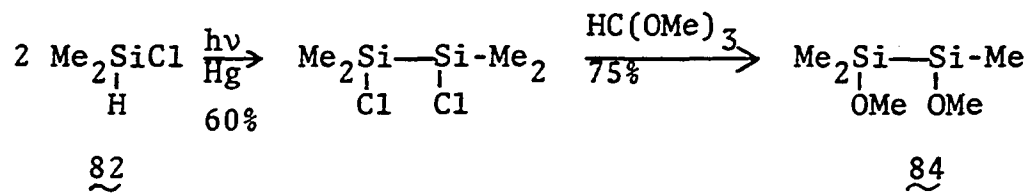
Scheme 19



The last step in the sequence, oxidation of 1,1-dimethyl-1-silacyclohexan-4-one 81 to the dienone 76 was a source of difficulty. This oxidation is reported to occur in the presence of either selenium dioxide-tert-butyl alcohol (126), or 2,3-dichloro-5,6-dicyanoquinone (DDQ) (127). The reaction of the saturated ketone 81 with selenium dioxide did produce the dienone 76, but the purification of the dienone away from foul-smelling organoselenium by-products was tedious and decreased the isolated yield considerably. Treatment of the saturated ketone with DDQ is reported to give the dienone in 62% yield in a much cleaner reaction. The DDQ reaction was attempted numerous times. Changing reaction conditions had no effect, the result was always the same, no dienone was obtained. Thus, it became obvious an alternate synthesis of the dienone 76 was necessary in order to obtain workable amounts of the compound.

The major obstacle in the previous synthesis was the introduction of the double bonds in the silacyclohexanone ring system. This obstacle was circumvented by starting with the double bonds already present and introducing the ketone functionality in the last step. The key compound in such a scheme is 1,1-dimethyl-1-silacyclohexa-2,5-diene 87. The unconjugated diene 87 could be obtained along with the isomeric 1,1-dimethyl-1-sila-cyclohexa-2,4-diene 86 from the coprolysis of 1,1,2,2-tetramethyl-1,2-dimethoxydisilane 84 and cyclopentadiene 85 (Scheme 20). In this reaction the

## Scheme 20



disilane 84 at high temperatures breaks down to dimethoxy-dimethylsilane and silylene (the silicon analogue of carbenes). The silylene then inserts into the cyclopentadiene and, with concomitant ring expansion, the isomeric mixture of silacyclohexadienes 86 and 87 are produced in 30-33% yield (65,130,131).

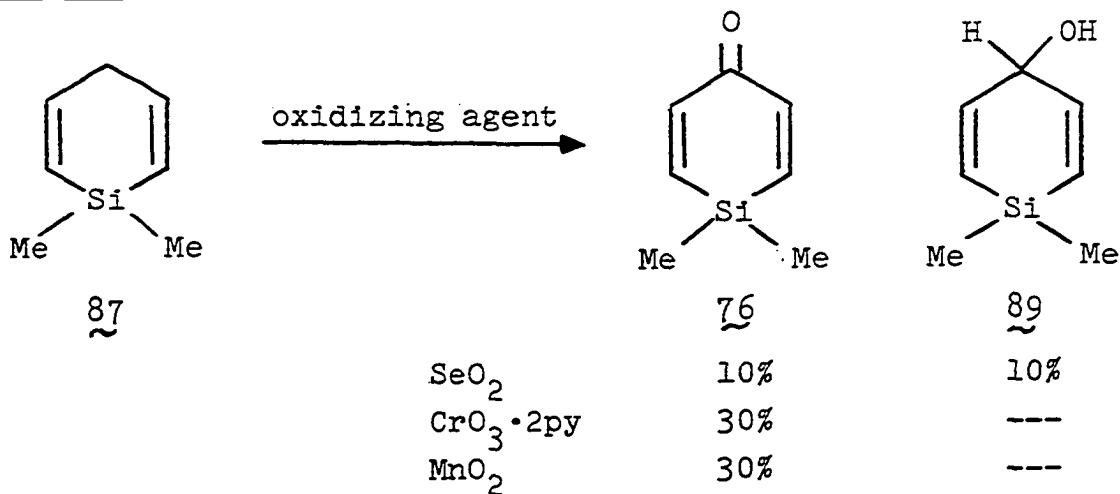
Separation of the isomeric dienes could only be achieved chemically as chromatographic attempts to separate the mixture failed. The isomers were separated by reacting the mixture of dienes with perfluoro-2-butyne in a sealed tube at 60°C for four hours, as described by Barton and Kline (66). The conjugated isomer 86 reacts in a Diels-Alder reaction with the butyne to give 2,3-bis(trifluoromethyl)-7,7-dimethyl-7-silabicyclo[2.2.2]-octa-2,5-diene 88, a thermal silene generator. The unconjugated isomer 87 is unaffected and can now be isolated in a pure form by distillation (Scheme 20).

The synthesis of the dimethoxydisilane 84 merits mention since it differs from previously reported methods (65,132). Previously, this compound was prepared by the action of sodium methoxide on 1,1,2,2-tetramethyl-1,2-dichlorodisilane 83 (132). The dichlorodisilane 83 was prepared by treatment of a mixture of acetyl chloride and aluminum chloride with hexamethyldisilane to yield a mixture of chlorodisilanes (132). Separation of the mixtures often requires tedious distillations. In this study the dichlorotetramethyldisilane 83

was more conveniently prepared by the mercury sensitized irradiation at 2537 Å of chlorodimethylsilane 82 (Scheme 20). This reaction is similar to the coupling of dimethoxymethylsilane reported by Childs and Weber (133). The yield of the dichlorodisilane 83 is 60% after two days and is obtained without the contamination of other chlorodisilanes. Conversion to the dimethoxy compound was accomplished by treatment with trimethylorthoformate at 60°C for twelve hours, following the procedure of Childs and Weber (133) for converting chlorosilanes to methoxysilanes. The product is purified by simple distillation.

The 4-position of 1,1-dimethyl-1-silacyclohexa-2,5-diene is ideally situated for allylic oxidation. The methylene was found to be quite active towards oxidation and could be converted directly to ketone 76 with a variety of oxidizing agents (Scheme 21).

Scheme 21



Treatment of diene 87 with selenium dioxide in refluxing 95% ethanol for 24 hours, produced the dienone 76 in 10% isolated yield along with an equal amount of the corresponding alcohol 89. Also accompanying the products were large amounts of unidentified organoselenium by-products. This oxidation suffered from the same purification problems as occurred with the selenium dioxide oxidation of 1,1-dimethyl-1-silacyclohexan-4-one 81. Therefore, other oxidizing agents were employed.

Collin's reagent (134), a chromium trioxide-pyridine complex, converted diene 87 to dienone 76 in 30% yield. No alcohol was found in the reaction products, but a large amount of unidentified acids was obtained, presumably arising from ring opening.

Activated manganese dioxide was found to be a milder oxidizing agent. It converted the diene to the dienone in 30% yield through stirring at room temperature in hydrocarbon solvent for 24 hours. With this method, purification involved only filtration followed by chromatography on silica gel. Furthermore, this oxidation could be carried out in the presence of 1,1-dimethyl-1-silacyclohexa-2,4-diene 86, the conjugated isomer, making separation of the isomeric mixture of dienes no longer necessary. The conjugated isomer 86 was untouched by manganese-dioxide and could be isolated from the reaction mixture by chromatography on silica gel. This was



not the case when a mixture of the conjugated and unconjugated dienes were oxidized with either selenium dioxide or Collin's reagent. No trace of the conjugated diene could be found. Also, no evidence of 1,1-dimethyl-1-silacyclohexa-2,4-dien-2-one was found in any of the oxidation reactions.

The overall isolated yield of the dienone 76, starting from commercially available dimethylchlorosilane, is about 5% in four steps. This amounted to a doubling of the yield over the previously used route, as well as considerable savings in the time necessary to effect the synthesis.

The dienone 76 was converted cleanly to the desired diazo compound 78 by standard procedures (Scheme 18). Thus, treatment of the dienone with para-toluenesulfonyl hydrazide yielded the white crystalline tosylhydrazone 77. The tosylhydrazone was converted to its sodium salt with sodium methoxide. Pyrolysis of the salt, at 110°C under a vacuum of 2.0 mm Hg, yielded the red diazo compound 78 (NMR, Figure 1). The isolated yield of the diazo compound starting from the dienone was 70%.

During the course of this study, the metalation of 1,1-dimethyl-1-silacyclohexa-2,4-diene was reported by Chernyshev and co-workers (135) (Scheme 22). The silacyclohexadienyl anion 90 formed upon treatment with n-butyllithium on the diene 86 was trapped with trimethylchlorosilane 91.

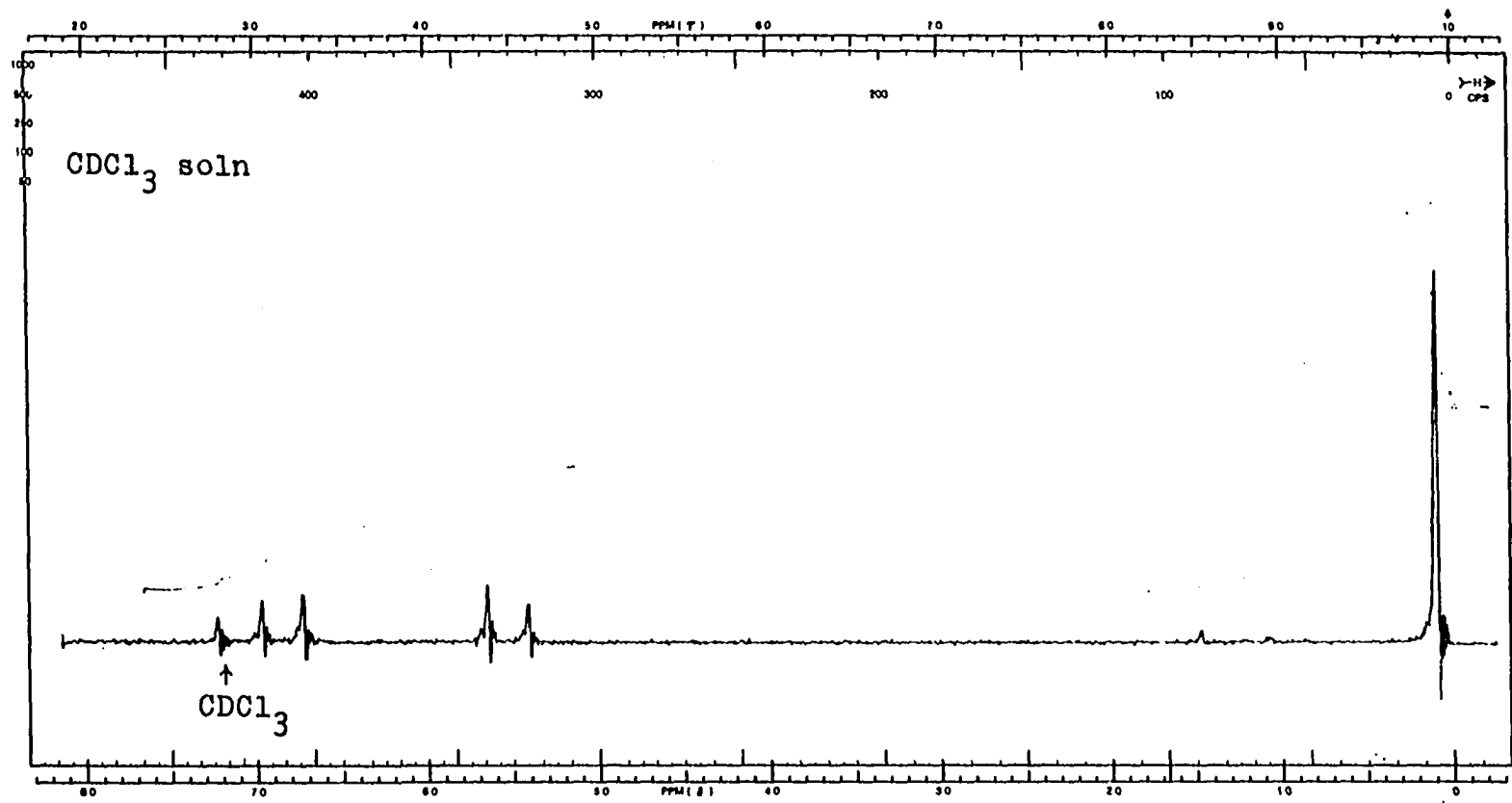
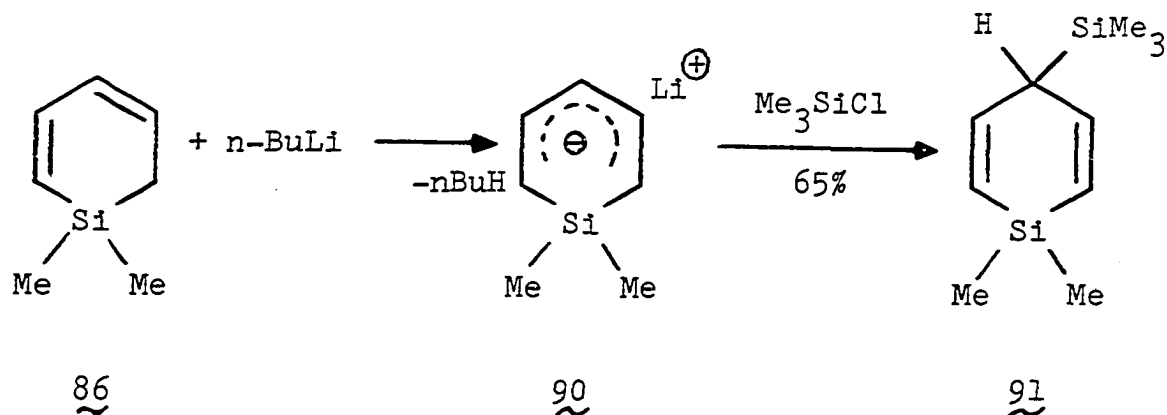


Figure 1. 60 MHz NMR spectrum of 1,1-dimethyl-4-diazo-1-silacyclohexa-2,5-diene (78)

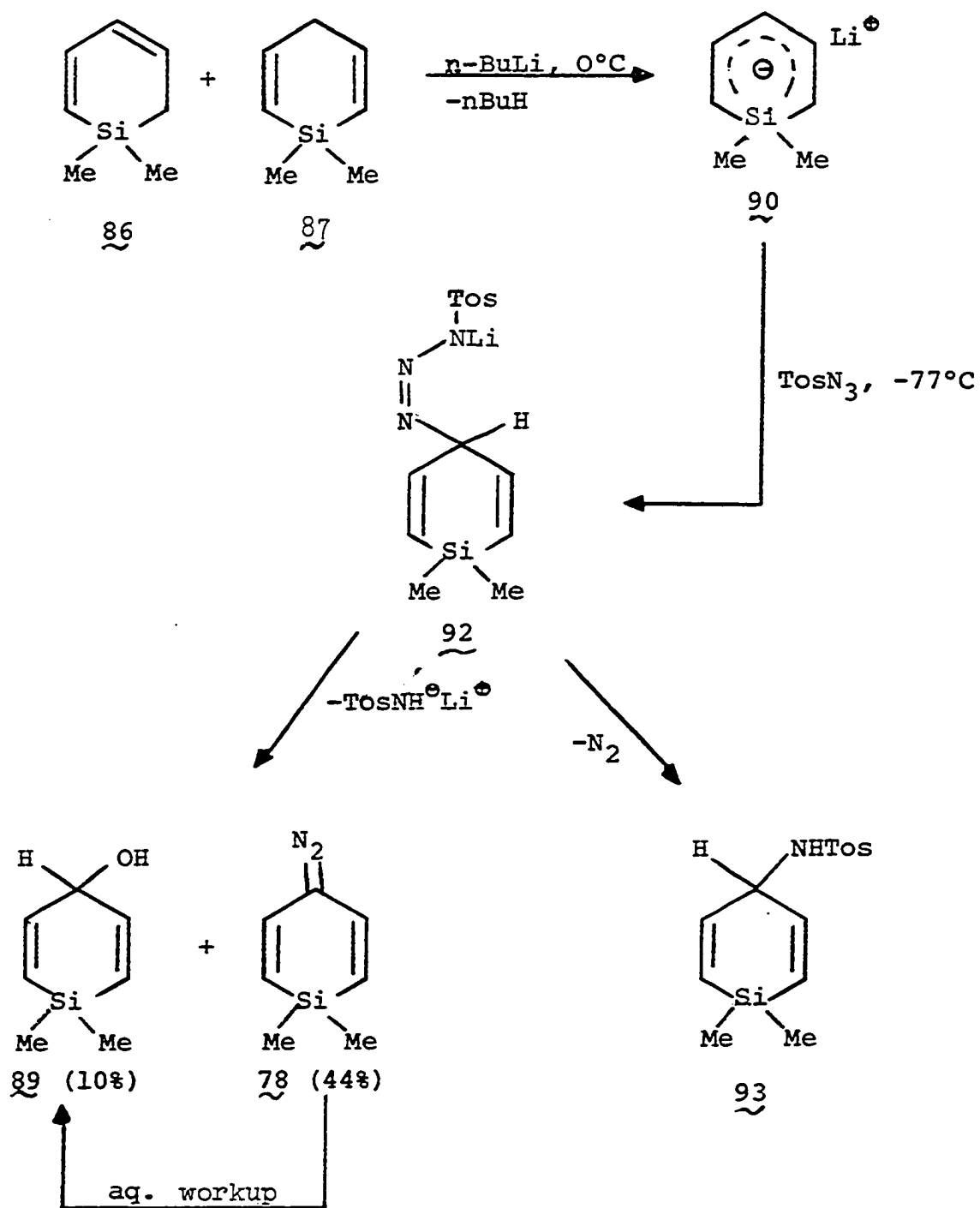
## Scheme 22



Trapping of the anion occurred only in the 4-position of silacyclohexadiene ring system. The case of formation of the silacyclohexadienyl anion suggested that it might provide a direct route to the diazo compound via the diazo transfer reaction first reported by von E. Doering and DePuy (136), in the formation of 1-diazocyclopenta-2,4-diene.

Thus, the isomeric mixture of dienes was treated with *n*-butyllithium in tetrahydrofuran at  $0^\circ\text{C}$ . The red silacyclohexadienyl anion **90** was immediately formed. Addition of the anion solution to a solution of *p*-toluenesulfonylazide in tetrahydrofuran at  $-77^\circ\text{C}$  produced a mixture of products (Scheme 23).

Scheme 23



The 4-diazo 78 compound was obtained in 44% yield along with a 10% yield of the 4-alcohol 89. The alcohol was shown to be a decomposition product of the 4-diazo compound resulting from the aqueous work-up. The amine 93 results from a loss of nitrogen from the initial tosyl-azide-silacyclohexadienyl anion intermediate 92.

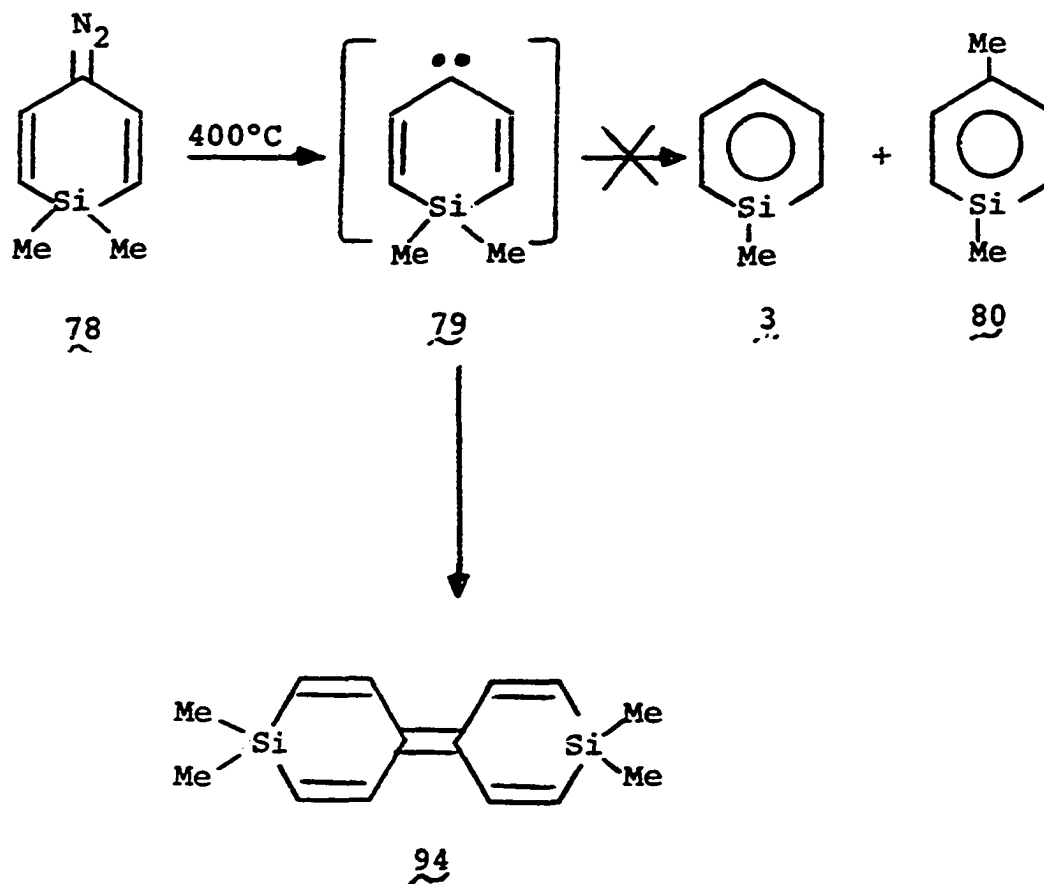
Formation of the 4-diazo-1,1-dimethyl-1-silacyclohexa-2,5-diene 78 from the carbanion 90 is the most convenient method of preparation. Comparison of yields, beginning with the dienes, shows the anion route produces the diazo compound in 44% isolated yield, while the ketone route gave only a 21% yield from the dienes. The diazo compound could now be obtained in a pure form in one step from the 1,1-dimethyl-1-silacyclohexadienes 86 and 87 without involving 1,1-dimethyl-1-silacyclohexa-2,5-diene-4-one 76 as an intermediate.

#### Reactions of 4-diazo-1,1-dimethyl-1-sila-cyclohexa-2,5-diene

Decomposition of diazo compound 78 was accomplished in the gas phase at 400°C in a vertical flow pyrolysis apparatus. The sample was introduced either by syringing microliter quantities through a septum or by slow evaporation with a stream of nitrogen into the heated tube to insure dilute conditions. Dilute conditions were maintained to promote the intramolecular rearrangement of carbene 79 to the desired silabenzenes 3 and 80. The pyrolysis produced a very complex

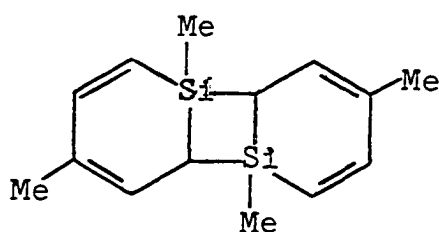
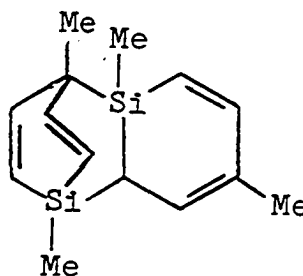
mixture of which the only identifiable product was a dimer 94 which was formed in 15% yield (Scheme 24). The structure of

Scheme 24



the dimer was determined largely from its NMR spectrum (Figure 2). A number of dimers are possible in the reaction if the desired silaxylene 80 is produced. The two most likely dimers based on normal silene behavior are the [2+2]

cycloaddition product 95 and the Diels-Alder adduct between two molecules of silaxylene 96. Simple dimerization of the

9596

carbene 94 must also be considered. Of these possible dimers, only the carbene dimer 94 fits the classic AB pattern found in the olefinic region of the product's NMR spectrum. (Figure 2). A large amount of unidentified nonvolatile silicon-containing material was also produced. No evidence of the desired rearrangement was observed.

The presence of the carbene dimer 94 indicated the conditions may not have been as dilute as desired in the vertical flow pyrolysis. Therefore, a vacuum horizontal pyrolysis of the diazo compound was attempted. The diazo compound was slowly distilled through a hot zone of 420°C and the products were trapped in a series of cold traps. Analysis of the products showed a small amount of carbene-dimer 94 (5%) along with a large amount of nonvolatile

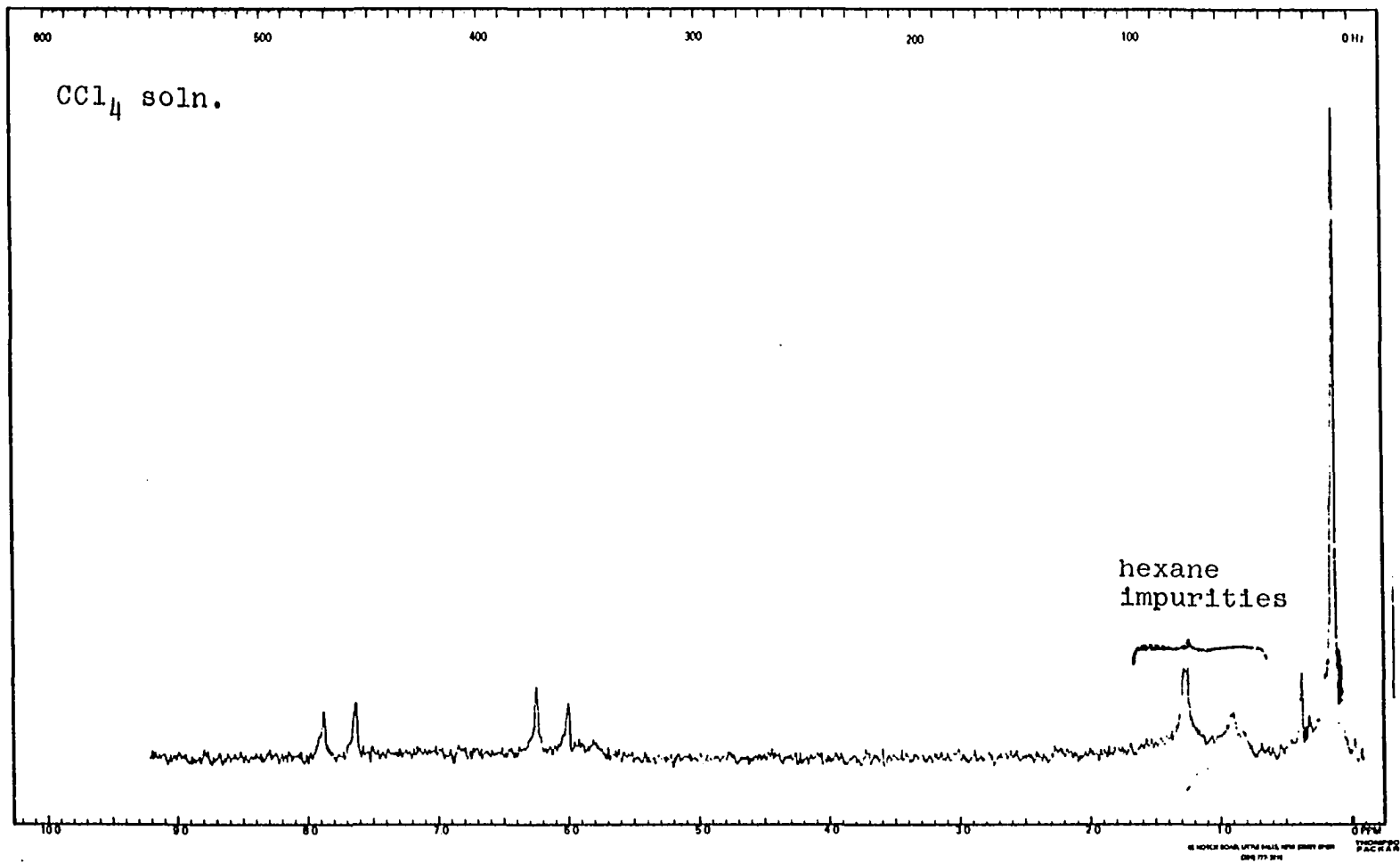


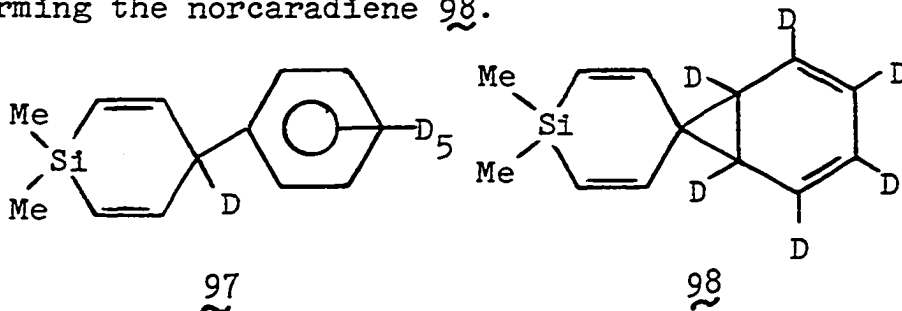
Figure 2. 60 MHz NMR spectrum of 1,1-dimethyl-1-silacyclohexa-2,5-dien-4-ylidene carbene dimer (94)

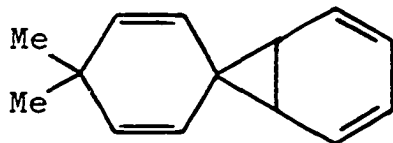
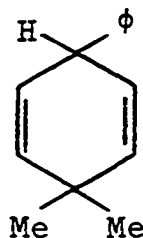


silicon-containing polymers. Again, no evidence for the formation of silabenzene 80 was found.

The presence of extraneous moisture in the vertical or vacuum pyrolysis resulted in the formation of varying amounts of 1,1-dimethyl-1-silacyclohexa-2,5-dien-4-one 76. Rigorous drying of all materials prevented the formation of this product. Presumably, the ketone is formed by insertion of the carbene into water, forming the alcohol 89. The alcohol, under these reaction conditions, then dehydrogenates to the ketone 76.

In another attempt to promote intramolecular rearrangements, a dilute solution (0.01 M) of the diazo compound 78 in benzene-6-D was pyrolyzed in a vertical flow system. The product mixture was much cleaner, only one major volatile product was observed. Unfortunately, this product turned out to be the result of addition of the carbene to the solvent 97. Conclusive identification of the adduct is complicated by the presence of deuterium. Consequently, it is not possible to distinguish between carbon deuterium insertion product 97 and addition to the  $\pi$ -bond of benzene forming the norcaradiene 98.



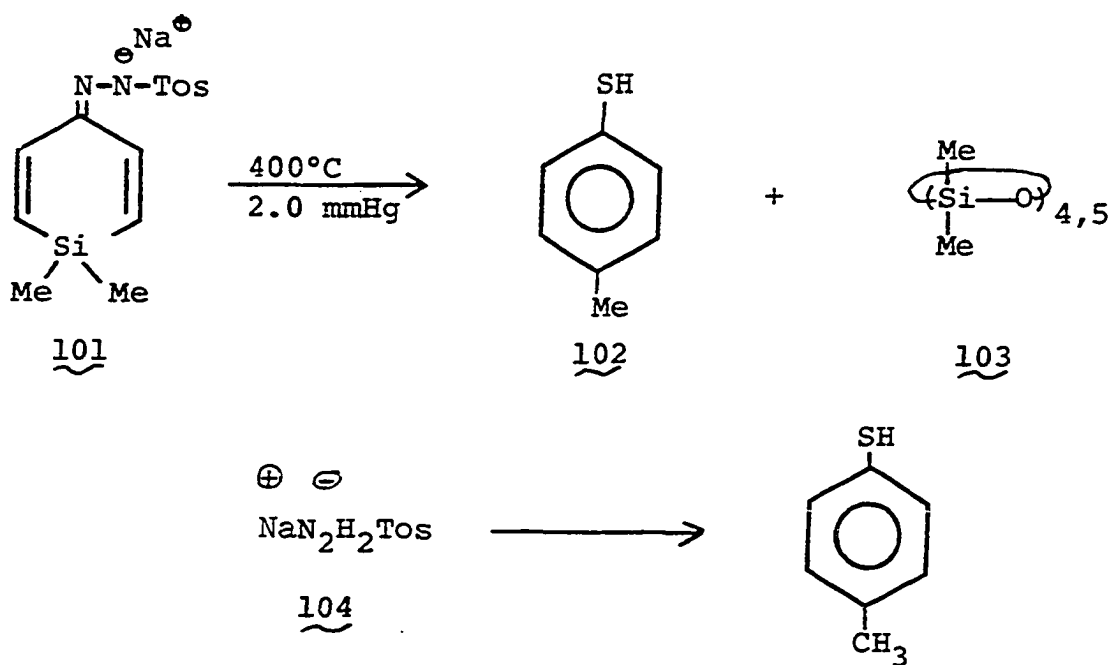
99100

The all-carbon analog of the diazo compound 71 also is known to react with benzene, but under photolytic conditions (135). The product, in that case, is the spironorcaradiene system 99. It was found to be a thermally unstable system, and rapidly rearranged to the aromatic system 100 upon heating. Thus, it is highly probable that adduct 97 is the isolated product since norcaradiene 98 would not be expected to survive the high reaction temperatures.

Decomposition of the lithium salt of the tosylhydrazone of 4,4-dimethylcyclohexa-2,5-dien-1-one 72 was also found to yield the rearrangement of the carbene to xylene. Therefore, it was hoped the salt of the silicon analog 101 would also undergo an analogous rearrangement. The sodium salt of the tosylhydrazone 101 was slowly dropped into a glass surface heated to 400°C under vacuum. The volatile products were trapped in cold traps. The products of the reaction were unexpected (Scheme 25). The major silicon-containing

products were the octamethyl and decamethyl cyclosiloxanes 103. The only other identifiable product was the surprising para-methylthiophenol 102. A large amount of intractable tar also occurred. The only logical source of the para-methylthiophenol 102 is the tosyl group. How deoxygenation at sulfur

Scheme 25

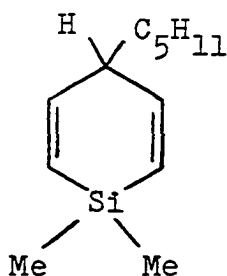
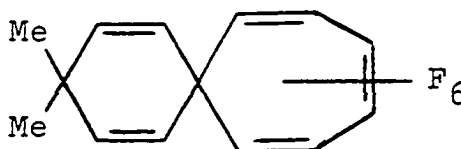


occurs is unknown, although the same process occurs when the sodium salt of the parent tosylhydrazide 104 is subjected to the same reaction conditions. Also, the oxygen liberated from the tosyl group is in some way responsible for the decomposition of the silacyclohexadiene ring that ultimately leads to the formation of the cyclic siloxanes 103.

Unfortunately, because of the unforeseen role of oxygen in

this reaction, the decomposition of the tosylhydrazone salt 101 cannot be used to study intramolecular rearrangements of 1,1-dimethyl-1-silacyclohexa-2,5-dienylidene 79.

Absence of evidence of the rearrangement of 1,1-dimethyl-1-silacyclohexa-2,5-dienylidene 79 to silaxylene 80 or silatoluene 3 in the thermal generation of the carbene, prompted an investigation of the photochemical behavior of this carbene. A 0.010 molar solution of the diazo compound ( $\lambda_{\text{max}} = 296 \text{ nm}$ ) in dry pentane was irradiated through Pyrex at  $3000 \text{ \AA}$  for ten hours. After removal of the pentane, one major compound was isolated in 83% yield. The product 105 was again the result of an interaction between the carbene and solvent. The pentane adduct (NMR, Figure 3) is a carbon-hydrogen insertion product, although it cannot be determined which carbon-hydrogen bonds of the pentane were attacked, nor was it of interest to our study. It

105106

became obvious the carbene could not be generated in the presence of carbon-hydrogen bonds without an interaction

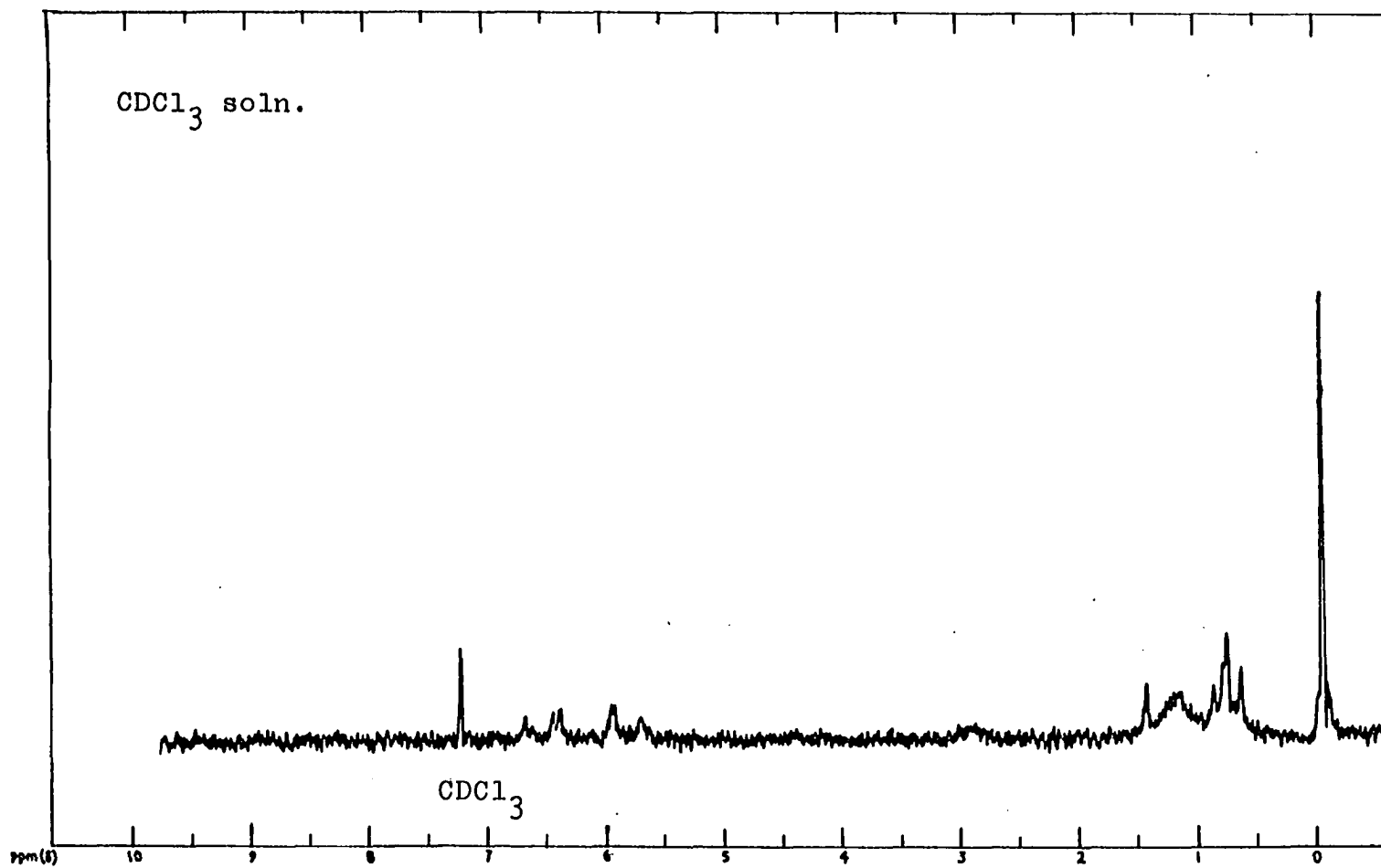


Figure 3. 60 MHz NMR spectrum of 1,1-dimethyl-4-pentyl-1-silacyclohexa-2,5-diene  
(105)

between solvent and the carbene. Consequently, the search for an inert solvent was initiated. Fluorocarbons seemed the most likely candidates since the increased strength of carbon-fluorine bonds over the carbon-hydrogen bonds make them more resistant to carbene insertion reactions. In fact, the carbon-fluorine bond apparently has not been found to take part in an intermolecular insertion reaction (137). Hexafluorobenzene, the solvent normally used as a carbene-inert solvent, was tried with some reservation. The carbon-carbon double bonds of hexafluorobenzene are attacked by 4,4-dimethylcyclohexa-2,5-dienylidene 73, the isolated product is the spirocycloheptatriene 106 (138). Therefore, hexafluorobenzene might not be inert to the carbene 79.

A solution of the 4-diazo compound 78 in hexafluorobenzene was sealed in a Pyrex nmr tube and irradiated at 3000 Å. The progress of the reaction was followed by NMR. After one hour the concentration of diazo compound was noticeably decreased, but no distinct new compound began to appear. At the end of twelve hours, all the diazo had decomposed. The mixture was shown to be very complex by its NMR spectrum. Only a flaky, polymeric material coated the sides of the nmr tube. Nothing but this flaky polymeric material was isolated.

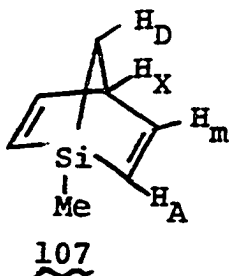
Perfluoro-n-hexane was the next solvent utilized. The diazo compound was much less soluble in perfluorohexane than

in hexafluorobenzene, but the solubility was sufficient for photochemical studies. Irradiation at 3000 Å, through Pyrex, again yielded only polymeric material. Changing the reaction conditions to irradiation through quartz at 2537 Å not only decreased the amount of polymer formed, but also produced a mixture of interesting products. The same set of products were also obtained in the mercury-photosensitized decomposition of the diazo compound at 2537 Å in the gas phase.

The product mixture proved difficult to separate. Elution through silica gel yielded a nonpolar fraction and a polar fraction. The polar fraction consisted of the previously mentioned unidentified polymer and cyclosiloxanes as evidenced by NMR and mass spectroscopy. The origin of the siloxanes is unknown. The nonpolar fraction would not pass through a gas chromatograph. Analysis of the sample was accomplished using normal-phase high pressure liquid chromatography (HPLC). The nonpolar fraction was found to contain at least three compounds, one of which was by far the major product. One minor product was identified to be the carbene dimer 94, the third was not present in sufficient quantities for spectra to be obtained.

Unfortunately, the major product has defied all purification attempts and has not been obtained in an analytically pure form. Preparative HPLC on  $\mu$ -Porasil gave a sample which was contaminated with a trace of carbene dimer 94.

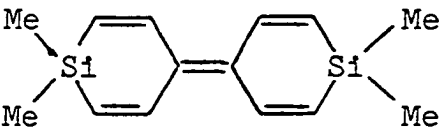
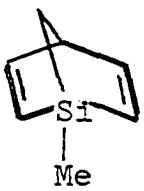
However, the sample was sufficiently pure to allow identification of the major product. This product was determined to be 1-methyl-1-silabicyclo[2.2.1]hepta-2,5-diene (1-methyl-1-silanorbornadiene) 107.



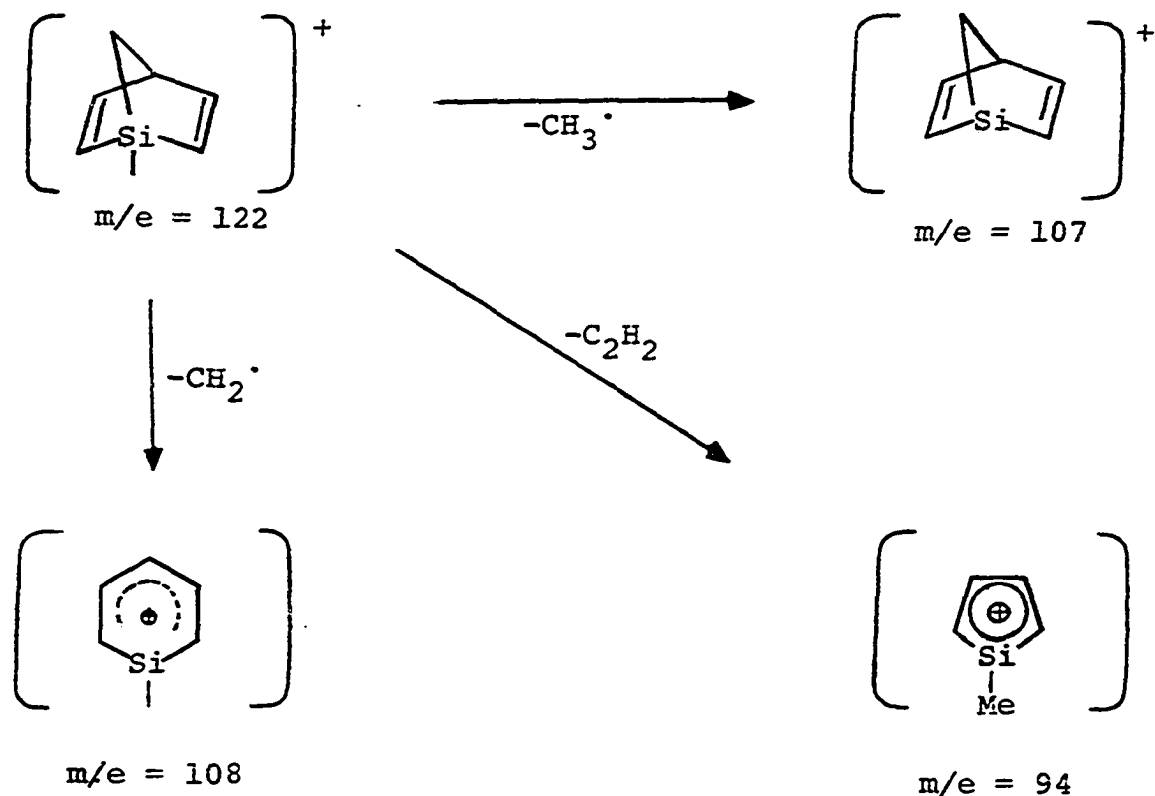
The presence of carbene dimer 94 complicated the analysis of the mass spectrum of 107. Table 2 shows the 70 eV mass spectrum of the carbene dimer 94 and contaminated 107. The peaks at  $\underline{m/e} = 244$  and 229 are assigned to 94 and not to 107 based on a calculation of the ratio of the intensities of  $\underline{m/e} 244$  to  $\underline{m/e} 229$  in both samples. The ratios are nearly identical (0.70 for 94 and 0.65 for contaminated 107). The remainder of the peaks found in contaminated 107 are not present in the mass spectrum of 94 and are totally consistent with 1-methyl-1-silanorbornadiene 107. Scheme 26 shows a breakdown pattern for these peaks.



Table 2. Mass spectra of the carbene dimer 94 and 1-sila-norbornadiene 107 (70 eV)

<u>m/e</u>	%	Exact mass
 <u>94</u>		
244	70	244.1099 C <sub>14</sub> H <sub>20</sub> Si <sub>2</sub>
229	100	
161	10	
160	10	ratio of rel. intensities
159	10	of <u>m/e</u> = $\frac{244}{229} = \frac{70}{100} = 0.70$
145	10	
107	5	
73	15	
 <u>107</u>		
and a trace of <u>94</u>		
244	26	244.1099 C <sub>14</sub> H <sub>20</sub> Si <sub>2</sub>
229	40	
122	100	122.0471 C <sub>7</sub> H <sub>10</sub> Si
108	40	ratio of rel. intensities
107	50	of <u>m/e</u> = $\frac{244}{229} = \frac{26}{40} = 0.65$
94	70	
57	40	
43	30	

## Scheme 26



Loss of methyl (P - 15,  $m/e = 107$ ) from the parent molecular ion ( $m/e = 122$ ) is quite prominent, as is loss of methylene (P - 14,  $m/e = 108$ ). The loss of ethylene (P - 28,  $m/e = 94$ ) is the major fragmentation observed.

The NMR spectrum of contaminated 107 helps confirm the presence of carbene dimer 94 (weak signal at  $\delta$  7.86 (d = J = 15 Hz). The remainder of the spectrum (Figure 4A) [(CDCl<sub>3</sub>)

$\delta$  -0.05, 0.00 (overlapped s, 10H), 3.11 (m, 1H), 5.85 (d of d,  $2H_A$ ,  $J_{AM} = 15$  Hz,  $J_{AX} = 2$  Hz), 6.57 (d of d,  $2H_M$ ,  $J_{MX} = 4$  Hz)] is quite indicative of the silanorbornadiene 107. Decoupling experiments (Figure 4B) established the presence of an AMX pattern for the olefinic and allylic protons. Integration of the spectrum shows a ratio of olefinic:allylic:silylmethyl protons equal to 4:1:10. The silylmethyl region which includes the bridgehead methylene protons ( $H_D$ ) is high, however, carbene dimer 94 will also add to the integration of this region. The chemical shifts of the olefinic and allylic protons correspond well with those of 1,1-dimethyl-1-silacyclohexa-2,5-diene 87 (Figure 5), whose protons are in a similar environment. Thus, although the sample is slightly impure, the NMR spectrum is totally consistent with 1-methyl-1-silanorbornadiene 107 as the major product of the reaction.

The formation of 107 is envisioned as occurring via an intramolecular insertion of carbene 79 into a carbon-hydrogen bond of a methyl on silicon (Scheme 27A). Precedence for this type of carbene rearrangement was recently found by Professor Orville Chapman.<sup>1</sup> He finds that photolysis of the corresponding carbon diazo compound 71 in

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<sup>1</sup>Professor Orville Chapman, Department of Chemistry, University of California at Los Angeles, Los Angeles, CA., personal communication.

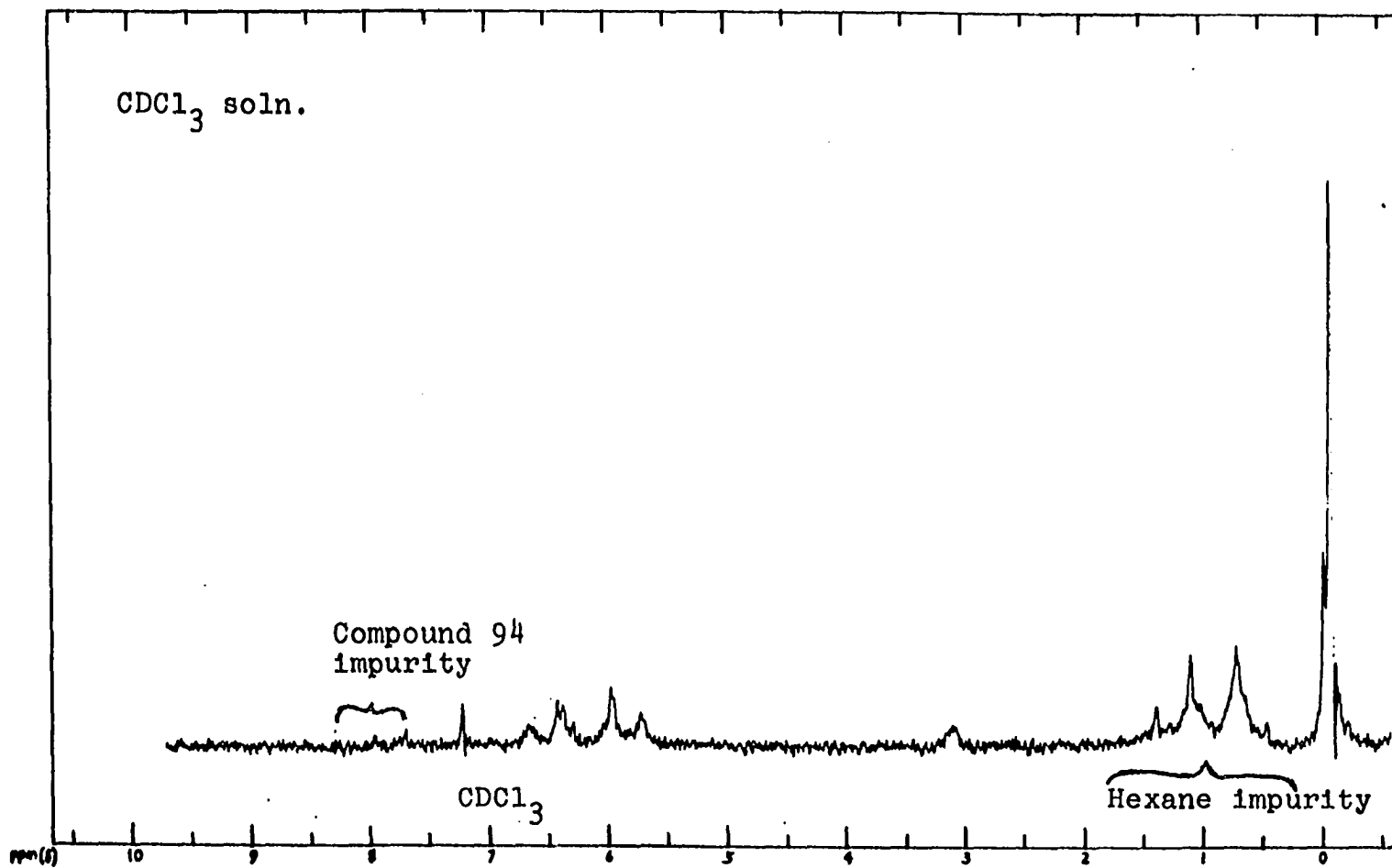


Figure 4A. 60 MHz NMR spectrum of 1-methyl-1-silabicyclo[2.2.1]hepta-2,5-diene  
(107)

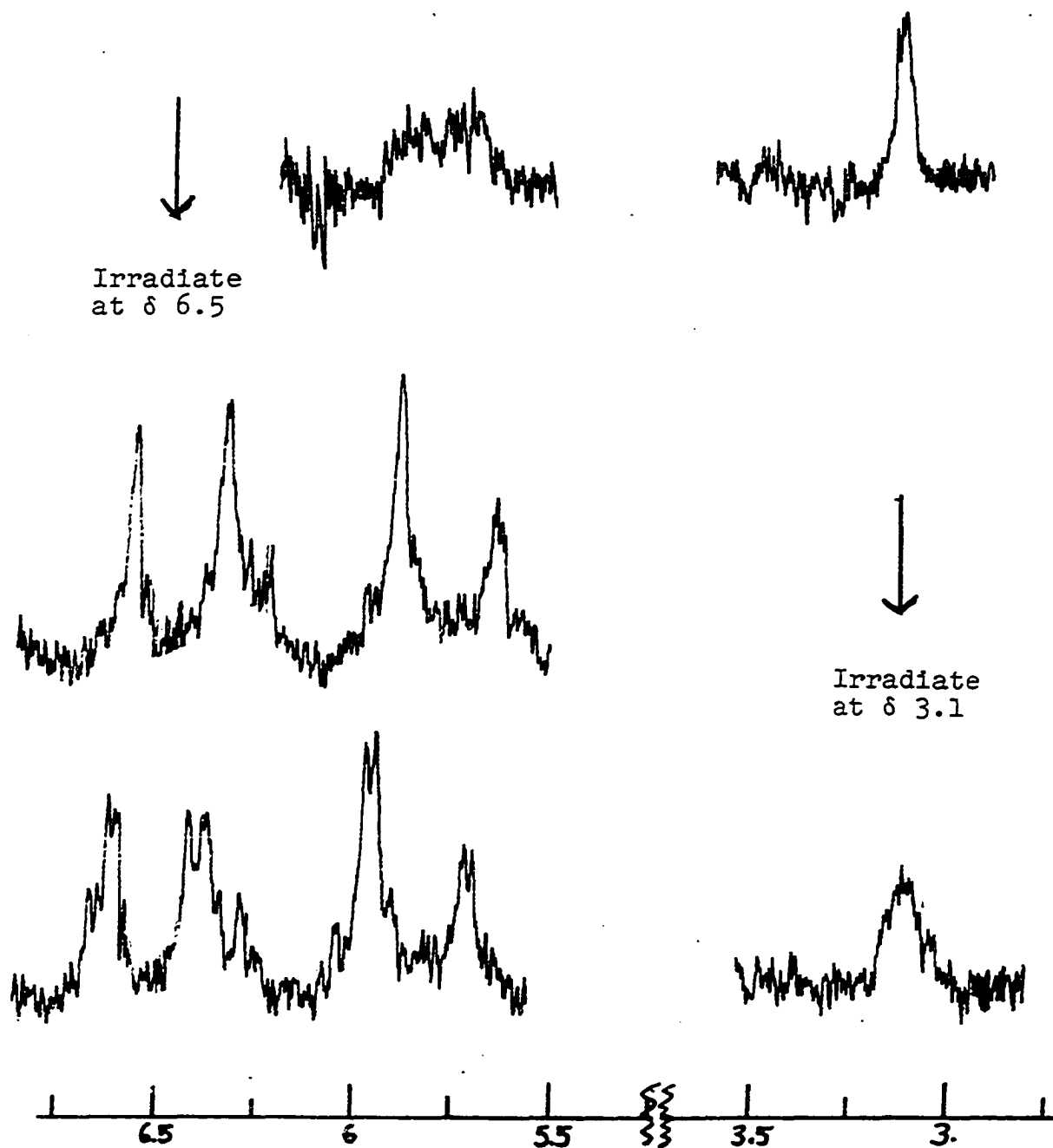


Figure 4B. 60 MHz NMR spectrum of spin-decoupling experiments of 1-methyl-1-silabicyclo[2.2.1]hepta-2,5-diene (107)

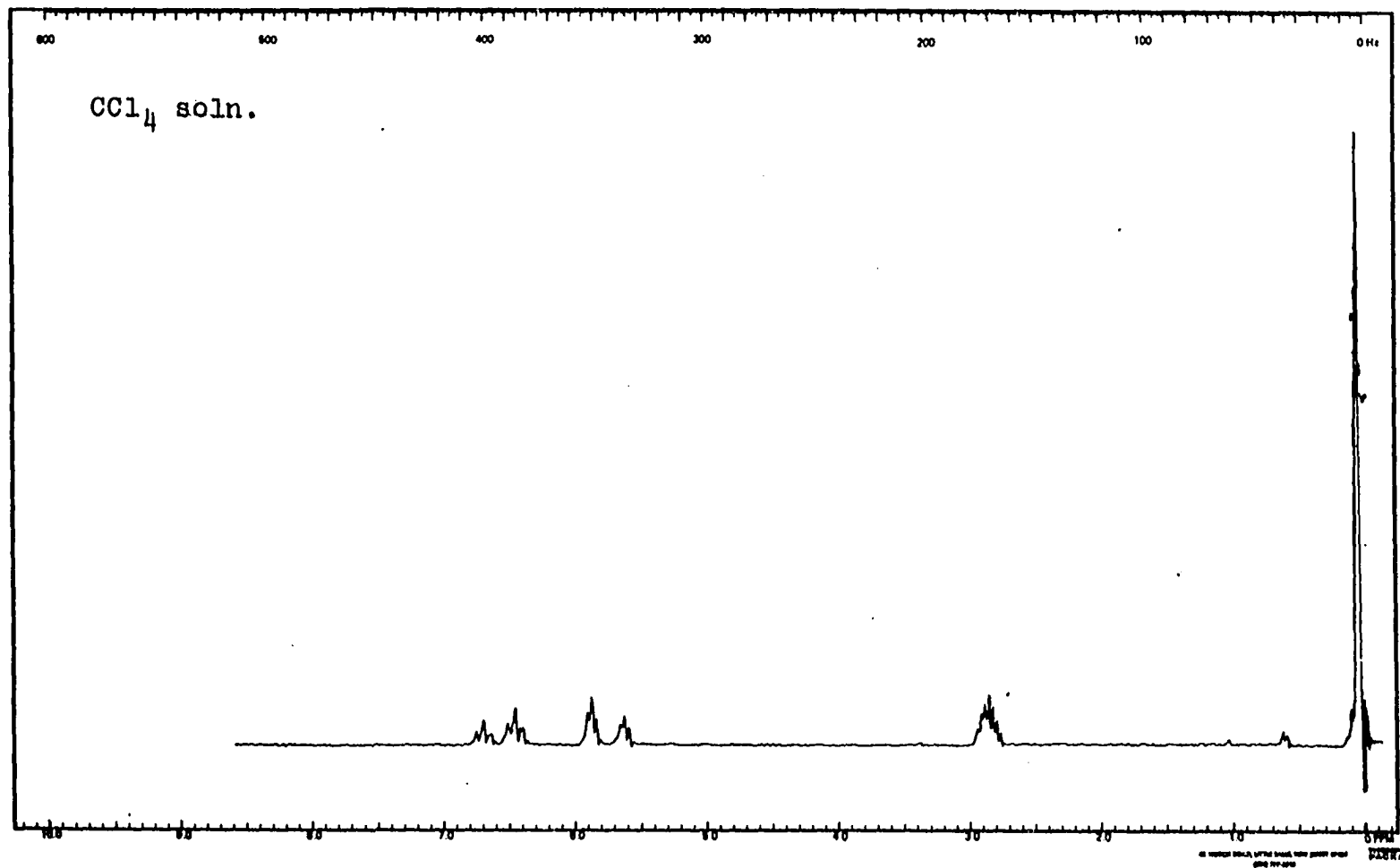
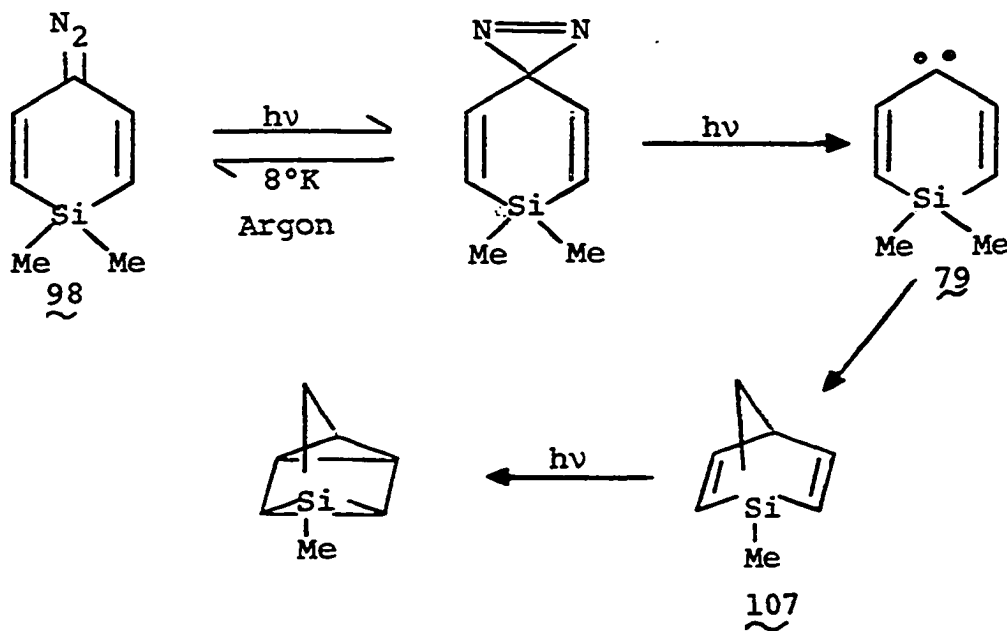


Figure 5. 60 MHz NMR spectrum of 1,1-dimethyl-1-silacyclohexa-2,5-diene (87)

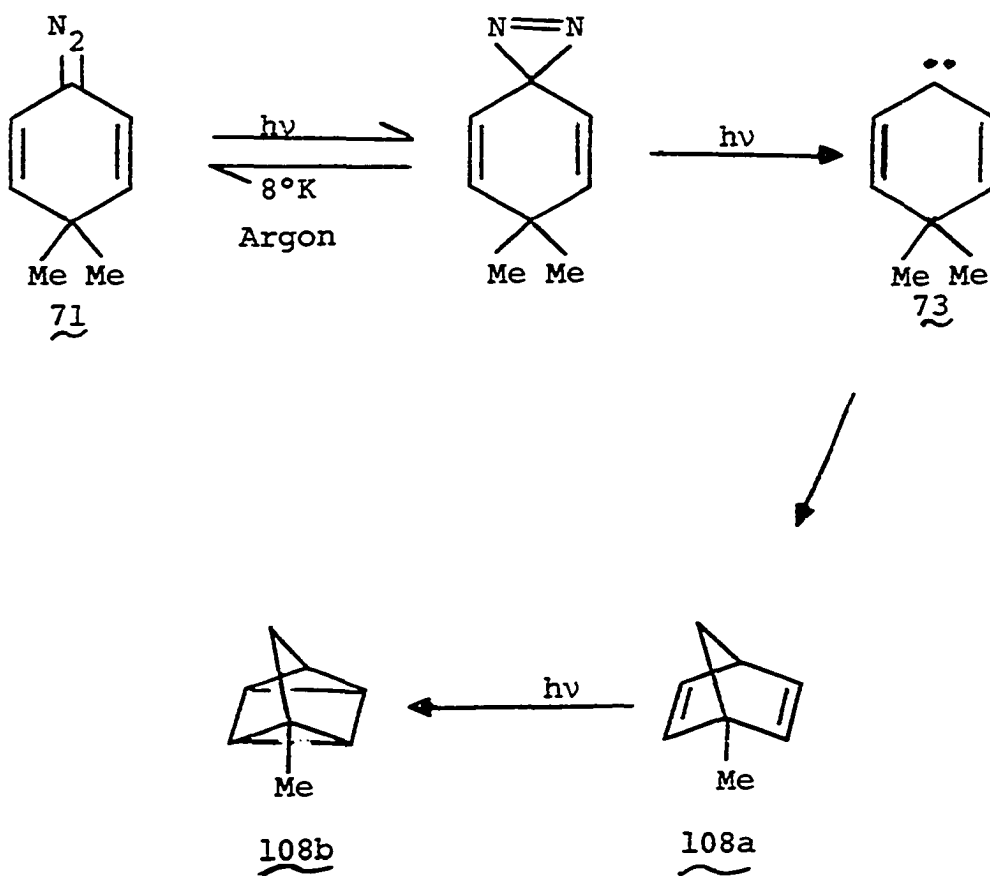
## Scheme 27A



an Argon matrix at 8°K causes the sequence of events depicted in Scheme 27B to occur. An equilibrium between the diazo compound and the isomeric diazarene is established, further irradiation causes decomposition to carbene 73. Carbene 73 then inserts into a carbon-hydrogen bond, in a fashion analogous to that proposed for carbene 79,

producing 1-methyl-1-norbornadiene 108a. Irradiating at this point converts 108a into quadricyclane 108b. These reactions are monitored by IR.

Scheme 27B





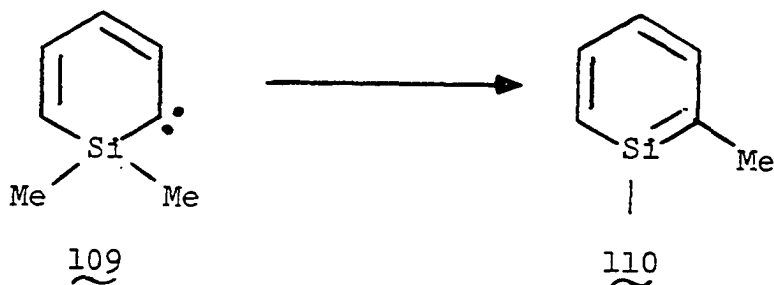
A sample of silyldiazo 78 was sent to Professor Chapman to investigate this reaction under his reaction conditions. Preliminary results indicate that the silicon system behaves in the same manner as the carbon system (Scheme 27B). The possibility of a silicon quadricyclane is also indicated, however, such a system would not survive the procedures used in the purification of the reaction mixture and will have to be reinvestigated in the future.

Thus, carbene 79, originally considered a silabenzene precursor, has instead opted to rearrange to 1-methyl-1-silanorbornadiene 107, the first example of silicon at the bridgehead of a norbornadiene ring system. Compound 107 should provide an interesting system for study in the future.

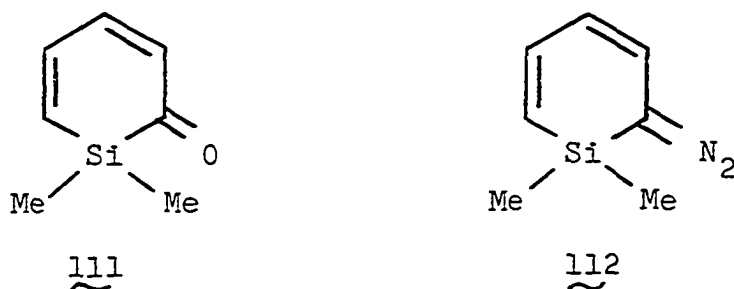
#### Attempts at the Preparation of

1,1-Dimethyl-1,1-silacyclohexa-3,5-dien-2-ylidene Carbene 109

Failure of both the thermal and photochemical reactions of 4-diazo-1,1-dimethyl-1-silacyclohexa-2,5-diene to yield a silabenzene resulted in the exploration of alternative routes. The recent observation of  $\alpha$ -silyl carbene rearrangements to silenes (100-105) suggested that the generation of the carbene in the 2-position 109 of the silacyclohexadiene ring system might effect a rearrangement to silabenzene 110 (Scheme 28). However, none of the normal precursors of the

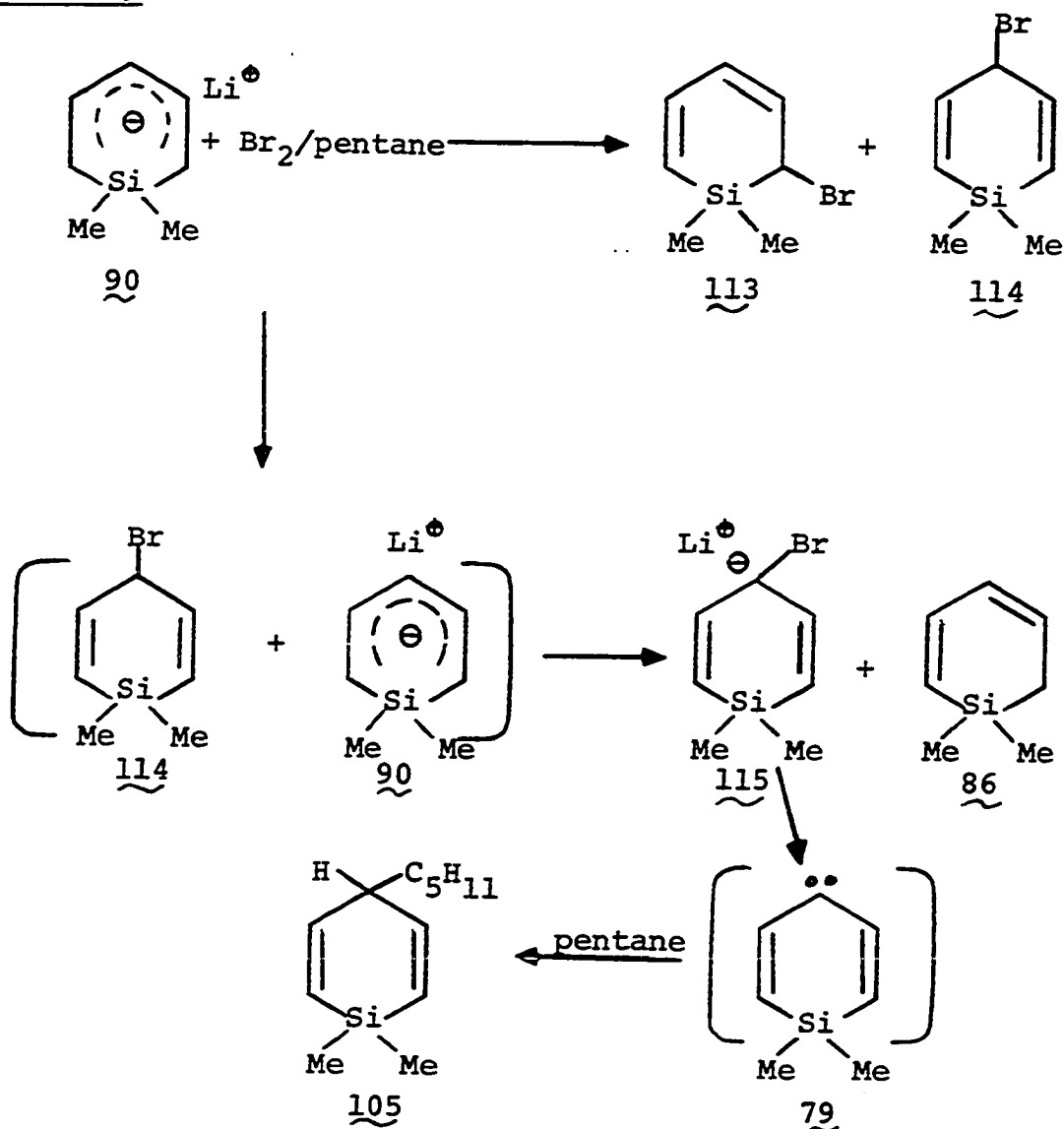
Scheme 28

2-carbene were known. The 2-ketone 111 was not produced by allylic oxidation of the diene ring system, nor was there evidence for the formation of the 2-diazosilacyclohexadiene ring system 112 in the diazo transfer reaction on the isomeric dienes. Therefore, the silacyclohexadiene ring system first had to be transformed into the desired precursors.



A convenient method of carbene generation is the  $\alpha$ -elimination of halogen from anions (127). Thus, the immediate precursor of the carbene could be 2-bromo-1,1-dimethyl-1-silacyclohexa-2,4-diene 113. Attempts to obtain this compound directly from the trapping of the anion of the silacyclohexadienes by bromine resulted in the formation of the pentane adduct 105 of the 4-carbene 79 (Scheme 29). The

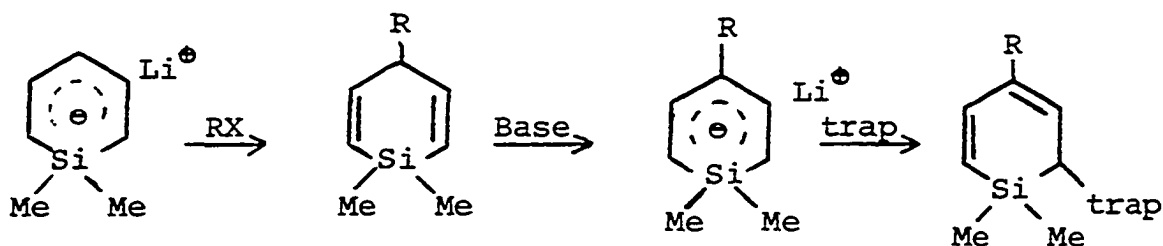
Scheme 29



pentane adduct arises from the 4-carbene 79, which is formed from the  $\alpha$ -elimination of bromide from anion 115. Anion 115 is the result of hydrogen abstraction from the 4-bromocyclohexadiene 114 by the original silacyclohexadienyl anion 90. Involvement of the silacyclohexadienyl anion 90 is consistent with the presence of the diene 86 in the product mixture. No

evidence of trapping in the 2-position by either bromine or pentane was observed. These results indicated that trapping of the intermediate, silacyclohexadienyl anion occurs primarily in the 4-position and that in order to functionalize the 2-position, the 4-position must first be blocked (Scheme 30).

Scheme 30

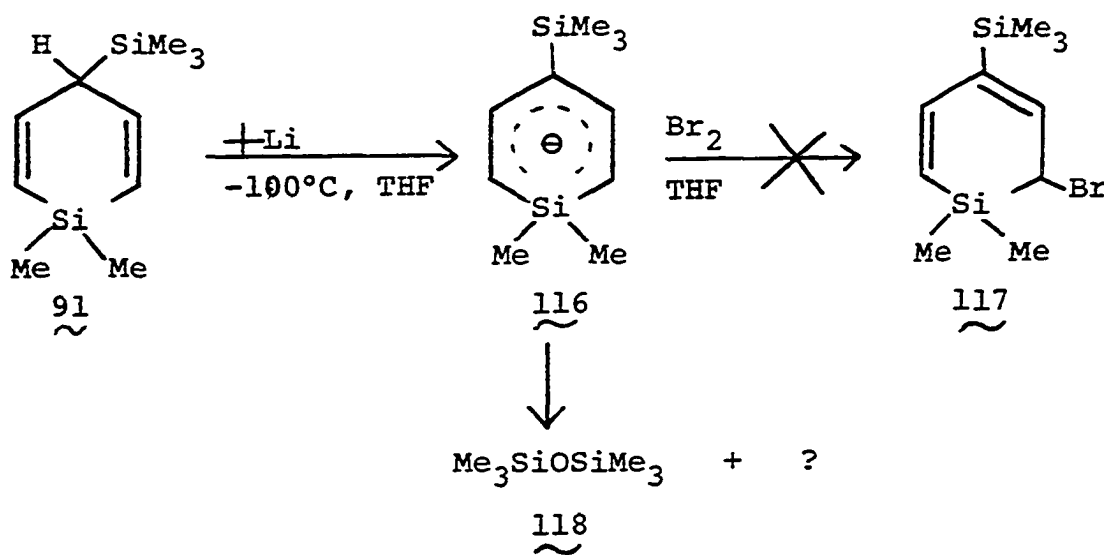


90  
~

A logical choice for the blocking group was the trimethylsilyl group. It is a sterically large group which should prevent trapping of the anion in the 4-position and force capture of the anion to occur in the 2-position. The 4-trimethylsilyl system 91 was known (135) and could be obtained with relative ease. Thus, only the 4-trimethylsilylsilacyclohexadiene isomer 91 was obtained upon capture of the silacyclohexadienyl anion by trimethylchlorosilane as reported by Chernyshev and co-workers (135). The blocked

system 91 readily formed the blocked anion upon treatment with *t*-butyllithium at  $-100^{\circ}\text{C}$  (Scheme 31). The anion 116 was trapped with a bromine/tetrahydrofuran solution in an attempt to obtain the 4-trimethylsilyl-2-bromosilacyclohexadiene system 117.

Scheme 31

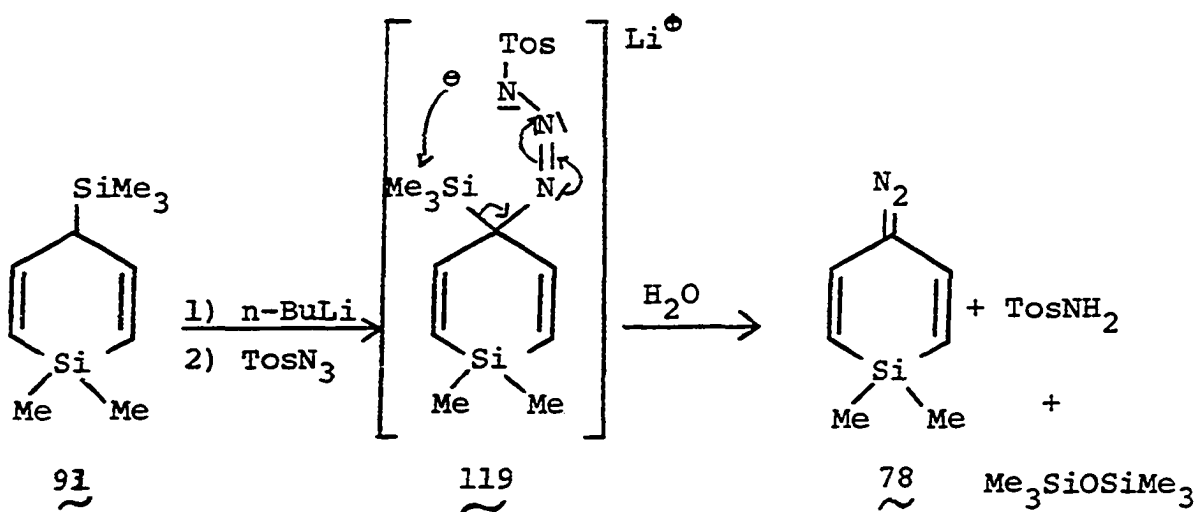


The products of the above reaction indicated the trimethylsilyl group was removed from the silacyclohexadiene ring. Thus, following an aqueous work-up, hexamethyldisiloxane 118 was a major product of the reaction. The remainder of the products by NMR appeared to be tetrahydrofuran silacyclohexadiene adducts; however, these compounds were unstable and could not be purified by chromatography. The desired

bromide (117) appeared to be too labile to be obtained in this manner.

Failure to obtain bromide 117 led to attempts to generate the 2-diazosilacyclohexadiene system combining both the blocking strategy and the diazo transfer reaction. Again, the 4-trimethylsilylcyclohexadiene ring system 91 was utilized. The anion 116 was generated with *n*-butyllithium at 0°C. The anion was then added to a cold solution of THF and tosyl azide. The products of the reaction were again unexpected (Scheme 32). The trimethylsilyl group was removed and the only diazo compound obtained was the 4-diazosilacyclohexadiene 78. The other product was presumably trimethylsilyltosylamine 120, which was hydrolyzed to tosylamine and hexamethyldisiloxane.

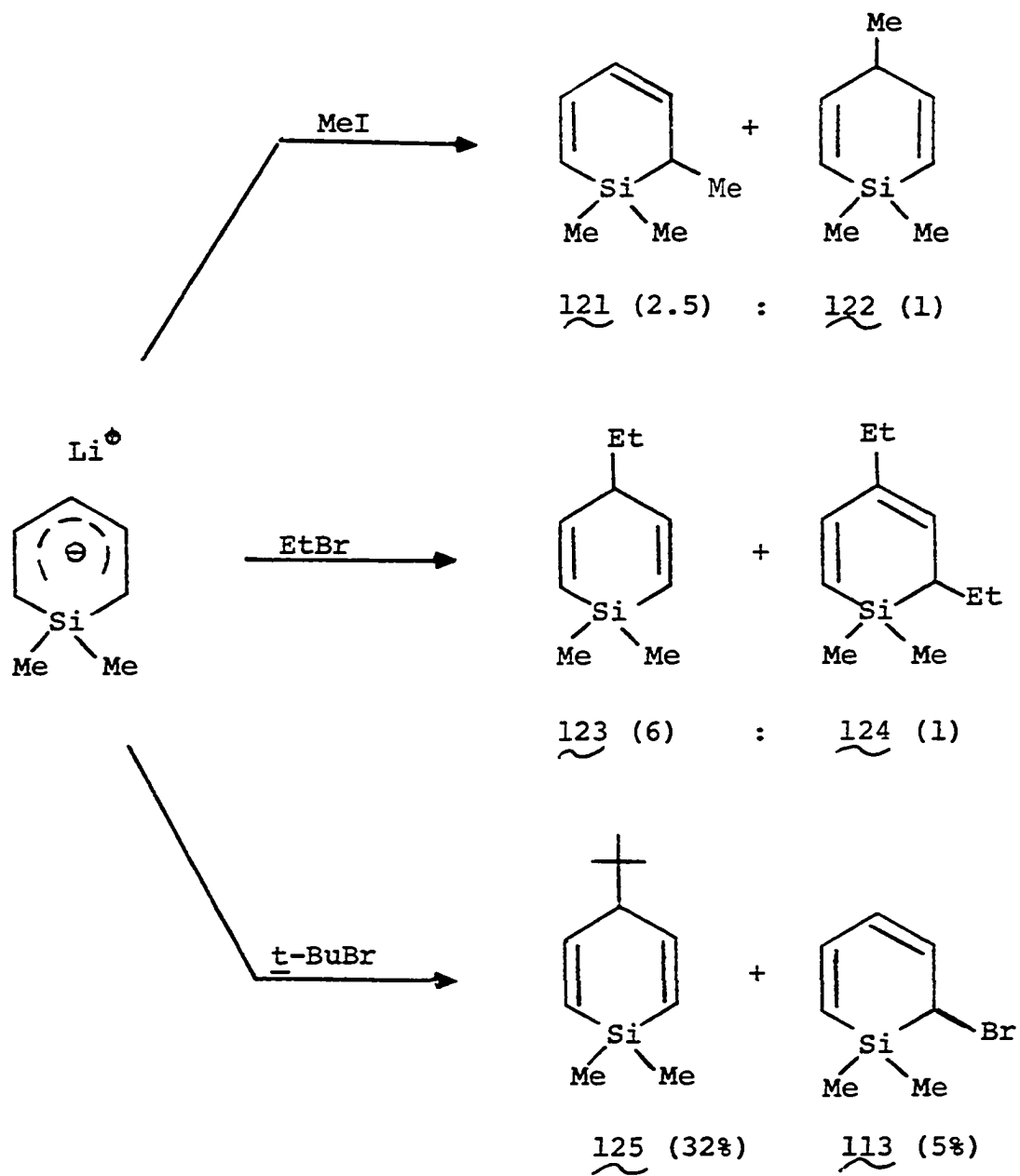
Scheme 32



The products could arise from capture of the anion by tosylazide in the 4-position, producing intermediate 119. This system then eliminates the anion of trimethylsilyl-tosylamine and the 4-diazo compound. The amine anion is protonated upon quenching with water. There was no indication of capture at the 2-position. It was now clear that the trimethylsilyl group was too labile to be a good blocking group. Therefore, a search for a suitable group was initiated.

Various alkylhalides were employed in the search for the best blocking group (Scheme 33). Methyl iodide trapped the anion in both the 2- and 4-position 121 and 122 in a 2.5:1 ratio. These products were encouraging for they showed the anion could indeed be trapped in the 2-position 121. However, because the methyl group has relatively little steric bulk and, due to the fact that the two isomers 121 and 122 could only be separated by preparative gas chromatography, larger alkyl halides were tried. Ethyl bromide improved the yield of the 4-blocked isomer 123, but was still complicated with the formation of a dialkylated product 124. The diethylsilacyclohexadiene 124 probably arises from formation of the blocked anion under the reaction conditions, followed by capture of this anion by a second ethylbromide. This was also encouraging for it showed that with the 4-position blocked, anion capture could proceed at the 2-position.

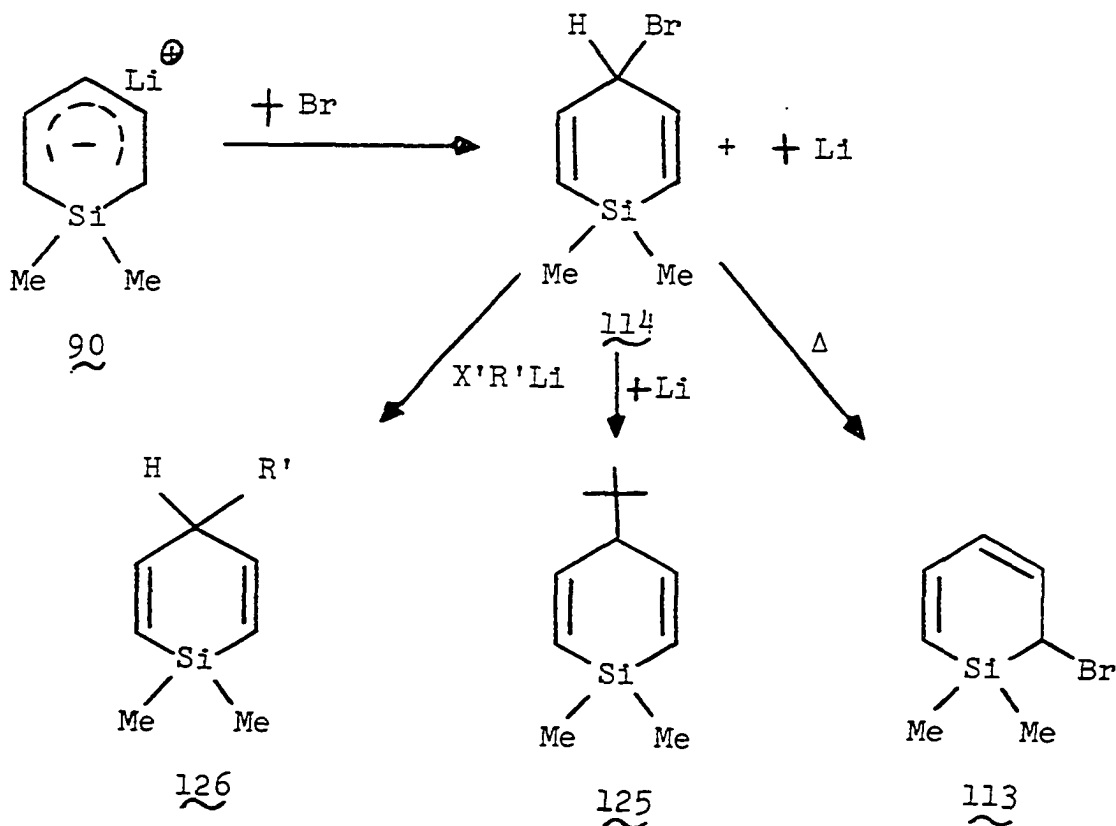
## Scheme 33





In an attempt to obtain an alkyl group, only in the 4-position the unlikely trap, t-butylbromide, was tried. The reaction produced a 32% yield of 4-t-butylsilacyclohexa-2,5-diene 125 (Figure 6), along with varying amounts of 2-bromo-silacyclohexadiene 114, which could occur from 4-bromo compound upon work-up. The reaction on the surface appears to be a displacement of bromide from a tertiary center. However, the formation of the 4-bromide 114 suggests that a lithium-halogen exchange occurs in the reaction (Scheme 34).

Scheme 34



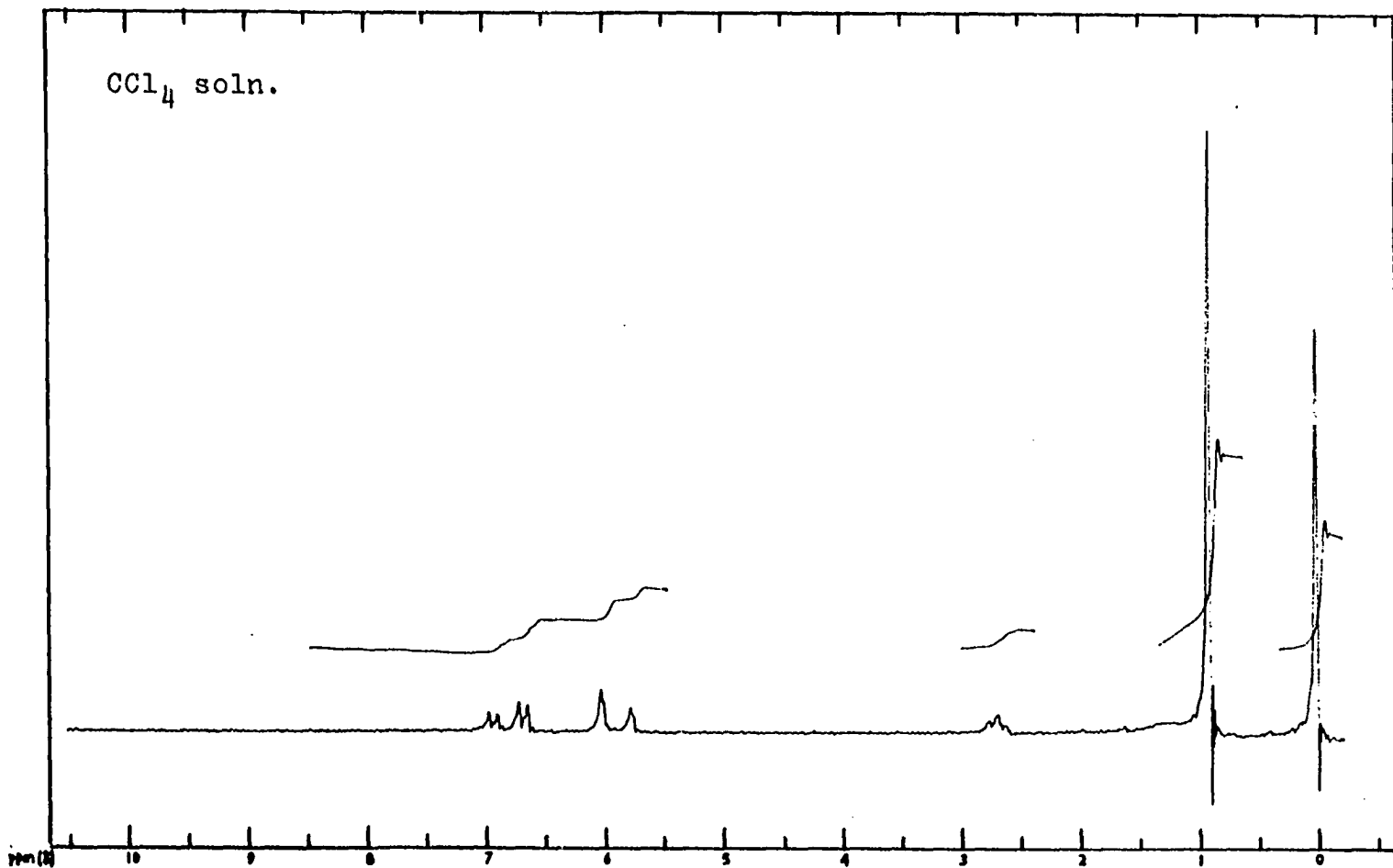
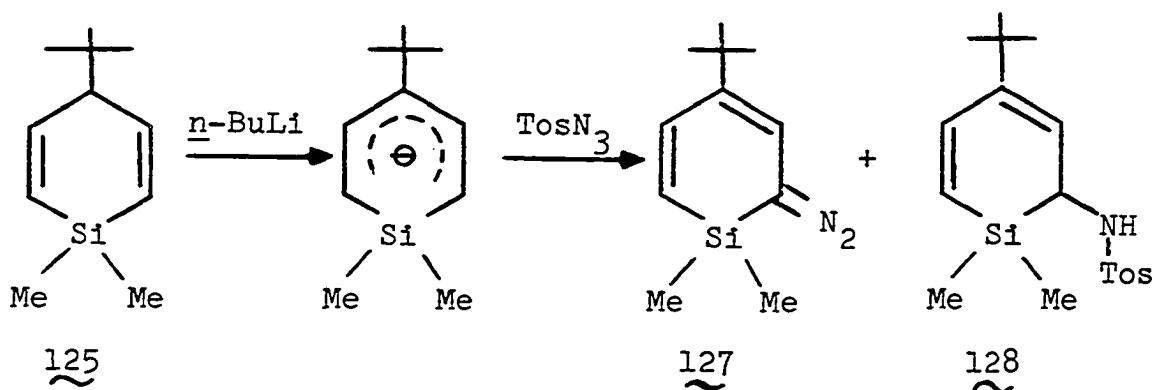


Figure 6. 60 MHz NMR spectrum of 1,1-dimethyl-4-t-butyl-1-silacyclohexa-2,5-diene (125)

In fact, when n-butyllithium is used to generate the original anion, two 4-blocked compounds are obtained, the 4-n-butyl and the 4-t-butylsilacyclohexadienes 126 ( $R'=\underline{n}\text{Bu}$ ) and 125. The 4-n-butyl system 126 is obtained by displacement of the intermediate bromide 114, by excess n-butyllithium. Only the 4-t-butyl compound is obtained when t-butyllithium is used to generate the original anion.

The 4-t-butylsilacyclohexadiene 125 fulfilled the requirements of the proper blocking group, it was sterically large and could not be easily removed. Thus, the diazo transfer reaction was attempted on the t-butyl system 125 (Scheme 35). A diazo compound was produced which showed a diazo band at  $2035\text{ cm}^{-1}$  in the IR. However, starting diene along with the tosylamine 128 were also present in the product mixture. The diazo compound 127 was very sensitive to heat

Scheme 35

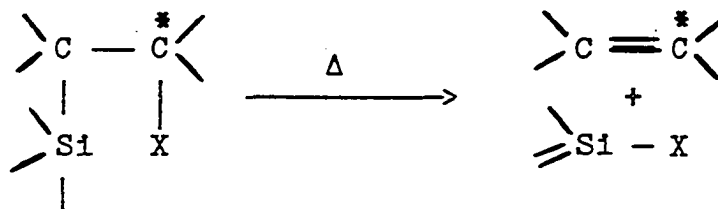


and light and unfortunately was not isolated after exhaustive attempts. Therefore, the question of whether an  $\alpha$ -carbene in the silacyclohexadiene ring system will rearrange to a silabenzene cannot be answered at this time.

The Synthesis and Pyrolysis of  
2,4-Bis-trimethylsilyl-1,1-dimethoxy-1-  
silacyclohexa-3,5-diene 133

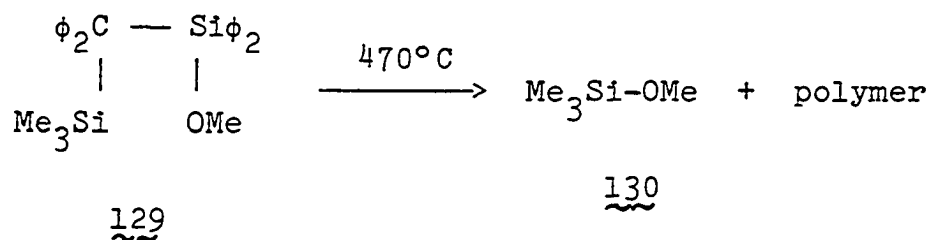
The facile decomposition of  $\beta$ -substituted organosilanes to give olefins and substituted silanes is a well-known reaction (139,140) (Scheme 36). Rutherford and Seideward (114) substituted the labeled carbon with silicon in an

Scheme 36



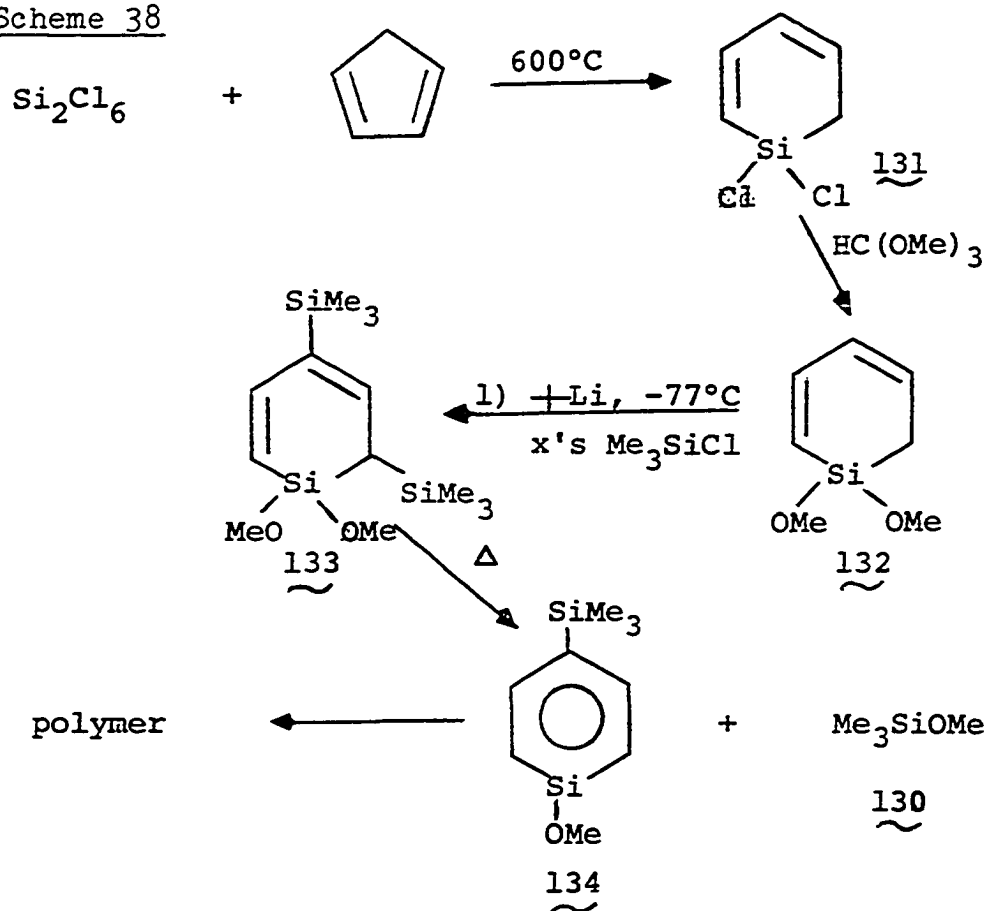
attempt to use this reaction in the formation of silenes. Unfortunately, when they pyrolyzed benzyldiphenylmethoxy-silane 129, they could only identify methoxytrimethylsilane 130 in the product mixture (Scheme 37). The remainder of

## Scheme 37



the product mixture was reported to be an unidentifiable polymeric material. Rutherford's rationale was adopted in a synthetic scheme directed toward silabenzene (Scheme 38).

## Scheme 38



The key step in this scheme is the pyrolytic elimination of methoxytrimethylsilane 130 from 2,4-bis-trimethylsilyl-1,1-dimethoxy-1-silacyclohexa-3,5-diene 133. Such an elimination requires the trimethylsilyl group and the methoxy group to be cis to one another in order for the formation of the necessary four-centered transition state to occur (141). Two methoxy groups were utilized so that the 2-trimethylsilyl group would always be properly aligned for this elimination.

This bis-trimethylsilyldimethoxysilacyclohexadiene ring was synthesized as shown in Scheme 38. Addition of dichlorosilylene to cyclopentadiene produced the dichlorosilacyclohexadiene 131 in 32% yield, as reported by Chernyshev et al., (130). The dichloride 131 was converted quantitatively to the dimethoxy system 132 upon treatment with trimethylorthoformate. The metalation of the dimethoxy compound was accomplished at  $-78^{\circ}\text{C}$  in the presence of excess trimethylchlorosilane with *t*-butyllithium. Use of two equivalents of the base resulted in the direct formation of the bis-trimethylsilyl system 133.

It is interesting to note that this system in the mass spectrum exhibits as the base peak the ion corresponding to the desired  $\beta$ -elimination, the ion of the silabenzene 134. Also present is a peak corresponding to an ion for methoxytrimethylsilane 130. The bis-trimethylsilyldimethoxysilacyclohexadiene 133 was pyrolyzed at various temperatures in

sealed NMR tubes. Pyrolysis required 200-220°C for 24 hours when either decalin or 1,2,4-trichlorobenzene were utilized as solvents. Analysis of the products always produced the same results, almost quantitative amounts of methoxytrimethylsilane were found along with a polymeric mess. All attempts to identify or purify the polymeric material were unsuccessful.

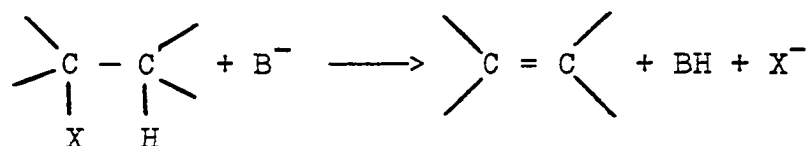
The fact that the elimination product methoxytrimethylsilane was formed indicated that the silabenzene 134 may have been formed. Vertical flow pyrolyses were carried out in an attempt to prevent the polymerization of the products. Complete reaction of the starting material required 450°C. The pyrolyses were carried out in both benzene-d-6 and without solvent. The results, again, showed almost quantitative formation of methoxytrimethylsilane along with polymer. A co-pyrolysis with benzophenone as a trap was tried. Again, formation of methoxytrimethylsilane was observed along with the same polymeric mixture. No evidence of benzophenone incorporation was found in the polymer.

The reaction of the bis-trimethylsilyldimethoxysilacyclohexadiene 133 may indeed produce a silabenzene species; however, as yet, the correct conditions for its observation have not been obtained. Addition of other traps, notably dienes and acetylenes, may prove to be the way to show the intermediacy of the silabenzene in this reaction.

Base Induced Eliminations as a Route  
to Silabenzene

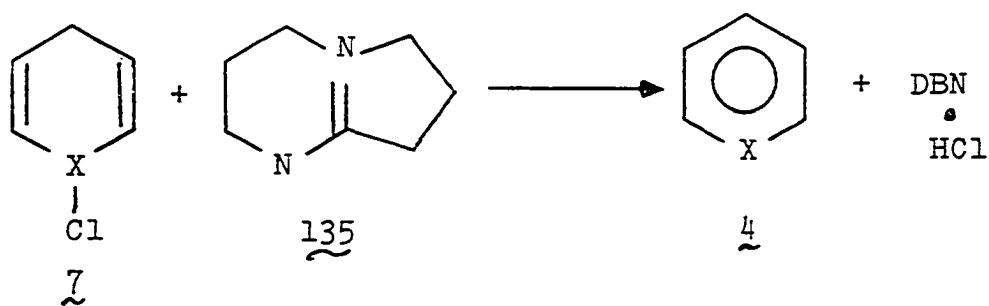
Olefins can be conveniently prepared by the base promoted  $\beta$ -elimination of hydrogen halides (142) (Scheme 39).

Scheme 39



Stibabenzene 4 (X = Sb) and bismabenzene 4 (X = Bi) have been prepared using a similar rationale (Scheme 40) (17). Ashe and co-workers (17) treat the corresponding heterochlorodiene 7 with the strong base diazobicyclo[4.3.0]non-5-ene 135.

Scheme 40



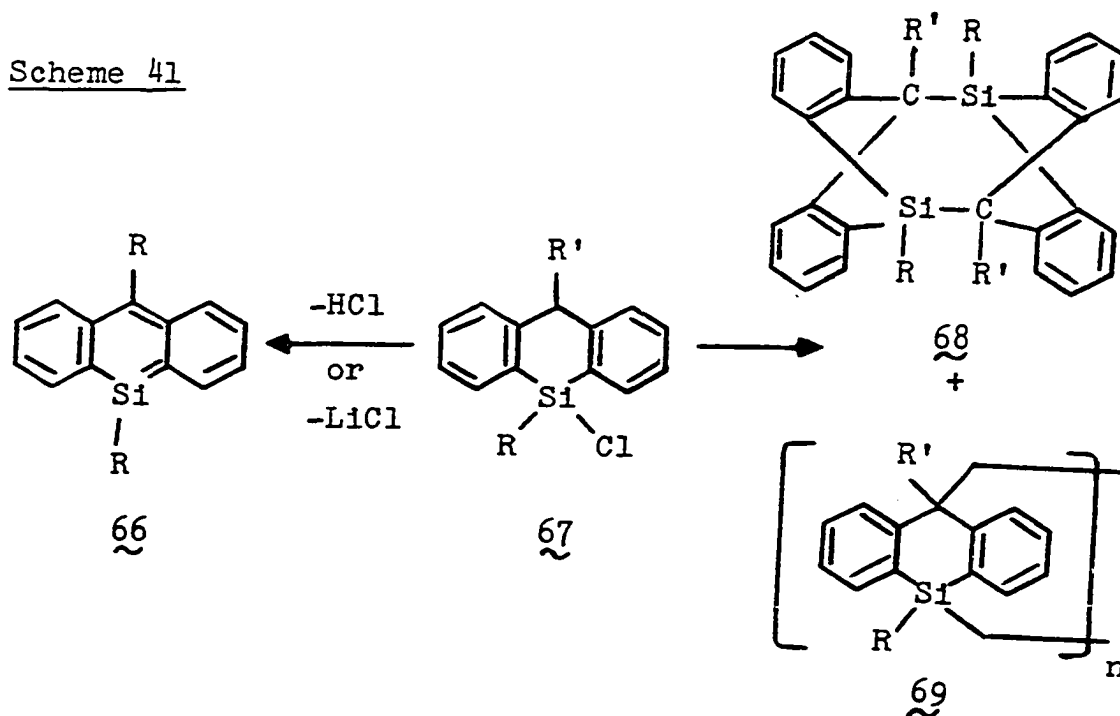
X = Sb, Bi

The base removes the hydrogen chloride yielding the heterobenzene 4.



The success of this type of reaction in producing heterobenzenes makes it very appealing as a potential route to silabenzene. In fact, there are two reports of attempts to obtain aromatic silicon species in this manner. The first involves the reaction of 9-chloro-9,10-dihydro-9-silaanthracene with alkyl lithiums (Scheme 41) (121,122,123).

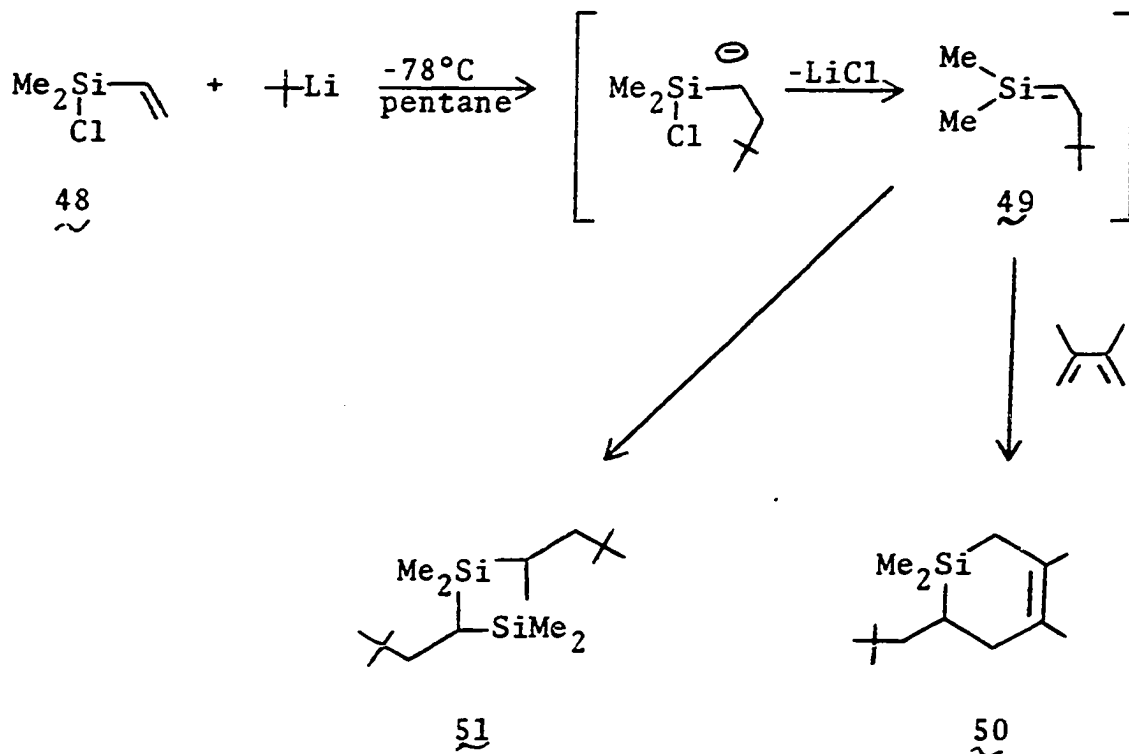
Scheme 41



Instead of the desired silaanthracene, the reaction produced dimer 68 and a polymeric substance, which the authors believe result from intermolecular substitution reactions of the silaanthracenyl anion. The second attempt is only mentioned in a review of hetero  $\pi$ -bonds by Jutzzi (12); it involves the attempted removal of hydrogen chloride from 1-chloro-1-methyl-1-silacyclohexa-2,4-diene. Quantitative loss of HCl is observed, however, no other products were identified.

The failure of these reactions to produce aromatic silicon species is not surprising when re-examined in view of the recent findings of Jones and Lim (111,112) (Scheme 42).

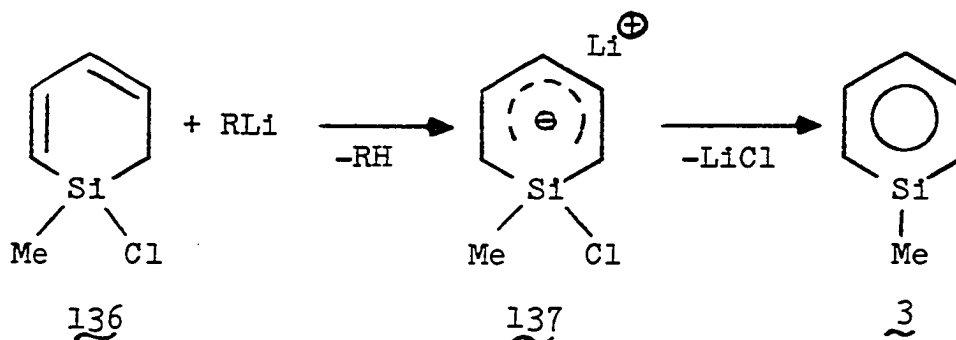
Scheme 42



They reported that the addition of t-butyllithium to vinyl-dimethylchlorosilane 48 resulted in products which could be attributed to silene 49 intermediacy. Formation of silene 49 is envisioned as occurring via the loss of lithium chloride from the anion obtained from t-butyllithium addition to olefin 48. This elimination of lithium chloride is very

similar to the elimination required to produce silabenzene 3 from the anion of 1-chloro-1-methyl-1-silacyclohexa-2,4-diene 137 (Scheme 43).

Scheme 43

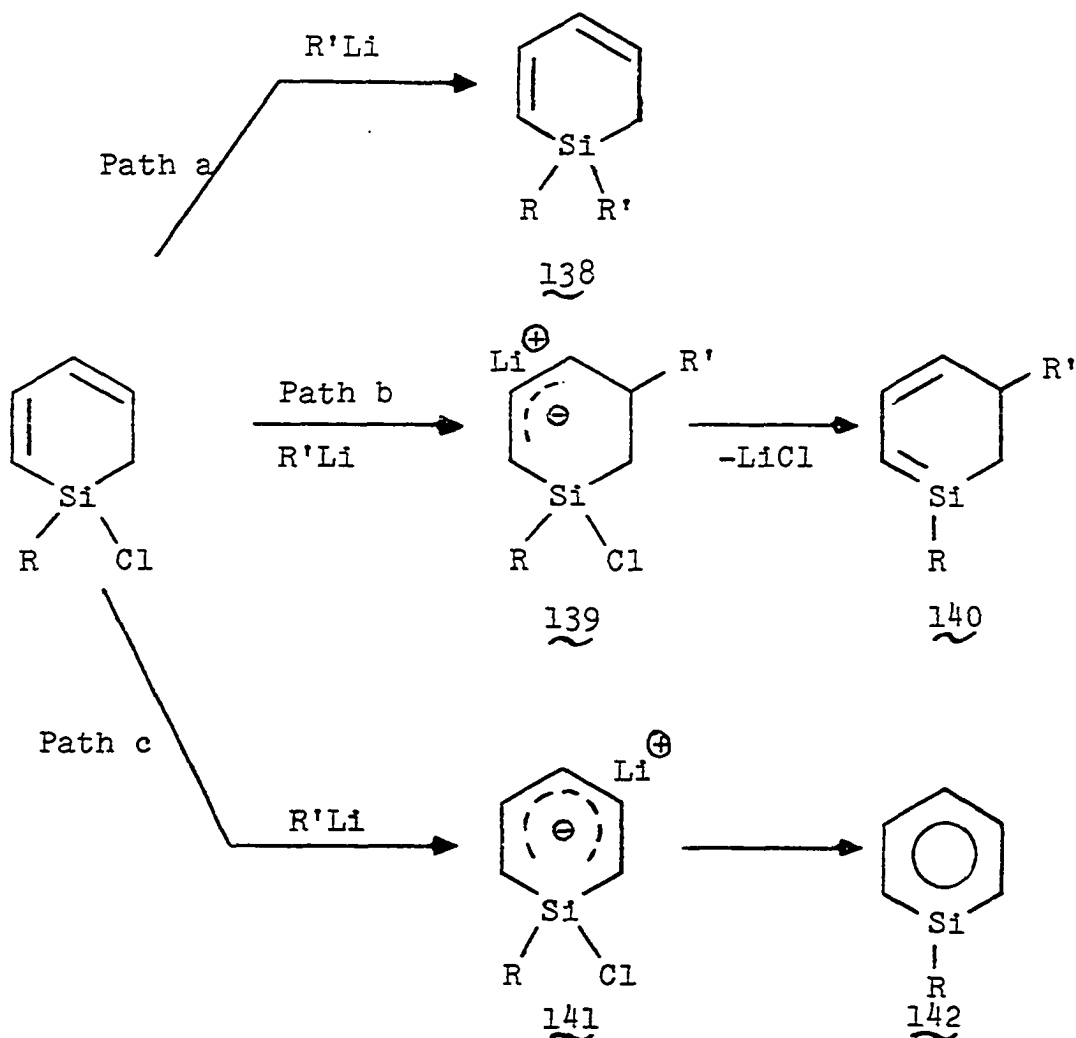


Interestingly, Jones and Lim (112) find the elimination occurs cleanly, at low temperatures, only in hydrocarbon solvents. Ether does work, but not as well, while tetrahydrofuran (THF) produces a complex mixture of products. All previous attempts to obtain aromatic silicon species from anionic eliminations have been performed in THF. Thus, the success of Jones and Lim in obtaining a silene intermediate in hydrocarbon solvents, demands a reinvestigation of the previous attempts at silabenzene.

The reaction of the chlorosilacyclohexadiene ring system with alkyl lithium has the potential of being a very complex reaction (Scheme 44). Three possible modes for reaction were envisioned. The first, displacement of the

silicon chloride by *t*-butyllithium would result in an alkyl-substituted silacyclohexadiene 138 (Path a, Scheme 44). The second mode involves nucleophilic addition of *t*-butyllithium to the  $\pi$ -system resulting in the formation of anion 139, which could eliminate lithium chloride, forming the conjugated silene 140 (Path b, Scheme 44). The addition of

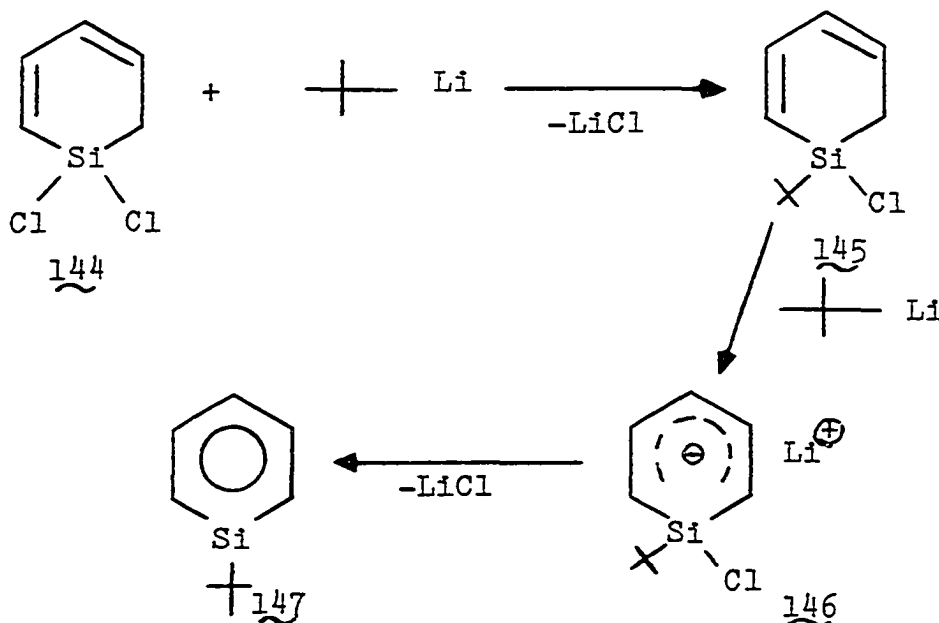
Scheme 44



alkyl lithiums to the diene system was not observed in the previous anion work involving dialkyl substituted silacyclohexadienes. The third mode, formation of silacyclohexadienyl anion 141, by abstraction of a proton, is the desired reaction. Loss of lithium chloride from anion 141 would result in the formation of silabenzene 142 (Path c, Scheme 44).

Consideration of these possibilities led to the choice of 1,1-dichloro-1-silacyclohexa-2,4-diene 144 as the system of study. Attack of *t*-butyllithium at silicon would be expected to occur only once (Scheme 45). A second displacement at silicon should not occur for steric reasons.

Scheme 45



Nucleophilic addition to the  $\pi$ -system was not expected, largely due to the fact that it had not occurred in dialkylsilacyclohexadiene systems. Therefore, reaction of dichlorodiene 144 with two equivalents of t-butyllithium should, after initial displacement of one chloride 145, result in the abstraction of a proton 146 and, hopefully, loss of lithium chloride will produce silabenzene 147 (Scheme 45).

Co-pyrolysis of hexachlorodisilane and cyclopentadiene produced dichlorocyclohexadiene 144 in 25% isolated yield, following the procedure of Chernyshev et al. (130). Dichloride 144 was obtained in a pure form immediately prior to use by preparative gas chromatography. It was dissolved in dry pentane and cooled to  $-77^{\circ}\text{C}$  under a nitrogen atmosphere. The t-butyllithium was added through a septum by syringe. No reaction was apparent at  $-77^{\circ}\text{C}$ , but, upon warming, a white precipitate began to form near  $-20^{\circ}\text{C}$ . The solid was presumably lithium chloride. With warming to room temperature, the mixture turned a tan color. Filtration, followed by solvent removal, left a viscous oil.

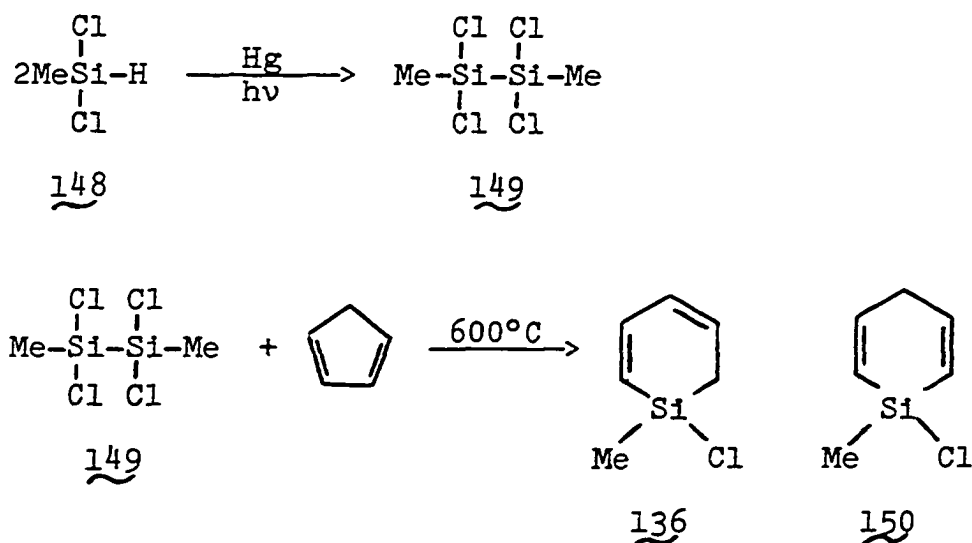
NMR indicated no starting material remained in the oil, t-butyl had been incorporated into the products, and the majority of the olefin absorptions had disappeared. The oil rapidly turned into a polymeric glass, which would not melt up to  $350^{\circ}\text{C}$ . The sample was not sufficiently volatile to obtain a mass spectrum. The reaction was repeated with

perfluoro-2-butyne being added after addition of t-butyllithium, in an attempt to trap any intermediates. The results were essentially the same. However, in this case, products derived from a reaction between the base and butyne were also present.

All the results in these reactions indicate that the t-butyllithium had attacked both at silicon and the  $\pi$ -system. If any proton abstraction occurred, it was masked by the other reactions.

Failure of 1,1-dichloro-1-silacyclohexadiene 144 to produce any conclusive results led to the investigation of the 1-chloro-1-methyl-1-silacyclohexadiene 136 (NMR, Figure 7). It was obtained from the co-pyrolysis of 1,1,2,2-tetrachloro-1,2-dimethyldisilane 149 and cyclopentadiene at ca. 600°C (Scheme 46) (65). Both the conjugated 136 and

Scheme 46



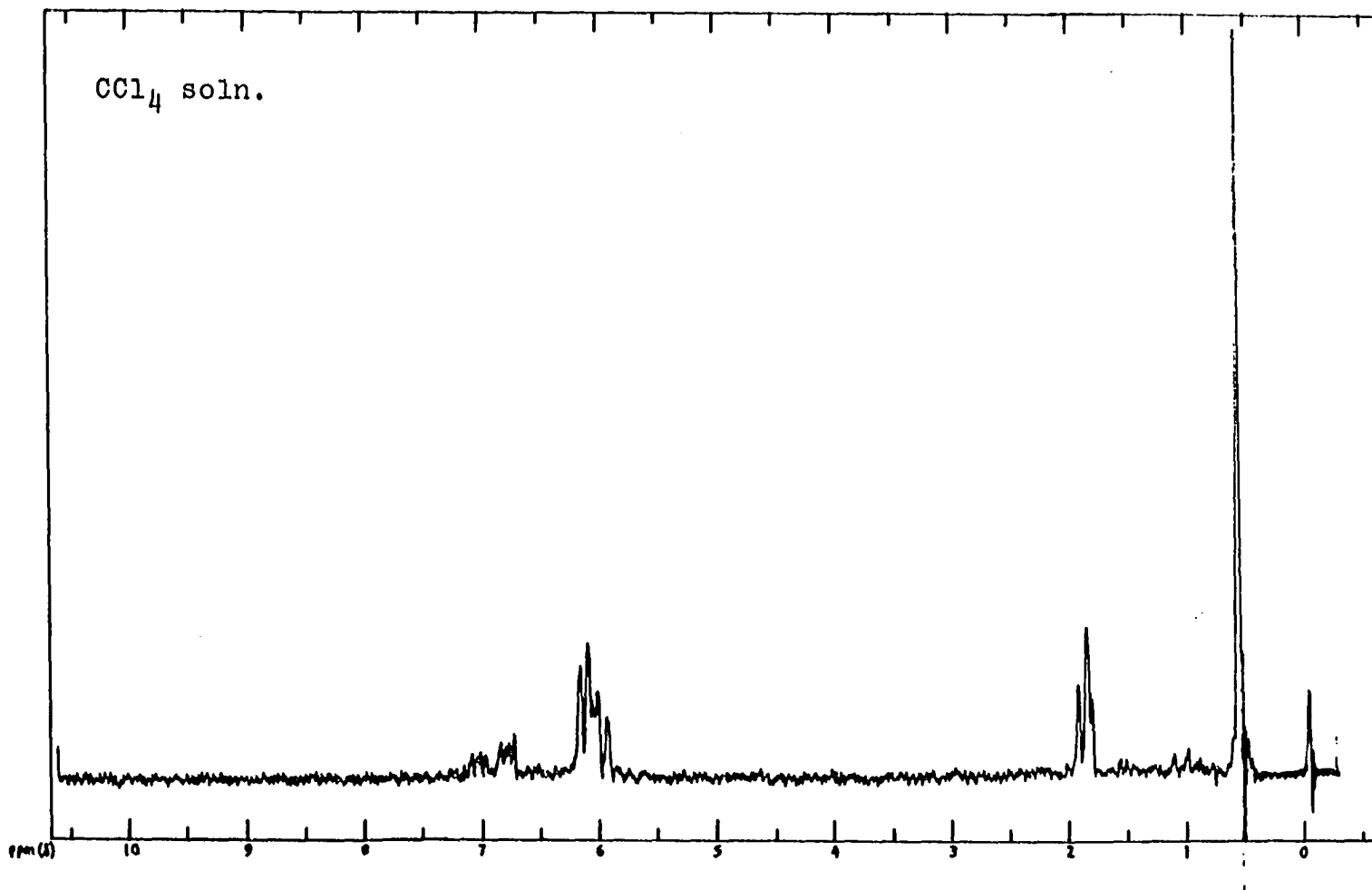
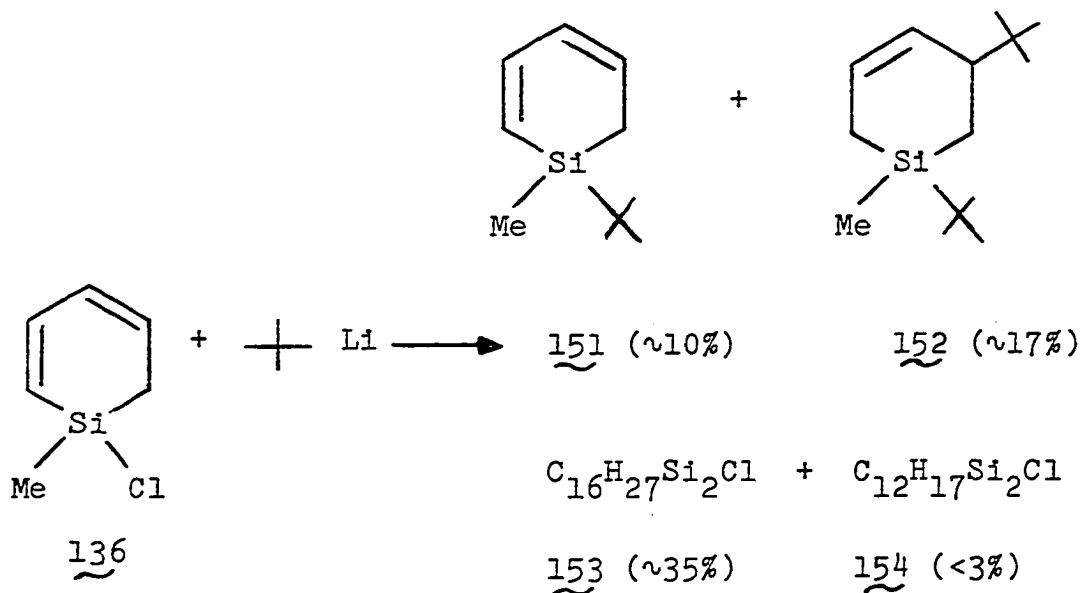


Figure 7. 60 MHz NMR spectrum of 1-chloro-1-methyl-1-silacyclohexa-2,4-diene  
(136)



unconjugated 150 isomers were obtained and could be separated by gas chromatography (65). The tetrachlorodisilane 149 was conveniently prepared by the mercury-photosensitized coupling of methylchlorosilane 148. In all reactions to follow, chlorosilacyclohexadienes 136 and 150 were always obtained immediately prior to use by preparative gas chromatography. This procedure was used to insure no hydrolysis of the chlorosilane had occurred prior to reaction.

Following the reaction conditions of Jones and Lim (112), chlorosilacyclohexadiene 136 was dissolved in dry pentane under nitrogen at  $-77^{\circ}\text{C}$ . The t-butyllithium was syringed into the flask and the reaction mixture was allowed to warm slowly. The order of addition of the reagents had no effect on the outcome of the reaction. A yellow color, along with a white precipitate, formed at  $-30^{\circ}\text{C}$ . Further warming intensified the yellow color and increased the amount of white solid. After allowing the mixture to stir at room temperature for an hour, excess methyl iodide was injected into the mixture to quench any anions which may have been present. In this, and in all succeeding cases, no incorporation of methyl was found. Filtration of the mixture yielded the white solid, lithium chloride, and a yellow oil. Analysis of the yellow oil by gas chromatography showed the reaction had produced a complex, but interesting array of products (Scheme 47).

Scheme 47

As was feared, *t*-butyllithium appears to have reacted with the chlorosilacyclohexadiene ring in the three ways previously considered (Scheme 44). The major products, 1,5-di-*t*-butyl-1-methyl-1-silacyclohex-3-ene **152** (NMR, Figure 8), and a mixture of isomers **153** having the molecular formula  $\text{C}_{16}\text{H}_{27}\text{Si}_2\text{Cl}$  (NMR, Figure 9), appear to be the result of nucleophilic addition of *t*-butyllithium to the  $\pi$ -system. However, in the case of 1,5-di-*t*-butyl-1-methyl-1-silacyclohex-3-ene **152**, it cannot be determined whether displacement of chloride from **136**, followed by addition of *t*-butyllithium to the  $\pi$ -system is the source of **152** (Path a, Scheme 48), or if **152** results from addition of

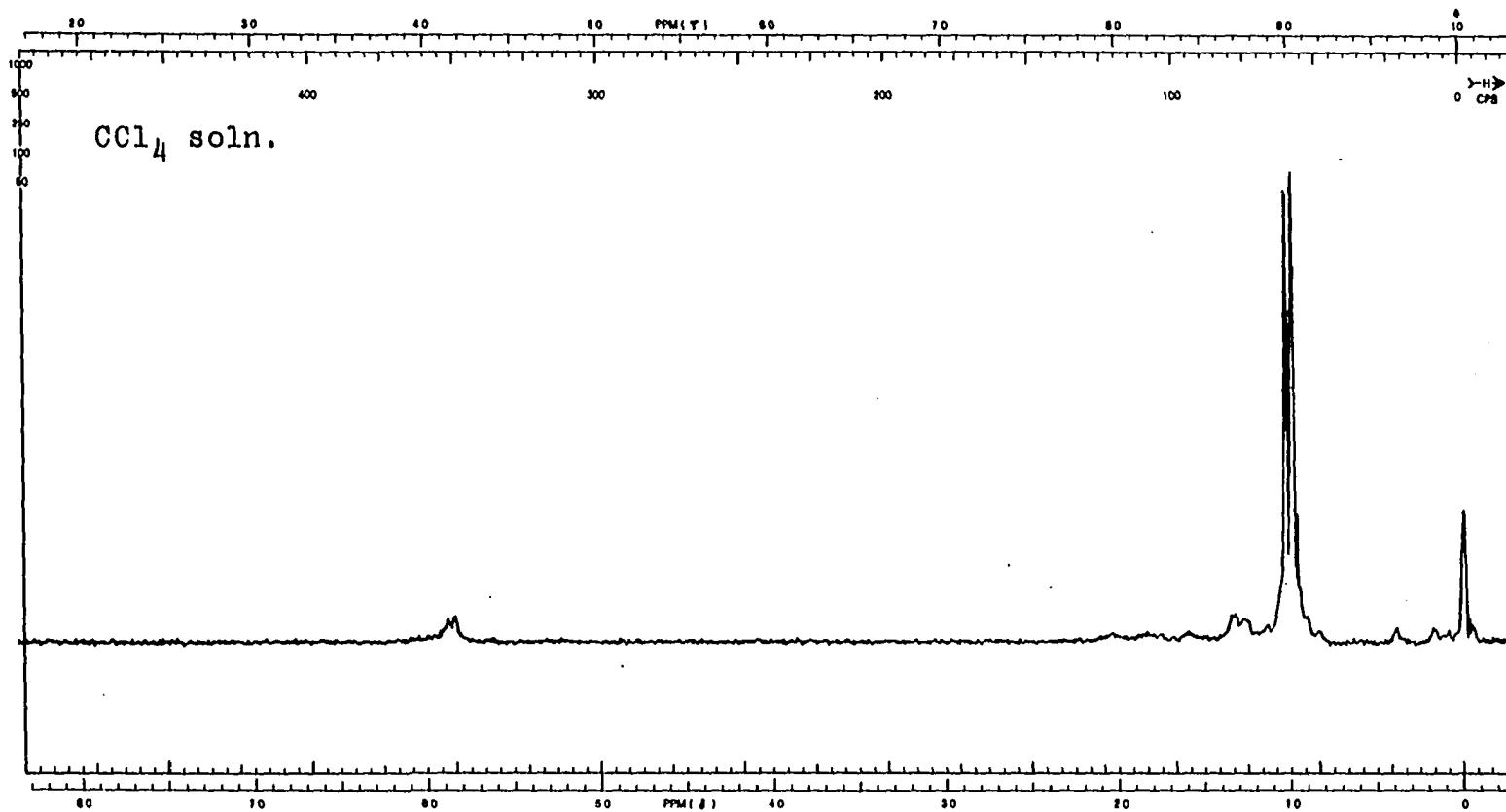


Figure 8. 60 MHz NMR spectrum of 1,5-di-*t*-butyl-1-methyl-1-silacyclohex-3-ene (152)

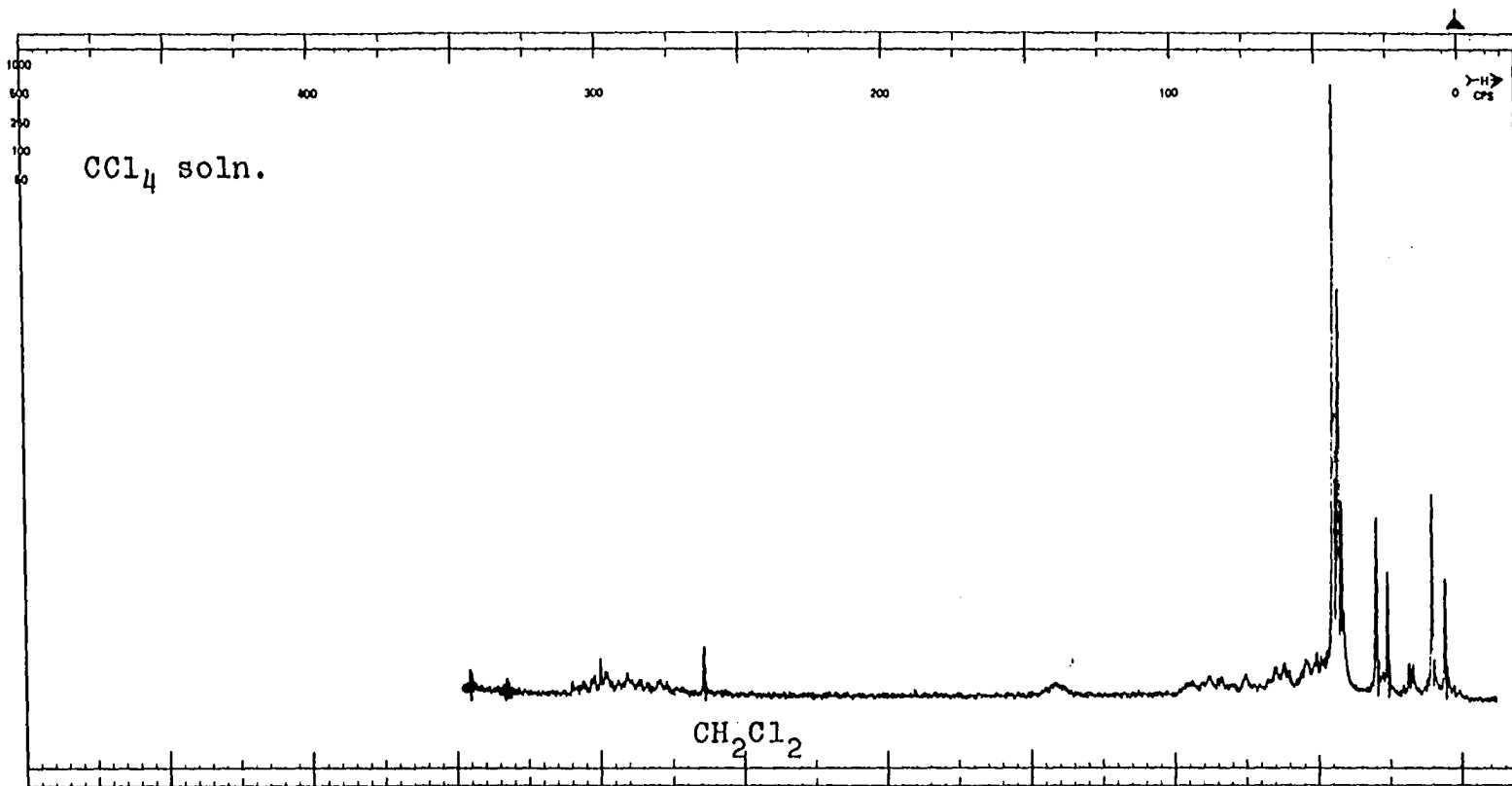
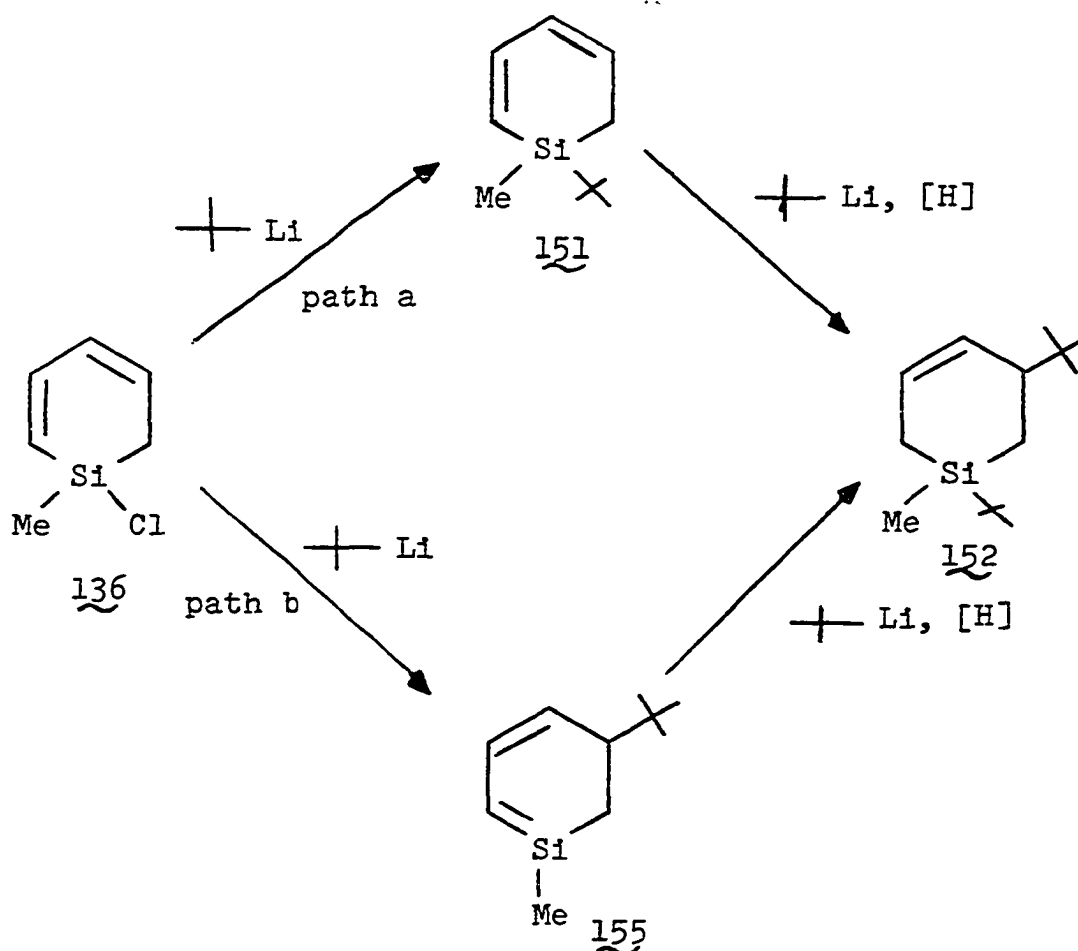


Figure 9. 100 MHz NMR spectrum of a mixture of  $C_{16}H_{27}Si_2Cl$  (153) isomers

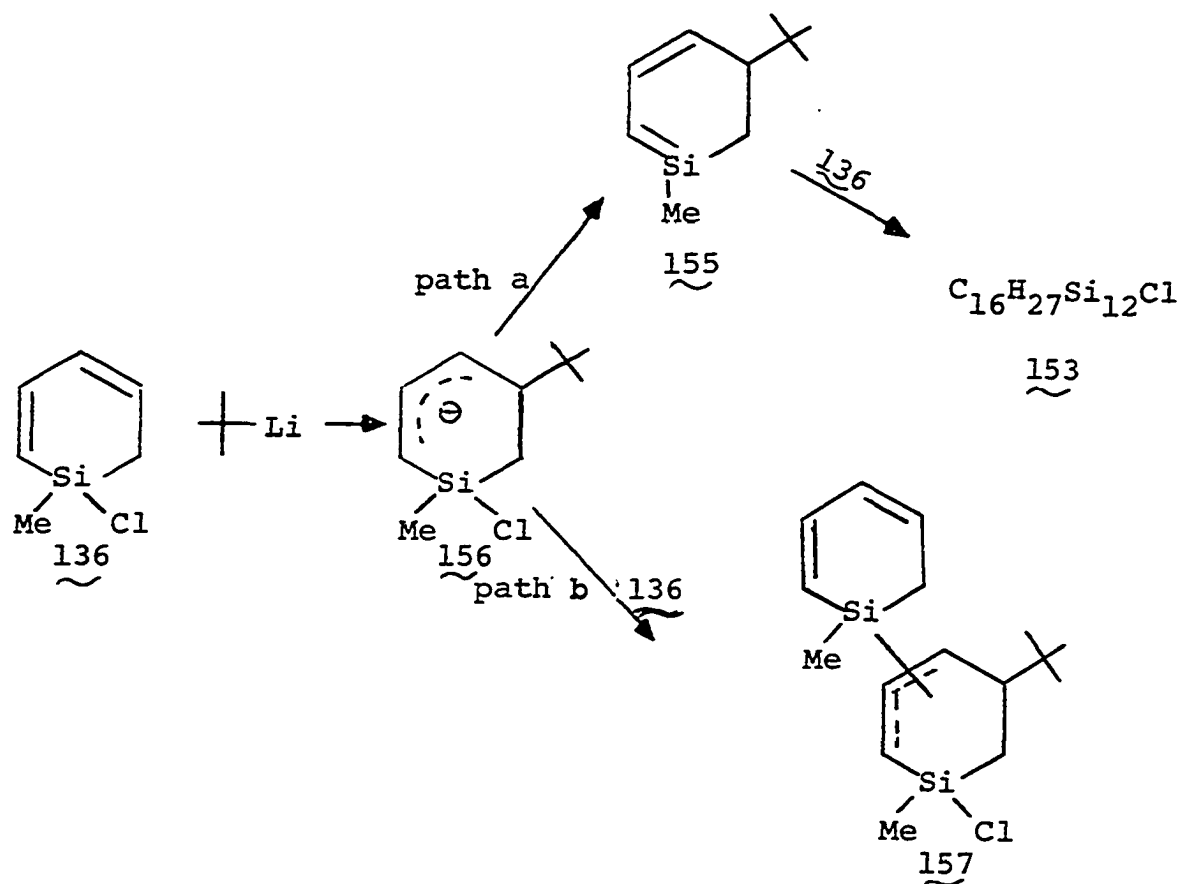
t-butyllithium across the silicon-carbon double bond of silene 155 (Path b, Scheme 48). A significant percentage,

Scheme 48



30-40%, of the product mixture has the correct mass (310.1333 measured, 310.1340 calculated for  $\text{C}_{16}\text{H}_{27}\text{Si}_2\text{Cl}$ ) for either an interaction of silene 155 with starting material (Path a, Scheme 49), or an attack of anion 156 on the silicon of the starting chlorodiene 136 yielding 157a and 157b (Path b, Scheme 49). The reaction was

## Scheme 49



repeated in the presence of a ten-fold excess of trimethylchlorosilane and although the yields are decreased slightly, the ratios of the products remained unchanged. Anion 156 was not intercepted by the trimethylchlorosilane indicating that Path b (Scheme 49) is not operative. This conclusion is based on the fact that, for 157 to form, the anion 156 must attack the silicon halogen bond of the starting material. Since no attack on trimethylchlorosilane occurred when it was present in a ten-fold excess, it seems highly

unlikely that anion 156 attacked the starting silyl halide 136. Thus, products having molecular weight of 310 most likely arise from an interaction of silene 155 and chlorosilane 136.

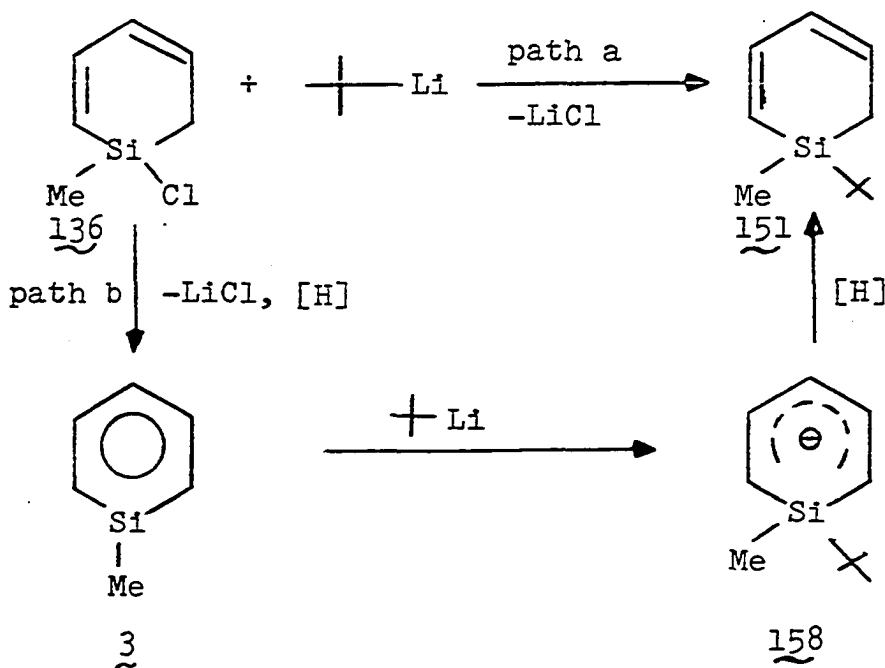
GCMS of the fractions containing mass 310 indicate that a mixture of isomers is present. NMR (Figure 9) confirms this in that the region from 0.0  $\delta$  to 0.8  $\delta$  shows at least four different silylmethyls. The shift of the silylmethyls at 0.4 and 0.5  $\delta$  is indicative of silicon bearing chlorine, while the methyls closer to 0  $\delta$  are probably on silicons bearing only carbon. Integration of the mixture gives the correct number of hydrogens (4 olefinic, 17 aliphatic, and 6 silylmethyl) for a product arising from an interaction between silene 155 and chlorosilacyclohexadiene 136 that destroys two  $\pi$ -bonds. However, the complexity of the NMR spectrum of this mixture does not provide a clue as to the exact nature of the products. Attempts to form the beta-naphthol silyl ether of the adduct with the hope of obtaining a crystalline material, have proven unsuccessful.

Examination of the possible ways in which silene 155 and chlorosilacyclohexadiene 136 can react does not help clarify the situation as there are numerous manners for the two systems to interact. Silene 155 and chlorosilacyclohexadiene 136 have the potential of behaving both as dienes and dieneophiles in Diels-Alder reactions with one another.

Furthermore, silene 155 can react with chlorosilacyclohexadiene 136 in a number of (2+2) cycloaddition reactions. All of these reactions can also produce a large number of stereoisomers. Thus, with the information in hand, the structure of 153 cannot be determined.

In addition to the large amount of products arising from *t*-butyllithium addition to the  $\pi$ -system of chlorosilacyclohexadiene 136, 10% of 1-*t*-butyl-1-methyl-1-silacyclohexa-2,4-diene 151 is also produced (NMR, Figure 10). This presumably arises from nucleophilic displacement of chloride at silicon by *t*-butyllithium (Path b, Scheme 50). However,

Scheme 50





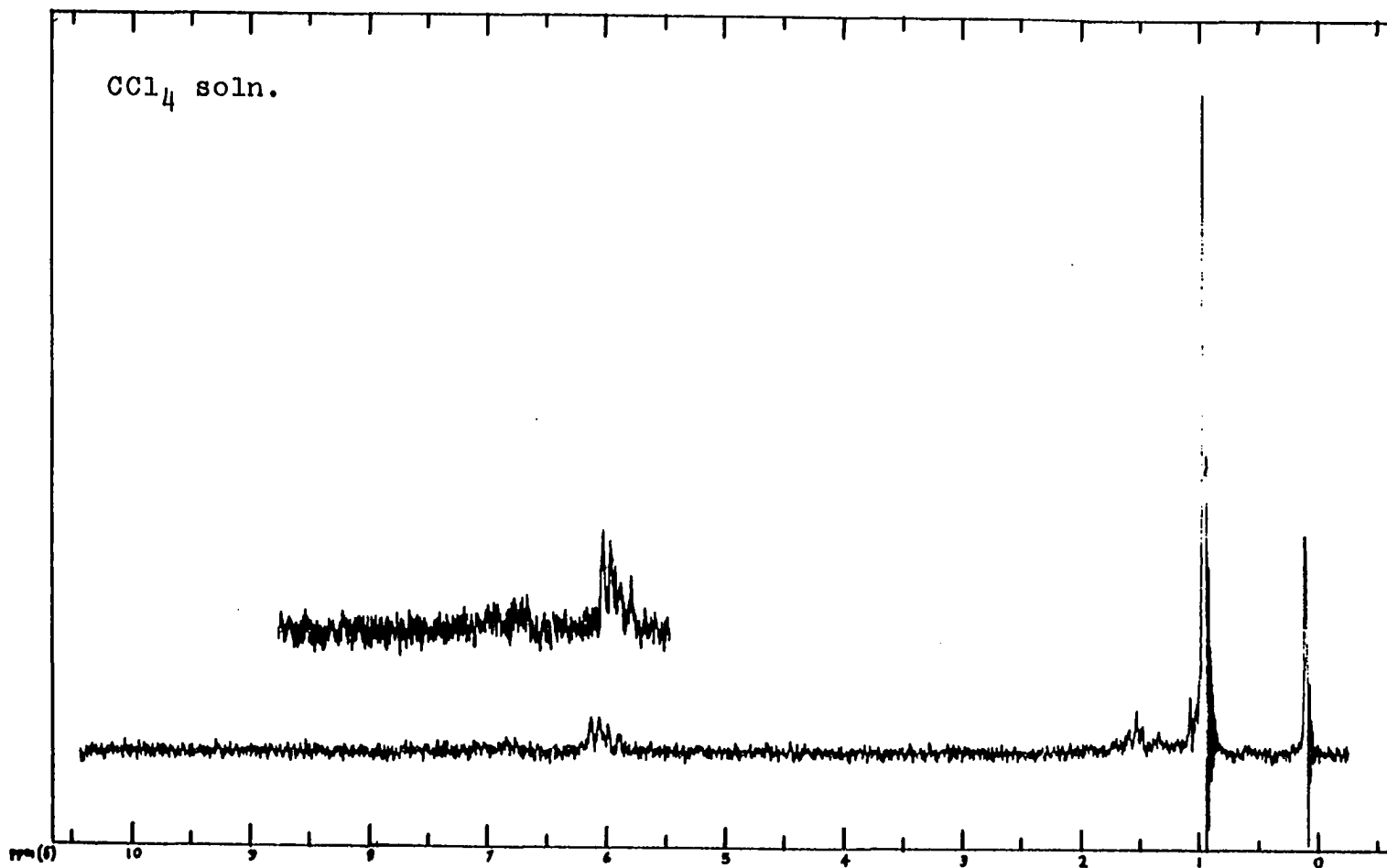
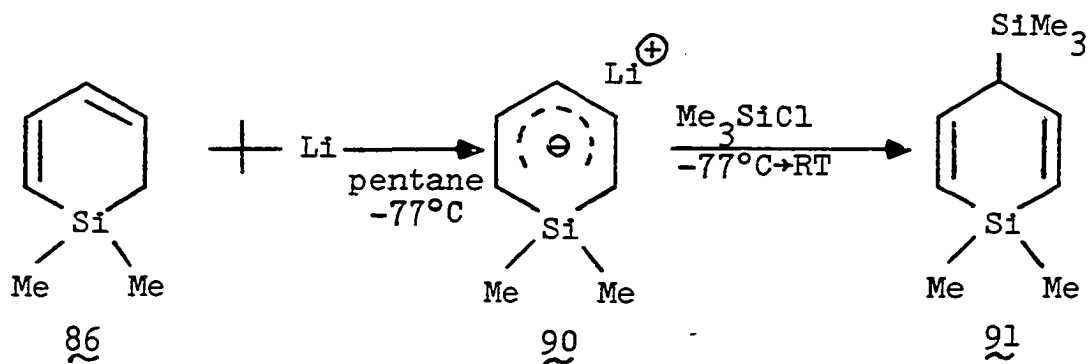


Figure 10. 60 MHz NMR spectrum of 1-t-butyl-1-methyl-1-silacyclohexa-2,4-diene (151)

there is a possibility that this product results from the addition of *t*-butyllithium to silabenzene 3 (Path b, Scheme 50). Again, the lack of any incorporation of methyl or trimethylsilyl groups upon addition of the corresponding halides to the reaction mixture, tends to rule out any long-lived anionic intermediates. Further arguments against anion 158 are found in the reaction of 1,1-dimethyl-1-silacyclohexa-2,5-diene 86 with *t*-butyllithium under the same reaction conditions, in the presence of excess trimethylchlorosilane. This reaction produces 4-trimethylsilyl-1,1-dimethyl-1-silacyclohexadiene 91 in 45% yield (130) (Scheme 51). Interestingly, no evidence of *t*-butyl addition to the  $\pi$ -system is found in this reaction. Thus, anion 90, which is

Scheme 51

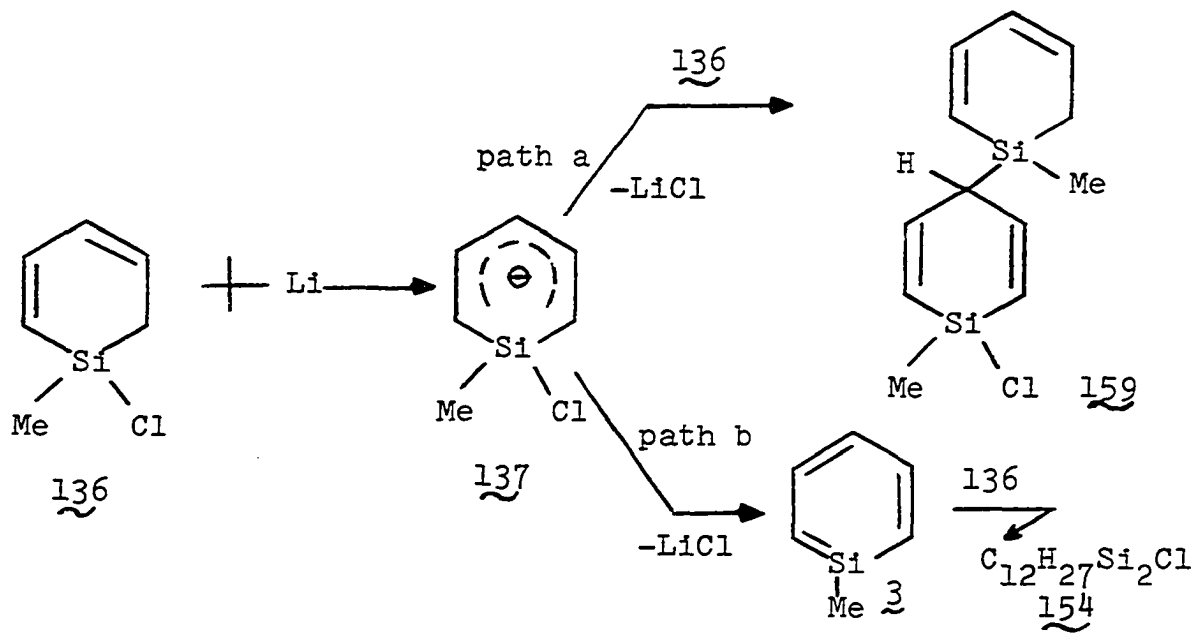


similar to anion 158, is trapped by trimethylchlorosilane under identical reaction conditions. Since no trapped anion 158 is found, it appears that anion 158 is not a precursor

of diene 151. Thus, t-butyl-1-methyl-1-silacyclohexa-2,4-diene 151 is apparently the result of t-butyl displacement of chloride from the starting material.

Although the majority of the products of this reaction (Scheme 47) are derived from pathways which do not involve silabenzene intermediates, there is a minor product, 154, which may require the formation of silabenzene 3. The product has a parent molecular ion of 252.9588 (measured), which fits well for a molecular formula of  $C_{12}H_{17}Si_2Cl$  (252.9558 calculated). This weight corresponds to a combination of one molecule of silabenzene 3 and one molecule of 1-chloro-1-methylsilacyclohexa-2,4-diene 136 (Path b, Scheme 52). However, the same molecular weight can be obtained from a nucleophilic displacement of anion 137 on

Scheme 52





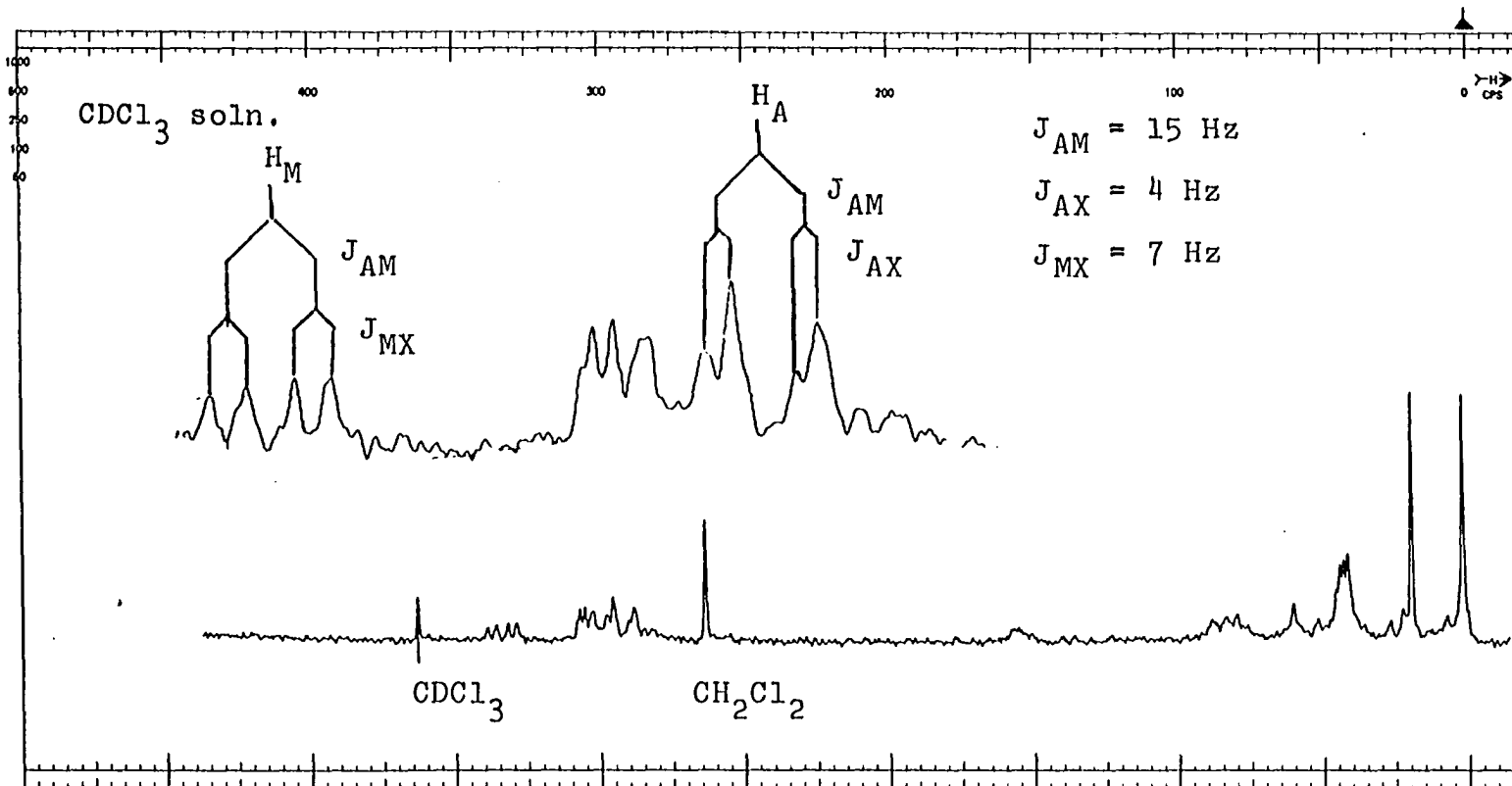
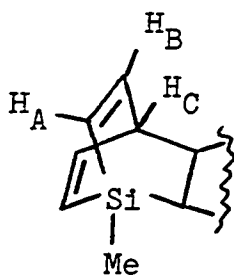
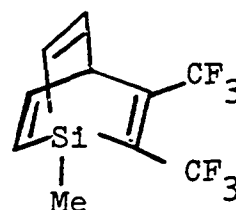


Figure 11. 100 MHz NMR spectrum of the Diels-Alder adduct of silabenzene and chlorosilacyclohexadiene (136)

The key feature is found in the splitting pattern of the olefin region (Expansion, Figure 11). The presence of two doublet of doublets centered at  $6.65 \delta$  ( $H_A$ ,  $J_{AB} = 7.5 \text{ Hz}$ ,  $J_{AC} = 2 \text{ Hz}$ ) and at  $5.85 \delta$  ( $H_B$ ,  $J_{BC} = 3.5 \text{ Hz}$ ), and a multiplet at  $3.15 \delta$  (Figure 11), strongly indicate the bicyclic portion of the adduct is of type 160. A similar type of AMX

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pattern is found in 2,3-bis-(trifluoromethyl)-1-methyl-1-silabicyclo[2.2.2]octa-2,5,7-triene 162 (Figure 15).

Unfortunately, there are a total of eight possible adducts of type 160 and these cannot be distinguished from one another at this time. Thus, although the true nature of the adduct is not known, it does appear that silabenzene 3 has reacted in a [4+2] manner.

The reaction of *t*-butyllithium with 1-chloro-1-silacyclohexa-2,4-diene was not affected by dilution, the adducts of the intermediate silene 155 and silabenzene 3 are still observed. Furthermore, no evidence was found for the dimer of either of these intermediates. This is quite surprising, especially considering that silenes are known

to dimerize quite readily. The lack of dimers may be due to the fact that both silabenzene 3 and silene 155 are conjugated systems. The few conjugated silenes (81→85) that have been studied do react in (2+4) manner rather than a [2+2] mode. However, because the structures of adducts 154 and 153 are not fully characterized, this analysis is largely conjecture and there cannot be further comments at this time.

The above reaction was repeated in the presence of excess butadiene in an attempt to trap the intermediates, silabenzene 3 and silene 155. The products previously observed in the reaction were completely eliminated. Instead, only one major product was now observed. This product had a parent molecular ion of 220.1633 (measured) which fits well for  $C_{14}H_{24}Si$ , (220.1647 calculated). The empirical formula is correct for a silene (155)-butadiene adduct. The reaction was repeated with butadiene and a ten-fold excess of trimethyl chlorosilane to verify that the adduct was not the result of an anionic intermediate. The yield of the adduct was decreased from 65% to 20% and a new product was observed. This product was identified as trans-1-trimethylsilyl-5,5-dimethylhex-2-ene 164 (NMR, Figure 12). This product is the trimethylsilyl trap of anion 163, produced by addition of *t*-butyllithium to butadiene (Scheme 54). Comparison of the NMR of 164 (Figure 12) and adduct 165 (Figure 13) show striking similarities. In

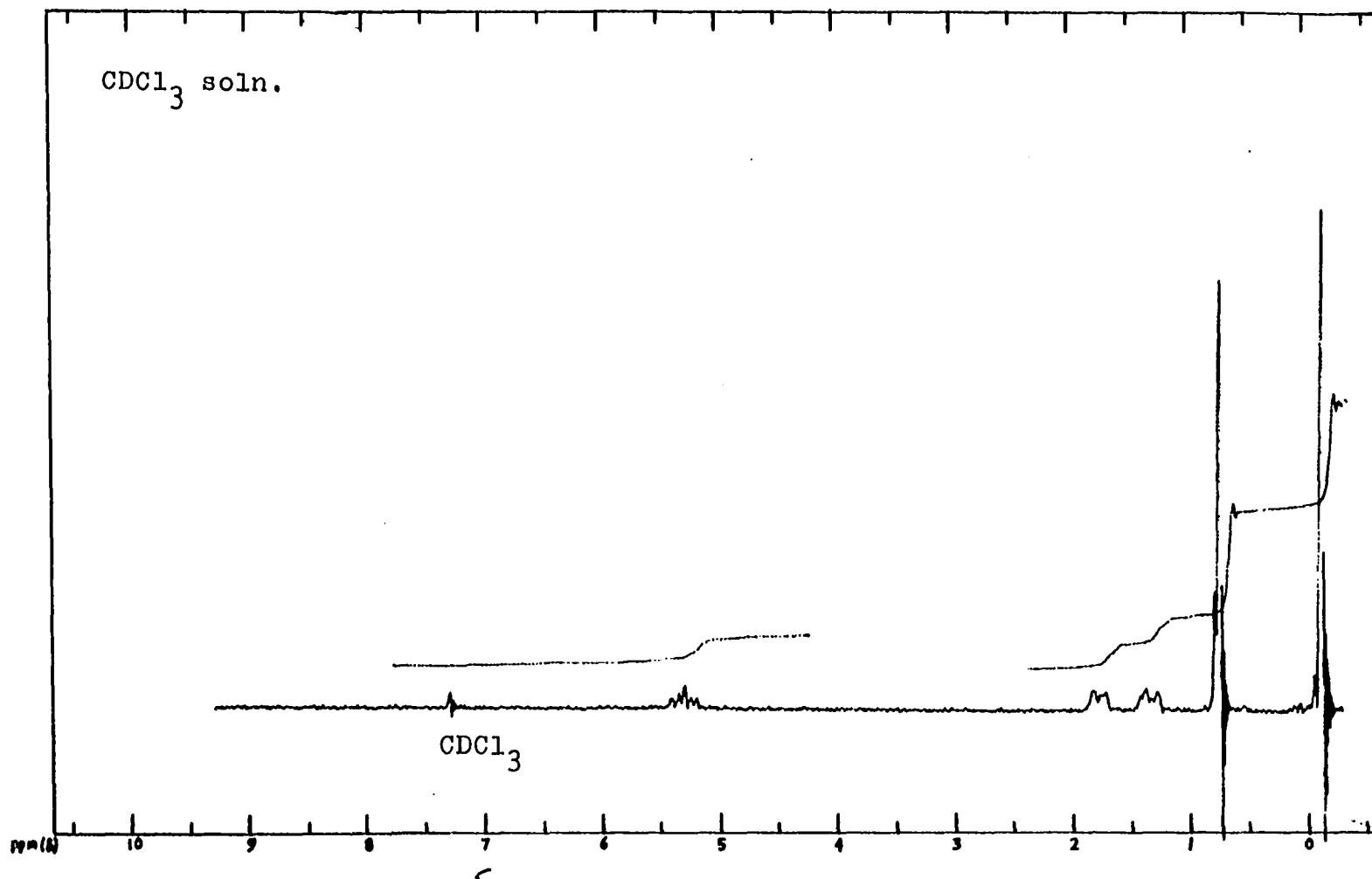


Figure 12. 60 MHz NMR spectrum of trans-1-trimethylsilyl-5,5-dimethylhex-2-ene (164)



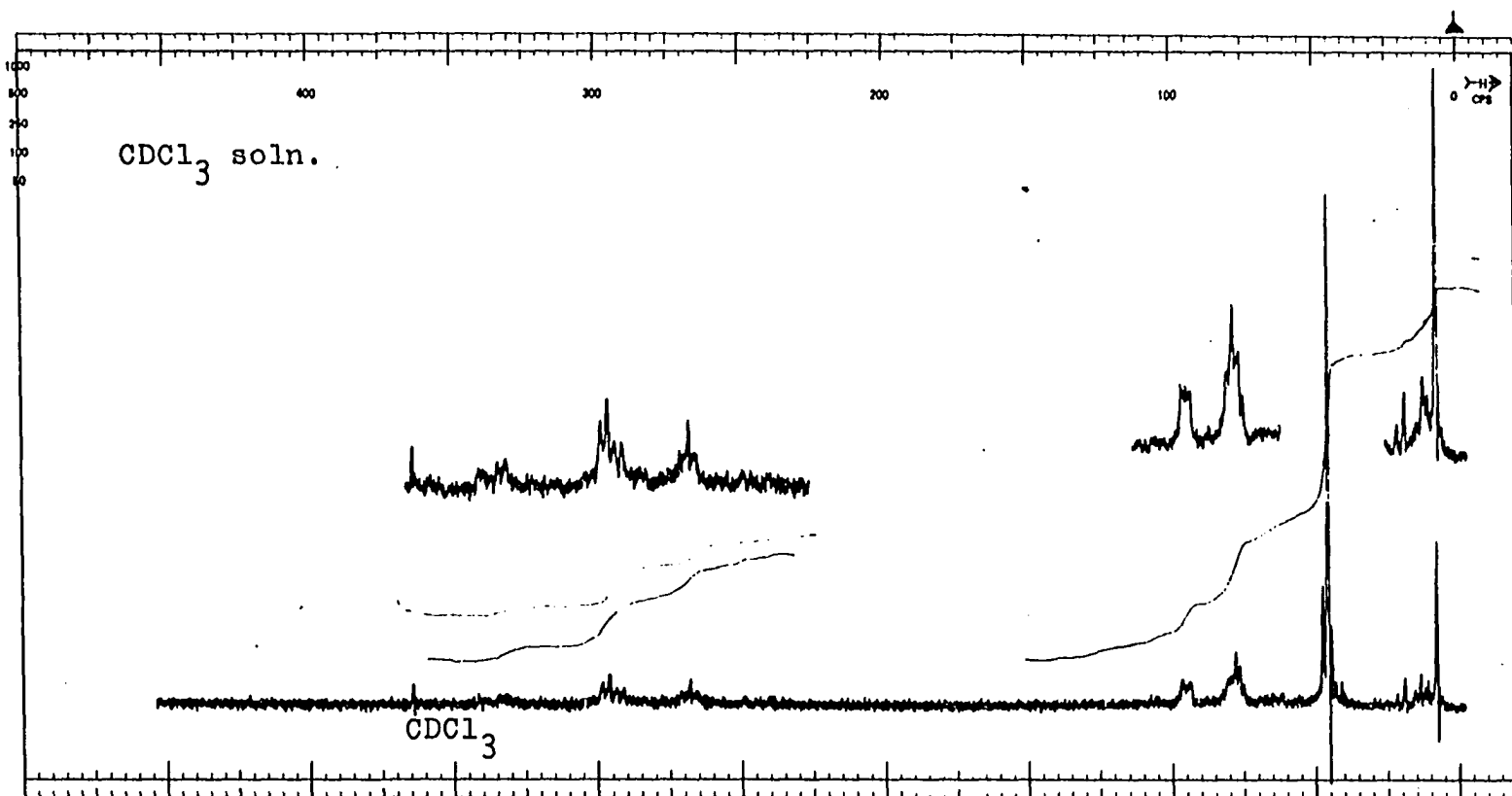
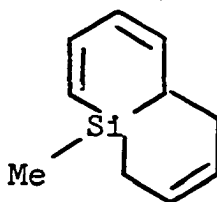
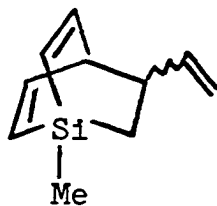
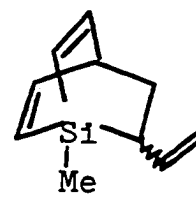


Figure 13. 100 MHz NMR spectrum of adduct (165)

fact, the only differences come from the substitution of the starting chlorosilane. Thus, adduct 165 is the result of nucleophilic substitution at silicon by the anion 163.

A second product occurred as less than 5% of the product mixture and could not be isolated in a pure form. GCMS indicates that this product fits a silabenzene-butadiene adduct (MW = 162.0870 measured,  $C_{10}H_{14}Si$ ). This adduct was not affected by the presence of excess trimethylchlorosilane. Thus, it is not the result of an anionic displacement. Possible structures for this adduct are 166, 167, and 168. Again, due to difficulties in isolating

166167168

the adduct and the large number of possibilities that exist for the adduct, the exact nature of the product must, at this time, remain in question.

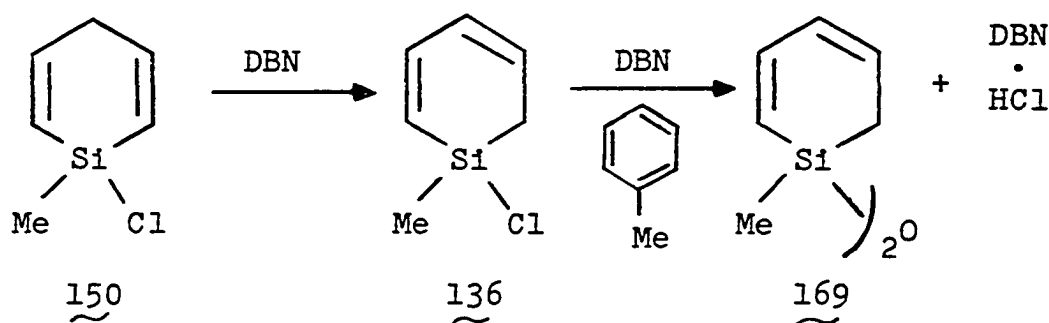
Although the reaction of t-butyllithium with 1-chloro-1-methyl-1-silacyclohexa-2,5-diene is complicated by many side reactions, the reaction does appear, to a small extent, to have produced silabenzene 3, indicating that base promoted eliminations of HCl from chlorodiene 136 constitute a

feasible route to silabenzene. However, in order for this type of reaction to be a successful method of generation of silabenzene, the side reactions of the base and chlorodiene must be eliminated. These side reactions should be eliminated with the use of a base less nucleophilic than *t*-butyllithium. An excellent nonnucleophilic base is 1,5-diazobicyclo[4.3.0]non-5-ene (DBN). It has been used successfully in the synthesis of Group V heterobenzenes (15).

The reaction of DBN with 1-chloro-1-methyl-1-silacyclohexa-2,4-diene 136 was carried out following the experimental procedures reported by Ashe for the synthesis of stibabenzene (15), reagents were dried immediately prior to use. In all cases, the DBN was added slowly to a cold (-77°C) solution of chlorodiene 136 and an appropriate trap. Either 2,3-dimethylbutadiene, benzaldehyde, or perfluoro-2-butyne were used as traps. A white precipitate formed immediately upon addition of the base. Upon warming to room temperature, a green color developed and the white solid was replaced by a green, globular substance. Filtration of the reaction mixture under nitrogen yielded a white solid and removal of solvent afforded a yellow-green oil. The yellow-green oil was identified by spectroscopic means to be almost pure disiloxane 169 (NMR, Figure 14, Scheme 55). The white solid (m.p. 105-113°C) was the hydrochloride salt of DBN. No evidence was found for incorporation of the trapping agents in the product mixture.

The reaction was repeated using 1-chloro-1-methyl-1-sila-cyclohexa-2,5-diene 150. Analysis of the reaction mixture by GC, thirty minutes after addition of DBN, revealed the 2,5-diene 150 had been isomerized to the 2,4-diene 136 (Scheme 55). This reaction again produced DBN-hydrochloride and only the conjugated disiloxane 169.

Scheme 55



The formation of the disiloxane 169 is somewhat perplexing. When the system was not exposed to water or air during work-up, the siloxane was still formed, indicating it could not have resulted from simple hydrolysis of the silylhalide.

The formation of DBN-hydrochloride is consistent with the formation of silabenzene. However, if silabenzene was formed, it should have been trapped by benzaldehyde, which

was present in excess during the reaction. Benzaldehyde is an excellent silene trap and should readily react with silabenzene. The products of the reaction were unaffected by the presence of benzaldehyde, strongly suggesting that silabenzene is not the origin of the observed products.

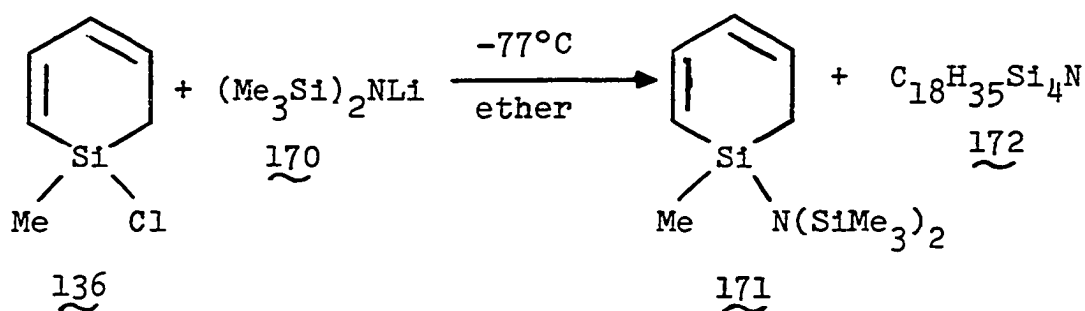
A possible source of the products is a complex which results from an interaction between chlorodiene 136 and DBN. Nitrogen bases are known to readily form expanded-valence complexes with chlorosilanes (143). DBN, a nitrogen base, could have formed such a complex upon addition to the reaction mixture. Thus, the white solid, observed immediately upon the addition of the base, could be this type of complex and not DBN-hydrochloride as originally thought. Decomposition of this complex could lead to the observed products. The structure of this complex and how it decomposes is, at this time, unknown. A complex of this type should also be unaffected by the trapping agents used.

The reaction of DBN and 136 produced no concrete evidence for silabenzene. The unwanted substitution reactions observed with t-butyllithium were eliminated, but apparent complexation between DBN and the starting material prevented the desired reaction from occurring.

Continuing the search for a suitable base to effect a clean synthesis of silabenzene, N-lithiohexamethyldisilazane 170 was employed. N-lithiodisilazane 170 is ideally suited

for the silabenzene reaction, being both a sterically hindered base, and also, quite soluble in hydrocarbon solvents. Treatment of chlorosilacyclohexadiene 136 with 170 at  $-77^{\circ}\text{C}$  in ether, produced a complex mixture (Scheme 56). Although the base is quite hindered, the displacement product 1-bis(trimethylsilylamino)-1-methyl-1-silacyclohexa-2,4-diene 171 was formed (NMR, Figure 14). However, the possibility that 171 is the result of addition of bistrimethylsilylamine to silabenzene 3 cannot be excluded at this time. Also produced in the reaction is a mixture of isomers all exhibiting a molecular ion of 377.1841 (measured), which correspond to an empirical formula of  $\text{C}_{18}\text{H}_{35}\text{Si}_4\text{N}$  (377.1847 calculated). Separation of the isomers could not be

Scheme 56



accomplished by either column or gas chromatography. The molecular formula,  $\text{C}_{18}\text{H}_{35}\text{Si}_4\text{N}$ , corresponds to an adduct of the displacement product 171 and silabenzene 3. The same

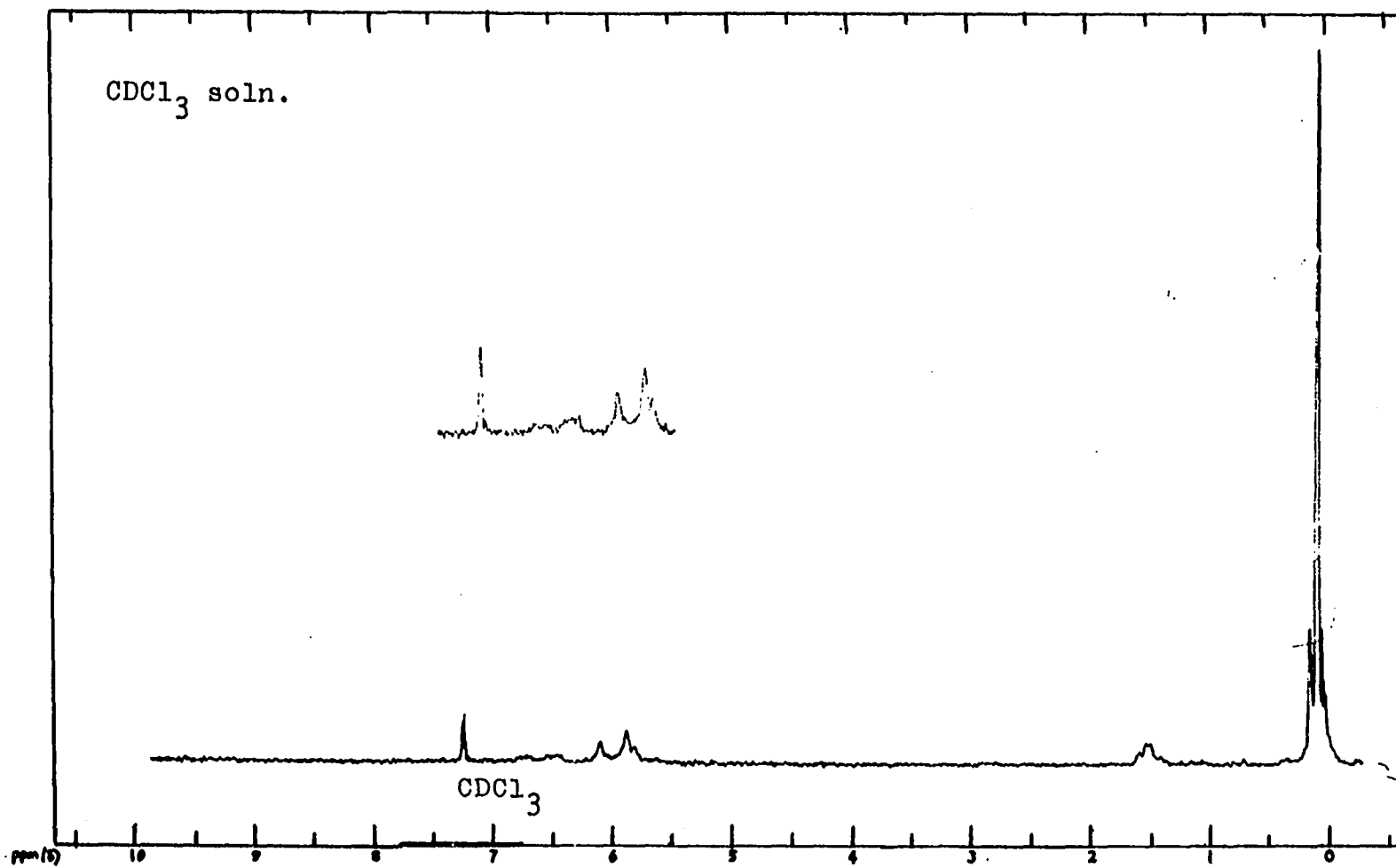


Figure 14. 60 MHz NMR spectrum of 1-(bis-trimethylsilylamino)-1-methyl-1-silacyclohexa-2,4-diene (171)

rationale used in determining the mode of formation of the adduct between silabenzene and 136 in the t-butyllithium reaction was utilized in the present case to rule out anionic displacements as a source of these adducts. As in the t-butyllithium reactions, neither the exact structure of these adducts could be determined, nor could it be determined if the displacement of chloride occurred before or after reaction with silabenzene. Nevertheless, it is apparent that the reaction did involve silabenzene.

The reaction was repeated in the presence of excess butadiene, in the hope of eliminating the formation of adduct 172. The product mixture was virtually identical to that observed in the reaction without butadiene. The only exception was the presence of a small amount of material which, by GCMS, was identical to the butadiene-silabenzene adduct described earlier. Obviously, butadiene does not readily react with silabenzene under these conditions.

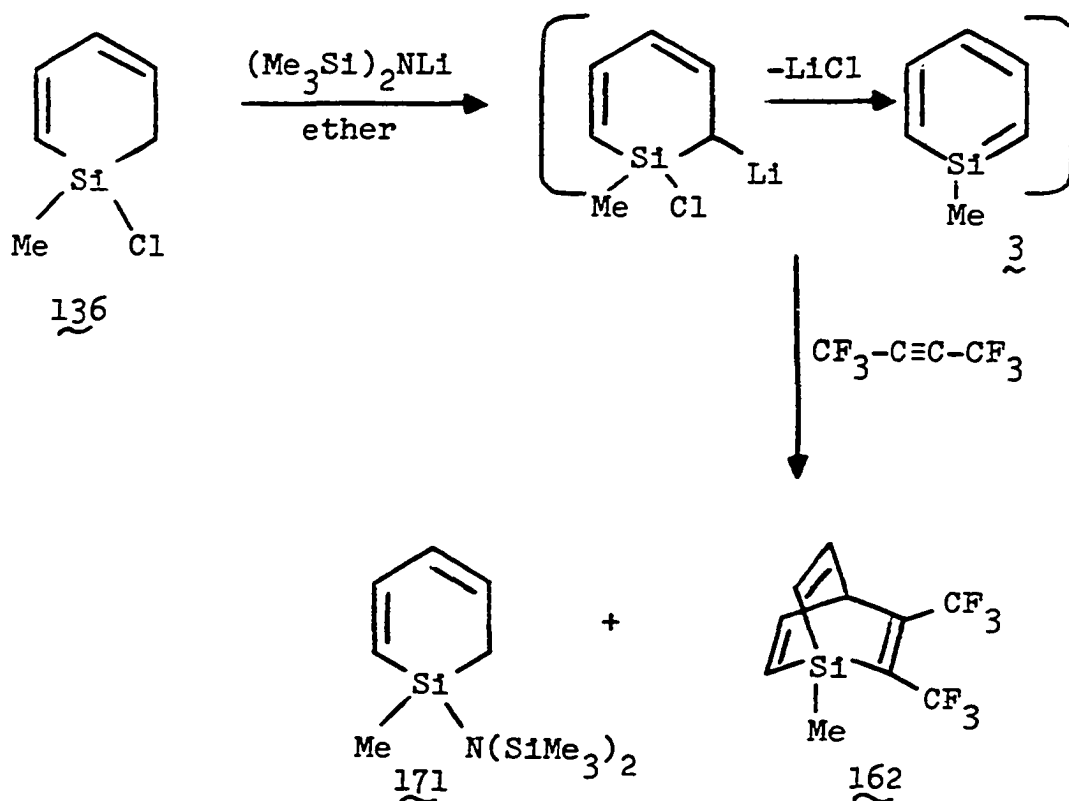
The fragmentary evidence obtained in the t-butyllithium studies indicates that silabenzene prefers to behave as a diene in a Diels-Alder reaction. If this is correct, a good dienophile should be an efficient trap for silabenzene. Selection of an appropriate dienophile was limited to those which would not react with N-lithiodisilazane 170. Perfluoro-2-butyne, a good dienophile, was chosen. The reaction was carried out under an atmosphere of perfluoro-2-butyne in ether. A very complex array of products was



obtained. However, practically all of these products were the result of interactions between the base and perfluoro-2-butyne. These products were not fully characterized after it was determined that chlorosilacyclohexadiene 136 was not involved in their formation. It seems that perfluoro-2-butyne was not as inert to N-lithiodisilazane 170 as originally considered.

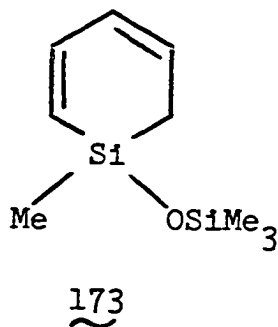
In addition to the base-butyne side products, the displacement product 171, hexamethyldisilazane, and a perfluoro-2-butyne-silabenzene adduct 162 were obtained in this reaction (Scheme 57). Introduction of a ten-fold excess

Scheme 57



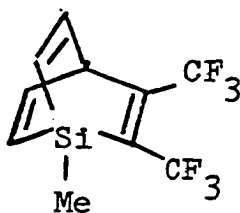
of trimethylchlorosilane decreased the yield of adduct 162 by half, but no evidence of any trimethylsilyl trapping products was found. Also, as in the t-butyllithium reactions, no dimers of silabenzene were found. Adduct 162 was also obtained when 1-chloro-1-methyl-1-silacyclohexa-2,5-diene 150 was subjected to these reaction conditions.

Before discussing the structure of adduct 162, a word of caution should be noted. It is imperative that all reagents and apparatus in the reaction be free of moisture. When this is not accomplished, or if the N-lithiodisilazane 170 is partially hydrolyzed, another product is obtained at the expense of adduct 162. This product is the mixed siloxane 173.



Adduct 162 could be obtained pure by preparative GC. Structure proof is based upon analysis of the  $H^1$ ,  $C^{13}$ ,  $F^{19}$ ,

and Si<sup>29</sup> NMR spectra, along with the IR and mass spectra of the system. A structure consistent with all of these data



162

is 2,3-bis(trifluoromethyl)-1-methyl-1-silabicyclo[2.2.2]-octa-2,5,7-triene 162, a Diels-Alder adduct between silabenzene 3 and perfluoro-2-butyne.

The mass spectrum of 162 merits discussion since the fragmentation pattern is not at all obvious (Table 3). The expected fragmentations, notably retro Diels-Alder reactions, producing either perfluoro-2-butyne and silabenzene, or acetylene and bistrifluoromethylsilabenzene, do not occur to an appreciable extent. Instead, the major fragments are the result of fluorine interactions. Exact mass measurements of the first three major fragments are shown in Table 3. A possible breakdown pattern is shown in Scheme 58. No reasonable structure is proposed for the base peak (163)<sup>+</sup> of the spectrum.

Table 3. 70 eV mass spectrum of 162

m/e	% of base peak	m/e	% of base peak	m/e	% of base peak
270	1.5	143	6	93	12
255	<1	142	8	87	7
244	<1	132	8	82	64
220	5	127	13	75	26
189	30	125	9	69	9
183	11	120	23	63	12
170	10	119	7	58	10
169	62	117	10	51	9
163	100	115	14	47	34
151	31	108	3		
146	8	101	15		
145	7	99	12		

Exact mass measurements

270.0301 measured

270.0305 calculated for  $C_{10}H_8SiF_6$ 

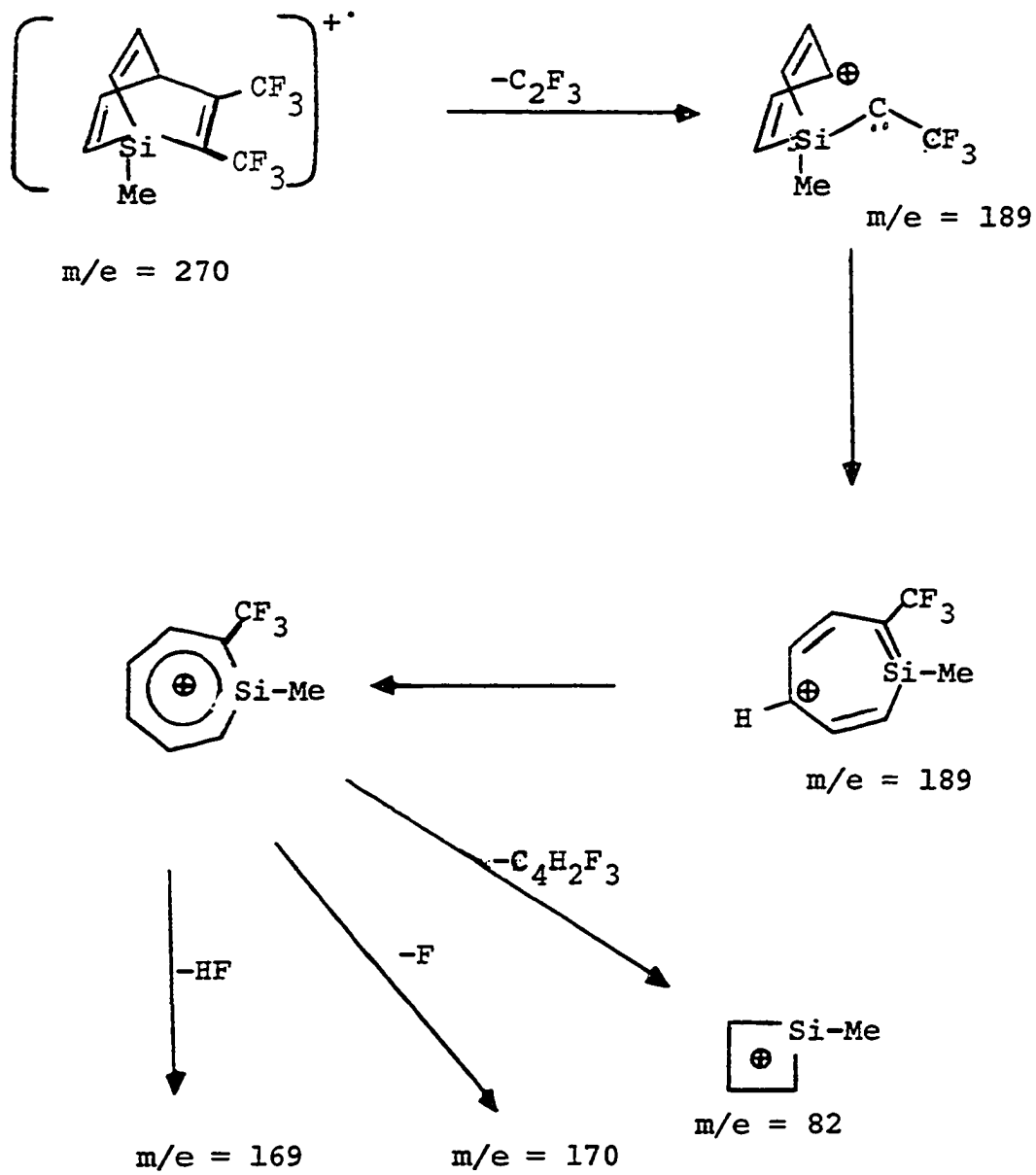
189.0313 measured

189.0347 calculated for  $C_8H_8F_3Si$ 

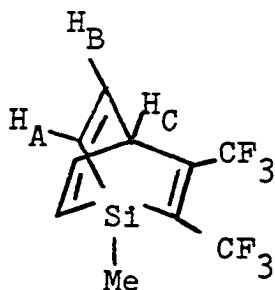
163.0157 measured

163.0171 calculated for  $C_7H_3F_4$

## Scheme 58



Proton NMR of 162 is very informative in assigning the structure of the adduct (Figure 15). The absorptions centered at 7.60  $\delta$  (d of d, 2H) are due to protons labeled  $H_B$ .

162

Protons labeled  $H_A$  are shifted upfield to 6.75  $\delta$  (d of d, 2H) due to the effect of the neighboring silicon. The vinylic proton  $H_C$  appears at 5.17  $\delta$  (overlapped t of t, 1H). The absorption at 0.81  $\delta$  (3H, quartet) is due to the methyl on silicon. It is split by long range  $\omega$ -coupling with a trifluoromethyl group,  $J = 1.5$  Hz. The pattern exhibited by protons  $H_A$ ,  $H_B$ , and  $H_C$  appears to be a first order AMX pattern. Spin-decoupling experiments (Figure 16) confirm this. A similar pattern is found for the corresponding Group V [2.2.2] systems (17).

$F^{19}$  NMR (Figure 17) and IR (broad band at 1150  $\text{cm}^{-1}$ ) show the presence of the trifluoromethyl groups. This is important, for  $C^{13}$  NMR only shows six carbons (Figure 18). The trifluoromethyl carbons, and the carbons bearing these groups, do not appear due to carbon-fluorine coupling. The

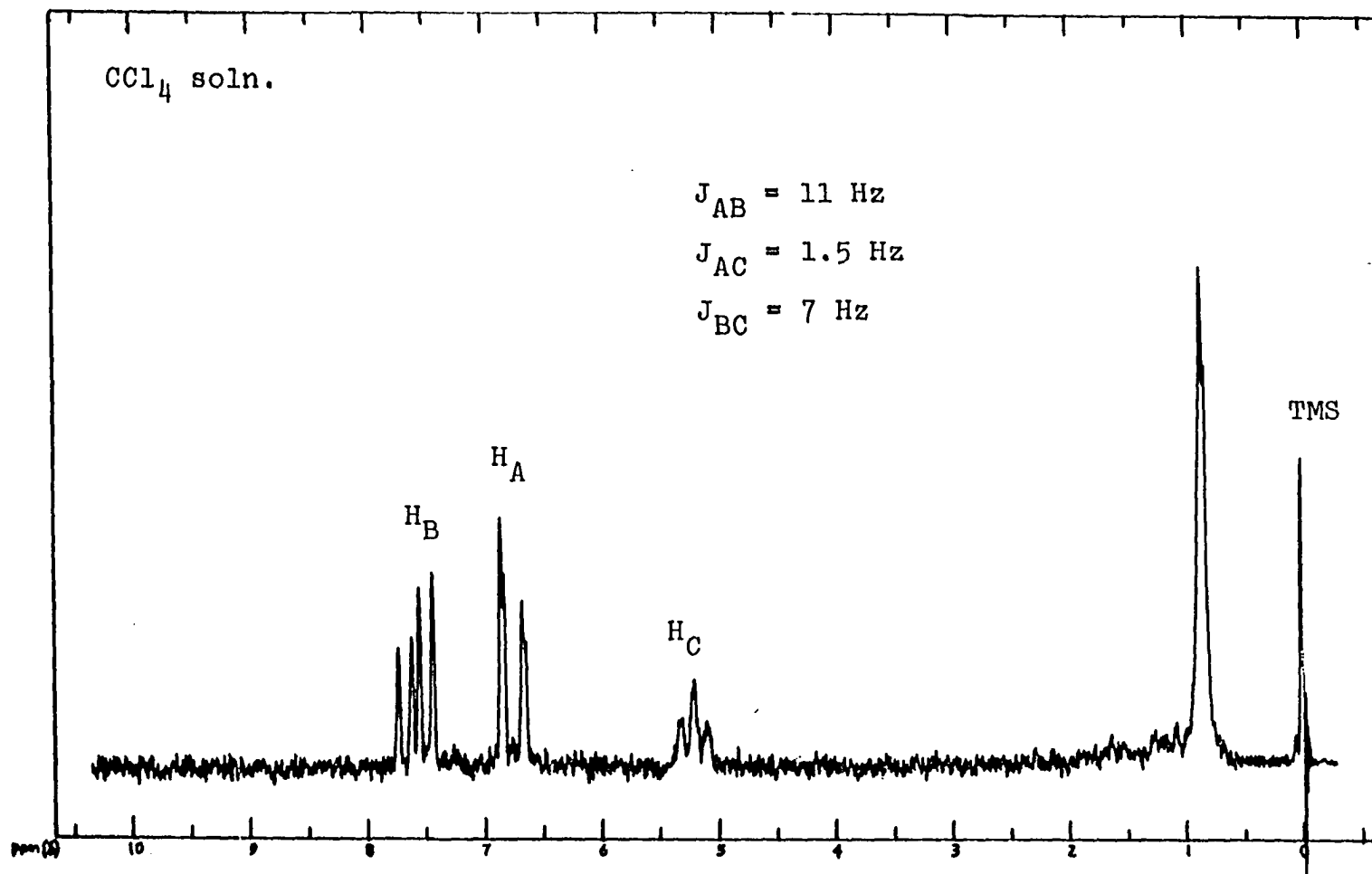


Figure 15. 60 MHz NMR spectrum of 2,3-bis(trifluoromethyl)-1-methyl-1-silabicyclo[2.2.2]octa-2,5,7-triene (162)

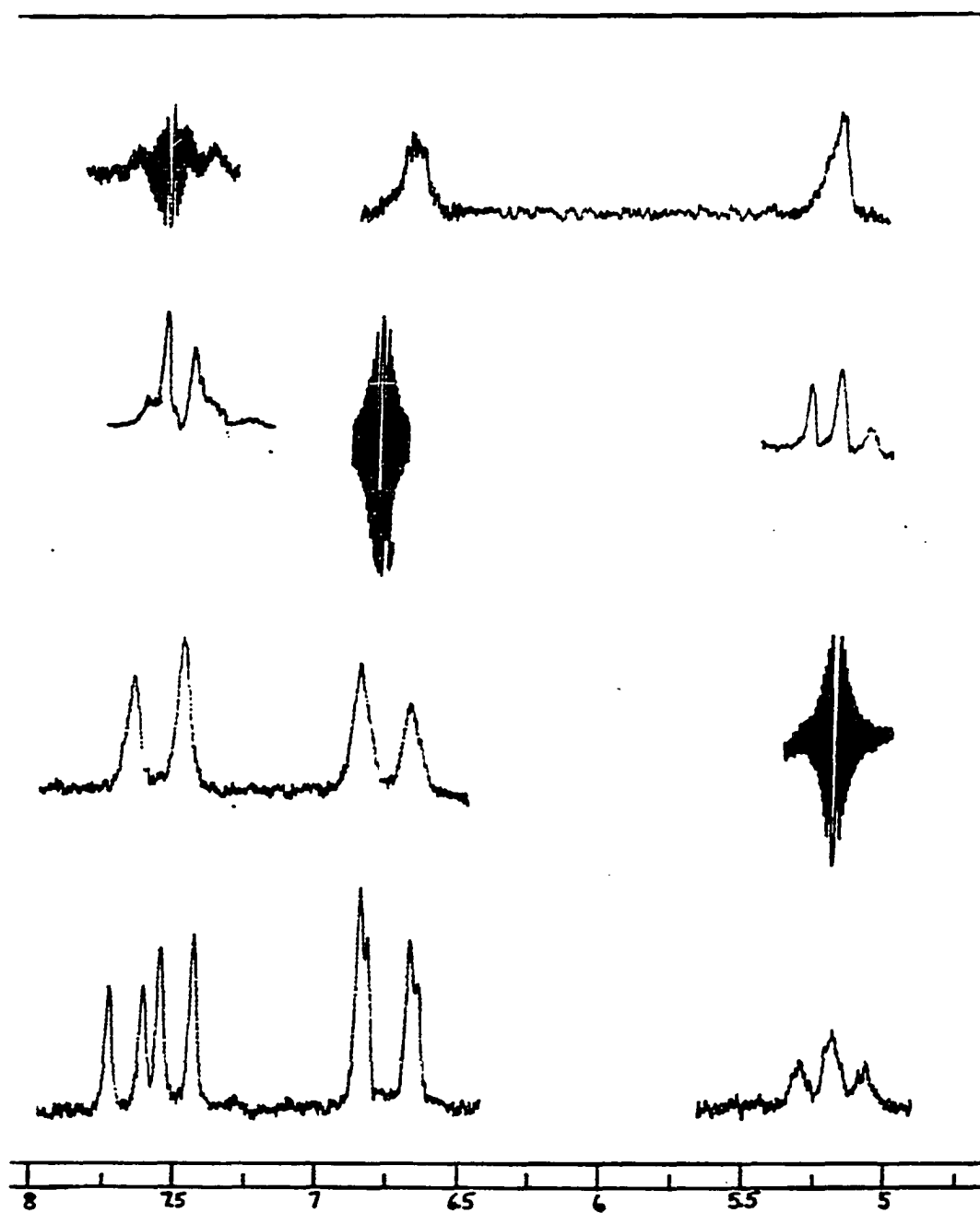


Figure 16. 60 MHz NMR of spin decoupling experiments of 2,3-bis(trifluoromethyl)-1-methyl-1-silabicyclo[2.2.2]octa-2,5,7-triene (162)



NO.	CURSOR	FREQ.	PPM	INTENS.
1	4256 -	4508.056 -	53.238	108032
2	4267 -	4521.484 -	53.397	327424
3	4277 -	4533.691 -	53.541	361472
4	4287 -	4545.898 -	53.685	153088
5	5073 -	5505.371 -	65.016	265728
6	5083 -	5517.578 -	65.161	812800
7	5093 -	5529.785 -	65.305	783616
8	5103 -	5541.992 -	65.449	268800

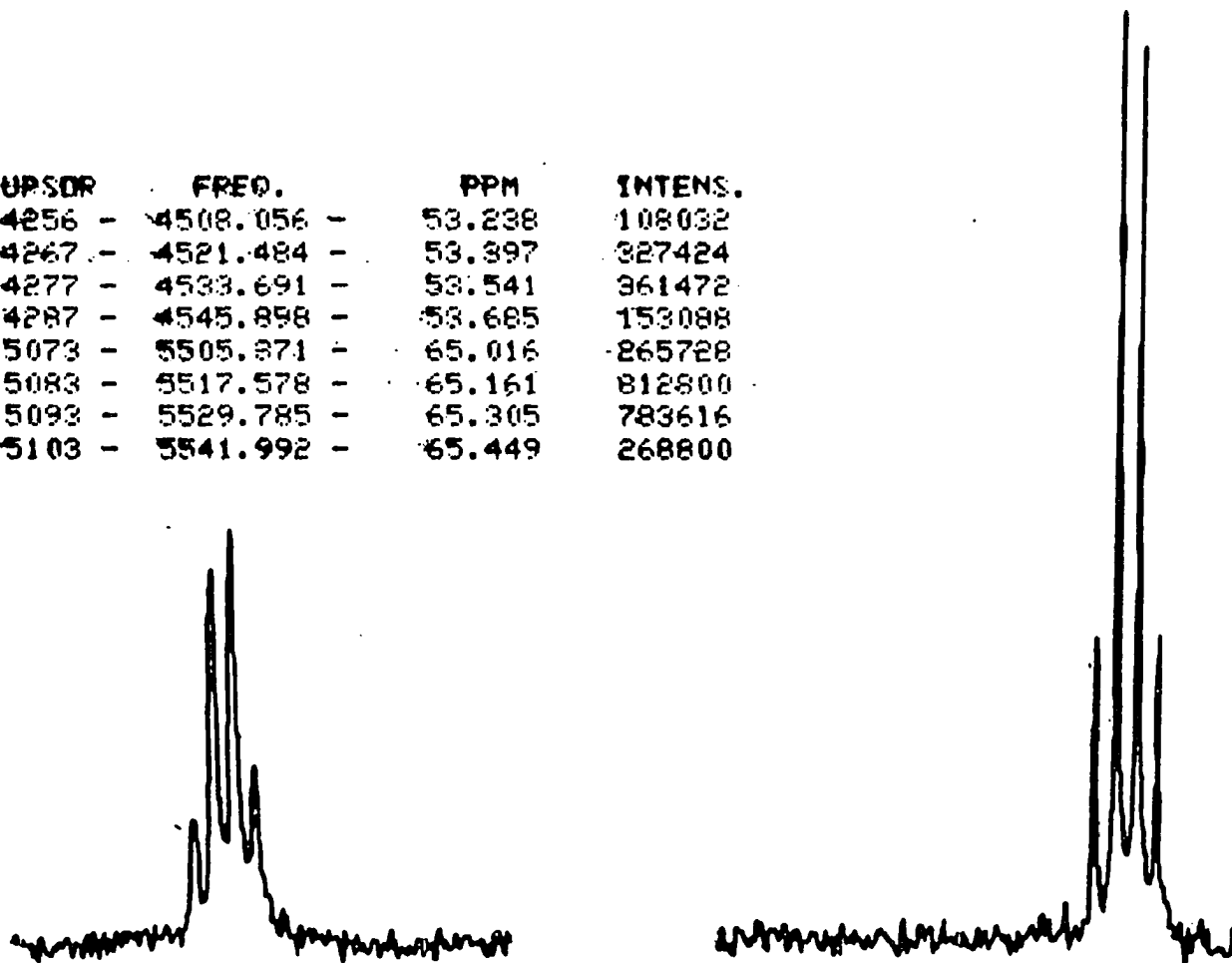


Figure 17.  $F^{19}$  NMR spectrum of 2,3-bis(trifluoromethyl)-1-methyl-1-silabicyclo[2.2.2]octa-2,5,7-triene (162)

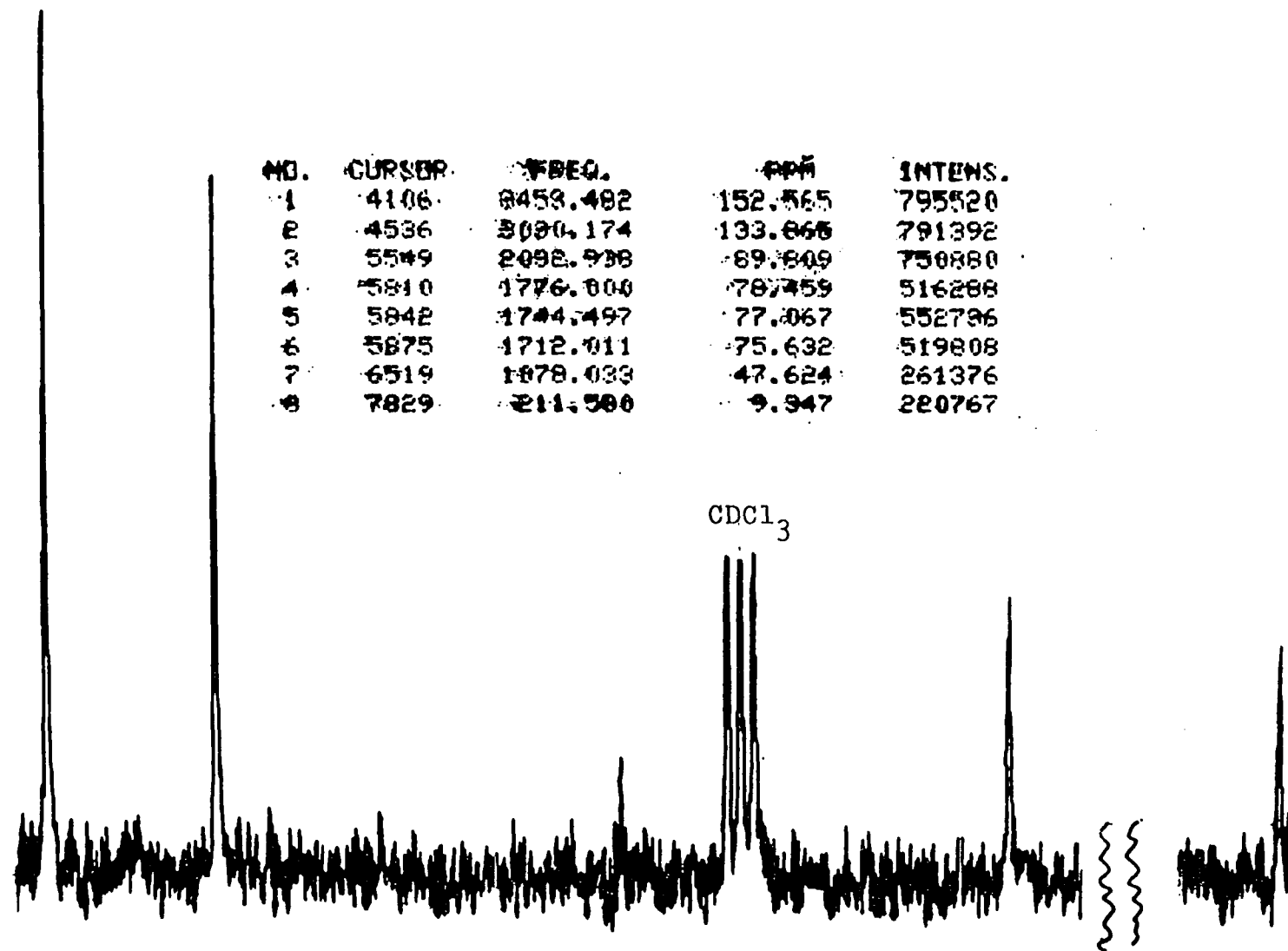
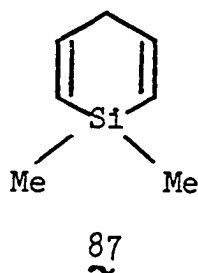
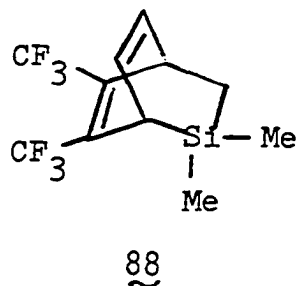


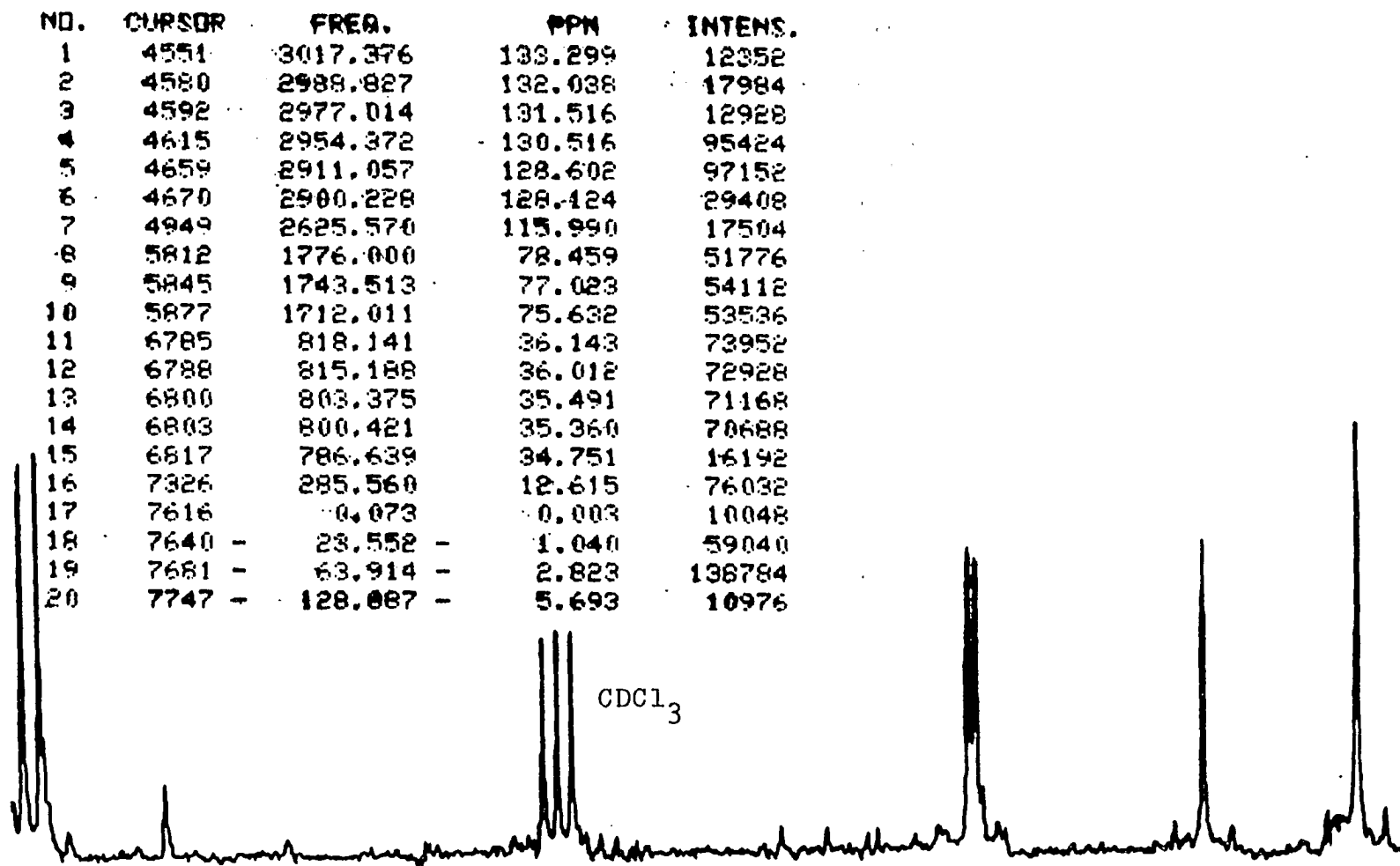
Figure 18.  $C^{13}$  NMR spectrum of 2,3-bis(trifluoromethyl)-1-methyl-1-silabicyclo[2.2.2]octa-2,5,7-triene (162)

coupling constants for these interactions are large enough ( $J_{CF}$ ,  $CF_2-F = 235$  Hz,  $J_{C-C-F} = 40-60$  Hz) to considerably broaden these peaks, making their detection difficult. Examination of the  $C^{13}$  NMR spectrum of 84 shows that it also does not exhibit the analogous four carbons (Figure 19).



$Si^{29}$  NMR places the absorption of the silicon atom in the adduct at 29.8 ppm above TMS. This compares quite well to the silicon absorption of 1,1-dimethyl-1-silacyclohexa-2,5-diene 87, which occurs at 30.8 ppm above TMS.

It is possible that formation of bicyclic adduct 162 may occur by two different pathways (Scheme 59). Path a involves a Diels-Alder reaction of silabenzene 3 with the butyne. Path b, on the other hand, yields adduct 162 via an anionic attack on perfluoro-2-butyne followed by anionic displacement of the silylchloride. Inclusion of a ten-fold excess of trimethylchlorosilane did not produce any capture of anions 137 or 174. These results tend to rule out an

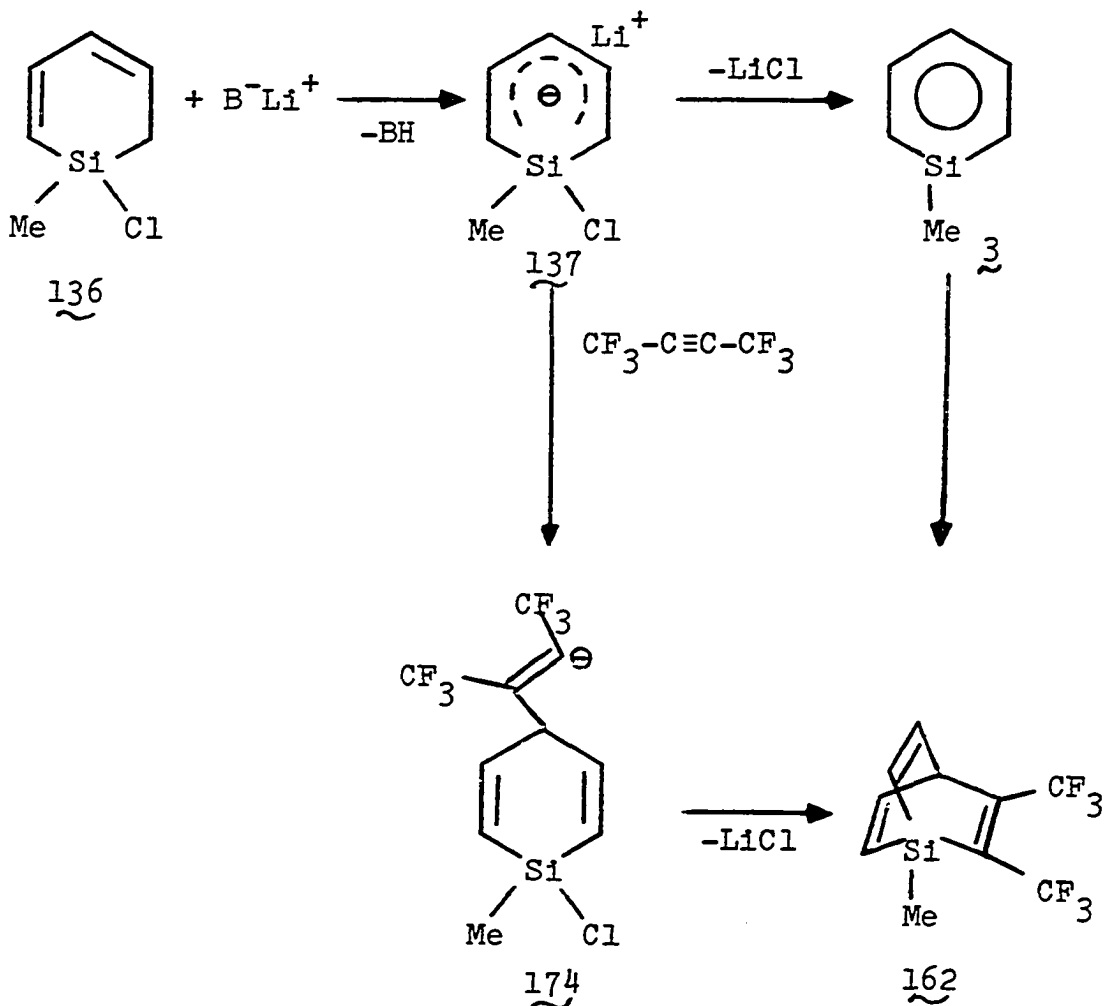


133

Figure 19.  $C^{13}$  NMR spectrum of 2,3-bis(trifluoromethyl)-7,7-dimethyl-7-silabicyclo[2.2.2]octa-2,5-diene 88

anionic mechanism for the formation of 162 and argue strongly for the intermediacy of silabenzene in this reaction.

Scheme 59

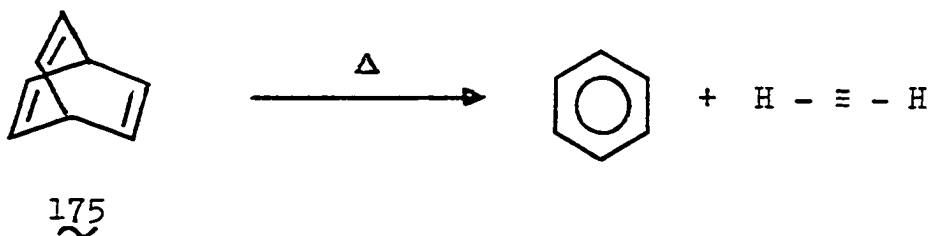


It is of interest to compare the results of these reactions to those of Ashe and co-workers (17). They have synthesized arsabenzene, stibabenzene, and bismabenzene in an analogous manner. Unlike the present results, these

heteroaromatics have been observed spectroscopically (14→19). Also, these systems all readily react with perfluoro-2-butyne, as does silabenzene, to form the corresponding bicyclic adducts. The Group V heteroaromatics were noted to increase in reactivity with atomic number. Attempts were made to observe silabenzene by NMR spectroscopy. The reaction was performed in an NMR tube. However, the fact that silabenzene readily reacted with the starting diene prevented its observation. The high reactivity of silabenzene does not reflect the stability of the system. Like silenes, a stable silabenzene may require either steric hindrance or metal complexation to effect its observation.

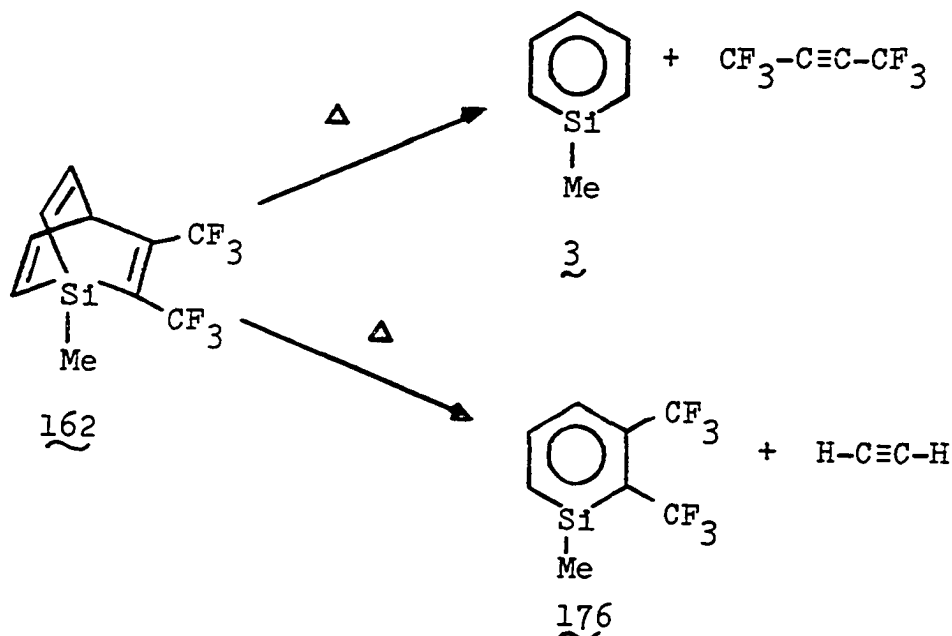
The first example of a silicon analog of bicyclo[2.2.2]octa-2,5,7-triene (barrelene) 175 is 2,3-bis(trifluoromethyl)-1-methyl-1-silabicyclo[2.2.2]octa-2,5-triene 162. Barrelene, upon heating to ca. 200°C, undergoes a retro-Diels-Alder reaction to acetylene and benzene (144) (Scheme 60). Thus, silabarrelene 162 may, itself, be a thermal

Scheme 60



source of silabenzene, if an analogous reaction occurs (Scheme 61). However, two possible retro-Diels-Alder

Scheme 61

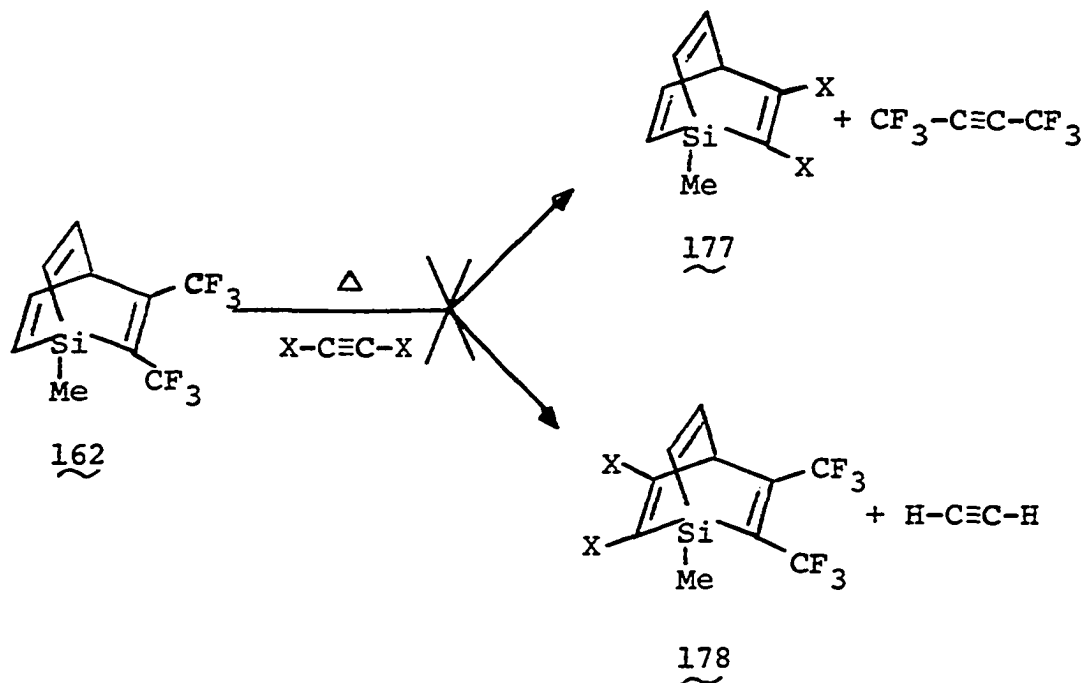


reactions are possible which complicate matters. Furthermore, the mass spectrum of 162 does not show large peaks corresponding to either fragmentation. This does not necessarily indicate the fragmentation will not occur thermally, but, in many instances, the mass spectrum is a good indication of the thermal behavior of a system.

Since silabenzene has already been shown to be very reactive, the pyrolysis was carried out in the presence of a trap. Another acetylene was chosen with the hope that an exchange of either acetylene or perfluoro-2-butyne with

the trap acetylene would occur (Scheme 62). Thus,

Scheme 62



silabarrelene 162, and bis-trimethylsilylacetylene were sealed in an evacuated and degassed NMR tube. The reaction was followed by NMR. The tube was heated to 250°C for 2 hours. After 22 hours, no reaction was apparent. The entire mixture turned to a black polymer after a total of 30 hours. Nothing could be identified from this polymer.

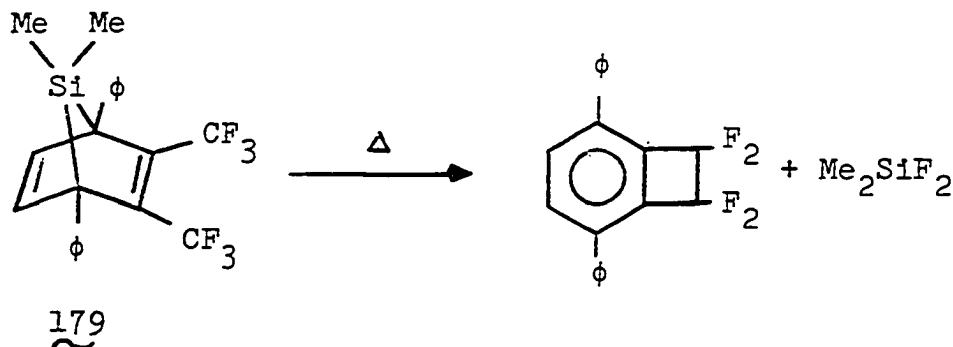
Di-t-butylacetylene was next attempted as a trap. Again, the acetylene trap and adduct 162 were placed in a sealed NMR tube. Heating began at 180°C and was slowly raised to a maximum of 300°C. No reaction was apparent up to 250°C after



41 hours. After an additional 72 hours at 300°C, all the silabarrelene had reacted, according to NMR. The tube was opened and the contents analyzed by GCMS. There was no evidence of any of the expected exchange products. In addition, the reaction was very dirty. It seems the system had completely decomposed.

It appears that silabarrelene 162 will not cleanly decompose to silabenzene. This may be due to the presence of the trifluoromethyl groups. The silicon-fluorine bond is a very strong bond and will form if given the opportunity. It is very possible that the system decomposes to form Si-F bonds, rather than decompose in the expected manner. An unexpected interaction of a trifluoromethyl and silicon in a thermal degradation is found in the neat pyrolysis of 1,4-diphenyl-2,3-bis(trifluoromethyl)-7-dimethylsilabicyclo[2.2.1]-heptadiene 179 (Scheme 63) (145). A different silabarrelene,

Scheme 63

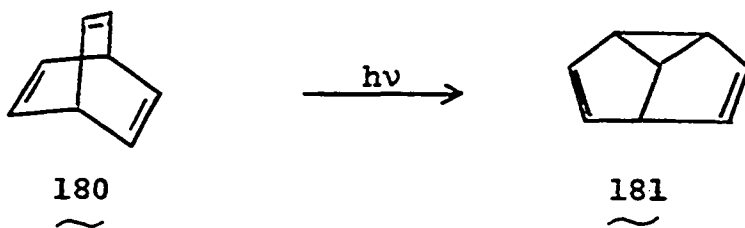


without trifluoromethyl groups, should thermally decompose to silabenzene. Towards this end, silabenzene was generated in the presence of other acetylenes.

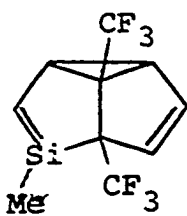
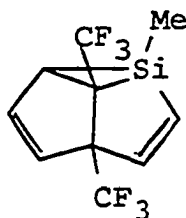
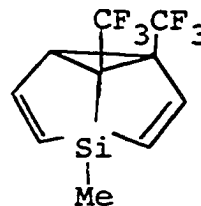
Preliminary evidence in attempts with diphenylacetylene showed that no trapping occurred. On the other hand, 3-hexyne did produce a small amount of a system which, by NMR, was consistent with the expected adduct. However, it was unstable and could not be fully characterized. This reaction shows potential, but requires further work.

Preliminary investigations into the photochemistry of silabarrelene 162 were also initiated. Barrelene, itself, when irradiated, undergoes a di- $\pi$ -methane rearrangement to semibullvalene 181 (Scheme 64) (146). If an analogous

Scheme 64



rearrangement occurred with silabarrelene 162 a large number of interesting products are possible. Included among these products are such as 182, 183, and 184. Thus, the photolysis

182183184

of 162 may ultimately result in the formation of species containing silacyclopropanes and/or silenes.

Silabarrelene 162 was photolyzed through quartz in benzene at 2537 Å for four hours. Preliminary analysis of the product mixture by GCMS and NMR indicates that a number of compounds isomeric with starting material are produced. However, a more complete analysis of these products by future investigations is required before the structures of these isomers can be determined.

## CONCLUSION

Although the generation of 1,1-dimethyl-1-silacyclohexa-2,5-dien-4-ylidene carbene did not result in silabenzene, it did yield the interesting product 1-methyl-1-silabicyclo[2.2.1]hepta-2,5-diene (1-silanorbornadiene), the first example of silicon at the bridgehead in a norbornadiene structure.

The syntheses of the various substituted silacyclohexadiene systems studied as potential silabenzene precursors has provided new insights into the chemical manipulations of the silacyclohexadiene ring system.

The goal of this endeavor, the generation of a silabenzene, was achieved in the base promoted elimination of HCl from 1-chloro-1-methyl-1-silacyclohexa-2,4-diene. Silabenzene proved to be very reactive and could not be isolated, however, its intermediacy was shown in a trapping reaction with perfluoro-2-butyne. This reaction produced 2,3-bis(trifluoromethyl)-1-methyl-1-silabicyclo[2.2.2]octa-2,5,7-triene (a 1-silabarrelene), a Diels-Alder adduct of silabenzene and perfluoro-2-butyne and the first example of the silicon analog of bicyclo[2.2.2]octa-2,5,7-triene (barrelene).

The generation of silabenzene and the synthesis of 1-silanorbornadiene and 1-silabarrelene should promote continued study of cyclic, unsaturated organosilicon compounds.

## EXPERIMENTAL

## Instrumentation

Routine proton NMR spectra were recorded either on a Varian model A-60, EM-360, or a Hitachi R20-B spectrometer. A Varian HA-100 spectrometer was used to record all 100 MHz spectra. Decoupling experiments were performed either on the Varian EM-360 or HA-100 spectrometer. All chemical shifts were reported as parts per million ( $\delta$  scale) using either tetramethylsilane or chloroform as internal standards.

$C^{13}$ ,  $F^{19}$ , and  $Si^{29}$  NMR spectra were recorded on a Bruker HX-90 NMR spectrometer equipped with a Nicolet 1089 data system.

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

Routine mass spectra were recorded on an Atlas CH-4 Mass Spectrometer. Exact mass measurements were obtained on a MS-902 Mass Spectrometer. Gas Chromatographic Mass Spectra (GCMS) were obtained on either a Perkin-Elmer 270 Mass Spectrometer or a Finnegan Model 4023 Mass Spectrometer.

Ultraviolet spectra (UV) were recorded on a Cary Model 14 spectrophotometer. All melting points (m.p.) were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Gas Chromatographic (GC) data were

obtained on a Varian-Aerograph Series 1700 Gas Chromatograph. Column size and packings will be reported as used. High Pressure Liquid Chromatography (HPLC) was performed on a Waters High Pressure Liquid Chromatograph equipped with UV and differential refractometer detectors.

### Procedures and Results

#### Standard procedures for flow pyrolysis

A vertical tube (17 mm x 30 cm) was packed with Vycor chips and prepurified nitrogen was passed through the tube. A liquid nitrogen-cooled trap was used to collect the pyrolysate. Samples to be pyrolyzed, either neat or as solutions, were dropped into the heated tube and allowed to collect in the cold traps.

#### Synthesis of 1,1-dimethyl-1-silacyclohexan-4-one (81)

The procedures of Benkeser and Bennett (129) and of Weber and co-workers (128) were followed to prepare this yellow oil, b.p. 46°C (1.0 mm Hg) (129), in 2-3% overall yield: NMR ( $\text{CCl}_4$ )  $\delta$  0.13 (s, 6H), 0.88 (t, 4H,  $J = 7.5$  Hz), 2.40 (t, 4H,  $J = 7.5$  Hz); IR (liquid film) 3120, 1675, 1250, and 780  $\text{cm}^{-1}$ .

Selenium dioxide oxidation of (81) to 4,4-dimethyl-4-silacyclohexa-2,5-diene-1-one 76 in t-butyl alcohol

The procedure of Weber and Laine (126) was followed. The yellow oil was obtained in 15% isolated yield: NMR ( $\text{CDCl}_3$ )  $\delta$  0.20 (s, 6H), 6.87 (center d of d, 4H,  $J = 14.5$  Hz); IR (film) 1635, 1580  $\text{cm}^{-1}$ ; mass spectrum (16 eV)  $m/e$  (rel intensity) 138 (24), 125 (33), 110 (100), 95 (28).

Attempted oxidation of (81) with DDQ

The procedure of Felix and Weber (127) was followed. The reaction did not produce dienone 76. Extension of reaction times, change of solvent to methylene chloride, toluene, or xylene did not alter the results. Freshly preparing the DDQ also had no effect on the reaction. In all cases, starting material 81 and a small amount of uncharacterized silicon polymer were obtained.

Mercury photosensitized coupling of dimethylchlorosilane (82)

In a dry 500 ml quartz tube, was placed 217 g (2.29 moles) of dimethylchlorosilane 82, boiling chips, and a drop of mercury. Nitrogen was passed through the liquid for thirty minutes prior to photolysis. The tube was equipped with two condensers and placed under a  $\text{N}_2$  atmosphere. Photolysis was accomplished in a Rayonet reactor with 2537 Å light for seven days. Distillation yielded 125 g (0.67

moles) (58% yield) of 1,1,2,2-tetramethyl-1,2-dichloro-disilane 83, b.p. 143-146°C (760 mm Hg): NMR (CCl<sub>4</sub>) δ 1.0 ppm (65); mass spectrum (70 eV) m/e (rel intensity) 186 (9), 151 (15), 93 (95), 73 (100), 58 (95).

Conversion of (83) to 1,1,2,2-tetramethyl-1,2-dimethoxydisilane (84) by trimethylorthoformate

In a dry 500 ml flask, equipped with a magnetic stirring bar, condenser, and CaCl<sub>2</sub> drying tube, was placed 260 g (1.39 moles) of 1,1,2,2-tetramethyl-1,2-dichlorodisilane 83 and 738 g (6.96 moles) of trimethylorthoformate. This mixture was heated at 60°C for twelve hours. Distillation of the reaction mixture yielded 185 g (1.04 moles) (75% yield) of 1,1,2,2-tetramethyl-1,2-dimethoxydisilane 84 boiling in the range 138°C to 151°C (760 mm Hg) (65): NMR (CCl<sub>4</sub>) δ 0.2 (s, 2H), δ 3.36 (s, 1H); mass spectrum (70 eV) m/e (rel intensity) 178 (86), 148 (100), 118 (18).

Preparation of 1,1-dimethyl-1-silacyclohexa-2,4- and -2,5-diene (86) and (87)

One equivalent of 1,1,2,2-tetramethyl-1,2-dimethoxydisilane 84 was mixed with three equivalents of cyclopentadiene and dropped into a 12" x 3/4" Vycor tube packed with quartz chips, swept with nitrogen, and heated to 520-550°C. The product was collected in a liquid nitrogen cooled flask and immediately fractionally distilled to prevent



dimerization of the excess cyclopentadiene. A 35-40% yield of a mixture of the 2,5- and 2,4-silacyclohexadienes was obtained, b.p. 125-129°C (760 mm Hg). This fraction was filtered through silica gel with hexane as a final purification procedure. At 520°, the mixture consisted of 2.5 parts 2,4-diene to 1 part 2,5-diene. Higher temperatures favored the conjugated isomer. The isomers could not be separated by GC on 15% SE-30, 20% DC-550, 10% Carbowax 20M, or 5% Dexsil 300, nor were they separated by HPLC on 1 ft.  $\mu$ -Porasil or 1 ft.  $\mu$ -Bondapak. 1,1-Dimethyl-1-silacyclohexa-2,5-diene 87: NMR ( $\text{CCl}_4$ )  $\delta$  0.1 (s, 6H), 2.80 (m, 2H), 6.75 (center d of m, 2H), 7.60 (center d of m, 2H) (see Figure 5); IR (film) 2980, 1655, 1607, 1375, 1245;  $\text{C}^{13}$  NMR (ppm) 144.9 (2C), 126.2 (2C), 33.9 (1C), -0.34 (1C), -1.18 (1C); mass spectrum (70 eV)  $\underline{m/e}$  (rel intensity) 124 (80), 109 (100), 93 (10), 81 (35); exact mass calculated for  $\text{C}_7\text{H}_{12}\text{Si}$ ,  $\underline{m/e} = 124.0708$ ; found:  $\underline{m/e} = 124.0706 \pm 0.0005$ . 1,1-Dimethyl-1-silacyclohexa-2,4-diene 86: NMR ( $\text{CCl}_4$ )  $\delta$  0.1 (s, 6H), 1.72 (d, 2H,  $J = 3$  Hz), 6.95 (m, 3H), 7.92 (m, 1H); mass spectrum (70 eV)  $\underline{m/e}$  (rel intensity) 124 (30), 109 (100), 81 (29).

#### Purification of 1,1-dimethyl-1-silacyclohexa-2,5-diene (87)

A mixture of 2.4 parts 86 and 1 part 87 was reacted with excess perfluoro-2-butyne in an evacuated, degassed sealed tube at 60°C according to the procedure of Barton and Kline

(66). The 2,5-silacyclohexadiene 87 was untouched and recovered pure by distillation b.p. 65-67°C (48 mm Hg). The product of the Diels-Alder reaction 2,3-(bis-trifluoromethyl)-7,7-dimethyl-7-silabicyclo[2.2.2]octa-2,5-diene 88 distilled at 78-80°C (14 mm Hg): NMR (CCl<sub>4</sub>) δ 0.11 (s, 6H), 0.48 (d, 2H, J = 3.8 Hz), 3.58 (d, 1H, 6.5 Hz), 4.12 (m, 1H), 6.16 (m, 2H); C<sup>13</sup> NMR (see Figure 19).

#### Oxidation of (87) by selenium dioxide

To a refluxing solution of 2.32 g (0.018 m) of 87 in 50 ml of 95% ethanol was added, dropwise over a three hour period, a solution of 2.0 g (0.18 moles) of selenium dioxide in 50 ml of 95% ethanol. The reaction mixture was refluxed an additional two hours, after which time most of the ethanol (80-90 ml) was distilled from the reaction vessel. The mixture was cooled, diluted with 100 ml of 95:5 pentane:chloroform, and filtered. The red-brown solution was washed three times with 75 ml of water and once with saturated NaCl and dried over anhydrous MgSO<sub>4</sub>. Filtration and removal of solvent yielded 1.97 g of a dark red oil. The oil was purified by column chromatography on silica gel. Elution with 95:5 hexane:diethylether produced 0.252 g (0.0018 moles) of pure 4,4-dimethyl-4-silacyclohexa-2,5-dien-1-one 76 (10.1% isolated yield). Elution with 90:10 hexane:diethylether gave 0.262 g (0.0018 moles) (10.4% isolated yield) of 1,1-dimethyl-1-silacyclohexa-2,5-dien-4-ol 89

(129): NMR ( $\text{CCl}_4$ )  $\delta$  0.07 (d, 6H,  $J = 3.5$  Hz), 1.8 (s, 1H disappears with  $\text{D}_2\text{O}$ ), 4.4 (m, 1H), 5.8 (center d of d,  $2\text{H}_A$ ,  $J_{AB} = 14.5$  Hz,  $J = 2$  Hz), 6.7 (center d of d;  $2\text{H}_B$ ,  $J = 4$  Hz); IR (film) 3320, 2980, 2960, 2900, 1640, 1618, 1583, 1410, 1370, 1247  $\text{cm}^{-1}$ .

Collins oxidation of a mixture of (86) and (87)

To a solution of 4.0 (0.032 moles) of a 2:1 mixture of 86 to 87 in 50 ml of  $\text{CH}_2\text{Cl}_2$  stirred under nitrogen at room temperature, was slowly added a solution of 35 g (0.15 moles) of Collins reagent (Chromium trioxide-pyridine complex), prepared by the method of Dauben and co-workers (134), in 100 ml of  $\text{CH}_2\text{Cl}_2$ . The reaction was followed by GC. After fifteen hours, no starting material could be detected. The reaction mixture was filtered through Celite. The Celite pad was washed with an additional 300 ml of  $\text{CH}_2\text{Cl}_2$ . The  $\text{CH}_2\text{Cl}_2$  was removed and replaced with 100 ml of hexane. The hexane solution was extracted three times with 100 ml of  $\text{H}_2\text{O}$  and once with saturated NaCl, and dried over anhydrous  $\text{MgSO}_4$ . Filtration and removal of the hexane left a yellow oil which was purified by column chromatography on silica gel. Elution with 95:5 hexane: $\text{Et}_2\text{O}$  yielded 1.29 g (0.0093) (29.2% isolated yield) of 4,4-dimethyl-4-silacyclohexa-2,5-dien-1-one 76.

"Activated" manganese dioxide oxidation of (87)

A solution of 1.02 g (0.0065 moles) of 87 in 100 ml of dry hexane was mixed with 6.1 g (0.07 moles) of activated manganese dioxide (Ventron) and stirred for twenty-four hours. The reaction mixture was filtered through a Celite pad and the pad was washed with 300 ml of  $\text{CH}_2\text{Cl}_2$ . Removal of the solvent left a yellow oil which was purified by column chromatography on silica gel. Elution with 95:5 hexane: $\text{Et}_2\text{O}$  yielded 0.27 g (0.0020) (30.1% isolated yield) of pure dienone 76.

"Activated" manganese dioxide oxidation of a mixture of (86) and (87)

A mixture of 3.34 g (0.027 moles) consisting of 2 parts 86 to 1 part 87 was reacted with 47 g (0.05 moles) of activated manganese dioxide (Ventron) as described above. Elution with hexane from a silica gel column yielded 1.61 g of 2,4-silacyclohexadiene 86, and 95:5 hexane: $\text{Et}_2\text{O}$  yielded 0.58 g of pure dienone 76. The 30% yield (0.58) is based on the amount of diene reacted.

Formation of the tosylhydrazone of 4,4-dimethyl-4-silacyclohexa-2,5-dien-1-one (77)

A solution of 0.100 g (0.73 mmoles) of dienone 76 in 20 ml of dry MeOH was added slowly to a stirring suspension of 0.135 g (0.73 mmoles) of tosylhydrazide in 30 ml of MeOH.

The mixture was heated to dissolve the hydrazide and then allowed to sit at 0°C for twelve hours, during which time tan crystals formed. These crystals were collected and recrystallized from EtOH·H<sub>2</sub>O. 0.190 g (0.62 mmoles) (85% yield) of tosylhydrazone 77, a white crystalline material, were obtained, m.p. 176-178°C: NMR (d<sub>6</sub>-acetone) δ 0.18 (s, 6H), 2.42 (s, 3H), 6.30 (center d of m, 2H), 6.91 (center d of m, 2H), 7.35 (d, 2H, J = 8.5 Hz), 7.81 (d, 2H, J = 8.5 Hz); mass spectrum (70 eV) m/e (rel intensity) 306 (3), 151 (27), 150 (32), 122 (100), 107 (60), 96 (55), 91 (44); exact mass calculated for C<sub>14</sub>H<sub>18</sub>SiN<sub>2</sub>SO<sub>2</sub>, m/e = 306.0858; found: m/e 306.0838 ± 0.003.

Procedure for the generation of 1,1-dimethyl-1-silacyclohexadienyl anion (90)

One equivalent of a 2:1 mixture of silacyclohexadienes 86 and 87 was dissolved in dry THF under a nitrogen atmosphere. The solution was cooled to 0°C. One equivalent of either n-butyllithium in pentane (Aldrich) or t-butyllithium in pentane (Aldrich or Ventron) was slowly syringed through a septum into the flask. The solution turned a deep red color upon addition of a one-half equivalent of base, and remained that color after addition was complete. The red solution was allowed to stir an additional thirty minutes to insure complete anion formation. This solution was then reacted with the desired reagents.

Formation of 1,1-dimethyl-4-diazo-1-silacyclohexa-2,5-diene (78)

Method I Tosylhydrazone 77 was generated as before from 1.04 (7.5 mmoles) of dienone 76. This solution was cooled to 0°C and 0.18 g (7.5 mmoles) of sodium was added to the methanol solution to generate sodium methoxide in situ. A red-orange color developed, and after thirty minutes the methanol was removed under vacuum. 2.16 g (6.6 mmoles) of a tan solid were obtained. This solid was used without further purification. This solid was rapidly heated to 110°-130°C under vacuum (0.2 mm Hg), 0.79 g (5.3 mmoles) (70% yield) of a red oil were collected. The red oil was identified as 1,1-dimethyl-4-diazo-1-silacyclohexa-2,5-diene 78: NMR (CDCl<sub>3</sub>) δ 0.10 (s, 6H), 5.55 (d, 2H, J = 14 Hz), 6.84 (d, 2H, J = 14 Hz), (see Figure 1); IR (film), 3010, 2970, 2900, 2050, 1576, 1528, 1308, 1245 cm<sup>-1</sup>; mass spectrum (70 eV) m/e (rel intensity) 150 (50), 122 (100), 107 (85), 95 (90); UV λ max (pentane) = 2960 Å, 2130 Å; exact mass calculated for C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>Si, m/e = 150.0613; found: m/e 150.0613.

Method II A 2:1 mixture of dienes 86 and 87 (2.14 g) (0.017 moles) was converted to anion 90 at 0°C with n-butyllithium in THF. This anion was slowly transferred by syringe to a flask cooled to -77°C which contained a THF solution of 3.8 g (0.020 moles) of tosylazide in THF under

nitrogen. After addition was complete, the dark brown mixture was allowed to stir for three hours while warming to room temperature. The reaction mixture was diluted with 200 ml of pentane and extracted six times with 150 ml portions of water and once with an equal volume of saturated NaCl. The pentane solution was dried over anhydrous  $\text{MgSO}_4$ , filtered, and the solvent removed. The residual, red oil was purified by chromatography on silica gel. Elution with hexane gave, after solvent removal, 1.12 g (0.0075 moles) (44% isolated yield) of the 4-diazo compound 78. Elution with 90:10 hexane: $\text{Et}_2\text{O}$  yielded, after solvent removal, 0.24 g (0.0017 moles) (10% isolated yield) of 1,1-dimethyl-1-silacyclohexa-2,5-dien-4-ol 89. Elution with 100% diethylether gave a 0.95 g (0.003) (19% yield) red-brown oil which crystallized to tan crystals (m.p. = 122-124°C), which were identified as the 4-tosylamine of 1,1-dimethyl-1-silacyclohexa-2,5-diene 93: NMR ( $\text{CDCl}_3$ )  $\delta$  -0.05 (s, 3H), -0.10 (s, 3H), 2.40 (s, 3H), 4.45 (center of m, 2H), 5.81 (center d of d, 2H,  $J = 3\text{Hz}$ ,  $J = 15\text{ Hz}$ ), 6.39 (center d of d, 2H,  $J = 4\text{ Hz}$ ,  $J = 15\text{ Hz}$ ), 7.30 (d, 2H,  $J = 9\text{ Hz}$ ), 7.82 (d, 2H,  $J = 9\text{ Hz}$ ); IR ( $\text{CCl}_4$  soln.) 3120, 3040, 2950, 1620, 1585, 1375, 1160; mass spectrum (70 eV)  $\underline{m}/\underline{e}$  (rel intensity) 293 (<1), 278 (10), 229 (18), 149 (35), 138 (100), 112 (20), 91 (28); Exact mass calculated for  $\text{C}_{14}\text{H}_{19}\text{O}_2\text{SNSi}$ ,  $\underline{m}/\underline{e} = 293.0906$ ; found:  $\underline{m}/\underline{e} = 293.0998$ .

Vertical flow pyrolysis of (78)

4-Diazo compound 78 was pyrolyzed neat following standard pyrolysis procedures stated previously. Sample introduction was accomplished by either slowly syringing microliter quantities, through a septum, into the tube or by evaporation of 78 from a reservoir suspended over the hot zone. Temperatures varied from 385° - 430°C. In a typical experiment, 0.70 g (0.0047 moles) of 78 was slowly dropped through a tube at 420°C under nitrogen. Analysis of the material condensed in cold traps yielded 0.49 g. Purification of the condensed material was accomplished by silica gel chromatography. Elution with hexane yielded 0.180 g (0.0007 moles) (15.7% yield) of a yellow, viscous oil which was identified as the dimer 94 of 1,1-dimethyl-1-silacyclohexa-2,5-dien-4-ylidene 79: NMR (CCl<sub>4</sub>) δ 0.15 (s, 6H), 6.13 (d, 2H, J = 15 Hz), 7.75 (d, 2H, J = 15 Hz); mass spectrum (70 eV) m/e (rel intensity) 244 (70), 229 (100), 161 (10), 160 (10), 159 (10), 145 (10), 107 (5), 73 (15); Exact mass calculated for C<sub>14</sub>H<sub>20</sub>Si<sub>2</sub>, m/e = 244.1104; found: m/e = 244.1100 ± .0007. Elution with varying ratios of hexane-ether produced 0.08 g of material bearing only silylmethyls: NMR (CCl<sub>4</sub>) δ 0.1 (broad singlet). This product was not identified further. No other material eluded from the column. If moisture was not rigorously excluded from the pyrolysis, varying amounts



of 4,4-dimethyl-4-silacyclohexa-2,5-dien-1-one 76 were eluded with 90:10 hexane:Et<sub>2</sub>O.

Vacuum pyrolysis of (78)

Pyrolysis of 78 at 420 - 450°C at 0.15 mm Hg was accomplished by evaporating through a stopcock small amounts of 78 into a heated tube packed with Vycor chips. Products were condensed into a series of liquid nitrogen traps. Analysis of the condensed material gave the same results as in the vertical flow pyrolysis of 78.

Vertical flow pyrolysis of (78) in benzene-d-6

Pyrolysis of 0.15 g (0.001 moles) of 78 in 5 ml of benzene-d-6 was accomplished in the standard fashion at 390°-400°C. Bulb-to-bulb distillation yielded 0.13 g (0.00063 moles) (63% yield) of benzene-carbene adduct 97. An analytical sample was obtained by GC chromatography on a 6 ft. by 1/4 in., 15% SE 30 on Chromosorb W column: NMR (benzene-d-6)  $\delta$  0.4 (s, 6H), 6.0 (d, 2H, J = 15 Hz), 6.75 (d, 2H, J = 15 Hz), 7.2 (broad signal from benzene); mass spectrum (70 eV)  $\underline{m/e}$  (rel intensity) 206 (60), 191 (58), 163 (14), 140 (40), 74 (60), 59 (100); Exact mass measurements: calculated for C<sub>13</sub>D<sub>6</sub>H<sub>10</sub>Si,  $\underline{m/e}$  = 206.1400; found:  $\underline{m/e}$  = 206.1344; for C<sub>12</sub>D<sub>6</sub>H<sub>7</sub>Si,  $\underline{m/e}$  = 191.1163; found:  $\underline{m/e}$  = 191.1159; for C<sub>10</sub>D<sub>2</sub>H<sub>5</sub>Si,  $\underline{m/e}$  = 163.0866; found:  $\underline{m/e}$  = 163.0860; for C<sub>5</sub>D<sub>5</sub>H<sub>6</sub>Si,  $\underline{m/e}$  = 140.0944; found:  $\underline{m/e}$  = 140.0943.

Flash vacuum pyrolysis of the sodium salt of the tosyl-hydrazone of 1,1-dimethyl-1-silacyclohexa-2,5-dien-4-one (101)

Onto a glass surface heated to 400°C under a vacuum of 2.0 mm Hg, was dropped, in small portions, 0.62 g (1.9 mm) of salt 101. Volatile decomposition products were condensed in a series of three liquid nitrogen cold traps. The contents of the first trap (0.31 g) (61% recovered) were analyzed by mass spectroscopy without exposure to air; mass spectrum (70 eV)  $\underline{m/e}$  (rel intensity) 355 (5), 281 (15), 207 (35), 124 (36), 91 (40), 58 (50), 43 (100); Exact mass measurements calculated for  $C_7H_{21}Si_4O_4$ ,  $\underline{m/e}$  = 281.0515; found:  $\underline{m/e}$  = 281.0522 ± .0014; calculated for  $C_7H_8S$ ,  $\underline{m/e}$  = 124.0345; found:  $\underline{m/e}$  = 124.0348 ± .0006; Peaks at  $\underline{m/e}$  = 355, 281, 207 correspond to P-15 peaks for the pentamer, tetramer, and trimer cyclosiloxanes.  $C_7H_8S$  is p-toluenethiol 102: NMR ( $CDCl_3$ ) δ 2.3 (s, H), 3.4 (s, 1H), 7.1 (m, 4H); NMR of mixture ( $CDCl_3$ ) δ 0.03 (s), 2.3 (s), 3.4 (s), 7.1 (m). The NMR spectrum of the mixture is consistent with the mass spectral findings. Attempts to isolate p-toluenethiol 102 ( $\underline{m/e}$  124) by GC on 6 ft. x 1/4 in. 15% SE 30 on Chromosorb W column resulted in the formation of dibenzylsulfide: NMR ( $CDCl_3$ ) δ 2.34 (s, 3H), 7.1 (m, 4H); IR ( $CCl_4$  soln.) 3080, 3040, 2960, 1495, 1250, 850  $cm^{-1}$ ; mass spectrum (70 eV)  $\underline{m/e}$  (rel intensity) 214 (100), 199 (5), 122 (8), 91 (40); Exact mass calculated for  $C_{14}H_{14}S$ ,  $\underline{m/e}$  = 214.0816; found:  $\underline{m/e}$  = 214.0809 ± .0011.

Flash vacuum pyrolysis of the sodium salt of tosylhydrazine

The sodium salt of tosylhydrazine, prepared by treatment of one equivalent of tosylhydrazine with one equivalent of sodium methoxide in methanol, was pyrolyzed under the same conditions as above. Analysis, by NMR, of the condensed material shows only p-toluenethiol 102, as identified by comparison of NMR to an authentic sample. NMR ( $\text{CDCl}_3$ )  $\delta$  2.3 (s, 3H), 3.4 (s, 1H), 7.1 (m, 4H).

Photolysis of (78) in pentane

In an evacuated, freeze-thaw-degassed tube, was sealed a solution of 0.043 g (0.3 mmoles) of diazo compound 78 in 30 ml of pentane. The Pyrex tube was irradiated with 3000 Å light in a Rayonet reactor for ten hours. Removal of solvent gave 0.063 g of material which, by GC, consisted of 83% (0.26 mmoles) of 1,1-dimethyl-4-pentyl-1-silacyclohexa-2,5-diene 105: NMR ( $\text{CDCl}_3$ ) (see Figure 3)  $\delta$  -0.01 (s, 3H), 1.00 (center broad m, 11H), 2.92 (m, 1H), 5.80 (center d of d, 2H,  $J = 15$  Hz,  $J = 2$  Hz), 6.56 (center d of d, 2H,  $J = 15$  Hz,  $J = 4$  Hz); IR (film) 2975, 2940, 2915, 2890, 1730, 1615, 1475, 1465, 1385, 1304, 1290, 1265  $\text{cm}^{-1}$ ; mass spectrum (70 eV)  $\underline{m/e}$  (rel intensity) 194 (40), 179 (16), 165 (12), 152 (15), 123 (65), 122 (30), 110 (35), 109 (100), 95 (25), 58 (35), 43 (73); Exact mass calculated for  $\text{C}_{12}\text{H}_{22}\text{Si}$ ,  $\underline{m/e} = 194.1491$ ; found:  $\underline{m/e} = 194.1493 \pm 0.001$ .

Photolysis of (78) in perfluorobenzene

In a Pyrex nmr tube was placed 0.011 g (0.07 mmoles) of 78 in 2 ml of perfluorobenzene. The sample was freeze-thaw-degassed and sealed under vacuum. Before irradiation at 3000 Å in a Rayonet reactor, the following NMR spectrum was obtained: (benzene-F-6)  $\delta$  0.02 (s, 6H), 5.51 (d, 2H,  $J = 15$  Hz), 6.83 (d, 2H,  $J = 15$  Hz). After twelve hours of irradiation, a flaky material coated the sides of the NMR tube. Analysis by NMR ( $\text{CCl}_4$ ) showed at  $\delta$  0.1 - 0.4 broad, hashed signals which indicate sample decomposition had occurred. The sample was not sufficiently volatile to obtain a mass spectrum.

Photolysis of (78) in perfluoro-n-hexane at 3000 Å

In a Pyrex tube was placed 0.319 (2.1 mmoles) of diazo compound 78 in 150 ml of perfluoro-n-hexane (Pierce). The solution was degassed during four freeze-thaw cycles and sealed under vacuum. Irradiation was accomplished in a Rayonet reactor with 3000 Å light for ten hours. The perfluoro-n-hexane solution was yellow in color and contained a yellow solid. The entire mixture was extracted three times with methylene chloride. Nothing remained in the fluorocarbon (by NMR). Removal of the solvent gave a red-orange oil which was unreacted starting material and an unidentified polymer: NMR ( $\text{CDCl}_3$ )  $\delta$  0.01 (s, 10H),

5.5 (d, 2H,  $J = 15$  Hz), 6.9 (d, 2H,  $J = 15$  Hz); IR (thin film)  $2050\text{ cm}^{-1}$ .

Photolysis of (78) in perfluoro-*n*-hexane at  $2537\text{ \AA}$

In a quartz tube equipped with a vacuum stopcock was placed 0.24 g (1.6 mmoles) of 78 in 80 ml of perfluoro-*n*-hexane (0.02 M). The solution was degassed and sealed under vacuum. The tube was irradiated in a Rayonet reactor with  $2537\text{ \AA}$  light for twenty hours. The reaction mixture was yellow and contained a large amount of solid material. The reaction mixture was extracted three times with methylene chloride, and the solvent removed, leaving a yellow oil. This oil was purified by column chromatography on silica gel. Elution with hexane gave a yellow oil. Elution with varying amounts of ether-hexane gave only a mixture of methylsiloxanes: NMR ( $\text{CCl}_4$ )  $\delta$  0.5 - 0.10 (overlapped s); mass spectrum (70 eV)  $m/e = 281, 207$ . The hexane fraction was further purified by HPLC on 3 ft.  $\mu$ -Porasil using hexane as solvent. At least two compounds are present, the major product was identified as 1-methyl-1-silabicyclo-[2.2.1]hepta-2,5-diene 107: NMR (see Figure 4a); IR (film) 3020, 2950, 2920, 2850, 1600, 1455, 1375, 1360,  $1245\text{ cm}^{-1}$ ; mass spectrum (see Table 2); exact mass calculated for  $\text{C}_7\text{H}_{10}\text{Si}$ ,  $m/e = 122.0552$ ; found  $m/e = 122.0472 \pm 0.0006$ . 107 was contaminated with a trace of carbene dimer 94, as evidenced by its NMR (Figure 2) and mass spectrum (Table

2). Compound 107 would not pass through a GC at temperatures from 80°C to 250°C on either a 5% SE 30 or 5% Dexsil 300 column.

Mercury photosensitized gas phase decomposition of (78)

An evacuated quartz tube containing a drop of mercury and 0.15 g (1.0 mmoles) of 78 was photolyzed at 2537 Å in a Rayonet reactor for four hours. A yellow polymer coated the sides of the vessel and would not dissolve in a variety of solvents. The tube was washed with CH<sub>2</sub>Cl<sub>2</sub>. Removal of CH<sub>2</sub>Cl<sub>2</sub> gave 0.095 g of a yellow oil. NMR indicates the same mixture of products is present as in the previous reaction. The mixture was purified in the same manner.

Attempted trapping of 1,1-dimethyl-1-silacyclohexadienyl anion (90) with bromine in pentane

Anion 90 was generated from 1.00 g (8.1 mmoles) of a mixture of silacyclohexadienes 86 and 87 with 8.1 mmoles of *t*-butyllithium, at room temperature, as before. A solution of 1.30 g of bromine (8.1 mmoles) in 30 ml of pentane was added to anion 90 over a ten minute period. The mixture was allowed to stir under nitrogen for four additional hours, after which, the mixture was diluted with 100 ml of pentane and washed three times with water and once with saturated NaCl. The pentane layer was dried over anhydrous MgSO<sub>4</sub>, filtered, and the solvent removed, yielding 1.2 g of a red

oil. Analysis by GC on an 8 ft. x 1/4 in. 20% DC 550 on Chromosorb W column at 160°C, showed one major product (76%). This product was identified as 1,1-dimethyl-4-pentyl-1-silacyclohexa-2,5-diene 105 by comparison to an authentic sample: NMR (CDCl<sub>3</sub>) δ -0.01 (s, 3H), 1.00 (center broad m, 11H), 2.92 (m, 1H), 5.80 (center d of d, 2H, J = 15 Hz, J = 2 Hz), 6.56 (center d of d, 2H, J = 15 Hz, J = 4 Hz).

Formation of 4-trimethylsilyl-1,1-dimethyl-1-silacyclohexa-2,5-diene (91)

A mixture of 2.00 g (16.1 mmoles) of silacyclohexadienes 86 and 87, and 2.20 g (20.0 mmoles) of trimethylchlorosilane were dissolved in 40 ml of dry THF under a nitrogen atmosphere. The mixture was cooled to -77°C and 16.1 mmoles of n-butyllithium was slowly syringed into the mixture. After addition was complete, the mixture was allowed to stir slowly, with warming to room temperature over an eight hour period. THF was removed under aspirator vacuum and replaced with 100 ml of chloroform. The lithium salts were filtered through Celite and the chloroform removed, leaving a brown oil. Distillation at 35°- 37°C at 0.6 mm Hg yielded 1.60 g (51%) of 4-trimethylsilyl-1,1-dimethyl-1-silacyclohexa-2,5-diene 91: NMR (CHCl<sub>3</sub>) δ 0.02 (3 overlapped s, 14H), 2.72 (apparent t, 1H), 5.65 (d of d, 2H, J = 15 Hz, J = 1.5 Hz), 6.66 (d of d, 2H, J = 15 Hz, J = 5 Hz) (135); mass spectrum (70 eV) m/e (rel intensity), 196 (4), 181 (5), 123 (3),

122 (5), 108 (75), 93 (14), 73 (100); Exact mass calculated for  $C_{10}H_{20}Si$ ,  $\underline{m/e} = 196.1104$ ; found:  $\underline{m/e} = 196.1142 \pm .001$ .

Attempted synthesis of 2-bromo-4-trimethylsilyl-1,1-dimethyl-1-silacyclohexa-3,5-diene (117)

A solution of 0.273 g (1.4 mmoles) of the 4-trimethylsilylcyclohexadiene 91 in 20 ml of THF was treated with 1.4 mmoles of t-butyllithium at  $-100^{\circ}C$  under nitrogen. The solution immediately turned a yellow-green color and was allowed to stir at  $-100^{\circ}C$  for one hour. At this time, 0.14 mmoles of bromine in 10 ml of THF was added slowly. The solution was gradually warmed to room temperature. The THF was removed under aspirator vacuum and replaced with chloroform. Filtration of lithium salts, followed by removal of the solvent, left 0.35 g of a brown oil. The brown oil was further purified by GC on an 8 ft. x 1/4 in. 20% DC 550 on Chromosorb W column at  $170^{\circ}C$ . Two major components, in equal amounts, were found. The first was hexamethyl-disiloxane: NMR ( $CCl_4$ )  $\delta -0.01$  (s); GCMS (70 eV)  $\underline{m/e}$  (rel intensity) 162 (0), 147 (100), 73 (19), 57 (12). The second component appeared to result from a reaction between THF and the silacyclohexadiene ring and was not investigated further: NMR ( $CCl_4$ )  $\delta -0.1$  (overlapped s) 1.0 - 2.0 (broad m), 3.1 - 4.2 (broad m), 5.1 - 5.3 (broad m); GCMS (70 eV)  $\underline{m/e}$  (rel intensity) 217 (108), 202 (5), 129 (16), 73 (11), 59 (8).



Diazo transfer reaction on the anion of (91)

The anion of 0.313 g (1.6 mmoles) of 4-trimethylsilylsilacyclonexadiene 91 was generated in THF under a nitrogen atmosphere by adding 1.6 mmoles of n-butyllithium. The red solution was allowed to stir for fifteen minutes, after which it was added to a solution of 0.32 g (1.7 mmoles) of tosylazide in THF at 0°C. A brown color developed upon addition of the anion. The solution was allowed to gradually warm to room temperature. To the reaction mixture was added 200 ml of pentane and the solution was extracted four times with H<sub>2</sub>O and once with saturated NaCl. The pentane layer was dried over anhydrous MgSO<sub>4</sub>, filtered, and the solvent removed. The resulting yellow-orange oil was purified by column chromatography on silica gel. Hexane elution yielded 0.12 g (0.8 mmoles) (50% yield) of 4-diazo-1,1-dimethyl-1-silacyclohexa-2,5-diene 78 as identified by comparison of NMR and IR spectra to authentic samples.

Trapping of silacyclohexadienyl anion (90) by methyl iodide

The anion of a mixture of 1.05 g (8.47 mmoles) of silacyclohexadienes 86 and 87 was generated in ether in the standard manner with 8.50 mmoles of n-butyllithium. To the red, anion solution was added 1.4 g (9.9 mmoles) of methyl iodide. After stirring for three hours, the ether solution was extracted with water, dried over anhydrous MgSO<sub>4</sub>, filtered, and the solvent removed to leave approximately

0.7 g (5 mmoles) of a mixture of 2.5 parts 1,1,4-trimethyl-1-silacyclohexa-2,5-diene 122 and 1 part 1,1,6-trimethyl-1-silacyclohexa-2,4-diene 121. The ratio of the products was determined both by GC and NMR. Analytical samples were obtained by preparative GC on a 12 ft. x 1/4 in. 20% DC 550 on Chromosorb W column at 130°C. 1,1,4-Trimethyl-1-silacyclohexa-2,5-diene 122: NMR (CDCl<sub>3</sub>) δ 0.0 (s, 3H), 1.02 (d, 3H, J = 7.5 Hz), 2.81 (m, 1H), 5.73 (center d of d, 2H, J<sub>AB</sub> = 15 Hz, J<sub>AX</sub> = 3 Hz), 6.59 (center d of d, 2H, J<sub>AB</sub> = 15 Hz, J<sub>BX</sub> = 4 Hz); mass spectrum (70 eV) m/e (rel intensity) 138 (15), 123 (100), 95 (98), 73 (86), 59 (50), 43 (40); 1,1,6-trimethyl-1-silacyclohexa-2,4-diene 121: NMR (CDCl<sub>3</sub>) δ -0.1 (s, 3H), 0.0 (s, 3H), 0.98 (d, 3H, J = 8 Hz), 1.56 (center q, 1H, J = 8 Hz), 5.81 (center m, 3H), 6.68 (m, 1H); mass spectrum (70 eV) m/e (rel intensity) 138 (45), 123 (95), 95 (100), 73 (85), 59 (73).

Trapping of silacyclohexadienyl anion (90) with ethylbromide

The anion of a mixture of 3.0 g (0.024 moles) of silacyclohexadienes 86 and 87 was generated in the standard fashion with 0.024 moles of n-butyllithium. To the stirring THF solution (50 ml) of the anion was added 2.7 g (0.024 moles) of ethylbromide in 10 ml of THF at 78°C. After stirring overnight, the mixture was filtered, and the THF was removed under aspirator vacuum and replaced with 100 ml of pentane. The pentane solution was extracted three times

with 100 ml of H<sub>2</sub>O, once with saturated NaCl, and dried over anhydrous MgSO<sub>4</sub>. Filtration and removal of the pentane yielded 2.4 g of a yellow oil which, by NMR and GC, was determined to be 6 parts 4-ethyl-1,1-dimethyl-1-silacyclohexa-2,5-diene 123 and 1 part 2,4-diethyl-1,1-dimethyl-1-silacyclohexa-3,5-diene 124. 4-Ethyl-1,1-dimethyl-1-silacyclohexa-2,5-diene 123: NMR (CDCl<sub>4</sub>) δ 0.0 (s, 6H), 0.78 (t, 3H, J = Hz), 1.4 (m, 2H), 2.85 (m, 1H), 5.8 (d of d, 2H, J<sub>AB</sub> = 15 Hz, J<sub>AX</sub> = 2H), 6.58 (d of d, 2H, J<sub>AB</sub> = 15 Hz, J<sub>BX</sub> = 5 Hz); IR (film) 3025, 2960, 2920, 1640, 1610, 1475, 1375, 1260 cm<sup>-1</sup>; mass spectrum (70 eV) m/e (rel intensity) 152 (43), 137 (100), 123 (55), 109 (35), 95 (50); 2,4-diethyl-1,1-dimethyl-1-silacyclohexa-3,5-diene 124: NMR (CDCl<sub>3</sub>) δ 0.0 (s, 6H), 0.8 (t, 6H, J = Hz), 1.4 (m, 5H), 5.9 (m, 2H), 6.4 (m, 1H); mass spectrum (70 eV) m/e (rel intensity) 180 (55), 165 (50), 151 (100).

#### Trapping of silacyclohexadienyl anion (90) with t-butylbromide

The silacyclohexadienyl anion of 3.38 g (0.027 moles) of diene 86 and 87 was generated at 0°C in THF with 0.027 moles of t-butyllithium. To the stirring anion solution, was added 3.7 g (0.027 moles) of t-butylbromide. The mixture was allowed to stir for ten hours, at which time a second equivalent of (0.027 moles) t-butyllithium was added, and the mixture was allowed to stir an additional twelve hours. Dilution with 100 ml of pentane, extraction with H<sub>2</sub>O, drying

over anhydrous  $\text{MgSO}_4$ , filtration, and removal of the pentane yielded 1.75 g of a yellow oil. The oil was purified by column chromatography on silica gel. Elution with pentane produced 1.54 g (0.009 moles) (32% isolated yield) of pure 4-t-butyl-1,1-dimethyl-1-silacyclohexa-2,5-diene 125. Elution with 90:10 pentane:ether produced 0.21 g (0.001) (4% isolated yield) of 2-bromo-1,1-dimethyl-1-silacyclohexa-3,5-diene 114. However, the yield of this product varies from reaction to reaction. When n-butyllithium is used to generate anion 90, the yield of 125 is reduced by one-third and is replaced by 4-n-butyl-1,1-dimethyl-1-silacyclohexa-2,5-diene 126. Analytical samples of 114, 126 and 126 were obtained by preparative GC on a 16 ft. x 1/4 in. 15% SE 30 on Chromosorb W column at 180°C. 4-t-Butyl-1,1-dimethyl-1-silacyclohexa-2,5-diene 125: NMR ( $\text{CCl}_4$ )  $\delta$  0.0 (s, 6H), 0.91 (s, 9H), 2.71 (m, 1H), 5.91 (d of d, 2H,  $J_{AB} = 15$  Hz,  $J_{AX} = 3$  Hz), 6.85 (d of d, 2H,  $J_{AB} = 15$  Hz,  $J_{BX} = 5$  Hz); IR (film) 3020, 2950, 2890, 2860, 1635, 1605, 1475, 1375, 1360, 1245  $\text{cm}^{-1}$ ; mass spectrum (70 eV)  $\underline{m/e}$  180 (9), 165 (10), 124 (50), 109 (50), 95 (10), 57 (100), 43 (40), 41 (40); Exact mass calculated for  $\text{C}_{11}\text{H}_{20}\text{Si}$ ,  $\underline{m/e} = 180.1334$ ; found:  $\underline{m/e} = 180.1334 \pm 0.0009$ ; 2-bromo-1,1-dimethyl-1-silacyclohexa-3,5-diene 114: NMR ( $\text{CCl}_4$ )  $\delta$  0.13 (s, 6H), 1.52 (d, 1H,  $J = 3$  Hz), 6.08 (m, 3H), 6.90 (m, 1H); IR (film) 3020, 2980, 2950, 2890, 1683, 1616, 1250, 840, 700  $\text{cm}^{-1}$ ; mass

spectrum (70 eV)  $\underline{m/e}$  (rel intensity) 202 (0), 123 (5), 122 (30), 107 (100), 81 (15), 79 (18), 57 (26); 4-n-butyl-1,1-dimethyl-1-silacyclohexa-2,5-diene 126: NMR ( $\text{CCl}_4$ )  $\delta$  0.0 (s, 6H), 0.9 (center m, 9H), 2.9 (m, 1H), 5.7 (d of d, 2H,  $J_{AB} = 15$  Hz,  $J_{AX} = 2$  Hz), 6.65 (d of d, 2H,  $J_{AB} = 15$  Hz,  $J_{BX} = 5$  Hz); mass spectrum (70 eV)  $\underline{m/e}$  (rel intensity) 180 (56), 165 (100), 138 (72), 124 (33), 123 (66), 109 (77), 95 (56), 59 (44), 57 (100), 43 (66); Exact mass calculated for  $\text{C}_{11}\text{H}_{20}\text{Si}$ ,  $\underline{m/e} = 180.1334$ ; found:  $\underline{m/e} = 180.1323 \pm 0.0009$ .

#### Diazo transfer reaction to the anion of (125)

To 0.198 g (1.1 mmoles) of 125 in THF at 0°C, was added 1.1 mmoles of n-butyllithium. A red solution resulted. The anion was added to 0.218 g (1.1 mmoles) of tosylazide in THF at 0°C. The resulting mixture was stirred at room temperature for two hours. The reaction mixture was diluted with 100 ml of pentane, extracted three times with  $\text{H}_2\text{O}$ , once with saturated NaCl, dried over anhydrous  $\text{MgSO}_4$ , filtered, and the pentane removed to leave a red oil. The IR spectrum of the crude reaction mixture showed that a diazo compound ( $2035 \text{ cm}^{-1}$ ) was present. NMR spectra and the GC retention times confirmed the presence of starting material 125. Attempts at purification by column chromatography on silica gel resulted in decomposition of the diazo compound. The only product of the reaction tentatively identified is

2-tosylamine-4-t-butyl-1,1-dimethyl-1-silacyclohexa-3,5-diene 128: NMR ( $\text{CCl}_4$ )  $\delta$  0.01 (s, 6H), 1.1 (s, 9H), 2.4 (s, 3H), 5.8 - 6.4 (m, 3H), 7.2 (d, 2H,  $J = 9$  Hz), 7.8 (d, 2H,  $J = 9$  Hz). The ring proton at the 2-position could not be detected, due to hexane impurities. IR (film) of mixture 3280, 3050, 2960, 2120, 2035, 1640, 1610, 1465, 1380, 1360, 1255, 1190, 1170  $\text{cm}^{-1}$ .

#### Co-pyrolysis of hexachlorodisilane and cyclopentadiene

Three equivalents of cyclopentadiene were mixed with one equivalent hexachlorodisilane and pyrolyzed in a horizontal flow pyrolysis system at 600°C, according to the procedure of Chernyshev and co-workers (130). Immediate distillation at 25 mm Hg yields a 25-35% yield of a fraction boiling between 63° and 70°C. This fraction was identified by NMR as a mixture of the conjugated and unconjugated dichlorodienes 131. The ratio of the conjugated isomer to the unconjugated is about 10:1 by NMR. Analytical samples were obtained by preparative GC on a 15 ft. x 1/4 in. 20% SE 30 on Chromosorb W column. 1,1-Dichloro-1-silacyclohexa-2,4-diene 131: NMR ( $\text{CCl}_4$ )  $\delta$  2.1 (d, 2H,  $J = 5$  Hz), 6.15 (m, 3H), 7.0 (d of m, 1H); mass spectrum (70 eV)  $\underline{m/e}$  (rel intensity) 166 (60), 164 (100), 131 (20), 129 (80).

Synthesis of 1,1-dimethoxy-1-silacyclohexa-2,4-diene (132)

To one equivalent of neat 1,1-dichloro-1-silacyclohexa-2,4-diene 131, under a nitrogen atmosphere, was added ten equivalents of trimethylorthoformate. The mixture was stirred at room temperature for twenty-four hours and at 80°C for twelve hours. Distillation at atmospheric pressure removed the excess orthoformate. The residue was distilled at 35 mm Hg. The fraction boiling at 75-80°C contained the desired 1,1-dimethoxy-1-silacyclohexa-2,4-diene 132: NMR (CCl<sub>4</sub>) δ 1.5 (d, 2H, J = 3.5 Hz), 3.45 (s, 6H), 5.95 (m, 3H), 6.85 (d of m, 1H).

Synthesis of 2,4-bis(trimethylsilyl)-1,1-dimethoxy-1-silacyclohexa-3,5-diene (133)

To a THF solution of one equivalent of 132 and three equivalents of trimethylchlorosilane cooled to -77°C, was added three equivalents of *t*-butyllithium. The reaction was allowed to warm to room temperature after which the mixture was stirred another two hours. Filtration and removal of the solvent yielded a red-orange oil. Preparative GC on a 3 ft. x 1/4 in. 15% SE 30 on Chromosorb W column at 150°C yielded 2,4-bis(trimethylsilyl)-1,1-dimethoxy-1-silacyclohexa-3,5-diene 133 and 4-trimethylsilyl-1,1-dimethoxy-1-silacyclohexa-2,5-diene in equal amounts. Compound 133: NMR (CDCl<sub>3</sub>) δ -0.15 (s, 9H), -0.10 (s, 9H), 1.48 (d, 1H, J = 7 Hz), 3.3 (s, 3H), 3.45 (s, 3H), 5.7 (d, 1H, J = 15 Hz),

6.32 (d of d, 1H,  $J = 7$  Hz,  $J = 2$  Hz), 7.0 (d of d, 1H,  $J = 15$  Hz,  $J = 2$  Hz); mass spectrum (70 eV)  $\underline{m/e}$  (rel intensity) 300 (50), 285 (20), 196 (100), 181 (95), 104 (10), 89 (55), 73 (60); Exact mass calculated for  $C_{13}H_{28}O_2Si_3$ ,  $\underline{m/e} = 300.1397$ ; found:  $m/e = 300.1356 \pm .0015$ ; Exact mass calculated for  $C_9H_{16}Si_2O$ ,  $\underline{m/e} = 196.0740$ ; found:  $\underline{m/e} = 196.0726 \pm .001$ ; 4-trimethylsilyl-1,1-dimethoxy-1-silacyclohexa-2,5-diene: NMR ( $CDCl_3$ )  $\delta$  0.10 (s, 9H), 2.9 (m, 1H), 3.49 (x, 3H), 3.56 (s, 3H), 5.75 (d of d, 2  $H_A$ ,  $J_{AB} = 15$  Hz,  $J_{AX} = 2$  Hz), 7.0 (d of d, 2  $H_B$ ,  $J_{AB} = 15$  Hz,  $J_{BX} = 4$  Hz).

Flow pyrolysis of (133) at 400°C in benzene

A solution of 0.36 g (2.0 mmoles) of 133 in 10 ml of dry benzene was pyrolyzed in a vertical nitrogen flow pyrolysis system. Products were condensed in a liquid nitrogen cooled trap. Analysis by GCMS indicates some starting material 133: mass spectrum (70 eV)  $\underline{m/e}$  (rel intensity) 300 (35), 285 (30), 196 (100), 181 (70); and methoxytrimethylsilane: NMR ( $CCl_4$ )  $\delta$  -0.05 (s, 3H), 3.3 (s, 1H); mass spectrum (70 eV)  $\underline{m/e}$  (rel intensity) 104 (10), 89 (100), 73 (70). NMR of the mixture shows peaks only at  $\delta$  0.0 and  $\delta$  3.3 and very little in the olefin region. Attempts at purification by GC on 15% SE 30 column, or HPLC on  $\mu$ -Porasil (Waters), were not successful.



Flow pyrolysis (133) at 400°C neat

0.34 g (2.0 mmoles) of 133 were pyrolyzed as above. Analysis of the condensed material produced the same results as in benzene. Only 133 and methoxytrimethylsilane were identified.

Static pyrolysis of (133) in decalin

In a NMR tube was placed 0.10 g (0.33 mmoles) of 133 in 3 ml of decalin. The solution was degassed and sealed. The reaction was monitored by NMR. After heating at 206°C for three hours, NMR indicated the presence of methoxytrimethylsilane ( $\delta$  0.0, s; 3.3, s) and starting material. After twenty-four hours, the reaction was stopped: NMR (decalin)  $\delta$  0.0 - 0.2 (overlapped s), 3.1 - 3.5 (overlapped s), 5.5 - 7.0 (weak undefined multiplets). Analysis by GC showed only a trace of 133 and a large amount of methoxytrimethylsilane. Attempts at purification by HPLC did not yield any identifiable material.

Static pyrolysis of (133) in 1,2,4-trichlorobenzene

A sealed, degassed NMR tube containing 0.11 g (0.37 mmoles) of 133 in 3 ml of 1,2,4-trichlorobenzene was heated to 200°C for fifteen hours. At this time, NMR indicated no starting material remained. The sample was heated to 60°C at 0.1 mm Hg to remove the solvent and methoxytrimethylsilane produced in the reaction, as evidenced by NMR. A yellow oil

remained which was further purified by chromatography on silica gel. Elution with 3:2 hexane:CHCl<sub>3</sub> gave a yellow oil. NMR indicated it was still a mixture: NMR (CDCl<sub>3</sub>) δ 0.1 (broad s), 3.4 (m), 6.0 - 6.5 (very broad m). The sample would not pass through the GC, thus nothing was identified in this mixture.

#### Flow pyrolysis of (133) with benzophenone

A benzene solution containing 0.36 g (0.0012 moles) of 133 and 2.19 g (0.012 moles) of benzophenone was pyrolyzed at 450°C. Analysis of the product mixture by HPLC on μ-Porasil (Waters) gave unreacted benzophenone, methoxytrimethylsilane, and the same unidentified mixture found in the previous pyrolyses.

#### Reaction of 1,1-dichloro-1-silacyclohexa-2,5-diene (131) with t-butyllithium in pentane

A solution of 0.38 g (2.2 mmoles) of 131 (obtained immediately prior to use by preparative GC) in 50 ml of pentane, was cooled under nitrogen to -77°C. Two equivalents (4.4 mmoles) of t-butyllithium were added slowly. Upon warming, a white precipitate formed. At room temperature, GC indicated no 131 remained. Filtration and removal of the solvent yielded 0.36 g of an orange oil. This sample would not pass through a GC. The oil rapidly turned into a glass which did not melt up to 350°C: NMR (CCl<sub>4</sub>) δ 0.8 - 1.6

(broad m, 12H), 5.5 - 6.3 (broad m, 1H). The product was not identified.

Reaction of (144) with *t*-butyllithium in the presence of perfluoro-2-butyne

To a pentane solution of 0.40 g (2.4 mmoles) of 144 was added 4.8 mmoles of *t*-butyllithium at  $-77^{\circ}\text{C}$  under a nitrogen atmosphere. Excess perfluoro-2-butyne was then condensed into the reaction vessel. The mixture was allowed to warm to room temperature. Filtration and removal of the solvent yielded 0.42 g of a tan oil which rapidly polymerized. Analysis of the oil by GC on a 16 ft. x 1/4 in. 15% SE 30 on Chromosorb W column, yielded only one compound which, by NMR, contained only *t*-butyl absorptions. It was not investigated further. NMR of tan polymers ( $\text{CCl}_4$ ) 0.8 - 1.3 (broad m, 7H), 5.4 - 6.8 (broad m, 1H). This polymer was not identified.

Mercury photosensitized coupling of methyldichlorosilane (148)

In a quartz tube was placed 210 g (2.84 moles) of 148, along with a drop of mercury. The sample was photolyzed for ten days in the same manner as was trimethylchlorosilane. Distillation at atmospheric pressure, b.p.  $150-157^{\circ}\text{C}$ , yielded

61 g (0.27 moles) of 1,1,2,2-tetrachloro-1,2-dimethyl-disilane 149. A 20% yield of 149 based on starting 148: NMR ( $\text{CCl}_4$ )  $\delta$  1.0 (s) (65).

Co-pyrolysis of (149) and cyclopentadiene

Three equivalents of cyclopentadiene were mixed with one equivalent of 149 and the mixture was pyrolyzed at 610°C in a vertical flow pyrolysis. The procedure of Kline was followed (65). A fractional distillation, immediately following pyrolysis, yielded a fraction (b.p. 68 - 73°C, 31 mm Hg) containing 80% 1-chloro-1-methyl-1-silacyclohexa-2,4-diene 136, 10% 1-chloro-1-methyl-1-silacyclohexa-2,5-diene 150, and 10% 1,1,2,2-tetrachloro-1,2-dimethyldisilane. Pure samples were obtained by preparative GC on a 20 ft. by 1/4 in. 20% DC 550 on Chromosorb W column. 1-Chloro-1-methyl-1-silacyclohexa-2,4-diene 136: NMR ( $\text{CCl}_4$ )  $\delta$  0.56 (s, 3H), 1.9 (m, 2H), 6.1 (m, 3H), 6.9 (d of m, 1H); IR (film) 3040, 3020, 2980, 1630, 1550, 1380, 1360, 1265  $\text{cm}^{-1}$ ; mass spectrum (70 eV)  $\underline{m/e}$  (rel intensity) 146 (21), 144 (55), 131 (37), 129 (100), 109 (11), 108 (67); 1-chloro-1-methyl-1-silacyclohexa-2,5-diene 150: NMR ( $\text{CCl}_4$ )  $\delta$  0.50 (s, 3H), 3.00 (m, 2H), 5.90 (d of t, 2H,  $J = 15$  Hz, 2Hz), 6.64 (d of t, 2H,  $J = 15$  Hz, 3.5 Hz); IR (film) 3010, 2980, 2920, 2880, 1670, 1618, 1405, 1375, 1260  $\text{cm}^{-1}$ ; mass spectrum (70 eV)  $\underline{m/e}$  (rel intensity) 146 (18), 144 (47), 131 (37), 129 (100),

109 (18), 100 (48); Exact mass calculated for  $C_6H_9SiCl$ ,  $m/e = 144.0161$ ; found:  $m/e = 144.0209 \pm .001$ .

Reaction of (136) with *t*-butyllithium in pentane

A solution of freshly GC prepped 136 (0.79 g, 5.4 mmoles) in 25 ml of pentane was cooled to  $-77^\circ C$  under a nitrogen atmosphere. To the cold solution was added 5.4 mmoles of *t*-butyllithium over a five minute period. The mixture was allowed to gradually warm to  $-30^\circ C$ , where a precipitate formed, and then to room temperature, where the solution was stirred for twelve hours. At this time, excess methyl iodide (2 ml) was injected into the mixture. Filtration through Celite, and removal of solvent by aspirator vacuum yielded 0.74 g of a yellow oil. This oil was further purified by column chromatography on silica gel. Pentane elution yielded 0.48 g of a material which, by GC on a 3 ft. x 1/4 in. 5% Dexsil 300 on Chromosorb P column, contained four components identified as the following:

1-*t*-butyl-1-methyl-1-silacyclohexa-2,4-diene 151 (5% of mixture): NMR ( $CCl_4$ ) (see Figure 10)  $\delta$  0.1 (s, 3H), 0.95 (s, 9H), 1.55 (m, 2H), 6.1 (m, 3H), 6.5 (m, 1H); IR (film) 3030, 3000, 2960, 2940, 2870, 1625, 1550, 1475, 1365, 1255  $cm^{-1}$ ; mass spectrum (70 eV)  $m/e$  (rel intensity) 166 (10), 151 (1), 109 (100), 58 (20), 57 (15), 43 (90); 1,5-di-*t*-butyl-1-methyl-1-silacyclohex-3-ene 152 (15% of mixture): NMR ( $CCl_4$ ) (see Figure 8)  $\delta$  0.05 (s, 3H), 1.0 (s, 9H),

1.06 (s, 9H), 1.2 - 1.5 (m, 5H), 6.85 (m, 2H); IR (film) 3020, 2950, 2920, 2890, 2850, 1615, 1465, 1360, 1240, 1190  $\text{cm}^{-1}$ ; mass spectrum (70 eV)  $\underline{m/e}$  (rel intensity) 224 (10), 209 (8), 166 (100), 138 (7), 124 (15), 110 (50); Exact mass calculated for  $\text{C}_{14}\text{H}_{28}\text{Si}$ ,  $\underline{m/e} = 224.1960$ ; found:  $\underline{m/e} = 224.1935 \pm .001$ ; an adduct between starting material 136 and silabenzene (compound 154) (2% of mixture): NMR (see Figure 11); IR (film) 3020, 2970, 2940, 2905, 1625, 1600, 1545, 1465, 1400, 1360, 1255  $\text{cm}^{-1}$ ; mass spectrum (70 eV)  $\underline{m/e}$  (rel intensity) 252 (3), 129 (3), 109 (20), 108 (100), 93 (20), 57 (10), 53 (12), 43 (15); Exact mass calculated for  $\text{C}_{12}\text{H}_{17}\text{Si}_2\text{Cl}$ ,  $\underline{m/e} = 252.0557$ ; found:  $\underline{m/e} = 252.0588 \pm 0.0012$ ; Exact mass calculated for  $\text{C}_6\text{H}_8\text{Si}$ ,  $\underline{m/e} = 108.0395$ ; found:  $\underline{m/e} = 108.0406 \pm .0006$ ; and an adduct between starting material 136 and silene 155, compound 153 (60% of mixture): NMR (see Figure 9); IR (film) 3010, 2960, 2900, 2870, 1630, 1600, 1475, 1390, 1360, 1255  $\text{cm}^{-1}$ ; mass spectrum (70 eV)  $\underline{m/e}$  (rel intensity) 310 (1), 295 (1), 253 (1), 166 (3), 109 (5), 57 (15), 43 (100); Exact mass calculated for  $\text{C}_{16}\text{H}_{27}\text{Si}_2\text{Cl}$ ,  $\underline{m/e} = 310.1340$ ; found:  $\underline{m/e} = 310.1333 \pm .001$ .

Reaction of (136) with t-butyllithium in the presence of excess trimethylchlorosilane

The preceding reaction was repeated with 0.417 g (0.0029 moles) of 136, 0.0029 moles of t-butyllithium, and

0.04 moles of trimethylchlorosilane present before addition of the base. After the same work-up, 0.35 g of the same mixture of products was obtained by column chromatography. GC shows the ratios of the products to one another are unchanged.

Reaction of dimethylsilacyclohexadienes (86) and (87), trimethylchlorosilane and *t*-butyllithium in pentane

To a solution of 0.13 g (0.001 moles) of dienes 86 and 87 in 20 ml of pentane under nitrogen and cooled to  $-77^{\circ}\text{C}$ , was added 0.001 moles of *t*-butyllithium. This solution was allowed to stir at  $-77^{\circ}\text{C}$  for one hour. At this time, 0.11 g (0.001 moles) of trimethylchlorosilane was added to the reaction mixture. The mixture was gradually warmed to room temperature, filtered, and the solvent removed. NMR of the mixture indicated two products, *t*-butyltrimethylsilane and 4-*t*-butyl-1,1-dimethyl-1-silacyclohexa-2,5-diene 91. GCMS confirmed the formation of 91: GCMS (70 eV)  $m/e$  (rel intensity) 196 (29), 100 (7), 109 (95), 73 (100).

The reaction of (136) with *t*-butyllithium in the presence of excess butadiene

In a dry flask cooled to  $-77^{\circ}\text{C}$ , was condensed an excess (about 10 ml) of butadiene. To the butadiene was added 0.480 g (0.0033 moles) of 136 in 30 ml of dry pentane. *t*-Butyllithium (0.0033 moles) was added to this mixture at

-77°C. The mixture was allowed to gradually warm to room temperature. Filtration through Celite and removal of the solvent by aspirator vacuum gave 0.73 g of a yellow oil, which was analyzed by GC on a 3 ft. x 1/4 in. 10% Apiezon L on Celite column at 180°C. The mixture contained a small amount of starting material, a product derived from 136, t-butyllithium, butadiene (compound 165) (70 mole % yield), and a trace of a silabenzene-butadiene adduct. Compound 165: NMR (see Figure 13) (CDCl<sub>3</sub>) δ 0.12 (s, 3H), 0.86 (s, 9H), 2.51 (m, 4H), 2.87 (m, 2H), 5.37 (m, 2H), 5.91 (m, 3H), 6.75 (d of m, 1H); IR (film) 3150, 3000, 2960, 2840, 1660, 1625, 1550, 1400, 1375, 965, 860 cm<sup>-1</sup>; C<sup>13</sup> NMR (CDCl<sub>3</sub>) ppm (rel intensity) 141.9 (1), 128.3 (1), 127.0 (1), 126.7 (1), 126.1 (1), 125.3 (1), 47.5 (1), 30.9 (5), 29.3 (3), 21.3 (7), 12.1 (.7), -3.2 (.5); mass spectrum (70 eV) m/e (rel intensity) 220 (5), 166 (4), 109 (100), 93 (6), 81 (10), 57 (15); Exact mass calculated for C<sub>14</sub>H<sub>24</sub>Si, m/e = 220.1647; found: m/e = 220.1633 ± .0011; Silabenzenebutadiene adduct: NMR (CDCl<sub>3</sub>) δ 0.1 (s), 0.7 (s), 1.3 (m), 2.8 (m), 5.7 (m), 6.0 (m), no integration was possible due to weakness of signals; mass spectrum (70 eV) m/e (rel intensity) 162 (39), 147 (48), 134 (100), 119 (65), 108 (46), 95 (97), 84 (26), 69 (99); Exact mass calculated for C<sub>10</sub>H<sub>14</sub>Si, m/e = 162.0865; found: m/e = 162.0870 ± .0006.



Reaction of (136) with t-butyllithium in the presence of both excess butadiene and trimethylchlorosilane

The above reaction was repeated with 0.377 g (0.0026 moles) of 136, and 0.0026 moles of t-butyllithium. Present in the pentane solution before addition of the base at -77°C were 136, 10 ml of butadiene, and 4 ml (0.03 moles) of trimethylchlorosilane. Following the above procedure yielded 0.188 g, which consisted of 10 mole % (by NMR) of trans-1-trimethylsilyl-5,5-dimethylhex-2-ene 164: NMR (see Figure 12) ( $\text{CDCl}_3$ )  $\delta$  -0.12 (s, 9H), 0.73 (s, 3H), 1.32 (m, 2H), 1.75 (m, 2H), 5.28 (m, 2H); IR (film) 3100, 2960, 2940, 1665, 1365, 1250, 970  $\text{cm}^{-1}$ ; mass spectrum (70 eV)  $m/e$  (rel intensity) 184 (18), 169 (6), 127 (34), 73 (100), 57 (26), 45 (20); and 20 mole % (by NMR) of adduct 165 described above. A trace of the silabenzene butadiene adduct is also present in the GC.

Reaction of (136) with 1,5-diazobicyclo[4.3.0]non-5-ene (DBN)

To 25 ml of dry toluene under a nitrogen atmosphere was added 0.39 g (27 mmol) of 136 and 2 ml of 2,3-dimethylbutadiene. The solution was cooled to -77°C and 0.34 g (2.7 mmol) of DBN in 2 ml of toluene was added to the reaction mixture. A white precipitate formed immediately upon addition. After warming to room temperature and stirring for two hours, a significant amount of 136 still remained. Two additional equivalents of DBN were added and

the mixture heated to 60°C for seventy-two hours. At this time, no 136 remained, by GC. Filtration under nitrogen yielded a white solid (m.p. 112-115°C), IR (KBr) 350 - 2800 broad, 1673, 1585, 1300  $\text{cm}^{-1}$ , and a brown oil. GC analysis of the oil indicated only one major product, 1-methyl-1-silacyclohexa-2,4-dienedisiloxane 169, as identified by comparison of the GC retention time to that of a known sample. Purification by column chromatography on silica gel yielded 0.15 g (0.6 mmoles) (24% isolated yield) of the disiloxane: NMR ( $\text{CDCl}_3$ )  $\delta$  0.05 (s, 3H), 1.45 (m, 2H), 5.9 (m, 3H), 6.67 (d of m, 1H); IR (film) 3020, 2985, 2950, 1615, 1535, 1350, 1250, 1035  $\text{cm}^{-1}$ ; mass spectrum (70 eV)  $\underline{m/e}$  (rel intensity) 234 (8), 219 (10), 206 (7), 156 (30), 143 (40), 119 (20), 117 (20), 57 (80), 43 (100); Exact mass calculated for  $\text{C}_{12}\text{H}_{18}\text{Si}_2\text{O}$ ,  $\underline{m/e}$  = 234.0896; found:  $\underline{m/e}$  = 234.0862  $\pm$  .001.

#### Reaction of (150) with DBN

A toluene solution of 0.13 g (0.9 mmoles) of 2,5-silacyclohexadiene 150 was subjected to the reaction conditions stated above. Only one equivalent of base was used. After thirty minutes, GC retention times indicated isomerization to the 2,4-diene had occurred. Filtration under nitrogen, after four hours at room temperature, yielded the DBN-hydrochloride (m.p. 107-115°C) and only the conjugated disiloxane 169 as identified above.

Reaction of (136) with DBN in the presence of benzaldehyde

A benzene solution of 0.60 g (4.2 mmoles) of 136 and 3 ml of benzaldehyde was cooled to 0°C under nitrogen and treated with 0.57 g (4.2 mmoles) of DBN. The reaction was allowed to warm to room temperature and then stir for twelve hours. Filtration under nitrogen yielded DBN hydrochloride (m.p. 110-115°C) and brown oil which was purified by column chromatography on silica gel. Pentane elution yielded 0.29 g (0.0012 moles) of disiloxane 169 (30% isolated yield). GCMS confirmed the formation of disiloxane. Unreacted benzaldehyde was also recovered.

Reaction of (136) with N-lithiohexamethyldisilazane (170)

A solution of 0.10 g (0.1 mmoles) of 136 and 20 ml of dry ether were cooled to -77°C. A pentane solution of base 170 (0.7 mmoles) was added and the mixture was allowed to warm to room temperature over a twenty-four hour period. Pentane was added and the solution was extracted with water. The pentane layer was dried over anhydrous MgSO<sub>4</sub> and the pentane was removed to leave 0.093 g of a brown oil. Analysis by GCMS shows only two products, 1-bis(trimethylsilylamino)-1-methyl-1-silacyclohexa-2,4-diene 171 (40% isolated yield) and adducts derived from silabenzene and 136 (compound 172). Compound 171: NMR (see Figure 14) (CDCl<sub>3</sub>) δ 0.06 (s, 18), 0.11 (s, 3H), 1.53 (m, 2H), 5.59 (m, 3H), 6.65 (d of m, 1H); IR (film) 3015, 2980, 2950, 2890, 1615, 1540, 1400, 1345,

1245,  $900\text{ cm}^{-1}$ ; mass spectrum (70 eV)  $\underline{m/e}$  (rel intensity) 296 (13), 253 (13), 146 (100), 129 (21), 99 (112), 73 (8); Exact mass calculated for  $\text{C}_{12}\text{H}_{27}\text{NSi}_3$ ,  $\underline{m/e} = 269.1454$ ; found:  $\underline{m/e} = 269.1438 \pm .002$ ; adduct 172: NMR ( $\text{CDCl}_3$ )  $\delta$  0.05-0.2 (overlapped s, 24H), 1.0-1.8 (broad m, 5H), 5.9-6.7 (broad m, 6H); IR (film) 3020, 2980, 2950, 2800, 1610, 1580, 1535, 1400, 1350, 1250, 910,  $835\text{ cm}^{-1}$ ; mass spectrum (70 eV)  $\underline{m/e}$  (rel intensity) 377 (37), 362 (19), 254 (10), 238 (10), 131 (53), 109 (100), 99 (26), 82 (6), 73 (24) (GCMS shows three isomers); Exact mass calculated for  $\text{C}_{18}\text{H}_{35}\text{Si}_4\text{N}$ ,  $\underline{m/e} = 377.1847$ ; found:  $\underline{m/e} = 377.1841 \pm .007$ .

Reaction of (136) with N-lithiodisilazane (170) in the presence of excess butadiene

To a solution of 0.45 g (0.0031 moles) of 136 in 5 ml of ether, was added a cold solution ( $-10^\circ\text{C}$ ) of 5 ml butadiene, and 0.59 g (0.0035 moles) of N-lithiodisilazane 170 in 30 ml of ether. The reaction was warmed to room temperature and allowed to stir for two hours, after which 2 ml of methyl iodide was added. Filtration through Celite and removal of the solvent left a yellow oil. Bulb-to-bulb distillation at  $80^\circ\text{C}$  (0.18 mm Hg) yielded a clear oil which contained four components, as analyzed by GC: 1) hexamethyldisilazane, identified by comparison of retention time to an authentic sample and mass spectrum (70 eV)  $\underline{m/e}$  (rel intensity)

161 (3), 146 (100), 131 (26), 73 (25); 2) 1-methyl-1-silacyclohexa-2,4-dienetrimethylsilyldisiloxane 173: NMR ( $\text{CCl}_4$ )  $\delta$  0.03 (s, 9H), 0.16 (s, 3H), 1.50 (m, 2H), 5.91 (m, 3H), 7.0 (d of m, 1H); IR (film) 3020, 2990, 2950, 1620, 1540, 1250, 1040; mass spectrum (70 eV)  $m/e$  (rel intensity) 198 (70), 183 (78), 171 (28), 158 (32), 143 (40), 133 (100), 109 (20), 73 (38); Exact mass calculated for  $\text{C}_9\text{H}_{18}\text{Si}_2\text{O}$ ,  $m/e = 198.0896$ ; found:  $m/e = 198.0886 \pm .005$ ; 3) 1-methyl-1-silacyclohexa-2,4-dienedisiloxane 169 (major product) as identified by comparison to an authentic sample; 4) a trace of the butadiene-silabenzene adduct (by GCMS). The residue of the bulb-to-bulb distillation contained three major components as analyzed by GC: disiloxane 169; 1-bis-(trimethylsilylamino)-1-methyl-1-silacyclohexa-2,4-diene 171; the adducts between silabenzene and 171 (compound 172). All products were identified by comparison to known samples.

Reaction of (136), N-lithiodisilazane (170) and perfluoro-2-butyne

To a dry ether solution at  $-77^\circ\text{C}$  containing 3 ml of perfluoro-2-butyne and 0.82 mmoles of N-lithiodisilazane 170, was added a solution of 0.12 g (0.82 mmoles) of 136 in 3 ml of ether. The reaction was allowed to warm to room temperature. Near  $-20^\circ\text{C}$ , the mixture became gelatinous. At room temperature, the brown-gelatinous material was filtered through Celite and the solid was washed with  $\text{CH}_2\text{Cl}_2$ .

The resulting solution was extracted with water three times and once with saturated NaCl, dried over anhydrous  $\text{MgSO}_4$ , filtered, and the solvent removed. (In this case, the mixture was analyzed directly by GC. In all subsequent reactions, the oil was first purified by column chromatography on silica gel to remove products derived from the base perfluoro-2-butyne interactions.) GC analysis on a 6 ft. x 1/4 in. 15% SE 30 column showed three major components: hexamethyldisilazane and 1-bis(trimethylsilylamino)-1-methyl-1-silacyclohexa-2,5-diene 171, both identified by comparison to authentic samples; and 1,2-bis(trifluoromethyl)-3-methyl-3-silabicyclo[2.2.2]octa-1,5,7-triene 162 (28.1% by GC): NMR (see Figure 15) ( $\text{CCl}_4$ )  $\delta$  0.81 (q, 3H,  $J = 1.5$  Hz), 5.17 (overlapped t of t, 1H,  $J = 1.5$  Hz, 7 Hz), 6.75 (d of d, 2H,  $J = 11$  Hz, 1.5 Hz), 7.60 (d of d, 2H,  $J = 11$  Hz, 7 Hz);  $\text{C}^{13}$  NMR (see Figure 18); IR (film) 3040, 1645, 1548, 1330, 1310, 1280, 1260, 1150  $\text{cm}^{-1}$ ; mass spectrum (see Table 3);  $\text{F}^{19}$  NMR (see Figure 17);  $\text{Si}^{29}$  NMR ( $\text{CDCl}_3$ ) 29.8 ppm above TMS; Exact mass calculated for  $\text{C}_{10}\text{H}_5\text{SiF}_6$ ,  $\underline{m/e} = 270.0300$ ; found:  $\underline{m/e} = 270.0300 \pm .0002$ . A large amount of solid material, which resulted from base butyne interactions, was also present and not characterized.

Reaction of (136), N-lithiodisilazane (170), and perfluoro-2-butyne in the presence of trimethylchlorosilane

The above reaction was repeated with 0.142 g (0.98 mmoles) of 136, 0.98 moles of base, 4 ml of perfluoro-2-butyne, and 3 ml (23 mmoles) of trimethylchlorosilane. The trimethylchlorosilane was added to the reaction mixture before 136. Analysis after normal work-up yielded, by GC, 6.6% of silabarrelene 162.

Reaction of (136), N-lithiodisilazane (170), and 3-hexyne

An ether solution of 0.20 g (1.4 mmoles) of 136 was added to an ether solution at  $-77^{\circ}\text{C}$  of 2 ml of 3-hexyne and 1.4 ml of N-lithiodisilazane 170. The reaction mixture was warmed to  $0^{\circ}\text{C}$  and stirred at  $0^{\circ}\text{C}$  for thirteen hours. The reaction was a light green color which disappeared on exposure to air. Filtration and removal of solvent gave a yellow oil. Analysis by GC on a 3 ft. x 1/4 in. Dexsil 300 column at  $160^{\circ}\text{C}$  showed a trace of a compound tentatively assigned as 1,2-diethyl-3-methyl-3-silabicyclo[2.2.2]octo-1,5,7-triene: NMR ( $\text{CCl}_4$ )  $\delta$  0.0 (s, 3H), 1.1 (t, 6H,  $J = \text{Hz}$ ), 2.0 (m, 4H), 4.4 (m, 1H), 5.7 (center m, 4H).

Reaction of (136) and N-lithiodisilazane (170) in the presence of diphenylacetylene

A pentane solution of 0.30 g (2.1 mmoles) of 136 and 1.50 g (8.5 mmoles) of diphenylacetylene was cooled to  $-77^{\circ}\text{C}$

and treated with 2.1 mmoles of N-lithiohexamethyldisilazane. The reaction was warmed to room temperature and stirred for thirteen hours. Filtration through Celite and removal of solvent gave a yellow oil which was purified by column chromatography on silica gel. Only disiloxane 169 and unreacted diphenylacetylene were eluted from the column with hexane. Identification was made by comparison with authentic samples.

#### Pyrolysis of (162) in bis-trimethylsilylacetylene

A degassed solution of 0.05 g (0.2 mmoles) of 162 in 1 ml of bis-trimethylsilylacetylene was sealed in an NMR tube and pyrolyzed at 250°C. After 30 hours, only a black polymer remained. Attempts at obtaining products away from the mixture by silica gel column chromatography were unsuccessful.

#### Pyrolysis of (162) in di-t-butylacetylene

An NMR tube containing 0.07 g (0.26 mmoles) of 162 in 2 ml of di-t-butylacetylene was degassed and sealed under vacuum. The reaction was followed by NMR. The adduct did not begin to react until heated to 240°C, total reaction of 162 required heating to 250°C for five days. Analysis of the reaction mixture by GCMS indicated a very complex mixture containing di-t-butylacetylene and a trace of 162. No other compounds could be identified.



Pyrolysis of (162) in benzene at 2537 Å

A solution containing 0.15 g (0.56 mmoles) of 162 in 10 ml of dry benzene was degassed and sealed in a quartz tube. Photolysis was accomplished in a Rayonet reactor at 2537 Å for four hours. The sample was exposed to methanol and then air. Removal of solvent left a yellow sweet smelling oil. GC on a 12 ft. x 1/2 in. 15% SE 30 on Chromosorb W column indicated the trace of starting material and one other major product. This product was obtained by preparative GC: NMR ( $\text{CCl}_4$ )  $\delta$  0.6 (s), 1.1 (m), 3.9 (m), 5.6 - 7.0 (complex pattern); mass spectrum (70 eV)  $\underline{m/e}$  (rel intensity) 270 (5), 225 (6), 214 (6), 213 (5), 175 (26), 189 (17), 183 (11), 182 (28), 177 (12), 171 (11), 170 (19), 169 (44), 165 (11), 164 (20), 163 (52), 159 (28), 152 (10), 151 (50), 146 (39), 145 (30), 144 (11), 140 (10), 139 (14), 133 (14), 127 (43), 125 (15), 121 (13), 120 (19), 119 (12), 115 (21), 114 (43), 108 (12), 101 (25), 99 (25), 95 (13), 93 (30), 91 (21), 85 (15), 83 (10), 81 (100), 79 (16), 78 (16), 77 (40), 75 (40); Exact mass calculated for  $\text{C}_8\text{H}_6\text{SiF}_5$ ,  $\underline{m/e} = 225.0159$ ; found:  $\underline{m/e} = 225.0162 \pm 0.001$ ; calculated for  $\text{C}_7\text{H}_7\text{SiF}_4$ ,  $\underline{m/e} = 195.0252$ ; found  $\underline{m/e} = 195.0342 \pm 0.005$ .

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