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SYNTHESES OF ELUSIVE UNSATURATED SILACYCLES

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Syntheses of elusive unsaturated silacycles

by

Gary Thomas Burns

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

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1981

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DEDICATION

To Steven

I. INTRODUCTION

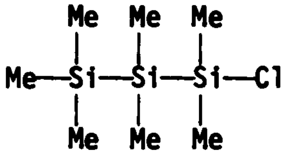
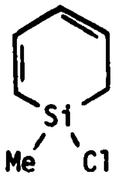
Since the establishment of the existence of (p-p)π bonded silicon compounds in 1966 by Nametkin and coworkers (1) and shortly thereafter by Gusel'nikov and Flowers (2), considerable interest has been focused on the attempts to generate, isolate, and utilize these reactive intermediates. This endeavor has recently culminated in the isolation of a stable compound containing a sterically hindered (p-p)π silicon-carbon double bond by A. Brook and coworkers (3).

This dissertation will describe the synthesis and reactions of 1-methyl-1-silabenzene and 6,6-dimethyl-6-silafulvene, two compounds containing a (p-p)π silicon-carbon double bond often postulated to be thermodynamically stable. The retro-ene elimination of propene from cyclic diallylsilanes used to prepare the aforementioned compounds was also utilized in the first synthesis of a C-unsubstituted silole and 2-methyl-2-silaindene. A new method for the generation of a (p-p)π silicon-carbon double bond was developed based upon the β-elimination of trimethylmethoxysilane. This method of forming a silicon-carbon (p-p)π double bond was utilized in the synthesis of silacyclobutenes, 6,6-dimethyl-6-silafulvene and 1,2-benzo-6,6-dimethyl-6-silafulvene. In addition, a synthesis of 1,1-dimethylsilole, two silacycloheptadienes and a nonannulated silepin were developed.

II. NOMENCLATURE

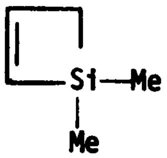
The nomenclature used in this dissertation will, with the exceptions described below, follow the conventions set down by IUPAC. Divalent silicon species will be named as derivatives of the parent silylene ($:SiH_2$). Simple organosilicon compounds will be named as derivatives of silane (SiH_4), while more complicated linear and cyclic systems will be named as sila-analogs of the corresponding carbon systems.

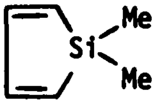
<u>Examples</u>:

$MeSiCl_2H$	Methyldichlorosilane
 $Me{-}\overset{Me}{\underset{Me}{Si}}{-}\overset{Me}{\underset{Me}{Si}}{-}\overset{Me}{\underset{Me}{Si}}{-}Cl$	1-Chloroheptamethyltrisilane
	1-Chloro-1-methyl-1-silacyclohexa-2,4-diene

The unsaturated four-membered rings containing one silicon atom will be named as derivatives of siletene. Silacyclopentadiene ring systems will be named as derivatives of siloles.

<u>Examples</u>:

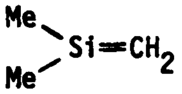
	1,1-Dimethylsiletene



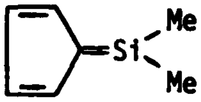
1,1-Dimethylsilole

All compounds containing silicon-carbon (p-p)π bonded silicon will be named as analogs of the corresponding unsaturated carbon system. 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, the term shall denote a cyclohexatriene ring system in which one carbon atom has been replaced by silicon. Substituents will be numbered in direct analogy with the carbon system.

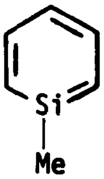
Examples:



2-Methyl-2-silapropene



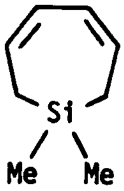
6,6-Dimethyl-6-silafulvene



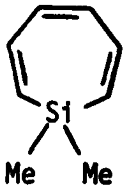
1-Methyl-1-silabenzene

Unsaturated seven-membered rings containing one silicon atom will be named as analogs of the corresponding carbon systems. Finally, when referring to a cycloheptatriene ring system containing one silicon atom, the term silepin shall be used.

Examples:



1,1-Dimethyl-1-silacyclohepta-3,5-diene



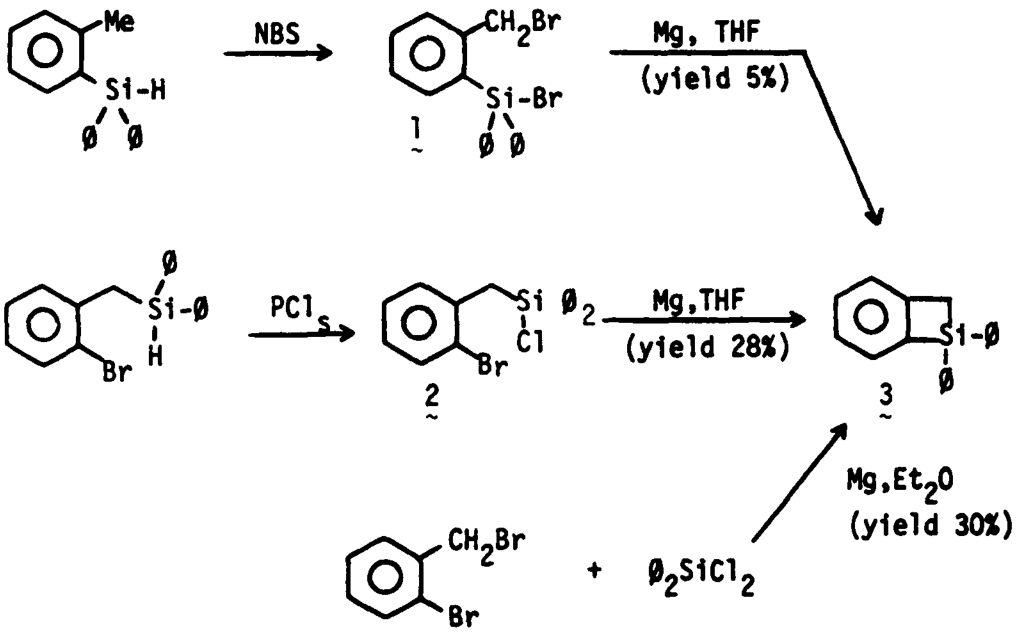
1,1-Dimethylsilepin

III. HISTORICAL

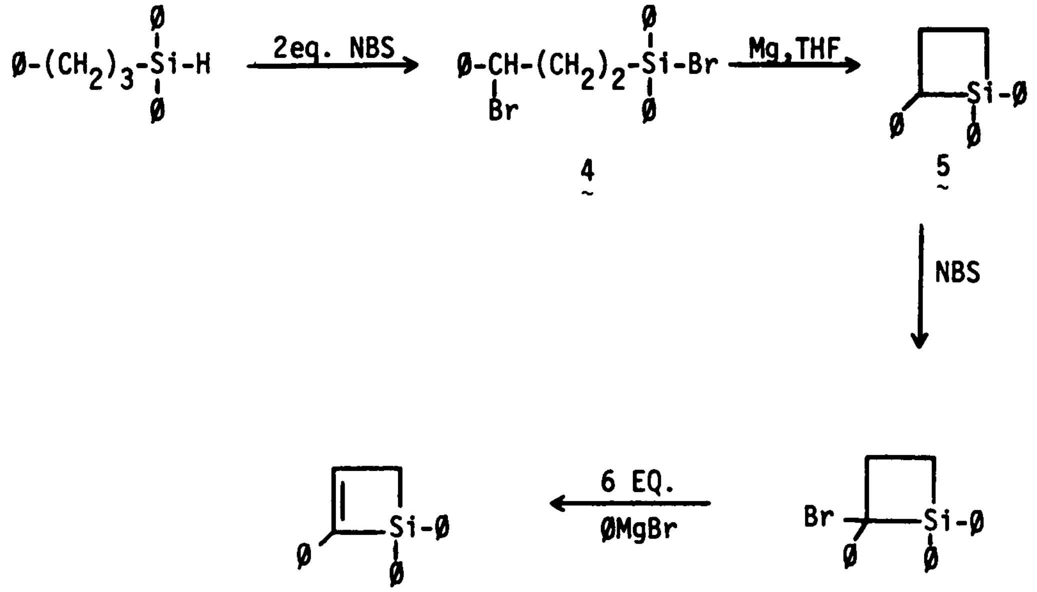
A. Siletenes

Study of the chemistry of silacyclobutenes or siletenes has long been hampered by their relatively poor accessibility. Multi-step syntheses, low overall yields plus lack of silicon functionality have characterized the approaches to date.

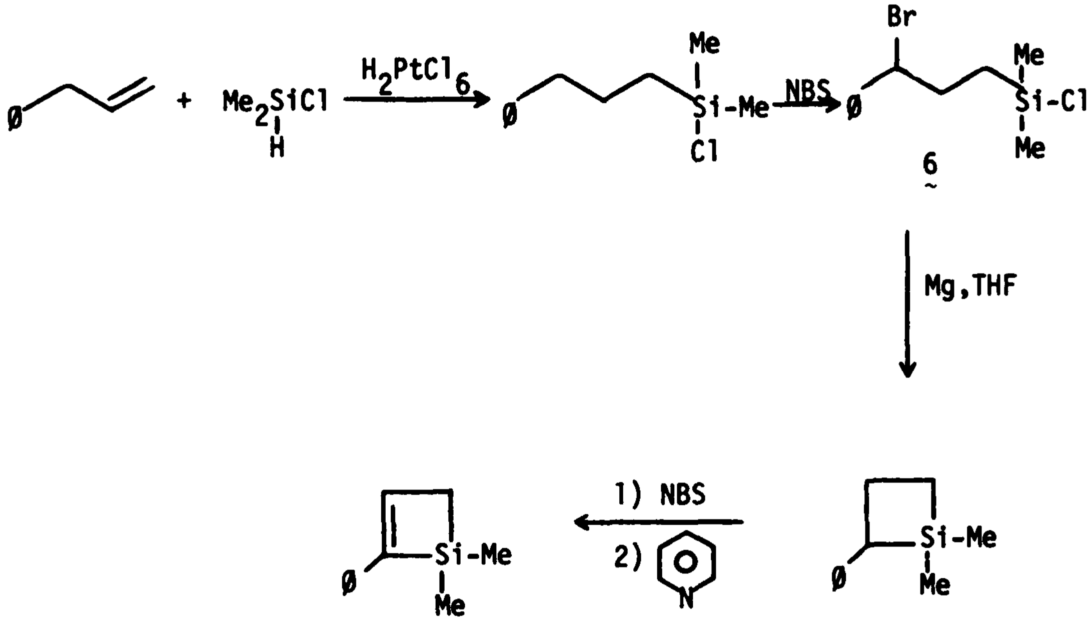
The first synthesis of a silacyclobutene was reported in 1964 by Gilman and Atwell (4). Intramolecular cyclization of either **1** or **2** with magnesium gave the diphenylbenzosilacyclobutene **3** although higher yields were obtained from **2**. A more convergent synthesis of **3** was accomplished by the magnesium induced coupling of o-bromobenzylbromide and diphenyldichlorosilane in ethereal solvents.



The first nonannulated siletene was prepared the following year by Gilman and Atwell (5,6). Their approach revolved around the ability to selectively brominate benzylic protons with NBS. Thus, dibromination of (3-phenylpropyl)diphenylsilane with NBS gave the dibromide 4. Purification of 4 was hampered by its low thermal stability. However, treatment of crude 4 with magnesium in THF gave the desired 1,1,2-triphenyl-1-silacyclobutane in a 52% yield. Benzylic bromination of 5 with NBS followed by dehydrohalogenation with an excess of phenylmagnesium bromide gave 1,1,2-triphenylsiletene in an overall yield of 8%.



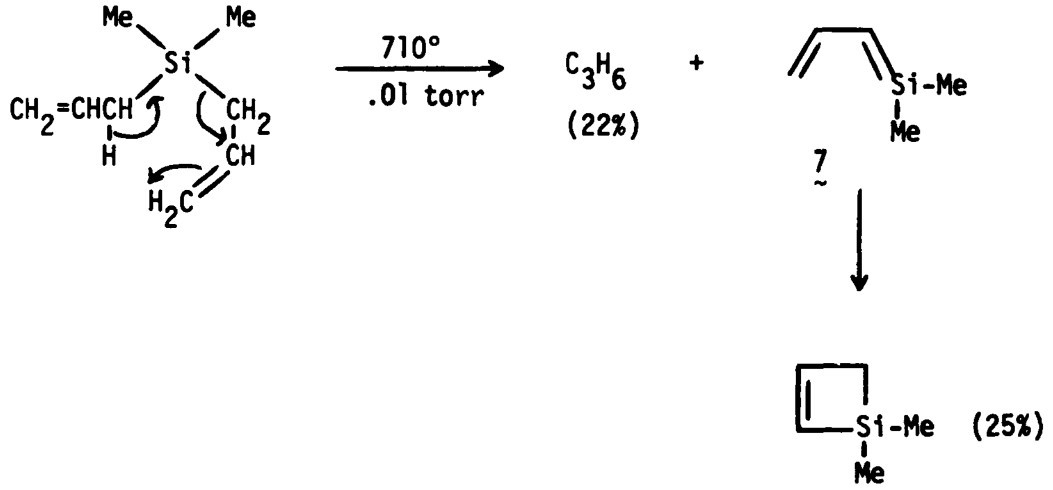
Nine years elapsed before another siletene synetheis appeared in the literature. In 1974, Weber and coworkers published a synthesis similar to Gilman and Atwell's for 1,1-dimethyl-2-phenylsiletene (7,8). Hydrosilylation of allyl benzene with dimethylchlorosilane followed by benzylic bromination with NBS gave the analogous dihalosilane 6. Intramolecular cyclization with magnesium afforded 1,1-dimethyl-2-phenyl-1-silacyclobutane in a 50% yield from allyl benzene. Desaturation to the siletene was accomplished by benzylic bromination with NBS followed by dehydrohalogenation with pyridine in methylene chloride. The overall yield from allyl benzene was 29%.



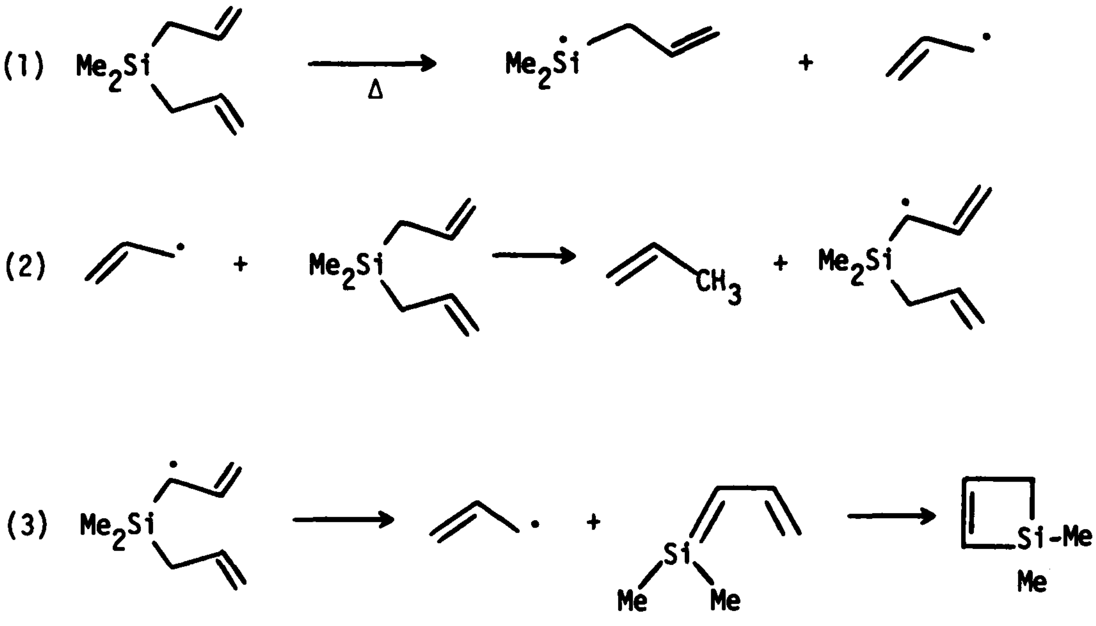
The first pyrolytic route to the siletene ring system was reported in 1978 by E. Block and L. Revelle (9). They found that flash vacuum pyrolysis (FVP) of dimethyldiallylsilane at 710°C and 0.1 torr afforded 1,1-dimethylsiletene in a 25% yield (41% based upon reacted starting material). The reaction mechanism favored by them involved the retro-ene elimination of propene as shown in Scheme 1. However, the alternate radical chain process involving abstraction of an allylic hydrogen from dimethyldiallylsilane by an allyl radical followed by disproportionation to the 1-silabutadiene 7 was not ruled out (Scheme 2).

Although allowing a relatively quick entry into the siletene ring system from readily available precursors, the introduction of functionality at silicon (R ≠ alkyl) was not tolerated. Thus, pyrolysis of diallylsilane was reported to give a very complex mixture of products while diallyldimethoxysilane passed through the pyrolysis system unscathed.

Scheme 1



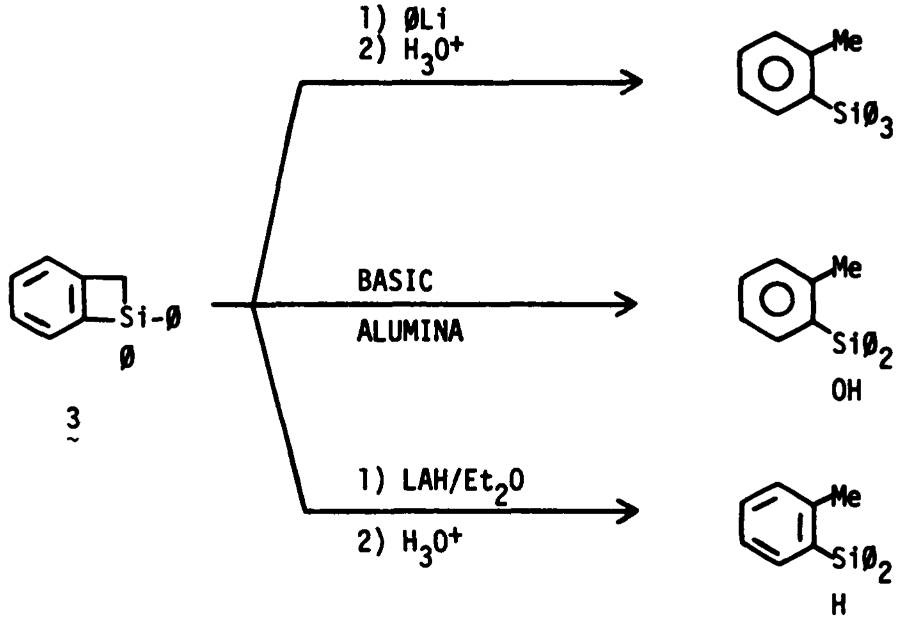
Scheme 2



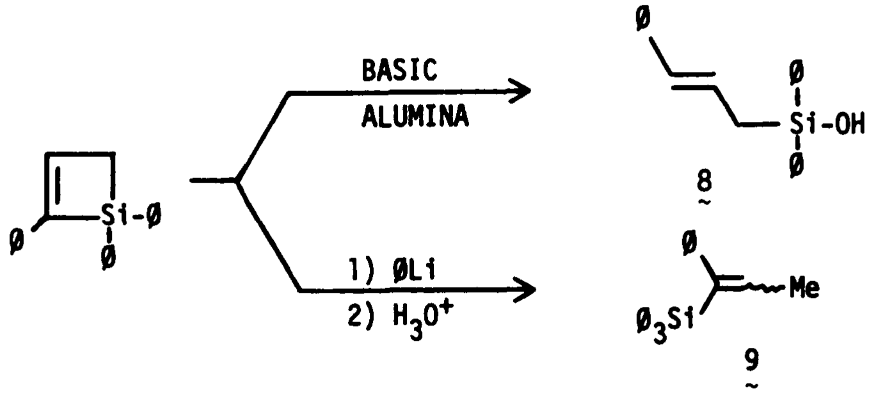
7

then (2), (3), etc.

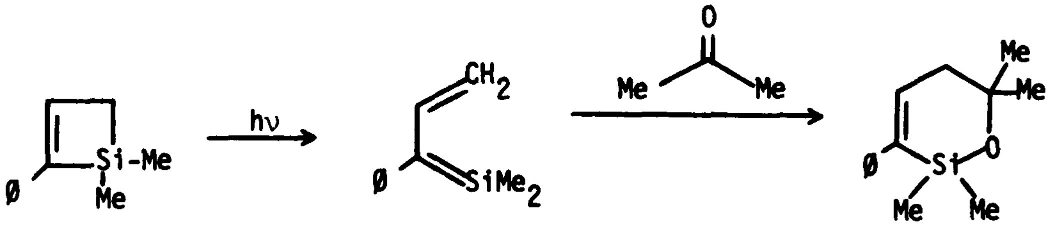
The known chemistry of both annulated and nonannulated siletenes is limited to a small number of reactions. Gilman and Atwell have reported that 3 rapidly decolorizes a solution of bromine in carbon tetrachloride (4) and reduces ethanolic solutions of silver nitrate (10). Chromatography of 3 over basic alumina gives diphenyl-o-tolylsilanol whereas treatment with phenyllithium followed by acid-hydrolysis gives o-tolyltriphenylsilane. Reduction of 3 with lithium aluminum hydride gives diphenyl-o-tolylsilane as the major product.



The behavior of nonannulated siletenes is analogous to that of the benzosiletenes, *i.e.*, chromatography of 1,1,2-triphenylsiletene over basic alumina results in cleavage of the silacyclobutene ring to give the silanol **8**, likewise, treatment with phenyllithium gives the ring opened product **9**.

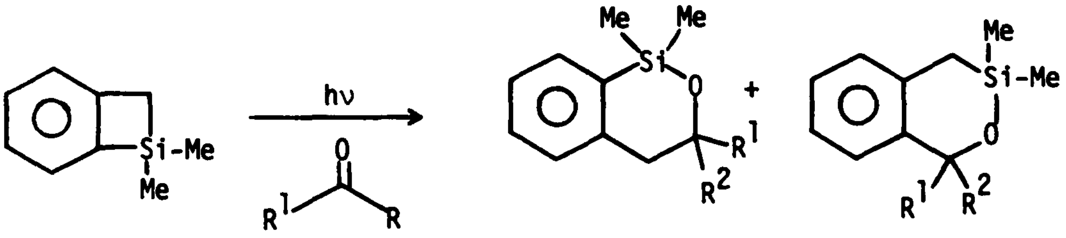


Valkovich and Weber have reported the photolytic ring opening of 1,1-dimethyl-2-phenylsiletene to the 1-silabutadiene 9 (8). The 1-silabutadiene was never isolated but was trapped *in situ* with acetone to give an 83% yield of 10.



9 10

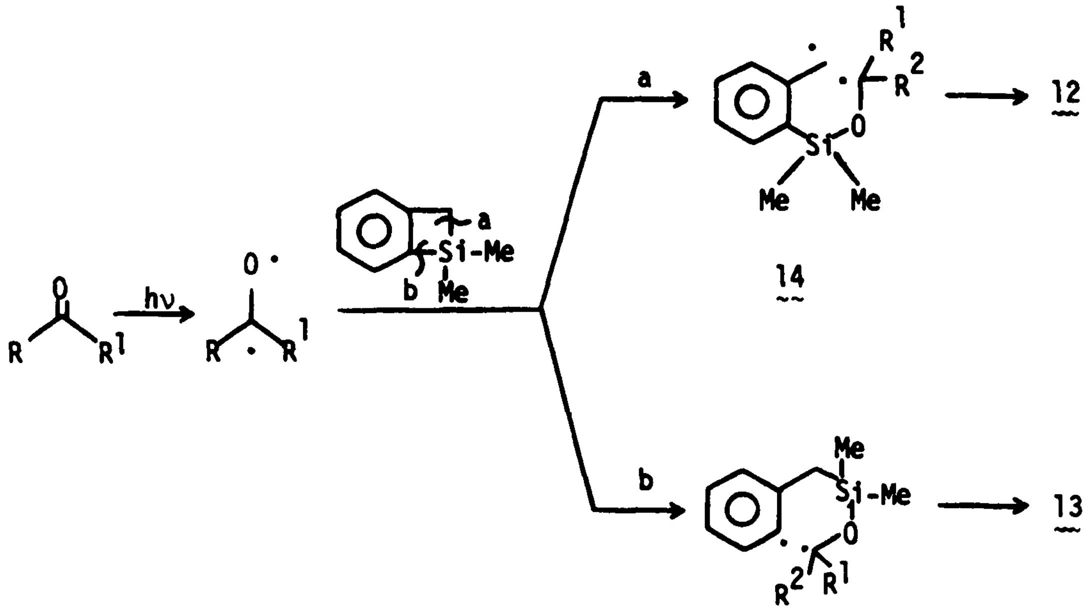
However, recent work by Okazaki *et al.* (11) brings into question Weber's interpretation of his results. They found that photolysis of 2,3-benzo-1,1-dimethyl-1-silacyclobutene 11 in the presence of carbonyl compounds afforded two isomeric products 12 and 13.



11 12 13

The formation of both 12 and 13 was explained by the mechanism shown in Scheme 3. Photoexcitation of carbonyl compound to the triplet diradical followed by attack on silicon by oxygen could result in the cleavage of either the silicon-benzyl bond (path a) or the silicon-phenyl bond (path b). Cleavage of the benzosilacyclobutene by path a would lead to the diradical 14 and ultimately to 12, whereas cleavage by path b would give rise to 13.

Scheme 3

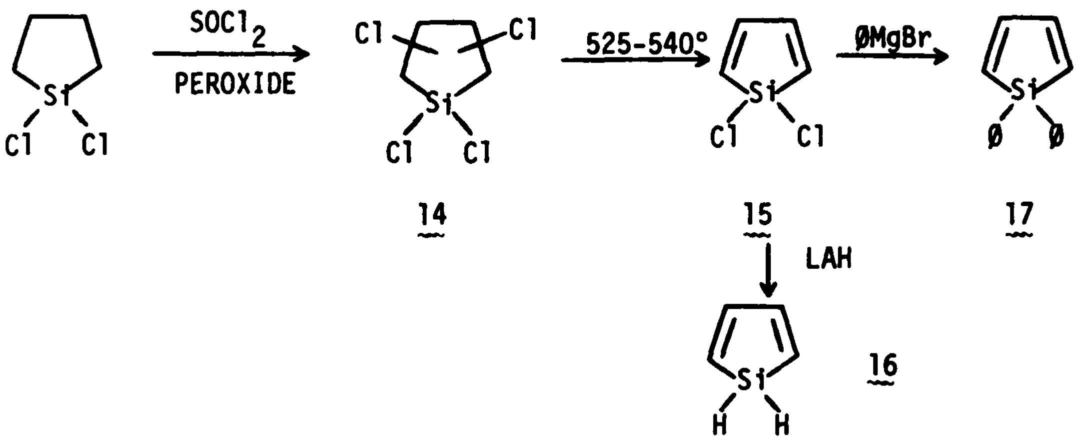


A similar interpretation as the one above could be used to explain Weber's results, where the formation of only one isomer was the result of the greater stability of a phenyl substituted allyl radical versus a vinyl radical.

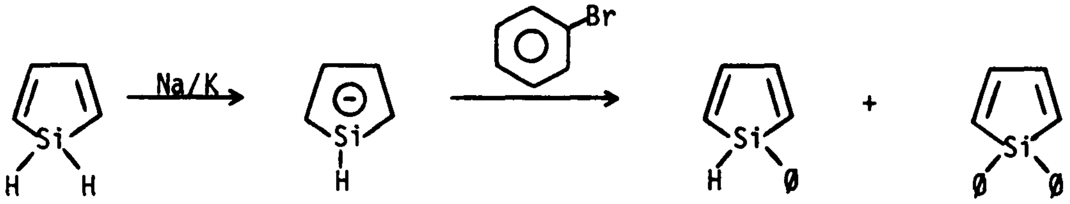
B. C-Unsubstituted Siloles

Although numerous siloles (5-silacyclopentadienes) have been prepared and characterized (12), the parent siloles, those with no ring substituents, have proven elusive to the synthetic silicon chemist. Over the years, several claims of a synthesis of an unsubstituted silole have appeared, only to be either retracted, found irreproducible by other workers, or prepared in such minute quantities to defy definitive structural assignments.

The first reports of a C-unsubstituted silole appeared in 1961 by Benkeser *et al*. (13,14). In these articles, they reported that free radical chlorination of 1,1-dichloro-1-silacyclopentane and the thermolysis of the resultant product **14** yielded 1,1-dichlorosilole **15** in high yields. Characterization of **15** was complete: NMR, IR, MS and b.p. were all reported. Furthermore, derivatization of the silole by either reduction with lithium aluminum hydride to **16** or phenylation with phenylmagnesium bromide to **17** was reported to be possible.



Benkeser and coworkers reported that synthesis of 16 also led to the first erroneous claim of a silaaromatic, the silacyclopentadienyl anion 17 (15,16). Entry into this system was reportedly by Na/K reduction of the parent silole 16. Proof of the intermediacy of 17 included; NMR data (three peaks, 2.70 τ, 2.90 τ, and 3.95 τ in a ratio of 1:1:0.5), measurement of the amount of evolved hydrogen (91% of theoretical), and quenching of the anion with bromobenzene to give 18 and 19.

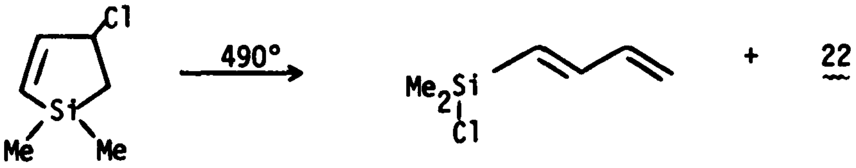


16 17 18 19

Unfortunately, the previous work was found to be irreproducible starting with the thermolysis of 14 and was retracted by Benkeser and Stanton in 1964 (17). In their re-examination of the pyrolysis of 14, Benkeser and coworkers found the major product to be 1-trichlorosilyl-1,3-butadiene (18), a conclusion later ratified by Nagai *et al.* (19).

Ironically, in one of their later investigations of the thermolysis of chlorosilacyclopentanes and chlorosilacyclopentenes, Benkeser and coworkers may have succeeded in preparing 1,1-dimethylsilole, but failed to characterize it (20). When 20 was pyrolyzed at 490°C in a vertical oven using nitrogen as the carrier gas, two products were obtained. The major product was identified as the intramolecular β-elimination product

1-(chlorodimethyl)silylbutadiene 21. The second product, 22, was never identified. However, the reported low thermal stability (a few hours at -78°C) and the concomitant appearance of a compound of higher molecular weight as 22 disappeared are in qualitative agreement with the properties found for 1,1-dimethylsilole in this dissertation. Furthermore, Nagai and coworkers have shown that in the pyrolysis of β-chloroethylsilanes, both β-elimination to give the chlorosilane and loss of HCl to give the vinylsilane occur in a ratio of $\sim$4:1 (19). This information in conjunction with the observed physical properties of 22 make it probable that 22 was 1,1-dimethylsilole.



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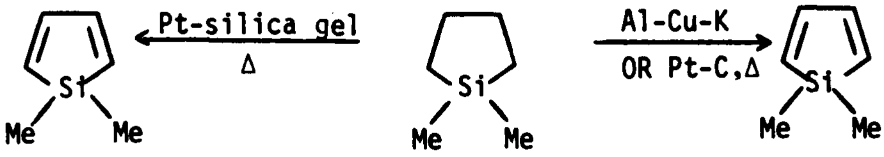
21

The next two claims for a synthesis of a C-unsubstituted silole came from Goubeau, Kalmar and Hofmann (21) and later by Nefedov and Manakov (22). Goubeau *et al*. reported that 1,1-dimethyl-1-silacyclopentane could be dehydrogenated over a catalyst consisting of 10% platinum-silica gel on 25% quartz wool. The yield of 1,1-dimethylsilole was quite low. From 54 grams of 1,1-dimethyl-1-silacyclopentane, only a few drops of the silole were obtained. Nefedov and Manakov also obtained a low yield (3%) of 1,1-dimethylsilole in the dehydrogenation of 1,1-dimethyl-1-silacyclopentane over a Al-Cu-K catalyst. A somewhat better yield (9%) was obtained with a platinum on carbon catalyst. Both of these claims have been dismissed by most researchers in this area after futile attempts to reproduce them.



The most substantiated claims for a synthesis of an unsubstituted silole have come from the research of Hwang and Gaspar in 1978 (23) and from Siefert et al. in 1980 (24) from the study of recoiling silicon-31 atoms with butadiene. P. Gaspar and coworkers found that fast-neutron irradiation of a phosphine-butadiene mixture produced two major products, one of which was identified as [^{31}Si]-1-silacyclopent-3-ene. The other major product was tentatively assigned the structure [^{31}Si]-1-silacyclopenta-2,4-diene based on its gas chromatographic behavior which suggested that it contained four carbons, the yield increased monotonically with the 1,3-butadiene mole fraction and the fact that nearly identical yields (20±3%) were obtained from 1:1 PH_3-butadiene and 1:1 PF_3-butadiene mixtures. Siefert et al. provided additional evidence for the assignment of [^{31}Si]-1-silacyclopenta-2,4-diene to this molecule by catalytically hydrogenating it to 1-silacyclopent-3-ene (24). However, Siefert et al. claim that 1-silacyclopenta-2,4-diene is stable for 12 hours at r.t. which is in disagreement with the behavior observed for

1-methylsilole and 1,1-dimethylsilole in this dissertation. This, in combination with the scanty product identification, brings into question the formation of 1-silacyclopenta-2,4-diene in the reaction of recoiling silicon atoms with butadiene.

C. Silabenzene

The aromatic stabilization afforded to cyclic, planar molecules possessing [4n + 2]π electrons has been utilized to generate a number of heteroatom-carbon multiple bonded species. Prior to the discovery of phosphabenzene (X=P) by Märkl in 1966 (25), the list of heterobenzenes was restricted to pyridine (X=N). Since that report, all of the Group V heterobenzenes (X = As, Sb, Bi) and borabenzene (X=B) have been prepared and characterized (26). They are all reasonably stable species either in solution or at low temperatures. Thus, stabilization of a number of weak π bonds has been achieved in a Hückel aromatic system.

X = N, P, Sb, Bi, B

The theoretical and experimental attempts to incorporate a silicon-carbon (p-p)π bond into a benzenoid framework will be covered in this section.

Several calculations on silabenzenes have been independently performed by P. H. Blustin (27,28), M.J.S. Dewar et al. (29), Dewar (30) and H. B. Schlegel et al. (31).

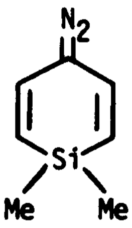
Blustin utilized an adaption of Frost's Floating Spherical Gaussian Orbital Model (FSGO) in his *ab initio* calculations on silabenzene in 1979. His calculations predict silabenzene to be a highly polarized molecule with a dipole moment of 2.85D, polarized such that the positive end is towards silicon. A relatively long $\text{C}\overset{\cdots\cdot}{\text{---}}\text{Si}$ bond of low bond order and low π-bond energy (D_π ∿6.9 kcal/mole *vs* $D_\pi(\text{C}\overset{\cdots}{\text{---}}\text{C})$ ∿38.5 kcal/mole) were also predicted. From these and other *ab initio* calculations on the π electron contribution to the molar magnetic susceptibility, Blustin concluded that the main obstacle to the formation of a silabenzene would be thermodynamic.

Contrary to the results of Blustin, both Dewar's MNDO/3 and Schlegel's *ab initio* calculations predicted silabenzene to be a stable although reactive molecule. Dewar and coworkers have calculated an aromatic stabilization energy (ASE) for silabenzene of 19.5 kcal/mole and a heat of formation of 13.7 kcal/mole. This is approximately 80 percent of the resonance energy attributed to benzene; the calculated values for benzene for the ASE and ΔH_f are 24.5 and 28.8 kcal/mole, respectively.

Using a standard STO-3G basis set, Schlegel *et al*. compared the relative stabilities of 1-silacyclohexadienylidene **23** to both singlet and triplet silabenzene **24**. They calculated the resonance energy of silabenzene at 22 kcal/mole or ∿ 2/3 the value calculated for benzene (32 kcal/mole). Further support for the aromatic character of silabenzene was found in the molecular orbital (MO) energies and MO coefficients. The usual benzenoid pattern of orbital energies (-0.461, 2x(-0.238), 2x(0.271), 0.571 Au calc'd for C_6H_6) was not strongly perturbed with the incorporation of a silicon atom in the benzene framework (-0.416, -0.278, -0.200, 0.256, 0.284, 0.494 Au).

The optimized geometries for both Blustin's and Schlegel's *ab initio* calculation are given in Table 1.

Although Schlegel's calculations indicate that the 4-silacyclohexadienylidene to silabenzene rearrangement is favorable, experimentally it has not been observed. In 1978, Barton and Banasiak (32) reported the preparation and thermolysis of the carbene precursors 25 and 26.



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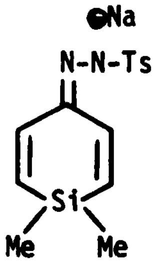
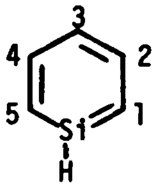


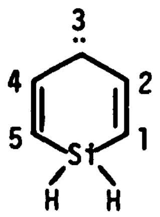
26

High dilution vacuum pyrolysis of 25 at 400° and 0.15 torr produced the carbene dimer 27 (Scheme 4) as the sole volatile product. In another attempt to promote intramolecular rearrangement of 24, a dilute solution of 25 in benzene-d_6 (.01 M) was pyrolyzed in a nitrogen flow system. The major volatile product was simply the adduct of the carbene and solvent, 28. No evidence for the intermediacy of a silabenzene was obtained in either case.

Table 1. Theoretically optimized geometry of silabenzene 23 and 4-silacyclohexadienylidene 24[a]



23



24

	Blustin	Schlegel		
Parameter[b]	23 (singlet)	23 (singlet)[c]	23 (triplet)[d]	24 singlet[e]
C(2)C(3)	1.420	1.395	1.406	1.511
C(1)C(2)	1.409	1.381	1.433	1.323
C(1)Si	1.819	1.722	1.759	1.844
C(3)H(3)	1.099	1.080	1.090	---
C(2)H(2)	1.088	1.086	1.076	1.086
C(1)H(1)	1.097	1.079	1.077	1.086
Si-H	1.446	1.419	1.428	1.425

---

[a] In each case, the initial structure had C_s symmetry (nonplanar skeleton) and optimization without constraints leads to C_{2v} symmetry (planar skeleton).

[b] Bond lengths in angstroms, angles in degrees.

[c] Total energy: -476.04320 au. Energy of triplet at this geometry: -475.86167 au.

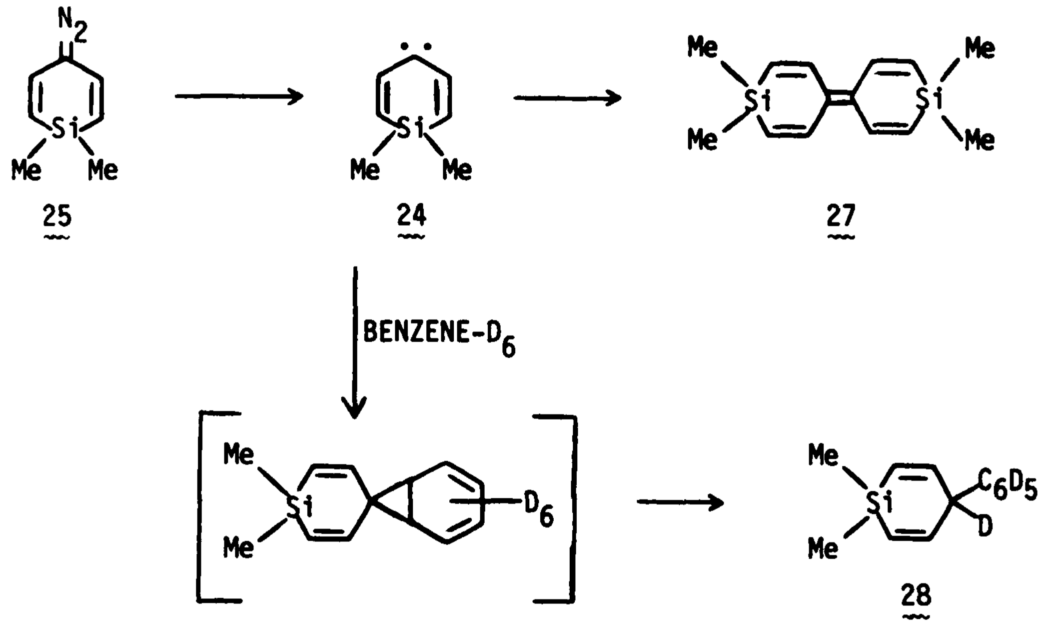
[d] Total energy: -475.87230 au.

[e] Total energy: -475.93878 au. Energy of triplet at this geometry -227.80701 au.

Table 1. (Continued)

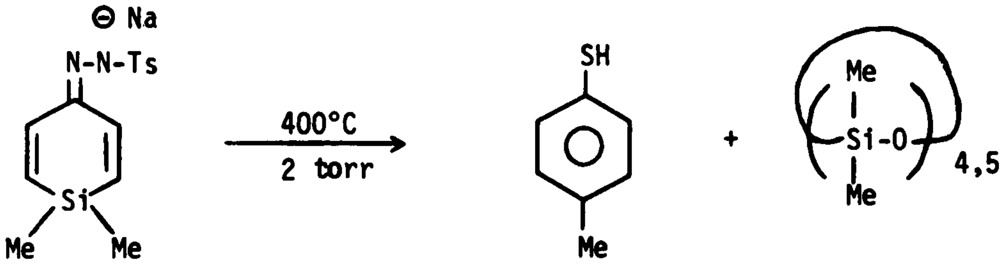
	Blustin	Schlegel		
Parameter[a]	23 (singlet)	23 (singlet)[c]	23 (triplet)[d]	24 singlet[e]
$C_2C_3C_4$	126.9	124.6	130.1	115.3
$C_1C_2C_3$	122.7	125.1	122.9	129.4
C_2C_1Si	122.5	117.4	115.3	121.7
C_1SiC_5	102.7	110.3	113.6	102.6
$C_2C_1H_1$	---	118.2	120.4	118.4
$C_1C_2H_2$	120.4	118.4	119.4	117.5
SiC_1H_1	123.0	---	---	---

Scheme 4



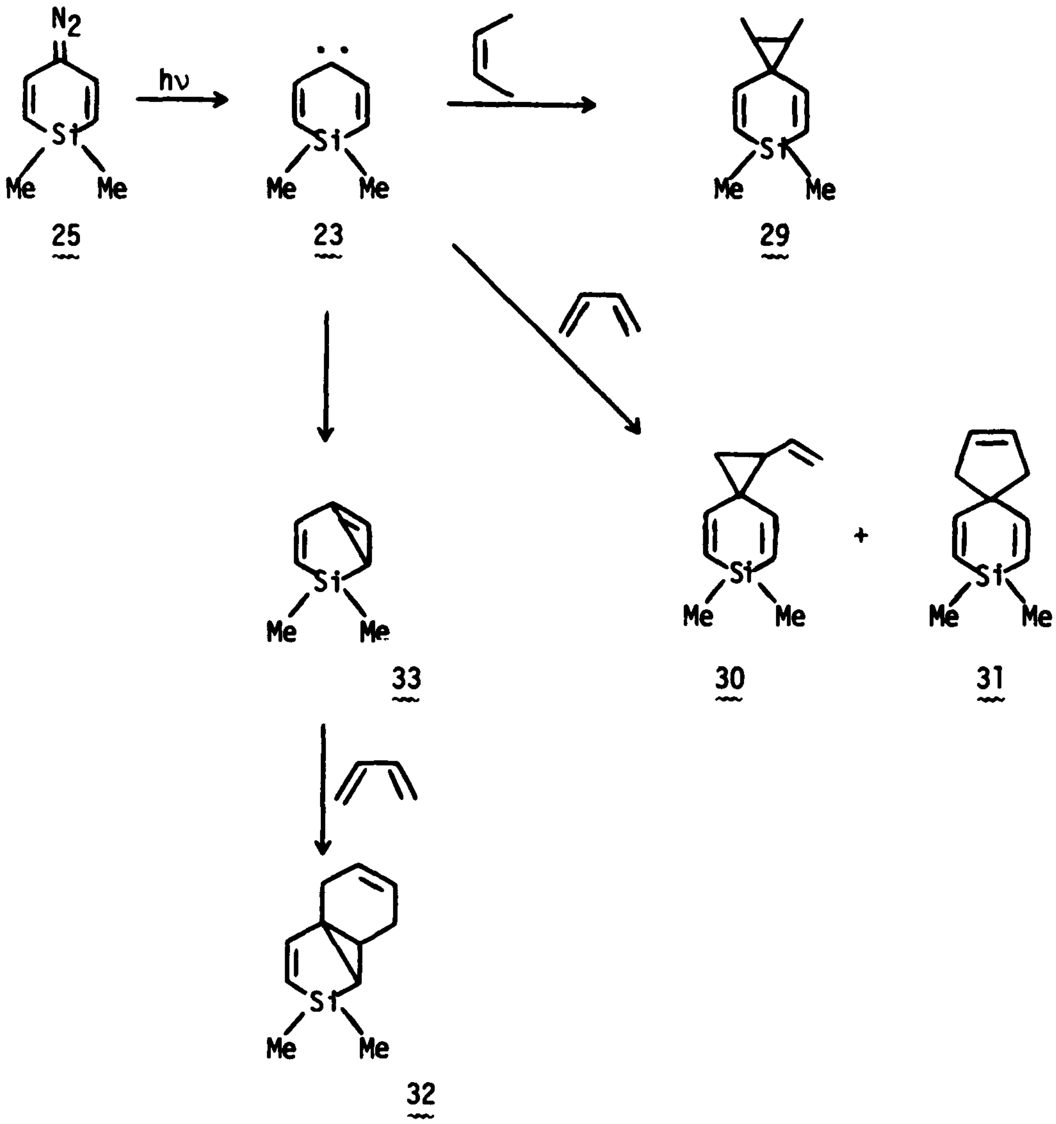
Since direct thermal decomposition of the lithium salt of the tosylhydrazone of 4,4-dimethylcyclohexa-2,5-dien-1-one had also been reported to yield xylene (33), the analogous reaction was attempted by Barton and Banasiak with 26 (Scheme 5). Unfortunately, the vacuum flow pyrolysis of 26 at 400°C produced octamethylcyclotetrasiloxane (D_4) and decamethylcyclopentasiloxane (D_5) as the major silicon containing products. The other identifiable product was p-methylthiophenol. The formation of p-methylthiophenol was not totally unexpected since it is also formed in the pyrolysis of the sodium salt of tosylhydrazone. However, the formation of D_4 and D_5 was unexpected and unexplained.

Scheme 5

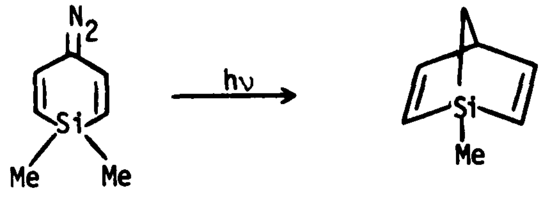


26

Both the gas phase pyrolysis and photolysis of 25 were reported by Coleman and Jones in 1979 (34). Although the results obtained from the vacuum pyrolysis (620°C, 5×10^{-3} torr) of 25 were identical to the earlier reports of Barton and Banasiak (32), the solution phase photolysis gave entirely different results. When a solution of 25 and *cis*-2-butene was irradiated with a Hanovia high pressure lamp, the expected carbene:olefin adduct 29 was obtained in a 54% yield (cis:trans ratio 92:8). However, the irradiation of a solution of 25 and butadiene yielded three products 30, 31, and 32 in the ratio of 53/9/38. Compounds 30 and 31 are the silicon analogs to the trapping of 4,4-dimethylcyclohexadienylidene with butadiene. Compound 32 was postulated to arise from 33, a product formally arising from a vinyl carbene to cyclopropene rearrangement.

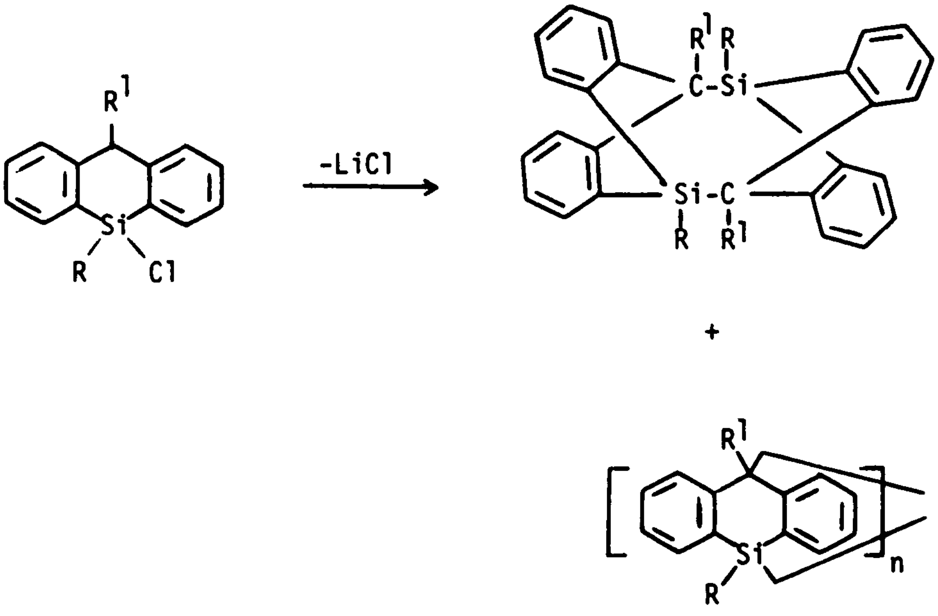


In striking contrast to the results of Coleman and Jones, Barton and Banasiak found that the gas phase photolysis of 25 or photolysis of 25 in an argon matrix resulted in the formation of 1-methyl-1-silanorbornadiene 34 (35).



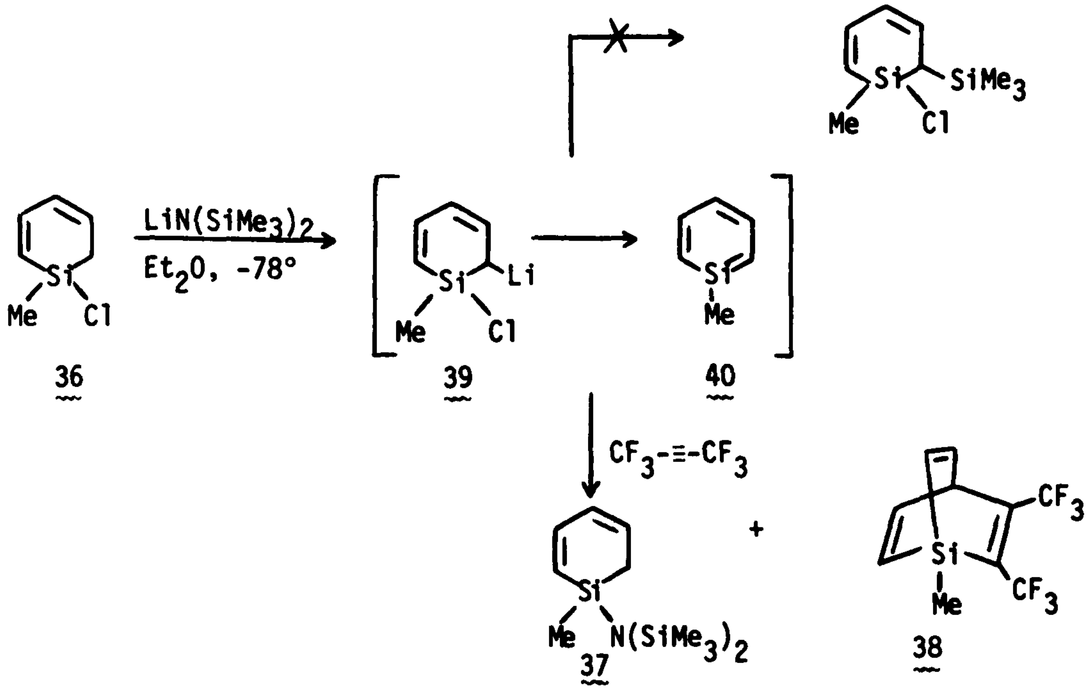
25 **34**

The first experimental evidence involving the generation and trapping of a silabenzene was presented in 1978 by Barton and Banasiak (36). The base induced elimination of HCl from 1-chloro-1-alkyl-1-silacyclohexa-2,4-dienes was reported in 1974 by P. Jutzi (26) to yield only polymeric material. Similarly, the elimination of HCl from 9-R-9-chloro-10-R'-9,10-dihydro-9-silaanthracenes **35** were reported to proceed *via* intermolecular substitution leading to dimeric and polymeric materials (37-39).



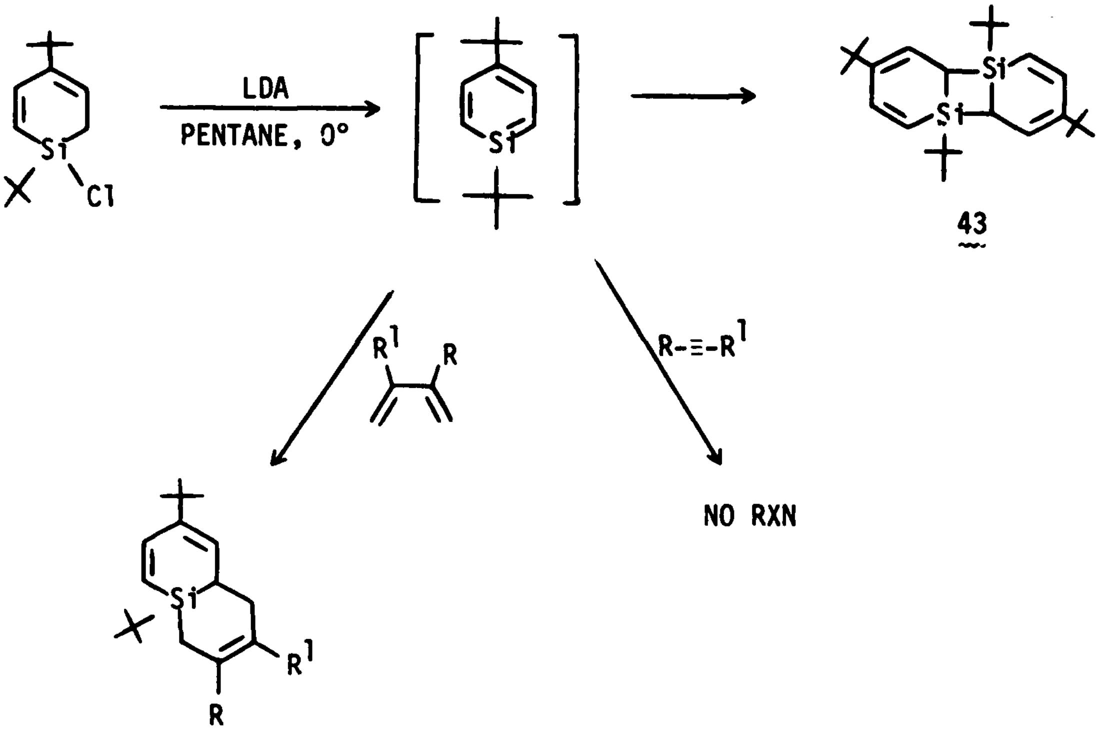
However, Barton and Banasiak found that treatment of 1-chloro-1-methyl-1-silacyclohexa-2,4-diene **36** with 1 equivalent of N-lithiodisilazane at

-78°C in the presence of perfluro-2-butyne yielded two major volatile products, 37 and 38. When a ten-fold excess of trimethylchlorosilane was included in the reaction mixture, no incorporation of a trimethylsilyl moiety was observed. Thus, the data were more consistent with a concerted elimination of LiCl from 39 followed by trapping of 1-methyl-1-silabenzene 40 in a [4+2] Diels-Alder fashion with perfluro-2-butyne than a step-wise mechanism involving carbanionic attack on acetylene by 39 followed by an intramolecular displacement of chloride. Two possible modes of formation for 37 were considered: either direct displacement of a chloride from silicon by the base, N-lithiodisilazane, or the addition of hexamethyldisilazane across the silicon-carbon double bond of 40. No attempt was made to distinguish the two possibilities. Inclusion of dienes into the reaction mixture gave no trapping products.



The method of Barton and Banasiak was later used by Märkl and Hofmeister to prepare 1,4-di-t-butyl-1-silabenzene 41 (40). When a solution of 1,4-di-t-butyl-1-chloro-1-silacyclohexa-2,4-diene, 42, was treated with one equivalent of lithium diisopropylamine, the [2+2] silene dimer 43 was obtained as the sole reaction product (Scheme 6). The inclusion of a diene trap into the reaction mixture completely suppressed the formation of 43 and yielded only the silene:diene adduct 44. Acetylenes failed to trap 41.

Scheme 6

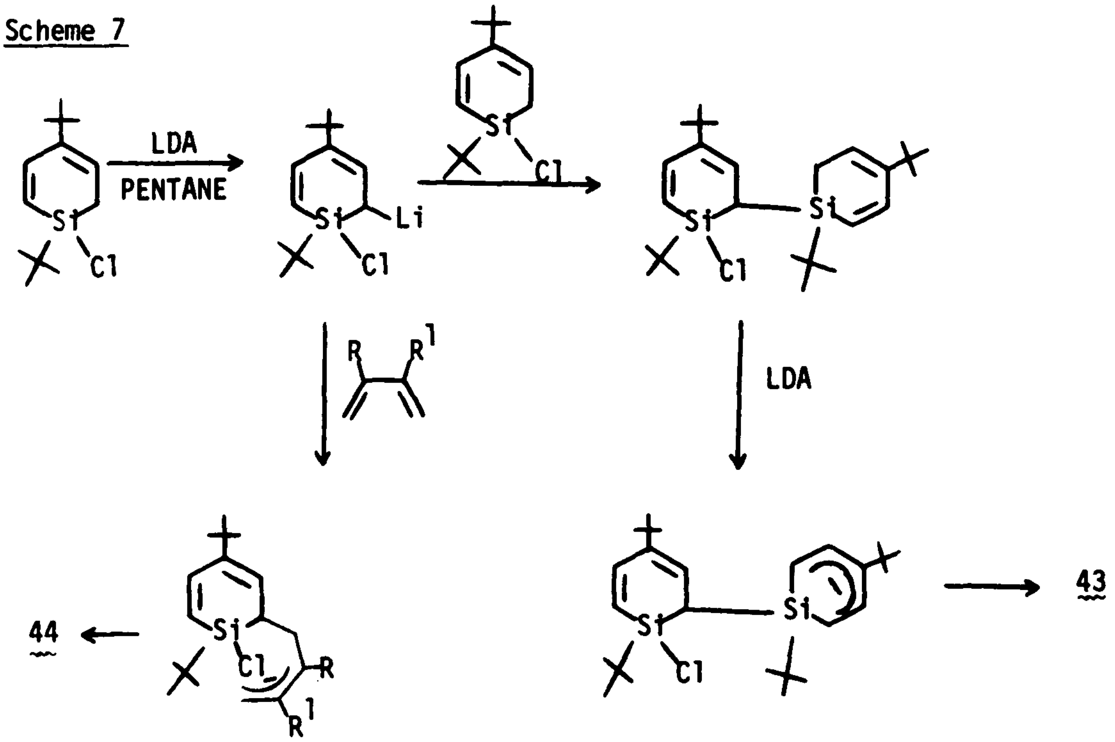


43

44 a) R=R^1=H
b) R=H, R^1=Me
c) R=R^1=Me

The latter two results, i.e., the trapping of a silabenzene with a diene, but not with an acetylene, are diametrically opposed to the earlier results of Barton and Banasiak. Märkl and Hofmeister dismiss the discrepancies on the basis of the greater steric hindrance of 41 in comparison to 40. However, while Barton and Banasiak tentatively ruled out a two-step anionic mechanism by their inability to intercept an anion when either trimethylchlorosilane or methyl iodide was included in the reaction mixture, Märkl and Hofmeister failed to do this simple experiment. Furthermore, the greater steric bulk of 41 should also hinder dimerization to 43. Thus, the discrepancies can also be explained by a mechanism shown in Scheme 7.

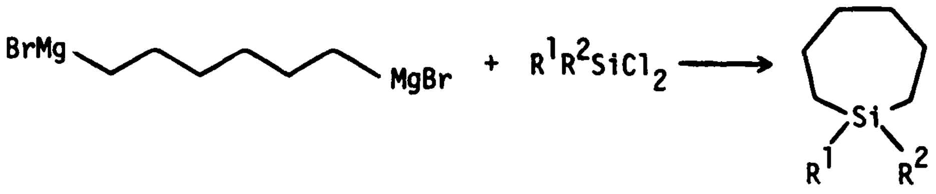
Scheme 7



The parent silabenzene has been recently prepared by both G. Maier *et al*. (41) and V. Solouki and coworkers (42) utilizing a retro-ene elimination of propene from a silacyclohexadiene. Furthermore, 1-methyl-1-silabenzene has been generated from a β-elimination of trimethylmethoxysilane by T. J. Barton and M. Vuper (43). Since both reactions were based upon methodology developed in this dissertation, their results are discussed in the Results and Discussion section.

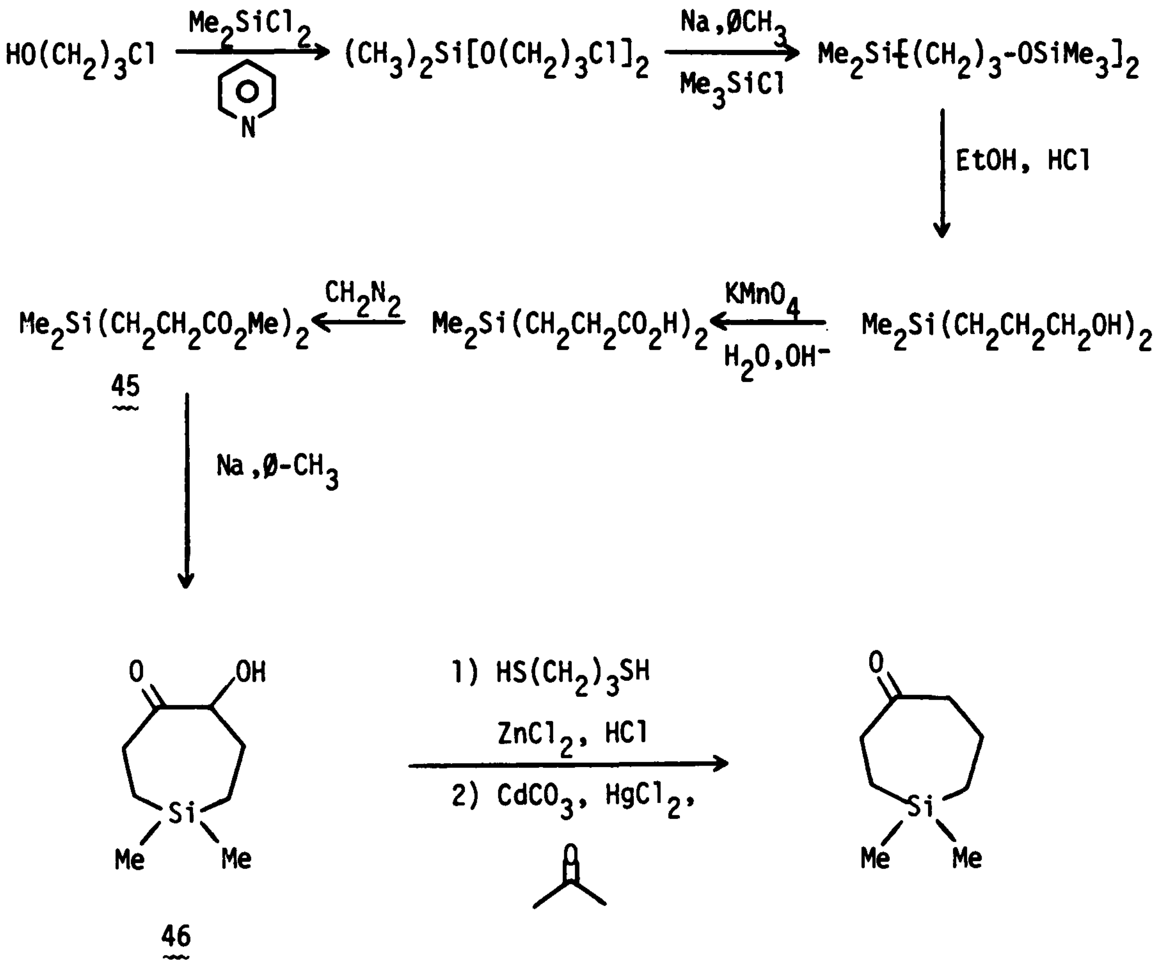
D. Nonannulated Seven-Membered Rings Containing One Silicon Atom

Prior to 1966, only four silacycloheptanes had been reported (44). These were all attainable, albeit in low yield, from the cyclization of 1,6-hexamethylenedimagnesium bromide with the corresponding dichlorosilane.



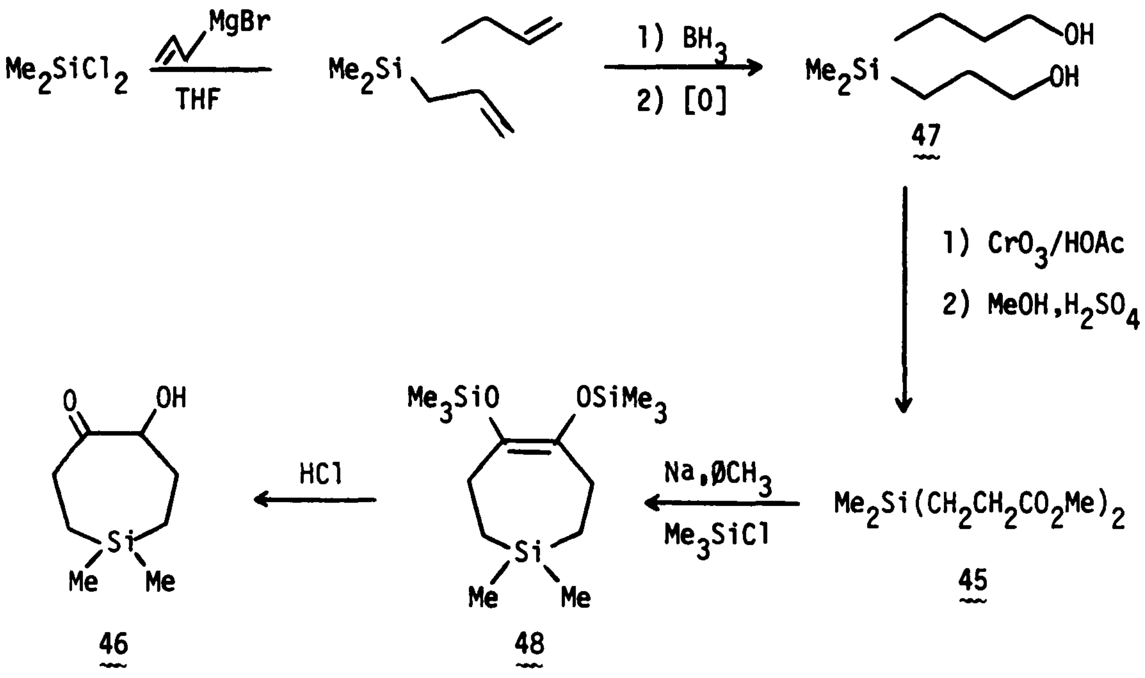
R^1 = Cl, R^2 = Cl
R^1 = Me, R^2 = Me
R = H, R^2 = H
R^1 = Me, R^2 = H

In 1966, Benkeser and Cunico reported the first general synthetic route into substituted silacycloheptanes (45). Starting with dimethyldichlorosilane, Benkeser and Cunico prepared the diester **45** in five steps by standard synthetic methodology. The yield for the first five steps was 10%. Treatment of **45** with sodium in refluxing toluene gave the acyloin condensation product 1,1-dimethyl-5-hydroxy-1-silacycloheptan-4-one **46** in a 28% yield (a 2.8% overall yield from dimethyldichlorosilane). Reduction of **46** to 1,1-dimethyl-1-silacycloheptan-4-one was accomplished by Cram and Cordon's method (46) in a 9% yield.

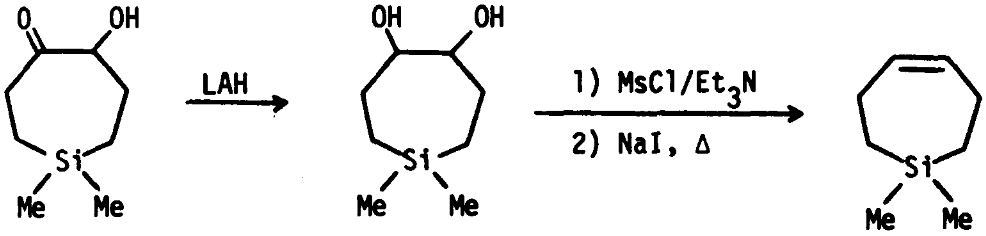


In 1971, Weber et al. (47) published an improved synthesis of 46 using newer synthetic methods (Scheme 8). Thus, hydroboration-oxidation of dimethyldiallylsilane gave the diol 47 in two steps from dimethyldichlorosilane in an 86% yield. Oxidation with Jones reagent followed by esterification of the crude diacid with methanol-H_2SO_4 gave the diester 45. A modification of the acyloin condensation by the addition of trimethylchlorosilane gave 48 in a 60% yield. Hydrolysis of 48 with 2N HCl gave 46 in an overall yield from dimethyldichlorosilane of 27%.

Scheme 8

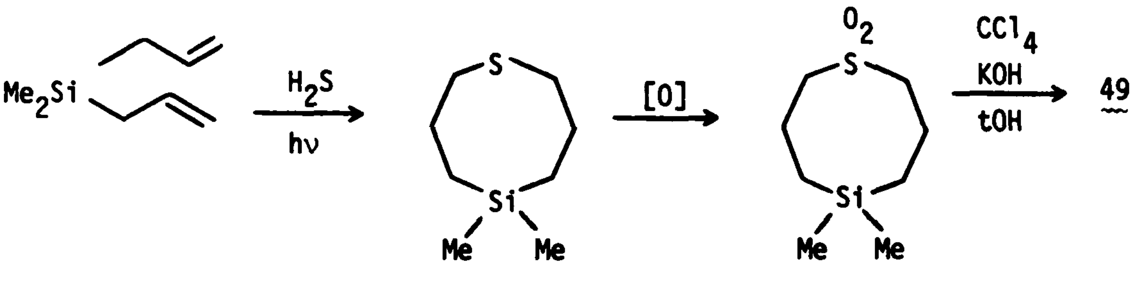


In subsequent work, Koenig *et al.* succeeded in converting 46 into 4,4-dimethyl-4-silacycloheptene (48). Reduction of the acyloin product 46 with lithium aluminum hydride gave the corresponding diol. Conversion of the diol into the dimesylate followed by treatment with NaI in refluxing methyl ethyl ketone yielded 1,1-dimethyl-1-silacyclohept-3-ene 49. The yield of 49 from 46 was 17%.



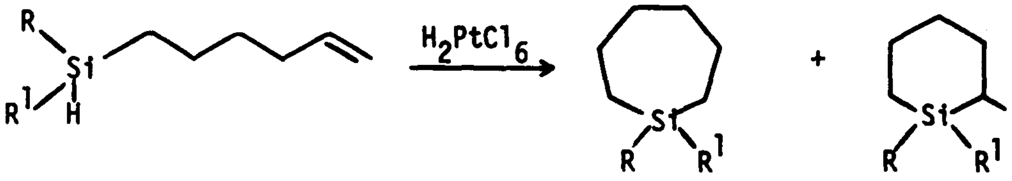
46 49

The low overall yield (4.6% from Me_2SiCl_2) and multitude of steps (eight) in the preparation of 49 prompted Weber and coworkers to develop an alternative synthesis. Photolytic addition of hydrogen sulfide to dimethyldiallylsilane yielded 1,1-dimethyl-1-sila-5-thiacyclooctane 50 in a 25% yield. Peracid oxidation of 50 to the sulfone 51 followed by a modified Ramberg-Backlund reaction gave 49 in an overall yield of 12% (from dimethyldiallylsilane). Likewise, 1,1-diphenyl-1-silacyclohept-4-ene was prepared from diphenyldiallylsilane in a 4% yield.



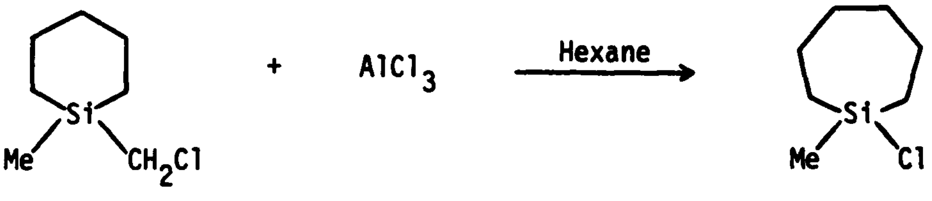
50 51

Ring closure by intramolecular hydrosilylation was studied in 1970 by Kobrakov and coworkers (49) and in 1974 by Swisher and Chen (50). Attempts to prepare silacycloheptanes by this method generally led to an approximately equal mixture of the six- and seven-membered silacycles. In the case where $R=R^1$-Et, the silacycloheptane 52c was the only non-oligomeric product reported. However, this is the only reported case where an intramolecular hydrosilylation afforded only the seven-membered ring. The lack of regiocontrol and tedious product separation has made this route unattractive for synthetic applications.



52 a) $R=R^1=Me$
b) $R=Me, R^1=CH_2Cl$
c) $R=R^1=Et$

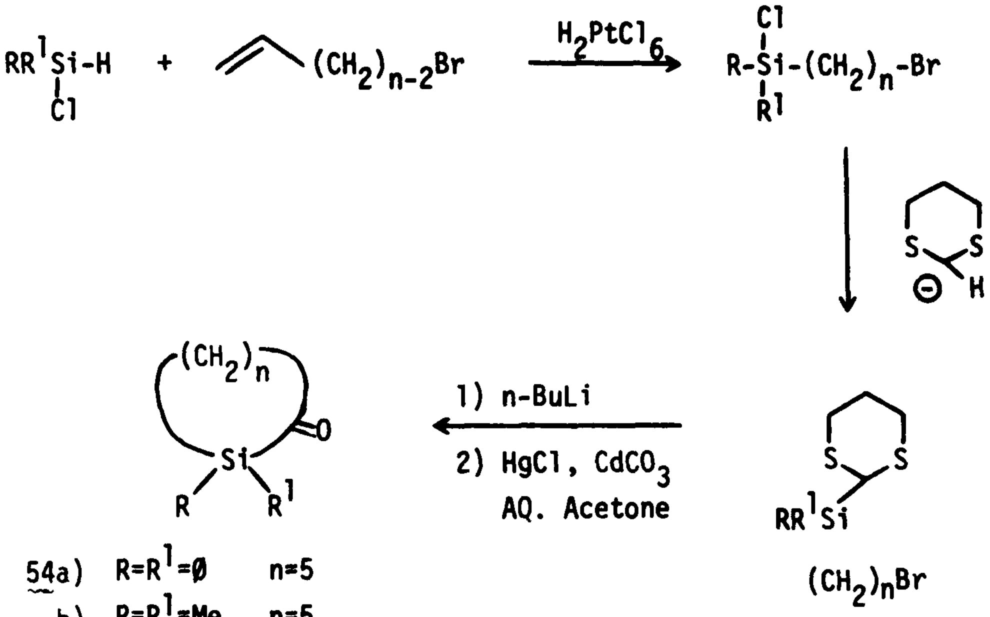
Ring expansion of 1-chloromethyl-1-methyl-1-silacyclohexane with $AlCl_3$ has been reported to give the chlorosilacycloheptane 53 in excellent yields (51).



53 (90%)

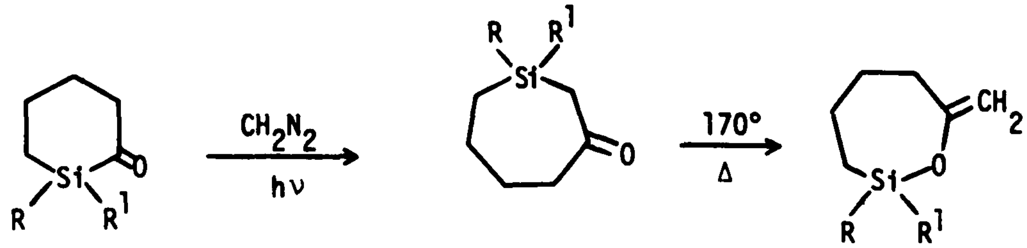
The first general route into cyclic acylsilanes was developed in 1974 by A. G. Brook and H. W. Kucera (52). Using the dithiane cyclization shown in Scheme 9, they were able to prepare 2,2-diphenyl-2-silacycloheptanone 54a and 2,2-dimethyl-2-silacycloheptanone 54b in yields of 8% and 18%, respectively.

Scheme 9



54a) R=R^1=Ø n=5
b) R=R^1=Me n=5

Brook and Kucera's synthesis of cyclic acylsilanes ultimately led to the synthesis of a number of cyclic β-ketosilanes (53). Treatment of the acylsilanes available from the dithiane cyclizations (Scheme 9) with diazomethane in the presence of light gave the ring expanded β-ketosilane. Thus, 3,3-dimethyl-3-silacycloheptanone 55a and 3-methyl-3-phenyl-3-silacycloheptanone 55b were prepared from the corresponding 2-silacyclohexanone 56. Thermally, 55 undergoes a 1,3-silyl shift to oxygen to give 57.

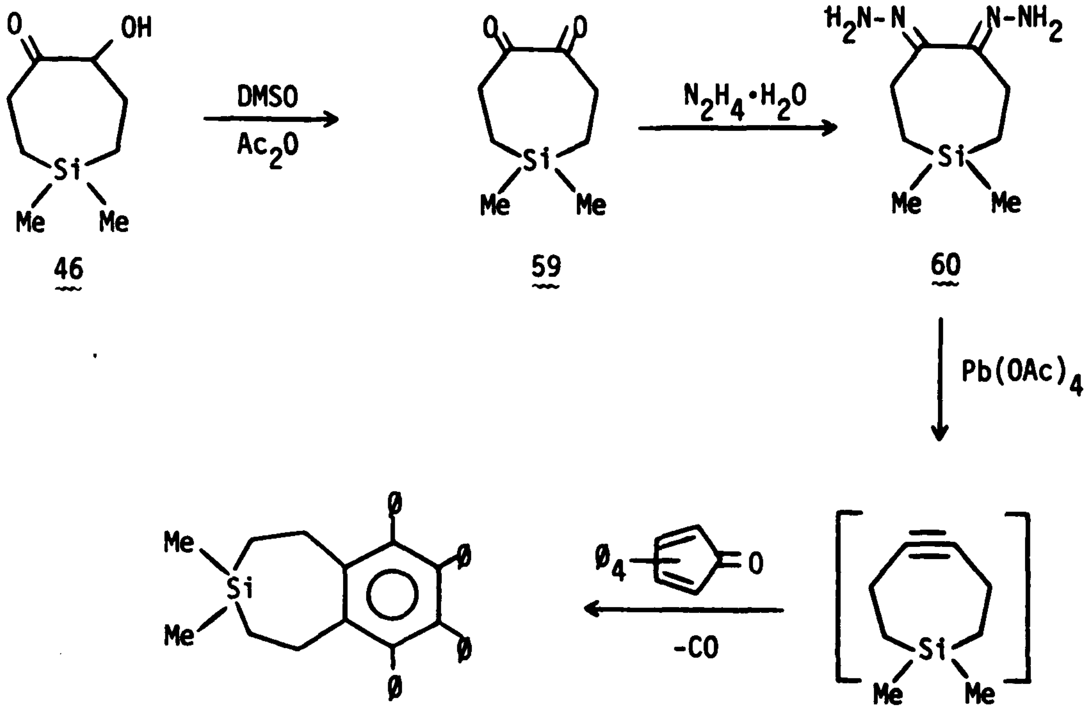


56 a) R^1=R=Me
b) R=Me, R^1=Ø

55 a) R=R^1=Me
b) R=Me, R^1=Ø

57 a) R=R^1=Me
b) R=Me, R^1=Ø

Undoubtedly, the most strained silaheptacycle is 4,4-dimethyl-4-silacycloheptyne 58 prepared by Karaev and Krebs in 1973 (54). Oxidation of 46 with DMSO in acetic anhydride gave the diketone 59 in a 40% yield. Conversion to the dihydrazone 60 followed by treatment with $Pb(OAc)_4$ yielded 58. Although 58 could not be isolated, its formation was confirmed by in situ trapping with tetraphenylcyclopentadiene to give 61.



46

59

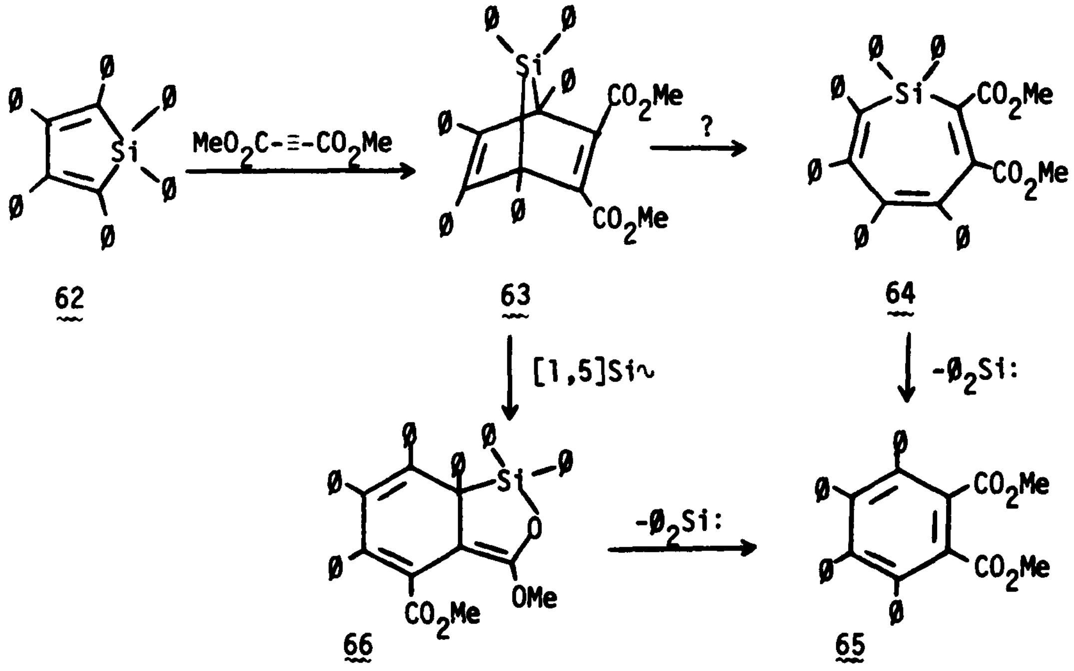
60

61

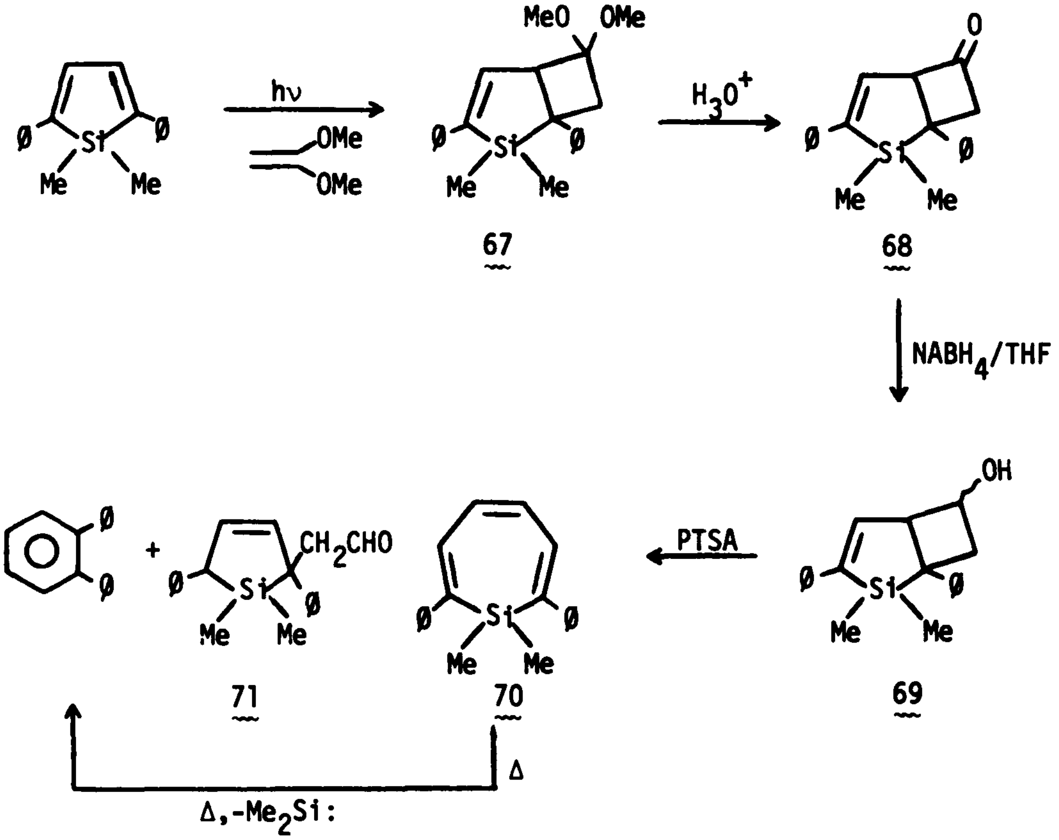
58

The ultimate goal in many of the synthetic routes to silaheptacycles has been their elaboration to silacycloheptatrienes (silepins). To date, this has not been accomplished except in the annulated systems (12,55).

Three literature reports of nonannulated silepins have appeared. The first report was by Gilman *et al*. in 1964 (56). They reported that the reaction of hexaphenylsilole 62 with dimethyl acetylenedicarboxylate gave the 7-silanorbornadiene 63. Treatment of 63 with ethanol gave a yellow material which was tentatively assigned the silepin structure 64. In support of this structure, decomposition of 64 gave the perphenylphthalate 65 (loss of ϕ_2Si:). The complete substitution of the material hindered the absolute identification until Barton and coworkers noted the IR absorption at 1626 cm^{-1} corresponded to a C=C stretch for an o-silyl-o-alkylkentene-acetal. This evidence in conjunction with other work in silole:dimethyl acetylenedicarboxylate adducts led to the assignment of structure 66 to this product (57).

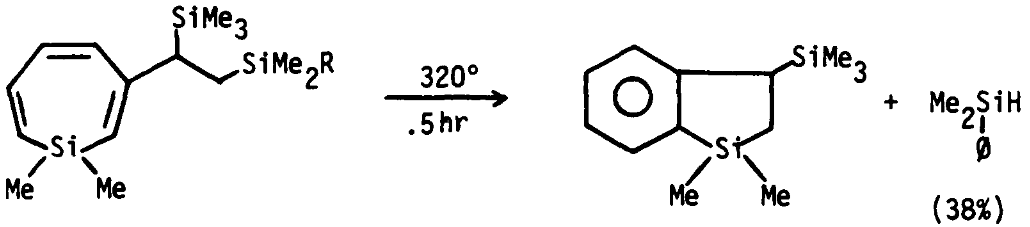


The first successful synthesis of a nonannulated silepin was by Barton *et al*. in 1974 (58). Photocycloaddition of 1,1-dimethoxyethane with 1,1-dimethyl-2,5-diphenylsilole afforded the [2+2] adduct 67 in a 70% yield. Hydrolysis to the ketone 68 followed by reduction of 68 with sodium borohydride gave the *ca*. 1:1 epimeric mixture of alcohols 69. Solvolysis of the pure endo alcohol, obtained by fractional recrystallization, with a catalytic amount of p-toluene sulfonic acid in benzene with azeotropic removal of water afforded three products; the silepin 70, o-terphenyl, and the silacyclopentene 71. The yields were 11%, 24% and 12%, respectively, for the last step (an overall yield of 3% for 70 from the starting silole). Thermally (250°, 15 min, sealed tube), the silepin extrudes dimethylsilylene to give o-terphenyl.



A one-step photochemical synthesis of certain mono- and disubstituted silepins was reported in 1976 by Ishikawa and coworkers (59). When vinylsilanes such as dimethylvinyl-, trimethylvinyl- and ethyldimethylvinylsilane are used as quenching agents in the photolysis of aryldisilanes, silepin derivatives are formed in 5-9% yield, in addition to the normal adducts 72a-e. Likewise, the photochemical reaction of aryldisilanes with 1-hexyne also gave silepin derivatives in 9-12% yield. The scope and mechanistic explanation are shown in Scheme 10. Although the silepins 73a-e and 74a-d are minor products of the reaction, the yields (5-12%) are comparable to Barton *et al.* (58) and have the advantage of only one step.

The thermolysis of silepins 73a+b failed to give the expected benzene derivatives generally observed. Instead, the silaindane 75 was obtained in both cases along with phenyldimethylsilane for 73b.

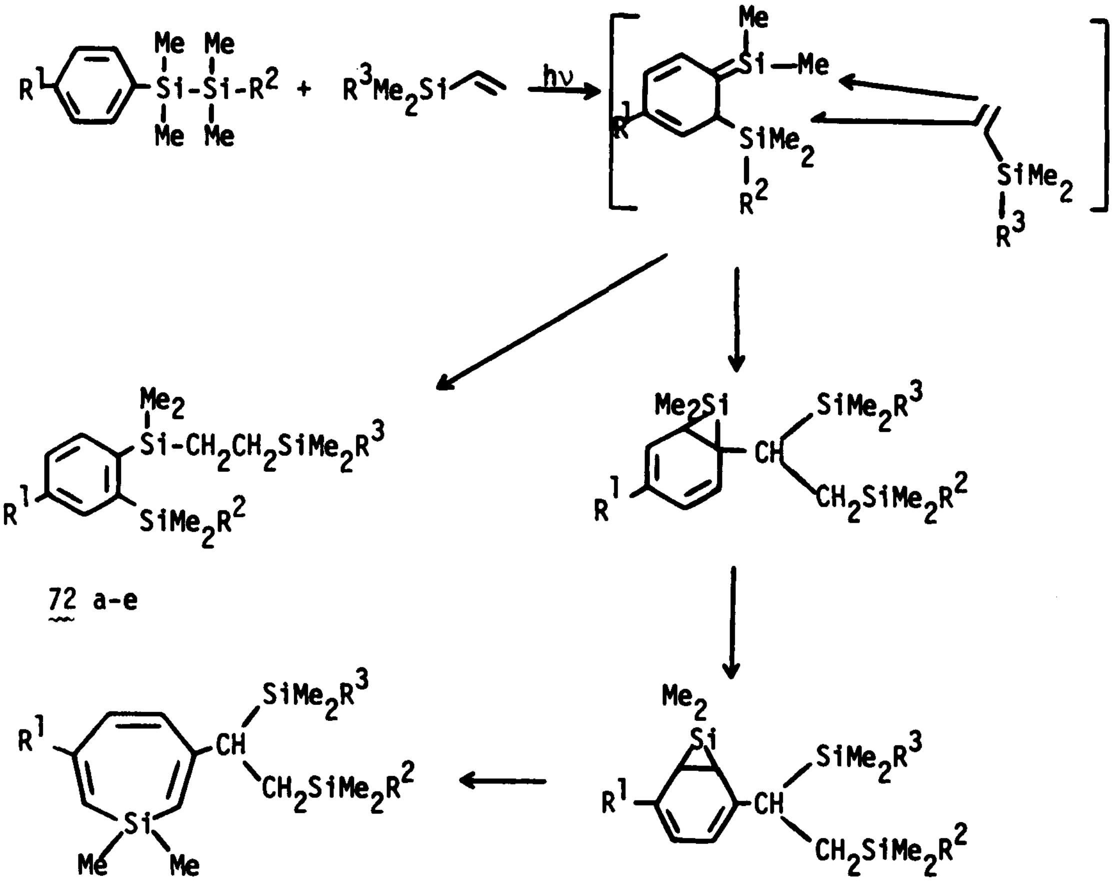


73a R=H
73b R=Ø

(42%)
75

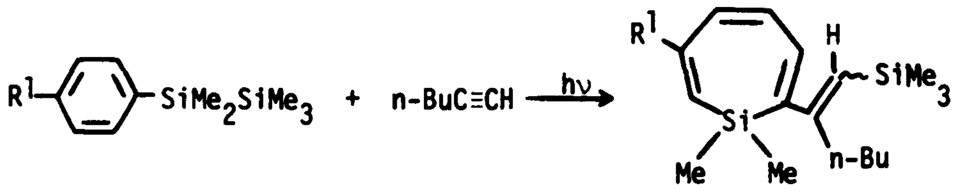
(38%)
(when R=Ø)

Scheme 10



72 a-e

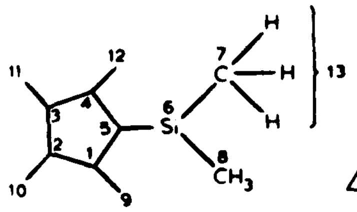
73 a) R^1=H, R^2=R^3=Me (7%)
b) R^1=H, R^2=Ø, R^3=Me (8%)
c) R^1=H, R^2=Me, R^3=Et (5%)
d) R^1=R^2=R^3=Me (7%)
e) R^1=R^2=Me, R^3=H (9%)



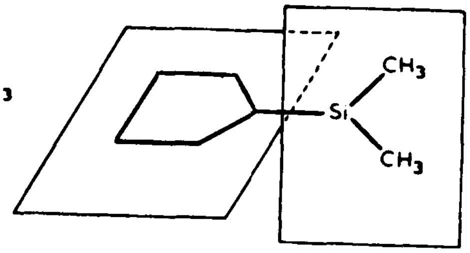
74 a) and b) R^1=H
c) and d) R^1=Me

E. Silafulvenes

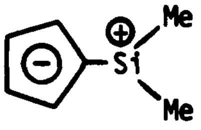
Calculations on 6,6-dimethyl-6-silafulvene by Ustynyuk et al. (60) led them to predict that it would be a stable, isolable molecule. Their CNDO/2 calculations showed 6,6-dimethyl-6-silafulvene to be planar with the planar conformation 76, 19.8 kcal/mole lower than the bisected conformation 77. Calculation of the dipole moment (5.47D) and the charge distribution (see Table 2) led them to believe that the major contribution to the stability of 6,6-dimethyl-6-silafulvene was the ylide structure 78.



76



77



78

Table 2. Total energies, bond lengths, charge densities and dipole moments, for conformations 76 and 77 of dimethylsilafulvene, as calculated via a CNDO/2 technique. For numbering of atoms, see structure 76

Parameter	76	77	Comment
E_{total}(eV)	-1653.77	-1652.91	
$r_{5,6}$ Å	1.962	2.060	
$r_{6,7} = r_{6,8}$	2.10	2.10	The parameters of $C_5H_4C(CH_3)_2$ (61)
$r_{1,5}$	1.475	1.475	
$r_{1,2}$	1.347	1.347	
$r_{2,3}$	1.462	1.462	

Table 2. (Continued)

Parameter	76	77	Comment
(r_{CH})	1.111	1.111	The mean (r_{CH}) calculated via CNDO/2
μ(D)	5.47	6.83	
q_1	-0.03	-0.01	
q_2	-0.03	-0.06	
q_5	-0.12	-0.19	
q_6	0.45	0.60	
q_7	-0.13	-0.15	
q_9	-0.03	-0.05	
q_{10}	-0.02	-0.03	
q_{13}	0.02	0.03	

However, work by Ahlrichs and Heinzman (62) contradicts Ustynyuk and coworkers' stand. Closed and open shell RHF calculations by Aldrichs and Heinzman on silenes show that their high degree of reactivity is not due to their thermodynamic instability but rather to the polarization of the silicon-carbon double bond. Furthermore, their results show a weakening of the (p-p)π bond when this polarization is increased. Thus, the contribution of ylide structure 78 to 6,6-dimethyl-6-silafulvene would be expected to enhance its reactivity.

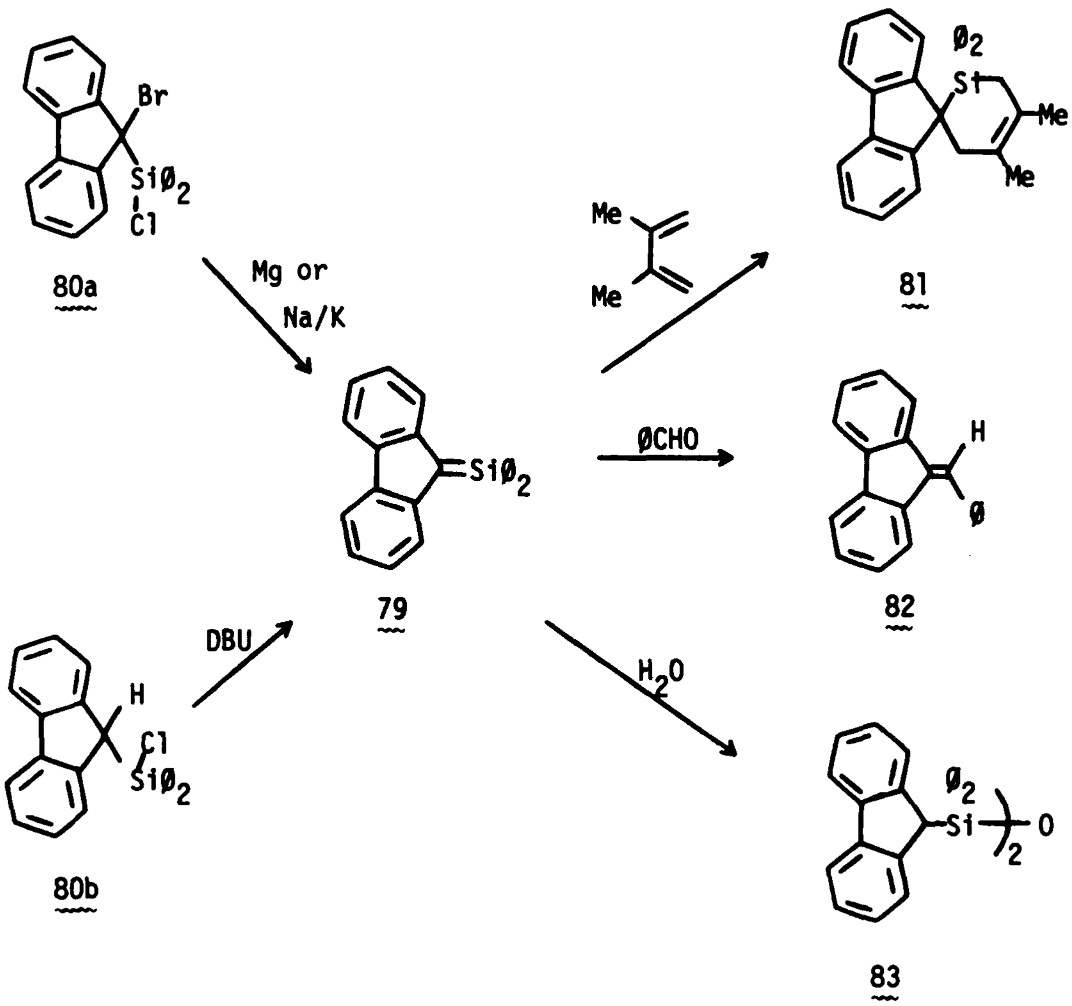
Since the initial reports on the first synthesis of 6,6-dimethyl-6-silafulvene from this dissertation (63-65), three other reports of a silafulvene have appeared. Two of the reports, those by Schubert and Rengstl (66) and Sekiguchi and Ando (67), utilize methods substantially different, hence these reports will be discussed in this section. The third, the report by Nakadaira and coworkers (68), mimics the method of preparation and results of those earlier reported (63-65). As such, this report will not be further examined.

In 1980, Schubert and Rengstl (66) reported the preparation of 6,6-diphenyl-6-sila-dibenzofulvene 79 via 80a and b. The evidence for the intermediacy of 79 was based on the following observations:

(1) When a solution of 80a and 2,3-dimethylbutadiene was treated with either magnesium metal or a sodium-potassium alloy, the corresponding silene:diene adduct 81 was obtained in a 3-5% yield.

(2) Treatment of 80b with DBU in the presence of benzaldehyde afforded phenylfulvene 82, the expected product from trapping the silene with benzaldehyde followed by extrusion of diphenylsilanone.

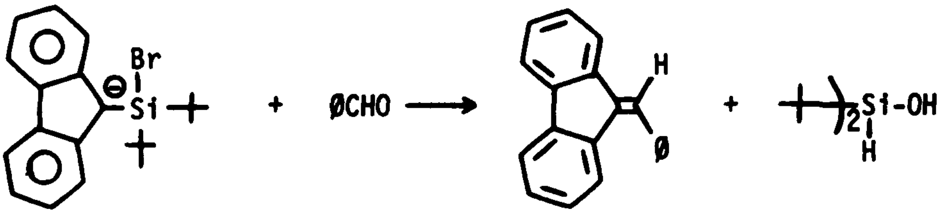
(3) Treatment of 80b with DBU in the presence of water gave the siloxane 83 in high yield.



Although the above data suggest the intermediacy of 79, it does not mandate it. In each case, the trapping data can be explained on the basis of the following known silicon chemistry:

(1) Chlorosilanes react with water to form siloxanes. Amine bases are typically employed to absorb the HCl produced in the reaction.

(2) α-Silyl anions react with carbonyls in the Peterson olefination reaction. This has been recently observed by Barton and Tully (69) for a di-t-butylfluorenyl silane 84 and benzaldehyde

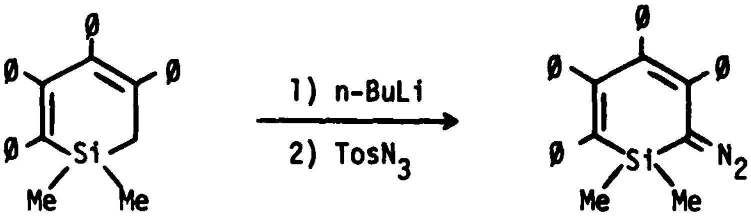


84 82

(3) Decomposition of the intermediate silaoxetane formed from trapping of the silene with benzaldehyde yields a silanone and an olefin. The silanone intermediate thus formed oligomerizes to cyclosiloxanes (70). Cyclosiloxanes were not reported in the reaction of 79 with benzaldehyde.

(4) The formation of a silene upon treatment of an α-halohalosilane with either Mg or Na/K has not been firmly established (71). Thus, while the probability of a silafulvene is good in the reactions reported by Schubert and Rengstl, their evidence is not as concrete as they claim.

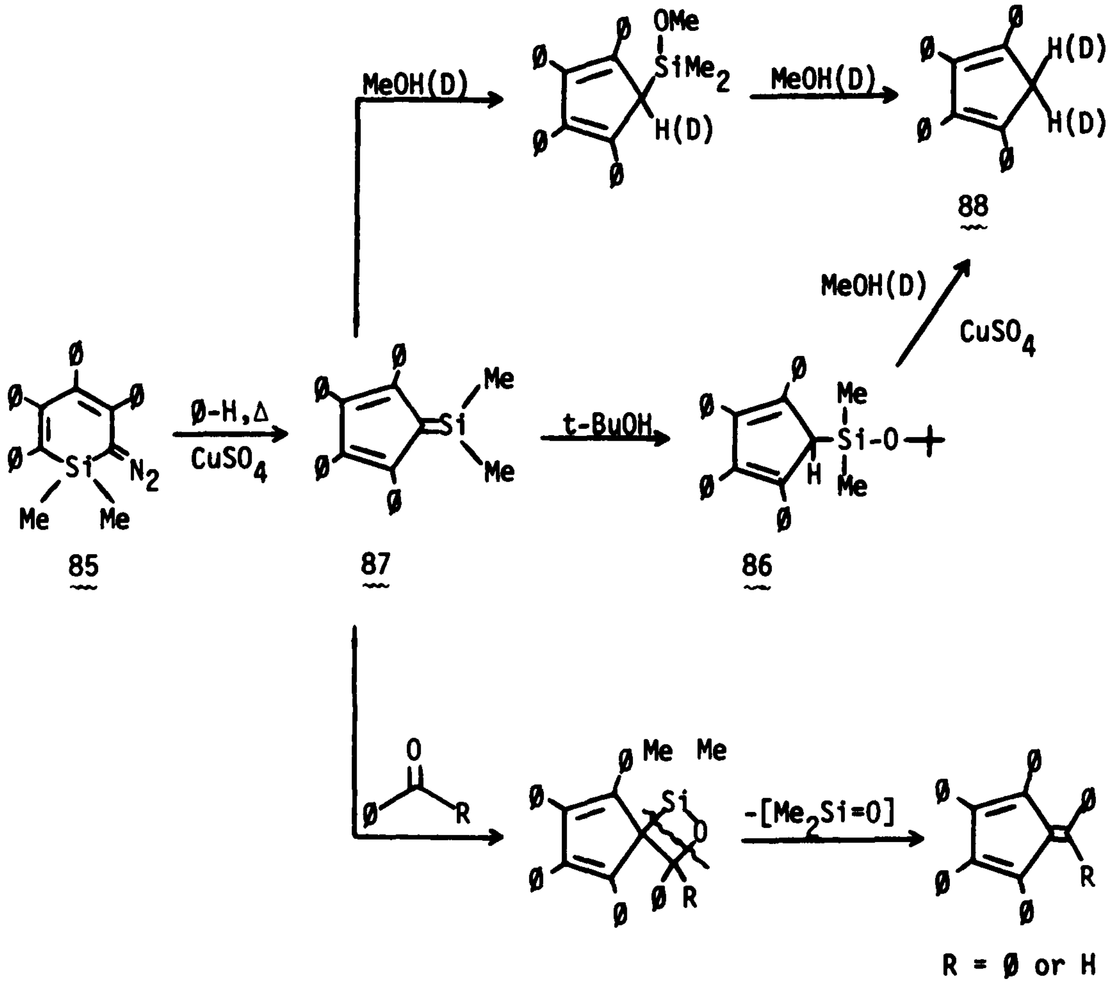
Very recently, Sekiguchi and Ando have reported (67) the synthesis of a 6-silafulvene via a silylcarbene rearrangement from a diazo-2-silacyclohexa-3,5-diene 85. The synthesis of 85 was accomplished by a modification of the method of Doering and Depuy (72). Treatment of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclohexa-2,4-diene with an equimolar amount of n-butyllithium followed by p-toluenesulfonyl azide afforded 85 in a 36% yield.



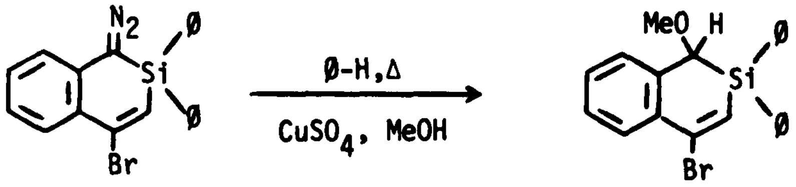
85

The carbene generated from 85 could generate either a silabenzene via a 1,2 methyl migration or a silafulvene via a 1,2 vinyl migration. When a benzene solution of 85 containing an excess of t-butyl alcohol was refluxed in a sealed tube in the presence of a catalytic amount of anhydrous cupric sulfate, the only product obtained was cyclopentadienyl-t-butoxysilane 86 in a 96% yield. This corresponds to the trapping of the silafulvene 87 with t-butyl alcohol. When methanol or methanol-d_1 was used in place of t-butanol, the major product was 1,2,3,4-tetraphenylcyclopentadiene 88 (91%). Control experiments established that under these conditions 86 was desilylated to 88. Hence, the formation of 88 was entirely consistent with the trapping of 87 with methanol.

Further evidence for the intermediacy of 87 was obtained in the thermolysis of a benzene solution of 85 with an excess of either benzophenone or benzaldehyde. When 85 was thermolyzed in the presence of benzophenone, 1,2,3,4,5,6-hexaphenylfulvene was obtained in 66% yield. When benzaldehyde was used as the trap, 1,2,3,4,6-pentaphenylfulvene was obtained. These are the expected decomposition products from the silaoxetane intermediate that would be formed from the trapping of a silafulvene with a carbonyl compound. Thus, all of the evidence obtained by Sekiguchi and Ando supports the intermediacy of a silafulvene arising from a 1,2 vinyl migration from silicon to carbon from an α-silylcarbene.



Surprisingly, when the diazo compound 89 was thermolyzed in a benzene solution with excess methanol, only the simple OH insertion product 90 was obtained.



89 90

IV. RESULTS AND DISCUSSION

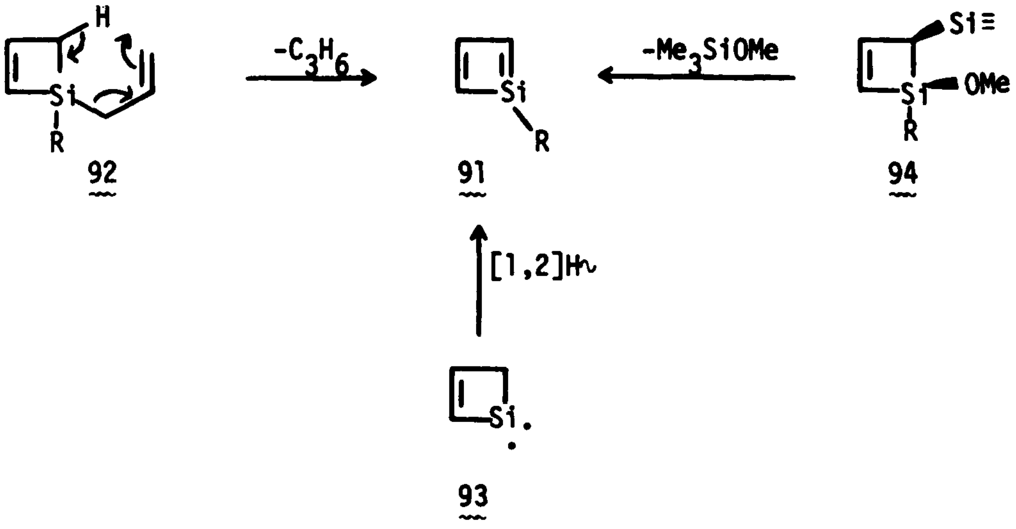
A. Syntheses of Siletenes and Attempted Syntheses of a Silacyclobutadiene

The idea of a synthesis of a silacyclobutadiene quickly personifies the rapidly advancing field of reactive intermediates in silicon chemistry. In a period of less than twelve years, organosilicon chemists have traversed the concept of the possibility of the existence of a silicon-carbon (p-p)π bond in an attempt to incorporate such a species into a potentially antiaromatic framework! The attempts to prepare this intriguing reactive silacycle is the subject of this section.

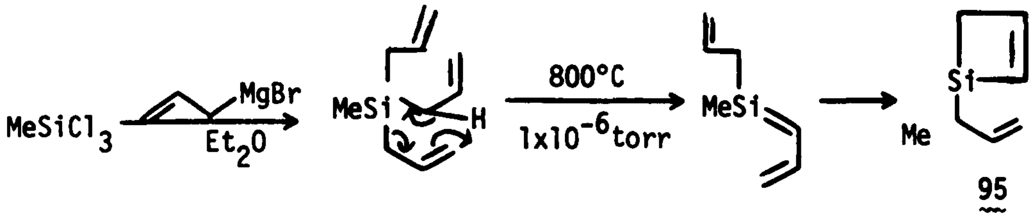
At the outset of this project, only three methods for the preparation of a siletene were known (see Historical section). However, none of these methods allowed for the general functionalization at either a ring carbon or the silicon. Since the ultimate goal was the generation of a silacyclobutadiene via an appropriate siletene, modification of existing methods and eventually development of a new route to siletene was required.

Three approaches to the synthesis of a silacyclobutadiene 91 were visualized; a retro-ene elimination of propene from the diallylsilane 92, intramolecular rearrangement of a silacyclobutenylidene 93, or a β-elimination of trimethylmethoxy silane from 94 (Scheme 11).

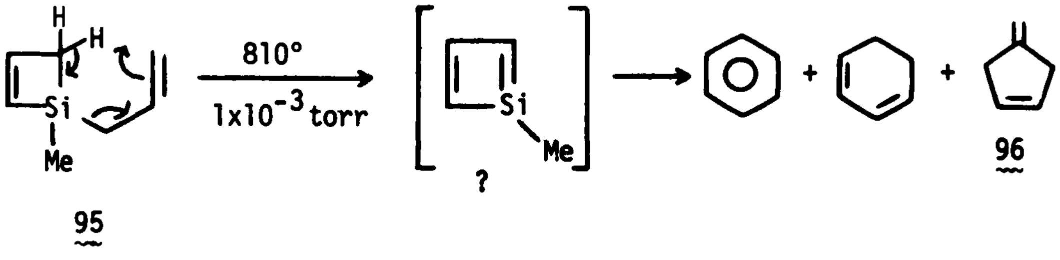
Scheme 11



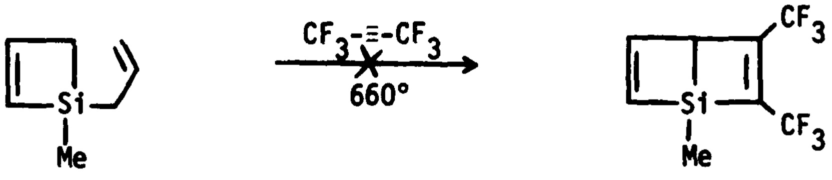
Examination of the literature clearly showed that the most expedient entry into a silacyclobutene ring system was the retro-ene method pioneered by Block and Revelle (9). Application of this route to the synthesis of 92 suggested the thermolysis of methyltriallylsilane, a simple dialkyldiallylsilane where one of the alkyl groups is an allyl. Methyltriallylsilane was prepared in an 80% isolated yield via the coupling of allylmagnesium bromide with methyltrichlorosilane (73). Vacuum flow pyrolysis (800°, 1×10^{-6} torr) of methyltriallylsilane afforded the desired methylallylsiletene amongst other products. Analytically pure 95 was obtained by preparative gas chromatography on a 12' 20% SE-30 column at 80°C.



In the presence of added traps, silenes generated in the gas phase undergo dimerization to 1,3-disilacyclobutanes (70). Flash vacuum pyrolysis (810°, 1×10^{-3} torr) of 95 failed to furnish evidence for the intermediacy of 1-methyl-1-silacyclobutadiene. GC analysis of the pyrolysate on a 12' 15% SE-30 column at 100°C revealed the presence of a number of products. The two major peaks were isolated by preparative gas chromatography and determined to be allylmethylsiletene 95 and a mixture consisting of benzene, 1,3-cyclohexadiene and 96 in a ratio of 1.5:1:2.6, respectively. Other than starting material, no silicon containing product could be identified.

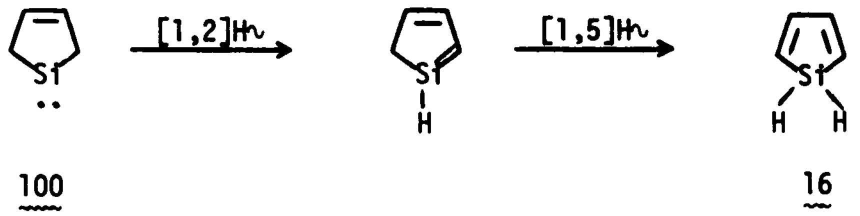


Although the absence of volatile silacyclobutadiene oligomers did not unequivocally rule out its intermediacy in the pyrolysis of 95, it did lower the probability. In an attempt to trap 1-methyl-1-silacyclobutadiene in a [4+2] Diels-Alder fashion, a copyrolysis of 95 and perfluoro-2-butyne was conducted (660° using a flow rate of perfluoro-2-butyne of 1 mL/4 sec). Analysis of the pyrolysate by GCMS showed the absence of a silacyclobutadiene:perfluoro-2-butyne adduct.

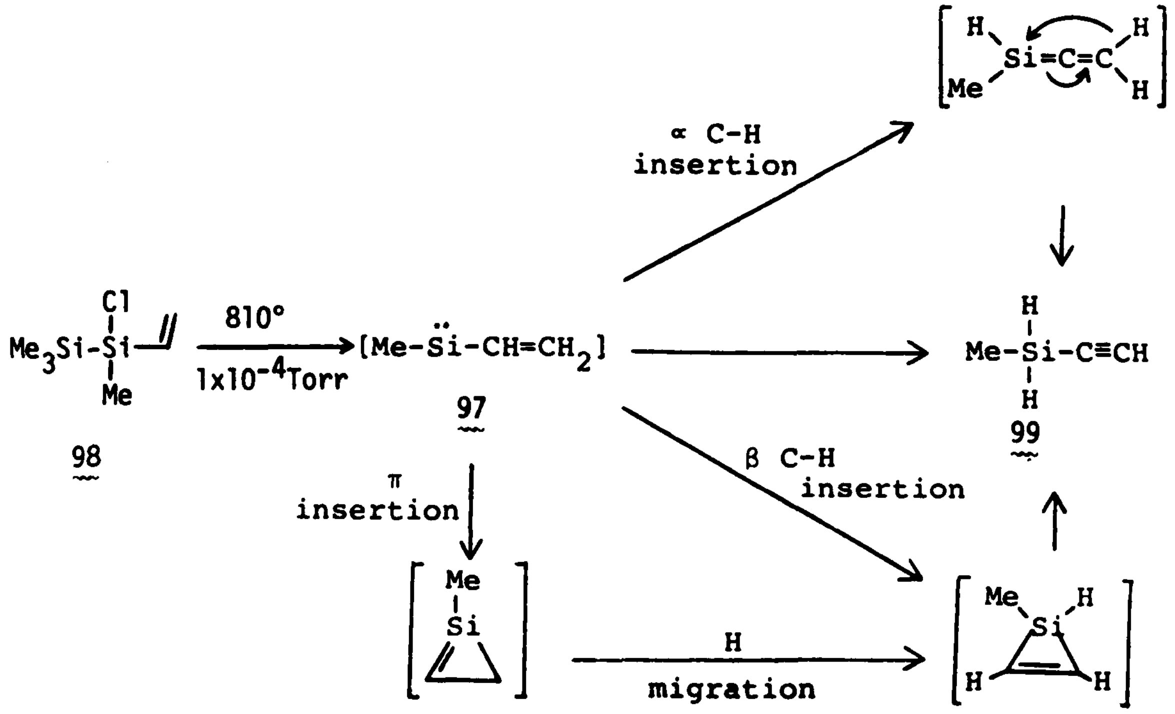


95

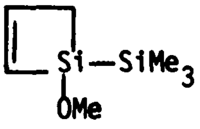
Another possible route into the silacyclobutadiene ring system was perceived to be through the silacyclobutenylidene 93. Recent results from the laboratories of both T. J. Barton and P. Gaspar indicate silylenes can undergo intramolecular rearrangements. Barton and Goure (74) have demonstrated that methylvinylsilylene 97 generated by alpha elimination of trimethylchlorosilane from 98 will isomerize to ethynylmethylsilane 99. Although the mechanistic origin of 99 has not been demonstrated, it is most likely to occur *via* one of the pathways shown in Scheme 12. Likewise, recent results from Gaspar (75) indicate the intramolecular rearrangement of silacyclopentenylidene 100 to silole 16.


[1,2]H~
[1,5]H~
Si
H
100
16

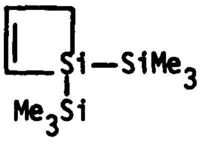
Scheme 12


Me$_3$Si-Si(Cl)(Me)-CH=CH$_2$
98
810°
1x10^{-4}Torr
[Me-S̈i-CH=CH$_2$]
97
α C-H insertion
[H(Me)Si=C=CH$_2$]
β C-H insertion
π insertion
H migration
Me-SiH$_2$-C≡CH
99

Two general methods for the generation of a silylene are commonly employed: the concerted alpha elimination of trimethylmethoxysilane from silicon (76), and the photochemical extrusion from a trisilane (77). The two most reasonable precursors of 93 would, therefore, be 101 and 102. However, the inability at that time to incorporate functionality at silicon in siletene syntheses disqualified 101 from further consideration.

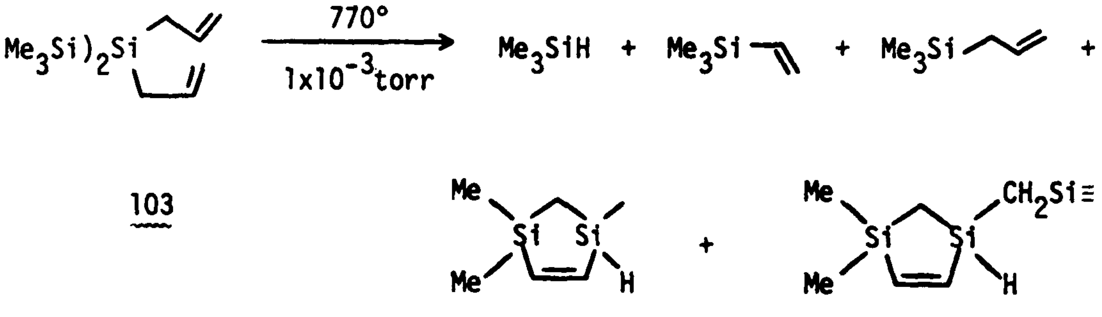


101



102

The synthesis of 102 appeared to be as simplistic as the pyrolysis of the easily prepared 2,2-diallyl-hexamethyltrisilane 103 should readily afford it. Utilizing this naive approach, 103 was prepared in 49% isolated yield by the coupling of allylmagnesium bromide with 2,2-dichlorohexamethyltrisilane. Flash vacuum pyrolysis (770°, 1×10^{-3} torr) of 103 afforded a light yellow liquid in a 66% mass recovery. Analysis of the pyrolysate by gas chromatography revealed the presence of five major products which were isolated by preparative gas chromatography on a 12' 20% OV101 column. The five products were identified as trimethylsilane (2%), trimethylvinylsilane (3%), trimethylallylsilane (7%), 3,3,5-trimethyl-3,5-disilacyclopentene 104 (4%) and 105 (14%) on the basis of their ^{1}H-NMR, low resolution mass spectrum, and comparison of their GC retention time with that of an authentic sample. The desired siletene 102 was not observed.

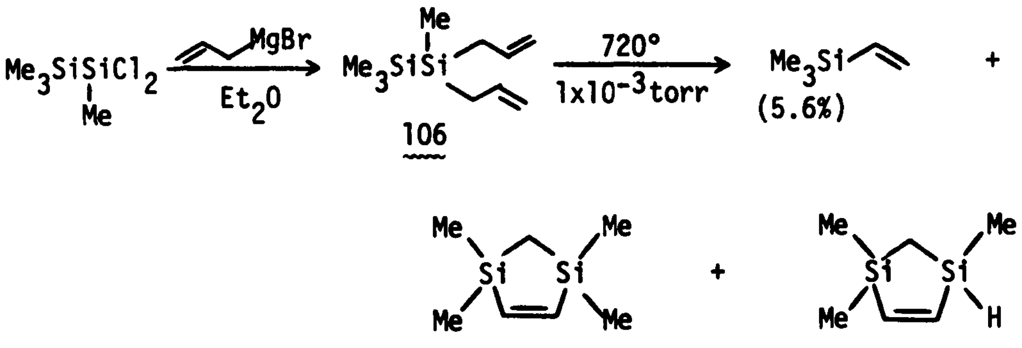


104

105

The absence of a silacyclobutene product in the pyrolysis of 103 was intriguing. In order to test whether the failure of 103 to yield 102 upon pyrolysis was due to a steric effect of the presence of a Si-Si bond, 1,1-diallyltetramethyldisilane 106 was prepared. The absence of trimethylsilylsiletene in the pyrolysate of 106 would indicate an incompatibility of a disilanyl unit in a retro-ene reaction. Furthermore, if trimethylsilylsiletene was formed, it could potentially be a precursor to a functionalized siletene via cleavage of the Si-Si bond. Coupling of allylmagnesium bromide and 1,1-dichlorotetramethyldisilane gave 106 in a 45% isolated yield. Flash vacuum pyrolysis (720°C, 1×10^{-3} torr) of 106 afforded a light yellow oil from which three products were isolated by preparative chromatography and identified on the basis of their ^{1}H-NMR, low resolution mass spectrum and GC retention time. The three products were trimethylvinylsilane (5.6%), 3,3,5-trimethyl-3,5-disilacyclopentene (6.3%) and

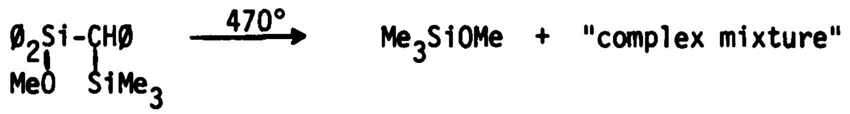
3,3,5,5-tetramethyl-3,5-disilacyclopentene (10.7%). Again, no silacyclobutene products were observed.



106

(10.7%) (6.3%)

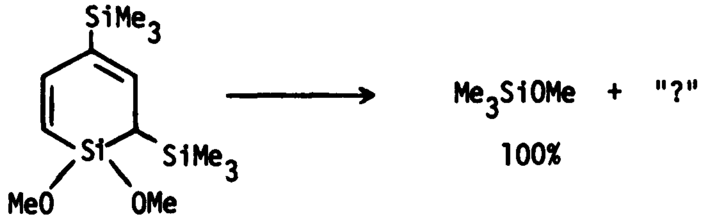
The third approach to the synthesis of a silacyclobutadiene was based on the β-elimination of trimethylmethoxysilane from 94 (R = Me). Although prior to the time of this dissertation work, thermal β-eliminations to generate a silicon carbon double bond had not been shown, sufficient evidence was available to warrant consideration of this approach. As early as 1975, Rutherford and Seidewand (78) reported an attempt to generate a silene in this manner. They reported that the thermolysis of 107 at 470° resulted in a 50% yield of trimethylmethoxysilane and a "complex mixture".



$$\underset{\text{MeO}}{\emptyset_2\text{Si}}\text{-}\underset{\text{SiMe}_3}{\text{CH}\emptyset} \xrightarrow{470°} Me_3SiOMe + \text{"complex mixture"}$$

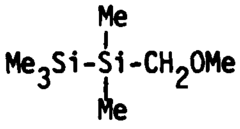
107

In another example of an unfruitful β-elimination, T. J. Barton (79) found that the static pyrolysis of 108 gave a quantitative yield of trimethylmethoxysilane. As in the case of Rutherford and Seidewand, products arising from a silene intermediate were not observed.



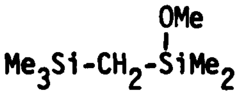
108

The two orientations possible for silene formation via a β-elimination of trimethylmethoxysilane are shown in 109 and 110. Examination of bond dissociation energies indicate that silene formation from 109 should be favored over 110. For 109, the two bonds being broken are a silicon-silicon bond ($D(Si\text{-}Si) = 80.5$ kcal/mole) and a carbon-oxygen bond ($D(C\text{-}O) = 91$ kcal/mole) and the two bonds being formed are a silicon-oxygen bond ($D(Si\text{-}O) = 128$ kcal/mole) and a silicon-carbon π bond ($D(Si{=}C) = 39$ kcal/mole) (80). Therefore, for 109, energy required for bond breaking is approximately the same as the energy of bond formation (-4.5 kcal/mole). Since in 110 a silicon-oxygen bond is both formed and broken, the two bonds to consider are the breaking of a silicon-carbon bond ($D(Si\text{-}C) = 89.4$ kcal/mole) and the formation of a silicon-carbon π bond ($D(Si{=}C) = 39$ kcal/mole). Therefore, based upon bond dissociation energies, the β-elimination of trimethylmethoxysilane from 109 should be favored by approximately 47 kcal/mole over 110 provided the same mechanistic pathway occurred for each.



$Me_3Si\text{-}Si(Me)_2\text{-}CH_2OMe$

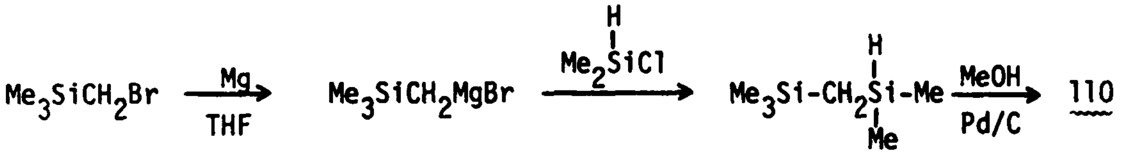
109



$Me_3Si\text{-}CH_2\text{-}Si(OMe)Me_2$

110

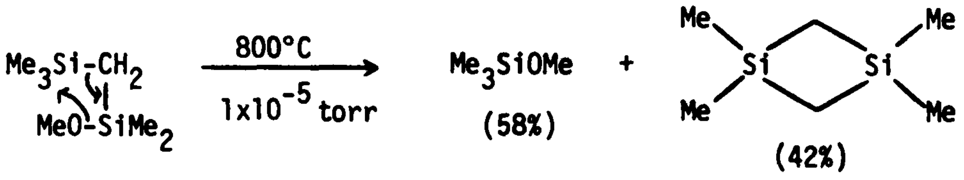
In order to assess the two possible β-eliminations, the two model systems 109 and 110 were prepared and thermolyzed. Preparation of 110 was accomplished in two steps in an overall isolated yield of 35%. Quenching of the Grignard reagent from bromomethyltrimethylsilane with dimethylchlorosilane afforded 110 in a 54% yield. Etherification of 111 by the method of Sommer and Lyons (81) utilizing a palladium on carbon catalyst gave 110.



$$Me_3SiCH_2Br \xrightarrow[THF]{Mg} Me_3SiCH_2MgBr \xrightarrow{HMe_2SiCl} Me_3Si\text{-}CH_2SiH(Me)\text{-}Me \xrightarrow[Pd/C]{MeOH} \mathbf{110}$$

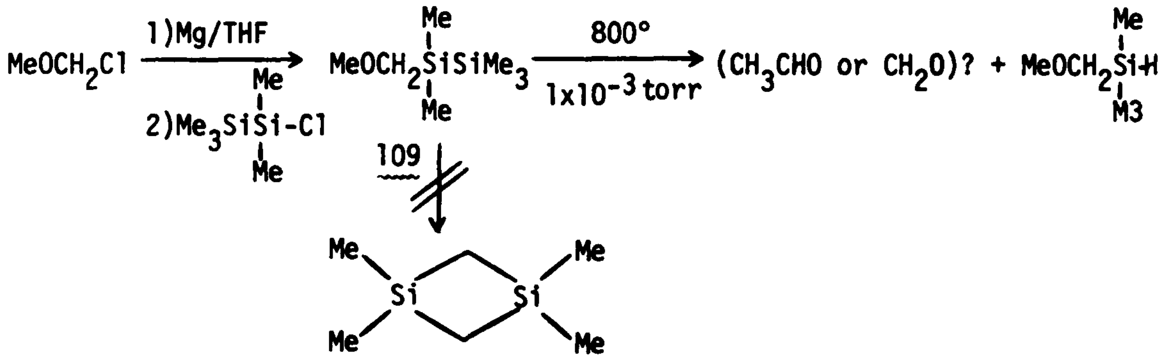
111

Flash vacuum pyrolysis (800°C, 1 x 10^{-5} torr) of 110 afforded trimethylmethoxysilane and 1,1,3,3-tetramethyl-1,3-disilacyclobutane in 58% and 42% yield, respectively (based on unrecovered 110). The formation of the disilacyclobutane, a prognostic product for the gas-phase generation of 2-methyl-2-silapropene, and trimethylmethoxysilane indicated the desired β-elimination; silene generation was occurring.



110

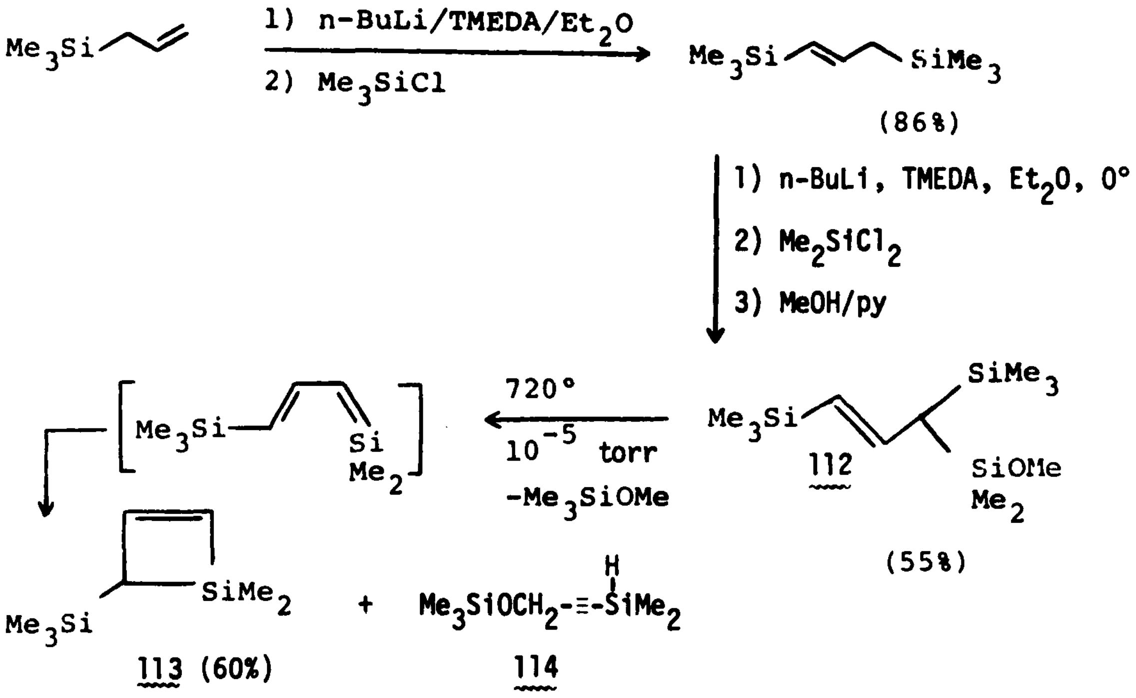
The alternative possible silene generator 109 was less encouraging. The synthesis of 109 was accomplished by the quenching of the Grignard reagent from chloromethyl methyl ether with chloropentamethyldisilane (82). A yield of 42% was obtained. Flash vacuum pyrolysis (800°C, 1 x 10^{-3} torr) of 109 afforded an acrid smelling clear liquid. Analysis of the pyrolysate by GCMS revealed the major product to be methoxymethyldimethylsilane. Neither trimethylmethoxysilane or 1,1,3,3-tetramethyl-1,3-disilacyclobutane, the products expected from a β-elimination, were observed in substantial amounts.



Comparison of the data obtained from the thermolysis of the model systems 109 and 110 clearly indicates the superiority of 110 for silene generation. Application of this method to the synthesis of siletenes suggested the thermolysis of 112. Two factors favored 112 as an entry point into siletes: (1) ease of synthesis, and (2) it tested whether the ring functionality necessary for a second β-elimination was compatible with this method of siletene generation.

The synthesis of 112 was accomplished by the sequence of metallation (83)/chlorosilane quenching shown in Scheme 13 in an overall isolated yield of 47%. Flash vacuum pyrolysis (720°, 1×10^{-5} torr) of 112 afforded a light yellow liquid in an 82% mass recovery. Distillation of the pyrolysate gave trimethylmethoxysilane (71% isolated yield) and 3-trimethylsilyldimethylsiletene 113 (60% isolated yield) as a clear colorless liquid. At high temperatures, the appearance of an additional product, tentatively assigned the structure 114 on the basis of its ^{1}H-NMR and low resolution mass spectrum was observed.

Scheme 13



The ability to incorporate functionality at silicon in a siletene via a beta elimination was demonstrated by the thermolysis of 115. The synthesis of 115 was effected by the metallation of 116 with n-BuLi followed by quenching with methyltrichlorosilane. After a nonaqueous work-up, the crude reaction mixture was treated with an equimolar mixture of methanol and pyridine to afford a 48% isolated yield of 115. Flash vacuum pyrolysis (740°, 1×10^{-4} torr) of 115 followed by fractional distillation of the pyrolysate gave a 74% yield of 4-trimethylsilylmethylmethoxysiletene 117. The ^{1}H-NMR spectrum of 117 (see Figure 1) showed that it was an approximately equal mixture of the cis- and trans-stereoisomers, which could not be separated.

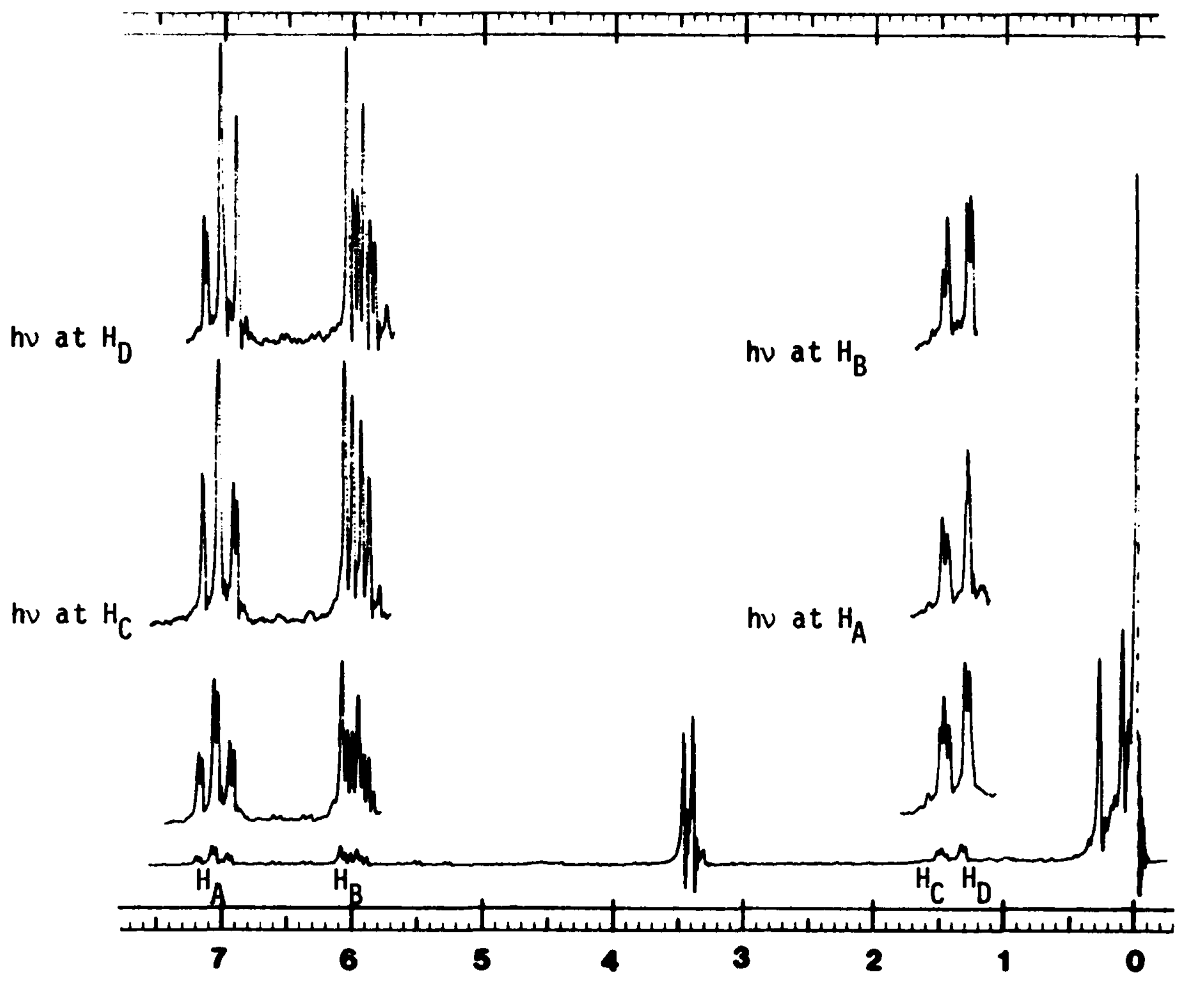
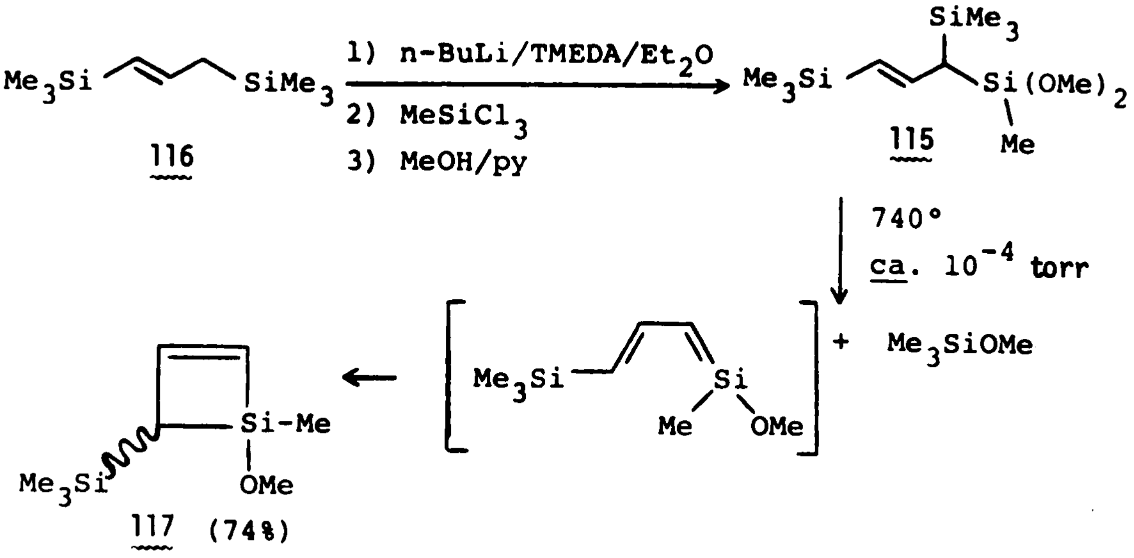
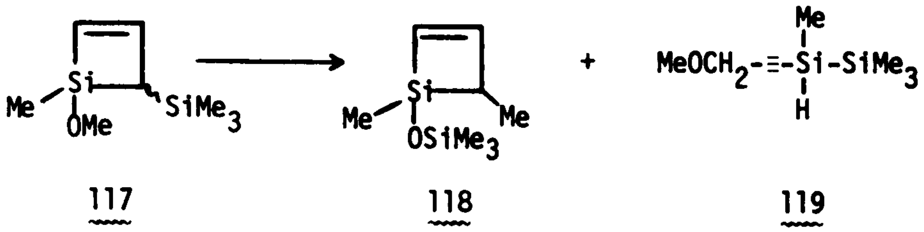


Figure 1. 60 MHz ^{1}H-NMR of a mixture of *cis*- and *trans*-4-trimethylsilyl-1-methoxy-1-methyl-1-silacyclobutene



Unfortunately, as in the pyrolysis of the allylsiletene 95, no evidence for the intermediacy of a silacyclobutadiene was obtained upon thermolysis of 117. Distillation (25°, 1×10^{-4} torr) of 0.2179 gm of 117 through a quartz tube packed with quartz chips and heated to 860°C afforded 0.155 gm (71% mass recovery) of a light yellow liquid. Analysis of the pyrolysate by gas chromatography revealed numerous products. The two major products were isolated by preparative chromatography on an 8'-20% DC-550 column and assigned the structures 118 and 119 based upon their ^{1}H-NMR and low resolution mass spectrum. The origin of 118 and 119 remain a mystery.



Since silene dimer formation or other evidence for a silacyclobutadiene intermediate was not garnered in the neat pyrolysis of 117, a copyrolysis of 117 and 2,3-dimethylbutadiene was conducted. Analysis of the pyrolysate showed only 2,3-dimethylbutadiene and products arising from it. A silene:butadiene adduct was not observed nor was trimethylmethoxysilane.

In summary, two possible silacyclobutadiene precursors were prepared and subjected to a variety of pyrolysis conditions. Although no evidence for the sought reactive intermediate was obtained, a new method of siletene synthesis based on a novel method of silene generation was developed (84). Furthermore, this method of siletene synthesis offers the following advantages over the previous methods available:

(1) It is amenable to a large scale synthesis.

(2) The yields are higher (28% to 35% overall yields) and highly reproducible.

(3) Functionality can be introduced at a ring carbon.

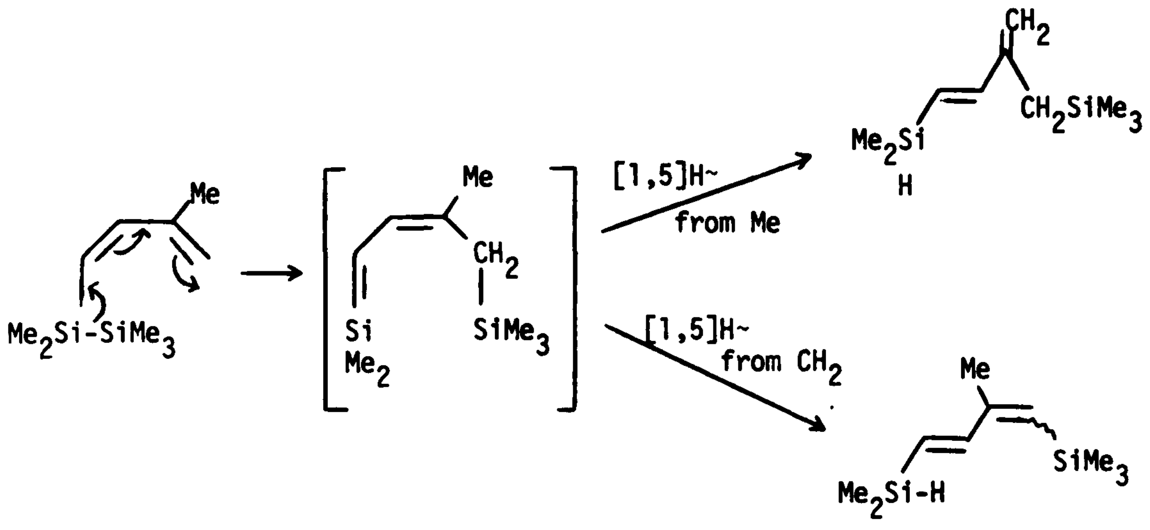
(4) Functionalization of silicon can be achieved.

B. Syntheses of 1-Methylsilole, 1,1-Dimethylsilole and 2-Methyl-2-silaindene

Although siloles (5-silacyclopentadienes) have proven to be quite interesting and important synthetic intermediates to ring systems such as 7-silanorbornadiene (85), siloxapinone (86), 1-silacyclopentadiene (87), and silepin (58), all of this work has been accomplished with siloles possessing at least two substituents on the ring-carbons.

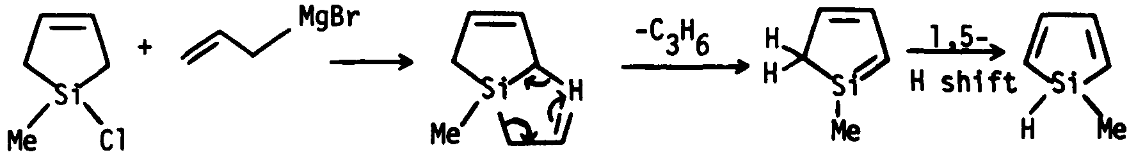
Reports of C-unsubstituted siloles have appeared in the literature four times only to be either withdrawn, found to be irreproducible or incompletely characterized (see Historical section).

The resolution of this long-standing synthetic problem was envisioned by the application of Block and Revelle's silene synthesis (9). It was expected that the thermolysis of 4-allyl-4-methyl-4-silacyclopentene would give 1-methylsilole as shown in Scheme 14. The rationale for this expectation was two-fold. The allylsilacyclopentene 120, being a diallylsilane, should undergo a retro-ene elimination of propene to give the intermediate silabutadiene 121. Earlier work by W. D. Wulff (88) had shown that a 1,5 hydrogen shift to silicon would occur in 1-silabutadienes possessing a gamma hydrogen to give a butadienyl silane.



Thus, a 1,5 hydrogen shift in the 1-silabutadiene 121 would give 1-methylsilole 122.

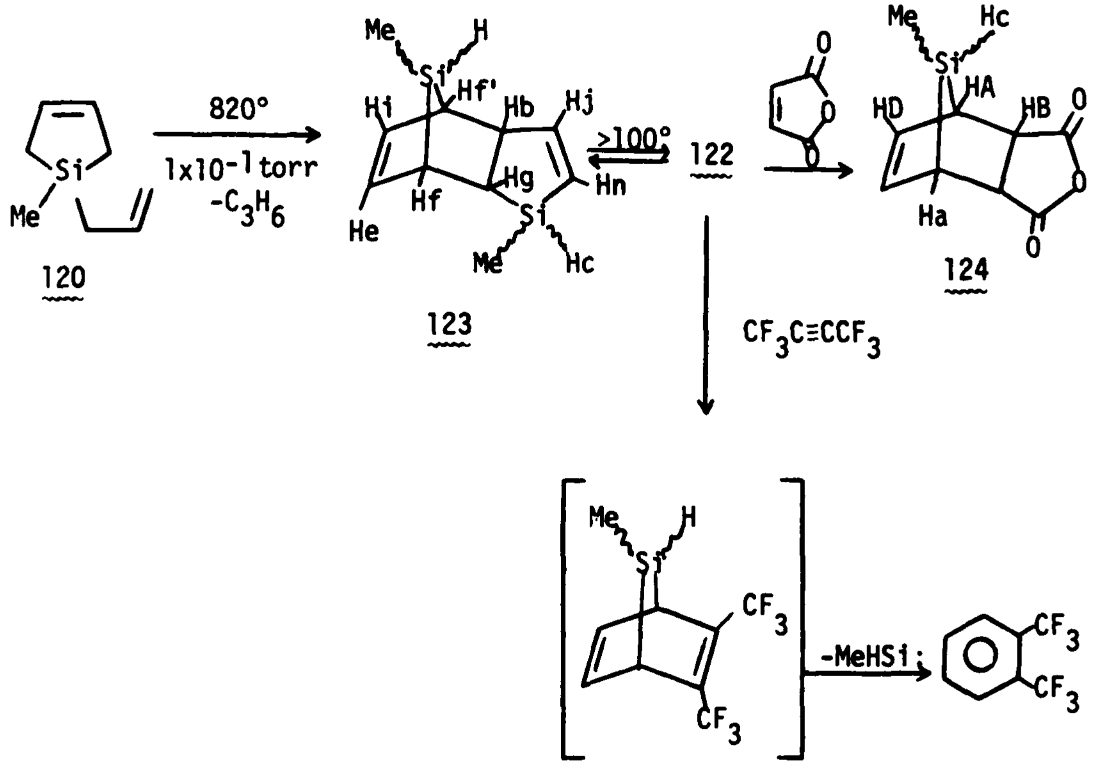
Scheme 14



120 121 122

Synthesis of the preposed precursor of 122, 4-allyl-4-methyl-4-silacyclopentene, 120, was accomplished by the coupling of 4-chloro-4-methyl-4-silacyclopentene with allylmagnesium bromide in 72% isolated yield. Vacuum-flow pyrolysis of 120 afforded a 71% yield of a light yellow oil (b.p. 42-44°C at 0.1 torr) whose high resolution mass spectrum (m/e 192.0784, calc'd for $C_{10}H_{16}Si_2$ 192.0791) was in accord with that expected of a dimer of 122. However, analysis of the oil by GCMS revealed two fractions with essentially identical mass spectra: m/e (% rel. int.) 192 (27, M^+), 177 (29, p-Me), 164 (24, P-C_2H_4), 147 (72, silaindane-H), 145 (100, silaindene-H), 121 (45, m/e 147-C_2H_2), 119 (17, m/e 145-C_2H_2), 105 (39), 92 (72), 95 (46), 93 (43), 69 (45), 55 (56), 53 (56). The two fractions were assumed to be the *endo*- and *exo*-adducts. The ^{1}H-NMR spectrum of the oil was entirely consistent with that of Diels-Alder dimer 123 existing as the inevitable mixture of isomers varying in stereochemistry at the two silicon atoms.

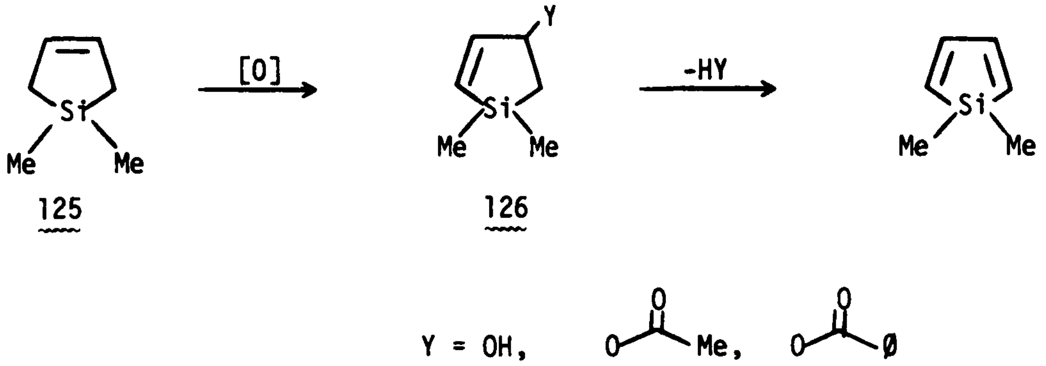
Heating of dimer 123 at 150°C (evacuated, sealed tube; no solvent) with the reactive dieneophiles maleic anhydride, TCNE, or dimethyl acetylenedicarboxylate, inevitably produced a violent explosion. Pyrolysis of 123 through a quartz tube packed with quartz chips heated at 400°C, and immediate trapping at -196°C in a trap containing TCNE revealed no evidence of trapping of 123 upon warming to room temperature. Evidence that these explosions were indeed the result of cracking of 123 and exothermic Diels-Alder reactions was obtained from a sealed-tube reaction of 123 and perfluoro-2-butyne. When 123 (0.2 g) and excess perfluoro-2-butyne were heated at 135°C for 13 hours, the only identifiable product was *o*-bis(trifluoromethyl)benzene. It is reasonable to assume that this arises from cracking of 123 to two molecules of 122, Diels-Alder addition of the acetylene, and extrusion of methylsilylene. Conclusive evidence came from heating a dilute toluene solution of 123 and maleic anhydride (sealed tube, degassed, 150°, 4.5 h) which afforded a 96% yield of adduct 124 as a viscous oil even after GLC purification. The mass spectrum [(m/e 194 (M^+, 0.9%), 165 (M-HCO, 43), 122 ($M-C_2O_3$, 75), 121 ($M-HC_2O_3$, 68), 120 ($M-H_2C_2O_3$, 32), 107 (m/e 122-CH_3, 45), 105 (m/e 120-CH_3, 41), 78 ($C_6H_6^+$, 100), 77 ($C_6H_5^+$, 26)], calc'd for $C_9H_{10}SiO_3$ 194.0399, measured m/e 194.0388) fit nicely for the Diels-Alder adduct. The NMR spectrum [δ 0.10 (d, J = 3 Hz, $h\nu$ at either H_c or $H_{c'}$, collapses to brd. s, 3H, SiMe), 2.48 (very broad hump which sharpens with $h\nu$ at H_D, 2H, H_A), 3.46 and 3.54 (two identical d of d with overlapped inner peaks, $h\nu$ at H_A collapses each to a s, $J_{AB} \sim J_{aB}$ = 1.5 Hz, each $\sim$ 0.5 H, H_B and $H_{B'}$), 3.75 (q, J = 3 Hz, Hν at at SiMe collapses to s, 0.5 H, H_C), 4.54 (broad q, J ∿ 3 Hz, hν at SiMe collapses to s, 0.5 H, $H_{C'}$), 6.15 (m, hν at H_A collapses to s, 2H, H_D)] clearly defines 124 as an equal mixture of the two expected isomers with opposite stereochemistry at silicon.



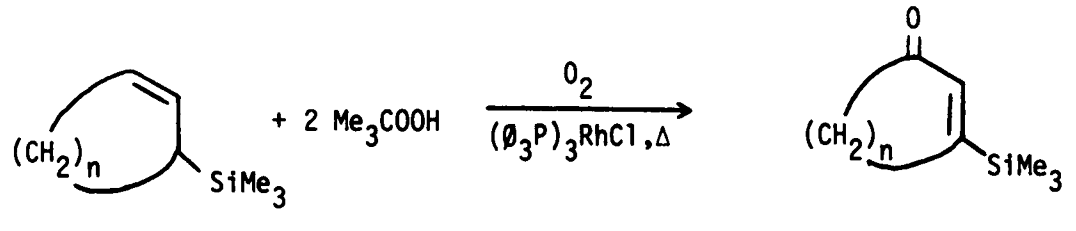
Thus, the thermally initiated retro-Diels-Alder reaction of 123 can provide a convenient, *in situ* source of 1-methylsilole 122.

The facile dimerization of 122 is surprising in light of the relative stabilities of cyclopentadiene and the heterocyclopentadienes, furan, thiophene, pyrrole, and 1,1-dimethylgermole (89). Since 1-methyl-1-silole was never isolated or directly observed, the substitution at silicon was varied in an effort to lower the barrier for dimer to monomer conversion in a hope to directly observe a C-unsubstituted silole. Thus, the synthesis of 1,1-dimethylsilole was undertaken for two reasons; the added steric bulk (methyl vs hydrogen) should hinder dimerization and the symmetry would enable easier identification of adducts.

The approach to the synthesis of 1,1-dimethylsilole revolved around the allylic oxidation of 4,4-dimethyl-4-silacyclopentene 125 to a 3-substituted silacyclopentene 126. Elimination of HY would then afford 1,1-dimethylsilole.

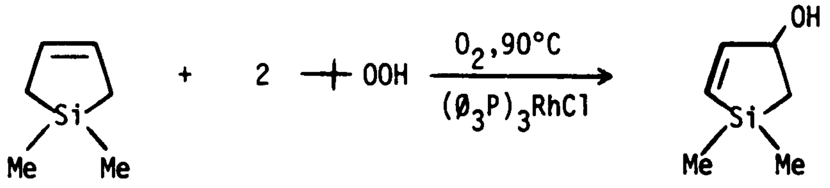


The initial attempt to allylically oxidize 125 was based on a report by Reuter and coworkers (90). They found that cycloalkenyl silanes 127 were oxidized to β-silyl-2-cycloalkenones 128 in good yields by bubbling molecular oxygen through a solution of 127, 2 equivalents of t-butylhydroperoxide and one mole percent of Wilkinson's catalyst.



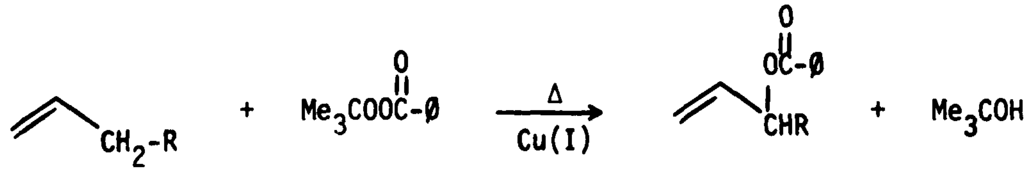
127 n=2-5 128 n=2-5

Attempts to prepare 4,4-dimethyl-4-silacyclopentenone by this method failed. Bubbling a slow stream of oxygen through a heated 1:2 (molar) mixture of 125 and t-butylhydroperoxide in the presence of one mole percent of Wilkinson's catalyst afforded the 4-silacyclopentenol 129 as the only identifiable product. The yield of 129 was low and highly variable; yields of less than one percent were obtained in many runs.



125 129

The low yields obtained in the above method prompted the use of another reagent. In 1959, Kharasch and coworkers (91) reported the oxidation of an allylic methylene via the copper(I) catalyzed decomposition of t-butyl peroxybenzoate.



Heating an equimolar mixture of 125 and t-butyl peroxybenzoate to 90°C in the presence of four mole percent of cuprous bromide initiated an exothermic reaction. After the exothermic reaction had subsided (∿30 minutes), the crude reaction mixture was chromatographed on silica gel (9:1, hexane:ethylacetate) to afford a 60% yield of 5-benzoyloxy-3,3-dimethyl-3-silacyclopentene 130.

Flow pyrolysis (540°, 0.01 torr) of 130 afforded benzoic acid (88%, condensed before the trap) and a yellow liquid which was determined to be 131, the dimer of dimethylsilole: (60% yield based on 130); NMR ($CDCl_3$) (Figure 2): δ (ppm), 0.10 (s, 3H), 0.08 (s, 3H), 0.06 (s, 3H), 0.23 (s, 3H), 1.57 (d of d, 1H, J_{CE} = 2.2 Hz, J_{CB} = 9 Hz), 1.85 (broad d, 1H), 1.99 (broad M, 1H, hν at He collapses 1H to d, J_{DF} = 6 Hz), 3.60 (d of d of d, 1H), 5.74 (d of d, J_{GE} = 2 Hz), 5.80 (overlapped d of d, 1H, J_{AB} = 6 Hz), 6.14 (overlapped d of d, 1H), 6.34 (d of d, 1H, J_{HG} = 10 Hz, J_{HE} = 25 Hz); calc'd for $C_{12}H_{20}Si_2$, 220.11036, measured m/e 220.11030.

When maleic anhydride (in $DCCl_3$) was included in the trap (liquid nitrogen cooled), examination of the resulting solution after pyrolysis

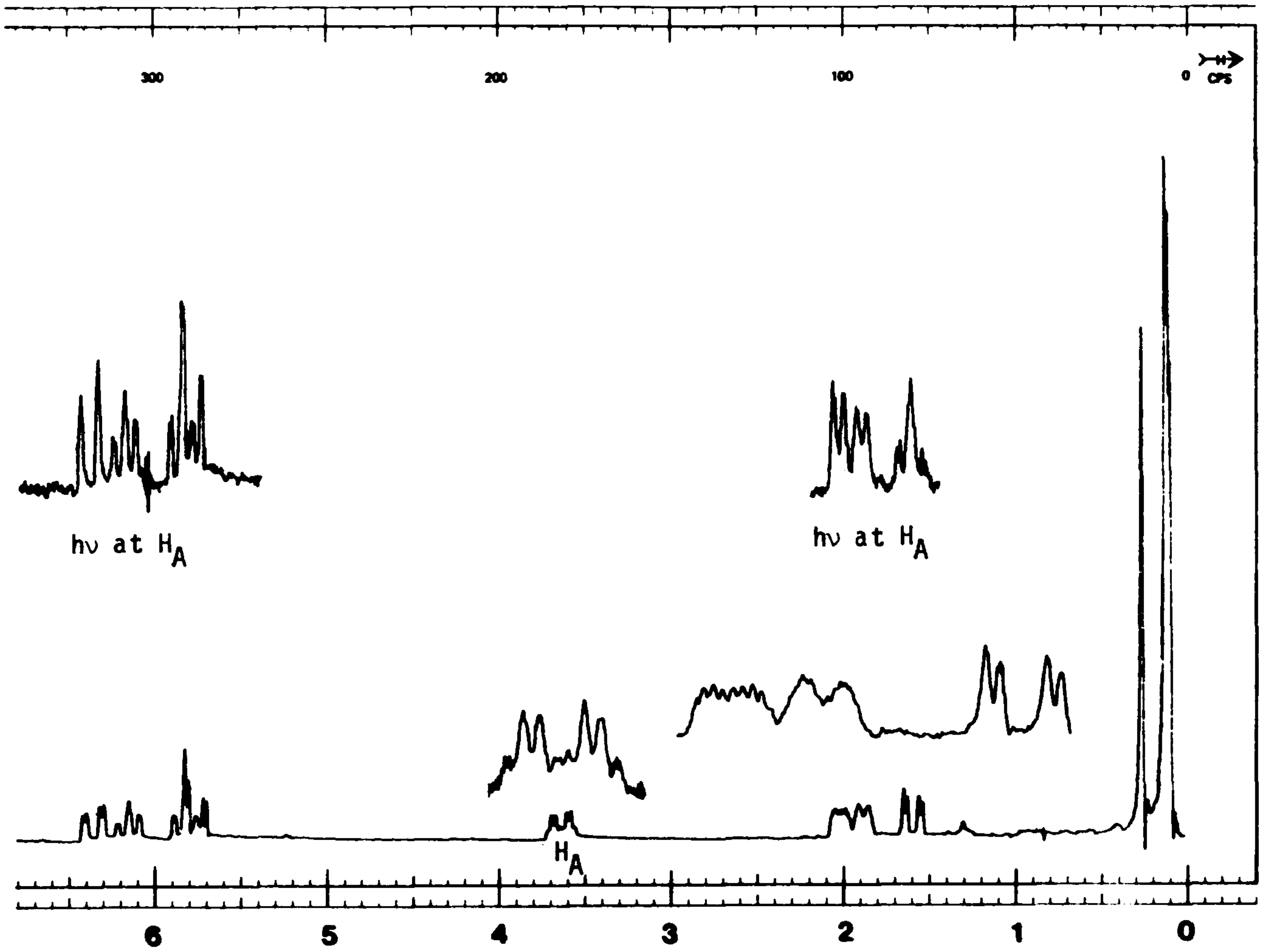


Figure 2. 100 MHz ^{1}H-NMR of dimers of 1,1-dimethylsilole 131

revealed that 1,1-dimethylsilole had been trapped as white, crystalline 132 in 66% yield. This same product (132) could be quantitatively obtained by heating dimer 131 with maleic anhydride at 160° in a sealed tube for 30 hours. [(132): m.p. 89.5 - 90.5°C; NMR ($CDCl_3$) (Figure 3): δ (ppm) 0.22 (s, 3H), 0.28 (s, 3H), 2.55 (m, 2H, $h\nu$ at H_C collapses to broad singlet), 3.32 (overlapped d of d, 2H, $h\nu$ at H_A collapses to s), 6.28 (overlapped d of d, 2H, $h\nu$ at H_A collapses to s); calc'd for $C_9H_9O_3Si$ (p-15) 193.03210, measured m/e 193.03192.]

Thus, it was obvious that dimer 131 was arising from dimerization of 1,1-dimethylsilole in the trap during warming to room temperature. Indeed, direct observation of monomeric 133 was possible by condensing the pyrolysate from 130 directly into an NMR tube containing $DCCl_3$, and cooled to -196°. PMR spectra recorded at -70° showed only a singlet at δ0.72 (6H, $SiMe_2$) and an AB quartet centered at δ6.40 (4H, vinyl, $J = 14$ Hz, $\nu_A = 6.78$, $\nu_B = 6.02$). The ^{13}C NMR spectrum at -70° further confirmed the structure of 133 as only the expected two vinyl absorptions (δ131.3 and 145.6) and a single Si-Me peak (δ-5.52) were observed. On warming the NMR sample in 10° increments to 10°C, the spectrum of dimer 131 slowly appeared. At 37°, dimerization was complete in 15 minutes.

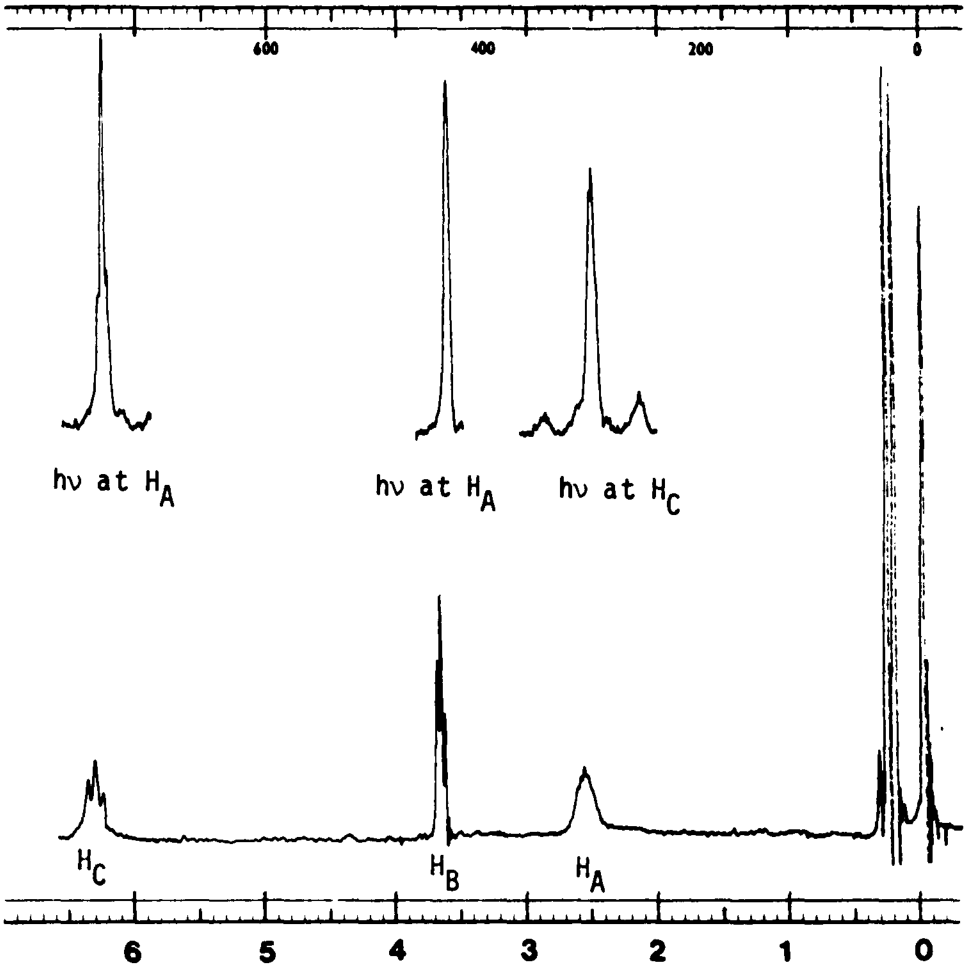
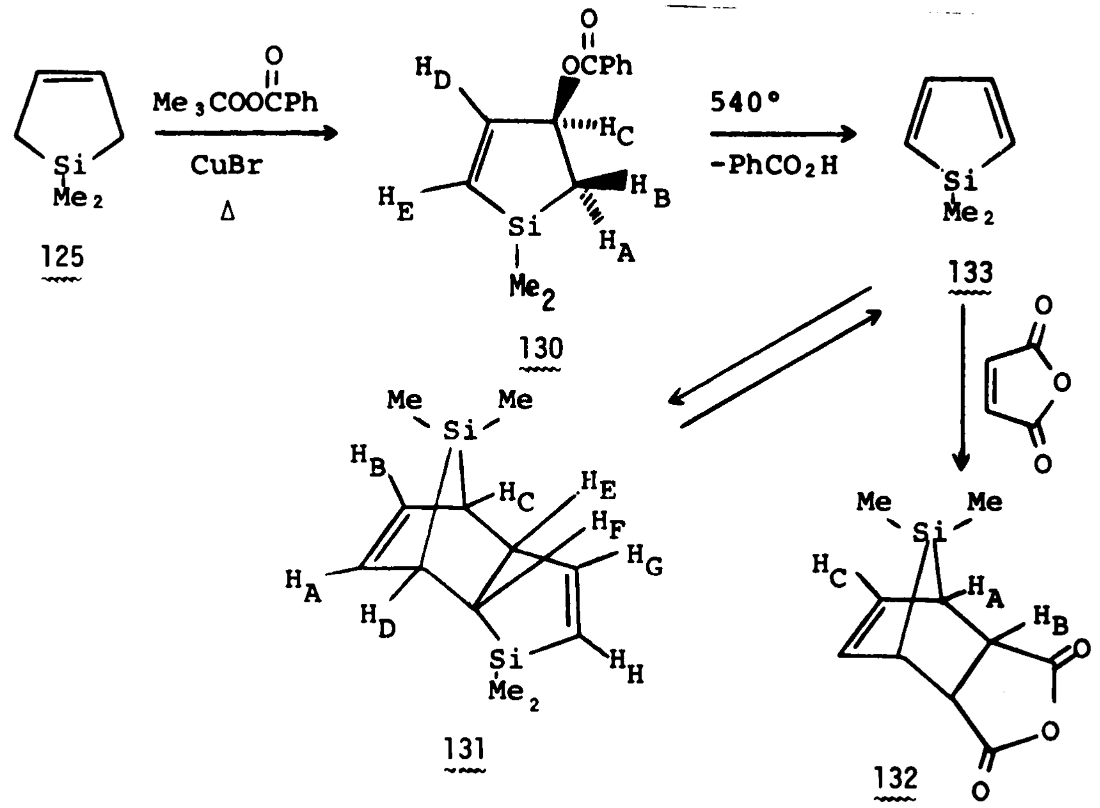
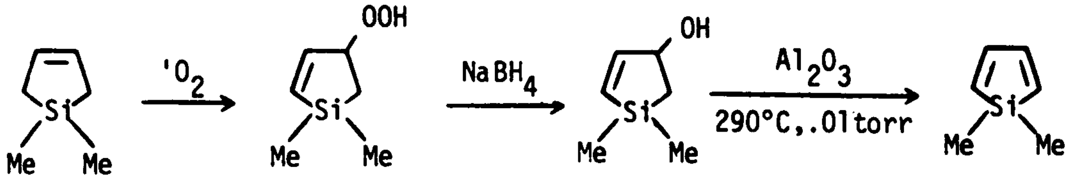


Figure 3. 60 MHz ^1H-NMR of the maleic anhydride 1,1-dimethylsilole adduct 132

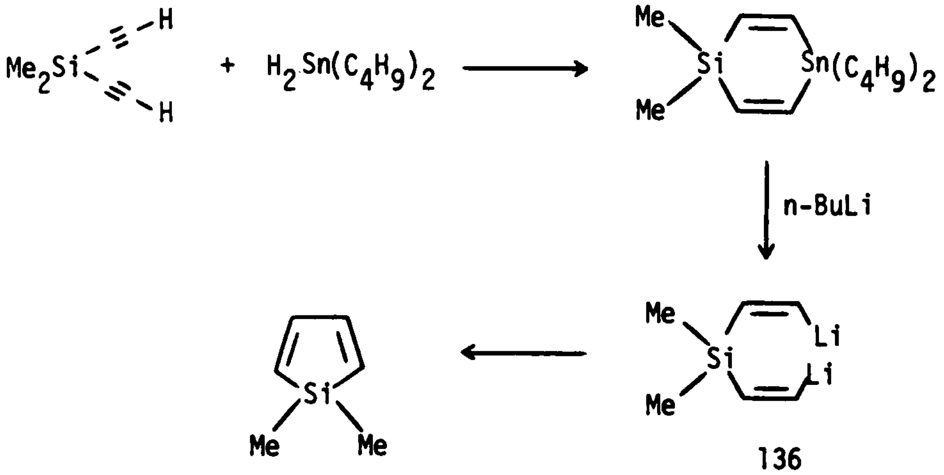


Thus, the generation and direct observation of 1,1-dimethylsilole was accomplished *via* the pyrolysis of 130. At the same time of this report (92), A. Laporterie and coworkers published an independent synthesis of 1,1-dimethylsilole based on a similar synthetic strategy (93); allylic oxidation of 125 followed by dehydration to 133. They were able to effect allylic oxidation of 125 with singlet oxygen to give the hydroperoxide 134 (94). Reduction of 134 with sodium borohydride afforded the silacyclopentenol 135 which could be dehydrated over an aluminum oxide catalyst at 290°C to give 1,1-dimethylsilole. They observed the identical reactions, including isolation and trapping, of 133 as reported in this dissertation.



134 135 133

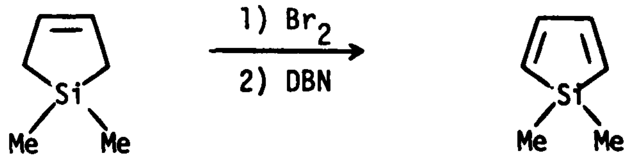
A recent private communication from H. Sakurai (95a) indicates that 1,1-dimethylsilole is also available from the intramolecular coupling of the dilithio species 136. The dilithio species 136 was prepared by hydrostannation of diethynyldimethylsilane followed by cleavage of the carbon-tin bond with n-butyllithium. Although Sakurai claims that 133 is a "stable" species, insufficient data were given to correlate it with the results obtained in this dissertation and those of Mazerolles and coworkers.



136

133

Phil Magnus has also recently communicated (95b) the synthesis of 1,1-dimethylsilole. His synthesis involves the bromination of 4,4-dimethyl-4-silacyclopentene followed by the elimination of two equivalents of HBr upon treatment with DBN to afford 133. Magnus claims 133 is a stable, isolable compound which reacts at room temperature with a variety of dienophiles. If Magnus' claim is correct, it would indicate that the dimerization observed from the pyrolysis of the benzoate 130 could be acid catalyzed. In order to check this possibility, a vertical vacuum pyrolysis was conducted with approximately 1 cm of basic alumina positioned between the hot zone and a trap containing $CDCl_3$ such that the gaseous pyrolysate would have to pass through the basic alumina. An NMR of the pyrolysate taken immediately upon warming of the trap to room temperature revealed only the monomeric silole 133. However, within 2.5 hrs at room temperature, the monomer had completely dimerized. As of yet, the dichotomy between the two results cannot be explained.

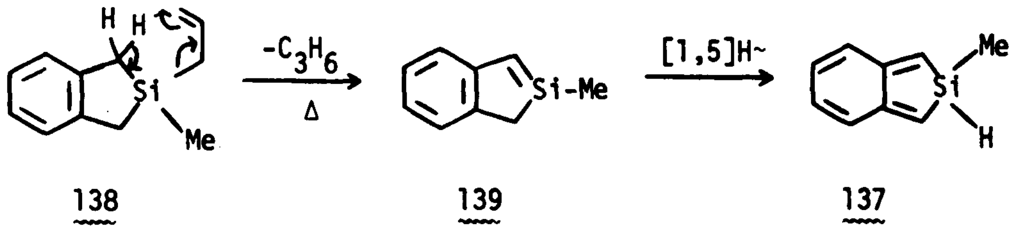


133

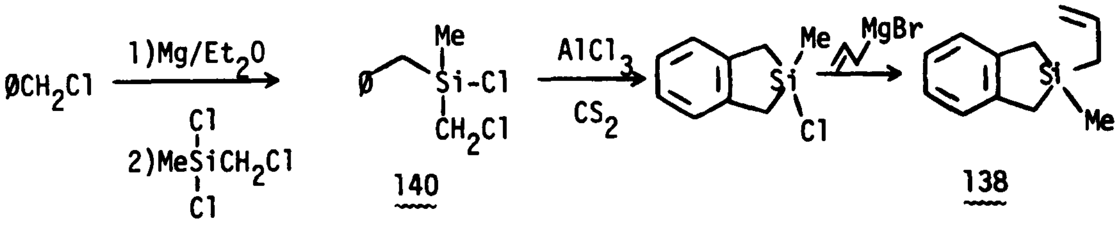
The success in the synthesis of a C-unsaturated silole *via* a sequential retro-ene elimination of propene followed by a 1,5 hydrogen shift prompted an investigation into the chemistry of isobenzosilole 137 based on this method. It was anticipated that the pyrolysis of

2-allyl-2-methyl-2-silaindane 138 would afford 137 via an intermediate 2-methyl-2-silaindene 139 (Scheme 15).

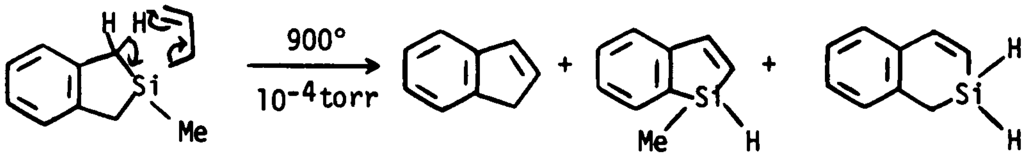
Scheme 15



The synthesis of 138 was achieved in three steps in an overall yield of 28%. Coupling of benzylmagnesium chloride with dichlorochloromethylmethylsilane afforded a 70% isolated yield of the chlorosilane 140. An intramolecular Friedel-Crafts alkylation gave 2-chloro-2-methyl-2-silaindane which was coupled with allylmagnesium bromide to give the desired 2-allyl-2-methyl-2-silaindane 138.



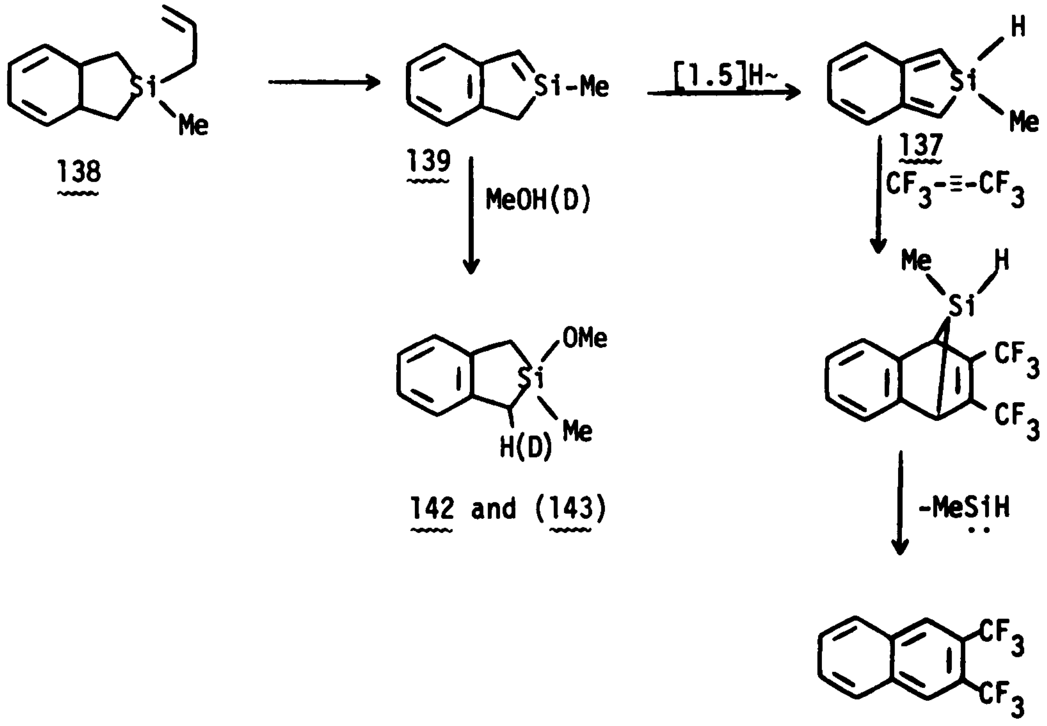
Distillation (25°, 1×10^{-4} torr) of 138 through a quartz tube packed with quartz chips and heated to 900°C afforded a light yellow oil in a 40% mass recovery. Analysis of the pyrolysate by gas chromatography on a 9' 3-% SE-30 column showed three major volatile products in addition to unreacted 138. The three products were isolated by preparative gas chromatography and assigned the structures of indene, 3-methyl-3-silaindene 140, and 141 based on their ^{1}H-NMR, high resolution mass spectrum, and IR. Although the yields 11%, 9% and 16%, respectively, were low, analysis of the crude pyrolysate by ^{1}H-NMR showed that these three products plus starting material comprised 79% of it.



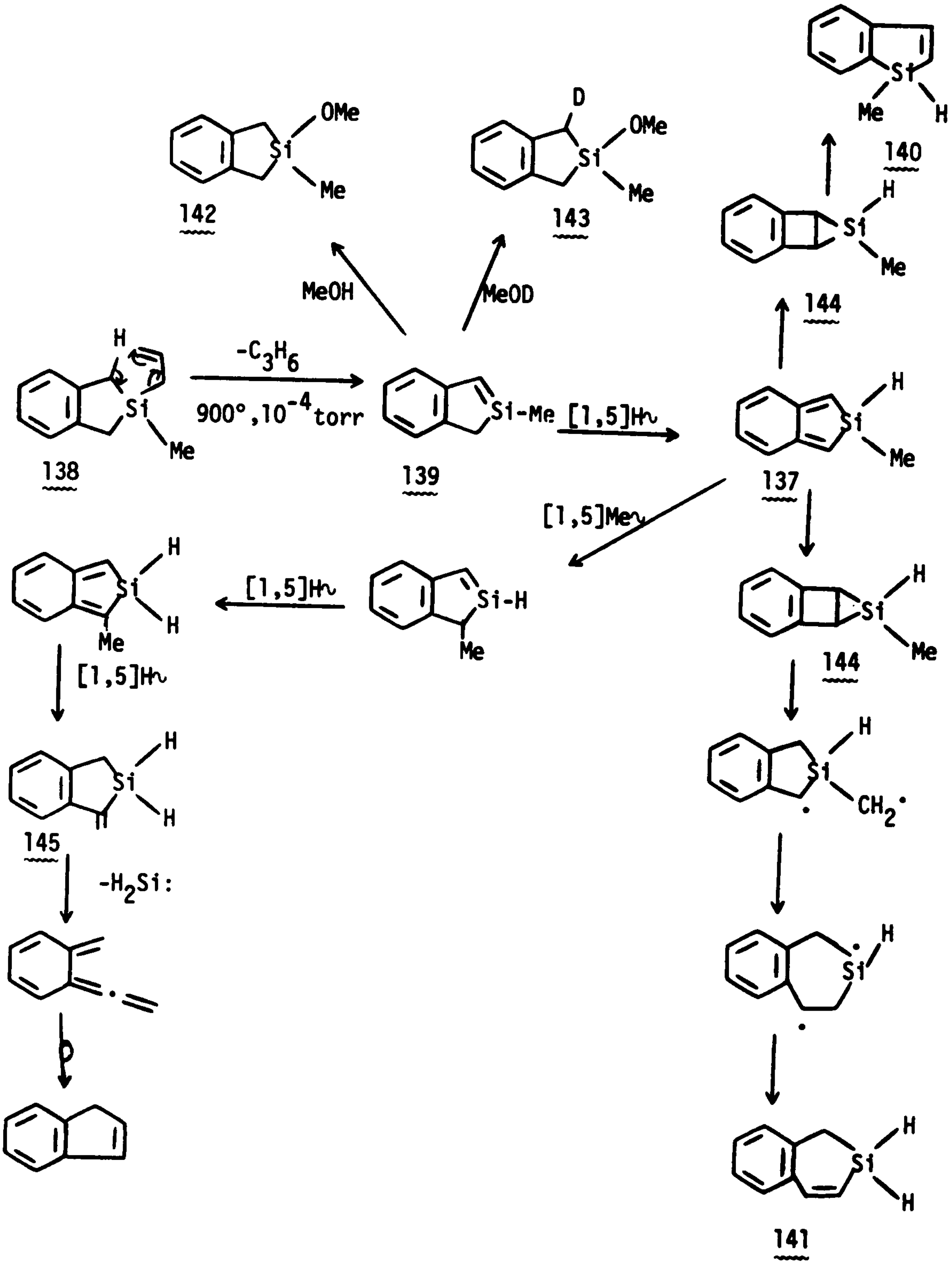
138 140 141

The formation of the two silicon containing products 140 and 141 was intriguing since both are isomeric with isobenzosilole 137 and presumably arise from it via an intramolecular rearrangement. A possible mechanism for the formation of the three products is shown in Scheme 16. The initial step, the retro-ene elimination of propene to give the 2-silaindene 139, was confirmed by methanol trapping experiments. Copyrolysis of 138 and methanol at 640° in a vertical nitrogen flow (5 ml/7 sec) system afforded 2-methyl-2-methoxy-2-silaindane 142 in 36% (based on reacted 138) as the sole volatile product. In order to insure that 142 arose from trapping of the 2-silaindene and not methanolysis of the allyl-silicon bond, a copyrolysis of 138 and MeOD was conducted. Analysis of the pyrolysate by gas chromatography revealed one major product which was isolated by preparative GC and identified as the monodeuteromethoxysilaindane 143 on the basis of its ^{1}H-NMR and low resolution mass spectrum. The absence of 140, 141, and indene in conjunction with the methanol trapping experiments clearly implicates 2-silaindene 139 as the initially formed intermediate.

In order to ascertain whether the isobenzosilole 137 is an intermediate in the formation of 140, 141, and indene, a copyrolysis of 138 and perfluoro-2-butyne was conducted at 640° in a vertical flow system. Careful analysis of the pyrolysate by GCMS revealed the formation of 2,3-(bis)trifluoromethylnaphthalene, the expected product from trapping of 137 followed by loss of methylsilylene. The formation of 140, 141 and indene was completely inhibited, implying the prior intermediacy of 137 for their formation.



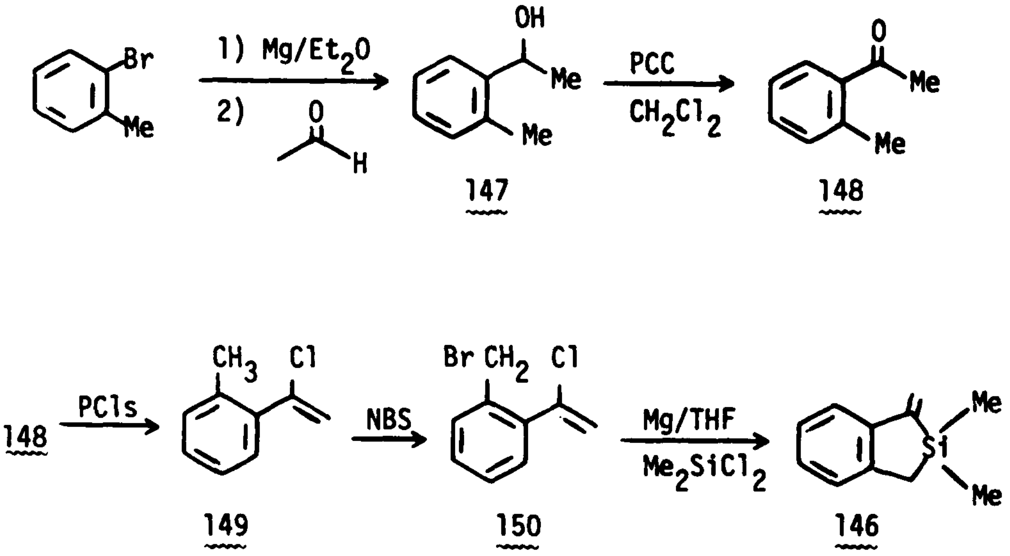
Scheme 16



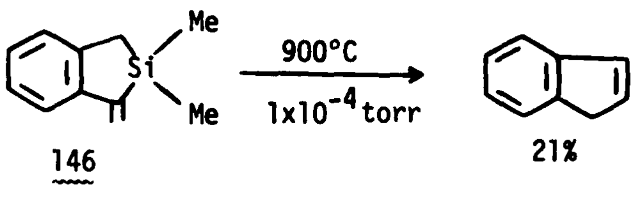
OMe
Me
142
D
OMe
Me
143
Me
H
140
H
Si
Me
144
MeOH
MeOD
H
Si
Me
138
$-C_3H_6$
900°,10^{-4}torr
Si-Me
139
[1,5]H~
H
Si
Me
137
[1,5]Me~
H
H
Me
[1,5]H~
Si-H
Me
H
Si
Me
144
[1,5]H~
H
H
145
$-H_2Si:$
H
$CH_2^{\bullet}$
H
Si
H
H
141

The formation of the products, except for the benzosilole 140, is not straightforward from 137 and requires more postulation than substantiation. The formation of 140 from isobenzosilole 137 can be explained by closure to the benzosilahausane 144. Cleavage of a silicon-carbon bond of the silacyclopropane ring followed by a 1,2-aryl shift gives the benzosilole 140. The formation of 141 can also be explained from the benzosilahausane 144 *via* cleavage of a carbon-carbon bond of the silacyclopropane followed by hydrogen abstractions and a 1,2 alkyl shift. However, this explanation requires the breaking of a carbon-carbon bond over a silicon-carbon bond in the silacyclopropane ring of the benzosilahausane, an occurrence which has not been substantiated experimentally.

If the formation of indene from 137 proceeds *via* 145, then an independent synthesis and thermolysis of 145 would also yield indene. For synthetic reasons, the dimethyl derivative 146 was chosen. The synthesis of 147 was accomplished in five steps from *o*-bromotoluene. Quenching of the Grignard reagent of *o*-bromotoluene with acetaldehyde afforded the benzyl alcohol 147 (64% isolated yield). Oxidation of 147 to the ketone 148 with pyridinium chlorochromate followed by treatment with PCl_5 gave the vinylchloride 149. Benzylic bromination with NBS gave benzyl halide 150 in an overall yield of 28% from *o*-bromotoluene. Ring closure of 150 to 146 was achieved by adding 150 to a stirring suspension of magnesium in a THF solution containing one equivalent of dimethyldichlorosilane. The yield for the ring closure was 17%.



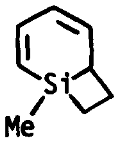
Vacuum pyrolysis of 146 at 900°C and 1×10^{-4} torr afforded a 21% yield of indene (based on unrecovered 146) as the sole volatile product. Thus, the formation of indene could come from an intermediate such as 146. However, whether indene arises from a concerted extrusion of silylene or a radical process is not known. It is also conceivable that indene, or for that matter 141, arises via a totally different pathway than the one shown in Scheme 16. The inability to further trap possible intermediates precludes knowing the exact mechanism(s).



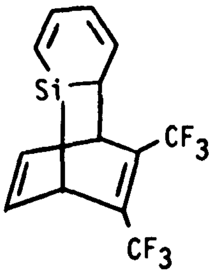
In summary, a sequential retro-ene reaction followed by a 1,4-hydrogen migration was utilized in the synthesis of the first C-unsubstituted silole (96) and in the synthesis of the highly reactive isobenzosilole 137. Furthermore, the isolation of a C-unsubstituted silole, 1,1-dimethylsilole, was accomplished (92).

C. Synthesis of 1-Methyl-1-Silabenzene

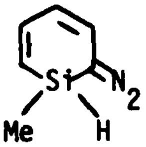
Although silatoluene 40 had been previously postulated by Barton and Banasiak (36) as an intermediate in the base induced elimination of HCl from 36, the reaction conditions precluded unambiguous identification. Thus, an alternative method of generation was sought; hopefully in a manner applicable to its isolation and trapping. Examination of the most common thermal silene generators, silacyclobutanes, 7-silabicyclo-[2.2.2]octa-2,5-dienes and α-diazosilanes revealed possible difficulties in their preceived adaptation towards a silabenzene. Thus, systems such as 151, 152, and 153, although potential precursors to a silabenzene, pose challenging synthetic problems and were deemed inappropriate.



151



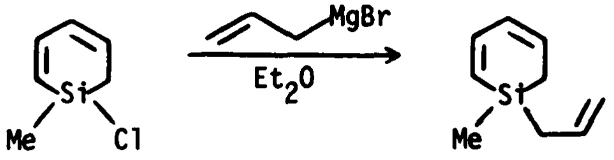
152



153

Application of Block and Revelle's (9) method of silene generation to the synthesis of a silabenzene prompted the investigation into the thermolysis of 1-allyl-1-methyl-1-silacyclohexa-2,4-diene **154**. Examination of **154** shows that it is basically a diallylsilane in which one of the allyl moieties has been incorporated into the ring system. Thermolytic behavior similar to other diallylsilanes would then yield a silabenzene under conditions conducive to trapping and isolation experiments.

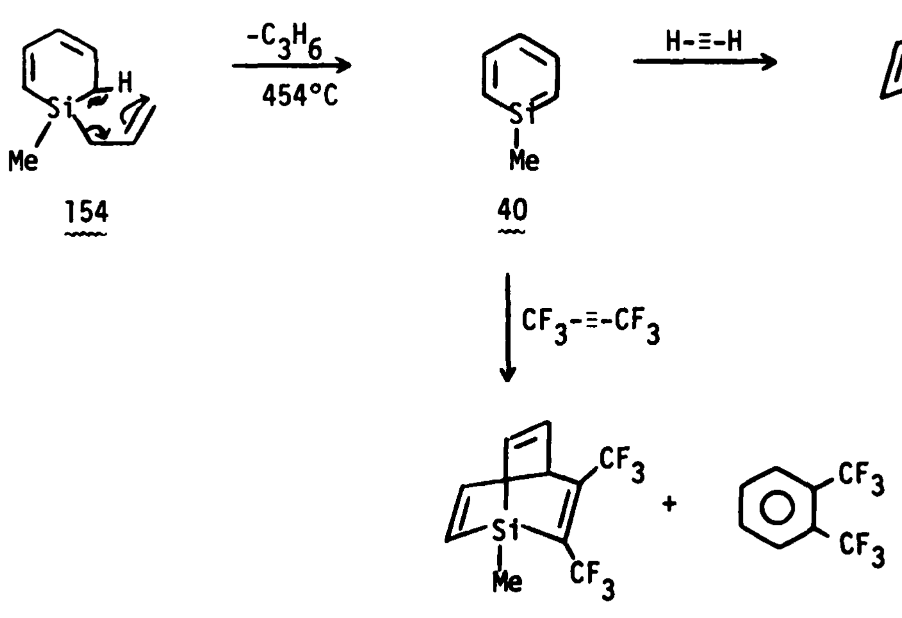
The synthesis of **154** was accomplished by the quenching of allylmagnesium bromide with the readily available methylchlorosilacyclohexadiene **36** (97,98) in 50-60% isolated yields.



36 **154**

Pyrolysis of **154** in a vertical nitrogen-flow system at 454°C yielded a light yellow oil which strongly effervesced upon warming to room temperature. Analysis of the pyrolysate by GCMS identified the gas as propene. The presence of propene in copious quantities in the pyrolysis of **154** suggested that the initial retro-ene elimination of propene was indeed occurring. However, GCMS analysis of the remainder of the pyrolysate failed to provide any evidence for the intermediacy of silabenzene **40**. The failure to observe identifiable products from silatoluene in the absence of traps in a nitrogen flow system was attributed to polymerization.

Examination of Barton and Banasiak's earlier results with silabenzene 40 (36) and Ashe and Gordon's results with bismabenzene (99) suggested the use of an acetylene as a trap. Pyrolysis of 154 in a vertical flow system at 454°C utilizing acetylene as both the carrier gas and the trap afforded a 33.6% yield (based on reacted 154) of 1-methyl-1-silacyclo[2.2.2]octatriene 155. The corresponding silabarralene 156 was obtained in $\sim$20% yield along with 1,2-bis(trifluoromethyl)benzene when perfluoro-2-butyne was used as the carrier gas (see Figures 4 and 5 for the NMR spectra of 155 and 156, respectively. These products, 155 and 156, are best explained by the trapping of 1-methyl-1-silabenzene in a [4+2] Diels-Alder reaction by the acetylene (100).



154

40

155

156

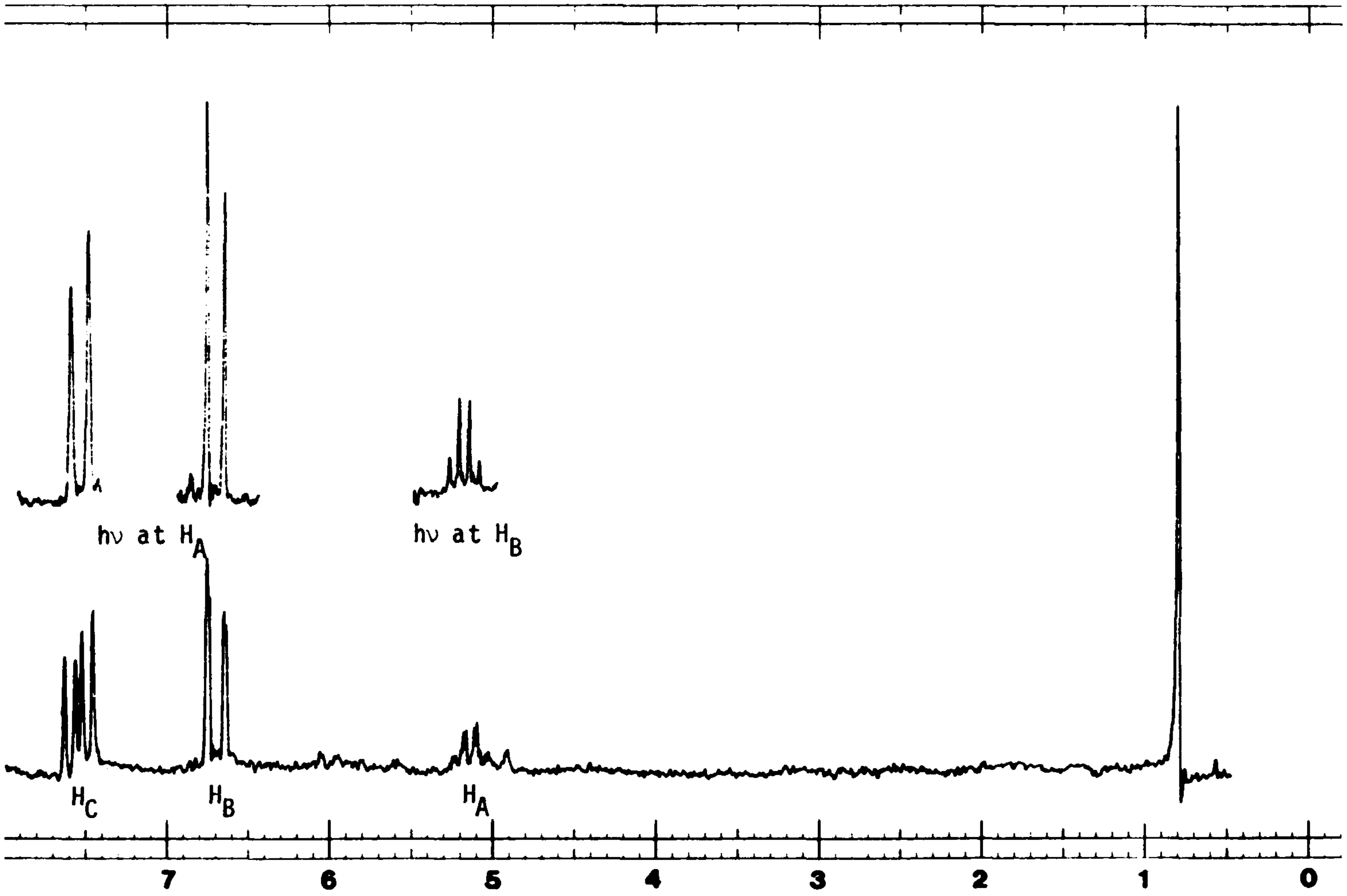


Figure 4. 100 MHz ^{1}H-NMR spectrum of 1-methyl-1-silabicyclo[2.2.2]octa-2,5,7-triene **155**

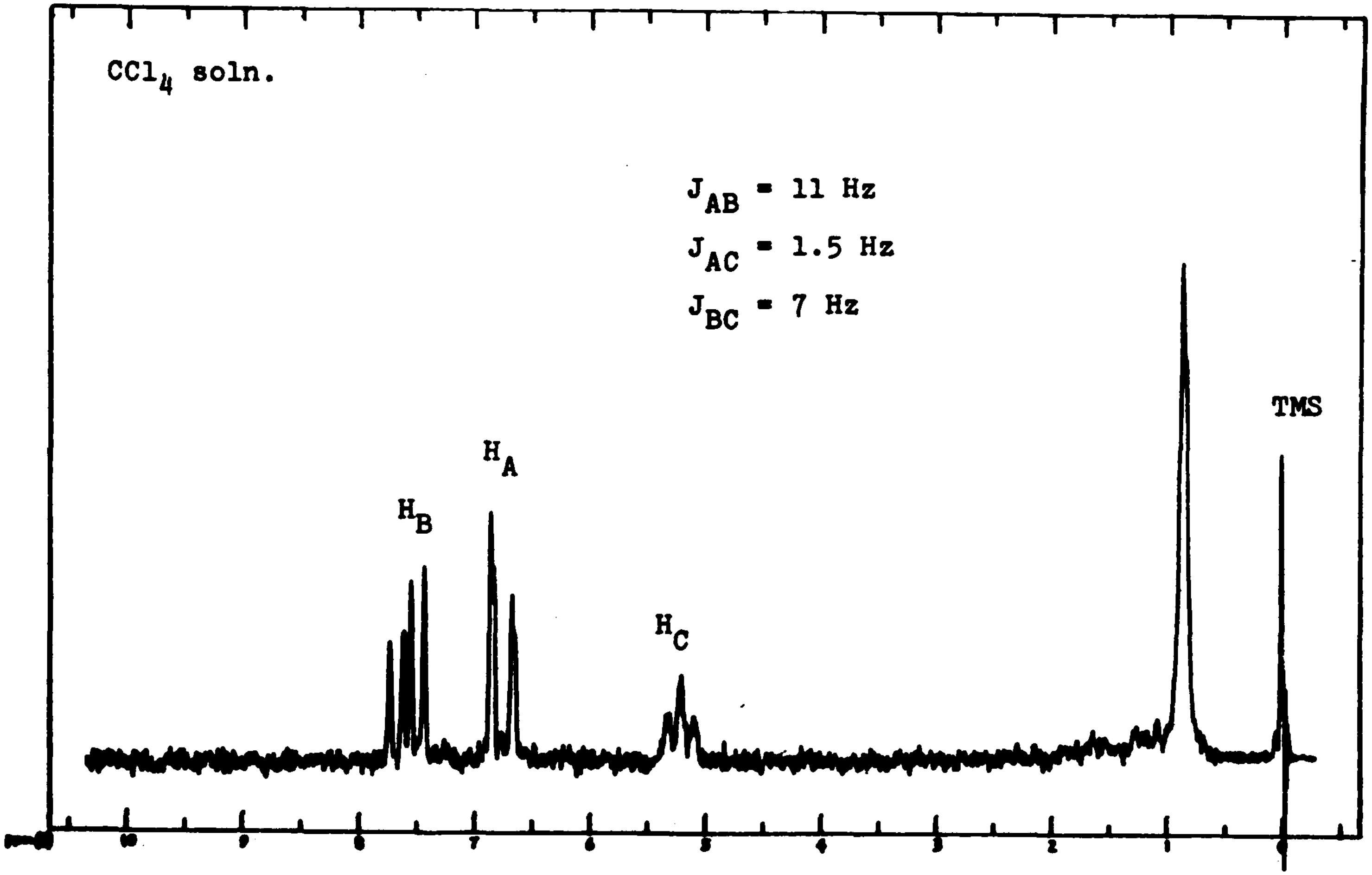


Figure 5. 60 MHz ^{1}H-NMR of 2,3-bis(trifluoromethyl)-1-methyl-1-silabicyclo[2.2.2]octa-2,5,7-triene 156

The yield of 155 appeared to decrease at higher temperatures (500° or higher). In part, this decrease in the yield of 155 can be attributed to the polymerization of acetylene, hence a decrease in trap concentration, as evidenced by the formation of of a brown oil at higher pyrolysis temperatures. However, another explanation lies in the gas phase electron diffraction study on the product, 1-methyl-1-silabicyclo-[2.2.2]octa-2,5,7-triene by Shen and coworkers (101) which indicates a rather significant amount of angular distortion about the silicon bridgehead. The observed $\angle$SiC=C valence angle of 109.9(±0.5)° and $\angle C_2SiC_6$ valence angle of 98.8(±0.3)° deviate substantially from the normal values of 120° and 109.5°, respectively (see Table 3 and Figure 6). Thus, the lower yields of 155 at higher temperatures might also be due to its thermal lability.

The origin of 1,2-bis(trifluoromethyl)benzene when perfluoro-2-butyne was used as the carrier gas and trap could be explained by an initial Diels-Alder reaction between perfluoro-2-butyne and 154 to give the bicyclo[2.2.2]octadiene 157. These types of systems have been shown by Barton and Kline (102) to extrude the bridge to afford a silene and 1,2-bis(trifluoromethyl)benzene. The synthesis of 157 was accomplished by sealing a neat solution of 154 and perfluoro-2-butyne in a thick-walled tube at room temperature for a day. Thermolysis of 157 at 500°C and 1×10^{-4} torr afforded 1,2-bis(trifluoromethyl)benzene in 90% yield (103). The only other observed products were 4-methyl-4-silacyclopentene and the silene dimer 158.

Table 3. Electron diffraction data for 1-methyl-1-silabicyclo[2.2.2]-octa-2,5,7-triene[a]

Independent Parameter	Value	Amplitude Parameter	Value
C-H_{avg}	1.091(7)Å	Si-C_{ave}	0.053(6)Å
C=C	1.348(3)	Si.C_3	0.066(6)
C-C	1.547(5)	C=C	0.046(3)
Si-C_{avg}[b]	1.865(10)	C_2.C_8	0.093(17)
ΔSi-C[c]	0.021(18)	C_2.C_9	0.125(46)
$\angle C_9SiC_2$	118.7(0.2)°	C_3.C_9	0.114(34)
$\angle SiC_2{=}C_3$	109.9(0.5)°	C-H	0.060(6)
$\angle HC_2Si$	119.6(6.5)°	---	---
$\angle HC_3C_2$	120.0	---	---
$\angle HC_9Si$	109.5	---	---

Dependent Parameter	Value
Si-C_9	1.844(30)Å
Si-C_2	1.885(8)
$\angle C_2SiC_6$	98.8(0.3)°
$\angle C_2C_3C_4$	119.4(0.7)°
$\angle C_3C_4C_5$	108.3(0.6)°

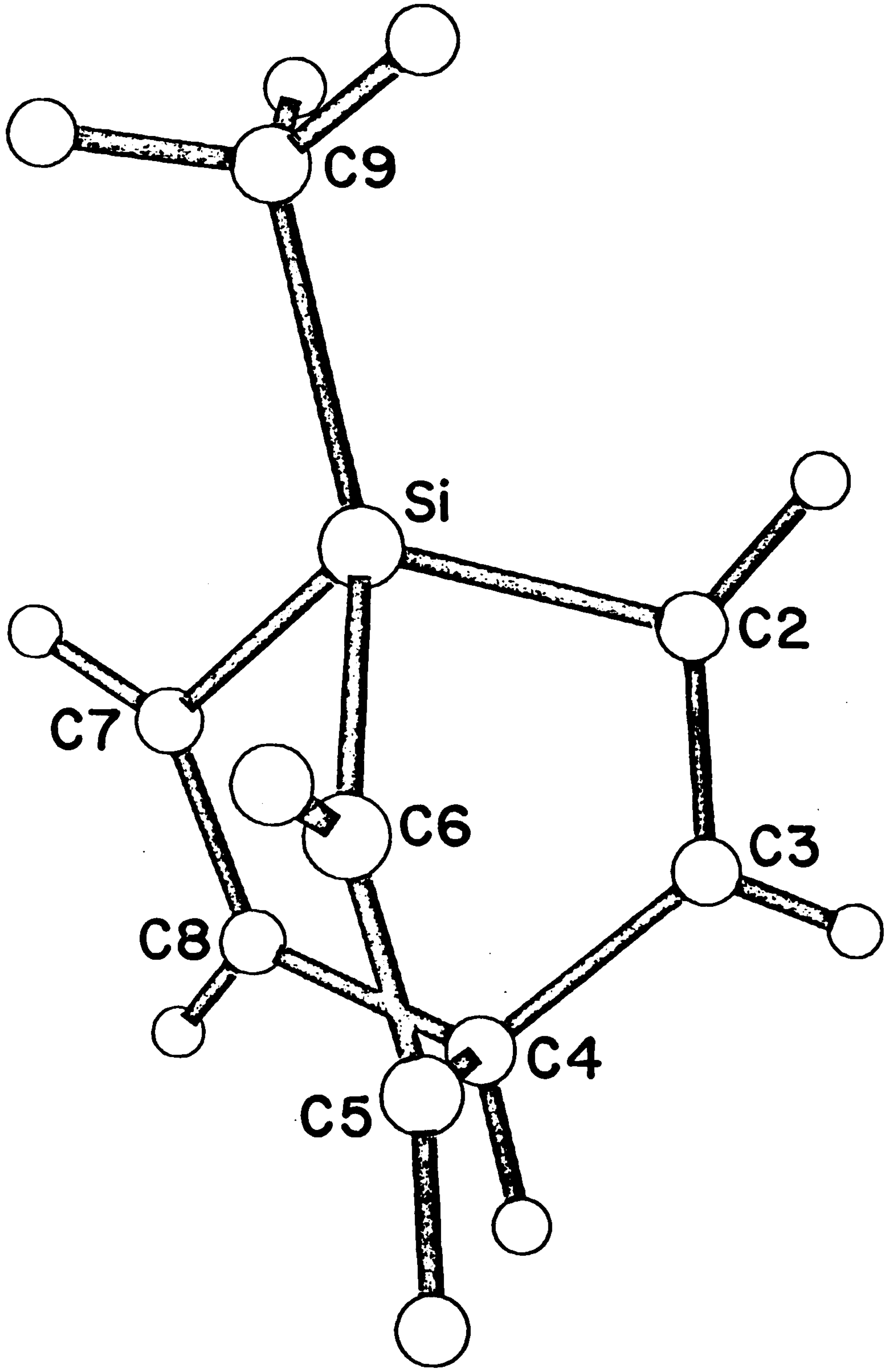
---

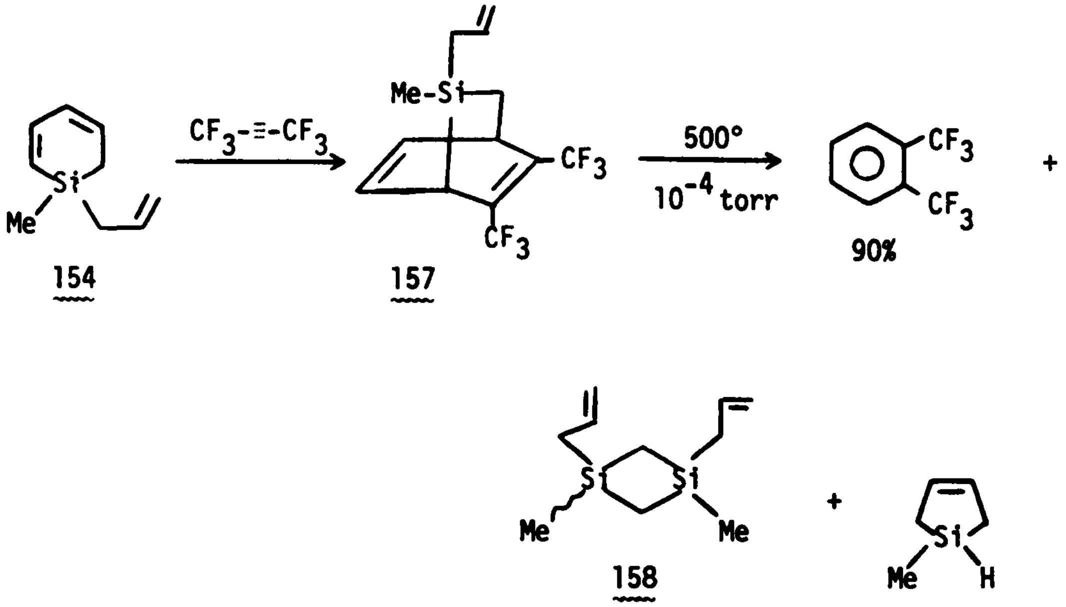
[a] Distances are reported as r_g values and angles are reported as r_α parameters. Reported errors are 3 values obtained from least squares analysis.

[b] Si-C_{avg} is the average value of Si-C_2 and Si-C_9.

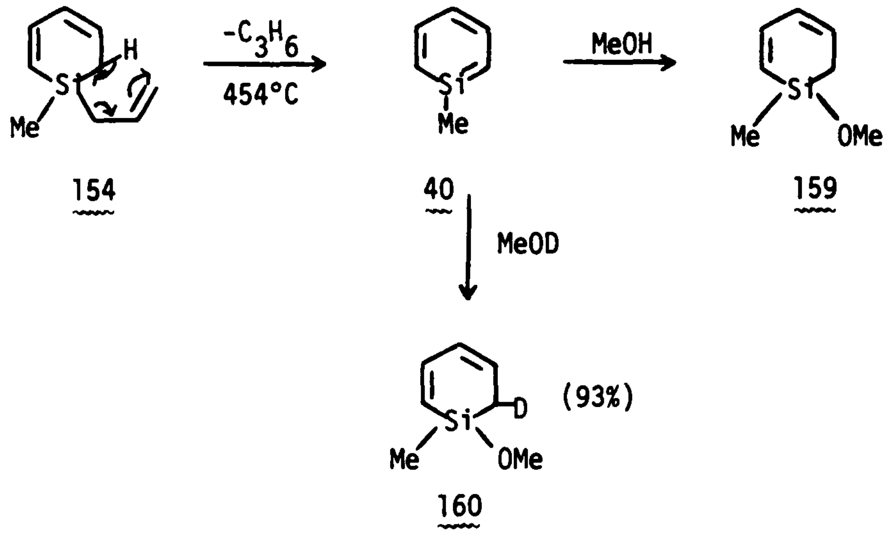
[c] Si-C is defined such that Si-C_2=Si-C_{avg} + ΔSi-C, and Si-C_9=Si-C_{avg}-ΔSi-C.

Figure 6. Electron diffraction picture for 1-methyl-1-silabicyclo-[2.2.2]octa-2,5,7-triene

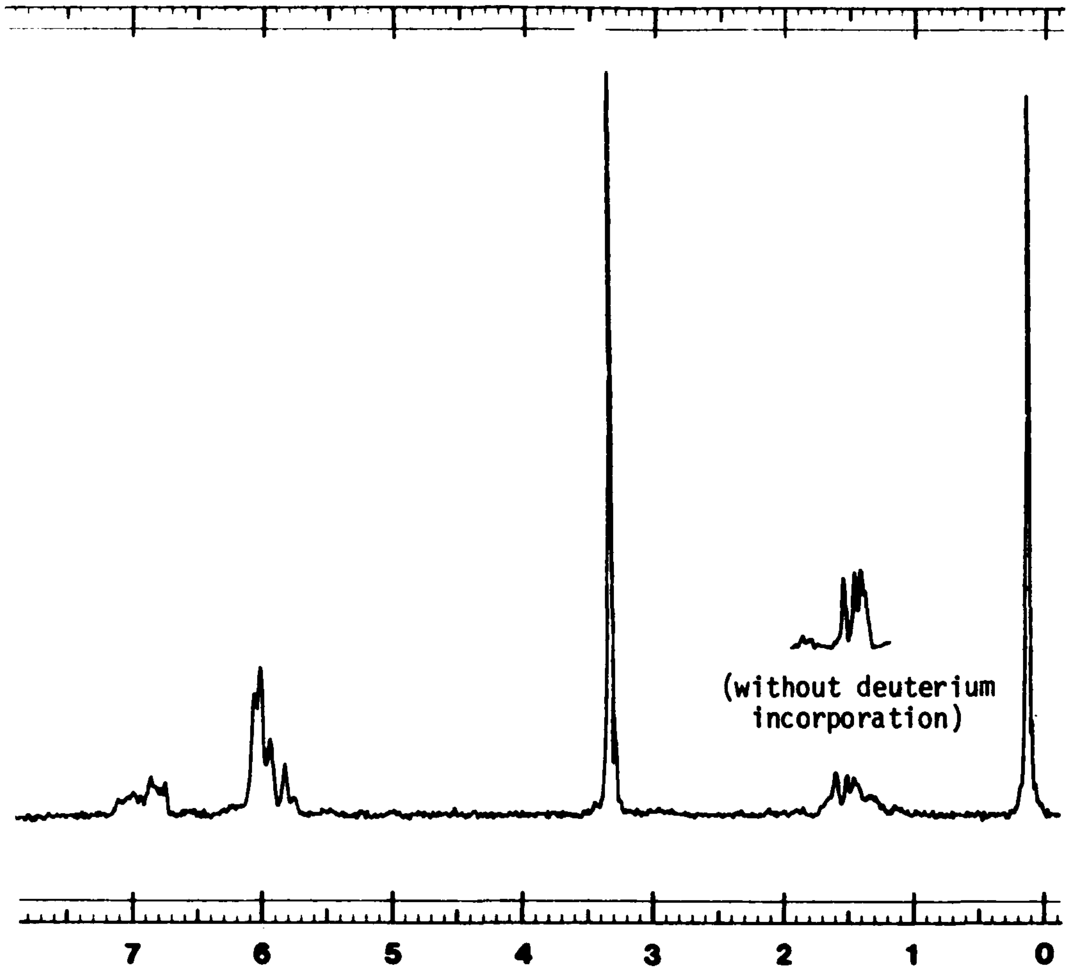

C9
Si
C2
C7
C6
C3
C8
C4
C5



Exclusive trapping of the silicon-carbon double bond in 1-methyl-1-silabenzene was accomplished using methanol as the trap (104,105). Co-pyrolysis of a mixture of 154 and a nine-fold excess of methanol in a nitrogen flow system at 454° afforded in 45% yield (based on reacted 154) the silabenzene:methanol adduct 159. To show that 159 arose from silene trapping and not methanolysis of an allyl-silicon bond, two experiments were performed. First, a copyrolysis of methanol and diallyldimethylsilane was conducted. If methanolysis was occurring in 154, then other allylsilanes would be expected to display similar behavior. However, no methanolysis products were observed in this thermolysis. Secondly, methanol-d_1 was used in place of methanol as the silene trap. If silabenzene 40 was being trapped, deuterium would be incorporated alpha to the silicon, whereas no deuterium incorporation would be expected for methanolysis. Copyrolysis of 154 with excess methanol-d_1 in a vertical nitrogen flow system at 454° yielded 160 (see Figure 7 for NMR of 160) in a 39% yield. The deuterium incorporation in 160 was determined to be 93% based on the relative intensities of the m/e 141/142 and 126/127 (loss of methyl) ions in its low and high resolution mass spectrum. Thus, the methanol copyrolysis experiments correspond to trapping of the silene and not methanolysis of a silicon-allyl bond.



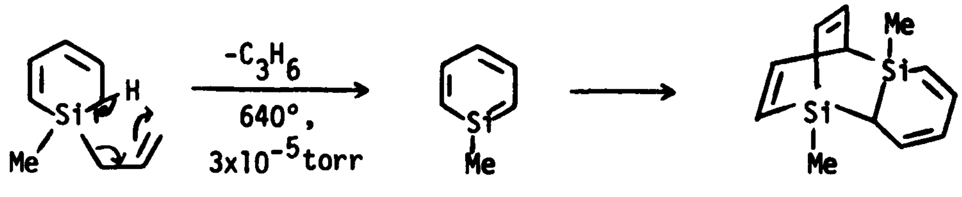
It is interesting to note that 159 was also obtained, albeit in considerably reduced yield, when a flow pyrolysis of neat 154 was conducted and the gaseous pyrolysate bubbled through methanol in a trap located ∿20 cm downstream from the heating zone. This observation has not been reported for other silenes and probably reflects the greater stability of 1-methyl-1-silabenzene.



(without deuterium incorporation)

Figure 7. 60 MHz ^{1}H-NMR of 1-methoxy-1-methyl-1-sila-6-deutero-hexa-2,4-diene 160

To minimize polymerization of 40, a high dilution vacuum pyrolysis of 154 was conducted at 640°C and 3×10^{-5} torr (106). Analysis of the pyrolysate by GCMS revealed one major volatile product whose mass spectrum was in accord with that expected of a dimer of 40: m/e (% rel. int.) 216 (8, M^+), 108 (100), 93 (63), 67 (18). The product was isolated in 18% after chromatography on silica gel (hexane) and confirmed to be the [4+2] dimer of 1-methyl-1-silabenzene 161 on the basis of its 100 MHz ^{1}H-NMR (Figure 8) high resolution mass spectrum and IR. A trimer of 1-methyl-1-silabenzene was also detected in the GCMS of the pyrolysate (∿ 10:1, dimer:trimer) although it was never isolated: m/e (% rel. int.) 324 (19), 138 (51), 123 (42), 108 (100), 93 (58).



154 40 161

Attempts to generate and trap 40 *via* a retro-Diels-Alder of the silabenzene dimers 161 completely failed. Thus, copyrolysis of 161 and methanol in a nitrogen flow system afforded none of the methanol:silabenzene adduct 159. Likewise, heating a degassed solution of 161 and diphenylacetylene in D_8-toluene at 150° in a sealed NMR tube showed the complete consumption of 161 after 8 hours. However, analysis of the

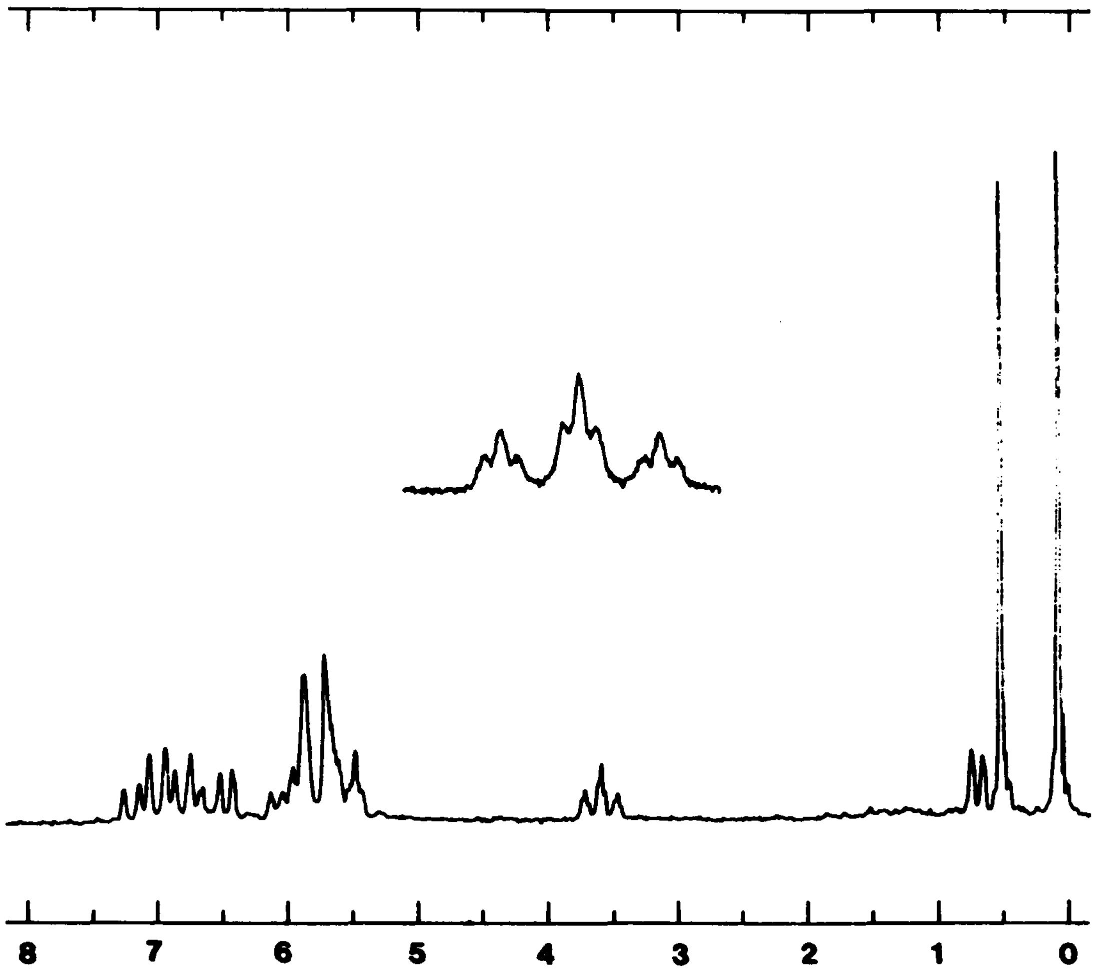
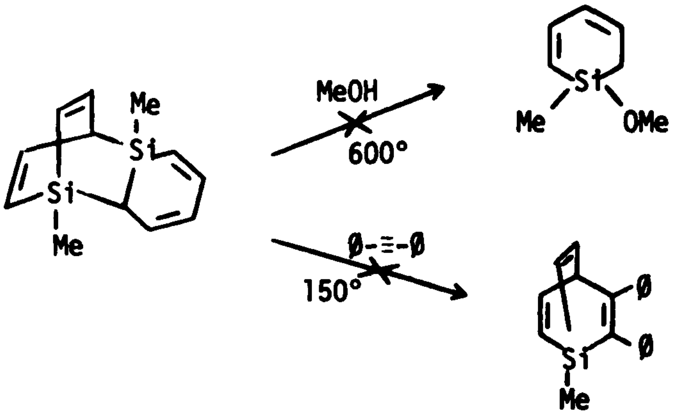
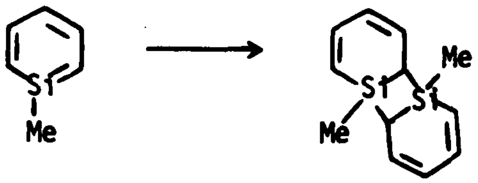


Figure 8. 60 MHz ^{1}H-NMR of [4+2] dimers of 1-methyl-1-silabenzene 161

pyrolysate by gas chromatography failed to give any evidence for the trapping of 40 with diphenylacetylene.



It is interesting to note that Dewar *et al.* (30) had predicted silabenzenes to dimerize in a head-to-tail fashion customary with other silenes and not in the [4+2] Diels-Alder fashion observed. Furthermore, Märkl and Hofmeister (40) have used Dewar's prediction to rationalize their head-to-tail dimer as arising from a silabenzene and not a displacement process (see Schemes 6 and 7).



(Dewar's prediction)

In collaboration with O. L. Chapman and C. L. Kreil, the argon matrix isolation of silatoluene was accomplished (105). Pyrolysis of 154 was accomplished by either passing a mixture of 154 in argon (1:500 v/v) through a quartz tube heated to 610°C or by cooling 154 to -40°C and allowing it to slowly vaporize through a 730°C tube and mix with argon (1:250 to 1:1000 v/v) upon exit from the hot zone. Deposition of the argon diluted pyrolysate on a CsI window cooled to 23 K allowed the IR spectrum to be obtained. Comparisons with the spectra of matrix-isolated authentic samples revealed that both propene and the starting diene 154 were present. Subtraction of these bands from the spectrum obtained from the pyrolysate gave the following bands attributed to 1-methyl-1-silabenzene (see Figure 9): 1530, 1500, 1410, 1360, 1268, 980, 965, 900, 890, 842, 770, 697, 655 and 563. No definitive assignments of these bands to specific vibrations were made.

The ultraviolet spectrum of 40 was obtained by depositing the argon-diluted pyrolysate on a sapphire window cooled to 26 K. Whereas, matrix isolated 154 possessed only one UV maxima at 2625 A°, the spectrum of the matrix-isolated pyrolysate possessed much longer wavelength absorption with considerable well-resolved vibrational structure (see Figure 10) as would be expected for the electronic transition corresponding to the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ band in benzene. Major UV maxima were at 3005, 3073, 3137 and 3221 A°.

The UV spectra of silatoluene follows the general trend of other heterobenzenes in that the bathochromic shift of the $\pi \rightarrow \pi^*$ transitions runs parallel to the fall of electronegativity of the heteroatom and the decreasing bond strength of the El=C bond (see

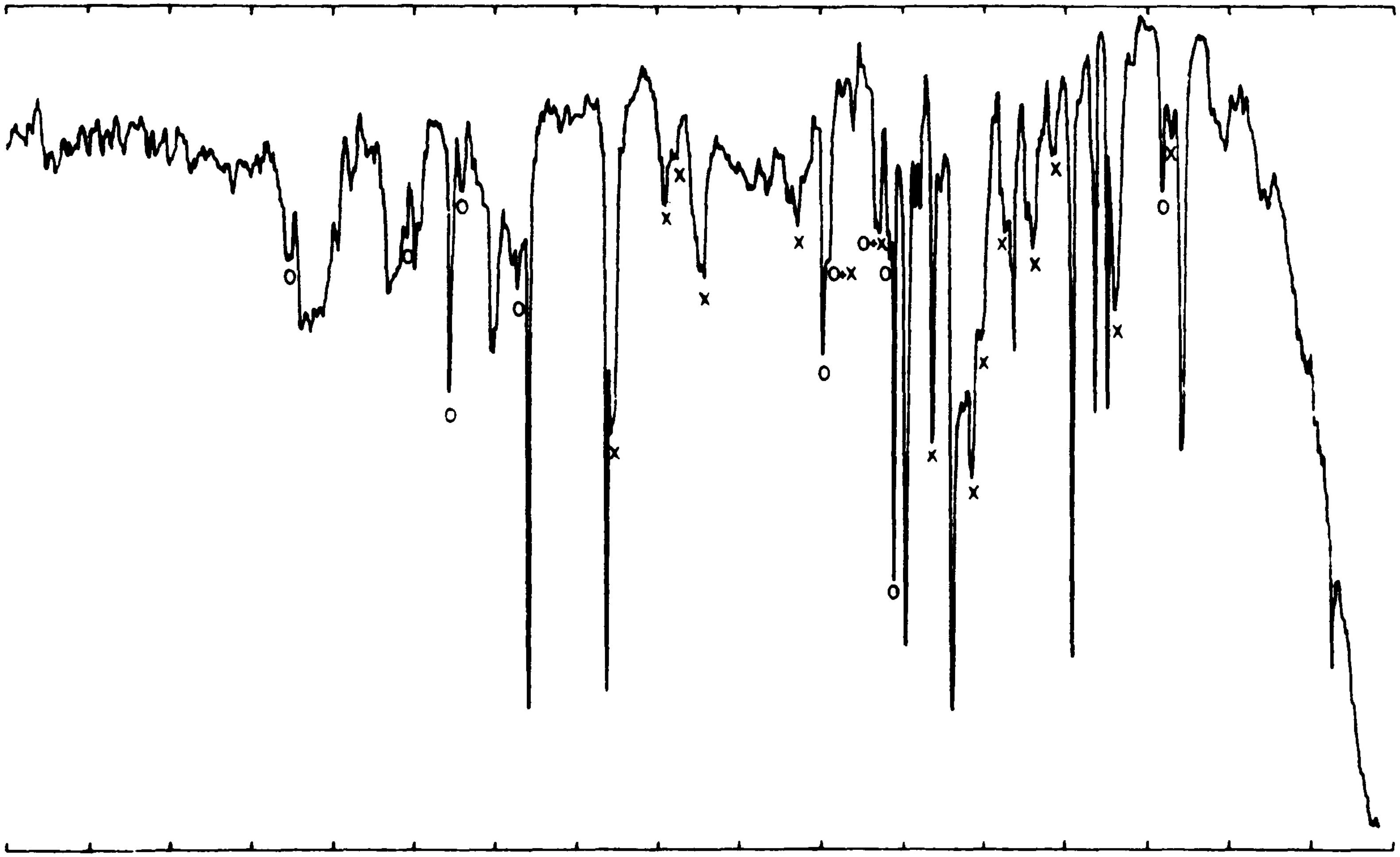
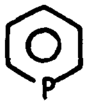


Figure 9. Infrared spectrum of silatoluene matrix isolated in argon at 23 K. Bands marked O are due to propene. Bands marked X are due to the starting diene

Table 4). The UV spectrum of **40** is also in good agreement with the prediction (29,31) that silabenzene would be an aromatic system.

Table 4. UV maxima and electronegativity values for heterobenzenes

					
$\lambda_{max}[A]^o$ $\pi \rightarrow \pi^*$	250	256	246	268	312
	192	200	213	219	236
Electronegativity[a]	3.0	2.5	2.1	2.0	1.90

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[a] Linus Pauling, The Nature of the Chemical Bond, 3rd edition; Cornell University Press: New York, 1960 (26).

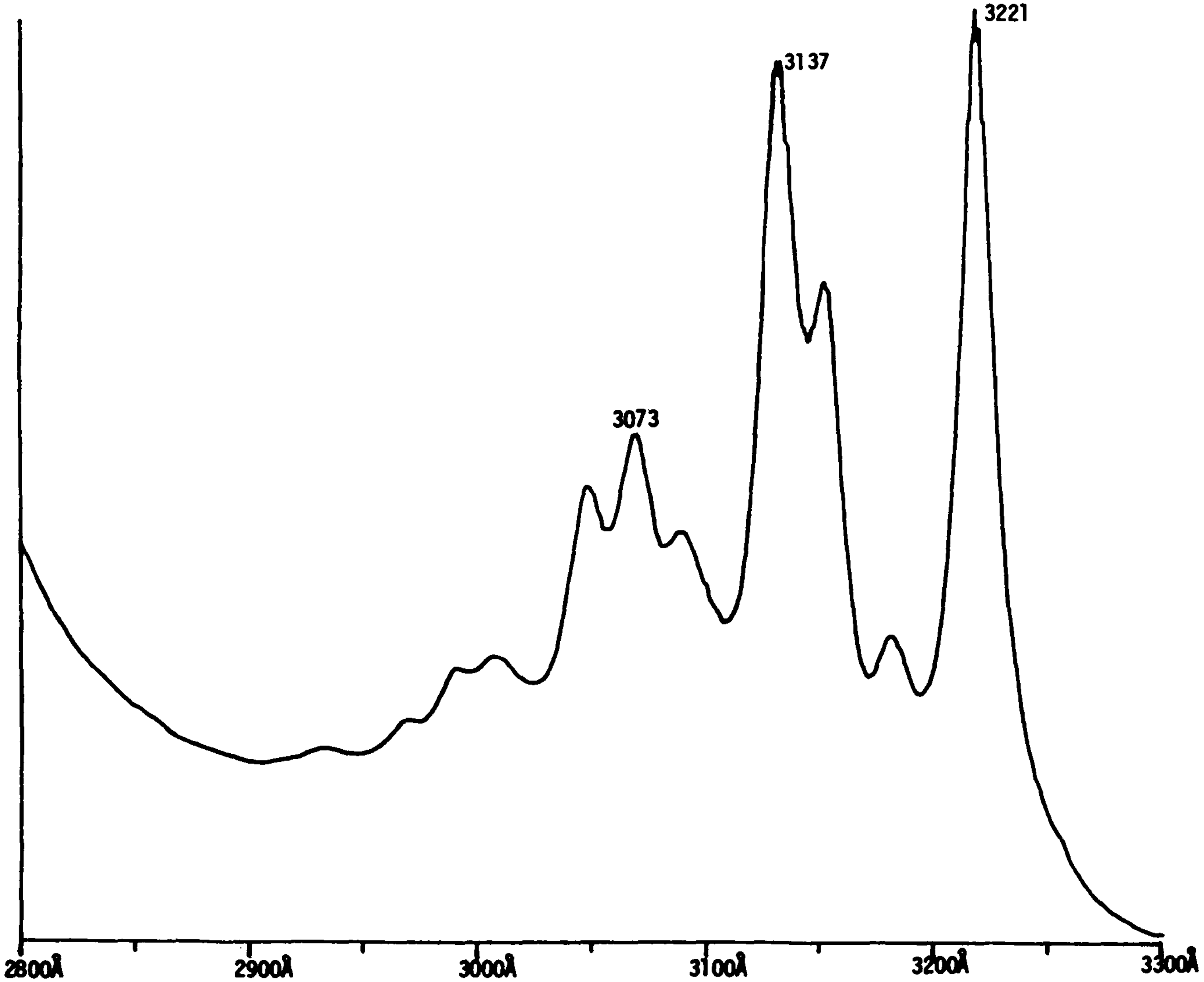


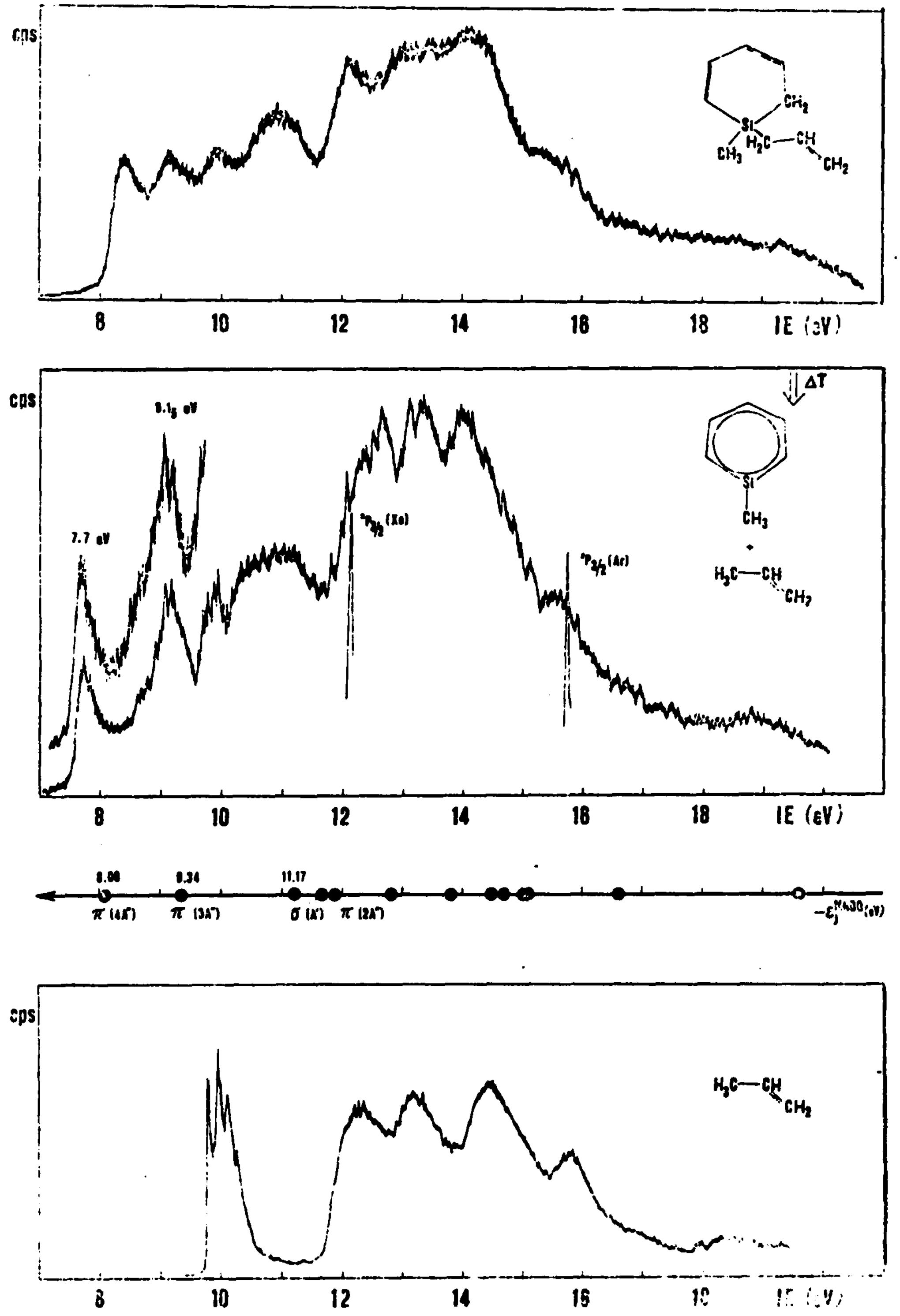
Figure 10. UV spectrum of 1-methyl-1-silabenzene in an argon matrix at 26 K

Definitive evidence that the observed matrix-isolated spectra were indeed arising from silatoluene was obtained by depositing the argon-diluted pyrolysate on a CsI window and obtaining the IR spectra. After matching the spectra with those previously reported, the matrix was coated with methanol ($\sim$ 1/2 the thickness of the argon layer) and allowed to warm to 180 K. At 180 K, the deposited material completely evaporated, and the products were isolated in a liquid nitrogen cooled trap. Analysis by GCMS and GC retention time showed only two major products, methoxysilane 159 and 154 in a 1:12.5 ratio. In the absence of added traps, warming the matrix produced a polymer which was not characterized.

In conjunction with H. Bock, R. A. Bowling and B. Solouki, the photoelectron (PE) spectrum of silatoluene was obtained (107). Pyrolysis of 154 in a modified heated inlet system of a Perkin-Elmer PS 16 photoelectron spectrometer (108) gave the PE spectrum shown in Figure 11. The two low-energy bands at 7.7 and 9.15 eV were assigned to the lowest radical cation states of silatoluene, whereas the third band centered at 10 eV coincided with the first band of propene.

The low first ionization energy of 7.7 eV is in accord with that predicted by a first order perturbation of silicon. Insertion of a silicon center in benzene yields a value of 8.2 eV for C_5H_5SiH (109). An additional attachment of a methyl group further lowers the ionization energy by $\sim$0.4 eV (60). Thus, the calculated value of $\sim$7.8 eV is in good agreement with the experimentally determined first ionization potential. In contrast, the second ionization potential should remain

Figure 11. Photoelectron spectrum of 1-methyl-1-silabenzene


cps
IE (eV)
8
10
12
14
16
18
ΔT
H$_3$C—CH—CH$_2$
CH$_3$
Si
7.7 eV
9.1$_5$ eV
$^2P_{3/2}$(Xe)
$^2P_{3/2}$(Ar)
8.06
9.34
11.17
π (4A")
π (3A")
σ (A')
π (2A")
$-\varepsilon_j^{MNDO}$(eV)

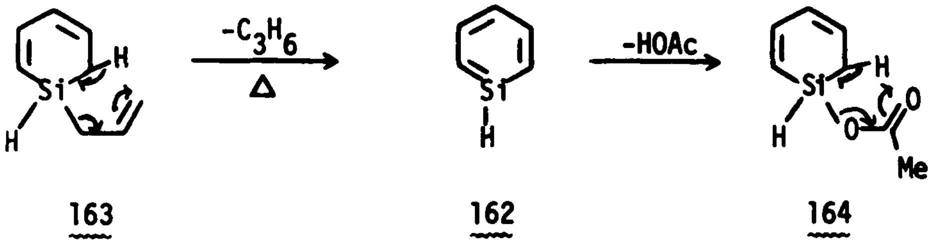
approximately constant and be comparable to IE_2 (9.15 eV) of toluene (110).

Since the initial reports on the generation, trapping, and isolation of 1-methyl-1-silabenzene from this dissertation (100, 106, 107), three other reports of a thermal generation of a silabenzene have appeared. All of these reports are based on methods developed in this dissertation.

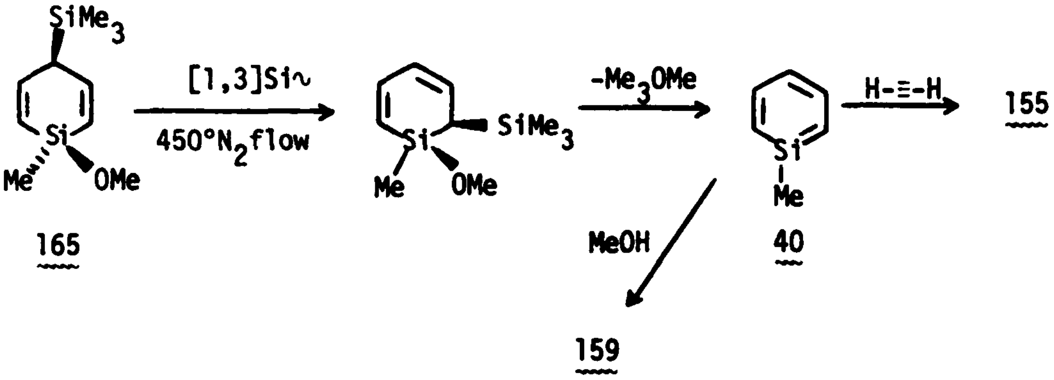
Utilizing the retro-ene elimination of propene, V. G. Maier *et al.* (41) and V. S. Solouki *et al.* (42) have recently prepared the parent silabenzene 162. V. B. Solouki *et al.* obtained the PE spectrum of silabenzene 162 via pyrolysis of 1-allyl-1-silacyclohexa-2,4-diene in a heated inlet system of a PE spectrometer. The experimentally determined first and second ionization potentials were 8.0 and 9.3 eV, respectively. This is in good agreement with the predicted values of 8.2 and 9.2 eV (109, 110).

The UV and IR spectra of the matrix-isolated parent silabenzene was obtained by G. Maier and coworkers (41). Pyrolysis of 163 or 164 followed by dilution of the pyrolysate with argon and deposition on a window cooled to 10 K gave a UV spectrum very similar to that of 1-methyl-1-silabenzene 40. The major absorptions in the B-band of silabenzene were 305, 313 and 320 nm. Comparison of these values with those obtained for 1-methyl-1-silabenzene (307.3, 313.7 and 322.1 nm) shows a bathochromatic shift of ∿2 nm on the B-band for a methyl substituent. For benzene, the shift is ∿5 nm for the addition of a methyl substituent.

The IR spectrum obtained by G. Maier and coworkers is also in good agreement with those obtained for 1-methyl-1-silabenzene. They observed bands at $\tilde{\nu}$ 418, 566, 698, 886, 1259, 1353, 1500, 1526 and 2217 (Si-H) cm^{-1} versus bands at $\tilde{\nu}$ = 563, 655, 697, 770, 842, 883, 890, 900, 980, 1268, 1360, 1410, 1500 and 1530 cm^{-1} for 40.

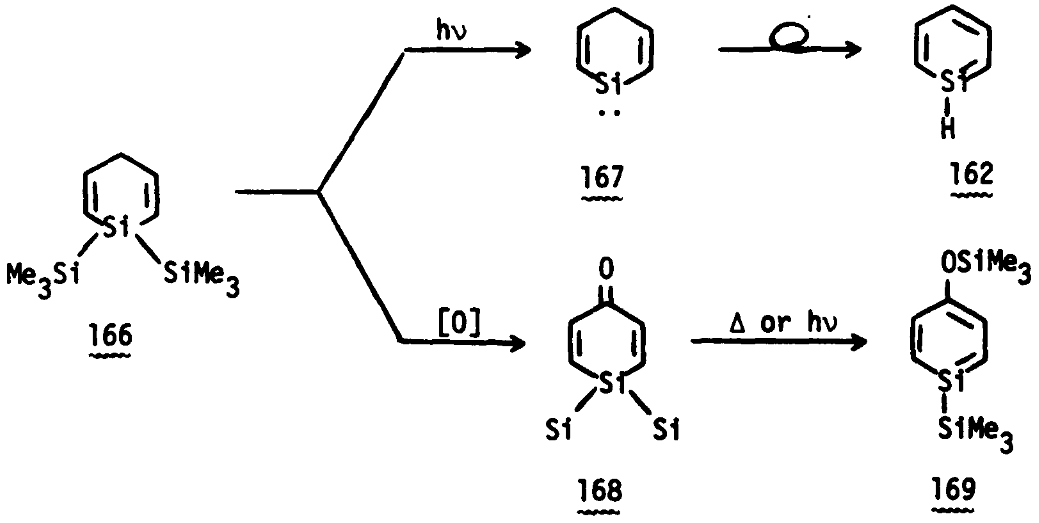


Barton and Vuper (43) have recently reported the synthesis of 1-methyl-1-silabenzene based on the beta elimination of trimethylmethoxysilane from 4-trimethylsilyl-methylmethoxysilacyclohexa-2,5-diene 165. Identical trapping results and temperature requirements for the generation of 40 were observed.



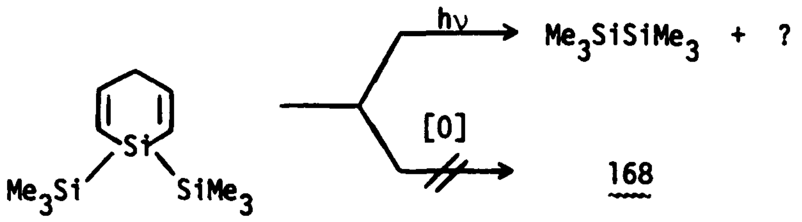
Although the gas phase pyrolysis of 154 cleanly affords 1-methyl-1-silabenzene, attempts to generate 40 from a solution phase thermolysis of 154 were less fruitful. When a mixture of 154, diphenylacetylene and diphenyl ether were degassed and heated to 290°C for several hours in a sealed tube, the only identifiable component was diphenyl ether. When more reactive dienophiles such as dimethylacetylenedicarboxylate or perfluor-2-butyne were used, the Diels-Alder adduct was obtained.

Attempts to prepare a silabenzene from the particularly promising precursor bis(trimethylsilyl)silacyclohexa-2,5-diene were unsuccessful. Two possible routes to a silabenzene from 166 were perceived. In analogy with other trisilanes (77), photolysis of 166 was expected to extrude the silylene 167 which could rearrange to silabenzene 162. Another route to a silabenzene from 166 was by oxidation to the silacyclohexadienone 168. A 1,5 silyl shift from silicon to oxygen would then afford silabenzene 169.

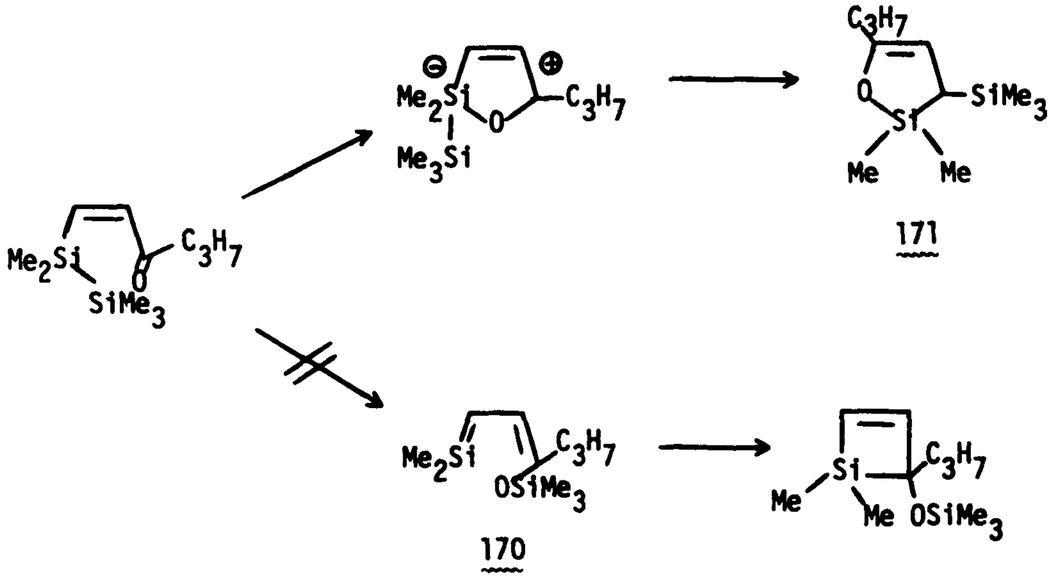


To this end, 166 was prepared by the quenching of 1,5-dilithio penta-1,4-diene (111) with 2,2-dichlorohexamethyltrisilane (112). After work-up, an 82% yield of 166 was obtained. Photolysis of 166 through quartz using a medium pressure Hanovia lamp for ∿30 hours saw the consumption of 166 with the concomitant formation of hexamethyldisilane as monitored by gas chromatography (74). No other volatile products were seen. Attempts to trap the silylene 167 by a cophotolysis with triethylsilane gave none of the expected silylene insertion product into triethylsilane.

Various attempts to oxidize 166 to the dienone 168 failed. Whereas, Barton and Banasiak (35) found that activated manganese dioxide readily oxidized 1,1-dimethyl-1-silacyclohexa-2,5-diene to 1,1-dimethyl-1-silacyclohexa-2,5-dien-4-one, the treatment of 166 with activated manganese dioxide for 18 hours afforded only unreacted 166 upon work-up. Similar results were obtained with SeO_2, pyridinium chlorochromate, and SeO_2 and *t*-butylhydroperoxide.



Recent work by Barton and S. Burns (113) illustrates the futility of the approach to 169 via the dienone 168. They have shown that disilanylenones do not rearrange under either thermal or photochemical conditions to 4-siloxy-1-silabutadienes 170. Instead, the silylenolether 171 is obtained.

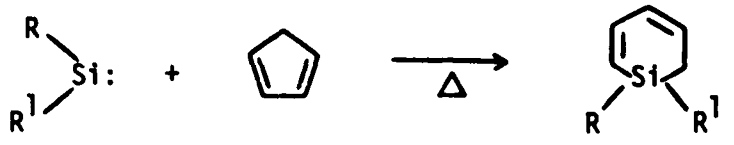


D. Syntheses of Nonannulated Seven-Membered Rings Containing One Silicon

In contrast to cycloheptatriene, which was obtained by Ladenburg (114) from atropine in 1881, the C-unsubstituted organosilicon analog, 1,1-dimethylsilepin, has not been reported in the literature, although mono- (59) and di-substituted (58) are now known. The silepin ring system is of interest as a potential precursor to the silicon analog of the tropylium cation and thus potentially the first example of a silylenium cation, a trivalent positive charged silicon, and the second example of a silaaromatic ring system.

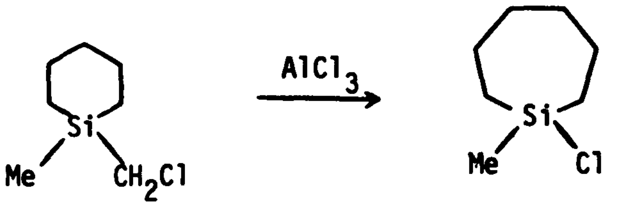
Although annulated silepins with functionality (Cl, H) on silicon are known -- a necessary requirement in order to serve as a precursor to a silepinium cation -- no conclusive evidence for a silylenium cation has been found from these systems. However, it should be noted that annulated silepins are poor models in which to look for a silylenium cation in view of the decreased stability of benzotropylium cations relative to the parent tropylium cation (115). The approaches to non-annulated silepins have not allowed the introduction of functionality on silicon. Thus, the goal of this section was to develop a quick entry into a seven-membered silacycle allowing for both functionality at silicon and the possible elaboration to a silepin.

Of the known silacycles, silacyclohexadienes 172 are the most readily accessible. Pyrolysis of cyclopentadiene and a silylene precursor affords the respective silacyclohexa-2,4-diene arising from addition of the silylene to cyclopentadiene. Utilizing this method, the silacyclohexadienes were R=Me, R^1=Cl (116), R=R^1=Cl (97), or R=R^1=Me (97) are all readily available in one step in yields of 25-40%. Thus, the initial attempts to prepare seven-membered silacycles were based upon a one carbon ring expansion of a silacyclohexadiene.

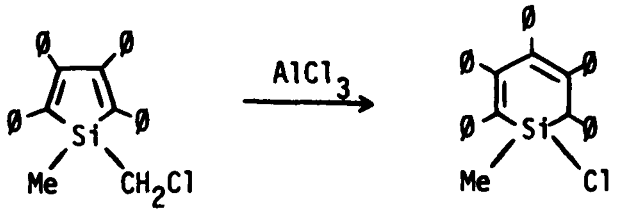


172

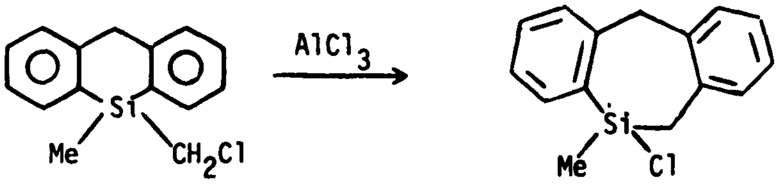
As mentioned in the Historical section, Nametkin and coworkers (51) have found that aluminum trichloride catalyzes the migration of an alkyl group from silicon to carbon in α-halomethylsilanes and have utilized this method in the preparation of methylchlorosilacycloheptane from chloromethylmethylsilacyclohexane. Vinyl (117) and benzo groups have also been shown to migrate from silicon to carbon to give a ring expanded product.



(Ref. 51)

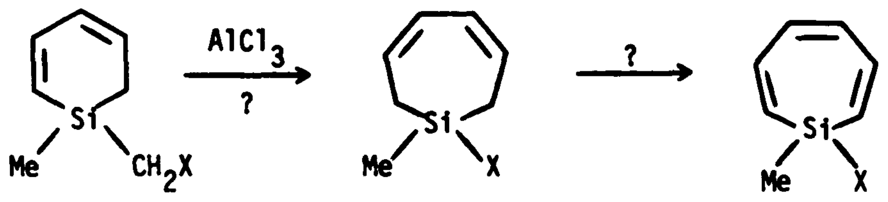


(Ref. 117)



(Ref. 55)

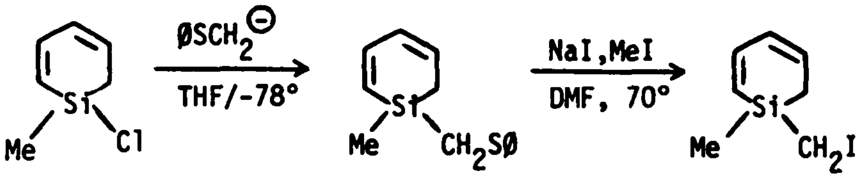
Application of this method suggested the synthesis of **173** which could be ring expanded to **174** using a Lewis acid. The diene **174** would then provide an entry point into the synthesis of functionalized silepins.



X = I, Cl X = Cl X = Cl

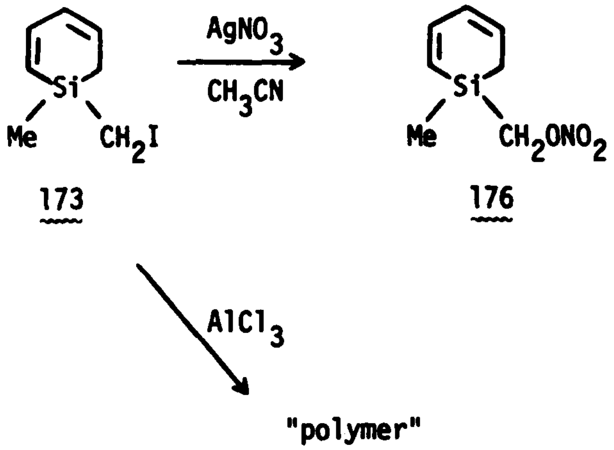
173 174

The synthesis of 172 (X=I) was achieved by a one-carbon homologation of methylchlorosilacyclohexadiene 36, by the method of Corey and Jautelat (118). Thus, treatment of 36 in a THF solution at -78°C with the anion of thioanisole afforded, after work-up, a 41% yield of 175. The other major product was thioanisole, apparently formed by an abstraction of a proton from the highly acidic ring methylene (119). Treatment of 175 with 1 equivalent of sodium iodide and >10 equivalents of methyl iodide in DMF at 70°C for 12 hours afforded a 70% yield of 173 (X=I).

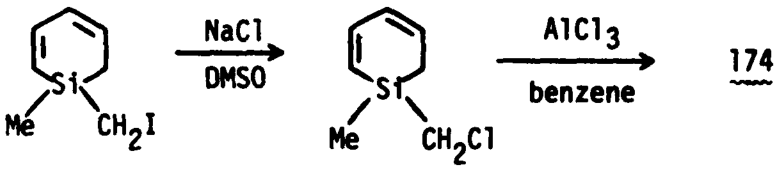


36 175 173

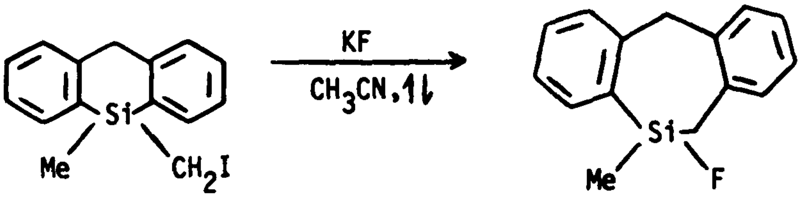
Treatment of 173 with $AlCl_3$ in hexane, CS_2, or D_6-benzene resulted in the loss of starting material as monitored by either NMR or gas chromatography. However, none of the ring expanded product 174 could be detected by either NMR, gas chromatography or GCMS. Attempts to ring expand 173 to 174 with silver salts also failed. Treatment of 173 with silver nitrate in acetonitrile afforded the nitrate ester 176 as the sole product (100% yield based on NMR).



Since most of the ring expansions in the literature were from the chloromethylsilane, 173 (X=I) was converted to the chloromethylsilane in 49% by stirring 173 (X=I) with >10 equivalents of NaCl in DMSO for four hours at room temperature in the hope of facilitating the expansion of 173 to 174. Addition of 173 (X=Cl) to a degassed suspension of freshly sublimed $AlCl_3$ (∿15 mole percent) in dry benzene immediately produced a reddish-orange coloration and a mildly exothermic reaction. Analysis of the reaction by gas chromatography showed two volatile products. The larger peak was isolated by preparative gas chromatography on an 8', 30% SE-30 column and identified as 174 on the basis of its GCMS and 60 MHz ^{1}H-NMR. However, attempts to repeat this reaction showed the yield of 174 was variable and always less than 10%.

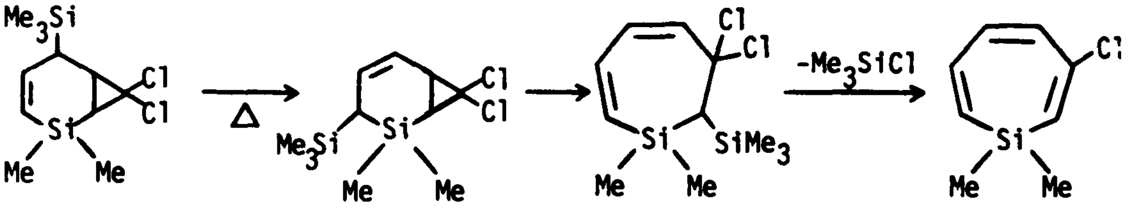


J. Corey and coworkers have also developed an anionic method of ring expansion (120). Refluxing iodomethyldibenzosilacyclohexadiene **177** with potassium fluoride in acetonitrile was reported to give ring expanded fluorosilane **178** in good yield. Application of this method of ring expansion to **173** (X=I) afforded in low yield a volatile product tentatively assigned the structure **174** (X=F) on the basis of its GCMS spectrum and 60 MHz ^{1}H-NMR. Attempts to increase the yield of **174** (X=F) by monitoring the progress of the reaction by gas chromatography revealed the steady consumption of starting material over a ten hour period with a concomitant, but much slower formation of **174**. At best, the yield of **174** was estimated to be less than 10 percent.



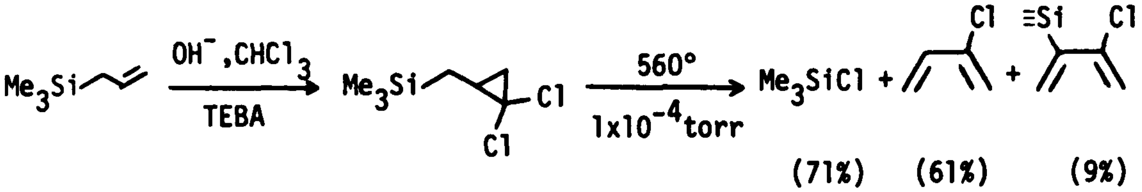
177 **178**

The low yields for the ring expansion step, as well as the low yield in converting **36** to **173**, made these two methods unattractive as entry points into functionalized silepins. At this point, an approach based on 179 was begun. The bicyclo[4.1.0]silaheptene 179 conceivably offered two novel entries into a silepin ring system, both of which should be amenable to functionalization at the ring silicon. Thus, it was hoped that thermolysis of 179 would result in a thermal [1,3] silyl shift followed by an unprecedented thermal homo [1,5] silyl migration. This would set up a beta elimination of trimethylchlorosilane from 180 which would introduce the last double bond and yield silepin 181. Precedent for [1,3] silyl migrations has been obtained by Barton and Vuper (43) in 4-trimethylsilylsilacyclohexa-2,4-dienes. Although homo [1,5] silyl shifts are not known, homo [1,5] hydrogen migrations have been reported in several instances (for example, see reference 121). This in combination with Ashe's studies (122) which show [1,5] silyl migrations in 5-trimethylsilylcyclopenta-1,3-dienes are 10^6 times faster than [1,5] hydrogen migrations, suggests 179 as a possible precursor to 181.



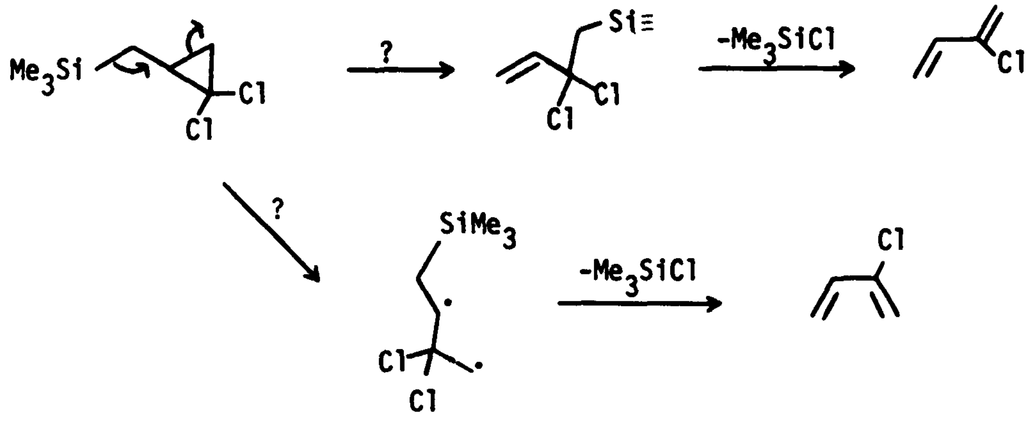
179 180 181

It is also possible that 179 could undergo a homo [1,3] silyl shift to directly yield 180. In order to investigate this possibility, a simple model system, dichlorocyclopropane 182 was prepared and thermolyzed. The synthesis of 182 was achieved by phase transfer of dichlorocarbene (123) to trimethylallylsilane in 53% yield. Vacuum pyrolysis of 182 at 560° and 1×10^{-4} torr afforded a light yellow pyrolysate consisting of four volatile components. The four components were isolated by preparative gas chromatography and identified as trimethylchlorosilane (71%), 182, 2-chlorobutadiene (61%), and 2-chloro-3-trimethylbutadiene (9%) on the basis of their ^{1}H-NMR, low resolution mass spectrum, and comparison with authentic samples.



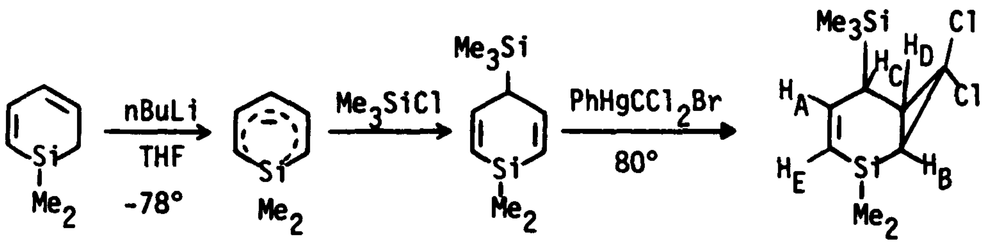
182

Although the products, especially trimethylchlorosilane and 2-chlorobutadiene, are consistent with a homo [1,3] silyl shift followed by a beta elimination, they do not demand this interpretation. Thermolytic homolysis of a cyclopropane bond to give the diradical 183 followed by loss of trimethylchlorosilane or HCl will also explain the formation of the products. However, the important aspect of this thermolysis was that it showed beta trimethylsilyldichlorocyclopropanes such as 182, serve as thermal diene synthons. Thus, further substantiating that 179 is a reasonable silepin precursor.



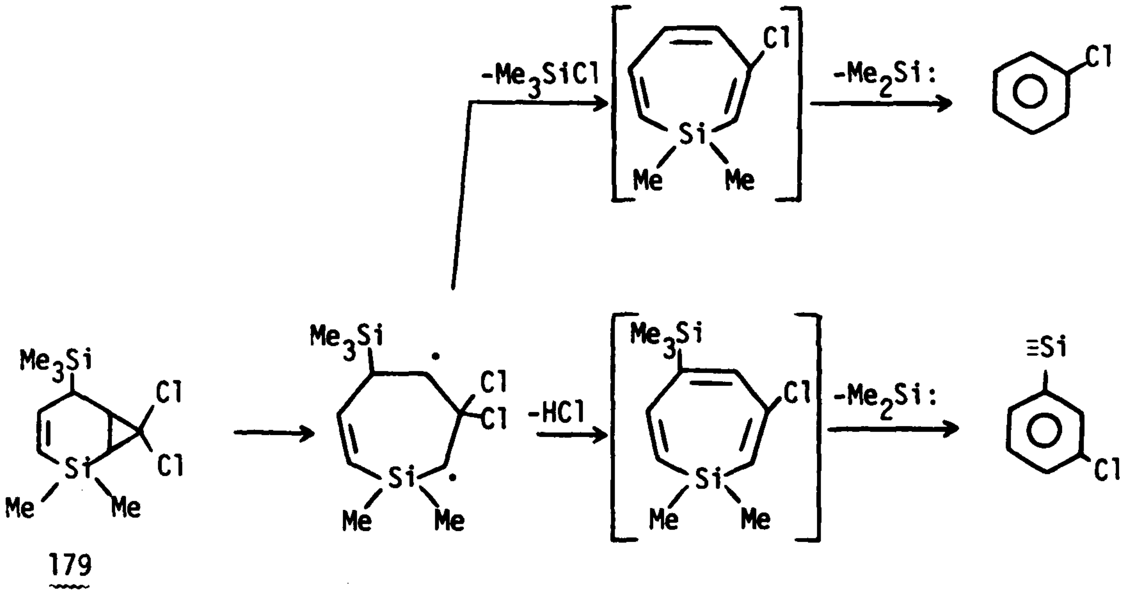
183

The synthesis of 179 was achieved in two steps from 1,1-dimethyl-1-silacyclohexa-2,4-diene in 47%. Metallation of 184 (*n*-BuLi, THF, -78°) (119) followed by quenching of the resulting pentadienyl anion with trimethylchlorosilane afforded 1,1-dimethyl-4-trimethylsilyl-1-silacyclohexa-2,5-diene, 185, in 66% yield. Reaction of 185 with dichlorocarbene, generated from the corresponding Seyferth and Lambert reagent (124), produced 179 in 72% yield.



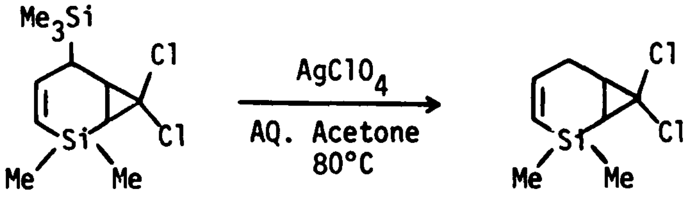
184 185 179

Pyrolysis of 179 in a vertical nitrogen flow (35 mL/min) system at 460°C produced a mixture of four major volatile components. The four products were isolated by preparative gas chromatography on a 5' 3% OV-101 column and identified as trimethylchlorosilane, $PhSiMe_3$, PhCl, and $Me_3SiPhCl$ (isomer mixture) on the basis of their 60 MHz ^1H-NMR and low resolution mass spectrum. Of these products, Me_3SiCl and PhCl are certainly consistent with the formation of silepin 181 and subsequent decomposition (58). All of the products are consistent with the ring opening of the cyclopropane to a diradical followed by loss of either HCl or trimethylchlorosilane to give the corresponding silepin which, under the pyrolysis conditions, extruded dimethylsilylene.



In an attempt to stimulate milder decomposition of 179 with electrophilic assistance to chloride loss, norcarene 179 was reacted with silver perchlorate in aqueous acetone (80°, 2 hrs). The only silicon-containing product isolated was the desilated narcarene 186 in

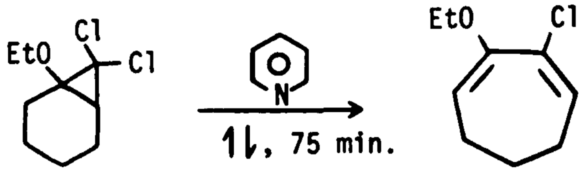
35% yield. In contrast to silver perchlorate, treatment of 179 with ethanolic silver nitrate afforded only unreacted 179.



179

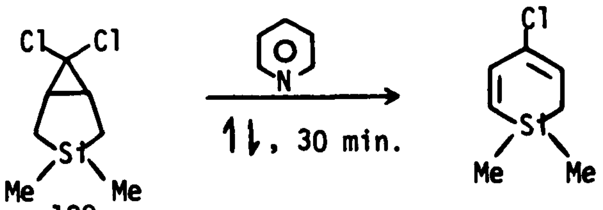
186

Parham *et al*. (125) had also observed an inertness of dichlorobicyclo[4.1.0]heptane, 187, towards solvolysis with alcoholic silver nitrate. However, they were able to obtain ring opening of 187 in good yield in refluxing pyridine (75 min). When 179 was subjected to refluxing pyridine for 90 min, the only volatile product observed was unreacted 179. This result is even more surprising considering that the corresponding ring expansion from the dichlorobicyclo[3.1.0]silahexane 188 to the 4-chlorosilacyclohexa-2,4-diene occurs more readily than the conditions reported by Parham.



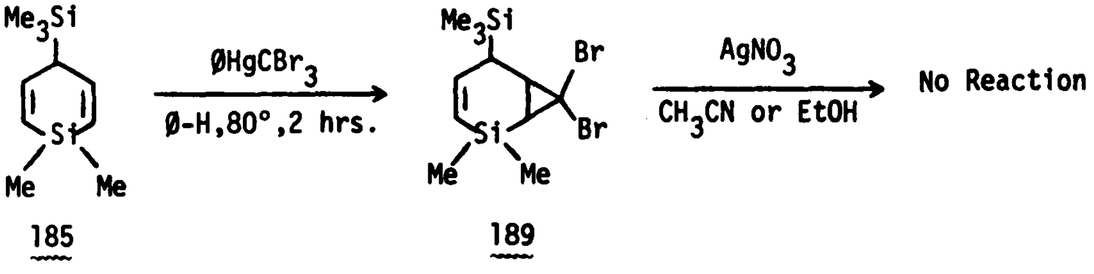
187

(83%)

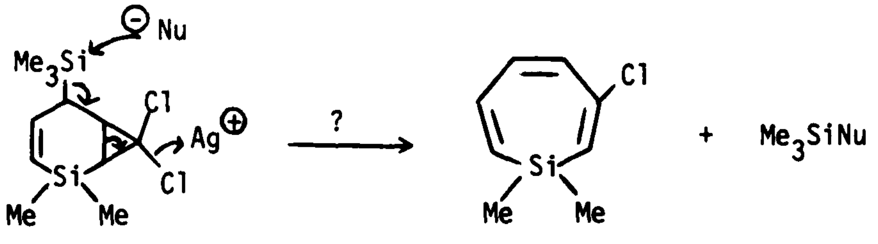


188

In 1967, Sandler (126) reported a rate enhancement in the solvolysis of 7,7-dibromobicyclo[4.1.0]heptane over 7,7-dichlorobicyclo[4.1.0]heptane and an increased yield of the ring expanded product (36% vs 24%). Thus, the solvolysis of 1,1-dimethyl-4-trimethylsilyl-7,7-dibromo-1-silabicyclo[4.1.0]hept-2-ene, 189, was attempted. The synthesis of 189 was achieved in 33% yield from the reaction of 185 with dibromocarbene ($\phi HgCBr_3$, C_6H_6, reflux 2 hrs). Treatment of 189 with silver nitrate in refluxing acetonitrile for 20 hrs afforded unreacted 189 as the sole volatile material. Similar results were obtained with 95% ethanol as the solvent. In contrast, Rosenburg and Zuckerman (127) found that treatment of 1,1-dimethyl-7,7-dibromo-1-silabicyclo[4.1.0]heptane with silver ion in 95% methanol results in the immediate precipitation of silver bromide. However, they reported that at least nineteen products were formed with none predominating.

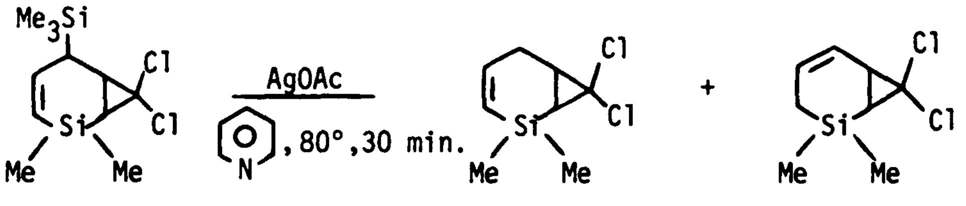


Another possible route into a silepin ring system from 179 was to initiate the decomposition of 179 using nucleophilic assistance to loss of trimethylsilyl. The reagents chosen initially for this were silver acetate and silver fluoride. With these reagents, the incoming nucleophile ($F^{\ominus}$ or $^{\ominus}OAc$) would form a very thermodynamically stable bond (Si-F or Si-O) and at the same time the silver ion would provide electrophilic assistance to the loss of chloride.



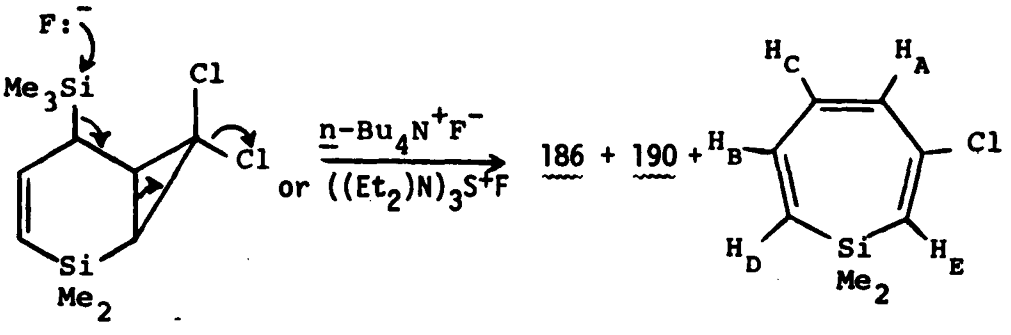
179

Treatment of 179 with excess silver fluoride in HMPA at 55°C for six hrs afforded unreacted 179 as the sole volatile material. The lack of even desilylated material suggested that the low solubility of silver fluoride was responsible for the recovery of 179. This problem was circumvented by the use of silver acetate in pyridine, in which it is soluble. Addition of 179 to an excess of silver acetate in pyridine at 80°C resulted in the immediate formation of a dark brown precipitate. Upon work-up, the only volatile materials obtained were the desilylated silanorcarenes 190 and 186.



179 186 190

The inability to effect ring opening with silver acetate or silver fluoride prompted the use of a variety of fluoride sources. The three most common fluoride sources -- potassium fluoride, cesium fluoride and tetra-n-butylammonium fluoride -- and tris(diethylamino)sulfonium fluoride were tried. Heating a mixture of 179 with either potassium fluoride or cesium fluoride in either acetonitrile or dimethylsulfoxide afforded, after work-up, 186 and 190 as the major volatile products. However, treatment of a THF solution of 179 at -23°C with either $(n\text{-Bu})_4N^+F^-$ or $(Et_2N)_3S^+F^-$ afforded a 3% yield of the silepin 191 (see Figure 12) in addition to an 18-22% yield of a mixture consisting of 186 and 190. Attempts to increase the yield of 181 by variation of solvent (ether, HMPA, HMPA:THF, pentane) reaction time and temperature failed to increase the yield of 181 and in most cases decreased it.



179

191

The inability to ring expand a six-membered ring to a seven-membered ring suggested the direct synthesis of silacycloheptenes and silacycloheptadienes from acyclic precursors. These, in turn, could serve as precursors to silepins.

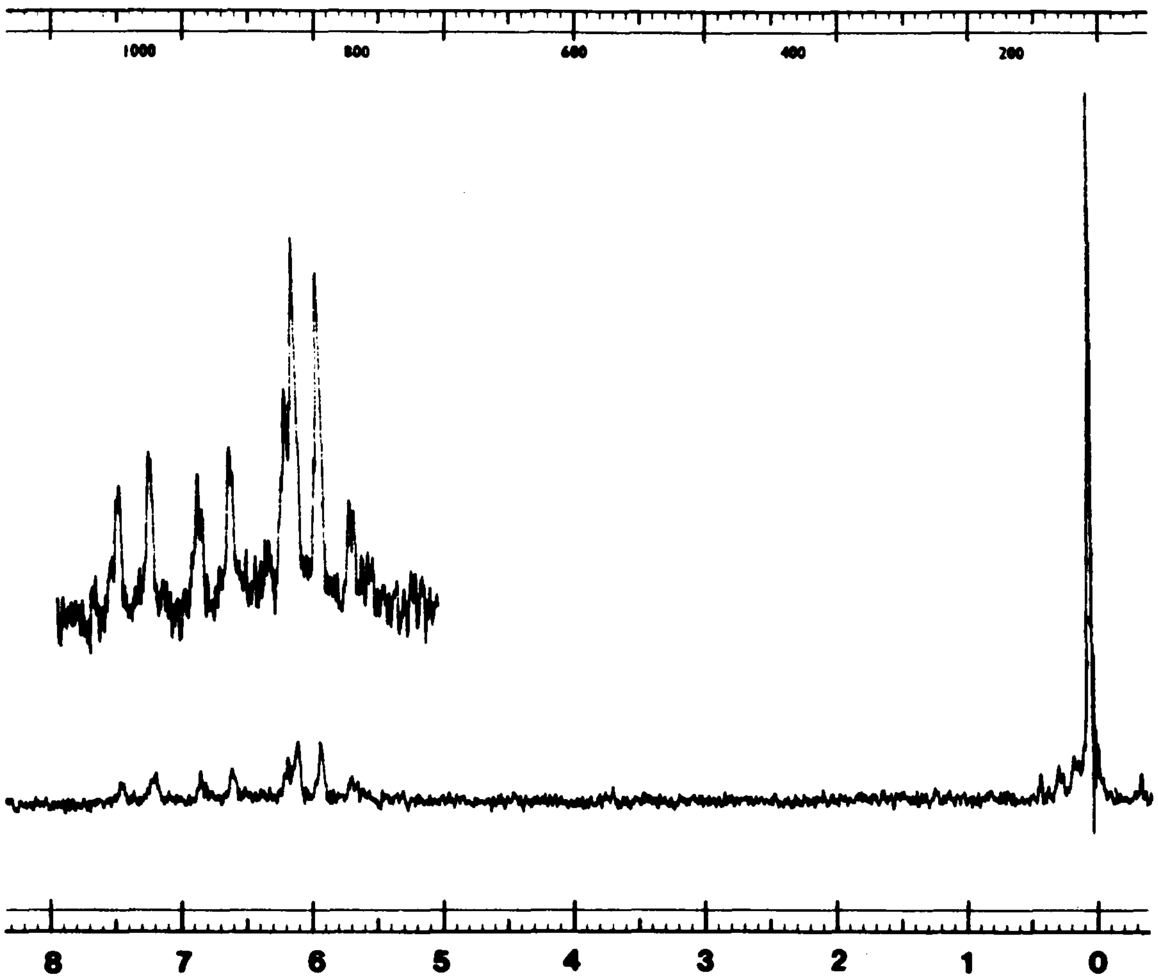
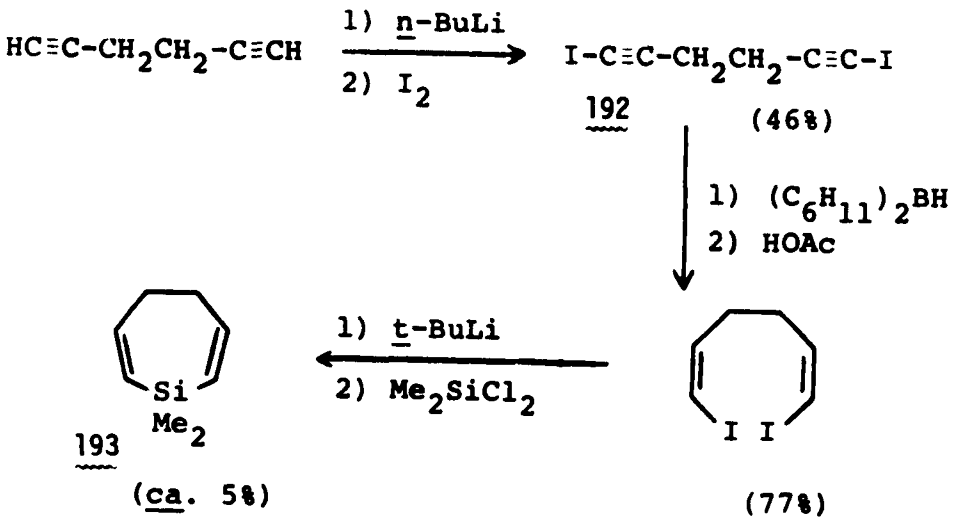


Figure 12. 60 MHz ^{1}H-NMR of 3-chloro-dimethylsilepin 181

The first attempt to synthesize the silacycloheptadiene ring (Scheme 17) involved cyclization and introduction of the silicon both in the final step. To this end, 1,6-diiodohexa-1,5-diene 191 was synthesized in 46% yield from iodination of the dianion of 1,5-hexadyne [(1) BuLi, THF/HMPA (10:1), -78° - (2) I_2, PMR (CCl_4) δ 2.58 (2)]. Reduction (128) of 192 with bis(cyclohexyl)borane afforded 1,6-diiodo-1,5-hexadiene, PMR (CCl_4) δ 2.28 (m, 4H), 6.20 (m, 4H)] in 77% yield. Treatment of 1,6-diiodo-1,5-hexadiene with t-butyllithium (C_5H_{12}, -23°C) followed by quenching with dichlorodimethylsilane yielded a light yellow oil from which 7,7-dimethyl-7-silacyclohepta-1,5-diene 193 could be isolated in ca. 5% yield only after tedious, preparative gas chromatography. The structure of 193 [GCMS (70 eV) m/e 138 (1), 123 (10), 97 (12), 95 (17), 79 (19), 78 (100), 59 (36%)] was largely determined from the PMR spectrum [δ (CCl_4) 0.30 (s, 6H, $SiMe_2$), 2.40 (t, 4H, J = 2.5 Hz, $-CH_2CH_2-$, collapses upon hν at δ 6.65), 5.67 (d, 2H, J = 14 Hz, vinyl), 6.65 (d of t, 2H, collapses to d, J = 14 Hz, with hν at δ 2.4) (see Figure 13).

Scheme 17



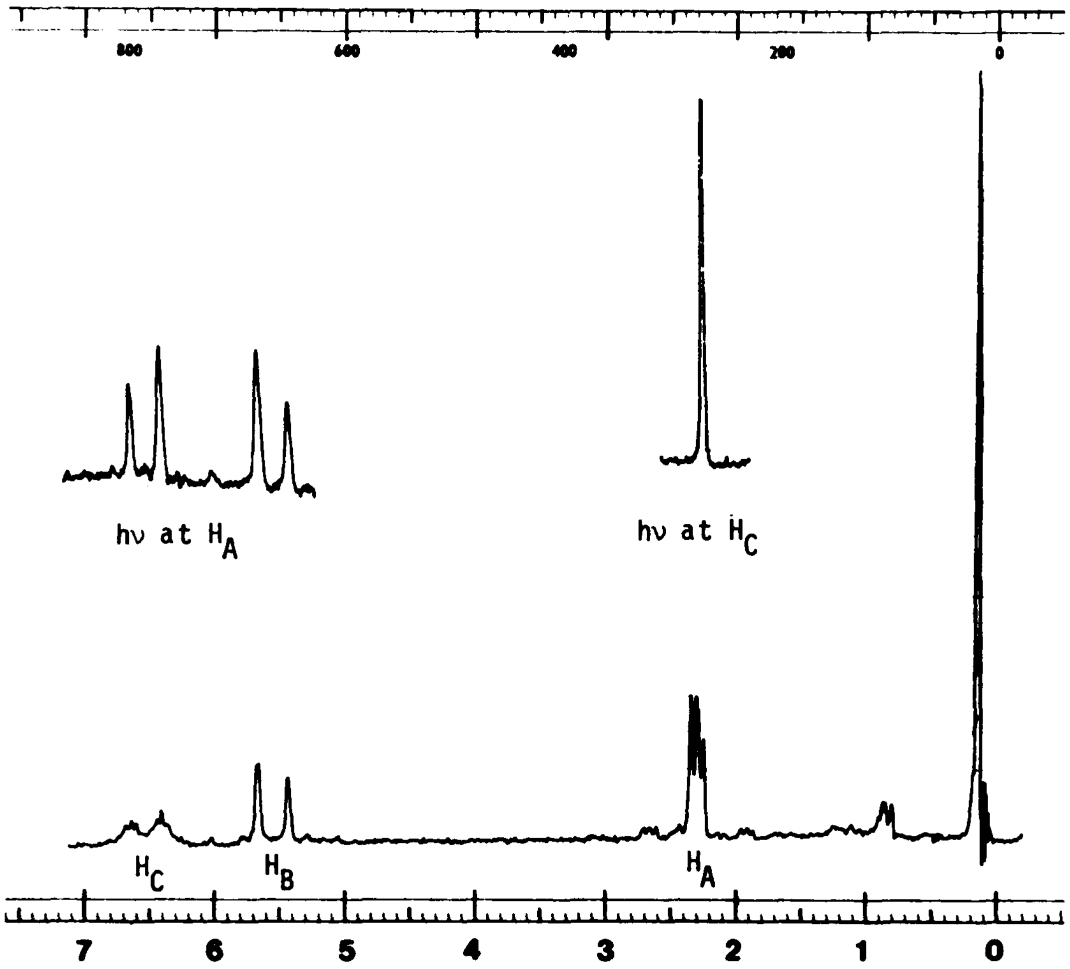
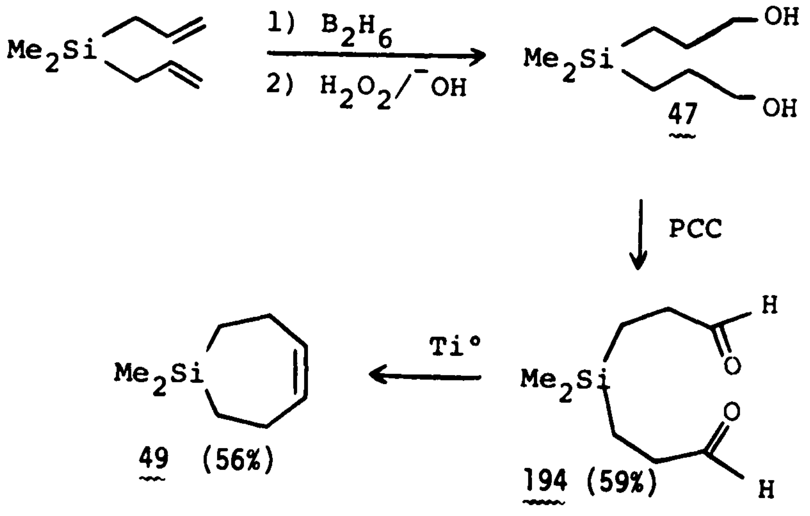


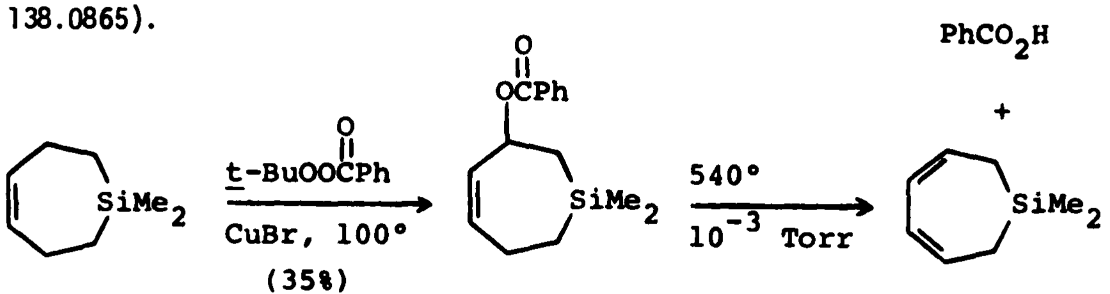
Figure 13. 60 MHz ^{1}H-NMR of 7,7-dimethyl-7-silacyclohepta-1,5-diene, 193

Although the synthesis of **193** was successful, the very low yield and rather difficult separation procedure prompted a search for a more convenient route to this ring system. Conversion of a silacycloheptene to a silacycloheptadiene by a variety of processes appeared possible, but the existing methods (47,48) of silacycloheptene synthesis (*vide supra*) were of too low a yield to lend themselves to this scheme. Thus, a simpler and more efficient conversion of diallyldimethylsilane to a silacycloheptene was sought. This was accomplished (Scheme 18) by the pyridinium chlorochromate (PCC) oxidation of the known diol **47** (from hydroboration/oxidation of diallyldimethylsilane) (**47**) to afford 4,4-dimethyl-4-silahepta-1,7-dial **194** in 59% yield. Cyclization of **194** with titanium by the procedure of McMurray and Kees (129) afforded 5,5-dimethyl-5-silacycloheptene **49** in 56% yield (GC). Although not maximized, the overall yield of this simple, three-step procedure, 29%, almost triples the best literature yield for **49**.

Scheme 18



Further unsaturation of silacycloheptene 49 was initiated by allylic oxidation with t-butyl peroxybenzoate in the presence of cuprous bromide (91). The resulting benzoyloxysilacycloheptene 195 was isolated in 35% yield by column chromatography and showed a single spot by TLC. Although the mass spectrum [m/e (% rel. int.) 260 (M^+, <1), 245 (2), 179 (52), 138 (36), 127 (13), 123 (32), 105 (100), 95 (16), 77 (42); calc'd for $C_{15}H_{20}O_2Si$, 260.1233, measured m/e 260.1236] and infrared spectrum (C=O 1720, C-O 1270) were quite consistent with structure 195, the PMR spectrum revealed it to be a mixture of at least two isomers (SiMe singlets at δ 0.0, 0.03, 0.05 and 0.2), presumably the two expected from the intermediate allylic radical. No extensive attempts were made to separate the isomers of 195. This isomer mixture was subjected to flash vacuum pyrolysis (540°, 10^{-3} torr, 30.5 cm horizontal quartz-packed tube with 1.9 cm IC) to effect elimination of benzoic acid (47%) and afford 6,6-dimethyl-6-silacyclohepta-1,3-diene 196 in 47% yield. The structure of 196 was confirmed by its PMR spectrum (see Figure 14) [δ (CCl_4) 0.08 (s, 6H), 1.32 (d, 4H, J = 6 Hz, collapses to s with $h\nu$ at ca. δ 5.6), 5.6 (strongest peak in mult. ca., 0.5 ppm wide, 4H)] and mass spectrum (calc'd for $C_8H_{14}Si$, 138.0865; measured m/e 138.0865).



49   195 (+ isomer)   196 (47%)

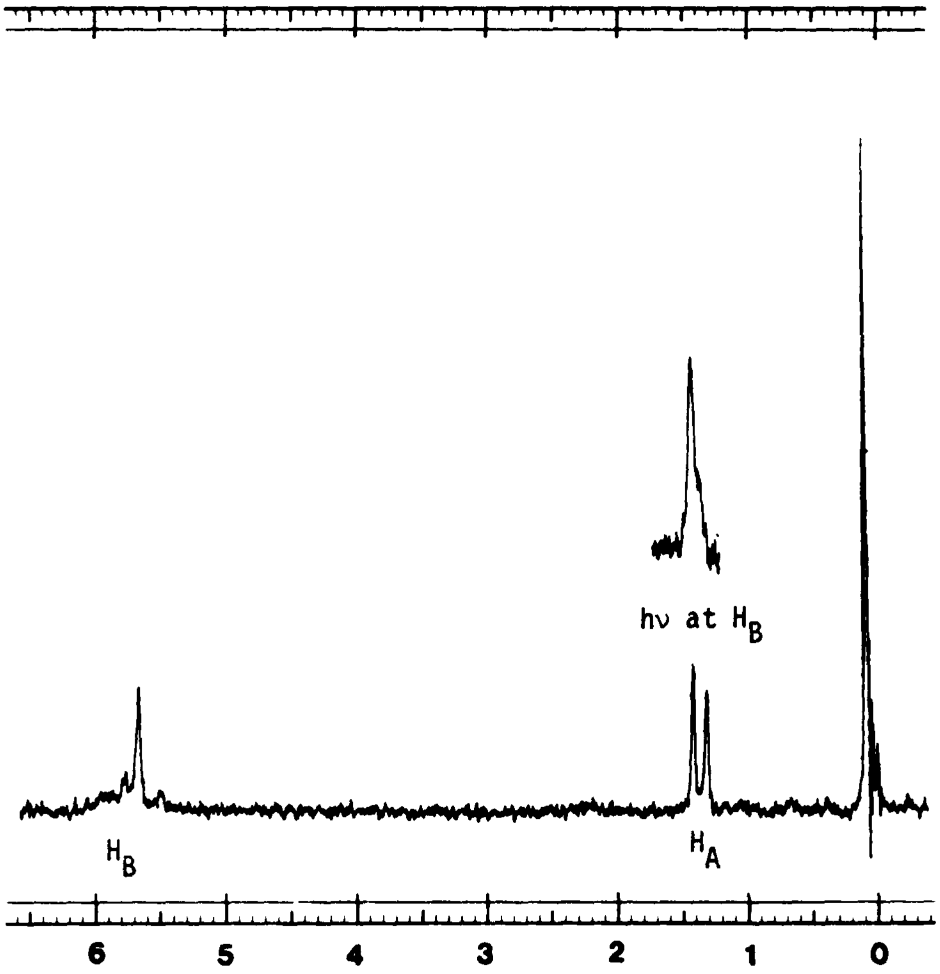


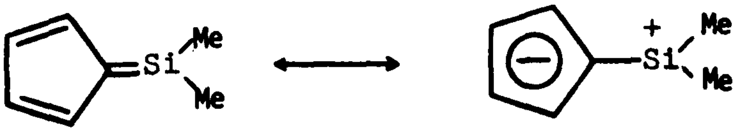
Figure 14. 60 MHz ^{1}H-NMR of 6,6-dimethyl-6-silacyclohepta-1,3-diene, 196

Addition of 196 to a degassed solution of DDQ in D_6-benzene resulted in the immediate discharge of the deep red color and the formation of a blackish precipitate. After stirring for 12 hrs at 55°C, no starting material was left. Analysis of the crude reaction showed a trace amount of a material tentatively assigned the structure of dimethylsilepin based on its low resolution mass spectrum: m/e (% rel. int.) 136 (28), 121 (85), 105 (21), 58 (100). However, the low yield defied complete spectral characterization.

In summary, an improved synthesis of a silacycloheptene -- nearly tripling the yield of the old route -- two new syntheses of a silacycloheptadiene, and a novel, though somewhat limited, synthesis of 3-chlorodimethylsilepin were achieved.

E. Syntheses of Silafulvenes

6- Silafulvene 76 has been suggested as a molecule containing a silicon-carbon double bond which could be a stable compound. This idea is derived from the qualitative view that the less electronegative the element in the 6-position, the more available will be the six π-electrons to the cyclopentadienyl ring. The CNDO calculations of 76 by Ustynyuk et al. (60) do indeed predict a large ground-state dipole moment.



76

However, the lack of "stability" of silenes might be to a large extent due to the enhanced reactivity because of this bond polarity rather than the weakness of the (p-p)π bond (62). Thus, the syntheses of silafulvenes were undertaken.

The retro-ene route to silenes introduced by Block and Revelle (9) has recently been employed to prepare silatoluene (100) and methylsilacyclopentadiene (96); thus, allylcyclopentadienyldimethylsilane 197 should thermally eliminate propene to yield 76. Synthesis (130) of 197 was accomplished in 72% yield from the coupling of cyclopentadienyldimethylsilyl chloride (131) and allylmagnesium bromide. The NMR spectrum indicated that 197 is a mixture of isomers, 5- and 1-cyclopentadienyl silanes in the respective ratio of 3.6:1 (based on the areas of the SiMe singlets at δ -0.05 and 0.15). The 1-isomer is formed from 1,5-hydrogen migration on the ring (122). As pyrolysis was the ultimate fate of 197, no attempt was made to separate the isomers.

Pyrolysis of 197 was conducted in a vacuum flow system (800°, 6×10^{-4} torr) and afforded, in 17% isolated yield, a white, crystalline material (mp 106 - 107.5°) whose mass spectrum was consistent with a dimer of 198 (calc'd for $C_{14}H_{20}Si_2$, 244.1105; measured 244.1101). However, the NMR spectrum (see Figure 15) [δ (CCl_4) -1.44 (s, 0.6H), -0.53 (s, ∿3H), 0.30 (narrow mult. of 3 spikes, ∿3H), 0.52 (like mult. at δ 0.30, ∿4H), 3.47 (brd. s, ∿1.3H), 3.74 (brd. s, ∿0.7H), 6.46 - 7.13 (hump, 7H)] was far too complex and unsymmetrical to fit any dimeric structure which could be imagined. Thus, the structure was determined to be that of 199 by single-crystal X-ray diffraction.

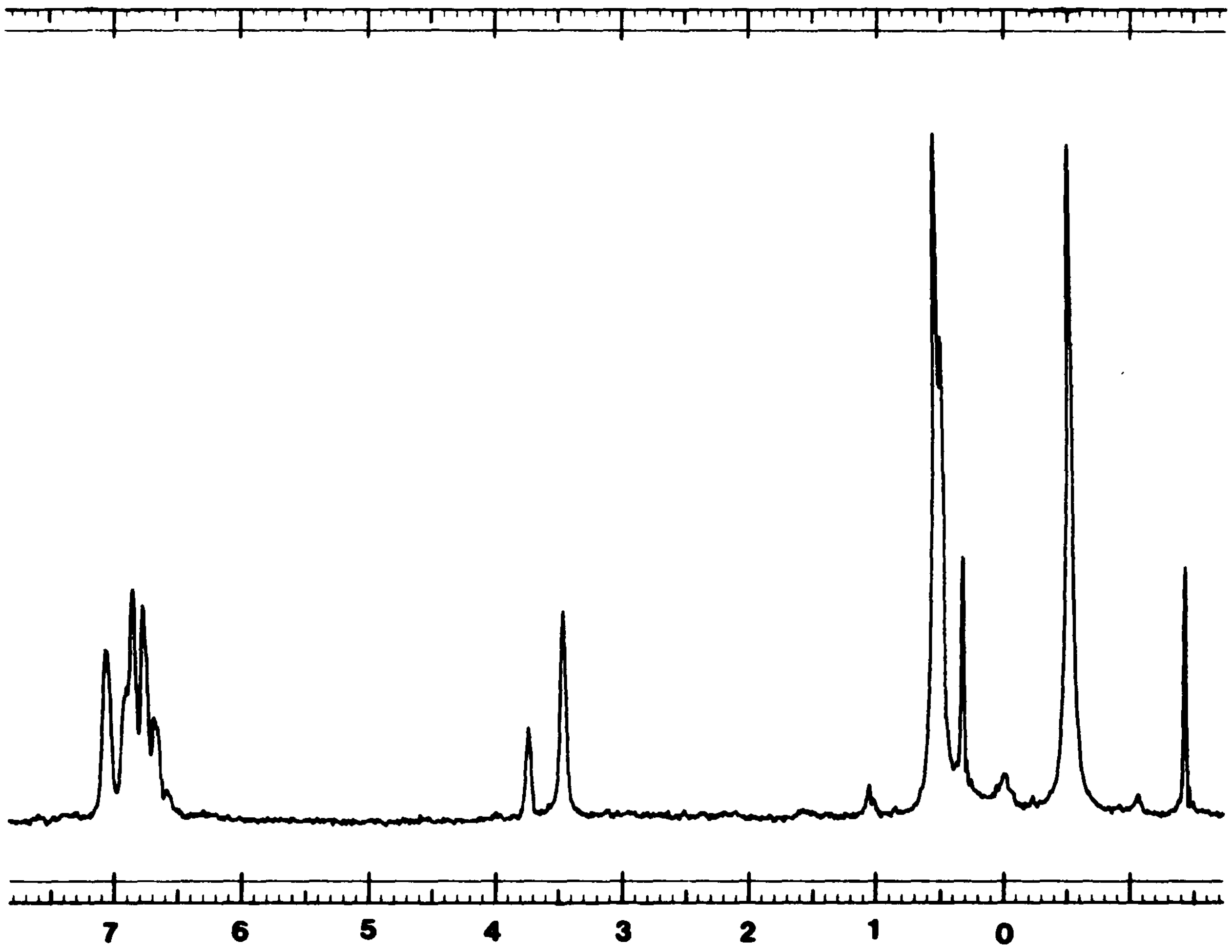
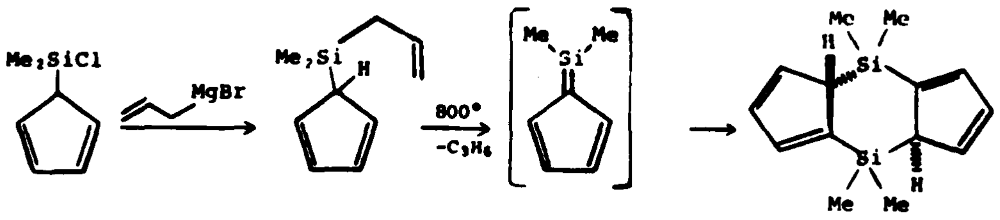


Figure 15. 60 MHz ^{1}H-NMR of 6,6-dimethyl-6-silafulvene dimers 199



197 198 199

Figure 16 is a computer generated perspective drawing of the final X-ray model of dimer 199. The molecule uses a crystallographic inversion center as a symmetry element. The cyclopentadiene fragment is essentially planar with a mean deviation from the best least-squares plane of 0.016 Å. The 1,4-disilacyclohexane is in the chair conformation. All bond distances and angles agree well with generally anticipated values.

Preliminary X-ray photographs displayed monoclinic symmetry and accurate cell constants, obtained by a least-squares fit of fifteen diffractometer measures 2θ- values, where a = 9.386(1), b = 9.115(1), c = 8.925(1) Å and β = 108.09(1)°. The systematic extinctions were uniquely compatible with space group $P2_1/n$ and a calculated ($z = 2$) and measured density of $\sim$1.12 g/cc required that the dimer be centrosymmetric. All accessible diffraction maxima with $2\theta \leq 150°$ were collected on a four-circle diffractometer using graphite monochromated CuKα (1.54178 Å) X-rays and an ω-scan technique. A total of 1427 intensities were collected in this manner, and after correction for Lorentz, polarization and background effects, 1361 (95%) were judged observed $(F_o^2 \geq 3\sigma(F_o^2))$.

A three-dimensional Patterson synthesis was readily deconvoluted to yield the Si position, and the resulting Si phased electron density synthesis yielded all nonhydrogen atoms. Hydrogen atoms were located on

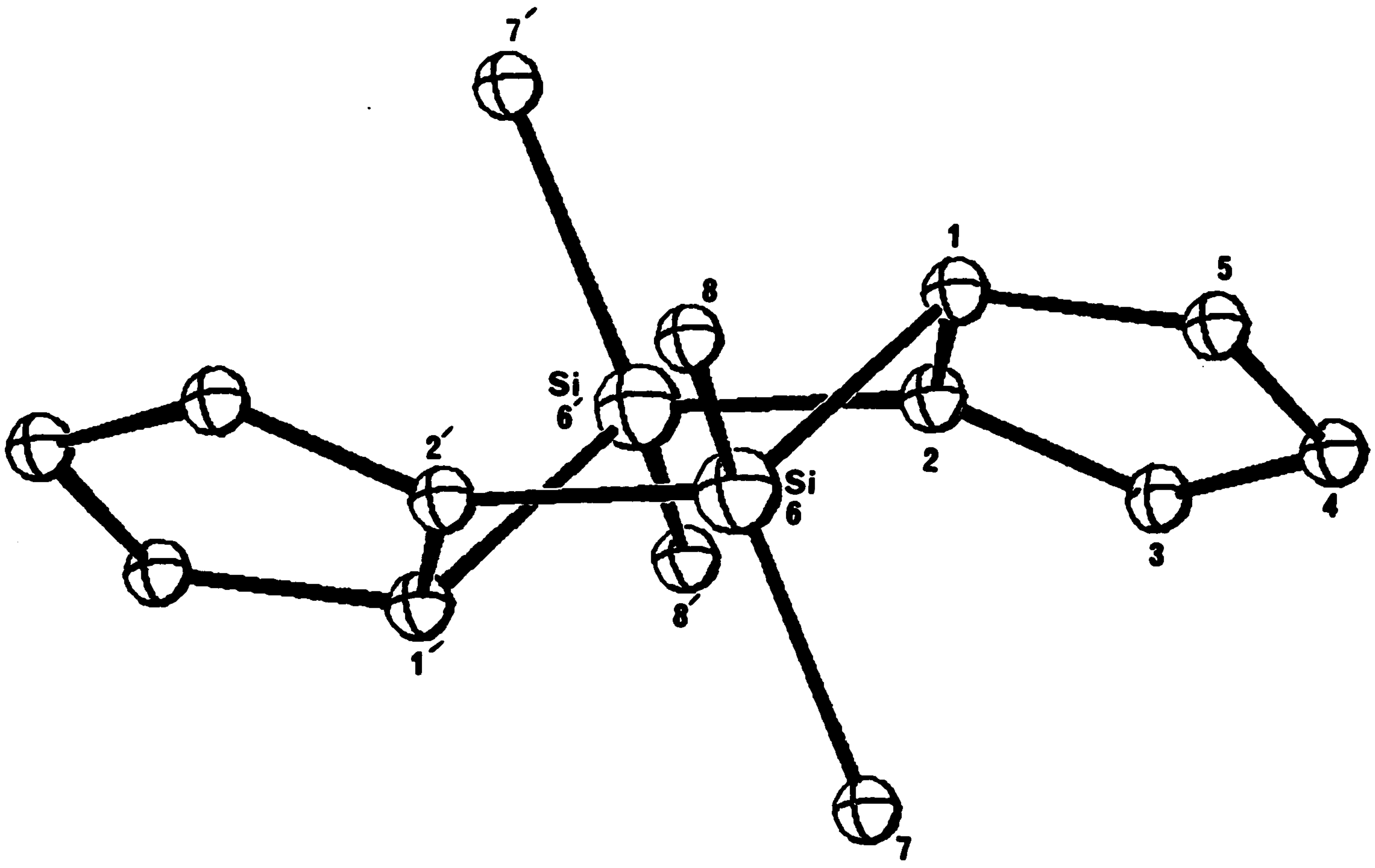
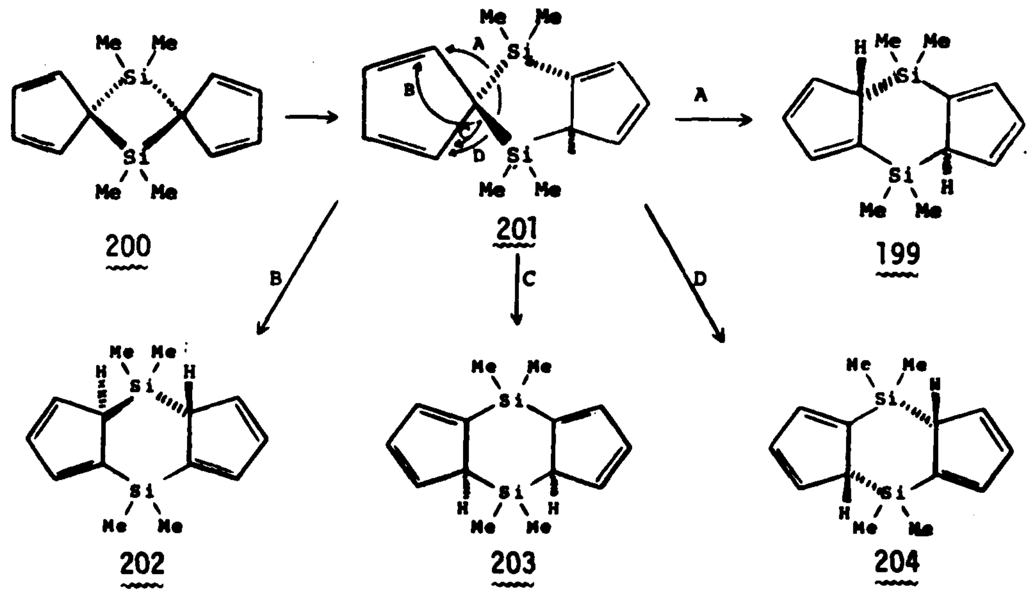


Figure 16. A computer generated drawing of silafulvene dimer 199. Hydrogens are omitted for clarity

a difference electron density synthesis computer after partial refinement. Full-matrix least-squares refinements using anisotropic thermal parameters for all nonhydrogen atoms have converged to a current crystallographic residual to 0.078 for the observed data.

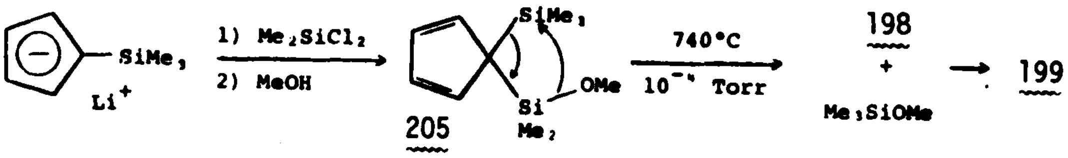
Since the highly symmetrical structure of 199 clearly did not fit the NMR spectrum, several crystals were first shown by photographs to be crystallographically identical to the crystal whose structure was determined, and then dissolved to obtain the same NMR spectrum as before. However, heating to 75° in the NMR probe caused coalescence to two broad singlets centered at δ ca. 6.1 and δ ca. -0.3, and cooling back to ambient temperature reproduced the original spectrum. The same spectrum, but with significant changes in relative peak areas, could be obtained by dissolving crystals of 199 in $DCCl_3$ at -30° and immediately obtaining the NMR spectrum at that temperature.



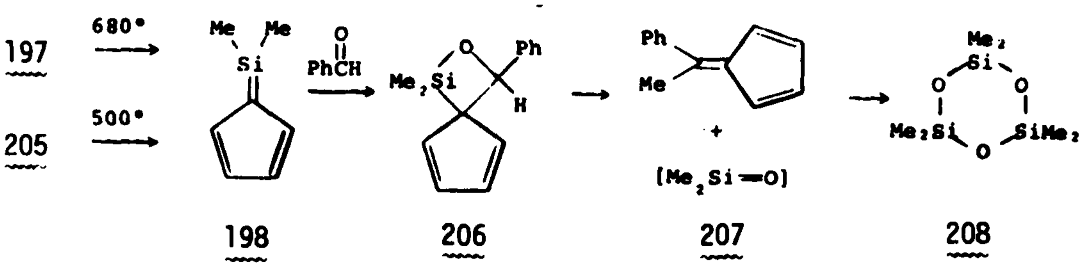
This latter result effectively eliminates the possibility that isomerization is occurring through prototropic rearrangements, since prototropic rearrangements in cyclopentadienyl silanes always occur slowly compared to the NMR time scale (122,132). Thus, in solution, 199 immediately established an isomeric equilibrium through a variety of facile 1,5-sigmatropic silyl migrations. The possible isomers of 199, which could interconvert by 1,5-silyl migrations, include structures 200 through 204.

While 199 could be formed directly from dimerization of 198, precedents in silene chemistry (71) suggest that the initial dimer be 1,3-disilacyclobutane 200.

In order to strengthen the claim that thermolysis of 197 affords 198, an alternate route to 198 was investigated. 1-Dimethylmethoxysilyl-1-trimethylsilylcyclopentadiene, 205, was prepared in 52% yield from the coupling of trimethylsilylcyclopentadienyl lithium and dichlo dichlorodimethylsilane followed by methanolysis [colorless oil; calc'd for $C_{11}H_{22}OSi_2$, m/e 226.1209, measured 226.1206]. The NMR spectrum of 205 [(CCl_4) δ -0.07 (s, 9H), -0.13 (s, 6H), 3.36 (s, 3H), 6.94 (AA'BB' center, 4H)] reveals the interesting fact that 205 is locked at room temperature as the 1,1-isomer. Presumably, this is due to attractive interaction of the methoxy oxygen and the Me_3Si group possible only in this isomer. Thermolysis of 205 (740°C, 10^{-4} torr) also afforded dimer 199 in 31% yield accompanied by the extrusion product, trimethylmethoxysilane, in 34% yield.

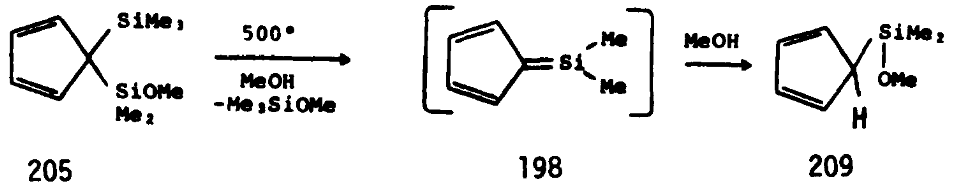


That silafulvene 198 is indeed initially formed is indicated by the results of nitrogen-flow pyrolyses of both 197 (680°) and 205 (500°) in the presence of excess benzaldehyde. Cycloaddition (71) of the carbonyl group and the Si-C double bond of 198 to 206 followed by extrusion and trimerization of dimethylsilanone 207 afforded hexamethylcyclotrisiloxane 208 in 17% and 20% yields, respectively.

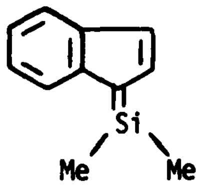


When 205 is copyrolyzed with benzaldehyde, 6-phenylfulvene is also formed (27%, GCMS and NMR analysis). Taken alone, this proves nothing since trimethylsilylcyclopentadiene will, itself, thermally react with benzaldehyde to produce this fulvene. However, in conjunction with hexamethylcyclotrisiloxane 208, this product provides strong evidence for the intermediacy and trapping of 198.

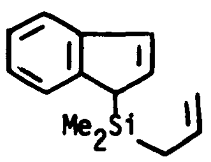
A N_2-flow copyrolysis of 197 and methanol (660°) produced a complicated product mixture. However, the milder (500°) copyrolysis of 205 and methanol afforded the desired product 209 of alcohol addition across the Si-C π bond of 198 in 58% yield. Adduct 209 was shown to decompose at 600° in a flow experiment, thus providing a rationalization for the failure of the copyrolysis of 198 and methanol.



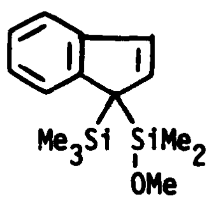
In an attempt to freeze out the [1,5] silyl shifts from the initially postulated disilacyclobutane 200, it was decided to prepare the benzosilafulvene 210. In order for the disilacyclobutane formed from dimerization of 210 to ring expand, the aromaticity of the benzene ring would have to be lost, therefore increasing the likelihood of isolating the disilacyclobutane. Both the allylsilane 211 and the 3-trimethylsily-3-dimethylmethoxysilylindene 212 were considered to be probable precursors to 210.



210

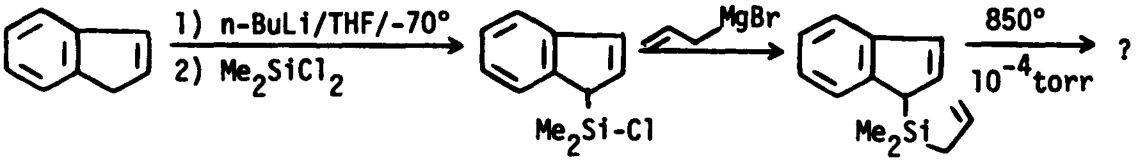


211



212

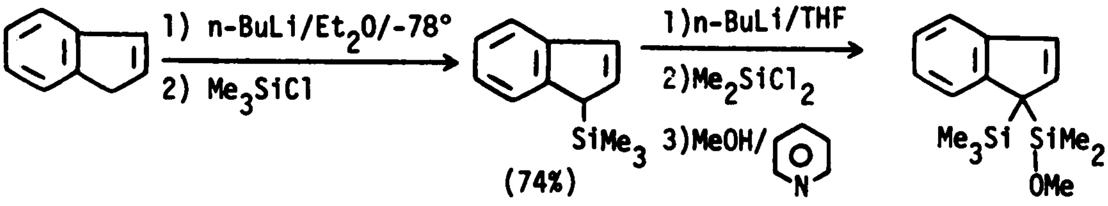
The synthesis of 211 was achieved by inverse addition of the anion of indene (*n*-BuLi, THF, -70°) to a solution of dimethyldichlorosilane in THF to afford 213 in 41% yield. Coupling of the chlorosilane 213 with allylmagnesium bromide afforded 211 in an overall yield of 31%. Distillation of 211 (25°, 1×10^{-4} torr) through a quartz tube packed with quartz chips and heated to 850°C yielded a light orange pyrolysate. Analysis of the pyrolysate by chromatography (gas, column and thin-layer) revealed a hideous mixture of products; none of which were identified.



213 211

The inability to generate 210 from 211 prompted the investigation into the thermolysis of 212. The synthesis of 212 was accomplished in 39% *via* the sequential metallation-chlorosilane quenching shown in Scheme 19. Analysis of the NMR of 212 indicated that it was a mixture of the 3,3 and the two 1,3 isomers in a ratio of 3:1:1, respectively. As pyrolysis was the ultimate fate of 212, no attempt was made to separate the isomers.

Scheme 19



(53%) 212

Distillation of 212 (25°, 1 x 10^{-4} torr) through a quartz tube packed with quartz chips and heated to 660° afforded in 37% a white crystalline material whose mass spectrum was consistent with a dimer of 210 (calc'd for $C_{22}H_{24}Si_2$, 344.14166, measured 344.14125). The presence of a broad singlet at δ 3.98 (4 H's) and a sharp singlet at δ 0.97 (6 H's) clearly revealed the material was the dimer 214 (see Figure 17). The formation of 214 can be explained by a mechanism similar to that of 6,6-dimethyl-6-silafulvene, namely, by initial dimerization of benzosilafulvene 215 to give a disilacyclobutane followed by a [1,5] silyl migration and a subsequent [1,5] hydrogen migration to rearomatize the benzene ring. In addition to 214, a 98% yield of trimethylmethoxysilane was obtained.

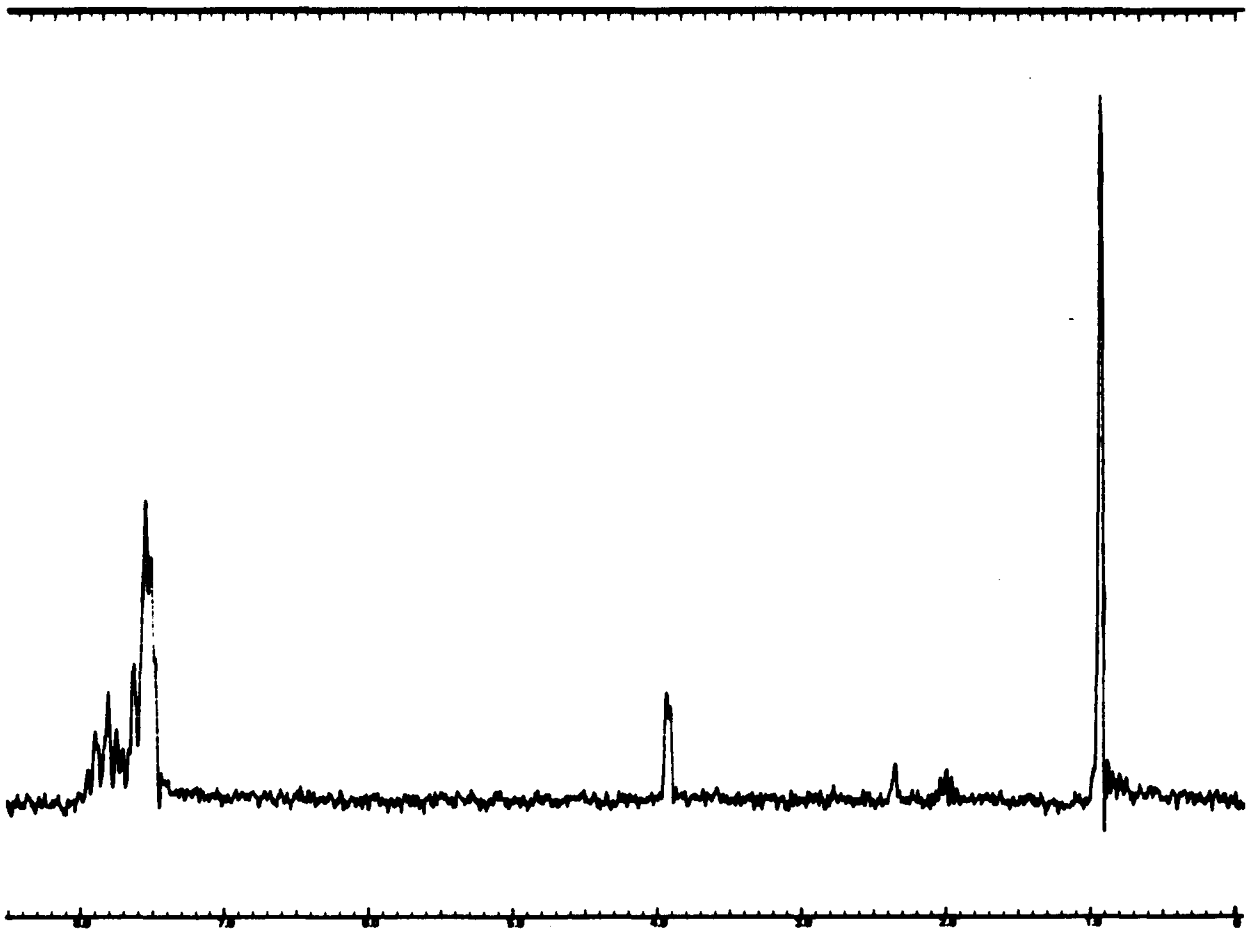
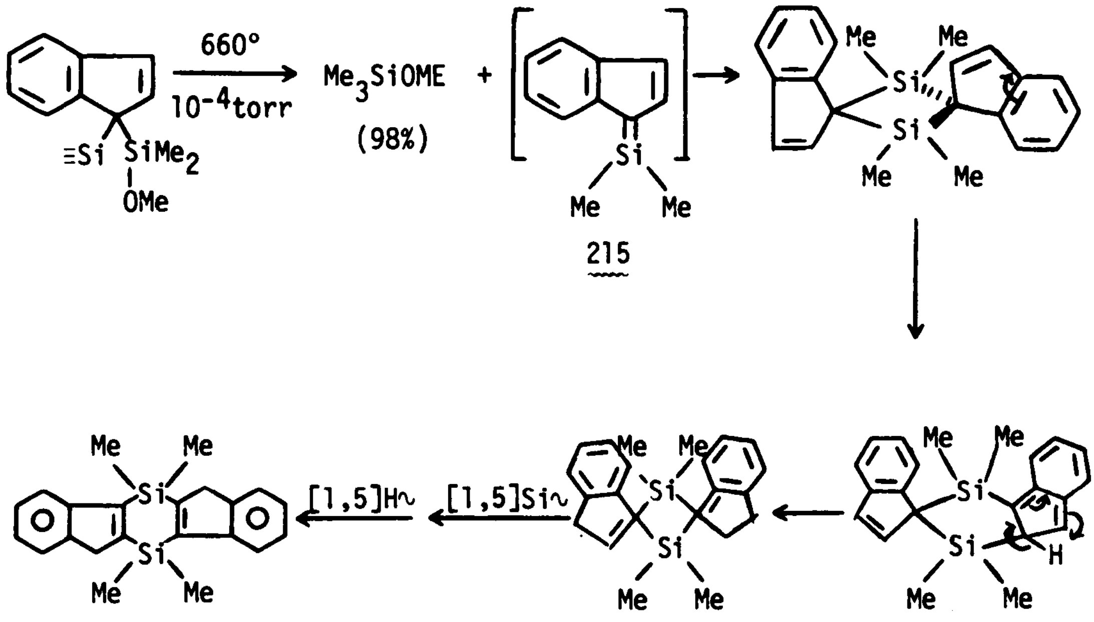
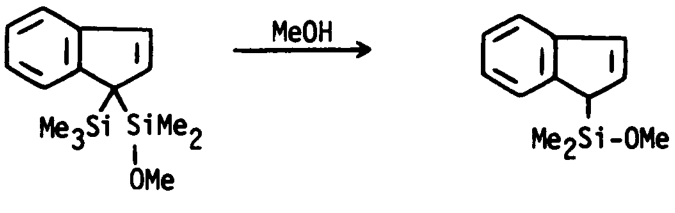


Figure 17. 60 MHz ^{1}H-NMR of benzosilafulvene dimers 214



214 (37%)

Copyrolysis of 214 with methanol in a vertical nitrogen flow system at 520° afforded in 65% yield (based on unrecovered 214) the benzosilafulvene methanol adduct 216, thus proving the intermediacy of 215.



214

216 (65%)

V. CONCLUSION

It was found that diallylsilanes in which one of the allyl groups is incorporated in a ring system undergo a thermal retro-ene elimination of propene to generate a silicon-carbon $(p\text{-}p)\pi$ bond within the ring. Thus, the thermolysis of 4-allyl-4-methyl-4-silacyclopentene provided a convenient route into 1-methylsilole. Both 1-methylsilole and 1,1-dimethylsilole, generated from the thermolysis of 5-benzoyloxy-3,3-dimethyl-3-silacyclopentene, were found to rapidly dimerize at or before room temperature when neat. In solution, 1,1-dimethylsilole was shown to dimerize completely only after ∿15 minutes at 37°C. The dimers of both siloles were shown to be a convenient *in situ* source of the monomer *via* a thermal retro-Diels-Alder.

In a similar fashion, thermolysis of 1-allyl-1-methyl-1-silacyclohexa-2,4-diene was shown to yield 1-methyl-1-silabenzene -- the first thermal and unambiguous generation. In collaboration with O. Chapman and H. Bock, the first UV, IR, and PE spectra of 1-methyl-1-silabenzene were obtained. Trapping experiments with methanol and methanol-d_1 gave the expected silene:alcohol adduct. In the presence of the acetylenes, perfluoro-2-butyne and acetylene, 1-methyl-1-silabenzene was trapped in a [4+2] Diels-Alder fashion to afford the corresponding silabarralene. In the absence of added traps, a [4+2] Diels-Alder dimer of 1-methyl-1-silabenzene was obtained.

It was conclusively shown that a beta elimination of trimethylmethoxysilane occurs upon thermolysis of trimethylsilyldimethylmethoxysilyl methanes to yield a silicon-carbon (p-p)π bond. Utilizing this novel method of generation, a new method of siletene syntheses was developed. This method of silene generation was further utilized to generate 6,6-dimethyl-6-silafulvene and 6,6-dimethyl-6-silabenzofulvene. Products isolated from both fulvenes suggest an initial head-to-tail dimerization of the silicon-carbon double bond followed by sigmatropic migrations to expand the ring. In the case of 6,6-dimethyl-6-silafulvene, the dimeric product rapidly interconverts through 1,5 silyl migrations in solution.

In addition, new methods for the syntheses of seven-membered rings containing silicon were developed. An improved synthesis of 1,1-dimethyl-1-silacyclohept-4-ene and the first two syntheses of a non-annulated silacycloheptadiene were achieved. Furthermore, evidence was obtained for the intermediacy of a silacycloheptatriene in the thermolysis of 1,1-dimethyl-4-trimethylsilyl-7,7-dichloro-1-silabicyclo[4.1.0]hept-2-ene. Although in low yield, the synthesis of 3-chloro-dimethyl silepin was achieved by the nucleophillic ring opening of a dichloro-silabicyclo[4.1.0]heptene.

VI. EXPERIMENTAL

A. Instrumentation

Routine proton NMR spectra were recorded either on a Varian model A-60, EM-360, or a Hitachi R-20B spectrometer. A Varian HA-100 spectrometer was used to record all 100 MHz spectra and a JEOL FX-90 spectrometer was used to record all 90 NHz spectra. Decoupling experiments were performed either on the Varian EM-360 or HA-100 spectrometer. All chemical shifts were reported as parts-per-million (δ scale) using either tetramethylsilane, benzene, chloroform, or acetone as internal standards.

^{13}C NMR spectra were recorded on a JEOL FX-90 spectrometer. ^{29}Si NMR spectra were recorded on a Bruker HX-90 NMR spectrometer equipped with a Nicollet 1089 data system.

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

Exact mass measurements were obtained on a MS-902 mass spectrometer. Gas chromatographic mass spectra (GCMS) were obtained on a Finnegan Model 4023 mass spectrometer.

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.

Unless otherwise specified, all GC yields were calculated from predetermined response factors and are based on the amount of starting material used.

B. Procedure and Results

1. Synthesis of methyltriallylsilane

A three-necked round-bottom flask was equipped with a reflux condensor with a drying tube, a pressure equalized addition funnel with a nitrogen inlet and a mechanical stirrer. The apparatus was flame dried and thoroughly flushed with nitrogen. The flask was charged with 0.675 L (0.545 moles) of 0.808 M allylmagnesium bromide in ether (133). To this stirring solution was added 20.0 gms (0.13 moles) of methyltrichlorosilane at a rate sufficient to maintain a gentle reflux. After the addition was complete, the flask and contents were cooled to -20° (CCl_4/Dry Ice) and 0.125 L of a 10% NH_4Cl solution was added over a 90 minute interval. After warming to room temperature, the two layers were separated and the ether layer dried over $MgSO_4$, filtered, and the solvent stripped by rotary evaporation. The residue was distilled at 88-90°/43 torr to afford 21.2 gms (98.2%) of methyltriallylsilane: NMR (CCl_4) δ 0.00 (s, 3H), 1.53 (d, 6H, J = 8 Hz), 4.64-6.17 (m, 9H); mass spectrum (70 eV) m/e (% rel. int.) 166 (2), 125 (100), 97 (35), 85 (13), 83 (21), 59 (68); ^{29}Si NMR, 81.38 ppm.

2. Synthesis of 1-methyl-1-allyl-1-silacyclobutene 95

Methyltriallylsilane was slowly distilled (25°C, 9×10^{-4} torr) through a quartz tube packed with quartz chips and heated to 820°C. The pyrolysate was collected in a liquid nitrogen trap and represented a 55% mass recovery. Compound 95 was isolated by preparative gas chromatography on a 12' x 1/4" 20% SE-30 on Chromosorb W column at 80°C and identified on the basis of its spectra: NMR (CCl_4) δ 0.32 (s, 3H), 1.48 (d, 2H, J = 2 Hz), 1.75 (d, 2H, J = 8 Hz), 4.68-5.15 (m, 2H), 5.56-6.07 (m, 1H), 6.17 (d, 2H, J = 8 Hz), 7.12 (d of t, J = 8 Hz, J = 2 Hz); mass spectrum (70 eV) m/e (% rel. int.) 124 (1), 109 (17), 96 (58), 83 (100), 67 (11), 55 (27), calc'd for $Si_1C_7H_{12}$ 124.07083, measured 124.07078, IR (neat) 3180, 3160, 2960, 2920, 1635, 1512, 1250, 895.

3. Vacuum pyrolysis of 95

Compound 95 was slowly distilled (25°, 1×10^{-3} torr) through a quartz tube packed with quartz chips and heated to 810°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 66% mass recovery. The four major products were isolated by preparative GC on a 12' x 1/4" 15% SE-30 on Chromosorb W column at 100°C. Benzene, cyclohexa-1,3-diene, and allylsiletene 95 were identified by comparison of their NMR and GC mass spectrum with those of the authentic material. Compound 96 was identified on the basis of its 60 MHz ^1H-NMR: (CCl_4) δ 253 (broad s, 4H), 4.72 (m, 2H), 6.11 (broad s, 2H).

4. Synthesis of 103

A 250 mL, three-necked round-bottom flask was equipped with a reflux condensor with a drying tube, a pressure equilized addition funnel with a nitrogen inlet, and a mechanical stirrer. The flask was charged with 100 mL of freshly distilled ether from LAH and 6.456 grams (0.0264 moles) of 2,2-dichlorohexamethyltrisilane. To this stirring solution was added 0.080 L (0.064 moles) of 0.80 M allylmagnesium bromide in ether over a 90 minute interval. After the addition was complete, the reaction was allowed to stir at room temperature for 1.5 hours. The flask and contents were then cooled to -20°C and 50 mL of 10% NH_4Cl added over 30 minutes. The two layers were separated and the ether layer further washed with water. After drying over Na_2SO_4, the ether was filtered and removed by rotary evaporation. The residue was distilled at 142-145°/22 torr to afford 3.31 grams of 103 (49% yield): NMR (CCl_4) δ 0.15 (s, 18H), 2.71 (d, 4H, J = 8 Hz), 4.69-5.09 (m, 4H), 5.47-6.24 (m, 2H); mass spectrum (70 eV) m/e (% rel. int.) 256 (2), 241 (2), 215 (12), 155 (16), 154 (14), 142 (16), 141 (84), 131 (14), 127 (39), 117 (11), 116 (11), 115 (12), 99 (10), 85 (10), 73 (100), 59 (35), calc'd for $C_{12}H_{28}Si_3$ 256.14989, measured 256.14976.

5. Vacuum pyrolysis of 103

Compound 103 was distilled (25°, 1×10^{-3} torr) through a quartz tube packed with quartz chips and heated to 820°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 46% mass recovery. Five major products were isolated by preparative gas chromatography on a 12' x 1/4" 20% OV101 on Chromosorb P column using a temperature program of 80°C to 250°C at 2° per minute. Trimethylsilane (2%), trimethylvinylsilane (3%), and trimethylallylsilane (7%) were identified by comparison of their GC mass spectrum and proton NMR with that of an authentic sample. The fourth major product (4% GC yield) was identified as 3,3,5-trimethyl-3,5-disilacyclopentene 104 on the basis of its spectra: NMR (CCl_4) δ -0.26 (center of apparent AB coupled to Si-H, J = 2 Hz, J = 4 Hz; irradiation at Si-H (δ 4.42) collapses to apparent doublet, presumably AB with wings hidden in baseline), 0.19 (s, 6H), 0.22 (d, 3H, J = ∿3 Hz, collapses to singlet with irradiation at δ 4.42), 4.42 (m, 1H), 7.08 (s, 2H); mass spectrum (70 eV) m/e (% rel. int.) 142 (27), 141 (7), 127 (100), 101 (11), 99 (13), 85 (12), 73 (13), 67 (13), 59 (16), calc'd for $C_6H_{14}Si_2$ 142.06341, measured 142.06422. The fifth major product was identified as 105 (14%) on the basis of its spectra: NMR ($CDCl_3$) δ -0.46 to -0.06 (overlapped multiplet, 4H), 0.02 (s, 9H), 0.09 (s, 3H), 0.11 (s, 3H), 3.37 (apparent pentet, 1H, collapses to singlet with irradiation in the region of -0.46 to -0.06), 6.08 (s, 2H); mass spectrum (70 eV) m/e (% rel. int.) 214 (2), 199 (100), 171 (35), 141 (13), 113 (10), 99 (11), 92 (12), 85 (11), 73 (40), 59 (24), calc'd for $Si_3C_9H_{22}$ 214.10294, measured 214.10199.

6. Synthesis of 1,1-diallyltetramethyldisilane 106

To a stirring solution of 8.09 gms (0.0433 moles) of 1,1-dichlorotetramethyldisilane in 40 mL of dry ether was added 0.125 L (0.10 moles) of 0.80 M allylmagnesium bromide in ether over a one hour interval.

After stirring for an additional 5 hours, the reaction was cooled to -20°C (CCl_4/Dry Ice) and ∿20 mL of a 10% NH_4Cl solution was added. The two layers were separated and the ether layer further washed with water. After drying over Na_2SO_4, the ether was filtered and the solvent removed *via* rotary evaporation. Distillation of the residue at 38-43°C/0.1 torr afforded 3.87 gms (45%) of 106: NMR (CCl_4) δ 0.09 (s, 12H), 1.62 (d, 4H, J = 8 Hz), 4.59-4.99 (m, 4H), 5.36-6.09 (m, 2H); mass spectrum (70 eV) m/e (% rel. int.) 198 (2), 157 (98), 129 (67), 117 (29), 85 (14), 73 (100), calc'd for $Si_2C_{10}H_{22}$ 198.12601, measured 198.12599.

7. Vacuum pyrolysis of 1,1-diallyltetramethyldisilane 106

Diallylsilane 106 was distilled (25°, 1×10^{-3} torr) through a quartz tube packed with quartz chips and heated to 720°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented an 83% mass recovery. Three major products and starting material were isolated by preparative gas chromatography on a 12' x 1/4" OV101 on Chromosorb P column at 170°C. Trimethylvinylsilane (5.6%) was identified by comparison of its GC mass spectrum, GC retention time, and proton NMR with that of an authentic sample. The second major product, 3,3,5-trimethyl-3,5-disilacyclopentene (6.3%), had spectra identical with those reported in the pyrolysis of 103. The third major product, 3,3,5,5-tetramethyl-3,5-disilacyclopentene (10.7%), was identified on the basis of its spectra: NMR ($CDCl_3$) δ -0.38 (s, 2H), 0.16 (s, 12H), 7.15 (s, 2H); GCMS, m/e (% rel. int.) 156 (29), 143 (13), 141 (100), 113 (15), 73 (25), 63 (17), 59 (17), 45 (14), 43 (23). Both the NMR and mass spectra match those published by Fritz and coworkers (134).

8. Synthesis of trimethylsilyl(dimethylsilyl)methane **111**

A 500 mL two-necked round-bottom flask was fitted with a reflux condensor with drying tube, a stirring bar, and a pressure equilized addition funnel with a nitrogen inlet. The flask was flame-dried and thoroughly flushed with nitrogen and 2.697 gms (0.111 moles) of magnesium powder and 150 mL of dry THF were then added. To this stirring solution was added 16.7 gms (0.10 moles) of trimethylbromomethylsilane in 10 mL of THF over a 90 minute interval. After stirring for an additional 30 minutes, 9.40 gms (0.10 moles) of dimethylchlorosilane was added over 40 minutes. The reaction mixture was cooled to room temperature, poured into 300 mL of pentane, filtered through celite and the filtrate distilled. The fraction boiling at 118-120°C was collected to afford 7.82 gms (54% yield) of **111**. NMR (CCl_4) δ -0.31 (d, 2H), 0.04 (s, 9H), 0.08 (d, -H), 4.03 (m, 1H).

9. Synthesis of trimethylsilyl(dimethylmethoxysilyl)methane **110**

To a stirring suspension of 0.71 gms of 5% Pd/charcoal in 35 mL of methylene chloride was added sequentially 3.44 gms (0.0236 moles) of **111** followed by the slow addition of 0.755 gms (0.0236 moles) of absolute methanol over a 45 minute interval. After the evolution of hydrogen ($\sim$20 minutes) had subsided, the solution was filtered through celite and the filtrate distilled at 57-59°C/35 torr to afford 2.71 gms of **110**: GCMS (70 eV) m/e (% rel. int.) 161 (p-Me, 100), 131 (70), 89 (11), 73 (41), 59 (75).

10. Vacuum pyrolysis of trimethylsilyl(dimethylmethoxysilyl)methane 110

Compound 110 was distilled (25°C, 1×10^{-4} torr) through a quartz tube packed with quartz chips and heated to 860°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a mass recovery of 92%. Trimethylmethoxysilane (58%), 1,1,3,3-tetramethyl-1,3-disilacyclobutane (42%) and unreacted 110 were isolated by preparative gas chromatography on an 8' x 1/4" 20% DC550 on Chromosorb P column using a temperature program of 100° to 130° at 2°/min, and identified by comparison of their proton NMR and GC mass spectra with those of an authentic sample.

11. Preparation of methoxymethylpentamethyldisilane 109

Methoxymethylpentamethyldisilane was prepared by the method of Tamao and Kumada (82). To a flask containing 6.69 gms (0.25 moles) of magnesium turnings, 0.40 gms of mercuric chloride, and 15.0 gms (0.090 moles) of pentamethylchlorodisilane in 150 mL of dry THF was added 21.8 gms (0.27 moles) of chloromethyl methyl ether over a 4 hour period. After stirring overnight (*ca*. 12 hours), the reaction mixture was poured into an ice/saturated NH_4Cl solution. The aqueous layer was extracted with hexane. After drying over $MgSO_4$, the hexane layer was filtered and the filtrate concentrated *in vacuo*. The residue was distilled with the fraction boiling 108-110° at 102 torr being collected. Yield 6.639 gms (42%): NMR (CCl_4) δ 0.07 (broad s, 15H), 3.11 (s, 2H), 3.27 (s, 3H); mass spectrum (70 eV) m/e (% rel. int) 161 (*p*-Me, 19), 313 (43), 89 (23), 75 (41), 73 (100), 59 (37).

12. Vacuum pyrolysis of methoxymethylpentamethyldisilane 109

Methoxymethylpentamethyldisilane was distilled (25°, 1×10^{-3} torr) through a horizontal quartz tube packed with quartz chips and heated to 800°C. The pyrolysate was collected in a trap cooled with liquid nitrogen. Analysis of the pyrolysate on an 8' x 1/4" 20% DC550 column at 80°C showed the absence of a peak in the area where 1,1,3,3-tetramethyl-1,3-disilacyclobutane would come off. The presence of starting material was confirmed by GC retention time.

13. Preparation of 1,3-bis(trimethylsilyl)propene 116

To a stirring solution of 17.98 gms (0.126 moles) of trimethylallylsilane in ether at 0°C (under nitrogen) were added 15.95 gms (0.156 moles) of tetramethylethylenediamine followed by slow addition of 66.0 mL (0.126 moles) of a 2.40 M n-BuLi/hexane solution. After stirring for 5 hours at 0°, 15.0 gms (0.139 moles) of trimethylchlorosilane was added. Stirring was continued for 30 minutes and then the reaction mixture was poured into ice and water. After separating the two layers, the ether layer was further washed with water and then dried over $MgSO_4$, filtered and the filtrate concentrated *in vacuo*. The residue was distilled at 70-73° at 6 torr to afford 20.18 gms of 116 (86% yield): NMR (CCl_4) δ -0.16 (s, 9H), -0.13 (s, 9H), 1.38 (d, 2H, J = 7Hz), 5.21 (d, 1H, J = 19 Hz), 5.88 (center of d of t, 1H, J = 19 Hz, J = 7 Hz).

14. Preparation of 1,3-bis(trimethylsilyl)-3-dimethylmethoxysilylpropene 112

To a stirring solution of 4.38 gms (0.0236 moles) of 116 in 70 mL of dry ether at 0°C (under a nitrogen atmosphere) were added 2.47 gms (0.0242 moles) of TMEDA followed by the slow addition of 10.0 mL of a 2.4 M n-BuLi/hexane solution. After stirring for ∿4 hours at 0°C, the anion was syringed into a flask containing 10.64 gms (0.083 moles) of dimethyldichlorosilane in 250 mL of ether at room temperature. The solution was stirred for several hours. The ether was then removed by rotary evaporation and the residue taken up in pentane. The pentane was filtered through celite and the filtrate added to a stirring solution of 3.95 gms (0.123 moles) of methanol and 9.78 gms (0.124 moles) of pyridine in 200 mL of hexane. The precipitated pyridinium hydrochloride salts were filtered and the filtrate concentrated by rotary evaporation. Distillation of the residue at 74-76°C at 0.1 torr afforded 3.57 gms (55%) of 112: NMR (CCl_4) δ 0.00 (s, 2 $SiMe_3$, 18H), 0.03 (s, 6H, $SiMe_2$), 1.23 (d, $J = 10$ Hz, $Si\text{-}CH_2\text{-}Si$, 1H), 3.3 (s, OMe, 3H), 5.18 (d, $Me_3SiC\underline{H}{=}$, $J = 18$ Hz), 5.82 (d of d, $Me_3Si\text{-}C{=}C\underline{H}$, $J = 10$ and 18 Hz, $h\nu$ at δ 1.23 collapses to d, $J = 18$ Hz); mass spectrum m/e (% rel. int.) 274 (20), 259 (35), 171 (100), 156 (58), 89 (35), 73 (90), calculated for $C_{12}H_{30}Si_8O$ m/e 274.1605, measured m/e 274.1607.

15. Vacuum pyrolysis of 1,3-bis(trimethylsilyl)-3-dimethylmethoxysilylpropene 112

Compound 112 was distilled (25°, 1×10^{-5} torr) through a horizontal quartz tube packed with quartz chips and heated to 700-720°. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented an 82% mass recovery. Trap to trap distillation of the pyrolysate afforded two fractions. The first fraction was identified as trimethylmethoxysilane (71%, NMR yield) by comparison of its spectra with those of an authentic sample. The second fraction (b.p. ∿40° at 0.1 torr) was identified as 4-trimethylsilyldimethylsiletene 113 (56%, NMR yield) on the basis of its spectra: NMR (CCl_4) δ 0.0 (s, $SiMe_3$, 9H), 0.33 (s, $SiMe_2$, 6H), 1.23 (apparent t actually overlapped d of d, 1H), 6.2 (d of d, J = 1.5 and 7.5 Hz, hν at δ 1.2 collapses to d with J = 7.5 Hz, 1H), 7.13 (d of d, J = 1.7 and 7.5 Hz, hν at δ 1.2 collapses to d with J = 7.5 Hz, 1H); mass spectrum (70 eV) m/e (% rel. int.) 170 (24), 155 (46), 127 (15), 73 (100), 59 (15), calc'd for $C_8H_{18}Si_2$ m/e 170.0947, measured 170.0947; IR (neat) 3080, 2980, 2920, 1500, 1250 cm^{-1}. Attempts to GC prep the pyrolysate failed to afford the siletene which apparently decomposed on the column. Instead, trimethylmethoxysilane and a compound tentatively assigned structure 114 on the basis of its spectra were obtained: NMR (CCl_4) δ 0.06 (s, 9H), 0.12 (d, 6H, collapses to singlet with hν at 3.99), 3.99 (m, Si-H, 1H, partially collapses with hν at 0.12), 4.24 (d, J = 2Hz, 1H).

16. Synthesis of 1,3-bis(trimethylsilyl)-3-methyldimethoxysilylpropene 115

To a starting solution of 8.49 gms (0.0457 moles) of 116 and 4.67 gms (0.0457 moles) of TMEDA in 100 mL of dry ether at 0°C (under a nitrogen atmosphere) was added 19.5 mL (0.0468 moles) of a 2.4 M n-BuLi in hexane solution over 30 minutes. After stirring for 3 hours at 0°C, the anion was transferred into a flask containing 25.5 gms (0.171 moles) of methyltrichlorosilane in 200 mL of ether cooled to 0°C. The solution was stirred for several hours at 0°C. The ether was then removed by rotary evaporation and the residue taken up in pentane. The pentane was filtered through celite and the filtrate added to a stirring solution of 6.33 gms (0.198 moles) of methanol and 15.65 gms (0.198 moles) of pyridine in 350 mL of hexane. The precipitated pyridinium hydrochloride salts were filtered and the filtrate concentrated by rotary evaporation. Distillation of the residue at 80-81° at 0.1 torr afforded 6.38 gms (48%) of 115: NMR (CCl_4) δ 0.0 (s, $SiMe_3$, 9H), 0.02 (s, $SiMe_3$, 9H), 0.04 (s, SiMe, 3H), 1.3 (d, J = 10 Hz, $SiC\underline{H}_2Si$, 1H), 3.4 (s, OMe, 6H), 5.22 (d, J = 18 Hz, 1H), 5.82 (d of d, J = 10 and 18 Hz); mass spectrum (70 eV) m/e (% rel. int.) 290 (27), 275 (37), 186 (80), 171 (27), 156 (15), 132 (25), 73 (100), 59 (28), calc'd for $Si_3C_{12}H_{30}O_2$ m/e 290.1554, measured m/e 290.1557.

17. Vacuum pyrolysis of 1,3-bis(trimethylsilyl)-3-methyldimethoxysilylpropene 115

Compound 115 was distilled (25°C, 1 x 10^{-4} torr) through a horizontal quartz tube packed with quartz chips and heated to 740°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 95% mass recovery. Fractional distillation of the pyrolysate afforded 4-trimethylsilyl-1-methyl-1-methoxy-1-silacyclobut-2-ene 117 in 74% yield as an approximately equal mixture of *cis* and *trans* stereoisomers: b.p. 45-50° at ∿ 0.5 torr; NMR (CCl_4) δ 0.0 (s, 2 $SiMe_3$), 0.02 (s, SiMe), 0.25 (s, SiMe), 1.28 (d, Si-C$\underline{H_2}$-Si, J = 2Hz, hν at *ca.* δ 7 collapses to 2), 1.43 (apparent t, actually overlapped d of d, hν at δ 7 or δ 5.9 collapses to d, Si-C$\underline{H}$-Si), 3.33 (s, SiOMe), 3.38 (s, SiOMe), 5.94 (d, SiC$\underline{H}$=, J = 7.5 Hz), 5.88 (d of d, SiC$\underline{H}$=, J = 7.5 Hz and 2.5 Hz, hν at δ 1.43 collapses to d with J = 7.5 Hz), 6.96 (center of apparent t of d which is actually an overlapped pair of d of d at δ 7.01 and δ 6.91, J = 6.8 and 2 Hz for the upfield d of d, and J = 6.4 and 1.5 Hz for the other, hν at δ 1.43 collapses the downfield d of d to a d with J = 6.4 Hz, and hν at δ 1.28 collapses the upfield d of d to a d with J = 6.8 Hz); mass spectrum (70 eV) m/e (% rel. int.) 186 (27), 171 (40), 144 (55), 117 (49), 89 (90), 73 (100), 59 (66), calc'd for $C_8H_{18}Si_2O$ m/e 186.0896, measured m/e 186.0891; IR (neat) 3040, 2960, 1495, 1250, 1090, 840 cm^{-1}.

18. Vacuum pyrolysis of 117

Compound 117 was distilled (25°, 1×10^{-4} torr) through a quartz tube packed with quartz chips and heated to 760°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 71% mass recovery. Two major products were isolated by preparative gas chromatography on an 8' x 1/4" DC550 on Chromosorb W column at 140°C. The first product was identified as 1,4-dimethyl-1-trimethylsiloxy-1-silacyclobut-2-ene 118 on the basis of its spectra: NMR (CCl_4) δ 0.00 (s, 3H), 0.10 (s, 9H), 0.97 (d, 3H), 1.40 (m, 1H), 5.32 (d of d, J = 14 and 2.5 Hz, collapses to d with hν at 1.40 with J = 14 Hz, 1H), 6.45 (d of d, J = 14 and 4 Hz, collapses to d with hν at 1.40 with J = 14 Hz, 1H); mass spectrum (70 eV) m/e (% rel. int.) 188 (3), 187 (7), 180 (M^+, 40), 171 (100), 143 (76), 133 (24), 131 (14), 117 (66), 78 (11), 73 (56), 66 (12), 59 (32). The second product was identified as 119 on the basis of its spectra: NMR (CCl_4) δ 0.09 (s, 9H), 0.19 (d, collapses to s with hν at 4.49, 3H), 3.36 (s, OMe, 3H), 4.37 (s, 2H), 4.49 (m, collapses to s with hν at 0.19, 1H); mass spectrum (70 eV) m/e (% rel. int.) 186 (13), 171 (24), 143 (59), 141 (17), 131 (21), 117 (70), 115 (10), 96 (18), 89 (64), 73 (86), 59 (100).

19. Flow pyrolysis of 117 and 2,3-dimethylbutadiene

A solution consisting of 150 μL of 117 and 500 μL of 2,3-dimethylbutadiene was slowly dripped into a vertical quartz tube packed with quartz chips and heated to 580°C. The pyrolysate was swept into a trap cooled with liquid nitrogen by a continuous nitrogen stream of *ca.*

30 mL/minute. Analysis of the pyrolysate by GC mass spectra revealed the absence of a silacyclobutadiene:2,3-dimethylbutadiene adduct.

20. Synthesis of 4-allyl-4-methyl-4-silacyclopentene 120

To a stirring solution of 1.35 L (1.08 moles) of 0.80 M allylmagnesium bromide in ether was added 83.5 gms (0.632 moles) of 4-chloro-4-methyl-4-silacyclopentene in 400 mL of ether over a 3 hour interval. After stirring at room temperature for 5 hours, the reaction was cooled to -20°C and 400 mL of a 10% NH_4Cl solution was added dropwise over 2 hours. The two layers were separated and the ether layer further washed with water and then dried over $MgSO_4$. After filtering, the ether was removed by rotary evaporation and the residue distilled at 42-44° at 12 torr to afford 63.1 gms (72%) of 120: NMR (CCl_4) δ -0.04 (s, 3H, SiMe), 1.05 (s(br), 4H, ring CH_2), 1.41 (center of apparent d of t actually overlapped d of d, $J_{vic} = 8$ Hz, $J_{1,3\text{-}\underline{trans}} \sim J_{1,3\text{-}\underline{cis}} \sim 1$ Hz, allylic CH_2, 2H), 4.49-4.74 (vinyl mult., 2H), 5.29-5.72 (vinyl mult., 3H); mass spectra (70 eV) m/e (% rel. int.) 138 (1), 97 (100), 96 (66), 95 (28), 69 (14), 43 (20), calc'd for $C_6H_{14}Si$ m/e 138.0865, measured m/e 138.0862.

21. Vacuum pyrolysis of 4-allyl-4-methyl-4-silacyclopentene 120

Compound 120 was distilled (25°, 4×10^{-4} torr) through a horizontal quartz tube packed with quartz chips and heated to 820°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 68% mass recovery after allowing the propene to escape. Two major fractions (presumably *endo*- and *exo*-adducts) were isolated by preparative gas chromatography on a 10' x 1/4" OV101 on Chromosorb W column at 110°C and identified as Diels-Alder dimers of **122** existing as a mixture of isomers varying in the stereochemistry at the two silicon atoms. Both fractions had essentially identical mass spectra: m/e (% rel. int.) 192 (27, M^+), 177 (29, P-Me), 164 (24, P-C_2H_4), 147 (72, silaindane-H), 145 (100, silaindene-H), 121 (45, m/e 147-C_2H_2), 119 (17, m/e 145-C_2H_2), 105 (39), 96 (72), 95 (46), 93 (43), 69 (45), 55 (56), 53 (56); the NMR spectrum (CCl_4) of the major fraction was the least complicated: δ 0.42 (SiMe, center of three d's *ca*. 1:2:1), 1.84 and 2.00 (Hg, centers of two sets of d of d of d, hν at H_b or H_f collapses to four d's), 2.83 (H_f and $H_{f'}$, center of complex mult., partially collapses with hν at H_c, H_e, H_i or H_j), 3.39 (H_b, sym. apparent pentet), 4.00 (H_c, center of mult. which collapses to broad s with hν at SiMe), 4.91 (H_a, mult. collapsing to s with hν at SiMe), 5.99 (H_h, d of d with low field d overlapping upfield part of H_i, hν at H_c collapses to sharp d), 6.12 (H_i, broad t collapsing to d with hν at H_f), 6.72 (H_j, broad d becoming shapr with hν at H_c, or broad s with hν at H_h), 6.45 (broad t, collapses to d with hν at H_f; mass spectra (70 eV) calc'd for $C_{10}H_{16}Si_2$ m/e 192.07906, measured 192.07837. The NMR spectrum of the minor fraction (19.2%) was also consistent with that of a Diels-Alder dimer of **122**: NMR ($CDCl_3$) δ 0.21 (SiMe, center of three d's *ca*. 1:2:1), 2.12 (center of complex multiplet), 3.75 (m, partially collapses with hν at 0.21), 4.32 (m, partially collapses with hν at 2.12), 4.75 (broad singlet), 5.62-6.0 (m, partially collapses with 3.75), 6.08-6.35

(broad m), 6.50 (apparent d of t, collapses to d with hν at 3.75); mass spectra (70 eV) calc'd for $C_{10}H_{16}Si_2$ m/e 192.07906, measured m/e 192.07722.

22. Attempted reaction of silole dimers 123 with TCNE

In a thick walled tube fitted with a joint were placed 0.4347 gms (0.00226 moles) of 123 and 0.7148 gms (0.00558 moles) of tetracyanoethylene (TCNE). The tube was degassed by the freeze-thaw method and sealed. Within 30 minutes of placing the sealed tube in an oil bath heated to 90°C, a violent explosion occurred.

23. Reaction of silole dimers 123 with maleic anhydride

A solution of 1.0572 gms (0.00551 moles) of 123, 1.0841 gms (0.0111 moles) of maleic anhydride, and 5 mL of toluene was degassed and sealed in a heavy walled tube. The tube was heated at 160°C for 4.5 hours. After opening, the solution was filtered and the solvent removed under reduced pressure. The residue, a light orange oil, was identified as a mixture of syn and anti isomers of the maleic anhydride:methylsilole adduct 124 on the basis of its spectra: NMR ($CDCl_3$) δ 0.10 (d, $J = 3$ Hz, hν at either H_C or $H_{C'}$, collapses to broad s, 3H, SiMe), 2.48 (very broad hump which sharpens with hν at H_D, 2H, H_A), 3.46 and 3.54 (two identical d of d with overlapped inner peaks, hν at H_A collapses each to a s, $J_{AB} \sim J_{aB} = 1.5$ Hz, each ∼ 0.5 H, H_B and $H_{B'}$), 3.75 (q, $J = 3$ Hz, hν at SiMe collapses to s, 0.5 H, H_C), 4.54 (broad q, $J \sim 3$ Hz, hν at SiMe collapses to s, 0.5 H, $H_{C'}$), 6.15 (m, hν at H_A collapses to s, 2H, H_D);

mass spectra (70 eV) m/e (% rel. int.) 194 (M^+, 0.9%), 165 (M-HCO, 43), 122 ($M-C_2O_3$, 75), 121 ($M-HC_2O_3$, 68), 120 ($M-H_2C_2O_3$, 32), 107 (m/e 122-CH_3, 45), 105 (m/e 120-CH_3, 41), 78 ($C_6H_6^+$, 100), 77 ($C_6H_5^+$, 26), calc'd for $C_9H_{10}SiO_3$ m/e 194.0399, measured m/e 194.0388).

24. Reaction of silole dimers 123 with perfluoro-2-butyne

A solution of 0.2051 gms (1.07 mmoles) of 123 and excess perfluoro-2-butyne was degassed and sealed in a heavy walled tube. The tube was heated to 135°C for 13 hours. The major volatile product, 1,2-bis(trifluoromethyl)benzene was identified by comparison of its GC retention time and GCMS with that of an authentic sample.

25. Rhodium catalyzed oxidation of 4,4-dimethyl-4-silacyclopentene

A slow stream of oxygen was bubbled through a solution of 5.0 mL of 4,4-dimethyl-4-silacyclopentene, 0.20 gms of t-butylhydroperoxide and 150 mg of Wilkinson's catalyst. The solution was heated to 90° for 1-2 hours. Trap to trap distillation of the volatile products yielded a clear liquid (1-3 mL) from which 1,1-dimethyl-4-hydroxy-1-silacyclopent-2-ene 129 was isolated by preparative gas chromatography on a 10' x 1/4" 20% SE-30 on Chromosorb W column at 120°C. Compound 129 was identified on the basis of its spectra: NMR (CCl_4) δ 0.11 (s, 3H), 0.22 (s, 3H), 0.56 (center of d of d, J = 6 and 15 Hz, 1H), 1.31 (center of d of d, J = 15 Hz and 8 Hz, 1H), 3.40 (s, 1H, disappears with the addition of D_2O), 4.63 (d of d of d of d, J = 8, 6, 2 and 2 Hz, 1H), 5.89 (d of d, J = 10 and 2 Hz, 1H), 6.61 (d of d, J = 10 and 2 Hz, 1H); mass spectrum

(70 eV) m/e (% rel. int.) 128 (37), 115 (11), 113 (100), 111 (23), 110 (27), 60 (3), 59 (6), 58 (74); IR (CCl_4) 3300 (broad, OH). All spectra fit well with those reported in the literature (94).

26. Oxidation of 4,4-dimethyl-4-silacyclopentene with *t*-butyl peroxybenzoate

A 25 mL round-bottom flask equipped with a reflux condensor and stirring bar was sequentially charged with 4.054 gms (0.0362 moles) of 4,4-dimethyl-4-silacyclopentene, 7.03 gms (0.0362 moles) of *t*-butyl peroxybenzoate and 0.224 gms (0.0015 moles) of cuprous bromide. The flask was flushed with nitrogen and then placed in a 90°C oil bath. Within 2 minutes, the solution turned a turquoise blue and an exothermic reaction occurred. After approximately 30 minutes, the reaction subsided. Elution of the crude reaction material through silica gel (9/1, hexane/ethyl acetate) afforded a 60% yield of 5-benzoyloxy-3,3-dimethyl-3-silacyclopentene **130**: NMR (CCl_4) δ (ppm) 0.21 (s, 3H), 0.28 (s, 3H), 0.82 (d of d, 1H, $J_{AB} = 15$ Hz, $J_{AC} = 6$ Hz), 1.57 (d of d, 1H, $J_{BC} = 9$ Hz), 5.90 (m, 1H), 6.14 (d of d, 1H, $J_{DE} = 10$ Hz, $J_{EC} = 2$ Hz), 6.75 (d of d, 1H, $J_{DC} = 3$ Hz), 7.28-8.21 (m, 5H); IR (neat) 3080, 3060, 2960, 2930, 1720, 1605, 1450, 1320, 1270, 1110, 905, 850, 800, 710 cm^{-1}; mass spectrum (70 eV) m/e (% rel. int.) 232 (1), 217 (4), 179 (26), 110 (20), 105 (100), 95 (30), 77 (43), 59 (15), calc'd for $C_{13}H_{16}O_2Si$ m/e 232.09196, measured m/e 232.09133.

27. Vacuum pyrolysis of 5-benzoyloxy-3,3-dimethyl-3-silacyclopentene 130

Compound 130 (0.5643 gms, 0.00242 moles) was slowly dripped into an evacuated (1×10^{-3} torr) vertical quartz tube packed with quartz chips and heated to 520°C. Approximately three inches below the heating zone, a white solid condensed and was identified as benzoic acid (0.2596 gms, 88%) by comparison of its spectra with that of an authentic sample. Upon warming of the trap cooled with liquid nitrogen, 0.159 gms (60%) of a light yellow liquid was obtained and was identified as the dimer of 1,1-dimethylsilole 131 on the basis of its spectra: NMR ($CDCl_3$) δ (ppm), 0.10 (s, 3H), 0.08 (s, 3H), 0.06 (s, 3H), 0.23 (s, 3H), 1.57 (d of d, 1H, $J_{CE} = 2.2$ Hz, $J_{CB} = 9$ Hz), 1.85 (broad d, 1H), 1.99 (broad m, 1H, $h\nu$ at H_E collapses 1H to d, $J_{DF} = 6$ Hz), 3.60 (d of d of d, 1H), 5.74 (d of d, $J_{GE} = 2$ Hz), 5.80 (overlapped d of d, 1H, $J_{AB} = 6$ Hz), 6.14 (overlapped d of d, 1H), 6.34 (d of d, 1H, $J_{HG} = 10$ Hz, $J_{HE} = 2.5$ Hz); mass spectrum (70 eV) m/e (% rel. int.) 220 (25), 215 (25), 162 (100), 147 (31), 146 (55), 145 (76), 135 (36), 110 (38), 95 (54), 59 (38), 57 (72), calc'd for $C_{12}H_{20}Si_2$ m/e 220.11036, measured m/e 220.11030.

28. Reaction of 133 with maleic anhydride

Compound 130 (0.5990 gms, 0.00258 moles) was slowly dripped into an evacuated (1×10^{-3} torr) vertical quartz tube packed with quartz chips and heated to 520°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and containing a solution of 0.2603 gms

(0.00265 moles) of maleic anhydride in 1.0 mL of $CDCl_3$. Upon completion of the pyrolysis, nitrogen was bled into the system and the trap was allowed to warm to room temperature. Removal of the solvent by rotary evaporation yielded 0.4258 gms of a light yellow oil. A white crystalline solid was sublimed (130°, 1×10^{-2} torr) from the oil. Fractional crystallization of this material from hexane:chloroform yielded white needles (m.p. 89.5-90.5°C) which were identified as the maleic anhydride:1,1-dimethylsilole adduct 132 on the basis of its spectra: NMR ($CDCl_3$) δ (ppm) 0.22 (s, 3H), 0.28 (s, 3H), 2.55 (m, 2H, hν at H_C collapses to broad singlet), 3.32 (overlapped d of d, 2H, hν at H_A collapses to s), 6.28 (overlapped d of d, 2H, hν at H_A collapses to s); mass spectrum (70 eV) m/e (% rel. int.) 193 (P-15, 1), 179 (75), 136 (32), 121 (31), 110 (39), 105 (33), 95 (71), 78 (53), 75 (37), 58 (100), calc'd for $C_9H_9O_3Si$ (P-15) 193.03210, measured m/e 193.03192; IR ($CHCl_3$) 1860 and 1780 cm^{-1} (C=O).

An aliquot of the material in the trap was removed before the solvent was removed and analyzed by NMR. Integration of the spectrum showed that it consisted of a mixture of the dimethylsilole:maleic anhydride adduct 132 (70.6%) and unreacted maleic anhydride (29.4%). This corresponded to a 66% yield (based on amount of 5-benzoyloxy-3,3-dimethyl-3-silacyclopentene used) of 132.

29. Reaction of 131 with maleic anhydride

A solution of 0.106 gms (0.482 mmole) of 131, 0.106 gms (1.08 mmoles) of maleic anhydride, and 0.30 mL of d_6-benzene was degassed and sealed in a NMR tube. The tube was heated to 160°C with occasional monitoring by NMR. After 30 hours, the signals due to 131 and maleic anhydride had disappeared and had been replaced by those of the maleic anhydride:dimethylsilole adduct 132.

30. Isolation of 1,1-dimethylsilole 133

5-Benzoyloxy-3,3-dimethyl-3-silacyclopentene was distilled (25°, 1×10^{-4} torr) through a horizontal quartz tube packed with quartz chips and heated to 620°C. The pyrolysate was collected in a jointed NMR tube containing ∿0.4 mL of d_2-methylene chloride. The tube was sealed and transferred to the probe of a JOEL FX-90 spectrometer and allowed to warm to -70°C in the probe. A 90 MHz ^{1}H-NMR taken at -70°C showed only a singlet at δ 0.72 (6H, $SiMe_2$) and an AB quartet centered at δ 6.40 (4H, vinyl, $J = 14$ Hz, $\nu_A = 6.78$, $\nu_B = 6.02$). The ^{13}C NMR spectrum taken at -70° further confirmed the isolation of 133 as only the expected two vinyl absorptions (δ 131.3 and 145.6) and a single Si-Me peak (δ -5.52) were observed. On warming the NMR sample in 10° increments to 10°C, the spectrum of the dimer 131 very slowly appeared. At 37°C, dimerization was complete in 15 minutes.

31. Synthesis of 140

To a stirring suspension of 5.76 gms (0.237 moles) of magnesium in 250 mL of ether was added 26.78 gms (0.212 moles) of benzyl chloride over a 4 hour interval. This Grignard solution was transferred *via* a double tipped needle to a stirring solution of 34.62 gms (0.211 moles) of chloromethylmethyldichlorosilane in 500 mL of ether. The solution was stirred for 3 hours at room temperature. The solvent was then stripped *via* rotary evaporation and the residue taken up in hexane. Filtration of the hexane followed by concentration of the filtrate afforded ∿45 mL of a light brown oil. Distillation of the oil at 110-113°C at 0.1 torr afforded 32.5 gms (70%) of **140**: NMR (CCl_4) δ (ppm) 0.10 (s, 3H), 2.13 (s, 2H), 2.50 (s, 2H), 7.0 (s, 5H).

32. Synthesis of 2-chloro-2-methyl-2-silaindane

To a stirring solution of 32.5 gms (0.148 mole) of **140** in 200 mL of CS_2 was added 4.40 gms (0.033 mole) of aluminum trichloride. After refluxing for 12 hours, the solution was filtered through celite. The filtrate was concentrated by rotary evaporation. Distillation of the residue at 87.89° at 0.1 torr afforded 20.0 gms (74% yield) of the title compound: NMR (CCl_4) δ 0.58 (s, 3H), 2.23 (s, 4H), 7.0 (m, 4H).

33. Synthesis of 2-allyl-2-methyl-2-silaindane **138**

To a stirring solution of 14.07 gms (0.077 mole) of 2-chloro-2-methyl-2-silaindane in 100 mL of ether at -70°C were added 120 mL (0.096 mole) of a 0.80 M allylmagnesium bromide in ether solution. After the addition was complete, the solution was allowed to warm to room temperature. The organic solution was stirred for several hours, quenched with 10% ammonium chloride, washed with water, and dried with sodium sulfate. After removal of solvent, distillation gave 7.85 gms of **138** (b.p. 100-102°/0.01 torr): NMR (CCl_4) δ 0.22 (s, 3H), 1.67 (d, 2H, J = 8 Hz), 2.02 (s, 4H), 4.63-5.04 (m, $CH_3\text{-}CH{=}C\underline{H_2}$, 2H), 5.38-6.12 (m, CH_2-C<u>H</u>-CH_2, 1H), 7.0 (m, 4H); mass spectrum (70 eV) m/e (% rel. int.) 188 (5), 147 (100), 146 (96), 145 (39), 119 (13), 105 (10), calc'd for $C_{12}H_{16}Si$, 188.10213, measured m/e 188.10239.

34. Vacuum pyrolysis of 2-allyl-2-methyl-2-silaindane 138

The pyrolysis of 138 was carried out by evaporating it (25°, 1×10^{-4} torr) through a horizontal quartz tube packed with quartz chips and heated to 860°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 36% mass recovery. Three products in addition to unreacted 138 were obtained that were isolated by preparative gas chromatography on a 9' x 1/4" SE-30 on Chromosorb W column using a temperature program of 140° to 210° at 2° per minute. The major product 141 (16%) was identified on the basis of its spectra: NMR (CCl_4) δ 2.24 (t, 2H), 4.08 (t, 2H), 6.59 (center of AB quartet, 2H, $\nu_A = 5.93$, $\nu_B = 7.25$), 7.01 (broad s, 4H); IR (neat) 3060, 3020, 2140 (Si-H), 1600, 1585, 1550, 950, 860 cm^{-1}; mass spectrum (70 eV) m/e (% rel. int.) 146 (100), 145 (67), 143 (27), 131 (39), 119 (14), 118 (16), 117 (15), 116 (12), 115 (36), 105 (24), 53 (30), calc'd for $C_9H_{10}Si$ m/e 146.05518, measured 146.05503. The coupling constant of 14 Hz is consistent with that expected for a cis vinyl silane (135). The lack of coupling between the vinyl hydrogen and the silyl hydride is also observed in 1-methyl-1-silacyclohexa-2,4-diene.

The second major product was identified as indene (11%) on the basis of its spectra: NMR (CCl_4) δ 3.62 (t, 2H, J = 2 Hz), 6.62-7.73 (m, 6H); mass spectrum (70 eV) m/e (% rel. int.) 116 (100), 115 (89), 89 (16), 63 (16), 57 (16). All spectra fit with those of authentic samples. The third major product was identified as 1-methylbenzosilole 140 (9.2%) on the basis of its spectra: NMR (CCl_4) δ 0.38 (d, J = 4 Hz, 3H), 4.59 (q, J = 4 Hz, 1H), 6.84 (center of AB quartet, J = 10 Hz, 2H, ν_A = 6.16, ν_B = 7.32), 7.09-7.63 (aromatic m, 4H); mass spectrum (70 eV) m/e (% rel. int.) 146 (100), 145 (76), 143 (11), 131 (63), 119 (12), 105 (57), 103 (10), 77 (13), 53 (39), calc'd for $C_9H_{10}Si$ m/e 146.05518, measured 146.05477.

35. Copyrolysis of 138 and methanol

A solution consisting of 0.2649 gms (1.41 mmoles) of 138 and 0.8166 gms (0.0255 mole) of methanol was slowly dripped into a vertical quartz tube packed with quartz chips and heated to 640°C. A continuous nitrogen stream of 5 mL per 7 seconds was used to sweep the pyrolysate into a trap cooled with liquid nitrogen. The major product, 2-methyl-2-methoxy-2-silaindane 142 (36%) was isolated by preparative gas chromatography on a 6' x 1/4" SE-30 column at 190° and was identified on the basis of its spectra: NMR (CCl_4) δ 0.30 (s, 3H), 2.01 (center of AB quartet, 4H, J = 18 Hz, ν_A = 2.14, ν_B = 1.88), 3.38 (s, -OMe, 3H), 7.0 (m, 4H); mass spectrum (70 eV) m/e (% rel. int.) 178 (46), 163 (23), 146 (100), 133 (37), 131 (16), 59 (65), calc'd for $C_{10}H_{14}SiO$ m/e 178.08140, measured 178.08112. Compound 142 was independently prepared by adding an equimolar mixture of pyridine and methanol to a stirring solution of 2-chloro-2-methyl-2-silaindane in pentane. After filtration to remove the precipitated pyridinium hydrochloride, the filtrate was distilled at 93-96°C to afford a 46% yield of 142. The spectra obtained from the independently prepared 142 were identical with those reported above.

36. Copyrolysis of 138 and methanol-d_1

A solution consisting of 0.228 gms (1.21 mmoles) of 138 and 0.6603 gms (0.020 moles) of methanol-d_1 was slowly dripped into a vertical quartz tube packed with quartz chips and heated to 660°C. A continuous nitrogen stream of 5 mL per 7 seconds was used to sweep the pyrolysate into a trap cooled with liquid nitrogen. The major product, 1-deutero-2-methyl-2-methoxy-2-silaindane 143 (17%), was identified on the basis of its spectra: NMR (CCl_4) δ 0.30 (s, SiMe, 3H), 2.01 (center of AB quartet with multiplet underneath, total of 3H, J_{AB} = 18 Hz, ν_A = 2.14, ν_B = 1.88), 3.38 (s, -OMe, 3H), 7.0 (m, 4H); mass spectrum (70 eV) m/e (% rel. int.) 179 (48), 164 (26), 147 (82), 146 (46), 134 (38), 132 (14), 59 (100).

37. Copyrolysis of 138 and perfluoro-2-butyne

Compound 138 (0.381 gms, 2.03 mmoles) was slowly dripped into a vertical quartz tube packed with quartz chips and heated to 640°C. Perfluoro-2-butyne (10 mL/15 seconds) was used as both the carrier gas and the trap. 2,3-Bis(trifluoromethyl)naphthalene was isolated by preparative gas chromatography and identified on the basis of its spectra: NMR ($CDCl_3$) δ 7.33-8.43 (m); mass spectrum (70 eV) m/e (% rel. int.) 264 (100), 245 (32), 214 (41), 195 (47), 175 (26), 159 (29), 145 (13), 126 (15), 125 (19), 99 (14), 98 (36), 75 (23), 74 (25), 69 (31), 63 (18), 62 (13).

38. Synthesis of 147

A 1-liter three-necked round-bottom flask was fitted with a reflux condensor with drying tube, a pressure-equilized addition funnel with a nitrogen inlet and a stirring bar. The apparatus was flame dried under a stream of nitrogen and then charged with 5.61 gms (0.231 mole) of magnesium turnings and 100 mL of ether. To this stirring solution was added 34.2 gms (0.200 mole) of o-bromotoluene over a 2.5 hour interval. After the Grignard formation had begun, the solution was further diluted with 400 mL of ether. To the stirring Grignard solution were added 11.82 gms (0.268 mole) of acetaldehyde at a rate to maintain a steady reflux. Stirring was continued for 1.5 hours after the addition was complete. The organic solution was then quenched with 125 mL of 0.1 N HCl, washed with water, and dried over sodium sulfate. After filtration, distillation of the filtrate at 99-101°C at 1.0 torr afforded 17.30 gms (64%) of 147 (literature b.p. 120-130° at 29.0 torr (136)).

39. PCC oxidation of 147 to 148

To a stirring suspension of 105 gms (0.486 mole) of pyridinium chlorochromate (PCC) in 500 mL of methylene chloride were added 33.0 gms (0.243 mole) of 147 over a 15 minute period. The solution immediately turned black. After stirring for 2.5 hours at room temperature, the solution was filtered through celite and the filtrate concentrated by rotary evaporation. The residue was taken up in hexane, filtered through celite and the hexane removed to afford 27.84 gms (85%) of 148 as a light orange liquid: NMR (CCl_4) δ 2.33 (s, 3H), 2.37 (s, 3H), 6.95-7.60 (m, 4H).

40. Synthesis of 149

To a stirring solution of 40.0 gms (0.192 mole) of phosphorus pentachloride in 200 mL of CCl_4 at 65°C were added 24.55 gms (0.183 mole) of 148. After stirring for approximately 3 hours at 65°C, the reaction was stopped and the solvent removed by rotary evaporation. The residue was eluted through silica gel with hexane to afford 24.0 gms (87%) of compound 149: NMR (CCl_4) δ 2.39 (s, 3H), 5.27 (broad s, 1H), 5.57 (broad s, 1H), 7.12 (broad s, 4H).

41. Synthesis of 150

A solution of 4.599 gms (0.030 mole) of 149, 5.46 gms (0.0307 mole) of N-bromosuccinimide, and 80 mL of CCl_4 was refluxed for several hours and then filtered through celite. The filtrate was concentrated by rotary evaporation. Elution of the residue through silica gel with hexane afforded 5.244 gms (76%) of 150: NMR (CCl_4) δ 4.59 (s, 2H), 5.60 (d, J = 1 Hz, 1H), 5.73 (d, J = 1 Hz, 1H), 7.32 (m, 4H); mass spectrum (70 eV) m/e (% rel. int.) 232 (11), 230 (14), 152 (90), 144 (80), 116 (100), 114 (95), 89 (65), 55 (95), 53 (75), calc'd for C_9H_8BrCl m/e 229.94979, measured 229.94897.

42. Ring closure of 150 to 146

To a stirring solution of 2.66 gms (0.0266 mole) of dimethyldichlorosilane, 1.217 gms (0.050 mole) of magnesium powder and 80 mL of dry THF was added 4.522 gms (0.0195 mole) of 150 over a 45 minute period at a rate sufficient to maintain a slow reflux. After stirring for 16 hours at room temperature, the organic solution was poured into hexane and filtered. The filtrate was carefully concentrated by rotary evaporation. Distillation of the residue at 79-81° at 0.1 torr afforded 0.559 gms (16%) of 146: NMR (CCl_4) δ 0.26 (s, 6H), 2.00 (s, 2H), 5.38 (d, 1H, $J = 2$ Hz), 6.12 (d, 1H, $J = 2$ Hz), 6.90-7.55 (m, 4H); mass spectrum (70 eV) m/e (% rel. int.) 174 (78), 159 (100), 143 (11), 133 (23), 131 (48), 115 (22), 105 (18), 77 (10), 59 (44), 53 (17), calc'd for m/e $C_{11}H_{14}Si$ 174.08648, measured 174.08541.

43. Vacuum pyrolysis of 146

The pyrolysis of 146 was carried out by evaporating (25°C, 1×10^{-4} torr) 0.7254 gms (4.17 mmoles) of 146 through a quartz tube packed with quartz chips and heated to 920°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 79% (0.571 gm) mass recovery. Indene (21%) was identified by comparison of its GC retention time and GC mass spectrum with that of an authentic sample. The other major volatile material was identified as unreacted 146 on the basis of its GC mass spectrum and GC retention time.

44. Synthesis of 1-allyl-1-methyl-1-silacyclohexa-2,4-diene 154

To a stirring solution of allylmagnesium bromide (0.081 moles) in ether were added 10.0 gms (0.069 mole) of 1-methyl-1-chloro-1-silacyclohexa-2,4-diene over a period of one hour. After stirring for an additional 30 minutes, the reaction was cooled to -20°C (Dry Ice/CCl_4) and 60 mL of a 10% ammonium chloride solution was added over 1 hour. The organic solution was warmed to room temperature and the two layers separated. The ether layer was then washed with water, dried over magnesium sulfate, filtered and the filtrate concentrated by rotary evaporation. Distillation of the residue afforded 4.97 gms (61.4%) of 154: b.p. 63-65° at 12 torr; NMR (CCl_4) δ 0.08 (s, 3H), 1.50 (m, 4H), 4.58-5.02 (vinyl mult., 2H), 5.34-6.15 (vinyl mult., 5H); mass spectrum (70 eV) m/e (% rel. int.) 150 (5), 135 (1), 109 (100), 93 (14), 83 (25), 81 (49), 67 (19), 55 (19), 43 (51), calc'd for $C_9H_{14}Si$ m/e 150.08648, measured 150.08493; IR (neat) 3090, 3040, 3000, 2920, 1630, 1550, 1250, 1150, 900, 820 cm^{-1}.

45. Copyrolysis of 154 and acetylene

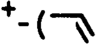
Compound 154 (0.455 gm, 3.03 mmoles) was slowly dripped into a vertical quartz tube packed with quartz chips and heated to 424-428°C. Acetylene (prepurified by passing through first concentrated sulfuric acid and then basic alumina) was used as both the carrier gas and the reactant. A flow rate of 20 mL per minute was used. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 76% (0.348 gm) mass recovery. 2-Silabarralene 155 (34%) was isolated by preparative gas chromatography on a 26' x 1/4" SE-30 on Chromosorb W column at 150°C and identified on the basis of its spectra: NMR ($DCCl_3$) δ 0.81 (s, 3H, SiMe), 5.15 (q of q, $1H_A$, $J_{AB} = 1.6$ Hz, $J_{AC} = 7$ Hz, $h\nu$ at 6.57 collapses to q), 6.57 (d of d, $3H_B$, $J_{BC} = 11$ Hz, $h\nu$ at 5.15 collapses to d), 7.41 (d of d, $3H_C$, $h\nu$ at 5.15 collapses to d); mass spectrum (70 eV) m/e (% rel. int.) 134 (12), 119 (100), 108 (27), 93 (78), 67 (20), 53 (22), calc'd for $C_8H_{10}Si$, m/e 134.0552, measured 134.0547.

46. Copyrolysis of 154 and perfluoro-2-butyne

Compound 154 (0.295 gm, 1.97 mmoles) was slowly dripped into a vertical quartz tube packed with quartz chips and heated to 452°C. Perfluoro-2-butyne was used as both the carrier gas and the reactant. A flow rate of 10 mL per 34 seconds was used. The pyrolysate was collected in a trap cooled with a Dry Ice/acetone bath. After evaporation of the excess perfluoro-2-butyne, a brown oil remained from which two major products were isolated by preparative gas chromatography on a 10' x 1/4" 20% DC-550 on Chromosorb W column at 150°C. The first product was identified as 1,2-bis(trifluoromethyl)benzene on the basis of its spectra: NMR (CCl_4) δ 7.86 (multiplet); mass spectrum (70 eV) m/e (% rel. int.) 214 (73), 195 (69), 164 (28), 163 (11), 145 (100), 125 (19), 114 (9), 95 (18), 75 (23), 69 (26), 50 (11). The second major product was identified as silabarralene 156 (*ca.* 20%) on the basis of its spectra: NMR (CCl_4) δ 0.83 (s, 3H, SiMe), 5.20 (overlapped t of t, 1H, $J = 1.5$ and 7 Hz), 6.76 (d of d, 2H, $J = 1.5$ and

11 Hz), 7.60 (d of d, 2H, J = 7 and 11 Hz); mass spectrum (70 eV) m/e (% rel. int.) 270 (2), 189 (30), 183 (11), 169 (62), 163 (100), 151 (31), 120 (23), 82 (64), 75 (26), 47 (34). All spectral data reported for 156 fit well with those in the literature (36).

47. Synthesis of 157

A solution of 1.412 gms (0.0094 mole) of 154 and 7.4 gms (0.0457 mole) of perfluro-2-butyne was degassed and sealed in a heavy walled tube. The tube was heated to 29°C for 24 hours. After evaporation of the excess perfluro-2-butyne, a light yellow oil remained. Distillation at 53-56°C at 0.1 torr afforded a 60% yield (1.76 gms) of 154: NMR (CCl_4) δ 0.08 (s, 3H, SiMe), 0.48 (d, 2H, J = 4 Hz, collapses to singlet with hν at 4.15), 1.50 (d, 2H, J = 8 Hz, $C\underline{H_2}CH{=}CH_2$), 3.66 (d, 1H, J = 6 Hz, collapses to broad s with hν at ∿6.10), 4.15 (m, 1H, collapses to broad triplet with hν at ∿6.10 collapses to d with J = 6 Hz with hν at 0.48), 4.63-6.53 (5H, vinyl m); mass spectrum (70 eV) m/e (% rel. int.) 295 (1), 195 (100), 170 (15), 157 (11), 145 (18), 97 (31), 83 (34), 70 (19), calc'd for $C_{12}H_{11}F_6Si$ (*p*-Me) m/e 297.05343, measured 297.05476, calc'd for $C_{10}H_{18}F_6Si$ (p^+-( + H)) 270.02996, measured 270.03092.

48. Vacuum pyrolysis of 157

The vacuum pyrolysis of 157 was carried out by evaporating (25°C, 1×10^{-3} torr) it through a horizontal quartz tube packed with quartz chips and heated to 550°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 94% mass recovery.

The three major products were isolated by preparative gas chromatography on a 12' x 1/4" SE-30 on Chromosorb W column at 120°C. The major product was identified as 1,2-bis(trifluoromethyl)benzene (83%) by comparison of its GC retention time and GC mass spectrum with those of an authentic sample. The second major product was the head-to-tail silene dimer 158 (85%) which was identified on the basis of its spectra: NMR (CCl_4) δ 0.00 (s, 4H, $SiC\underline{H}_2Si$), 0.22 (s, 6H, SiMe), 1.64 (d, 4H, J = 8 Hz), 4.61-5.04 (m, 4H, $CH_2CH{=}C\underline{H}_2$), 5.37-6.03 (m, 2H, $CH_2{-}C\underline{H}{=}CH_2$); mass spectrum (70 eV) m/e (% rel. int.) 196 (1), 181 (3), 168 (4), 156 (15), 155 (93), 129 (13), 128 (14), 127 (100), 115 (18), 113 (32), 99 (18), 97 (10), 85 (16), 83 (11), 73 (19), 71 (15), 69 (15), 59 (49), 55 (12), calc'd for $C_{10}H_{20}Si_2$ m/e 196.11036, measured 196.11021. The third product was identified as 4-methyl-4-silacyclopentene (2.3%) on the basis of its spectra: NMR (CCl_4) δ 0.20 (d, 3H, J = 4 Hz), 1.40 (m, 4H), 4.24 (m, 1H, Si-H), 5.80 (broad s, 2H); mass spectrum (70 eV) m/e (% rel. int.) 98 (65), 97 (100), 83 (77), 81 (23), 70 (54), 67 (11), 57 (11), 55 (55), 54 (14), 53 (27).

49. Copyrolysis of 154 and methanol

A solution of 0.1840 gm (1.23 mmoles) of 154 and 0.3586 gm (0.0112 mole) of methanol was dripped into a vertical quartz tube packed with quartz chips and heated to 456°C. A continuous stream of nitrogen (8 mL per minute) was used to sweep the pyrolysate into a trap cooled with liquid nitrogen. A mass recovery of 79% was obtained. One major product, in addition to unreacted 154, was isolated by preparative gas chromatography on a 10' x 1/4" 13% SE-30 on Chromosorb W column at 125°C and identified as 1-methoxy-1-methyl-1-silacyclohexa-2,4-diene 159 (45%) on the basis of its spectra: NMR (CCl_4) δ 0.17 (s, 3H, SiMe), 1.56 (m, 2H, $SiC\underline{H}_2C$=), 3.37 (s, 3H, OMe), 5.95 (m, 3H, vinyl), 6.95 (m, 1H, vinyl); mass spectrum (70 eV) m/e (% rel. int.) 140 (11), 125 (97), 112 (12), 108 (14), 95 (30), 75 (40), 59 (100), 43 (21), calc'd for $C_7H_{12}OSi$ m/e 140.0658, measured 140.0652. Compound 159 was independently prepared by adding 1-chloro-1-methyl-1-silacyclohexa-2,4-dienes to an equimolar mixture of triethylamine and methanol in hexane. After filtration and concentration of the filtrate by rotary evaporation, the product was isolated by preparative GC on a 10' x 1/4" 13% SI-30 on Chromosorb W column at 120°C. The spectra obtained for 159 prepared in this way were identical to those reported above.

50. Copyrolysis of 154 and methanol-d_1

A solution of 0.1495 gm (9.95 mmoles) of 154 and 0.3257 gm (0.0987 mole) of methanol-d_1 was slowly dripped into a vertical quartz tube packed with quartz chips and heated to 450°C. A continuous nitrogen stream of 8 mL/minute was used to sweep the pyrolysate into a trap cooled with liquid nitrogen. A mass recovery of 77% was obtained. The major product, 6-deutero-1-methyl-1-methoxy-1-silacyclohexa-2,4-diene 160 (39%), was isolated by preparative gas chromatography on a 10' x 1/4" 13% SE-30 on Chromosorb W column at 120°C and identified on the basis of its spectra: NMR (CCl_4) δ 0.20 (s, 3H, SiMe), 1.52 (m, 1H), 3.37 (s, 3H, OMe), 5.95 (m, 3H, vinyl), 6.95 (m, 1H, vinyl);

mass spectrum (70 eV) m/e (% rel. int.) 141 (30), 126 (65), 113 (14), 109 (24), 96 (31), 76 (16), 75 (52), 59 (100), calc'd for $C_7H_{11}DSiO$ m/e 141.07202, measured 141.07203. Comparison of the relative intensities of the m/e 141 and 126 (loss of methyl) ions showed a 93% deuterium incorporation.

51. Vacuum pyrolysis of 154

Compound 154 was distilled (25°C, 1×10^{-5} torr) through a horizontal quartz tube packed with quartz chips and heated to 640°C. The pyrolysate was collected in a trap cooled with liquid nitrogen. Analysis of the pyrolysate on a 10' x 1/4" 1.5% OV101 on Chromosorb W column using a temperature program of 100° to 220° at 6°/minute showed one major product. The product was isolated by elution of the pyrolysate through silica gel with hexane and was identified as 161 (18%) on the basis of its spectra: NMR (CCl_4) δ 0.12 (s, 3H, SiMe), 0.57 (s, 3H, SiMe), 0.80 (d, $J_{DE} = 6$ Hz, collapses to s with $h\nu$ at δ 6.04, 1 H_d), 3.66 (overlapped d of d of d of d, 1H_A, $J_{AB} \sim J_{AB'} = 7$ Hz, $J_{AC} \sim J_{AC'} = 2$ Hz, collapses to broad s with $h\nu$ at δ 7.0), 6.04 (d of d, $J_{ef} = 10$ Hz, $J_{DE} = 6$ Hz, collapses to d with $h\nu$ at δ 0.80, 1 H_E), 7.09 and 6.93 (each d of d, $J_{BC} \sim J_{BC'} = 12$ Hz, each collapses to a d with $h\nu$ at δ 3.66, 1 H_b and 1 $H_{B'}$), 6.60 (d of d, $J_{gi} = 6$ Hz, $J_{Fg} = 14$ Hz, 1 H_g), 5.52 - 5.93 (partially resolved m, 4H, H_c, $H_{c'}$, H_i, H_f); mass spectrum (70 eV) m/e (% rel. int.) 216 (7), 138 (21), 123 (15), 110 (4), 109 (12), 108 (100), 93 (53), 82 (3), 81 (4), 67 (14), 55 (4), calc'd for $C_{12}H_{16}Si_2$ m/e 216.07906, measured 216.07909.

52. Copyrolysis of 161 and methanol

A solution of 0.252 gm (1.17 mmoles) of 161 and 1.0 mL of methanol was slowly dripped into a vertical quartz tube packed with quartz chips and heated to 600°C. A nitrogen stream of 10 mL per 24 seconds was used to sweep the pyrolysate into a trap cooled with liquid nitrogen. Analysis of the pyrolysate on a 10' x 1/4" 15% SE-30 on Chromosorb W column at 160°C showed the absence of the expected trap 159 by GC retention time.

53. Attempted reaction of 161 and diphenylacetylene

A solution of 161, excess diphenylacetylene and toluene-d_8 was degassed and sealed in a NMR tube. The tube was heated to 150°C with occasional monitoring by NMR. After 8 hours, starting material 161 had disappeared. However, no new signals in the NMR were observed.

54. Synthesis of 1,5-diiodopenta-1,4-diene

To a refluxing solution of 25.4 gms (0.100 mole) of iodine in 200 mL of carbon disulfide were added 16.0 gms (0.0535 mole) of 1,1-di(*n*-butyl)-1-stannacyclohexa-2,5-diene (111). After refluxing for 10 hours, the carbon disulfide was removed by rotary evaporation and the residue distilled at 70-73°C at 0.07 torr to afford 16.0 gms (100%) of *cis,cis*-1,5-diiodopenta-1,4-diene. NMR (CCl_4) δ 3.0 (t, 2H, $J = 6$ Hz), 6.32 (m, 4H); mass spectrum (70 eV) m/e (% rel. int.) 320 (14), 193 (62), 167 (16), 127 (51), 67 (11), 66 (100), 65 (61), 63 (17), 62 (10).

55. Synthesis of 1,1-bis(trimethylsilyl)-1-silacyclohexa-2,5-diene 166

To a stirring solution of 4.232 gms (0.0132 mole) of 1,5-diiodopenta-1,4-diene in 20 mL of pentane (distilled from sodium) at -44°C (Dry Ice/acetonitrile) was added 0.0268 mole of *t*-butyl lithium. After stirring for 2 hours at -44°C, the solution was transferred into a one-liter round bottom flask containing 600 mL of ether and cooled to -78°C. Concurrent with the addition of the dilithio species was the addition of 3.262 gms (0.0133 mole) of 2,2-dichlorohexamethyltrisilane. The ether solution was stirred for 1 hour at -78°C and then allowed to warm to room temperature. The ether was removed by rotary evaporation and the residue eluted through silica gel with hexane to afford 2.592 gms (82%) of 166: NMR (CCl_4) δ 0.12 (s, 18H), 2.94 (m, 2H), 5.65 (d of t, 2H, J = 15 and 2 Hz, collapses to d with $h\nu$ at δ 2.94 with J = 15 Hz), 6.56 (d of t, 2H, J = 15 and 4 Hz, collapses to d with $h\nu$ at δ 2.94 with J = 15 Hz); mass spectrum (70 eV) m/e (% rel. int.) 240 (12), 225 (20), 181 (17), 167 (34), 166 (31), 151 (24), 141 (10), 116 (20), 109 (15), 93 (23), 83 (11), 73 (100), 59 (31), calc'd for $C_{11}H_{24}Si_3$ m/e 240.11859, measured 240.11846.

56. Attempt to oxidize 166 with activated manganese dioxide

To a stirring slurry of ∿15 gms of activated manganese dioxide (prepared according to the procedure of Goldman (137)) in ∿50 mL of benzene was added 0.00472 mole (1.133 gms) of 166. The slurry was stirred for 18 hours at room temperature and then filtered through celite. The filtrate was concentrated by rotary evaporation.

Analysis of the residue by IR did not show a C=O stretch. Attempts to isolate a product through column chromatography on silica gel also failed to yield 166 as determined by NMR analysis of the various fractions.

57. Attempt to oxidize 166 with PCC

To a stirring solution of 0.364 gm (1.69 mmoles) of PCC in 7.0 mL of methylene chloride was added 0.209 gm (0.87 mmole) of 166. The solution turned a dark brown immediately upon addition of 166. After stirring for 4 hours at room temperature, the solution was filtered and the filtrate concentrated by rotary evaporation. Analysis of the residue by NMR did not indicate the presence of the oxidized product.

58. Attempt to oxidize 166 with selenium dioxide and *t*-butyl hydroperoxide

To a stirring solution of 0.0564 gm (0.508 mmole) of selenium dioxide, 0.20 mL of *t*-butyl hydroperoxide, and 5 mL of methylene chloride was added 0.196 gm (0.815 mmole) of 166. Stirring was continued at room temperature for 36 hours followed by extraction of the reaction with benzene. The benzene was washed with water and saturated sodium chloride. Removal of the benzene afforded a small amount of residue which, by NMR, was not the desired product.

59. Synthesis of 175

A solution of 4.42 gms (0.0191 mole) of 175, 10 mL of methyl iodide, 3.0 gms (0.020 mole) of sodium iodide, and 20 mL of dimethylformamide (dried over molecular sieves, type 4A) was heated to 70°C for 12 hours, after which it was poured into pentane. The pentane was washed with water, dried over magnesium sulfate, and filtered. Concentration of the filtrate by rotary evaporation yielded 10 mL of a brown oil. Distillation at 100°C at 0.1 torr afforded 3.33 gms (70%) of 173: NMR (CCl_4) δ 0.26 (s, 3H, SiMe), 1.54 (m, 2H), 1.97 (s, 2H), 5.64-5.99 (m, 3H), 6.47-6.86 (m, 1H); mass spectrum (70 eV) (% rel. int.) 250 (1), 235 (1), 123 (23), 109 (100), 81 (16), 67 (9), calc'd for $SiC_7H_{11}I$ m/e 249.96748, measured 249.96788.

61. Attempted ring expansion of 173 with aluminum trichloride

A general method for the attempts to ring expand 173 is as follows: aluminum trichloride (10-30 mg) was placed in a NMR tube along with the appropriate solvent. Argon was bubbled through the solution and then 60-100 mg of 173 were introduced *via* syringe. The tube was heated in an oil bath with occasional monitoring by NMR and gas chromatography.

62. Reaction of 173 with silver nitrate

To a stirring solution of 7.0 mL of acetonitrile saturated with silver nitrate was added 0.500 mL of 173. The solution was stirred for 1 hour and then poured into ether. The ether was washed with water, dried over magnesium sulfate and filtered. The filtrate was concentrated by rotary evaporation. The residue was identified as the nitrate ester 176 on the basis of its NMR spectrum: (CCl_4) δ 0.31 (s, 3H), 1.62 (m, 2H), 4.08 (s, 2H), 5.62-6.08 (m, 3H), 6.56-6.98 (m, 1H).

63. Synthesis of 1-chloromethyl-1-methyl-1-silacyclohexa-2,4-diene

A solution of 1.244 gms (0.00497 mole) of 173, 2 gms (0.0342 mole) of sodium chloride and 20 mL of dimethyl sulfoxide was stirred for 4 hours at room temperature and then poured into hexane. The hexane was washed with several portions of water, dried over sodium sulfate and filtered through a plug of glass wool. Concentration of the filtrate followed by chromatography of the residue on silica gel with hexane afforded 0.384 gm (49%) of 1-chloromethyl-1-methyl-1-silacyclohexa-2,4-diene: NMR (CCl_4) δ 0.25 (s, 3H, SiMe), 1.59 (m, 2H), 2.75 (s, 2H), 5.61 - 6.10 (m, 3H), 6.52 - 6.95 (m, 1H); mass spectrum (70 eV) m/e (% rel. int.) 160 (3.4), 158 ($M^{+\cdot}$, 10), .45 (2), 143 (5), 109 (100), 93 (18), 83 (11), 81 (27), 79 (47), 78 (14), 77 (14), 67 (15), 65 (19), 63 (31), 55 (11), 53 (18).

64. Ring expansion of 1-chloromethyl-1-methyl-1-silacyclohexa-2,4-diene with aluminum trichloride

Freshly sublimed aluminum trichloride (0.0185 gm, 0.139 mmole) and benzene were transferred into a NMR tube in a dry box under a nitrogen atmosphere. To this suspension was added 0.1496 gm (0.944 mmole) of the chloromethylsilacyclohexadiene. The solution immediately turned a reddish-orange and a mildly exothermic reaction occurred. Analysis of the reaction by GC indicated the formation of a volatile product which was isolated by preparative gas chromatography on an 8' x 1/4" 20% SE-30 on Chromosorb W column using a temperature program of 120° at 2° per minute. The product was tentatively assigned the structure 174 on the basis of mass spectrum (70 eV): m/e (% rel. int.) 160 (9), 158 ($M^{+\cdot}$, 29), 143 (23), 122 (19), 117 (14), 115 (14), 95 (24), 93 (43), 92 (13), 81 (11), 80 (35), 79 (100), 78 (37), 77 (22), 65 (21), 63 (40), 53 (12).

65. Ring expansion of 173 with potassium fluoride

A solution of 0.1923 gm (0.769 mmole) of 173, 0.0766 gm (1.32 mmoles) of potassium fluoride and 2 mL of dry acetonitrile was heated to 72°C for 12 hours at which point all of the starting material had been consumed. One volatile product was observed in the reaction mixture by gas chromatography and was isolated by preparative gas chromatography on an 8' x 1/4" SE-30 on Chromosorb W column at 120°C. The material was assigned the structure of 174 (X=F) on the basis of its GC mass spectrum: m/e (% rel. int.) 142 (43), 127 (29), 101 (16), 99 (27), 87 (10), 80 (33), 79 (83), 78 (35), 77 (97), 76 (16), 63 (35), 62 (14), 47 (100).

66. Synthesis of 182

To a stirring solution of 2.157 gms (0.019 mole) of trimethylallylsilane, 40 mg of triethyl benzyl ammonium chloride and 3.8 mL (0.095 mole) of 50% sodium hydroxide were added 1.492 gms (0.0190 mole) of ethanol-free chloroform. Stirring was continued for 2 hours and then the solution was poured into pentane. The pentane was washed with water, dried with sodium sulfate, filtered and concentrated by rotary evaporation. The residue was distilled at 92°C at 1.0 torr to afford a 53% yield of 182: NMR (CCl_4) δ 0.09 (s, 9H), 0.86 (m, 2H), 1.12 (m, 1H), 1.52 (m, 2H); mass spectrum (70 eV) m/e (% rel. int.) 196 (1), 181 (1), 161 (1), 145 (1), 95 (4), 93 (11), 88 (14), 73 (100), 53 (32).

67. Vacuum pyrolysis of 182

The pyrolysis of 182 was carried out by dripping 182 (0.4258 gm, 2.17 mmoles) into a vertical quartz tube packed with quartz chips, heated to 560°C and evacuated to 1×10^{-4} torr. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented an 85% mass recovery. In addition to starting material, three major products were isolated by preparative gas chromatography on an 8' x 1/4" 20% DC-550 on Chromosorb W column using a temperature program of 120° to 210° at 2° per minute. The first product was identified as trimethylchlorosilane (71%) by comparison of its spectra with those of an authentic sample. The second product was identified as 2-chlorobuta-1,3-diene (61%) by comparison of its spectra with those of a commercial sample. The third product was identified as 2-chloro-2-trimethylsilylbutadiene (9%) on the basis of its spectra: NMR (CCl_4) δ 0.12 (s, 9H), 5.34 and 6.31 (centers of apparent d's, presumably the inner peaks of AB quartets, 2H each); mass spectrum (70 eV) m/e (% rel. int.) 162 (0.4), 161 (0.13), 160 (M^+, 1.2), 147 (20), 145 (58), 95 (37), 93 (100).

68. Synthesis of 4-trimethylsilyl-1,1-dimethyl-1-silacyclohexa-2,5-diene 185

To a stirring solution of 9.51 gms (0.077 mmole) of 1,1-dimethyl-1-silacyclohexa-2,4-diene in 170 mL of dry THF at -78°C was added 0.078 mole of n-butyllithium over 10 minutes. After stirring for 45 minutes at -78°C, the anion was transferred (via a double tipped needle) into a solution of 21.45 gms (0.198 mole) of trimethylchlorosilane in 200 mL of THF at -78°C. The solution was stirred for 30 minutes at -78°C and then warmed to room temperature and stirred there for 1 hour. The solvent was then stripped by rotary evaporation and the residue taken up in pentane. The pentane was filtered and the filtrate concentrated. Distillation of the residue at 75-76°C at 0.5 torr afforded 9.89 gms (66%) of 185: NMR ($CDCl_3$) δ 0.02 (3 overlapped s, 15H), 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); mass spectrum (70 eV) m/e (% rel. int.) 196 (4), 181 (5), 123 (3), 122 (5), 108 (75), 93 (14), 73 (100), calc'd for $C_{10}H_{20}Si$ m/e 196.11036, measured 196.11083.

69. Synthesis of 179

A solution of 2.573 gms (0.0131 mole) of 185, 5.766 gms (0.0131 mole) of phenyl(dichlorobromomethyl)mercury, and 70 mL of benzene was refluxed for 2 hours. Within 10-15 minutes after heating was begun, a white precipitate formed. The slurry was poured into pentane and the precipitated phenylmercuric bromide (4.318 gms, 92%) was collected. The filtrate was concentrated by rotary evaporation. Distillation of the residue afforded 0.639 gms of 185 and 1.98 gms (72% yield) of 179: b.p. 87-89°/0.1 torr; NMR (CCl_4) δ 0.13 (s, 9H, $SiMe_3$), 0.14 (s, 3H, SiMe), 0.26 (s, 3H, SiMe), 0.92 (d, 1 H_B, $J_{BD} = 13$ Hz), 1.71 (d, 1 H_D, $J_{BD} = 13$ Hz), 2.21 (d of d, 1 H_C, $J_{AC} = 5$ Hz, $J_{CE} = 2$ Hz), 5.25 (d of d, 1 H_E, $J_{AE} = 15$ Hz, $J_{CE} = 2$ Hz), 6.35 (d of d, 1 H_A, $J_{AE} = 15$ Hz, $J_{AC} = 5$ Hz); mass spectrum (70 eV) m/e (% rel. int.) 278 (<1), 241 (3), 227 (12), 157 (36), 155 (100), 136 (59), 95 (27), 93 (76), calc'd for $Si_2C_{10}H_{16}Cl$ ($\underline{m}$-HCl + CH_3) m/e 227.0486, measured 227.0491, calc'd for $Si_2C_{11}H_{18}Cl$ ($\underline{m}$-H_2Cl) m/e 241.0638, measured 241.0636.

70. Vacuum pyrolysis of 179

Compound 179 (0.2681 gm, 0.96 mmole) was slowly dripped into a vertical quartz tube packed with quartz chips and heated to 460°C. A continuous nitrogen stream (35 mL/min) was used to sweep the pyrolysate into a trap cooled with liquid nitrogen. A mass recovery of 87% was obtained. Four major products, trimethylchlorosilane, chlorobenzene, trimethylsilylbenzene, and trimethylsilylchlorobenzene, were isolated by preparative gas chromatography on a 5' x 1/4" OV225 on Chromosorb W column at 95°C. All of their spectra fit those of authentic samples.

71. Reaction of 179 with silver perchlorate

To a solution of 0.828 gm (3.99 mmoles) of silver perchlorate in aqueous acetone was added 0.3915 gm (1.41 mmoles) of 179. A brown precipitate formed immediately. After heating for 2 hours at 80°C, the solution was poured into pentane. The pentane was washed with water, dried with magnesium sulfate, and filtered. The filtrate was concentrated by rotary evaporation to yield 0.251 gm of a light yellow oil. The major reaction product was isolated by preparative gas chromatography on an 8' x 1/4" 20% DC-550 on Chromosorb W column at 160°C and was identified as the desilylated norcarene 186 (36%) on the basis of its spectra: NMR (CCl_4) δ 0.06 (s, 3H), 0.19 (s, 3H), 0.81 (d, H_D, 1H, J_{DC} = 13 Hz, hν at δ 1.83 (H_C) collapses to s), 1.83 (d of t, H_C, 1H, J_{DC} = 13 Hz, J_{BC} = 4.5 Hz, hν at δ 2.55 (H_B) collapses to d), 2.55 (overlapped d of d of d, H_B, 2H, J_{BC} = 4.5 Hz, J_{AB} = 4 Hz), 5.42 (broad d, H_E, 1H, J_{AE} = 14 Hz, hν at H_B collapses to sharp d), 6.31 (d of t, H_A, 1H, J_{AE} = 14 Hz, J_{AB} = 4 Hz, collapses to sharp d with hν at H_B); m/e (% rel. int.) 157 (1), 155 (3), 115 (12), 113 (18), 95 (30), 93 (83), 79 (12), 78 (100); calc'd for C_7H_8SiCl ($\underline{m}$-HCl + CH_3) 155.00838, measured m/e 155.00796.

72. Attempted reaction of 179 with silver nitrate

To a stirring solution of 0.0813 gms (0.479 mmole) of silver nitrate in 3 mL of absolute ethanol was added 0.131 gm (0.47 mmole) of 179 in one portion. A brown precipitate formed immediately. After stirring for 2 hours at room temperature, the reaction was checked by gas chromatography which showed unreacted 179 as the sole volatile material. Excess silver nitrate (∿200 mg) in 95% ethanol was added and stirring was continued for one hour. The solution was then poured into hexane and the hexane washed with water, dried over magnesium sulfate and filtered. The hexane was removed by rotary evaporation and the residue taken up in carbon tetrachloride. An NMR of the residue showed only 179.

73. Attempted reaction of **179** with pyridine

A solution of ∿75 mg of **179** and 1.0 mL of pyridine was degassed by bubbling argon through it and then refluxed for 90 minutes. A NMR taken at this point showed no change in the spectrum.

74. Synthesis of **189**

A solution of 3.416 gms (6.45 mmoles) of phenyl(tribromomethyl)-mercury, 1.27 gms (6.45 mmoles) of **185** and 50 mL of benzene was refluxed for 1.5 hours. Within 30 minutes after heating was begun, a white precipitate formed (PbHgBr). The slurry was poured into hexane and the precipitated PhHgBr collected (1.86 gms, 81%). The filtrate was concentrated and the residue distilled at 104-106°C at 0.05 torr to afford 0.794 gm of **189** (33%): NMR ($CDCl_3$) δ 0.12 (s, 9H), 0.16 (s, 3H), 0.29 (s, 3H), 1.12 (d, 1H, $J = 13$ Hz), 1.88 (d, 1H, $J = 13$ Hz), 2.23 (d of d, 1H, $J = 4$ Hz, $J = 2$ Hz), 5.32 (d of d, 1H, $J = 15$ Hz, $J = 2$ Hz), 6.72 (d of d, 1H, $J = 15$ Hz, $J = 2$ Hz).

75. Attempted reaction of **189** with silver nitrate

A solution of 0.151 gm (0.889 mmole) of silver nitrate, 0.2506 gm (0.681 mmole) of **189** and 17 mL of acetonitrile was refluxed for 20 hours. The reaction was then poured into hexane and the hexane washed with water, dried with magnesium sulfate and filtered. The filtrate was concentrated by rotary evaporation. Elution of the residue through silica gel with hexane afforded unreacted **189** as the only identifiable material.

76. Reaction of 179 with silver acetate in pyridine

To a slurry suspension of 0.196 gms (1.17 mmole) of silver acetate in 3.0 mL of dry pyridine at 80°C was added 0.2412 gm (0.865 mmole) of 179 in one portion. The solution immediately turned a dark brown. After heating for 5.5 hours at 80°C, the solution was poured into pentane and the pentane was washed with water. The organic solution was dried over magnesium sulfate, filtered and concentrated by rotary evaporation. Two products, in addition to unreacted 179, were isolated by preparative gas chromatography on an 8' x 1/4" 10% SE-30 on Chromosorb W column using a temperature program of 120° to 210° at 2° per minute. One of the products was identified as 186 on the basis of its spectra which matched those earlier reported. The second product was identified as 190 on the basis of its spectra: NMR (CCl_4) δ -0.02 (s, 3H), 0.17 (s, 3H), 0.94 (d, 1H, $J = 12$ Hz, collapses to s with $h\nu$ at δ 2.18), 1.06 (broad s, 2H), 2.18 (d of t, 1H, $J = 12$ Hz, $J = 2$ Hz, collapses to d with $h\nu$ at 5.70 with $J = 12$ Hz, collapses to t with $h\nu$ at 0.94 with $J = 2$ Hz), 5.70 (broad d, 2H, collapses to broad s with $h\nu$ 2.18); mass spectrum (70 eV) m/e (% rel. int.) 155 (2), 131 (5), 115 (15), 113 (24), 112 (12), 95 (28), 93 (70), 79 (14), 78 (100), 65 (17), 63 (16), 53 (11), 52 (10), 51 (10), calc'd for C_7H_8SiCl (m-HCl + CH_3) m/e 155.00838, measured 155.00796.

77. Reaction of 179 with tetrabutylammonium fluoride

To a stirring solution of 0.4789 gm (1.72 mmoles) of 179 and 6.0 mL of the THF at -44°C were added 1.70 mmoles of tetra-*n*-butylammonium fluoride (1.0 M in THF) over 15 minutes. The solution was stirred for 1 hour at -44°C and then allowed to warm to room temperature. The organic solution was poured into pentane. The pentane was washed with several portions of water, dried over magnesium sulfate and filtered. The filtrate was concentrated by rotary evaporation. Two products were isolated by preparative gas chromatography of the residue on an 8' x 1/4" 10% SE-30 on Chromosorb W column using a temperature program of 130° to 210° at 2° per minute. The major product was identified as 190 (18%) on the basis of its spectra which were identical with those reported earlier. The second product was identified as 3-chloro-1,1-dimethylsilepin 181 (3%) on the basis of its spectra: NMR ($CDCl_3$) δ 0.13 (s, 6H), 6.01 (d of d, H_D, 1H, J_{BD} = 14 Hz, J_{DC} = 2.5 Hz), 6.26 (center of d of m, H_C, 1H, J_{AC} = 14 Hz, hν at δ 7.13 (H_A) collapses to broad s), 6.26 (broad s, H_E, 1H), 6.87 (d of d, H_B, 1H, J_{BD} = 14 Hz, J_{BC} = 2 Hz, hν at H_C collapses to d), 7.13 (broad d, H_A, 1H, J_{AC} = 14 Hz, hν at H_C collapses to broad s, hν at H_D sharpens d); GCMS (70 eV) m/e (% rel. int.) 172 (5), 171 (2), 170 (14), 157 (34), 155 (100), 131 (3), 129 (10), calc'd for $C_8H_{11}Si$ m/e 170.03186, measured 170.08196.

78. Reaction of 179 with tris(diethylamino)sulfonium fluoride (TESF)

Tris(diethylamino)sulfonium fluoride was prepared by the method of Middleton (138).

To a stirring solution of 0.225 gm (0.807 mmole) of 179 in 3.3 mL of a 10:1 THF:HMPA at -23°C was added 0.862 mmole of TESF over a 10 minute interval. The solution was stirred at -23°C for 1 hour and then warmed to room temperature. After stirring at room temperature for 10 hours, the solution was poured into pentane and the pentane washed with water, dried over magnesium sulfate and filtered. The filtrate was concentrated by rotary evaporation. Analysis of the residue by gas chromatography and GC mass spectroscopy revealed the presence of 3-chloro-1,1-dimethylsilepin **181** (3%) and compound **190** (22%).

79. Synthesis of 1,6-diiodohexa-1,5-diyne

To a stirring solution of 8.377 gms (0.107 mole) of hexa-1,5-diyne in 250 mL of a 10:1 THF:HMPA mixture at -78°C was added 0.218 mole of *n*-butyllithium over a 30 minute interval. After stirring for 1 hour at -78°, 55 gms (0.218 mole) of iodine in 100 mL of THF were added and the reaction mixture allowed to warm to room temperature. After stirring for an additional 10 hours, the THF solution was poured into hexane and the two layers separated. The hexane layer was washed with a 2% sodium bisulfite solution, water and saturated sodium chloride. After drying over magnesium sulfate, the hexane was removed by rotary evaporation to give a brown solid. Recrystallization from ethanol and water afforded 16.1 gms (46%) of 1,6-diiodohexa-1,5-diene: NMR (CCl_4) δ 2.58 (s).

80. Synthesis of *cis,cis*-1,6-diiodohexa-1,5-diene

To a stirring solution of 0.103 mole of borane-tetrahydrofuran complex at 0°C were added 17.03 gms (0.207 mole) of cyclohexene. After stirring for 2 hours at 0°C, 16.10 gms (0.0488 moles) of

1,6-diiodohexa-1,5-diyne in 30 mL of THF were added. The solution was stirred for 3 hours and then 10 mL of glacial acetic acid were added and stirring was continued for 24 hours. The organic solution was then poured into hexane and the hexane washed with several portions of water, dried over magnesium sulfate and filtered. The hexane was removed by rotary evaporation. Elution of the residue through silica gel with hexane afforded 12.518 gms (77%) of 191: NMR (CCl_4) δ 2.28 (m, 4H), 6.20 (m, 4H).

81. Synthesis of 193

To a stirring solution of 1.207 gms (3.61 mmoles) of 1,6-diiodohexa-1,5-diene in 50 mL of pentane at -23°C was added 0.0074 mole of *n*-butyllithium over a 30 minute interval. After stirring for 90 minutes, 0.468 gm (3.63 mmoles) of dimethyldichlorosilane was added in one portion. The solution was stirred at -23°C for 30 minutes, warmed to room temperature and filtered. The filtrate was concentrated. The silacycloheptadiene 193 was isolated by preparative gas chromatography of the residue on a 6' x 1/4" 10% OV101 on Chromosorb W column at 110°C and was identified on the basis of its spectra: NMR (CCl_4) δ 0.30 (s, 6H, $SiMe_2$), 2.40 (t, 4H, $J = 2.5$ Hz, collapses upon hν at δ 6.65), 5.67 (d, 2H, $J = 14$ Hz, vinyl), 6.65 (d of t, collpases to d, $J = 14$ Hz, with hν at δ 2.40); mass spectrum (70 eV) m/3 (% rel. int.) 138 (1), 123 (10), 97 (12), 95 (17), 79 (19), 78 (100), 59 (36).

82. Synthesis of diol 47

To a stirring solution of 0.110 mole of BH_3 in 110 mL of THF was added 15.36 gms (0.109 mole) of diallyldimethylsilane. The solution was stirred for 1.5 hours at 0°C followed by the slow addition of 20 mL of 3N sodium hydroxide. To this solution were added 20 mL of 30% hydrogen peroxide. Ether (ca. 200 mL) was then added and the two layers separated. The ether layer was washed with saturated sodium chloride, dried over magnesium sulfate, filtered and evaporated. The residue was perculated through a short column of silica gel with ethyl acetate. The ethyl acetate was evaporated and the residue distilled at 133-140° at 1.5 torr to afford 16.04 gms of 47 (84%): NMR (D_6-acetone) δ 0.00 (s, 6H), 0.51 (m, 4H), 1.55 (m, 4H), 3.50 (broad t, 4H).

83. Oxidation of 47 to dial 194

To a stirring suspension of 24.60 gms (0.114 mole) of pyridinium chlorochromate, 2.30 gms (0.028 mole) of sodium acetate and 250 mL of methylene chloride were added 6.748 gms (0.0383 mole) of 47 in one portion. After stirring for 2 hours, the reaction mixture was poured into 600 mL of pentane and the pentane filtered through celite. Removal of the solvent afforded a yellow-green residue which was eluted through florisil with ether to afford 4.488 gms (68%) of 194: b.p. 74-76° at 0.1 torr; NMR (CCl_4) δ 0.00 (s, 6H), 0.72 (t, 4H, $J = 8.5$ Hz), 2.33 (d of t, 4H, $J_{AB} = 8.5$ Hz, $J_{BC} = 2$ Hz), 9.62 (t, 2H, 2 Hz); mass spectrum (70 eV) m/e (% rel. int.) 157 (M^+-15, 5), 115 (100), 101 (29), 99 (23), 92 (14), 91 (22), 85 (42), 75 (39), 61 (17), 59 (69), 57 (23), calc'd for $C_7H_{13}SiO_2$ (p'-CH_3) m/e 157.06848, measured 157.06825.

84. McMurray coupling of 194

A stirring suspension of 4.8 gms (0.0311 mole) of titanium trichloride, 4.8 gms of zinc-copper couple (129) in 150 mL of 1,2-dimethoxyethane (distilled from calcium hydride and degassed with argon) was refluxed for 1.5 hours (under argon). To this refluxing solution was added 0.788 gm (4.58 mmole) of dial 194 in 10 mL of 1,2-dimethoxyethane over a 24 hour interval. After the addition of 194 was complete, the solution was refluxed for an additional 18 hours. After filtration through celite, the DME was removed by distillation. The residue was GC prepared on an 8' x 1/4" 20% DC-550 on Chromosorb W column to afford 5,5-dimethyl-5-silacycloheptane 49 (56%): NMR (CCl_4) δ 0.00 (s, 6H), 0.57 (m, 4H, collapses to s with hν at δ 2.17), 2.17 (m, 4H, collapses to d with hν at δ 0.57 with J = 4 Hz), 5.8 (t, 2H, J = 4 Hz, collapses to s with hν at δ 2.17); mass spectrum (70 eV) m/e (% rel. int.) 140 (3), 125 (8), 112 (56), 97 (100), 72 (17), 59 (32), 58 (10), 55 (11), calc'd for $C_8H_{16}Si$ m/e 140.1021, measured 140.1027.

85. Allylic oxidation of 49 with *t*-butyl peroxybenzoate

A solution of 1.896 gms (13.5 mmoles) of 49, 3.063 gms (0.0158 mole) of *t*-butyl peroxybenzoate and 0.1432 gm of cuprous bromide was heated to 80°C in an oil bath until the reaction was initiated. After the reaction had subsided (∿10-15 minutes), the solution was heated for an additional 30 minutes at 80°C. Chromatography of the crude reaction material on silica gel with 90:10 hexane:ethyl acetate afforded 1.194 gms of 195 (34%) as a mixture of isomers: NMR (CCl_4) δ 0.00 (s, SiMe), 0.03 (s, SiMe), 0.05 (s, SiMe), 0.20 (s, SiMe), 0.67-1.21 (m), 1.27-1.50 (m), 2.27-2.67 (m), 5.87-6.16 (m), 7.23-7.74 (m), 8.04-8.34 (m); mass spectrum (70 eV) m/e (% rel. int.) 260 (M^+, <1). 245 (2), 179 (52), 138 (36), 127 (13), 123 (32), 105 (100), 95 (16), 77 (42), calc'd for $C_{15}H_{20}O_2Si$ m/e 260.1233, measured 260.1236; IR (CCl_4) C=O 1720, C-O 1270.

86. Vacuum pyrolysis of 195

Compound 195 (0.2254 gm, 0.867 mmole) was slowly dripped into a vertical quartz tube packed with quartz chips, heated to 560°C, and evacuated to 1×10^{-3} torr. The pyrolysate (0.0815 gm) was collected in a trap located approximately 12 inches below the hot zone. A white solid (0.0489 gm) condensed approximately six inches below the hot zone and was identified as benzoic acid (47% yield). The major product of the pyrolysate was isolated by preparative gas chromatography on an 8' x 1/4" 20% DC-550 column at 140°C and was identified as silacycloheptadiene 196 on the basis of its spectra: NMR (CCl_4) δ 0.08 (s, 6H), 1.32 (d, 4H, J = 6 Hz, collapses to s with $h\nu$ at ca. δ 5.6), 5.6 (strongest peak in mult. ca. 0.5 ppm wide, 4H); mass spectrum (70 eV) m/e (% rel. int.) 138 (55), 123 (88), 97 (20), 95 (100), 83 (13), 79 (20), 78 (34), 73 (62), 72 (37), 59 (71), 58 (24), 55 (18), 53 (19), calc'd for $C_8H_{14}Si$ m/e 138.0865, measured 138.0865.

87. Reaction of 196 with DDQ

To a degassed suspension of DDQ (0.180 gm, 0.793 mmole) in 1.0 mL of benzene-d_6 was added 0.0717 gm (0.520 mmole) of 196 in one portion. The deep red color was immediately discharged and the solution turned black. The tube was heated for 12 hours at 55°C after which the solution was filtered through florisil. Analysis of the filtrate by GC mass spectroscopy revealed the presence of 196 and a trace amount of a compound tentatively assigned the structure of 1,1-dimethylsilepin on the basis of its mass spectrum: m/e (% rel. int.) 138 (28), 121 (88), 105 (21), 58 (100).

88. Synthesis of cyclopentadienyldimethylsilyl chloride

Cyclopentadienyldimethylsilyl chloride was prepared by the method of Shologon and Romatsevich (131) in which dichlorodimethylsilane was coupled with one equivalent of cyclopentadienyl anion: b.p. 37-39°C at 10 torr (lit. b.p. 37-40°/7 torr).

89. Synthesis of allylcyclopentadienyldimethylsilane 197

A solution of cyclopentadienyldimethylsilyl chloride (12.013 gm, 0.0758 mole) in 75 mL of freshly distilled (from $LiAlH_4$) ether was added dropwise to a stirred solution of allylmagnesium bromide in ether (170 mL of a 0.89 M solution) under nitrogen. After 8 hours stirring, the solution was cooled to -20°C, and 75 mL of a 10% NH_4Cl solution was added in a dropwise fashion over a 45 minute period. The organic layer was separated, washed with water, dried over magnesium sulfate and evaporated to yield 12.3 gms of a light yellow oil. Distillation at 36-39°C/1 mm Hg afforded 8.9 gms (72%) of colorless 197. The NMR spectrum indicated 197 to be a mixture of the 5- and 1-cyclopentadienylsilanes in the respective ratio of 3.6:1 based on the areas of the Si-Me singlets at δ -0.05 and 0.15: NMR (CCl_4) δ -0.05 (s, SiMe), 0.15 (s, SiMe), 1.54 (d, 2H, J = 8 Hz), 3.01 (broad s, 1H), 4.68-5.10 (m, 2H, $CH_2CH{=}C\underline{H_2}$), 5.45-6.23 (m, 1H, $CH_2C\underline{H}{=}CH_2$), 6.55 (broad hump, 4H); mass spectrum (70 eV) m/e (% rel. int.) 164 (7), 149 (3), 123 (100), 99 (11), 95 (32), calc'd for $C_{10}H_{16}Si$ 164.10213, measured m/e 164.10217.

90. Vacuum pyrolysis of allylcyclopentadienyldimethylsilane 197

Through a quartz tube packed with quartz chips heated to 800°C were slowly distilled 0.2882 gm of 197 at 5×10^{-4} torr. The pyrolysate was collected in a liquid nitrogen cooled trap. The crystalline material was collected by suction filtration, and then chromatographed with hexane on silica gel to yield dimer 199 in 17% yield. The yield was determined to be essentially the same in the pyrolysate of a separate pyrolysis by GC using tetradecane as an internal standard. Properties of 199: m.p. 106-107.5°C; NMR (CCl_4) δ -1.44 (s, 0.6 H), -0.53 (s, ca. 3H), 0.52 (similar to mult. at δ 0.3, ca. 4H), 3.47 (broad s, 1.3 H), 3.74 (broad s, 0.7 H), 6.46-7.13 (hump, ca. 7H); mass spectrum (70 eV) m/e (% rel. int.) 244 (40), 229 (100), 185 (6), 183 (6), 170 (11), 169 (14), 145 (15), 107 (24), 105 (11), 95 (10), 93 (21), 83 (12), 81 (12), 73 (34), 69 (10), 67 (10), 59 (23), 58 (21), 55 (11), 53 (16), calc'd for $C_{14}H_{20}Si_2$ m/e 244.1104, measured m/e 244.1101.

91. Synthesis of 1-dimethylmethoxysilyl-1-trimethylsilylcyclopentadiene 205

To a stirring solution of 1.8214 gms (0.0132 mole) of cyclopentadienyltrimethylsilane in 70 mL of dry THF at -78°C (under a nitrogen atmosphere) were added 0.018 mole of n-butyllithium. The solution was stirred for 1.5 hours at -78°C followed by the addition of 1.80 gms (0.0140 mole) of dimethyldichlorosilane in one portion. After stirring for 1 hour, the solution was warmed to room temperature and the solvent evaporated. The residue was extracted with hexane and the hexane filtered. The filtrate was cooled to -78°C and an equimolar mixture of methanol and pyridine (0.014 mole) was added. The solution was warmed to room temperature, filtered, and the solvent evaporated. The residue was eluted through florisil with hexane to afford 1.557 gms (52%) of 205: NMR (CCl_4) δ -0.07 (s, 9H), -0.13 (s, 6H), 3.36 (s, 3H), 6.94 (AA'BB' center, 4H); mass spectrum (70 eV) m/e (% rel. int.) 226 (18), 211 (22), 138 (12), 122 (100), calc'd for $C_{11}H_{22}OSi_2$ m/e 226.1209, measured 226.1206.

92. Synthesis of trimethylsilylcyclopentadiene

To a stirring solution of 16.0 gms (0.242 mole) of cyclopentadiene in 300 mL of THF at -78°C were added 0.15 mole of n-butyllithium over a 15 minute period. After stirring for 30 minutes, 30 mL of trimethylchlorosilane was added and the solution allowed to warm to room temperature. The solvent was evaporated and the residue extracted with hexane. The hexane was filtered through celite. After evaporation of the hexane, the residue was distilled at 71-75°C/59 torr to afford 14.5 gms (70%) of trimethylsilylcyclopentadiene (lit. b.p. 50° at 30 torr).

93. Vacuum pyrolysis of 205

Compound 205 was distilled (25°, 1×10^{-4} torr) through a horizontal quartz tube packed with quartz chips and heated to 740°C. The pyrolysate was collected in a trap colled with liquid nitrogen. Two major products were isolated from the pyrolysate by preparative gas chromatography on a 6' x 1/4" 20% SE-30 on Chromosorb W column at 190°C and were identified as trimethylmethoxysilane (34%) and the silafulvene dimers 199 (31%) by comparison of their spectra with those of an authentic sample.

94. Copyrolysis of allylcyclopentadienyldimethylsilane and benzaldehyde

A solution of 197 (0.2807 gm, 1.69×10^{-3} mol) and freshly-chromatographed benzaldehyde (1.0267 gms, 9.69×10^{-3} mol) was added at a rate of 1 mL/50 minutes via a motor-driven syringe into a vertical quartz tube packed with quartz chips and heated to 680°C. Dry nitrogen was used as a carrier gas at a flow rate of 50 mL/minute. The pyrolysate was collected in a trap cooled with liquid nitrogen. The 0.9443 gm of pyrolysate collected represents a 92% mass recovery.

Hexamethylcyclotrisiloxane (D_3) was isolated by preparative GC on a 10 ft, 20% DC-550/Chromosorb P column at 140°C. Identification was made by GCMS and NMR comparison. The yield of 16.8% was obtained by GC with diphenylmethane as a standard.

95. Copyrolysis of **205** and benzaldehyde

A solution of 0.1057 gm (0.468 mmole) of **205** and 0.665 gm (6.27 mmoles) of freshly chromatographed benzaldehyde was dripped into a vertical quartz tube packed with quartz chips and heated to 500°C. A nitrogen stream of 10 mL per 29 seconds was used to sweep the pyrolysate into a trap cooled with liquid nitrogen. A mass recovery of 86.2% was obtained. Two major products were isolated from the pyrolysate. Hexamethylcyclotrisiloxane (D_3) (29%) was isolated by preparative gas chromatography on a 12' x 1/4" 20% SE-30 on Chromosorb W column at 120° and was identified by comparison on its spectra with those of an authentic sample. The other major product, 6-phenylfulvene (27%) was isolated by column chromatography of the pyrolysate on silica gel with hexane, and was identified by comparison of its spectra with those reported in the literature (139).

96. Copyrolysis of **197** and methanol

A solution of 0.498 gm (3.04 mmoles) and 1.5 mL of methanol was slowly dripped into a vertical quartz tube packed with quartz chips and heated to 600°C. A nitrogen flow rate of 3.0 mL per second was used to sweep the pyrolysate into a trap cooled with liquid nitrogen.

Analysis of the pyrolysate by both GC retention times and GC mass spectroscopy failed to reveal the presence of cyclopentadienyldimethylmethoxysilane.

97. Copyrolysis of 207 and methanol

A solution of 207 (0.122 gm, 0.540 mmole) in methanol was slowly dripped into a vertical quartz tube packed with quartz chips and heated to 500°C. A nitrogen flow rate of 20 mL per minute was used to sweep the pyrolysate into a trap cooled with liquid nitrogen. Cyclopentadienyldimethylmethoxysilane was isolated by preparative gas chromatography on a 6' x 1/4" 30% SE-30 column and represented a 50% yield. Positive identification was made by comparison of its NMR and GC mass spectra with those of an authentic sample.

98. Synthesis of cyclopentadienyldimethylmethoxysilane 209

Compound 209 was prepared in 32% yield by reacting cyclopentadienyldimethylchlorosilane with excess methanol and triethylamine in ethyl ether. After filtration and removal of the solvent, the residue was distilled at 53-56° at 83 torr: NMR (CCl_4) δ -0.1 (s, 3H), 3.2 (broad s, 1H), 3.5 (s, 3H), 6.6 (broad unresolved mult., 4H); mass spectrum (70 eV) m/e (% rel. int.) 154 (7), 139 (13), 109 (7), 89 (100), 59 (70).

99. Synthesis of 3-indenyldimethylchlorosilane 213

To a stirring solution of 7.529 gms (0.0647 mole) of indene in 100 mL of dry THF at -78°C was added 0.0672 mole of *n*-butyllithium.

After stirring at -78°C for 15 minutes, the solution was warmed to 0°C and transferred via a double ended needle into a stirring solution of 31.92 gms (0.247 mole) of dimethyldichlorosilane in 150 mL of THF at -78°C. Stirring was continued for 10 minutes and then warmed to room temperature. After stirring for an additional 1.5 hours, the THF was evaporated and the residue extracted with hexane. The hexane was filtered and the filtrate concentrated by rotary evaporation. Distillation of the residue at 114-124° at 0.1 torr afforded 5.918 gms (44%) of 213: NMR (CCl_4) δ 0.10 (s, 3H), 0.20 (s, 3H), 3.63 (broad s, 1H), 6.46-7.58 (m, 6H).

100. Synthesis of 211

To a stirring solution of 5.918 gms (0.0284 mole) of 213 in 50 mL of ether at -78°C was added 0.036 mole of allylmagnesium bromide in ether. The solution was warmed to room temperature and stirring was continued for 4 hours. The organic solution was washed with water and dried over sodium sulfate. The ether solution was filtered and the filtrate concentrated by rotary evaporation. Elution of the residue through silica gel with hexane afforded 211 as a light yellow oil (69% yield): NMR (CCl_4) δ 0.07 (s, 3H), 0.15 (s, 3H), 1.67 (d, 2H, $J = 8$ Hz, $C\underline{H}_2CH{=}CH_2$), 3.67 (broad s, 1H), 4.79-5.18 (m, 2H, $CH_2CH{=}C\underline{H}_2$), 5.49-6.19 (m, 1H, $CH_2C\underline{H}{=}CH_2$), 6.67-7.67 (m, 6H).

101. Vacuum pyrolysis of 211

Compound 211 was distilled (25°C, 2×10^{-5} torr) through a horizontal quartz tube packed with quartz chips and heated to 770°C.

The pyrolysate was collected in a trap cooled with liquid nitrogen. Upon warming the trap to room temperature, an orange oil was obtained. Attempts to chromatograph the pyrolysate on silica gel with hexane afforded no single, clean fraction that was identifiable. Analysis of the pyrolysate by gas chromatography showed no volatile materials.

102. Synthesis of 3-trimethylsilylindene

To a stirring solution of 9.92 gms (0.0855 mole) of indene in 120 mL of ether at -78°C was added 0.0882 mole of n-butyllithium over a 20 minute period. The anion was stirring for 1.5 hours at -78°C and then quenched with 12.87 gms (0.118 mole) of trimethylchlorosilane. The solution was warmed to room temperature and stirred there for 12 hours. The organic solution was then washed with water, dried over magnesium sulfate, and filtered. The filtrate was concentrated by rotary evaporation. Elution of the residue through silica gel with hexane afforded 11.93 gms (74%) of 3-trimethylsilylindene: NMR (CCl_4) δ 0.08 (s, 9H), 3.52 (broad s, 1H), 6.58-7.59 (m, 6H).

103. Synthesis of 212

To a stirring solution of 3.205 gms (0.0171 mole) of 3-trimethylsilylindene in 200 mL of ether at -78°C was added 0.0176 mole of n-butyllithium over a 15 minute period. After stirring for 1 hour at -78°C, 2.341 gms (0.0181 mole) of dimethyldichlorosilane were added in one portion. The reaction mixture was warmed to room temperature and stirred for an additional 2 hours. The solution was then cooled to 0°C and 0.0181 mole of an equimolar mixture of pyridine and methanol was added. After stirring for 2 hours, the ether was evaporated and the residue extracted with hexane. Removal of the hexane afforded a light orange oil which was distilled at 50-52°/0.05 torr: yield 2.498 gms (53%); NMR (CCl_4) δ -0.31 (s, SiMe), -0.23 (s, SiMe), -0.18 (s, $SiMe_3$), -0.15 (s, $SiMe_2$), 0.20 (s, SiMe), 0.24 (s, SiMe), 3.30 (s, OMe), 3.50 (broad s, 1H), 6.44-7.54 (s, 6H); mass spectrum (70 eV) m/e (% rel. int.) 276 (5), 261 (3), 172 (100), 89 (25), 73 (70), 59 (12), calc'd for $C_{15}H_{24}Si_2O$ m/e 276.13658, measured 276.13767. The NMR clearly defines **212** as a mixture of the three possible isomers of a 1,3-disubstituted indene.

104. Vacuum pyrolysis of 212

The pyrolysis of **212** was carried out by evaporating (25°C, 1×10^{-4} torr) it through a horizontal quartz tube packed with quartz chips and heated to 660°C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 67% mass recovery. The major product, trimethylmethoxysilane (98%) was identified by comparison of its GC retention time and GC mass spectrum with those of an authentic sample. The benzosilafulvene dimer **214** was isolated by column chromatography of the pyrolysate on silica gel with chloroform and represented a 37% yield: NMR (D_6-benzene) δ 0.97 (s, 12H), 3.98 (broad s, 4H), 7.5-8.0 (m, 8H); mass spectrum (70 eV) m/e (% rel. int.) 344 (46), 326 (45), 271 (14), 270 (16), 269 (21), 172 (35), 157 (23), 155 (11), 145 (23), 143 (14), 131 (21), 128 (22), 155 (12), 104 (11), 73 (100), 59 (40), calc'd for $C_{22}H_{24}Si_2$ m/e 344.14166, measured 344.14125.

105. Copyrolysis of 212 and methanol

A solution of 0.3593 gm (1.302 mmoles) of 212 and 1.0 mL of methanol was slowly dripped into a vertical quartz tube packed with quartz chips and heated to 520°C. A continuous stream of nitrogen ($\sim$30 mL/minute) was used to sweep the pyrolysate into a trap cooled with liquid nitrogen. The major product, 3-dimethylmethoxysilylindene, was isolated by preparative gas chromatography on a 12' x 1/4" 20% SE-30 on Chromosorb W column at 170° and represented a 65% yield (based on unrecovered starting material): NMR (CCl_4) δ -0.12 (s, 3H), -0.10 (s, 3H), 3.36 (s, 3H, OMe), 3.46 (broad s, 1H), 6.47-7.61 (6H); mass spectrum (70 eV) m/e (% rel. int.) 204 (86), 159 (12), 91 (11), 89 (100), 59 (40), calc'd for $C_{12}H_{16}SiO$ m/e 204.09705, measured 204.09644. Dimethylmethoxysilylindene was independently synthesized by adding 7.448 gms (0.0577 mole) of dimethdichlorosilane to a stirring solution of 0.0515 mole of the anion of indene in 200 mL of ether at -23°C. After warming to room temperature and stirring there for several hours, the solution was cooled back down to -23°C and an excess of an equimolar mixture of pyridine and methanol was added. The salts were removed by filtration. The filtrate was concentrated and the residue distilled at 134-137°C at 0.1 torr to afford 3.72 gms (35%) of 3-dimethylmethoxysilylindene. The spectra were identical with those reported above.

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