Selected descriptive and mechanistic considerations of (p-p) (π) bonded silicon intermediates

John Alfred Kilgour

Iowa State University

Follow this and additional works at: https://lib.dr.iastate.edu/rtd

Part of the Organic Chemistry Commons

Recommended Citation
Kilgour, John Alfred, "Selected descriptive and mechanistic considerations of (p-p) (π) bonded silicon intermediates " (1975).
Retrospective Theses and Dissertations. 5784.
https://lib.dr.iastate.edu/rtd/5784
INFORMATION TO USERS

This material was produced from a microfilm copy of the original document. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the original submitted.

The following explanation of techniques is provided to help you understand markings or patterns which may appear on this reproduction.

1. The sign or “target” for pages apparently lacking from the document photographed is “Missing Page(s)”. If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting thru an image and duplicating adjacent pages to insure you complete continuity.

2. When an image on the film is obliterated with a large round black mark, it is an indication that the photographer suspected that the copy may have moved during exposure and thus cause a blurred image. You will find a good image of the page in the adjacent frame.

3. When a map, drawing or chart, etc., was part of the material being photographed the photographer followed a definite method in "sectioning" the material. It is customary to begin photoing at the upper left hand corner of a large sheet and to continue photoing from left to right in equal sections with a small overlap. If necessary, sectioning is continued again — beginning below the first row and continuing on until complete.

4. The majority of users indicate that the textual content is of greatest value, however, a somewhat higher quality reproduction could be made from "photographs" if essential to the understanding of the dissertation. Silver prints of "photographs" may be ordered at additional charge by writing the Order Department, giving the catalog number, title, author and specific pages you wish reproduced.

5. PLEASE NOTE: Some pages may have indistinct print. Filmed as received.

Xerox University Microfilms
300 North Zeeb Road
Ann Arbor, Michigan 48106
KILGOUR, John Alfred, 1946-
SELECTED DESCRIPTIVE AND MECHANISTIC
CONSIDERATIONS OF (p-p) π BONDED
SILICON INTERMEDIATES.

Iowa State University, Ph.D., 1975
Chemistry, organic

Xerox University Microfilms, Ann Arbor, Michigan 48106

THIS DISSERTATION HAS BEEN MICROFILMED EXACTLY AS RECEIVED.
Selected descriptive and mechanistic considerations
of (p-p) π bonded silicon intermediates

by

John Alfred Kilgour

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

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1975
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEDICATION</td>
<td>iii</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>iv</td>
</tr>
<tr>
<td>HISTORICAL</td>
<td>1</td>
</tr>
<tr>
<td>RESULTS AND DISCUSSION</td>
<td>40</td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
<td>79</td>
</tr>
<tr>
<td>LITERATURE CITED</td>
<td>97</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>104</td>
</tr>
</tbody>
</table>
DEDICATION

To Dr. David L. Randall, Susan and O.
INTRODUCTION

The investigation of (p-p) π-bonded silicon compounds forms a history in miniature of chemistry. A prolonged infancy consisting of false starts and misinterpreted results has emerged only recently as an area of growing interest and increasing understanding. The driving force for this investigation has been an attempt to find (p-p) bonded silicon species analogous to the well established carbon compounds also of group IV.

The first attempt dates back to 1866 when Dilthey (1) reported the pyrolysis of diphenylsilanediol to produce diphenylsilanone. In 1889 Gatterman (2) reacted ammonia with dichlorosilanes and claimed silylimines as products. In 1912 Schlenk and Renning (3) claimed the first silaalkene as the product of dehydration of diphenylmethylsilanol. With these publications the field of (p-p) bonding of silicon was initiated, although on shaky grounds as all experiments eventually proved to be incorrect. Attempts at isolation of silicon multiple bonds were abandoned with the realization that the products obtained were oligomers or polymers of the desired structure.

Along with some technological advances, progress in the area depended on a basic philosophical change. Emphasis had to shift from isolation of products to
trapping of reactive intermediates: from synthesis to mechanistic interpretation. That change first came in a paper by Adrianov and Sokolov (4) who proposed dimethyl-polysiloxanes. The result has been a wide range of \((p-p)\pi\) bonded silicon intermediates proposed as necessary parts of particular mechanistic schemes.

This thesis will consider the use of intermediate \((p-p)\pi\) bonded silicon species in explaining the mechanistic details of selected reactions. More particularly, disilene additions to carbonyls, acetylenes and dienes will be examined in order to elaborate their mechanistic details. In the course of this study, a related mechanism involving a proposed silacyclopropane intermediate is elucidated.
HISTORICAL

Theoretical Considerations of Silicon Multiple Bonding

Theoretical treatments of silicon as a participant in (p-p) \( \pi \) bonding have been sporadic and often contradictory through the last thirty years. Pitzer (5), using pictorial representations, explained the lack of (p-p) \( \pi \) bonding by silicon in terms of repulsion of inner shell electrons. This repulsion might prohibit an atom below the second row from approaching a second atom near enough to form an effective (p-p) \( \pi \) bond. Further, while silicon might be able to approach near enough to second row elements, the difference in size between the 2p and 3p orbitals would prohibit effective overlap. These arguments are no longer used, which is reasonable in view of known matching of valence orbital sizes, even between disparate atoms as exemplified by tellurophene.

Mulliken (6) proposed calculating overlap integrals in order to provide a more quantitative evaluation of (p-p) \( \pi \) bonding. He calculated inner shell repulsions and found them no greater for third row than for second row elements. He found the (2p-2p) \( \pi \) overlap to be greater than the (3p-3p)\( \pi \) overlap, but the calculated \( \sigma \) overlap for the third row elements was more favorable than for
carbon. He concluded the lack of isolated silicon (p-p) $\pi$ bonds is due to the relatively stronger $\sigma$ bonds available via polymerization. Attridge (7), in a review article, criticized Mulliken's results as being ambiguous due to the necessity of artificially constraining the parameter $\xi$ (used to adjust the calculations for inter-atomic distance) in order to achieve the reported results.

Curtis (8,9) has done EHMO and CNDO calculations for ethylene, silaethylene and disilaethylene. His results indicate (p $\pi$-d $\pi$) overlap as the dominating factor in the stability of the $\pi$ bonded silicon systems. The relative overlap populations thus calculated suggested an order of stability ethylene $>$ disilaethylene $>$ silaethylene. The same order was observed in calculations of the rotational barriers which predicted silaethylene (9 kcal) $<$ disilaethylene (34 kcal) $<$ ethylene (111 kcal). The high value for ethylene is disappointing, although Curtis defended it by comparison to Herzberg's estimate for singlet twisted ethylene at 115 kcal/mole. The CNDO calculation for silaethylene predicted a very polar and thus very reactive species which should behave like a "carbanion-siliconium ion." While the disilaethylene was not predicted to be polar, the d orbitals might stabilize an adjacent radical as well as the $\pi$ bond. A relatively low difference (34 kcal) between the double bond and
triplet diradical species suggested significant reactivity. Curtis predicted the disilaethylene, though reactive, might be isolated if provided with bulky t-butyl substituents.

Damrauer and Williams (10) did CNDO/2 calculations for silaethylene and some fluorinated silaethylenes. They supported Curtis' conclusions concerning the polarity of the silaethylene systems. In addition they noted the influences on this polarity by the introduction of fluorines at silicon and carbon. They predicted a reversal in the mode of dimerization on changing from silaethylene to tetrafluorosilaethylene.

Dewar and co-workers (11) did MINDO/3 calculations for several unsaturated silicon compounds. They calculated the π bond strength for silaethylene as 42.3 kcal/mol. This value was in agreement with a calculation by Walsh (12) (28-46 kcal) on the basis of Flowers and Gusel'nikov's (13) kinetic data, and a value supported by Curtis (9). Dewar disagreed with Curtis in his evaluation of the disilaethylene. Dewar's results predicted the silicon-silicon π bond strength to be 20.0 kcal/mole, thus weaker than silaethylene. Perhaps his most intriguing calculation is that for silabenzene which he predicted to be a stable species with a heat of dimerization no greater than for olefins.

Schlegel, Wolfe and Mislow (14a) have applied Ab Initio calculations to silaethylene. In doing so, they have
predicted a theoretical infrared spectrum for silaethylene. The spectrum should include a band at 1490 cm\(^{-1}\) for silaethylene.

Ustynyuk and co-workers (14b) have recently performed CNDO/2 calculations on dimethylsilafulvene. A comparison of two conformations (one conformation with the silylmethyl groups in the plane of the cyclopentadiene, and one with silylmethyl groups perpendicular to the plane of the cyclopentadiene ring) offered two results which supported a stable silicon-carbon double bond. First, the critical carbon-silicon bond length was 0.098 Å shorter for the planar conformation. Second, the energy difference between the two conformations was 19.8 kcal, again favoring the planar species.

**Experimental Evidence for Silicon Multiple Bonding**

The real renaissance of (p-p) \(\pi\) bonded silicon chemistry came in 1966 with the trapping of intermediate 1,1-dimethyl-1-silaethylene by Nametkin and co-workers (15,16), and shortly thereafter by Flowers and Gusel'nikov (13,17). The last decade has seen increasing research, not only on silaalkenes, but also on silylimines, silanones and disilenes. In spite of the stability suggested by the most recent theoretical calculations, the majority of the experiments depended on trapping the \(\pi\) bonded silicon
intermediates, rather than isolation. Thus one direction of investigation has centered on using a number of trapping agents to discover the types of reactions π bonded silicon might enter into. A second direction has explored various precursors as possible π bonded silicon generators. Yet a third direction has seen the development of chemical, pyrolytic and photochemical methods for generation. After the initial burst of random, descriptive chemistry, the area has begun to mature and explore the mechanistic details of π bonded silicon species. As the area has grown, a number of reviews have appeared summarizing the progress (7,18-21).

Silaalkenes

Easily the most explored type of (p-p)π bonded silicon compounds is the silaalkene. Silacyclobutanes have provided the most extensively used pyrolytic generator for silaalkenes (13,15-17,22-37b). Generation has normally been achieved in flow pyrolysis systems ranging in temperature from 510° (32) for 1,1-dimethyl-2-phenyl-1-silacyclobutane, to 600° for 1,1-dimethyl-1-silacyclobutane (15,16), to 750° (15,16) for 1,1-dichlorosilacyclobutane. Although this temperature range has not been rigorously established, Weber and co-workers (32) suggested that it reflects the relative stability of the incipient silaalkene.
Thus, if correct, electron withdrawing groups on silicon destabilize the silaalkene while phenyl substituents offer significant stabilization. In addition, there has been one report (38) of 1,1-diphenylsilacyclobutane being used as a photochemical generator for 1,1-diphenyl-1-silaethylene. Apparently the phenyls are necessary on the silicon, since 1,1-dimethyl-2-phenyl-1-silacyclobutane does not yield the corresponding silaalkene on photolysis (32).

Closely related to the silacyclobutanes is 1,1,3,3-tetramethyl-1,3-disilacyclobutane. At 700° this cleaves to form two molecules of 1,1-dimethyl-1-silaethylene (35,39). The extreme conditions prohibit the use of disilacyclobutane for synthesis.

Carbosiloxanes have been used extensively for generating both silaalkenes and silanones. The series includes a number of moderately sized cyclic systems composed of various combinations of \( \text{Me}_2\text{SiCH}_2 \) and \( \text{Me}_2\text{SiO} \) units. Pyrolysis of the rings from 480° (40) to 750° (39) produces both 1,1-dimethyl-1-silaethylene and 1,1-dimethylsilanone.

Barton and co-workers (26,27,41) have shown that 2,3-bis(trifluoromethyl)7,7-dimethyl-7-silabicyclo[2.2.2]-octa-2,5-diene is an efficient generator of 1,1-dimethyl-1-silaethylene. When this system was pyrolyzed at 400° under nitrogen flow conditions, 1,1-dimethyl-1-silaethylene
was generated. In addition, they used the system to generate the π bonded silicon photochemically.

Slutsky and Kwart (42) observed the isomerization of cis-4,4-dimethyl-4-silahexa-1,5-diene to the trans diene in a flow system at 500-580°C. The results were attributed to a Cope rearrangement followed by a reverse Cope rearrangement, with 1,1,3-trimethyl-1-silahexa-1,5-diene as the intermediate species. His kinetic study found the Arrhenius parameters similar to those for normal Cope rearrangements.

Sakurai and co-workers (43,44) photolyzed mono- and disilacycloclohexadienes 1 and 4 as shown in Scheme 1. The isolated products of the reactions suggested the hexatriene intermediates 2 and 5. Thus one or two π bonded silicon were created from a photochemical Cope reaction. Perhaps one of the more interesting products was the 3-silacyclobut-2-ene (3). Upon heating, this system opened in a reverse (2+2) cyclo addition to form silahexatriene 2 which then reclosed via a thermal Cope rearrangement to the original silacycloclohexadiene 1.
Scheme 1

1. $R=H, Ph$

2. $R=H$

3. $SiMe_2(OMe)$

4. $R=H, Ph$

5. $R=H$

$hv$
Valkovich and Weber (45) also used a silacyclobutene as a silaalkene generator. 3,3-Dimethyl-3-phenyl-3-silacyclobutene was photolyzed in the presence of acetone to yield 3,3,5,5-tetramethyl-2-phenyl-3-sila-4-oxycyclohexene. The proposed mechanism was initiated by ring opening of the silacyclobutene to intermediate 1,1-dimethyl-2-phenyl-1-silabuta-1,3-diene. The product was presumed to be either the result of a (4+2) cycloaddition of the silabutadiene and the carbonyl, or a (2+2) cycloaddition of the silicon-carbon double bond and the carbonyl followed by rearrangement to the observed product.

Acyclic silanes have also been claimed as silaalkene precursors. Fritz and Grobe (46) pyrolyzed tetramethylsilane at 710° and found a host of products, including 1,1,3,3-tetramethyl-1,3-disilacyclobutane, which was described as coming from dimerization of 1,1-dimethyl-1-silaethylene. Gowenlock and co-workers (47) repeated this pyrolysis. Their kinetic studies supported the mechanism via the silaalkene.

Similar pyrolytic work has been done with trimethylsilane. Davidson and Lambert (48,49) have done kinetic studies from 670-750°. They found the Arrhenius parameters to be consistent with a silaalkene intermediate generated from an initial homolytic cleavage of either the silicon-hydrogen or silicon-carbon bond. Ring and co-workers (50)
pyrolyzed trimethylsilane at 710°. Their results showed disilacyclobutanes arising from both 1,1-dimethyl-1-silaethylene and 1-methyl-1-silaethylene. This suggested silaalkene generation by loss of either methane or hydrogen.

Acyclic silanes have also been used as photochemical generators of silaalkenes. Strausz and co-workers (51) photolyzed methylsilane and claimed products indicating silaethylene as an intermediate. Sommer and co-workers (52) photolyzed methylpentaphenyldisilane in the presence of methanol. They isolated the product of trapping 1,1-diphenyl-1-silaethylene generated by the loss of triphenylsilane from the starting disilane.

Some attempts have been made to generate silaalkenes chemically. Kumada and co-workers (53) have reacted sodium ethoxide with a series of halomethyldisilanes as shown in Scheme 2. The proposed mechanism starts with a concerted attack on the silicon, breaking the silicon-silicon bond, with concomitant ejection of the halide anion, thus forming an intermediate silaalkene (6); the trapping of 6 by the alcohol solvent completes the sequence.

Scheme 2

\[
\text{EtO}^- \quad \text{Me} \quad \text{Si} \quad \text{Si} \quad \text{CH}_2 \quad X \quad \text{Me} \quad \text{Si} \quad \text{CH}_2 \quad \text{EtOH} \quad \text{Me} \quad \text{Si} \quad \text{CH}_3 \quad \text{OEt}
\]
Hopper and Fine (54) have recently performed a similar reaction using tris-(2,2,4,4-tetramethyl-3-oxa-2,4-disilapentyl) borane. The direction of generation was reversed, with initial attack of the ethoxide anion on boron to produce a silaalkene and the trimethylsilanol anion. Jarvie and Rowley (55) have also proposed 1,1-dimethyl-1-silaethylene as an intermediate in the reaction of benzophenone with dimethylsilylmagnesium bromide. Though they favored the silaalkene mechanism, they did allude to other possibilities.

The existence of a silaalkene intermediate has been explored using three different methods. In 1968 Flowers and Gusel'nikov (13) used 1,1-dimethyl-1-silacyclobutane under static pyrolytic conditions to generate 1,1-dimethyl-1-silaethylene. The kinetic data indicated a homogeneous first-order reaction, thus implying a unimolecular mechanism for the reaction. Since the Arrhenius parameters for the reaction were similar to those for cyclobutane, they proposed a mechanism starting with the homolytic cleavage of either the silicon-carbon or carbon-carbon bond. This was followed by fragmentation to produce ethylene and 1,1-dimethyl-1-silaethylene. The mechanism to this point was completely reversible. The intermediate silaalkene might then dimerize to form the isolated 1,1,3,3-tetramethyl-1,3-disilacyclobutane. In support of an actual double
bonded species as an intermediate, they noted that toluene did not alter the rate constant. Further, if the intermediate were a triplet diradical, then a spin inversion would be necessary during the decomposition. This was not consistent with the measured A factor.

Support for the original homolytic cleavage has been steadily growing. Nametkin and co-workers (22,23,24) pyrolyzed 1,1,3-trimethyl-1-silacyclobutane at 560°. In addition to 1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutane, they isolated trimethylallylsilane. They argued that homolytic cleavage occurred to produce the 2,2-dimethyl-2-silapentane 1,4-diradical. Hydrogen was abstracted from the terminal methyl by the primary radical thus forming the isolated trimethylallylsilane.

More recent experiments in the laboratories of Weber and co-workers (32), Barton and co-workers (35) and finally Sommer and co-workers (37a) have examined the pyrolysis of 2-methyl- and 2-phenyl-1,1-dimethyl-1-silacyclobutane. All three studies have shown a preference to form the more substituted silaalkene. This was best explained if the reaction originated by cleavage of the carbon-carbon bond of silacyclobutane.

Barton and McIntosh (25) have found evidence for the silaalkene from flash pyrolysis experiments. After condensing the flash pyrolysis products of
1,1-dimethyl-1-silacyclobutane on a salt plate at -196°, they observed a new infrared band at 1407 cm\(^{-1}\). This band disappeared on warming and was ascribed to a silaalkene. Schlegel, Wolfe and Mislow (14a) found this absorption value to be reasonable based on their calculations for silaethylene.

The most common method of establishing the presence of silaalkenes is via trapping reactions. In fact, the descriptive knowledge of silaalkenes consists mostly of reactions with trapping agents. The first evidence for silaalkene intermediates came from dimerization (13,15-17, 22-24), as they easily form stable dimeric products. This dimerization has become the standard proof of silaalkene intermediates from new precursors such as methylsilanes (46-49) and bicyclic systems (25, 41).

Early work by Nametkin and co-workers (22-24), and Flowers and Gusel'nikov (13,17) indicated that the generation of silaalkenes from silacyclobutanes was reversible. This suggested that silaalkenes should add to olefins, and indeed the pyrolysis was inhibited by ethylene. They also found that 1,1-dimethyl-1-silaethylene was trapped by propene via an intermediate to form 1,1,3-trimethyl-1-silacyclobutane.

Nametkin and co-workers (24) first observed the addition of 1,1-dimethyl-1-silaethylene to a diene.

Using
isoprene as a trap, only 1,4,4-trimethyl-4-silacyclohexene and 2,4,4-trimethyl-4-silacyclohexene were isolated. Noting that the silicon of the isolated silacyclohexene was always in the 4 position, he favored a direct 1,4 addition over a two step mechanism initiated by a 1,2 addition. Valkovich and Weber (36) have claimed a 1,4 addition of 1,1-dimethyl-1-silaethylene to acrolein which produced 4,4-dimethyl-4-sila-3-oxycyclohexene. There was, however, no evidence contradicting a mechanism starting with a 1,2 addition to the carbonyl.

Gusel'nikov and Flowers (17) discovered that sila-alkenes would add to ammonia or water to form silylamines and silanols. This fact was later used by Nametkin and co-workers (39) to show the presence of 1,1-dimethyl-1-silaethylene from the pyrolysis of cyclocarbosiloxanes by trapping with water. It was a small step from water to alcohol, and Sommer and co-workers (31,37a) have added a series of alcohols to the pyrolysis of silacyclobutanes. Their results showed little difference in alcohols, though steric factors have some influence. The affinity silaalkenes have for alcohols led Roark and Sommer (29) to propose addition to enols as the mechanism of silylvinyl-ether formation from silaalkenes and enolizable carbonyls. They later changed their minds (37) and proposed a concerted ene type mechanism.
Trapping by alcohols has been virtually the only evidence for silaalkene generation under solution chemistry conditions. Two of the attempts at chemical generation (53,54) have been done in alcohol solutions and isolation of the alcohol addition products was the only proof of a silaalkene intermediate. Photochemical generation of silaethylenes by Sommer and co-workers (38,52) has been done with alcohol trapping as the sole means of silaalkene identification. Sakurai and co-workers (43) used methanol to trap a silaalkene intermediate from the photolysis of silacyclohexadienes and from moderate warming of silacyclobutene (3).

In 1972 Barton and co-workers (26) and Kline (27a) discovered that 1,1-dimethyl-1-silaethylene adds to ketones and aldehydes. They identified products which indicated a Wittig type addition of methylene to the carbonyl compound. The silicon was found in cyclic siloxanes and the carbonyl compound as an olefin as shown in Scheme 3. Using 1,1-dimethyl-1-silacyclobutane (7) or 2,3-bis(trifluoromethyl)-7,7-dimethyl-7-silabicyclo[2.2.2]octa-2,5-diene (8), as generators, they proposed the formation of a silaoxetane 9 as an intermediate. This ring then cleaved to form the isolated olefin 10 and dimethylsilanone (11). The mechanism finished with oligomerization of dimethylsilanone to form the observed cyclic siloxanes. There was no
direct evidence for the siloxetane intermediate, nor were the details of formation and reaction discussed.

Shortly thereafter, Sommer and co-workers (29-31) enlarged the selection of aldehydes and ketones. The products observed were in agreement with the Wittig type addition via the siloxetane mechanism. He noted, however, that the formation of the siloxetane might not be via a concerted addition. A second product appeared to arise from either addition to the enol or via a concerted ene reaction to the carbonyl. Aromatic carbonyls gave a
somewhat better yield than aliphatic carbonyls. No particular explanation was offered for this difference in yields.

Valkovich and Weber (36) added silaalkenes to the α, β unsaturated aldehyde acrolein. In addition to the 1,4 addition product, a Wittig type addition product was observed. Again an intermediate siloxetane was proposed as part of the reaction mechanism.

Valkovich and Weber (45) photolyzed 3,3-dimethyl-2-phenyl-3-silacyclobutene in the presence of acetone. In this reaction, a carbonyl added in a proposed [2+4] manner to intermediate 1,1-dimethyl-2-phenyl-1-silabuta-1,3-diene. Whether the product was the result of initial 1,4 or 1,2 addition is a matter of speculation.

Sommer and co-workers (37a) added silaalkenes generated from pyrolysis of silacyclobutanes to imines. The products were similar to the carbonyl addition and included the expected olefin 14 and cyclodisilazane 15, as shown in Scheme 4. The reaction was presumably initiated by generation of silaalkene 6 which added to N-phenylbenzaldimine to form intermediate azasilacyclobutane 12, in analogy to the previous silaoxetane 9. Fission of the azasilacyclobutane would produce styrene and silylimine 13, the latter of which would dimerize to 1,3-diphenyl-2,2,4,4-tetramethylcyclodisilazane (15), as shown by path a. When the
pyrolysis was carried out in the presence of a ketone, the intermediate silylimine 13 was trapped, presumably via the azasilaoxetane 16 (path b). In this case the isolated products included cyclic siloxanes and N-phenylbenzophenimine.

Scheme 4
Other trapping agents for 1,1-dimethyl-1-silaethylene include tetrafluorosilane (34) which formed 3-methyl-1,1,1,3-tetrafluoro-1,3-disilabutane, and acetonitrile (28) which formed cyanomethyltrimethylsilane. It should be noted that all additions were consistent with the theoretical predictions concerning the polarity of the silicon-carbon double bond.

Perhaps no compound has better proven the perversity of chemicals than $\alpha$-silyl carbenes. There are about as many different reactions of these compounds as there are experiments. Two of these reactions are of interest here. By analogy to carbon systems, the $\alpha$-silylcarbene might insert into one of the other substituents on silicon to form ring systems of 3 or larger. Alternatively, a rearrangement might occur to form a silicon-carbon double bond. Obviously, neither or both could happen.

Skell and Goldstein (56) pyrolyzed dichloromethyltrimethylsilane at 260-280° in the presence of sodium-potassium vapor under helium flow as shown in Scheme 5. They suggested that these conditions generated trimethylsilylcarbene. The carbene then allegedly inserted into a carbon-hydrogen bond to form intermediate 1,1-dimethyl-1-silacyclop propane, followed by rearrangement to form the isolated product dimethylvinylsilane.
Urry and Connolly (57) and Connolly (58) worked with a series of chloromethylsilanes. Reaction with alkali metals was proposed to yield $\alpha$-silylcarbenes. The mechanism then called for cyclization to a silacyclop propane which underwent nucleophilic attack by the original $\alpha$-silylcarbanion to yield the isolated linear products. The presence of the carbene was demonstrated by insertion to form 1,1,2-trimethylsilacyclopentane from n-butylchloromethyldimethylsilane.

Ando and co-workers (59) pyrolyzed trimethylsilylphenyldiazomethane at 500$^\circ$ under a nitrogen flow. The first reported product was 3,3-dimethylbenzo-3-silacyclopentene. The proposed mechanism began with formation of trimethylsilylphenylcarbene followed by insertion to give 1,1-dimethyl-2-phenyl-1-silacyclop propane. The silacyclop propane was presumed to rearrange via 1,1-dimethyl-2,5-dihydro-2,3-benzosilole to produce the isolated product.
In a later paper on the same pyrolysis, Ando and co-workers (60) reported trapping experiments with a series of ketones. The evidence indicated that once the trimethylsilylphenylcarbene was generated, it rearranged to 1,1,2-trimethyl-2-phenylsilaethylene. The silaethylene was trapped by ketones to yield products consistent with those previously discussed. The rearrangement to the benzosilacyclopentene was competitive, as a significant amount was observed.

Ando and co-workers (61) pyrolyzed trimethylsilyl-carbomethoxydiazomethane at 360° under nitrogen flow. They isolated dimethylmethoxysilylmethylketene and produced the expected 2-alkoxydimethylsilylpropionate by heating the ketene with an alcohol. The implication was that a silicon-carbon double bond may not arise from this carbene, even though the products appeared to come from a silaalkene. The origin of the dimethylmethoxysilylmethylketene was not clear, though it might have arisen from rearrangement of 1,1,2-trimethyl-2-carbomethoxy-1-silaethylene (Scheme 6).
Hazledine and co-workers (62) pyrolyzed trimethylsilyldiazomethane and isolated an uncharacterized dimer. Shortly thereafter, Kreeger and Schechter (63) repeated the experiment and isolated 1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutane which was taken as evidence for a silaalkene intermediate. The reaction, a vacuum flow pyrolysis at 440°, was repeated with isopropanol and with benzaldehyde. In both cases, silaalkene trapping products were isolated. Deuterium labeling experiments showed the origin of the 1,1,2-trimethyl-1-silaethylene was not from an intermediate silacyclop propane. A second product of this reaction was dimethylvinylsilane, the product associated with proposed silacyclop propane mechanisms. No direct evidence was found to substantiate silacyclop propane as the precursor to the dimethylvinylsilane.
Ando and co-workers (59,64) studied the photolysis of \( \alpha \)-silyldiazoe compounds. Although trimethylsilylphenyldiazomethane showed only carbene trapping products, trimethylsilylcarboethoxydiazomethane rearranged to 1,1,2-trimethyl-2-carboethoxy-1-silaethylene. The silaethylene was trapped by deuterated alcohol to give ethyl 2-alkoxytrimethylsilyl-2-deuteropropionate. Since a series of alcohols was used, a rearrangement avoiding the silaethylene as shown by Ando and co-workers (61) may be ruled out. Moreover, the deuterium labeling experiment ruled out silacyclop propane intermediates.

Kreeger and Schechter (63) photolyzed trimethylsilyldiazomethane. The results of trapping experiments with various alcohols and diethylamine supported a methyl shift to form intermediate 1,1,2-trimethyl-1-silaethylene. Evidence against an intermediate 1,1-dimethyl-1-silacyclopropane was obtained from trapping with 0-deuterated alcohols.

Silanones

Andrianov and Sokolov (4) revived the investigation of silanones. Polydimethylsiloxanes were pyrolyzed at temperatures of 150-200°C. They proposed intermediate dimethylsilanone to account for the observed products
which were varying length polymeric siloxanes related to each other and the starting material by units of \( \text{Me}_2\text{SiO} \).

The bulk of the work in this area has centered on redistribution of cyclosiloxanes and cyclocarbosiloxanes. A series of articles by Nametkin and co-workers (39, 65-67) described their work in pyrolyzing several ring sizes of cyclosiloxanes and cyclocarbosiloxanes. They noticed changes in ring size by units of \( \text{Me}_2\text{SiO} \) and \( \text{Me}_2\text{SiCH}_2 \), with formation of the six membered cyclotrisiloxane from all systems, and disilacyclobutane from the cyclocarboxysiloxanes. Kinetics experiments indicated the reaction was first order, having an Arrhenius dependence: \( k=10^{12.0} \exp (-61,000/RT) \), sec \(^{-1} \). They proposed the degradation of the siloxanes via a four centered transition state similar to 17a or 17b, leading to the expulsion of either \( \text{Me}_2\text{Si}=\text{O} \) or \( \text{Me}_2\text{Si}=\text{CH}_2 \). This proposal was supported by pyrolyzing cyclocarbosiloxanes in the presence of water. The isolated product was hexamethylsiloxane, the addition product of water to two molecules of 1,1-dimethyl-1-silaethylene.
At first, the 1,1,3,3,5,5,7,7-octamethyl-2,6-dioxa-1,3,5,7-tetrasilacyclooctane appeared to provide an interesting competitive test of the stabilities of 1,1-dimethyl-1-silaethylene and dimethylsilanone. To some extent this may be valid, but the authors chose to neglect this factor. Instead, they credited the slight preference for 1,1-dimethyl-1-silaethylene formation to the greater ability of oxygen to coordinate with a nonadjacent silicon in forming the four centered transition state.

Davidson and Thompson (40) did a kinetic study of the pyrolysis of octamethyltetrasiloxane. The products from their pyrolysis were hexamethylcyclotrisiloxane and deca-methylcyclopentasiloxane. Their study showed the reaction to be first order and to have Arrhenius parameters similar to Nametkin's systems. Dimethylsilanone was proposed as the intermediate, and the kinetic data used to calculate the value of the silicon-oxygen $\pi$ bond at 37.8 kcal/mole.
Interestingly, pyrolysis experiments in the presence of ethylene, propene and butadiene inhibited the formation of the ten membered ring, but not the six membered ring. This was consistent with the formation of a silanone intermediate. It also suggested a possible trap for silanones -- a feat so far done only by siloxanes and itself. Unfortunately, Davidson and Thompson did not report any products of the trapping.

Disilenes

With the increasing evidence for silicon multiple bonding to second row elements, the next obvious direction was toward silicon-silicon multiple bonding. Peddle and co-workers (68,69) investigated this area starting in 1969 by synthesizing a series of 7,8-disilabicyclo[2.2.2]octa-2,5-dienes (18,19,20). When pyrolyzed, these produced a benzene derivative and an intermediate they believed to be a silicon-silicon double bonded species. Deuterium labeling experiments established the reversibility of this reaction. They also demonstrated the dienophilic character of tetramethyldisilene (21) in reactions with anthracene, naphthalene and 1,4-diphenyl-1,3-butadiene. Pyrolysis in the absence of a diene trap produced a novel result. Rather than dimerizing in the manner of other silicon
compounds with multiple bonds, the tetramethyldisilene rearranged to several linear and cyclic disilenes.

Scheme 7

\[ \text{Me-Si-Ph} \]
Addition to acetylenes

In 1961 Vol'pin and co-workers (70-72) initiated a series of experiments designed to synthesize and characterize silacyclopropene 22 or "silirene." He predicted the empty 3d orbital of silicon would stabilize the three membered ring via (p-p-d)\(\text{π}\) overlap, and thus be analogous to the cyclopropenium cation. He generated what he thought to be dimethylsilylene from the reaction of dimethyl-dichlorosilane and sodium, and from pyrolysis of poly-dimethylsilanes. These reactions were done in the presence of diphenylacetylene to produce what Vol'pin called a "silirene."

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{Si} & \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

22

His conclusions were based on infrared spectra and elemental analysis. An inertness to bromination confirmed his conclusion as to the aromatic character of "silirene".

The structure proposed by Vol'pin was quickly discounted. West and Bailey (73) repeated Vol'pin's work and
used vapor phase osmometry to arrive at a molecular weight of 475. This result, combined with NMR data on the corresponding tetratoly product, led them to propose 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexa-1,4-diene as the compound actually produced in the reaction. Johnson and co-workers (74) studied the mass spectrum of the "silirene" and found the parent ion (m/e 472) and degradation pattern consistent with disilacyclohexadiene. But the real coup de grâce came from Bokii and Struchkov (75). Working with samples supplied by Vol'pin, they investigated the structure of the proposed "silirene". Using x-ray crystallography, they also found the structure to be a disilacyclohexadiene.

With the establishment of the correct structure for the addition product of dimethylsilylene and diphenylacetylene, attention centered on two different aspects. One concerned the mechanism of formation. The other was simply a descriptive study of different silylene generators and their addition to acetylenes. Both of these problems were attacked by Gilman and co-workers (76,77). They enlarged the descriptive knowledge to include both diphenyl- and dimethylsilylenes generated from pyrolysis of 7-silanorbornadiene systems. In both cases the 1,4-disilacyclohexadiene was found as the product of addition to diphenylacetylene.
Gilman and co-workers (76) were the first to propose a mechanism for the formation of the 1,4-disilacyclohexadiene, tentatively put forth with the acknowledgement that their "experimental evidence does not allow a distinction to be made between [their] route and others." They proposed the route shown in Scheme 8.

There were essentially two key steps to their mechanism; the first was addition of the generated dimethylsilylene (23) to diphenylacetylene to form silacyclop propane 24. This
step was proposed in agreement with Vol'pin's earlier work. The proposal gained support from findings by Skell and Goldstein (78) that the ground state for silylene is a singlet. Thus it might be expected to react with an acetylene in much the same manner as a singlet carbene (79). The second key step involved the dimerization of silacyclop propane 24 to eventually form the tricyclic intermediate 25 which could open to the observed 1,4-disilacyclocyclohexadiene 26. This sequence, though unsupported by any substantial evidence, was proposed in analogy to rearrangement of bis-triphenylcyclopropenyl to hexaphenylbenzene (80).

Atwell and Weyenberg (81,82) continued work in the area, expanding the methods of silylene generation to include pyrolysis of 1,1,2,2-tetramethyl-1,2-dimethoxydisilane. In doing so, they found cause to change the mechanistic proposal for the addition of silylenes to acetylenes. The key experiment is shown in Scheme 9.
In pyrolysis of a silylene generator with 2-butyne and tolane, the only mixed isomer has the methyl in the 2 and 3 positions. None of the mixed isomer with the methyl in the 2 and 5 positions was found. This ruled out the dimerization mechanism. Dimerization of 1,3-diradical 27 was also proposed.

This proposal was shelved as unlikely since no 1,1-dimethyl-2,3,4,5-tetraphenylsilole was found. They felt the silole would be a certain product of 27 in a solution having a high concentration of diphenylacetylene.
Barton and co-workers (83) have generated dimethylsilylene photochemically in the presence of diphenylacetylene to produce the 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyldisilacyclohexadiene.

The flow pyrolysis method was first used for the silylene-acetylene reaction by Chernyshev and co-workers (84) using hexachlorodisilane and acetylene. Later, Atwell and Uhlman (85) used 1,1,2,2-tetramethyl-1,2-dimethoxydisilane in a flow pyrolysis with 2-butyne. While it is probable they produced the corresponding disilacyclohexadiene 26, Atwell and Uhlman reported only the production of hexamethyldisilacyclobutene (28, R=Me). Although they had no direct evidence, they proposed the mechanism shown in Scheme 10.

Scheme 10
They felt the second silylene addition occurred via insertion of silylene $23$ into the silicon-carbon bond. They drew an analogy to carbene insertion into the silicon-carbon bond of small rings (86a).

More recently, Haas and Ring (86b) pyrolyzed disilane with acetylene in a recirculating flow system at 370°. Silylene generation was indicated by the presence of silane and trisilane among the products. Also isolated were a series of ethynylsilanes. While no evidence was presented, they suggested that these products came from silacyclopropene via homolytic cleavage of a silicon-carbon bond followed by a hydrogen shift. Thus a 1,3-diradical similar to $27$ is implied. However, neither silole nor 1,4-disilacyclohexadiene was isolated.

Throughout the history of this problem, there has been a growing background of mass spectral data. Work by Johnson and co-workers (74) and later Maruca and co-workers (87) had suggested a reverse Diels-Alder reaction as the second fragmentation of 1,4-disilacyclohexa-2,5-dienes. While this seemed likely, it was not until work by Atwell and Weyenberg (82) that strong evidence was found. They worked with a series of unsymmetrical disilacyclohexadienes, and showed that the second loss is that of an acetylene made from the 2 and 3 or 5 and 6 carbons of the original ring. All three studies agreed that the
third loss was the expulsion of silylene from the proposed disilacyclobutene intermediate to form a possible silacyclop propane.

**Addition to alkenes**

Any consideration of a mechanism for the addition of silylenes to acetylenes must be done in light of similar additions to alkenes. As with addition to acetylene, Nefedov and co-workers (88-90) were the first to carry out silylene addition to alkenes. Most of his work involved reactions of dihalosilanes with alkali metals to generate the silylene in the presence of an alkene. Much of this work was removed from the area of silylene additions by Weyenberg and co-workers (91,92) who showed these reactions did not involve silylene. There are, however, numerous conditions which have been used to generate silylenes for reaction with alkenes, including: pyrolysis of halosilanes through vaporized alkali metals (78), pyrolysis of polysilanes (89, 90), pyrolysis of 7-silanorbornadienes (82,88), bombardment of phosphorus precursors by fast moving neutrons (93-97), and also by photolysis of polysilanes (98,99).

Both mono- and dienes have been the target of dimethylsilylene additions. Skell and Goldstein (100) observed the apparent insertion of dimethylsilylene into the C-H bond of ethylene. The mechanism proposed used intermediate 1,1-dimethylsilacyclop propane which rearranged to the
observed product. They supported this mechanism with two other reactions which might have formed the intermediate silacyclop propane, and did form the isolated dimethylvinylsilane.

At about the same time, Nefedov and Manakov (89,90) generated dimethylsilylene (23) in the presence of ethylene to yield dimethylvinylsilane (31), 1,1,3,3-tetramethyl-1,3-disilacyclohexane (32), 1,1-dimethyl-1-silacyclopentane (33) and polymers of silicon and ethylene units as shown in Scheme 11. The proposed mechanism started with dimethylsilylene addition to the double bond to form silacyclop propane 29. This was followed by homolytic silicon-carbon bond cleavage of the ring to create 1,3-diradical 30. The products were then produced by hydrogen shift, dimerization, addition to ethylene, or copolymerization of 30 with ethylene.
The greatest effort in this area has been with silylene addition to butadienes. Atwell and Weyenberg (82) added silylenes generated from 1,1,2,2-tetramethyl-1,2-dimethoxydisilane and several 7-silanorbornadiene systems to 2,3-dimethyl-1,3-butadiene. The silylene 23 was proposed to add to a single double bond to form a silacyclopropane 34, which in turn underwent a 1,3 shift of silicon to produce the isolated product, 1,2,4,4-tetramethyl-4-silacyclopentene (35).
This mechanism was partially supported by work of Gaspar and co-workers (101). Addition of silylene to trans, trans-2,4-hexadiene yielded equal amounts of cis and trans-3-5-dimethyl-4-silacyclopentene. The mechanistic implication of these products was that addition could not be via concerted 1,4 addition. Recent work by Tang and co-workers (96) indicated that silylene is a ground state singlet similar to dimethylsilylene, which Skell and Goldstein (78) have shown is also a singlet. In view of this, Gaspar favored addition of the silylene to form a silacyclopropane which opened to a diradical similar to 36. The diradical then closed to give both the cis and trans products.

Gaspar and co-workers (101) generated dimethylsilylene in the presence of 1,3-cyclohexadiene. The isolated
products were 7,7-dimethyl-7-silanorbornene and 3,3-dimethyl-3-sila-1,4,6-heptatriene. Gaspar selected 7,7-dimethyl-7-silabicyclo[4.1.0]hepta-2-ene as a common intermediate for both products. The proposed mechanism proceeded by homolytic cleavage of the silacyclop propane portion of the molecule. Carbon-carbon bond cleavage could produce, via a 1,3-diradical, the 3,3-dimethyl-3-silahepta-1,4,6-triene. Silicon-carbon bond cleavage would lead to 7,7-dimethyl-7-silanorbornene.

Sakurai and co-workers (44) isolated two 2-vinyl-1-silacyclop propane derivatives. In both cases the silacyclop propane can be rearranged -- one thermally, one photochemically -- to a silacyclopentene. The thermal rearrangement occurred at fairly low temperatures and was consistent with the above mentioned mechanisms.

Ishikawa and Kumada (99) have worked with the photochemical generation of silylenes in the presence of cyclohexene. Their most recent work claimed 7,7-dimethyl-7-silanorcarane as a product. Although isolation has not been successful, the experiment, if valid, adds further evidence of silylene's ability to add to alkenes to produce silacyclop propane.
RESULTS AND DISCUSSION

Addition to Benzaldehyde

By late 1972, the study of silicon multiple bonding was beginning to burgeon into an area of major interest in silicon chemistry. The major efforts, including work at Iowa State University, were in the areas of silaalkenes and, to a lesser extent, silanones. The dimensions of disilene chemistry were relatively unexplored, with only the limited work of Peddle and co-workers (68,69) having been successful.

The descriptive chemistry of disilenes was limited to a few Diels-Alder reactions and internal rearrangements. Thus a logical starting place for research into disilene chemistry was the investigation of reactions with various possible chemical traps. The disilabicyclooctadienes synthesized by Peddle were used as tetramethyl-disilene generators.

The first proposed extension of descriptive disilene chemistry was reaction with a carbonyl compound. There are several reasons for the choice of a carbonyl for a trap of disilene. Silicon has shown a relatively high affinity for oxygen in general. Thus it might be predicted that disilene would react with a carbonyl. Secondly, Peddle had shown that disilene reacts in an apparent (4+2) manner. Carbonyl compounds would certainly not undergo this type
of addition, and thus offer a chance to test disilene in a possible (2+2) type addition. However, the largest single reason for choosing carbonyl compounds for addition was successful work, initiated at Iowa State University, on the addition of silaalkenes to various aldehydes and ketones.

Benzaldehyde was chosen as a trap for tetramethyl-disilene. The choice of benzaldehyde was supported by both practical and theoretical reasons. Obviously, benzaldehyde is cheap, available, and easily handled. It also has the advantage of being a liquid and thus could act as a solvent for the reaction. This ability to act as a solvent was particularly useful as the reactions were done in a vertical pyrolysis column under nitrogen flow. The benzaldehyde solution was dripped through at a controlled rate.

The chemical characteristics of benzaldehyde were the dominant factor in its choice as a carbonyl compound. Most important is that benzaldehyde is a nonenolizable aldehyde. Work involving carbonyl trapping of silaalkenes had been plagued by some ambiguities due to possible reaction with the enol form instead of the keto tautomer. The use of benzaldehyde obviates this problem. Furthermore, benzaldehyde is relatively stable to the reaction conditions.
2,3-Benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]-octa-2,5-diene (19) was dissolved in an excess of benzaldehyde. The solution was pyrolyzed by slowly dripping it through a pyrolysis column under a nitrogen flow at 500° C. The isolated products included naphthalene, trans-stilbene (21.4%), hexamethylcyclotrisiloxane (14.1%), and octamethylcyclotetrasiloxane (10.2%). Likewise, 1-phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (18) was pyrolyzed with an excess of benzaldehyde in a nitrogen flow system at 480° C. The products were biphenyl, trans-stilbene (23.9%), hexamethylcyclotrisiloxane (16%), and octamethylcyclotetrasiloxane (13.8%).

Research on reactive intermediates is often centered on mechanisms. After discovering several products from the pyrolysis of tetramethyldisilene and benzaldehyde, the objective became to rationalize a mechanistic pathway. Certainly the observed products are not the primary products of an easily recognized reaction. Thus, part of the need to outline a detailed mechanism is to demonstrate that the observed products are indeed the result of a reaction of disilene and benzaldehyde.

Attention was first focused on the origin of trans-stilbene. Peddle and co-workers (68,69) had never observed any of the isolated secondary products. Disilabicyclooctadiene 18 was pyrolyzed in the flow system at 480° with the
results supporting Peddle's results. Benzaldehyde was also pyrolyzed in the flow system with no evidence found for trans-stilbene. Thus whatever the mechanism of the original pyrolysis, the observed products were the result of a reaction between benzaldehyde and the disilene 21.

Peddle had provided some evidence that the disilene reactions do not involve the separation of the silicon atoms. Nevertheless, it is possible that the observed reaction was actually a silylene reaction. For this reason, 1,1,2,2-tetramethyl-1,2-dimethoxydisilane was pyrolyzed with benzaldehyde in the nitrogen flow system at 500°C. The identified products include dimethyldimethoxysilane, some polysilanes, and starting benzaldehyde. No evidence was found for stilbene.

One early proposal was a mechanism depending on the dimerization of phenylcarbene to produce trans-stilbene. While several mechanisms might incorporate phenylcarbene as a key intermediate, the proposal in Scheme 13 has the advantage of providing for the generation of the observed cyclosiloxanes.
Since phenylcarbene is the key intermediate in this mechanism, it provides a method for testing the mechanism. Jones (103) has reported the pyrolysis of the sodium salt of benzaldehyde tosylhydrazone. The products he isolated include a 2:1 ratio of heptafulvene to stilbene. Hedaya
has pyrolyzed the salt of benzaldehyde tosylhydrazone at temperatures over 600°. His results indicated a ring contraction to produce fulveneallene. The pyrolysis of disilabicyclooctadiene 19 with benzaldehyde was repeated specifically to look for heptafulvalene. NMR analysis showed a large peak for trans-stilbene and no evidence for heptafulvalene or fulveneallene.

Further evidence against phenylcarbene was found in the pyrolysis with cyclohexene. The normal mixture of disilabicyclooctadiene 19 was pyrolyzed with an excess of cyclohexene. The mixture was analyzed by gas chromatography/mass spectroscopy and showed no evidence for 7-phenylnorcarane or any other C_{13}H_{10} isomer. These results rule out phenylcarbene as an intermediate in the original pyrolysis. For this reason the mechanism in Scheme 13 must be rejected.

The foundation for a more reasonable mechanism had been established in the study of silaalkene addition to aldehydes and ketones. As outlined in the historical section, several groups have studied this particular reaction. While little direct evidence is available, there is an agreement on the probable mechanism as outlined in Scheme 3.

The products of the silaalkene additions are strikingly similar to those of the disilene addition, and suggest a
similarity of mechanism. This has led to the proposal
in Scheme 14. The initially formed tetramethyldisilene
(21) adds to benzaldehyde forming an intermediate disila-
oxetane 37. The disilaoxetane cleaves, generating silanone
11 and silaalkene 38. The silanone oligomerizes to form
the cyclic siloxanes. The silaalkene adds to a second
molecule of benzaldehyde to form silaoxetane 39. Finally,
this silaoxetane cleaves to form more silanone 11 and
stilbene.

Scheme 14
This mechanism requires silaalkene formation. It explains all of the observed products, particularly the trans-stilbene. The mechanism does not, however, make any stereochemical predictions. Perhaps this is just as well, as the reaction conditions would obliterate any specific stereochemistry imparted to the stilbene. At 500°, the stilbene is completely isomerized to the trans isomer which is the only one found.

The formation of the cyclosiloxanes via this mechanism has been well established. In addition to the mechanistic proposals of the silaalkene additions, a great deal of work with cyclosiloxanes has been done. The results indicate the formation of cyclosiloxanes from silanone intermediates.

Certainly a key intermediate in this mechanism is 1,1-dimethyl-2-phenyl-1-silaethylene. As mentioned in the historical, silaalkenes easily dimerize to the corresponding disilacyclobutanes. Thus one test of this mechanism is the isolation of 1,1,3,3-tetramethyl-2,4-diphenyl-1,3-disilacyclobutane. The ratio of benzaldehyde to disilene generator was lowered to 2:1 and finally 1:1 in attempts to isolate the disilacyclobutane. It is necessary to use small amounts of benzaldehyde due to the preference of silaalkenes for carbonyls in place of dimerization. However, even at a 1:1 ratio no evidence was found for the predicted disilacyclobutane.
As is often the case with negative evidence, the result only casts doubt on the proposal without providing a definitive answer. The evidence supports any mechanism not involving a silaalkene. On the other hand, it may be that the silaalkene is formed and reacts with benzaldehyde before it can undergo dimerization. The amount of benzaldehyde present is undoubtedly critical. Too much benzaldehyde present will swamp out the dimerization reaction; too little benzaldehyde may be insufficient to generate the silaalkene, or might leave reactive disilene available to trap the silaalkene. Since these conditions may overlap, it is possible that an intermediate silaalkene cannot be trapped by dimerization.

Were there no reasonable alternative to the silaethylene mechanism, then the absence of isolated disilacyclobutane might not be so damaging to that proposal. However, there is a reasonable alternative as shown in Scheme 15.
Once the disilaoxetane 37 is formed, it may be in equilibrium with the open chain 1,4-diradical 40. Alternatively, the disilene 21 may react with benzaldehyde to directly form 40. Peddle and co-workers (68,69) have shown that disilene may have a good deal of diradical character, thus direct addition is entirely reasonable.

The 1,4-diradical 40 may then add a second molecule of benzaldehyde to eventually form the disiladioxane 41. This cyclic system is ideally designed to fragment via a
concerted reaction to form stilbene and silanone. The stereochemistry which might be imparted to the stilbene in this path is obliterated by the high temperature.

The obvious key to this mechanism is the cyclic intermediate 41. With this in mind, 41 was synthesized from reaction of 1,1,2,2-tetramethyl-1,2-dichlorodisilane with dihydrobenzoin in the presence of triethylamine. The disiladioxane was pyrolyzed in a nitrogen flow system at 500° C. Trans-stilbene and siloxanes were isolated with no evidence for extraneous products. The results support the disiladioxane mechanism.

To date, the available evidence provides no clear choice between these two mechanisms. Both mechanisms involve key intermediates which have been shown to give the products under the reaction conditions. The absence of disilacyclobutane favors the disiladioxane mechanism but is not unequivocal proof.

**Disilene and Silylene Addition: A Common Intermediate**

Success with addition of disilene to benzaldehyde prompted a further extension of disilene chemistry. One of the earliest reactions of silaalkenes was addition to an unconjugated double bond in an apparent (2+2) cycloaddition. It was therefore a logical step to attempt disilene addition to an unsaturated system.
2-Butyne was chosen as a target for the disilene addition. Aside from being readily available at the time, there should be a minimum of steric hindrance to addition, and several of the possible products had been reported in the literature, thus facilitating identification. Peddle had shown that disilene will add, in an apparent Diels-Alder manner, to 1,4-diphenyl-1,3-butadiene. That reaction was done at 260° for 24 hours in a sealed tube. Similar conditions were adopted for the present investigation, modified to 18 hours.

1-Phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]-octa-2,5-diene (18) was pyrolyzed in a sealed tube at 250° for 18 hours with 2-butyne. Two products were identified: a quantitative yield of biphenyl, expected if disilene were to be extruded, and octamethyl-3,6-disilacyclohexa-1,4-diene (26a) in a 20% yield. This second product provided the stimulus to investigate several rather intriguing mechanistic possibilities. It happens that this disilahexadiene is also the product of dimethylsilylene (23) addition to 2-butyne. The obvious question is where, if anywhere before the product, do the mechanisms of these reactions merge?

If the assumption is made that the disilene reacts as a unit, then the reaction could proceed via the mechanism which follows. The mechanism most reasonably begins
with an apparent [2+2] addition of tetramethyldisilene (21) to 2-butyne to form hexamethyl-3,4-disilacyclobutene (28a). The disilacyclobutene could open via a reversible four electron electrocyclication to yield hexamethyl-1,4-disilabuta-1,3-diene (43). The isolated product, then, is the Diels-Alder adduct of the disilabutadiene with a second molecule of 2-butyne (Scheme 16).

The first step is perhaps unprecedented, but not entirely surprising. The second step is far more radical. Single silicon-carbon double bonded systems are still relatively novel and the presence of two in one system is unknown. At the very least, chemical intuition would predict this to be a very reactive species with the equilibrium, if one exists at all, being far to the side of the disilacyclobutene. The possibility of disilabutadiene is not completely unprecedented; certainly silaalkenes, though new, are now well established. Furthermore, the carbon analogue of disilacyclobutene is well known, and easily undergoes a ring opening reaction to butadiene at 100-150°. In fact, for the carbon system the equilibrium favors the open butadiene.

Returning to the dimethylsilylene addition to 2-butyne, the question is where might this reaction share a common intermediate with the disilene addition? Scheme 16 shows several mechanistic possibilities for both the
silylene and disilene additions. There are several possible junction points and all are at least potentially reversible. Any joint mechanism must take into consideration the facts already established for the silylene addition. The mechanism must account for 1,2,3,3,6,6-hexamethyl-4,5-diphenyl-3,6-disilacyclohexa-1,4-diene (26) as the only mixed isomer from the reaction of dimethylsilylene with 2-butyne and diphenylacetylene. In doing so, the proposal must not allow the formation of a silole.

Scheme 16

\[ \text{Me}_2\text{Si} \rightarrow \text{MeSi} \rightarrow \text{MeSi} \]
In confirmation of earlier results of Atwell and Weyenberg (81, 82), 1,1,2,2-tetramethyl-1,2-dimethoxydisilane (42) was pyrolyzed with a mixture of 3-hexyne and 2-butyne in a sealed tube at 225° for 18 hours. The products isolated were octamethyl-3,6-disilacyclohexa-1,4-diene (26a), 1,2,4,5-tetraethyl-3,3,6,6-tetramethyl-3,6-disilacyclohexa-1,4-diene (26c), and 4,5-diethyl-1,2,3,3,6,6-hexamethyl-3,6-disilacyclohexa-1,4-diene (26b). The last isomer, the mixed isomer, supports the conclusion that Atwell and Weyenberg arrived at from their reaction of dimethylsilylene with 2-butyne and diphenylacetylene. The stereochemistry of the mixed isomer was determined by the mass spectral degradation pattern. As Atwell and Weyenberg had shown, the second loss is a reverse Diels-Alder reaction to eject an acetylene from one side of the disilacyclohexadiene. The mixed isomer from 2-butyne and 3-hexyne shows a second loss of 54 or 82 to m/e of 183 or 155. The loss of either acetylene, and no mixed acetylene, confirms the stereochemistry of the mixed isomer.

Atwell and Uhlman (85) published the synthesis of hexamethyl-3,4-disilacyclobutene (28a). This compound was chosen as a possible common intermediate for the silylene and disilene addition reactions. The synthesis was duplicated with slightly different results. As shown in Scheme 17, along with disilacyclobutene 28a and
hexamethyl-3,5-disila-4-oxycyclopentene (44), a 25.5% yield of disilacyclohexadiene 26a was isolated. These were the only identifiable compounds isolated from the reaction. If Atwell and Uhlman isolated this last compound, they failed to report it in their communication.

Scheme 17

![Chemical structure](attachment:image)

The hexamethyl-3,4-disilacyclobutene (28a) was pyrolyzed in a sealed tube with 2-butyne for 18 hours at 225° C. These are the same conditions for the silylene addition to acetylene, and milder conditions than those for the disilene addition. The isolated products were hexamethyl-3,5-disila-4-oxycyclopentene (44) and octamethyl-3,6-disilacyclohexa-1,4-diene (26a) (31.4%). As shown in Scheme 16, the discovery of the disilacyclohexadiene 26a supports disilacyclobutene 28a as a possible intermediate in both reactions. Since the conditions of this pyrolysis
are compatible to both the silylene and disilene additions, if a disilacyclobutene is generated it would form the desired products.

The isolation of hexamethyl-3,5-disila-4-oxycyclopentene (44) was entirely expected. Atwell and Uhlman (85) reported the extremely rapid and exothermic reaction of the disilacyclobutene 28a with oxygen at room temperature. This experiment was repeated, in order to obtain an authentic sample, by bubbling oxygen through a solution of the disilacyclobutene 28a. On the other hand, when hexamethyl-3,4-disilacyclobutene was left in a sealed tube with 2-butyne for 24 hours, only starting material was found. These results suggest the much more rapid reaction with oxygen than with an acetylene. Thus, if there is oxygen present at the start of the reaction, it will react first to make disilaoxycyclopentene 44. This will serve to decrease the yield of disilacyclohexadiene.

The isolation of octamethyl-3,6-disilacyclohexa-1,4-diene (26a) does support disilacyclobutene 28a as a possible intermediate. However, it does not prove that the necessary stereochemistry is obtained. To show this, hexamethyl-3,4-disilacyclobutene (28a) was pyrolyzed with 3-hexyne. The conditions were the same as above, 18 hours at 225° C. Oxycyclopentene 44 was again isolated, this time along with 1,2-diethyl-3,3,4,5,6,6-hexamethyl-3,6-disilacyclohexa-1,4-diene (26b) (39%). The latter was identified by comparison
with a previously prepared authentic sample. As before, the mass spectrum showed a reverse Diels-Alder reaction to prove the stereochemistry of the product. With the completion of this experiment, disilacyclobutene was a very good prospect as a common intermediate since it produces the correct product with the required stereochemistry.

The mechanism shown in Scheme 16 proposes a reversible loss of silylene from disilacyclobutene \(28\) to form silacyclop propane \(24\). The pyrolysis of hexamethyl-3,4-disilacyclobutene with 3-hexyne refutes this loss of silylene as a major pathway. If the reaction is initiated by loss of silylene \(23\) to form silacyclop propane \(24\), then the next step would be dimerization of two silacycloprenes to form the isolated disilacyclohexadiene. The reaction was run with a fourfold excess of 3-hexyne; thus at any one time there would have to be a 50/50 mixture of tetramethyl-3-silacyclop propane \(24a\) and 1,2-diethyl-3,3-dimethyl-3-silacyclop propane \(24b\). Since these should dimerize in a random manner, there should be a product ratio of 1:2:1 of octamethyl-3,6-disilacyclohexa-1,4-diene \(26a\) to 1,2-diethyl-3,3,4,5,6,6-hexamethyl-3,6-disilacyclohexa-1,4-diene \(26b\) to 1,2,4,5-tetraethyl-3,3,6,6-tetramethyl-3,6-disilacyclohexa-1,4-diene \(26c\). However, only the mixed isomer was found, and the loss of silylene may be ruled out.
Likewise the reversible loss of disilene \textsuperscript{21} is excluded under these conditions. Since the reaction was done with a fourfold excess of 3-hexyne, if there was reversible loss of tetramethyldisilene, then there should be an aggregation of 1,2-diethyl-3,3,4,4-tetramethyl-3,4-disilacyclobutene \textsuperscript{(28b)}. This would result in the production of 1,2,4,5-tetraethyl-3,3,6,6-tetramethyl-3,6-disilacyclohexa-1,4-diene. Again, since none was found, this may be ruled out.

Scheme 16 proposes an equilibrium between the isolated hexamethyl-3,4-disilacyclobutene \textsuperscript{(28a)} and hexamethyl-1,4-disilabuta-1,3-diene \textsuperscript{(43)}. There is no direct evidence to either reject or support this mechanism. By way of analogy, the carbon system does undergo this equilibrium, and the open butadiene does undergo Diels-Alder addition with acetylenes to form cyclohexadienes. To date no one has shown an uncatalyzed addition of any silicon-silicon single bond to acetylene or any other multiple bond.

There is indirect evidence for this ring opening from more recent work with silacyclobutenes. Since the publication of this work with disilacyclobutene, Sakurai and co-workers \textsuperscript{(43)} have presented evidence that silacyclobutene \textsuperscript{5}, when heated, opens to silabutadiene \textsuperscript{4}. The silicon-carbon double bond thus created was trapped with an alcohol. More
recently, Valkovich and Weber (45) photolyzed 1,1-dimethyl-2-phenyl-κ-silacyclobut-2-ene in the presence of acetone. He proposed ring opening to a silabutadiene to account for the isolated products.

After establishing one common intermediate, the next step was to investigate the previous junction point. The key to this junction is a possible equilibrium between dimethylsilylene (23) and tetramethyldisilene (21). The character of this equilibrium will control the pathway of both reactions.

Under the conditions of the sealed tube reactions, there is no real difference in the nature of the isolated products. There is a difference in the yields, 20% for disilene versus 50% for the silylene reaction. This implies no more than a possible difference in the type of generator employed.

To probe the junction point, the conditions of the silylene reaction were altered. Instead of using a sealed tube at 225° the reaction was run at 480-500° in a flow pyrolysis system under a nitrogen flow. These are the conditions used by Atwell to generate disilacyclobutene 28a. When the reaction was repeated, not only was octamethyl-3,4-disilacyclobutene (28a) isolated, but also hexamethyl-3,6-disilacyclohexa-1,4-diene (26a). Thus, aside from being able to isolate the intermediate disilacyclobutene,
this reaction provides the same products as the sealed tube reaction. It would seem safe to propose that there is no change in mechanism.

The pyrolysis of both 1-phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octadiene (18) at 480° and 2,3-benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (19) gave different results than the silylene pyrolysis. The first product was disilacyclobutene 28a which was isolated as hexamethyl-3,5-disila-4-oxycyclopentene (44). In regard to disilacyclobutene formation, the silylene reaction is similar to the disilene reaction.

It is necessary to demonstrate that the disilaoxy-cyclopentene 44 comes only from the disilacyclobutene 28a. Atwell had already shown that this conversion is a rapid exothermic reaction. To further limit the sources of 44, 6,7-benzo-2,2,4,4-tetramethyl-2,4-disila-3-oxybicyclo[3.2.2]nona-6,8-diene (45) was synthesized (Scheme 18). 2,3-Benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (19) was treated with an equal molar amount of m-chloroperbenzoic acid (MCPBA) in carbon tetrachloride. The resulting disilaoxybicyclo[3.2.2]nonadiene was subjected to flow pyrolysis at 500° and 640°. In both cases the only material isolated was starting material. This result indicates the incorporation of oxygen into 45 takes place at some point after disilene generation.
The second product of the flow pyrolysis of 19 and 2-butyne is 1,2,3,3,5-pentamethyl-3,5-disilacyclopentene 50. A clue to the origin of this compound lies in two products discovered by Peddle in his research with disilene generation in the absence of a trap. Peddle isolated several compounds including 1,1- and 1,3-dimethyl-1,3-disilacyclobutane (48 and 49). He proposed a free radical mechanism to account for this as shown in Scheme 19.
The interesting intermediate in this mechanism is 1,1,2-trimethyl-1,2-disilacyclopropane (46). It appears as though the pyrolysis with 2-butyne has trapped this intermediate or a form of it. As shown in Scheme 20, once generated, the 1,1,2-trimethyl-1,2-disilacyclopropane may cleave homolytically as in Peddle's mechanism to form 1,3-diradical 47.
This diradical is then trapped by the 2-butyne to form the isolated disilacyclopentene 50. Alternatively, the 2-butyne could add to the disilacyclop propane directly. At the present time there is no evidence to choose between these mechanisms. A third alternative -- that of ring expansion of disilacyclobutene 28a -- may be ruled out as the five membered ring is not isolated from the silylene reaction whereas disilacyclobutene is isolated.

While this mechanism is speculative at this point, it is consistent with Peddle's results. Further, if it is correct, then the mechanism implies a difference between the silylene and disilylene reactions. If one assumes that disilacyclopentene 50 comes only from the reaction of disilene 21 (in rearranged form 46 or 47) and 2-butyne,
then silylene cannot be dimerizing to form disilene, as disilacyclopentene has not been isolated from the silylene reaction.

This evidence is only valid for the reaction mechanisms at 500° in a nitrogen flow system. It seems reasonable to assume, however, that since the silylenes produce essentially the same products at 500° as they do at 225°, the mechanisms are the same at both temperatures. Further, if there is a difference between the silylene and disilene reaction mechanisms at 500°, there is most probably a difference in the reaction mechanisms at 225°.

Since all reactions may produce disilacyclobutene, this evidence at best rules out the dimerization of dimethylsilylene to form tetramethyldisilene (Scheme 16). This suggests that the mechanism for silylene addition is that shown in Scheme 21. The generated silylene 23 adds to an acetylene in a possibly reversible reaction to form silacyclopropene 24. A second silylene then adds to form disilacyclobutene 28 which goes on to product via disilabutadiene 43.
As silylene type products are observed in both reactions of disilene with acetylene, the possibility remains that either the disilene or the disilabicyclo[2.2.2]octadiene systems are producing silylene. A test for this is to find a second type of chemical trap which gives a distinctly different product with silylene than with disilene. There are several possibilities that could be used for this trap.

As reviewed in the historical section, silylenes have been added to several dienes to form silacyclopentenes. Thus Atwell and Weyenberg (82) have pyrolyzed 1,1,2,2-tetramethyl-1,2-dimethoxydisilane with 2,3-dimethylbuta-1,3-diene to produce 1,2,4,4-tetramethyl-4-silacyclopentene.
On the other hand, Roark and Peddle (69) have added tetramethylidisilene to 1,4-diphenyl-1,3-butadiene to produce 3,6-diphenyl-4,4,5,5-tetramethyl-4,5-disilacyclohexene. In both cases the author reported only one product. While it seems reasonable that these were the only products of interest, no specific check was made for the alternate size ring.

Isoprene was chosen as a diene to react with both silylene and disilene in order to check for common products. 1,4,4-Trimethyl-4-silacyclopentene was synthesized from isoprene, dimethyldichlorosilane, and sodium according to the method of Weyenberg and co-workers (92). 1,4,4,5,5-Pentamethyl-4,5-disilacyclohexene was synthesized in an analogous manner from the reaction of isoprene, tetramethyldichlorodisilane and sodium. The reaction, however, provided only a low yield of a mixture which was difficult to separate. For this reason the reaction was altered to follow the method of Calas and co-workers (102) who used magnesium in hexamethylphosphoramide in place of sodium.

The reaction with magnesium in hexamethylphosphoramide produced satisfactory results in that the desired 1,4,4,5,5-pentamethyl-4,5-disilacyclohexene was formed in 5.4% yield. Interestingly, 1,4,4-trimethyl-4-silacyclopentene was also produced in 11.8% yield. The silacyclopentene is indicative of a mechanism involving a two step process. The mechanism
has similarities to the addition of 1,4-diphenyl-1,4-dilithiobutadiene to tetramethyldichlorodisilane. In that case there is also both a five and six membered ring formed. In both cases there is probably nucleophilic attack on the dichlorodisilane to replace either a chlorine or a dimethylchlorosilyl anion. In the first case the six membered ring is produced.

With the standards available, the proposed test reactions were done. 1,1,2,2-Tetramethyl-1,2-dimethoxydisilane was pyrolyzed with excess isoprene in a sealed tube at 245° for 18 hours. The only isolated product of interest was 1,4,4-trimethyl-4-silacyclopentene in 18.9% yield. No evidence was found for the six membered ring (<1%).

1-Phenyl-7,7,8,8-dimethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene was pyrolyzed with excess isoprene under the same conditions. The isolated products of interest were biphenyl and 1,4,4,5,5-pentamethyl-4,5-disilacyclohexene in 22.0% yield. No evidence was found for the five membered ring (<1%).

To show that the disilacyclohexene was not a product of silylene addition to silacyclopentene, the obvious test reaction was made. 1,1,2,2-Tetramethyl-1,2-dimethoxydisilane was pyrolyzed under the same conditions with 1,4,4-trimethyl-4-silacyclopentene. The results showed only starting silacyclopentene and no disilacyclohexene (<1%).
These results can only lead to the conclusion that there is no interchange or equilibrium between silylene and disilene or the disilylene generator under these conditions. Returning to the original problem, the mechanism for addition of disilene to acetylenes (as well as dienes) is independent of any silylene intermediate. The results lead to the conclusion that the mechanism in Scheme 22 is the most consistent with the evidence.

Scheme 22

In conclusion, it appears as though silylene and disilene arrive at the same products through merging
mechanisms. The point of juncture for these mechanisms is the production of a disilacyclobutene intermediate. Returning to Scheme 16, the silylene pyrolysis must start by formation of silylene which adds to an acetylene to produce silacyclopropene 24. Precedence for this addition comes from the silylene addition to olefins, where the accumulated evidence suggests initial silacyclopropane formation. This reaction may or may not be reversible. While there is no direct evidence disproving a special, nondiradical dimerization of the silacyclopropene, it seems more reasonable that the silacyclopropene efficiently traps silylene, thus forming disilacyclobutene 28. The disilacyclobutene then enters into an equilibrium with disilabutadiene 43, which in turn reacts with acetylene to form the isolated disilacyclohexadiene 26.

On the other hand, the disilene reaction, after generation of disilene, proceeds directly to disilacyclobutene formation. Whether this reaction is concerted or not is uncertain, though the lack of 1,2-disilacyclohexa-3,5-dienes is consistent with a concerted mechanism. As with the silylene reaction, once the disilacyclobutene is formed it may open to disilabutadiene. Again, a simple Diels-Alder reaction completes the mechanism. The concertedness of this reaction is also in doubt. Alternatively the acetylene may add to one silicon-carbon double
bond in a \((2+2)\) manner, followed by a \((1,3)\) shift to form the product. The absence of 1,2-disilacyclohexa-3,5-diene argues against a two step mechanism and favors a concerted \((4+2)\) addition.

A Proposed Silacyclopropane

Interest in silaalkene generators drew attention to a rearrangement of trimethylsilylphenyldiazomethane \((51)\) to 1,1-dimethyl-2,3-benzo-1-silacyclopent-2-ene \((53)\). The proposal by Ando and co-workers \((59)\) is shown in Scheme 23 and includes 1,1-dimethyl-2-phenyl-1-silacyclopropane \((52)\) as the key intermediate in the reaction. In light of work on \(\sigma\)-silylcarbenes by Skell and Goldstein \((56)\), and Connolly and Urry \((57,58)\), the proposed intermediate silacyclopropane \(52\) was a reasonable possibility. However, an intuitive suspicion of Ando's mechanism based on the "chemical gymnastics" required to make use of the silacyclopropane intermediate led to a closer investigation of what is actually happening.
The most convincing reason for questioning Ando's mechanism was work on phenylcarbenes (103). Work with p, m, and o-tolyldiazomethane has shown all three produce benzocyclobutene, along with other products, upon generation of the carbene. The same type of rearrangement was observed for diphenylcarbene in the production of dibenzocyclopentadiene. The general mechanism is that shown in Scheme 24.
The phenylcarbene rearrangement inspired the alternative mechanism shown in Scheme 25. Instead of requiring the relatively rare silacyclopropane intermediate, this mechanism makes use of the simple phenylcarbene rearrangement to give o-(trimethylsilyl)phenylcarbene (54). This carbene may then easily insert into the C-H bond of a silicon methyl to give the isolated product 53.
Fortunately a test was available to easily and definitively distinguish between these two mechanisms. If the trimethylsilylphenyldiazomethane is synthesized with a $^{13}$C label in the benzyl position, then that carbon might be followed through the course of the reaction. In Scheme 23 (Ando's mechanism) this $^{13}$C label is marked with an asterisk. After the silacyclop propane formation and ring opening, this carbon remains in the aliphatic portion of the molecule with two hydrogens attached. On the other hand, in the mechanism shown in Scheme 25, the labeled carbon is incorporated into the aromatic portion of the molecule and has no attached hydrogens.
Barium carbonate (20% $^{13}$C) was used as a source of carbon dioxide to make labeled benzoic acid from phenylmagnesium bromide. This was converted according to the procedure of Brook and Jones (104) to 20% $^{13}$C-trimethylsilylphenyldiazomethane. A proton nmr spectrum of the intermediate benzychloride showed $^{13}$C-H splitting for the benzyl hydrogen ($J_{13C-H}$ 120 Hz). This was used to verify the 20% $^{13}$C label in the benzyl carbon. The thermal decomposition of both unlabeled trimethylsilylphenyldiazomethane and labeled trimethylsilylphenyldiazomethane was accomplished in a gas chromatograph with the inlet port at 300° and the column temperature at 175°.

A proton nmr of the collected products identified both labeled and unlabeled compounds as 1,1-dimethyl-2,3-benzo-1-silacyclopent-2-ene (53). The two proton nmr's were identical ([CCl₄] $\delta$ 0.31 [s, 6H], 1.00 [t, 2H], 3.02 [t, 2H], 6.95-7.51 [m, 4H]) and showed no evidence for $^{13}$C-H coupling. This is in contrast to the labeled benzylchloride, and is best interpreted to mean that the labeled carbon is not bonded to a hydrogen. There are two such carbons (those at the bridgehead positions) in the product, and they are certainly not in the aliphatic region. Thus within the limits of proton nmr spectroscopy the Ando mechanism is rejected and the phenylcarbene mechanism is possible.
A $^{13}$C nmr study was performed. A comparison of relative intensities was made between a labeled and unlabeled sample. There was no change of relative intensities in the aliphatic portion of the spectrum (31.8, 11.47, and -1.59 ppm from TMS). The aromatic portion of the spectrum showed no enhancement for four of the peaks (153.11, 131.93, 129.20, and 125.56 ppm from TMS). The remaining peak at 139.86 ppm from TMS increased by a factor of 19.7 from the unlabeled to the labeled spectrum. Thus, virtually all of the label was in the aromatic portion of the molecule and concentrated at one position. The discovery of all the $^{13}$C label in the aromatic region is consistent with the phenylcarbene mechanism and refutes Ando's proposal.

An unequivocal assignment of carbon chemical shifts in the $^{13}$C nmr is not possible. Although no study has previously been made of benzosilacyclopentene, the closest analogous compound which has been studied is indane (105). For indane, and several related compounds, the hydrogen substituted carbons (124.4 and 126.2) in the aromatic region are significantly upfield from the bridgehead carbons (144.0). Within the limits of this analogy, the most reasonable assignment for the bridgehead carbons would appear to be at 153.11 and 139.86. Further speculation would select the farthest upfield peak at 139.86, which is the proposed position of attachment of silicon to
the aromatic ring. This assignment is consistent with the proton nmr results, and together the results very strongly support the phenylcarbene mechanism.

Mass spectral analysis of the labeled and unlabeled compounds was also done. The unlabeled compound showed a loss of 15 followed by a loss of 28. This is best explained by loss of a silylmethyl followed by loss of ethylene from the aliphatic portion of the molecule as shown in Scheme 26.

**Scheme 26**

\[
\begin{align*}
\text{m/e 162} & \quad \text{m/3 147} & \quad \text{m/e 119} \\
\text{[\text{m/e 162}]} & \rightarrow & \text{[\text{m/e 119}]} \\
\text{[\text{m/3 147}]} & \rightarrow & \text{[\text{m/e 119}]} 
\end{align*}
\]

The labeled compound showed the same degradation pattern. Mass spectral measured intensities showed the labeled parent ion \((\text{m/e} = 162/163)\) to have 24.8\% \(^{13}\)C label. This is in agreement with an earlier measured intensity for the benzoyl-trimethylsilanetoluene-p-sulphonylhydrazone which showed 24.3\% \(^{13}\)C label. The measured intensity of the peaks for
loss of methyl and ethylene (m/e = 119/120) showed 23.6% \(^{13}\text{C}\) label. An exact mass of the 119 peak (m/e 119.03185 ± 0.0006, calc. 119.0317) confirmed the formula of C\(_7\)H\(_7\)Si. If the assumptions are correct concerning which carbons are lost, then again the phenylcarbene mechanism is supported to the discredit of the silacyclop propane mechanism.

Work on this experiment was concurrently performed at Princeton University in conjunction with Dr. Maitland Jones, Jr. Samples of labeled and unlabeled 1,1-dimethyl-2,3-benzo-1-silacyclopent-2-ene were made by flash pyrolysis (420\(^\circ\) at 5mm) of the lithium salt of benzyltrimethylsilane toluene-p-sulphonylhydrazone. Proton nmr, \(^{13}\text{C}\) nmr, and mass spectral measurements made at Iowa State University completely supported the results reported above.

In conclusion, it would seem there is very little leeway in deciding between the silacyclop propane mechanism and the phenylcarbene mechanism. There cannot be a silacyclop propane intermediate in the rearrangement of trimethylsilyl-phenylcarbene to 1,1-dimethyl-2,3-benzo-1-silacyclopent-2-ene. In light of the evidence concerning the location of the original carbene carbon, it would be extremely difficult to imagine an alternative to the phenylcarbene rearrangement mechanism.

Since the completion of this work, Kreeger and Shechter (63) have published work with trimethylsilylcarbene. While
The evidence is not conclusive at this point, it does raise an interesting problem. Contrary to earlier work, it now appears that silylcarbenes do not undergo insertion to form silacyclop propane. In addition to altering current concepts of silacyclopropane, it should stir some mechanistic reexaminations of other proposed silacyclopropane intermediates.
EXPERIMENTAL

General

Infrared spectra (ir) were recorded on a Beckman 18A spectrophotometer. Routine nmr spectra were determined on a Varian model A-60 or Hitachi R20-B spectrometer, and chemical shifts are reported as parts per million (δ scale) from tetramethysilane as an internal standard. Routine mass spectra were obtained on an Atlas CH-4 spectrometer and an MS-902 spectrometer. High resolution mass spectra were run on the MS-902. Gas chromatographic/mass spectral (g.c.m.s.) analysis was done on a Perkin-Elmer 270 mass spectrometer. Routine analytical and preparative gas chromatography (g.c.) was done with an F & M 500 gas chromatograph.

Yields, unless otherwise indicated, were measured by g.c. analysis. A known amount of a standard was added to the reaction mixture and used to calculate yield. The exception to this procedure was for reactions of the disilene generators. In these cases the yield of naphthalene or biphenyl was assumed quantitative and yields based on them. In all cases, corrections were made for differences in thermal conductivities.

Flow pyrolysis was done by dripping the desired solution through a vertical tube (10 m x 30 cm) packed with
quartz chips. The solutions were dripped through the tube at a rate of 0.33 ml/min. The reactions were done under a nitrogen flow at 1 ml/sec. The products were trapped in a liquid nitrogen cooled trap for analysis and separation.

**Preparation of 2,3-benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (18)**

2,3-Benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]-octa-2,5-diene was prepared according to the method of Roark and Peddle (69). This procedure was sometimes modified to use sodium in place of lithium: nmr (CDCl₃) δ 0.00 (s, 6H), 2.0 (s, 6H), 3.40 (d of d, 2H), 6.10 (d of d, 2H), 7.10 (s, 4H); mass spectrum (70 eV) m/e (rel. intensity) 244 (36), 229 (4), 128 (10), 116 (100), 73 (48).

**Preparation of 1-phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (19)**

1-Phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]-octa -2,5-diene was prepared according to the method of Roark and Peddle (69) with sodium used in place of lithium: nmr (CDCl₃) δ 0.0 (s, 6H), 0.3 (s, 6H), 2.9 - 3.1 (m, 1H), 5.8 - 6.2 (m, 4H), 7.2 - 7.5 (m, 5H); mass spectrum (70 eV) m/e (rel. intensity) 270 (32), 255 (3), 154 (14), 116 (100).

**Preparation of cyclosiloxanes**

Hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, and decamethylcyclopentasiloxane were made
according to the method of Patnode and Wilcock (106). Hexamethylcyclotrisiloxane was identified: mass spectrum (70 eV) m/e (rel. intensity) 207 (100), 192 (8), 177 (4), 133 (7), 74 (8); and infrared (CCl₄) 2965 (w), 1270 (m), and 1030 (s) cm⁻¹. Octamethylcyclotetrasiloxane was identified: mass spectrum (70 eV) m/e (rel. intensity) 281 (100), 266 (7), 207 (5), 192 (4); and infrared (CCl₄) 2965 (w), 1265 (m), and 1085 (s). Decamethylcyclopentasiloxane was identified: mass spectrum (70 eV) m/e (rel. intensity) 355 (100), 340 (5), 281 (48), 266 (4); and infrared (CCl₄) 2965 (w), 1270 (m), and 1090 (s).

**Pyrolysis of 1-phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (19) with benzaldehyde**

A solution of 0.450 grams (1.06 m moles) of 1-phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene and 3.5 grams (33 m moles) of benzaldehyde was degassed via the freeze-thaw technique. The solution was dripped (1/3 ml/min) through a vertical pyrolysis column heated to 480° C under a nitrogen flow of 1 ml/sec. The products were collected in a liquid nitrogen trap. Analysis and separation was done by gas chromatography. The products were trans-stilbene (23.9% - identification by matching g.c. retention time, nmr and mass spectra with authentic sample (107)), hexamethylcyclotrisiloxane (16%), and
octamethylcyclotetrasiloxane (13.8%) (siloxanes identified by matching g.c. retention time, infrared, and mass spectra comparison with authentic samples (106)).

**Pyrolysis of 2,3-benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (18) with benzaldehyde**

0.122 grams (0.5 m moles) of 2,3-benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene was dissolved in 1.06 grams (10 m moles) of benzaldehyde. The solution was degassed and pyrolyzed in a nitrogen flow system at 500°C. The products were isolated and analyzed by gas chromatography. Products included naphthalene, trans-stilbene (21.4%), hexamethylcyclotrisiloxane (14.1%), and octamethylcyclotetrasiloxane (10.2%). All products were identified by g.c. retention time, nmr, infrared, and mass spectra comparison with authentic samples.

**Pyrolysis of 2,3-benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (18) with benzaldehyde**

A solution of 0.10 grams (0.41 m moles) of 2,3-benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene and 0.412 grams (3.9 m moles) of benzaldehyde were degassed via the freeze-thaw technique. The solution dripped through a vertical pyrolysis column heated to 500°C under a nitrogen flow. The products were trapped in liquid nitrogen. An nmr of the product solution shows no evidence for heptafulvalene (olefin H's at δ 5.88 (108)), but does show a peak for trans-stilbene (δ 6.93 (107)).
Pyrolysis of 2,3-benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (18) with benzaldehyde and cyclohexene

0.244 grams (1 m mole) of 2,3-benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene was added to 0.42 grams (4 m moles) of benzaldehyde and 0.82 grams (10 m moles) of cyclohexene. The solution was degassed and pyrolyzed at 500° C in a nitrogen flow system. The product was analyzed by gas chromatographic mass spectroscopy. No evidence was found for 7-phenylnorcarane, nor any other C_{13}H_{16} isomer.

Pyrolysis of 1-phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (19) in hexane

0.1 grams (0.37 moles) of 1-phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene was dissolved in 1.5 grams (17.5 m moles) of hexane. The solution was pyrolyzed in a nitrogen flow system at 480° C. Analysis by gas chromatography and gas chromatographic mass spectroscopy showed neither trans-stilbene nor cyclic siloxanes. Gas chromatography and g.c. mass spectroscopy identified a quantitative yield of diphenyl along with several polysilanes.

Pyrolysis of benzaldehyde

1.75 grams (16.5 m moles) of benzaldehyde were pyrolyzed under nitrogen flow at 480° C. Analysis of the
product by nmr and g.c.m.s. showed only starting benzaldehyde (96% recovery) and no evidence for trans-stilbene.

**Pyrolysis of 1,2-dimethoxy-1,1,2,2-tetramethyldisilane with benzaldehyde**

1.78 grams (0.1 moles) of dimethoxydisilane 42 was added to 2.12 grams (0.2 moles) of benzaldehyde. The solution was analyzed by g.c., and benzaldehyde (97%) isolated (identified by g.c. retention time and g.c.m.s.). No evidence was found for trans-stilbene or cyclic siloxanes.

**Preparation of 5,6-diphenyl-2,3,3,3-tetramethyl-2,3-disiladioxane (41)**

2.0 grams (9.3 m moles) of dihydrobenzoin was dissolved in 250 ml of dry, deoxygenated benzene. 1.9 grams (18.8 m moles) of dry triethylamine was added. 1.75 grams (9.3 m moles) of 1,2-dichloro-1,1,2,2-tetramethyldisilane was added and the solution refluxed under nitrogen for 12 hours. The solution was filtered to remove triethylamine hydrochloride. The benzene was distilled from the filtrate under reduced pressure, and then under high vacuum. The residue was identified as disiladioxane 41 (80%): nmr (CCl₄) δ 0.30 (s, 12H), 5.16 (s, 2H), 6.92 (s, 10H); infrared (CCl₄) 3080 (w), 3025 (w), 2950 (m), 2880 (w), 1500 (w), 1410 (m), 1380 (w), 1250 (s), 1200 (w), 1105 (s), 1070 (b); mass spectrum (70 eV) m/e (rel. intensity) 328 (1), 270 (17),
180 (100), 165 (25), 74 (28); mass spectrum calculated for $\text{C}_{18}\text{H}_{24}\text{O}_{2}\text{Si}_{2}$ m/e = 328.1315; found: m/e = 328.1310 + 0.0016.

Pyrolysis of 5,6-diphenyl-2,2,3,3-tetramethyl-2,3-disiladioxane (41)

0.5 grams (1.5 m moles) of 5,6-diphenyl-2,2,3,3-tetramethyl-2,3-disiladioxane (41) was dissolved in 10 ml of dry, deoxygenated benzene. The solution was dripped through a pyrolysis column at 500° under nitrogen flow. The products were separated by gas chromatography. They were trans-stilbene (73%) (identified by nmr and gas chromatographic comparison with authentic sample (107)), hexamethylcyclotrisiloxane (28%) and octamethylcyclotetrasiloxane (17%) (siloxanes identified by g.c. and g.c.m.s. comparison of authentic samples).

Preparation of 1,1,3-trimethyl-1-silacyclopent-3-ene

1,1,3-trimethyl-1-silacyclopent-3-ene was prepared according to the method of Weyenberg and co-workers (92): nmr ($\text{CCl}_{4}$) $\delta$ 0.15 (s, 6H), 1.20 (m, 4H), 1.72 (m, 3H), and 5.38 (m, 1H); and b.p. 55 - 65° (20 mm).

Reaction of 1-phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (19) with 2-butyne

1.08 grams (4 m moles) of 1-phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene was dissolved in 0.69 grams (13 m moles) of 2-butyne in a sealing tube. The tube
was sealed and heated at 250° for 18 hours. The products were biphenyl (identified by g.c. retention time, nmr and g.c.m.s. comparison with authentic samples (109)) and 20% octamethyl-3,6-disilacyclohexa-1,4-diene (identified by g.c. retention time, nmr, and mass spectral comparison with an authentic sample).

Pyrolysis of 1,2-dimethoxy-1,1,2,2-tetramethylsilane (42) with 2-butyne

The procedure and quantities used were those of Atwell and Uhlman (85). 1,2,3,3,4,4-hexamethyl-3,4-disilacyclobutene was isolated by distillation: b.p. 55 - 65° (25mm); nmr (CCl₄) δ 0.15 (s, 12H), 1.66 (s, 6H); mass spectrum (70 eV) m/e (rel. intensity), 170 (65), 155 (100), 116 (50), 73 (82); mass spectrum calculated for C₈H₁₈Si₂, m/e = 170.0947; found: m/e = 170.0942 ± 0.001 (85). After distillation, a solid crystalized from the residue and 3.2 grams (25.5%) of octamethyl-3,6-disilacyclohexa-1,4-diene was isolated and identified by g.c. retention time, nmr, and mass spectra comparison with an authentic sample.

Reaction of hexamethyl-3,4-disilacyclobutene (28a) with oxygen

Hexamethyl-3,4-disilacyclobutene was dissolved in carbon tetrachloride. Oxygen was bubbled through the solution. The solution became hot and gave a quantitative yield of 1,2,3,3,5,5-hexamethyl-3,5-disila-4-oxycyclopentene:
nnir (CCl₄) δ 0.08 (s, 12H), 1.70 (s, 6H). The carbon tetrachloride was distilled off: mass spectrum (70 eV) m/e (rel. intensity) 180 (61), 165 (100), 116 (18), 73 (30), 58 (13); mass spectrum calculated for C₈H₁₈Si₂O, m/e = 186.0896; found, m/e = 186.0902 ± 0.002 (85).

Pyrolysis of 1,2-dimethoxy-1,1,2,2-tetramethyldisilane (42) with 2-butyne and 3-hexyne

The procedure was that of Atwell and Weyenberg (82). A solution of 0.162 grams (0.91 m moles) of 1,2-dimethoxy-1,1,2,2-tetramethyldisilane, 0.108 grams (2.0 m moles) of 2-butyne, and 0.178 grams (2.0 m moles) of 3-hexyne was degassed in a tube. The tube was sealed under a vacuum and heated to 225 °C for 18 hours. The tube was opened and the products analyzed and separated by gas chromatography. The products were octamethyl-3,6-disilacyclohexa-1,4-diene (17.9%) (identified by comparison of g.c. retention time, nmr, and mass spectral comparison with authentic sample (82)), 1,2,3,3,6,6-hexamethyl-4,5-diethyl-3,6-disilacyclohexa-1,4-diene (19.5%) and 1,2,4,5-tetraethyl-3,3,6,6-tetramethyl-3,6-disilacyclohexa-1,4-diene (8.7%).

1,2,3,3,4,5,6,6-Octamethyl-3,6-disilacyclohexa-1,4-diene was identified: nmr (CCl₄) δ 0.10 (s, 12H), 1.80 (s, 12H) (82); mass spectrum (70 eV) m/e (rel. intensity), 224* (65), 209 (100), 155 (73), 97 (22), 73 (31); mass spectrum calculated for C₁₂H₂₄Si₂, m/e = 224.1417; found,
m/e = 224.1419 + 0.0012. 1,2,4,5-Tetraethyl-3,3,6,6-tetramethyl-3,6-disilacyclohexa-1,4-diene was identified: nmr (CCl₄) $ 0.10 (s, 12H), 1.00 (t, 12H), 2.26 (q, 8H); mass spectrum (70 eV) m/e (rel. intensity), 280 (100), 265 (37), 251 (96), 183 (55), 111 (16), 97 (18), 73 (49), 58 (30); mass spectrum calculated for C₁₆H₃₂Si₂, m/e = 280.0243; found, m/e = 280.0243 + 0.0014. 1,2,3,3,6,6-Hexamethyl-4,5-diethyl-3,6-disilacyclohexa-1,4-diene was identified: nmr (CCl₄) $ 0.10 (s, 12H), 1.00 (t, 6H), 2.26 (q, 4H); mass spectrum m/e (rel. intensity), 252 (100), 237 (85), 223 (68), 183 (40), 155 (75), 111 (35), 97 (37), 73 (44), 58 (40); mass spectrum calculated for C₁₂H₂₄Si₂, m/e = 252.1730; found, 252.1726 + 0.0013.

**Reaction of hexamethyl-3,4-disilacyclobutene (28a) with 2-butyne**

0.22 grams (4 m moles) of 2-butyne was degassed in a sealing tube. 0.17 grams (1 m moles) of hexamethyl-3,4-disilacyclobutene was added under nitrogen. The tube was degassed and sealed. The solution was heated for 18 hours at 225° C. The products were analyzed and isolated by gas chromatography. No starting material was found. The products were hexamethyl-3,5-disila-4-oxycyclopentene (81.4%) (identified by g.c. retention time and nmr comparison with authentic samples (85)) and (31.4% - corrected for presence
of 44) octamethyl-3,6-disilacyclohexa-1,4-diene (identified by g.c. retention time, nmr spectrum, mass spectrum, and exact mass comparison with an authentic sample (82)).

**Reaction of hexamethyl-3,4-disilacyclobutene (28a) with 3-hexyne**

0.33 grams (4 m moles) of 3-hexyne was degassed in a sealing tube. 0.17 grams of hexamethyl-3,4-disilacyclobutene was added under nitrogen. The tube was degassed and sealed. The tube was heated for 18 hours at 225° C. Analysis and isolation was done by gas chromatography. No starting material was found. Compounds isolated were hexamethyl-3,5-disila-4-oxy-cyclopentene (86%) (identified by g.c. retention time and nmr comparison with authentic samples (85)) and (39% - corrected for presence of 44) 1,2-diethyl-3,3,4,5,6,6-hexamethyl-3,6-disilacyclohexa-1,4-diene (identified by g.c. retention time, nmr spectrum, mass spectrum, and exact mass comparison with authentic samples). No octamethyl-3,6-disilacyclohexa-1,4-diene or 1,2,4,5-tetraethyl-3,3,6,6-tetramethyl-3,6-disilacyclohexa-1,4-diene was found.

**Pyrolysis of 2,3-benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (18) with 2-butyne**

1.22 grams (5 m moles) of 2,3-benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene was dissolved in 1.35 grams (25 m moles) of 2-butyne. The solution was
pyrolyzed in a nitrogen flow system at 500°. The product was analyzed and separated by gas chromatography. The isolated products were 1,2,3,3,5,5-hexamethyl-3,5-disila-4-oxy cyclopentene (4.1%) (identified by g.c. retention time, nmr, and mass spectral comparison of a known sample (85)) and 1,2,3,3,5-pentamethyl-3,5-disilacyclopentene (26.3%): nmr (CCl₄) δ -0.52 (d of d, 1H), -0.08 (d of d, 1H), 0.11 (s, 6H), 0.17 (d, 3H), 4.25 (m, 1H); infrared (CCl₄) 2945 (s), 2890 (m), 2840 (m), 2085 (s), 1248 (s); mass spectrum (70 eV) m/e (rel. intensity) 170 (20), 155 (100), 128 (56), 44 (42); mass spectrum calculated for C₈H₁₈Si, m/e = 170.0947; found, m/e = 170.0947 ± 0.001.

Pyrolysis of 1-phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (19) with 2-butyne

0.54 grams (2 m moles) of 1-phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene was dissolved in 3.24 grams (60 m moles) of 2-butyne. The solution was pyrolyzed in a nitrogen flow system at 480°. The solution was analyzed and separated by gas chromatography. 1,2,3,3,5-Pentamethyl-3,5-disilacyclopentene (28.3%) and 1,2,3,3,5,5-hexamethyl-3,5-disila-4-oxy cyclopentene (8.5) were isolated. Products were identified by g.c. retention time, nmr, and mass spectral comparison with known samples.
Preparation of 6,7-benzo-2,2,4,4-tetramethyl-2,4-disila-3-oxybicyclo[3.2.2]nona-6,8-diene (45)

1.0 grams (4.1 m moles) of 2,3-benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene was dissolved in carbon tetrachloride. 0.71 grams (4.1 m moles) of m-chloroperbenzoic acid was added and the reaction followed by nmr. After one hour of stirring at room temperature, the solution was extracted with an aqueous solution of sodium bicarbonate and then dried. The carbon tetrachloride was removed via rotoevaporation to isolate the 6,7-benzo-2,2,4,4-tetramethyl-2,4-disila-3-oxybicyclo[3.2.2]nona-6,8-diene: nmr (CCl\textsubscript{4}) δ 0.11 (s, 6H), 0.37 (s, 6H), 2.85 (d of d, 2H), 6.16 (d of d, 2H), 7.00 - 7.40 (m, 4H) (69).

Pyrolysis of 6,7-benzo-2,2,4,4-tetramethyl-2,4-disila-3-oxybicyclo[3.2.2]nona-6,8-diene (45) with 2-butyne

0.5 grams (1.92 m moles) of 6,7-benzo-2,2,4,4-tetramethyl-2,4-disila-3-oxybicyclo[3.2.2]nona-6,8-diene was dissolved in 2.1 grams (39 m moles) of 2-butyne. The solution was pyrolyzed in the flow pyrolysis system under nitrogen at 500°. NMR and gas chromatographic analysis showed no evidence of 1,1,3,3,4,5-hexamethyl-1,3-disila-2-oxycyclopent-4-ene. The butyne was distilled off and nmr and gas chromatography analysis repeated with only negative results. An nmr analysis indicated 95% recovery.
of starting 45. The reaction was repeated with negative results (78% recovery of 45, 11% benzene, and 4% biphenyl) at 640°.

Preparation of 1,1,2,2,4-pentamethyl-1,2-disilacyclohex-4-ene

5.1 grams (75 m moles) of isoprene was added to 9.31 grams (50 m moles) of 1,2-dichloro-1,1,2,2-tetramethyldisilane in 100 ml of dry hexamethylphosphoramide. 2.43 grams (0.1 moles) of magnesium was added and the solution was heated (80°) for three days. Hexane was added and extracted several times with water. After drying with magnesium sulfate the majority of hexane was removed by rotoevaporation. The residue was analyzed and separated by g.c. The products were 1,1,3-trimethyl-1-silacyclopent-3-ene (5.35%) (identified by g.c. and nmr comparison with an authentic sample) and 1,1,2,2,4-pentamethyl-1,2-disilacyclohex-4-ene (11.8%): nmr (CCl₄) δ 0.7 (s, 12H), 1.36 (m, 4H), 1.7 (m, 3H), and 5.27 (t. 1H); infrared 2960 (b), 1440 (w), 1250 (s), 1150 (w), and 1042 (m); mass spectrum (70 eV) m/e (rel intensity) 184 (56), 179 (42), 116 (100), 73 (48), and 45 (62); mass spectrum calculated for C₉H₂₀Si₂ m/e = 184.1103; found, m/e = 184.1114 ± 0.0018.
Pyrolysis of l-phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (19) with isoprene

1.35 grams (1.0 m moles) of disilabicyclo[2.2.2]octa-diene 19 was added to 0.73 grams (10.7 m moles) of isoprene in a tube. The solution was degassed and the tube sealed. The tube was heated for 18 hours at 245°. The tube was opened and the products analyzed and separated by g.c. The products were biphenyl and 1,1,2,2,4-pentamethyl-1,2-disilacyclohex-4-ene (22.0%). Both products were identified by g.c., nmr. and mass spectral (including exact mass of the disilacyclohexene) comparison with authentic samples.

Pyrolysis of 1,2-dimethoxy-1,1,2,2-tetramethyldisilane and isoprene

1.2 grams (6.75 m moles) of 1,2-dimethoxy-1,1,2,2-tetramethyldisilane was added to 0.93 grams (1.35 m moles) of isoprene in a tube. The solution was degassed and the tube sealed. The tube was heated for 18 hours at 245°. The tube was opened and the products were analyzed and separated by g.c. The products were dimethyldimethoxysilane and 1,1,3-trimethyl-1-silacyclopent-3-ene (18.9%) (identified by g.c., nmr, and mass spectral comparison with authentic samples). No evidence was found for 1,1,2,2,4-pentamethyl-1,2-disilacyclohex-4-ene (<1%).
Pyrolysis of 1,1,3-trimethyl-1-silacyclopent-3-ene with 1,2-dimethoxy-1,1,2,2-tetramethylidisilane

0.57 grams (4.5 m moles) of 1,1,3-trimethyl-1-silacyclopent-3-ene was added to 0.53 grams of dimethoxydisilane in a tube. The solution was degassed and sealed. The tube was heated for 18 hours at 245°. The 1,1,3-trimethyl-1-silacyclopent-3-ene was recovered (98%) and no evidence was found for 1,1,2,2,4-pentamethyl-1,2-disilacyclohex-4-ene (<1%).

Preparation of benzoyltrimethylsilane toluene-p-sulphonylhydrazone

Benzotrimethylsilane toluene-p-sulphonylhydrazone was prepared according to the method of Brook and Jones (104): nmr (CDCl₃) δ 0.08 (s, 9H), 2.4 (s, 3H), 7.3 (m, 9H); mass spectrum (70 eV) m/e (rel. intensity), 346* (7), 228 (38), 191 (35), 91 (92), 73 (100).

Preparation of trimethylsilylphenyldiazomethane (51)

Trimethylsilylphenyldiazomethane was made according to the method of Shechter and co-workers (110). Distillation at 80 - 135° (0.3 mm) yielded a red liquid: nmr (CCl₄) δ 0.15 (s, 9H), 7.0 (m, 5H) (104).

Pyrolysis of trimethylsilylphenyldiazomethane (51)

Trimethylsilylphenyldiazomethane was injected into a gas chromatograph with the inlet port at 300° and an SE-30
column at 175°. The product 1,1-dimethyl-2,3-benzo-1-silacyclopent-2-ene was isolated by cold trap at -78°: nmr (CCl₄) δ 0.31 (s, 6H), 1.00 (t, 2H), 3.02 (t, 2H), 6.95 - 7.51 (m, 4H) (59); mass spectrum (70 eV) m/e (measured intensity) 163 (3.4), 162 (21.5), 120 (0.48), 119 (3.25); ¹³C nmr ppm from TMS (intensity), 153.14 (317440), 139.86 (227456), 131.93 (1388928), 129.20 (1673984), 125.56 (2893056), 31.80 (652416), 11.47 (360448), -1.59 (551936).

Preparation of ¹³C labeled benzoyltrimethylsilane toluene-p-sulphonylhydrazone

 Phenylmagnesium bromide and 20% ¹³C labeled carbon dioxide were reacted to produce benzoic acid (109). The benzoic acid was converted to benzoyltrimethylsilane toluene-p-sulphonylhydrazone according to the method of Brook and Jones (104): nmr (CDCl₃) δ 0.08 (s, 9H), 2.41 (s, 3H), 7.80 - 6.75 (m, 9H); mass spectrum (70 eV) m/e (rel. intensity), 346 (6) m+, 228 (36), 191 (34), 91 (90), 73 (100), m/e (measured intensity) 346 (45.0), 347 (22.5). The ¹³C labeled is measured at 24.3%. An nmr of the intermediate benzylchloride shows the α carbon to have 20% ¹³C label: nmr δ 4.14 (s, 1.6H), 4.14 (d, 4H), 7.10 (s, 5H).

Preparation of ¹³C labeled trimethylsilylphenyldiazomethane

¹³C enriched trimethylsilylphenyldiazomethane was made from ¹³C enriched benzoyltrimethylsilane
toluene-p-sulphonylhydrazone according to the method of Shechter and co-workers (110). Distillation at 80 - 135° (0.3 mm) yielded a red liquid.

Pyrolysis of $^{13}$C enriched trimethylsilylphenyldiazomethane

$^{13}$C enriched trimethylsilylphenyldiazomethane was injected into a gas chromatograph with the injection port at 300° and an SE-30 column at 175°. The product $^{13}$C enriched 1,1-dimethyl-2,3-benzo-1-silacyclopent-2-ene was isolated with a cold trap at -78°: nmr (CCl$_4$) $\delta$ 0.31 (s, 6H), 1.00 (t, 2H), 3.02 (t, 2H), 6.95 - 7.51 (m, 4H) (59): mass spectrum (70 eV) m/e (measured intensity) 163 (13.2), 162 (32.5), 120 (2.1), 119 (5.5); mass spectrum calculated for C$_7$H$_7$Si m/e = 119.0317; found, m/e = 119.0318 ± 0.0006; $^{13}$C nmr ppm from TMS (intensity), 153.11 (124992), 139.86 (1183552), 131.93 (495616), 129.20 (608256), 125.56 (1042816), 31.80 (288640), 11.47 (177600), -1.59 (230336).
LITERATURE CITED

2. L. Gatterman, Ber. 22, 194 (1889).


107. Aldrich Chemical Co., Inc.


ACKNOWLEDGEMENTS

I would like to thank Dr. Thomas J. Barton for his inspiration, assistance, and understanding throughout my graduate career. His creativity, enthusiasm, and attitude toward science have left a vivid impression on me that has influenced my approach to chemistry.

The course of my career has been enjoyable due to the ideas, commiserations, and humor of my fellow graduate students. I am grateful for their help and friendship.

Special thanks are due to Dr. Philip Warner for going out of his way in time and effort to greatly aid in finishing this thesis.

Finally, great credit goes to my wife, Susan, for her love, patience, and encouragement. Without her this thesis would not have been possible.