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ITS CHARACTERIZATION AND REACTIONS

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TETRAMETHYL-1-SILACYCLOPROP-2-ENE:

ITS CHARACTERIZATION AND REACTIONS

by

Becky June Cornett

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ABSTRACT

TETRAMETHYL-1-SILACYCLOPROP-2-ENE: ITS CHARACTERIZATION AND REACTIONS

By Becky June Cornett

Chairman: Peter P. Gaspar.

The object of this research is to fully characterize and study some of the reactions of tetramethyl-1-silacycloprop-2-ene. The final characterization of this compound was accomplished by obtaining both silicon-29 and carbon-13 nuclear magnetic resonance spectra. The reactions studied included those with fluorenone, acetone, styrene, phenylacetylene, acetonitrile, t-butylcyanide, methyl isocyanate, phenyl azide, and azobenzene. Product analyses suggest that aside from addition reactions tetramethylsilacyclopropene can react either via a radical chain polymerization or an anionic chain polymerization mechanism with the latter being the more prevalent. Other reactions studied included the photolysis of tetramethylsilacyclopropene and its reactions in the presence of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$.

An appendix includes a study of trimethylsilyl radical disproportionation in the liquid phase to a sila olefin. Trimethylsilyl radicals in solution undergo disproportionation as well as recombination in a 1:5 ratio. The sila olefin formed by disproportionation was trapped by alcohols.

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I. INTRODUCTION

Although Volpin [1] predicted, as early as 1962, that sufficiently reactive silylenes should add to alkynes to form stable silacyclopropenes, they continued to elude scientists until 1976 when R.T. Conlin and P.P. Gaspar [2] obtained tetramethyl-1-silacycloprop-2-ene. The importance of isolating tetramethylsilacyclopropene lay not only in the verification that silylenes could add to acetylenes to form three-membered heterocycles but in the finding of an unusually stable highly strained new ring system. In the year following Conlin's original work three other groups reported the synthesis of several other silacyclopropenes [3,4,5]. The chemistry of this new ring system is just beginning to be explored. Because of their high reactivity silacyclopropenes offer the possibility of a wealth of unusual reactions. These reactions might lead to new compounds that are of interest themselves or that cannot be made by any other route.

By studying these reactions and understanding their mechanisms a better understanding of the bonding characteristics of silacyclopropenes can be gained.

Since tetramethyl-1-silacycloprop-2-ene is the least substituted silacyclopropene reported to date and, therefore, should be the most reactive, it was fully characterized and some of its reactions were studied. Because the synthesis of tetramethylsilacyclopropene is so intimately connected to the chemistry of silylenes, the formation and reactions of silylenes will be discussed before discussing silacyclopropenes.

1.0 STRUCTURES AND PHYSICAL PROPERTIES OF SILYLENES

Margrave and co-workers [6] have given us a good picture of the spectral and physical properties of difluorosilylene. Difluorosilylene is the most stable silylene, possessing a half life of one hundred fifty seconds in the gas phase at ambient temperature and 0.1 torr pressure. This stability allows its transport in the gas phase away from the reaction zone where it is formed for the study of its physical properties. Difluorosilylene has been studied in the gas phase by microwave [7], electron spin resonance [8], ultraviolet absorption [9], and by infrared [10] spectroscopy; in a solid matrix at low temperature by infrared [11] spectroscopy; and in the condensed phase by electron spin resonance [12] spectroscopy. The structures of other silylenes have also been determined from spectral studies and are shown below [12,13] along with some heats of formation.

Table 1: STRUCTURES OF SILYLENES

θ	$\theta(^{\circ})$	$r_{\circ} \text{ Si-R } (\text{\AA})$	$r_{\circ} \text{ Si-R}' (\text{\AA})$	method
R = H R' = Cl	102.8	1.56	2.06	a [17]
R = H R' = Br	102.9	1.56	2.23	a [17]
R = H R' = H	92.0	1.52	1.52	a [18]
R = F R' = F	101.0	1.59	1.59	b [10]

a = electronic spectra in vapor phase

b = microwave spectra in vapor phase

Table 2: HEATS OF FORMATION OF SILYLENES

SILYLENE	$\Delta H_{f,298}^{\circ}$ kcal/mole	method
SiH ₂	81 59	a [19] b [20]
SiF ₂	-148 -139	b [21] a [22]
SiCl ₂	-38	b [23]
SiBr ₂	-12 -10	b [23] b [24]
SiI ₂	18	b [23]

a = appearance potential from mass spectrum

b = kinetic study

The thermodynamic properties and electronic structures of diorganosilylenes are practically unexplored because silylenes with organic substituents do not have the stability of difluorosilylene and must be studied as highly

reactive intermediates. Only very recently has R. West [22] reported the preparation and spectroscopic characterization of dimethylsilylene in hydrocarbon glasses and inert gas matrices at low temperatures.

Complications in the reactions of carbenes because of their two low-lying electronic states 1A_1 and 3B_1 are well known. Experimental evidence and theoretical calculations [23,24,25] indicate that all silylenes which have been examined so far have a singlet ground electronic state [23,22]. These silylenes include SiH_2 , $SiHCl$, $SiHI$, SiF_2 , $SiCl_2$, and $SiMe_2$. That SiH_2 does have a singlet ground state was confirmed in a rather direct manner by fixed-frequency laser photoelectron spectrometry [26]. The singlet-triplet separation was determined to be less than or equal to 0.6 eV (≤ 14 kcal/mole). Although most reactions of silylenes involve the singlet ground state, it has been suggested that the photochemical extrusions of silylenes from polysilanes produce silylenes in an excited state [27]. Scavenger experiments done on reactions of recoiling silicon atoms have been interpreted as scavenging triplet $^{31}SiH_2$ [28,29] and $^{31}SiF_2$ [32].

2.0 PREPARATION OF SILYLENES

Silylenes may be prepared by several methods. These methods can be divided into five general categories:

1) reduction of halosilanes, 2) thermal degradation of the appropriate substrate, 3) photolysis of polysilanes,

4) reactions of atomic silicon and 5) rearrangement of disilenes to silylsilylenes.

2.1 REDUCTIONS

The first methods of preparation were reductions. The most intensively studied reaction in this class involves the reaction of silicon with silicon tetrahalides, a retro-disproportionation.

Despite the high temperatures (greater than 800°C) employed in this method, it is still used as a source of silylenes for synthetic and mechanistic studies.

The reductions of other metal halides by silicon have been reported [12].

Vapor phase reductions have been used to prepare dimethylsilylene [12,31].

Earlier reports of this reaction occurring in the liquid phase to produce silylenes were ambiguous. The intermediacy of dimethylsilylene was deduced from the product obtained in the following reaction [12,32].

However, it was demonstrated that the diene rather than the halosilane reacted initially with the alkali metal, and the role of the halosilane was merely to silylate a carbanion [33,34]. No firm evidence has been presented for the intermediacy of silylenes in these heterogeneous liquid phase reactions.

2.2 THERMOLYSES

Silylenes may be prepared from the thermal degradation of appropriate substrates. Proper choice of a substrate allows the use of very mild reaction conditions. One of the most widely used thermal methods is represented by the following general equation which may be written for the unsymmetrical thermolysis, with rearrangement, of disilanes [35].

Z = hydrogen, halogen, or alkoxy
X, Y = hydrogen, halogen, alkoxy, alkyl, or aryl

I.M.T. Davidson [36] discusses the thermodynamic factors that influence the formation of silylenes in the pyrolysis of silicon compounds. Atwell and Weyenberg have demonstrated the generality of this method for alkoxydisilanes [39,38]. By using alkoxydisilanes the thermolyses may be carried out at fairly low temperatures.

These reactions have a half life of approximately two hours in the liquid phase at the temperatures shown. In gas phase pyrolyses with ten to twenty second contact times in the hot zone, these reactions have half lives of only a few seconds when the temperatures are 150 degrees higher than those indicated. Temperatures between 500° and 525°C are needed for the gas phase decomposition of 1,2-dichlorodisilanes. Dihydro- and difluoro- disilanes require intermediate temperatures [37]. When the flash vacuum pyrolysis technique of Hedaya [39] is employed, even milder conditions can be utilized. Although temperatures above 600°C are used, the contact time is less than 0.1 second.

Kinetic studies and trapping experiments by Atwell and Weyenberg [38,40], Purnell and co-workers [41,42], and

M. A. Ring and co-workers [43,44,45,46] have established the intermediacy of silylenes in these reactions. The mechanism is believed to involve an α -elimination [12,17,37].

This type of elimination is characteristic of compounds having an atom with an unshared pair of electrons and a metal or metalloid bonded to a common atom.

Gilman and co-workers [47,48] were the first to report the extrusion of silylenes from the thermolysis of 7-sila-norbornadienes. The temperatures required for thermolyses vary over a wide range depending on the stability of the 7-silanorbornadiene. For example, the liquid phase pyrolysis of 1,4,5,6-tetraphenyl-7,7-dimethyl-7-sila-2,3-benzonorbornadiene required a temperature of 300° [47]; whereas, the

analogous 1,4-dihydro compound decomposed at 0°C [49], and 1,4-diphenyl-2-trichlorogermyl-7,7-dimethyl-7-silanorbornadiene decomposed in refluxing carbon tetrachloride [50].

It has not been firmly established that the decomposition of these compounds leads to free silylenes. Barton and co-workers [51] have provided evidence which suggests that the extrusion may proceed in a stepwise fashion; thus, silylene transfer may occur without the formation of free silylene.

Dimethylsilylene extrusion from the thermolysis of hexamethylsilacyclopropane was first reported by Seyferth [52] in 1975.

This is a very mild method which produces high yields of dimethylsilylene adducts when substrates are present.

Caution must be observed, however, in assuming that free dimethylsilylene is formed. The yield of the dimethylsilylene addition product dropped to zero when hexamethylsilacyclopropane and 2,3-dimethylbuta-1,3-diene were reacted without diluent. When hexamethylsilacyclopropane and styrene (or α -methylstyrene) were pyrolyzed together a silacyclopentane rather than a silacyclopropane was formed [53].

The absence of silylene adduct in both cases may be due to a competition between SiMe_2 loss from a diradical intermediate ($\text{Me}_2\dot{\text{Si}}-\text{C}(\text{CH}_3)_2-\dot{\text{C}}(\text{CH}_3)_2$) and trapping of that diradical intermediate by the substrate.

When the bispiro compound shown below was pyrolyzed in the presence of HSiEt_3 no silylene was intercepted [52].

One last thermal method will be discussed - the pyrolysis of monosilanes. Silylene formation has been suggested to occur in the following reactions [12].

The question concerning the formation of :SiH_2 from SiH_4 has remained controversial for over forty years. Two mechanisms proposed by Purnell and Walsh [54] which can account for the kinetics of the reaction are shown below.

Mechanism A: (H_2 elimination)

Mechanism B: (H atom formation)

John and Purnell favor mechanism A on thermodynamic grounds. The energy of activation for SiH_4 pyrolysis (55.9 kcal/mole) [54] is much less than the Si-H bond dissociation energy (estimated 77-94 kcal/mole) [55] for SiH_4 .

O.P. Strausz and P.S. Neudorfl [56] found that in the pyrolysis of MeSiH_3 and of Me_2SiH_2 both mechanism A and mechanism B are operative. They believe that a similar dual mechanism applies to the pyrolysis of silane.

Ring, Puentes, and O'Neal originally favored mechanism B [55,46,57]. However, recent shock tube studies [58] have caused them to change their stand in favor of mechanism A. Silane decomposition in a single pulse shock tube at temperatures between 1200-1300°K indicated that the initial reaction is hydrogen molecule elimination.

The decomposition rate and the first-order rate constant are independent of initial silane concentration and

are unchanged by up to a ten fold excess of toluene, indicating that no free radical decomposition occurs. Calculated RRKM and Ring's experimental Arrhenius parameters agree nicely with Purnell and Walsh's [54] Arrhenius parameters. The 3/2 order rate dependence in silane observed by Purnell and Walsh is predicted by the RRKM calculations and is, as they suspected, an artifact of pressure dependence.

Perhaps after 40 years the controversies concerning SiH_4 pyrolyses are coming to an end. Although all the questions concerning the mechanism of SiH_4 pyrolyses have not been answered, there does seem to be agreement that the initial process is formation of SiH_2 and H_2 .

2.3 PHOTOLYSES

In the last few years several photochemical sources of silylenes have been discovered. In 1970 Ishikawa and Kumada [62] reported that dodecamethylcyclohexasilane extruded dimethylsilylene units when it was irradiated for 20-40 hours with an ultraviolet light (2537°A).

The formation of dimethylsilylene was deduced from trapping experiments as well as from the appearance of the lower homologs of the starting material [60].

Linear and branched chain polysilanes $\text{Me}_3\text{Si}-(\text{SiMe}_2)_n-\text{SiMe}_3$ ($n=2-6$) [61,60], $\text{Me}_3\text{Si}-(\text{SiPh}_2)_2-\text{SiMe}_3$ [62], and $\text{Me}_3\text{Si}[\text{SiMe}(\text{SiMe}_3)]_n-\text{SiMe}_3$ ($n=1,2$) [61] also extrude silylenes upon irradiation. These silylenes have been trapped with Et_2MeSiH .

The photolysis of 1,2,3-trisilacycloheptane derivatives allows for the formation of "tailor-made" organosilylenes [63].

Unlike the other photochemical methods, this method is not restricted to only the production of dimethylsilylene. The synthesis of the starting trisilane can easily be altered so that the desired diorganosilylene can be formed.

Upon photolysis only the central silicon is extruded, and it is extruded in a highly stereospecific manner with retention of configuration at the Si^1 and Si^3 centers [64], i.e. when cis- and trans- 1,2,2,3-tetramethyl-1,3-diphenyl-1,2,3-trisilacycloheptane are photolyzed they yield cis- and trans- 1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane respectively.

The dimethylsilylene produced inserts into Si-H bonds with retention of configuration [68]. These results suggest a concerted elimination of singlet silylene.

Ramsey [27], however, suggests that the silylene is extruded in an excited state. By making the assumption that the above reaction is a concerted elimination and therefore proceeds with conservation of orbital symmetry, Ramsey has applied the Woodward-Hoffmann selection rules and has found that the electronic transition must be assigned to a $\sigma \rightarrow \sigma^*$ transition rather than the previously suggested $\sigma \rightarrow \pi$ (3d or 4p) transition. Assuming a $\sigma \rightarrow \sigma^*$ transition, a molecular orbital correlation diagram can be constructed from a linear combination of bonding and anti-bonding Si-Si σ orbitals.

Figure 1: Molecular Orbital Correlation Diagram for a $\sigma \rightarrow \sigma^*$ Transition

In the excited state, the half filled orbitals $\sigma^*(a_1)$ and $\sigma(b_1)$ of the trisilane correlate with the $sp^2(a_1)$ and the $p_x(b_1)$ orbitals of the silylene. In this simple approach the a_1 orbital decrease in energy is comparable to the b_1 orbital increase in energy; therefore, the rearrangement of the 1B_1 excited state of the trisilane to the lowest excited state 1B_1 of the silylene and the ground state of the disilane should be an energetically favored process with a low activation energy.

Construction of a correlation diagram for the photochemical reaction proceeding through a $\sigma \rightarrow \pi^*$ excited state indicates that the energy of the orbital containing the promoted electron in the trisilane increases during the rearrangement to the silylene and disilane.

Although there is evidence supporting a concerted elimination for these photochemical processes, Sakurai [63] points out that homolytic fission of a Si-Si bond followed by S_H2 attack of a silyl radical center on the remaining Si-Si bond cannot be excluded.

A free silylene may not be produced at all. The biradical intermediate could be acting as a silylene transfer agent.

There are several pieces of evidence suggesting that silylene extrusion may not be concerted. The relative rate of photolysis of dodecamethylcyclohexasilane in cyclohexane is highly dependent on the concentration of the cyclohexasilane [60]. When the irradiation is done in the presence of a large excess of HSiMeEt₂, HSiMe₂-SiMeEt₂ is produced in 46% yield and HSiMe₂-SiMe₂-SiMeEt₂ in 18% yield. In contrast, when Me₂SiCl₂ is used as the trapping agent the yield of Me₂ClSi-SiMe₂Cl is smaller than the yields of Me₂ClSi-SiMe₂-SiMe₂Cl and Me₂ClSi-(SiMe₂)₂-SiMe₂Cl. Kumada postulated that a direct reaction of photochemically excited polysilanes with the chlorosilane may be occurring [60]. Photolysis of permethylated linear polysilanes yields heptamethyltrisilane as a minor product. Kumada [66] and

co-workers propose that this product arises from homolytic scission of a Si-Si-bond to give silyl radicals which immediately abstract hydrogen.

Although the insertion into Si-H bonds is used as a touchstone for silylene formation, it is best to keep in mind that until the primary photochemical processes are established, the intermediacy of free silylenes in these photochemical processes should be regarded as probable but not proven.

2.4 REACTIONS OF ATOMIC SILICON

Reactions of atomic silicon are believed to involve silylene intermediates. P.W. Owen and P.S. Skell studied the reactions of thermally generated silicon atoms by simultaneously depositing the substrate and the silicon vapor on the liquid nitrogen cooled walls of an evacuated reaction flask [67,68,69]. The product distribution obtained can best be explained by formation of a singlet silylene intermediate which can insert into another substrate or polymerize to a nonvolatile polysilane. In some cases radical abstraction is available as a minor pathway.

Other insertion reactions of atomic silicon to form silylenes include the following:

Nuclear recoil techniques have also been employed to produce silicon atoms which are alleged to form intermediate silylenes. Formation of $\text{H}_3^{31}\text{SiSiH}_3$ and $^{31}\text{SiH}_4$ from fast neutron irradiation of $\text{PH}_3\text{-SiH}_4$ mixtures has been explained by the intermediacy of $^{31}\text{SiH}_2$. Gaspar and co-workers [70,71] have studied the reactions of recoiling silicon atoms in mixtures of phosphine, silane, disilane, and trisilane

and have suggested the following reaction scheme.

Reactions of recoiling silicon atoms in the presence of phosphine-1,3-butadiene mixtures have been studied by Y.N. Tang and co-workers [28,29] and by Gaspar and co-workers [72,99].

From product and scavenger studies Tang deduced that 80% of the silylene was in the triplet state and 20% was in the singlet state. The singlet state was determined to be the ground state. Similar conclusions were drawn for the reactions of PF_3 -1,3-butadiene mixtures [73,30]. In this system the ratio of singlet to triplet $^{31}\text{SiF}_2$ was 1 to 3.5 [30].

Recent studies by P.P. Gaspar and R.J. Hwang [72] of recoiling silicon atoms in the presence of 1,3-organic dienes cast some doubt on the intermediacy of singlet silylene. The products formed, even in the presence of silane, differ from the products of thermally generated silylene with the same substrates. This difference in products may be due to differences in reaction conditions, or it may be due to differences in the electronic states of the silylenes if the recoil systems do in fact produce $^{31}\text{SiH}_2$ as 80% triplet. In any case, it does reopen the question whether silylenes are important intermediates in recoil systems.

2.5 REARRANGEMENT OF DISILENES

Recent evidence by Barton [74] suggests another general route to silylenes may be the rearrangement of disilenes to silylsilylenes.

This reaction will be discussed in more detail in Section 3.2.

3.0 REACTIONS OF SILYLENES

As with any highly reactive intermediate, the chemistry of silylenes is a medley of the competitive reactions available to it under the conditions employed for its generation. The fate of the silylene will depend on the relative rates of reaction with itself, with the starting precursor, and with the added trapping agent.

Fortunately there are a variety of trapping agents which can compete with polymerization making silylene chemistry quite interesting.

3.1 INSERTIONS

Silylenes undergo insertion reactions into several types of single bonds. Much of what is known about silylene insertions comes from the study of silylene extrusions. For each thermal extrusion of a silylene from a disilane involving migration of hydrogen, halogen, or an alkoxy group there is a corresponding insertion of a silylene into a Si-H, Si-halogen, or Si-O bond. By the principle of microscopic reversibility the insertion and extrusion reactions should have the same transition state if the reactants and products lie on the same potential surface.

The transition state usually invoked for silylene insertion is a three centered configuration involving a bridging atom group.

Ring and co-workers [17] suggest that a rehybridization from sp^3 in the reactant silicon to dsp^3 at the acceptor silicon in the transition state is required.

The insertion reactions of silylenes into silicon-hydrogen bonds have been extensively studied. Direct

insertion occurs,

not hydrogen abstraction followed by radical recombination.

The absence of geminate recombination products excludes the radical pathway shown above. The direct insertion of silylene is taken as evidence that it is the singlet silylene which is inserting [31].

Two groups which have studied the insertions of silylene (from the pyrolysis of disilane) into Si-H bonds conclude that substituents on silicon do significantly affect the insertion rate into the remaining Si-H bonds. Sefcik and Ring [75] used a recirculating flow system at 350°C with a cold trap so products were condensed and not allowed to undergo secondary decomposition. Cox and Purnell [42] employed static pyrolyses at 320°C.

Table 3: Relative Insertion Rates of SiH_2 (per Si-H bond)

Trapping Agent	Sefcik and Ring [77]	Cox and Purnell [44]
Si_2H_6	1.0	1.0
SiMe_3H	1.6 ± 0.2	3.06
SiMe_2H_2	0.7 ± 0.01	1.59
SiMeH_3	0.4 ± 0.05	1.80
SiH_4	$0.3 \pm 0.1^*$	0.47
Si_3H_8 (primary SiH)		3.31
Si_3H_8 (secondary SiH)		2.46
SiClH_3	<0.01	

*from recoiling silicon atoms [70]

Although there are some differences in the results, the trends are similar. Ring has suggested that in the static system the products may undergo secondary decomposition. Under static conditions Ring obtained a value of 1.4 as the relative insertion rate of SiH_2 into SiMeH_3 [75]. Sefcik and Ring concluded that SiH_2 behaves as an electrophile. The differences in Si-H insertion rates were attributed to differences in the hydridic character of the Si-H bonds. The more hydridic the bond the greater the rate of insertion. Cox and Purnell attributed these differences to differences in Si-H bond dissociation energies. The weaker the bond the greater the rate of insertion. These two interpretations do not conflict. Based on IR stretching

frequencies of Si-H bonds the order of hydridic character decrease in the following order [76], $\text{Me}_3\text{SiH} > \text{Me}_2\text{SiH}_2 > \text{MeSiH}_3$, and the Si-H bond strengths increase in the following order [76], $\text{Me}_3\text{SiH} < \text{Me}_2\text{SiH}_2 < \text{MeSiH}_3$.

From studies of reactions of atomic silicon with silanes, Skell and Owen [69] conclude that silylsilylenes also exhibit electrophilic character. It is of interest to note that Sakurai and co-workers [64] found that Me_2Si photochemically extruded from 1,3-diphenyl-1,2,2,3-tetramethyl-1,2,3-trisilacycloheptane exhibited nucleophilic character. A rho value of +0.84 was obtained from the insertion reactions of Me_2Si into $\text{XC}_6\text{H}_4\text{SiMe}_2\text{H}$.

Silylenes insert into single bonds other than Si-H.

Silylenes also undergo insertions into alkoxy- and halo-substituted polysilanes.

These reactions do not seem to be general reactions for monosilanes. The insertion of SiMe_2 into dimethyldimethoxysilane is a kinetically unimportant reaction in the thermolysis of the starting disilane [40]. The Me_2Si prefers to insert into the methoxypolysilane starting material rather than into the methoxysilane. Photochemically generated Me_2Si did insert into the Si-O bond of dimethyldimethoxysilane [60] in the absence of methoxypolysilanes. That it is Si-O insertion and not Si-Si insertion in the reactions of the alkoxypolysilanes is consistent with the proposed transition state for the extrusion of silylenes (the reverse of insertion). The following reactions show that it is indeed Si-O insertion that is occurring.

The Si-Si insertion product was not detected.

Silicon-silicon bond insertion has, however, been postulated to explain both the high ratio of normal- to iso-tetrasilane products from the reactions of thermally generated silylene with trisilane [79] and the high reactivity of disilane versus silane toward the proposed

intermediate $^{31}\text{SiH}_2$ in recoil systems [70]. The observation that the ratio of normal- to iso-pentasilane from the insertion of SiH_3SiH into trisilane is lower than the ratio of normal- to iso-tetrasilanes from insertion of SiH_2 into trisilane has also been explained by Si-Si bond insertion [75].

That the thermal extrusion of the central SiH_2 of trisilane is unlikely was deduced from a comparison of the pre-exponential factor (A-factor) for silylene extrusion from $\text{H}_3\text{C-SiH}_2\text{-SiH}_3$ and from $\text{H}_3\text{Si-SiH}_2\text{-SiH}_3$ [17]. Hence the insertion of SiH_2 into Si-Si bonds, as previously proposed, is rendered improbable. A direct attempt to show Si-Si insertion failed [66].

Only recently has there been a clear demonstration of silicon-silicon bond insertion, and this was into the strained silicon-silicon bond of a disilacyclobutene [80].

Similarly silylenes will insert into strained silicon-carbon bonds [81]. Dimethylsilylene thermally generated from hexamethylsilacyclopropane in the liquid phase will insert into the Si-C bond of a silacyclopropane and of a silacyclopropene.

However, silylene thermally generated from Si_2H_6 did not insert into the silicon-carbon bonds of tetramethylsilane [42].

Recently Barton and co-workers [74] have shown that silylsilylenes and β -silylsilylenes can undergo intramolecular C-H insertions.

These reactions will be discussed in more detail in Section 3.2.

3.2 SELF REACTIONS

Generated in the absence of other reagents, silylenes usually polymerize.

O.M. Nefedov and co-workers [13] suggest that the formation of these oligomers and polymers most likely occurs via the initial formation of dimers which then react further owing to their instability. This idea gains some support from the studies of SiF_2 by Thompson and Margrave [82, 83,84,85]. When SiF_2 is co-condensed at -196°C with an unsaturated organic compound the products formed are based on Si_2F_4 units.

The reactive intermediate appears to be the biradical $\text{F}_2\text{Si}-\text{SiF}_2$.

Gaspar and Conlin have presented evidence for the gas phase dimerization of dimethylsilylene [86,87].

The suggested common intermediate for the formation of the disilacyclobutanes is the dimethylsilylene dimer, tetramethyldisilene $\text{Me}_2\text{Si}=\text{SiMe}_2$. Support for the intermediacy of this silylene dimer is found in the rearrangement of tetramethyldisilene itself. Tetramethyldisilene thermally generated from 7,8-disilabicyclo [2.2.2] octa-2,5-dienes rearranges to disilacyclobutanes [88].

Roark and Peddle [88] proposed the following as an unproven but possible mechanism.

The key feature of this mechanism is the 1,2-migration of a hydrogen from a carbon to a silyl radical center. As Barton and co-workers [74] point out, this hydrogen migration suggests that organosilyl radicals bearing an α -hydrogen are unstable; however, this is not the case. As an alternative to Roark and Peddle's mechanism Barton suggests that the tetramethyldisilene rearranges to trimethylsilylmethylsilylene which then inserts into a carbon-hydrogen bond to yield a disilacyclopropane. The disilacyclopropane then rearranges via an α -elimination to two silylenes which undergo intramolecular carbon-hydrogen bond insertions to give the products.

To test his hypothesis Barton generated trimethylsilyl-methylsilylene. Gas phase vacuum-flow pyrolysis of 2-chloroheptamethyltrisilane at 700°C produced 1,1-dimethyl-1,3-disilacyclobutane and 1,3-dimethyl-1,3-disilacyclobutane in 28% and 15% respectively.

This reaction alone does not exclude the possibility that the silylene may be rearranging to the disilene and then following Roark and Peddle's mechanism. However, Barton's group has found no evidence to indicate that trimethylsilylmethylsilylene rearranges to tetramethyldisilene.

The evidence indicates that it is the tetramethyldisilene which is rearranging to trimethylsilylmethylsilylene. In the pyrolysis of both the trisilane shown below and the precursor of the disilene, trimethylsilylmethylsilylene is trapped by trimethylsilane yielding a heptamethyltrisilane.

The 2,2,3,5-tetramethyl-2,3,5-trisilahehexane could arise from Si-H insertion of $\text{Me}_2\text{HSiCH}_2\dot{\text{Si}}\text{CH}_3$ or from Si-H addition across the Si-Si bond of 1,1,2-trimethyl-1,2-disilacyclopropane.

Pyrolyses using Me_3SiD as the trapping agent indicate that it is Si-D insertion of the silylene that is occurring.

Recently Sakurai and co-workers [6] reported the dimerization of several silylenes to disilenes which were trapped with anthracene. Co-thermolysis of 7-silanorbornadiene (or methoxypolysilanes) and anthracene in a sealed tube at 350°C gave a 2,3,5,6-dibenzo-7,8-disilabicyclo [2.2.2] octa-2,5-diene.

Formation of the 2,3,5,6-dibenzo-7,8-disilabicyclo-[2.2.2] octa-2,5-diene was rationalized in terms of a Diels-Alder type reaction between the disilene and the anthracene.

A route involving stepwise addition of silylene to anthracene has not been ruled out; however, the Diels-Alder route is favored by the authors.

Their results indicate that dimerization of silylenes competes with insertion into Si-O bonds of the precursor when methoxypolysilanes are used as the silylene source. There was no stereochemical preference in the dimerization of methylphenylsilylene. Under conditions in which the cis- and trans-1,2-diphenyl-1,2,-dimethyldisilenes were configurationally stable [90], a 1:1 mixture of the cis and trans isomers of the anthracene adducts was obtained. Methyl(tri-methylsilyl)silylene, on the other hand, dimerized stereoselectively in favor of one isomer which was tentatively assigned as the trans disilene.

In Sakurai's sealed tube experiments there was no indication that the disilenes rearranged to silylenes, a rearrangement which Barton [74] reported occurred in the gas phase.

The discrepancy between these experiments may arise from the different experimental conditions, but Sakurai reserved any explanation until a later date.

3.3 ADDITION TO OLEFINS

The reactions of carbenes with alkenes and alkynes to produce cyclopropanes and cyclopropenes respectively are well known. Silylenes can also be trapped by unsaturated organic compounds; however, cyclic products are not always obtained.

Skeell and Goldstein [91] provide the earliest claim of a silylene reacting with an olefin. Dimethylsilylene, produced from the reaction of Me_2SiCl_2 with alkali metal vapor at 260-280°C, reacted with ethylene to form dimethylvinylsilane.

A silacyclopropane intermediate was proposed; however, due to its thermal instability it was not isolated. The silacyclopropane was thought to undergo a rearrangement similar to the cyclopropane rearrangement to propylene.

Reactions of difluorosilylene with olefins depend on the olefin's substituents. Difluorosilylene that is co-condensed with ethylene seems to undergo dimerization before reaction with the olefin [84].

Recent evidence from both Seyferth [92] and Thompson [93] suggests that the reaction initially involves formation of a silacyclopropane which then undergoes further reaction.

When trifluoroethylene is the substrate monomeric SiF_2 seems to be the attacking species. The suggested intermediate is a silacyclopropane which rearranges to a vinylsilane.

Atwell and Weyenberg found that olefins were not reactive enough to compete favorably with the disilane precursor for silylenes that were thermally produced from substituted disilanes [37,38,94]. This finding hampered the investigation of silylene reactions with olefins.

The next report of a silylene addition to an olefin came five years later from the laboratory of Kumada [62]. Photochemically generated methylphenylsilylene added to cyclohexene to give 3-(methylphenylsilyl)cyclohexene.

A silacyclopropane was proposed as the intermediate. All attempts to isolate it failed, probably due to its kinetic instability; however, it was stable in solution under a nitrogen atmosphere. Methanol quenching of the reaction supported the intermediacy of a silacyclopropane [95]. In the presence of methanol, 22% of an alkoxy silane was formed, presumably from addition of methanol to the silacyclopropane ring.†

Kumada and co-workers suggested that the products were best explained by the formation of a silacyclopropane followed by a photochemical 1,3-hydrogen shift. Recent studies using silylenes with bulky substituents [96] suggest that this is indeed correct. Photochemically generated trimethylsilylphenylsilylene added readily to the double bonds of olefins to form silacyclopropanes which were identified by their ^1H NMR and from their methanolysis products.

† Seyferth [97] has since reported that silacyclopropanes do react with methanol to form alkoxy silanes.

Further photolysis of silacyclopentane C-1 and C-2 with a high pressure mercury lamp gave two new products, one resulting from a 1,2-hydrogen shift and one resulting from a 1,3-hydrogen shift.

Silacyclop propane C-3 afforded only non-volatile products upon irradiation.

Using hexamethylsilacyclop propane, a very mild source of dimethylsilylene, Seyferth and Annarelli [98] were the first to prepare silacyclop propanes by reacting a silylene with an olefin.

Identification of the silacyclopropanes was based on their methanolysis products and on their distinctive ^{29}Si nuclear magnetic resonance chemical shifts.

3.4 ADDITION TO DIENES

The addition of a silylene to a diene was first reported in 1968 by Atwell and Weyenberg [94].

Although the silacyclopentene formed was formally a product of 1,4-addition of the silylene, the reaction path involving prior formation of a vinyl-substituted silacyclopropane was preferred.

In 1974 Gaspar, Hwang, and Eckelman [99] reported the addition of thermally generated $:\text{SiH}_2$ to 1,3-butadiene, while

Ring and co-workers [100] reported the following reactions of silylenes with 1,3-butadienes in 1975.

The 1,2-disilacyclohex-4-ene formed suggests that silylsilylene may rearrange to disilene.

However, the above reaction sequence is only speculative and is in direct contrast to Barton's findings that tetramethyldisilene rearranges to the silylsilylene. The following sequence is just as likely.

Tang and co-workers [29,101,73] report that 1-silacyclopent-3-enes are formed when recoiling silicon atoms are generated in the presence of phosphine (or trifluorophosphine) and 1,3-butadienes.

In contrast to Tang's report, Gaspar, Hwang, and Eckelman [99,72] report that reactions of recoiling silicon atoms with phosphine-diene mixtures yield both 1-silacyclopent-3-ene and 1-silacyclopenta-2,4-diene.

When hexamethylsilacyclopropane was heated in a THF solution in the presence of 2,3-dimethylbutadiene Seyferth and Annarelli [102] isolated a silacyclopentene.

Chernyshev and co-workers [103] report the synthesis of silacyclopentenenes from additions of dichlorosilylene to dienes.

Experiments designed to elucidate the mechanism of addition of silylenes to 1,3-dienes include studies of the stereochemistry of addition and trapping experiments. A concerted 1,4-cycloaddition was precluded by the finding

of Gaspar and Hwang [104] that silylene added to trans-trans-2,4-hexadiene to give both the cis- and trans-2,5-dimethyl-1-silacyclopent-3-ene.

Although this result precludes a concerted cycloaddition, the following two mechanisms are consistent with the observed stereochemistry.

One mechanism involves a diradical being produced along the reaction coordinate either as a primary adduct or as a ring opened vinylsilacyclopropane followed by ring closure to either isomer. The other mechanism involves a vinylsilacyclopropane being formed in a concerted reaction and subsequently undergoing a suprafacial or antarafacial 1,3-sigmatropic rearrangements to form the isomers.

Gaspar and Hwang favored the diradical pathway because of the cumbersome transition state required for the concerted antarafacial rearrangement.

The intermediacy of a vinylsilacyclopropane was established by the methanol trapping experiments of Kumada and Ishikawa [105]. Photochemically generated methylphenylsilylene added to 2,3-dimethyl-1,3-butadiene in the absence of methanol yielding three products,

two of which can be explained by rearrangements of a vinylsilacyclopropane.

Formation of C-6 could be rationalized by a photochemical 1,1-addition of a Si-Si to the terminal unsaturated carbon atom accompanied by a 1,2-hydrogen shift. When the photolysis was done in the presence of methanol an alkoxy silane was formed in 6% yield.

The alkoxysilane is believed to arise from reaction of methanol with the proposed intermediate vinylsilacyclopropane.

These experimental results do not prove that the vinylsilacyclopropane rearranges to a silacyclopentene, only that a vinylsilacyclopropane is present. Nor do they rule out the possibility that the silacyclopentene formed in 7% yield in the presence of methanol could have come from 1,4-cycloaddition of the silylene and diene. However, recent product studies by Kumada [96] have shown that the silacyclopentene does not come from 1,4-addition but from photoisomerization of the vinylsilacyclopropane.

Further evidence for 1,2-addition as the primary step is seen in the structure of one of the two major products isolated by Gaspar and co-workers [106] from the addition of dimethylsilylene to 1,3-cyclohexadiene. Rearrangement of a 7,7-dimethyl-7-silanorcarene intermediate seems to be the source for the 3,3-dimethyl-3-sila-1,4,6-heptatriene product.

In the addition to cyclopentadiene, SiH_2 , like SiCl_2 , gives rise to only the conjugated silacyclohexadiene.

Dimethylsilylene, on the other hand, adds to cyclopentadiene to give both the conjugated and nonconjugated product [106]. Gaspar and co-workers suggested a mechanism involving formation of an initial 1,2-adduct followed by rearrangement.

The absence of the non-conjugated isomer in the SiH_2 and SiCl_2 reactions may be due to secondary decomposition, to conformational differences in the diradical, or to the operation of an entirely different mechanism.

M.E. Childs and W.P. Weber [107] have investigated the reaction of methyldimethoxysilylene with 1,3-cyclooctadiene. They proposed that the initial step was 1,2-addition of the silylene followed by C-C bond scission and transannular abstraction of a hydrogen.

No 9-methoxy-9-methyl-9-silabicyclo [4.2.1] nona-7-ene (the formal 1,4-adduct) was isolated.

Quite different results were obtained by Kumada [96]. Under photochemical conditions, trimethylsilylphenylsilylene added to 1,3-cyclooctadiene to give 9,9-disubstituted-9-silabicyclo [4.2.1] nona-7-enes.

Irradiation of the silacyclopropane itself also gave the silabicyclo [4.2.1] nona-7-dienes. Thermolysis of the silacyclopropane in a sealed tube at 200°C for one hour resulted in complete decomposition of the starting silacyclopropane. Four compounds whose molecular ions corresponded to $\text{C}_{25}\text{H}_{38}\text{Si}_2$ were produced but have not been identified.

Two examples of silylene additions to cyclooctatetraene have been reported. Chernyshev and co-workers [12,108] reported the addition of SiCl_2 to cyclooctatetraene. The products were believed to arise from SiCl_2 addition to a double bond or from insertion into a strained C-C bond of a valence isomer of cyclooctatetraene.

Barton and Juvet [109] investigated the addition of dimethylsilylene to cyclooctatetraene. They proposed an initial 1,2-addition followed by competing rearrangements.

There still are questions to be answered concerning the mechanism of silylene additions to dienes, but a general pattern seems to be emerging. The first step is similar to silylene addition to olefins and involves the addition of silylene to one of the double bonds of the diene forming a vinylsilacyclopropane. The mechanism of the rearrangement of the vinylsilacyclopropane to the final product is not fully

understood yet. It could involve a concerted rearrangement, or it could proceed via a diradical intermediate.

3.5 ADDITION TO ALKYNES

After seventeen years of investigation we are only just beginning to understand the reactions of silylenes in the presence of acetylenes. In 1962 Volpin [1] reported the isolation of 1,1-dimethyl-2,3-diphenyl-1-silacycloprop-2-ene.

What he had prepared was later shown to be a 1,4-disilacyclohexadiene [110,111].

Gilman, Cottis, and Atwell [47] suggested that if silacyclopropenes were formed in these reactions, they could dimerize, leading to 1,4-disilacyclohexadienes after rearrangement.

In 1968 Atwell and Weyenberg [94] carried out an elegant experiment showing that the 1,4-disilacyclohexadienes were not formed by π -dimerization of silacycloprenes. When sym-dimethoxytetramethyldisilane was thermalized in the presence of diphenylacetylene and dimethylacetylene three 1,4-disilacyclohexadienes were formed.

None of the 1,4-disilacyclohexadiene that would result from π -dimerization of the two different silacyclopropenes was isolated.

Although these results do rule out π -dimerization, they do not rule out the intermediacy of silacyclopropenes. In fact, methanolysis trapping experiments [37,112] suggest a silacyclopropene intermediate. When the reactions with acetylenes are carried out in the presence of methanol, the 1,4-disilacyclohexadienes are virtually eliminated and vinylalkoxysilanes are formed in comparable yields. These vinylalkoxysilanes presumably arise from addition of methanol to the silacyclopropenes.

Atwell and Weyenberg proposed that a very specific sigma-dimerization might be occurring — a dimerization across the Si-C bond.

A new perspective on the problem was gained when Atwell and Uhlman [113] isolated hexamethyl-1,2-disilacyclobut-3-ene from the flow pyrolysis of sym-dimethoxytetramethyldisilane in the presence of dimethylacetylene*. They proposed a mechanism involving silylene insertion into the Si-C bond of a silacyclopropene.

*It is important to note that experiments of Barton [114] indicate that considerable quantities of disilacyclohexadiene accompany the disilacyclobutene.

Barton and Kilgour [115] have demonstrated the involvement of the disilacyclobutene along the reaction coordinate which leads to the 1,4-disilacyclohexadiene by subjecting the disilacyclobutene to pyrolysis in the presence of acetylenes.

Recently, however, Sakurai and co-workers [80] reported the following reaction in which the 1,4-disilacyclohexadiene was obtained in only 1.2% yield.

The starting disilacyclobutene was recovered in 49% yield. These results contrast rather sharply with Barton's results. The authors offered no mechanistic discussion.

Two questions remain: How does the disilacyclobutene react with the acetylene to form the 1,4-disilacyclohexadiene, and how is the disilacyclobutene formed? Barton and Kilgour [114,115] propose the following scheme involving ring opening of the disilacyclobutene to a disilabutadiene which undergoes a 2+4 cycloaddition with the acetylene.

Two different mechanisms have been considered for the formation of the disilacyclobutene. One involves silylene insertion into the Si-C bond of the silacyclopropene and the other involves dimerization of the silylene followed by cycloaddition of the resulting disilene with the acetylene. Seyferth and Vick [81] have shown that, in the liquid phase, dimethylsilylene will insert into the Si-C bond of a silacyclopropene.

By allowing preformed silylene dimer to react with 2-butyne in the liquid phase, Barton and Kilgour [114] have shown that silylene dimerization followed by cycloaddition is also a viable route to 1,4-disilacyclohexadienes.

When this reaction was done in a gas phase flow system, no 1,4-disilacyclohexadiene was isolated. However, they did find evidence for the addition of tetramethyldisilene to 2-butyne.

Barton and Kilgour have shown that under static conditions 1,4-disilacyclohexadienes can be formed by the following reaction sequence: 1) silylene dimerization 2) disilene and acetylene cycloaddition 3) disilacyclobutene and acetylene addition. In the gas phase the disilene will cycloadd to the acetylene; however, the reaction conditions are not appropriate for subsequent ring opening and Diels-Adler addition. The authors suggest that silacyclopentene σ -dimerization may account for most of the 1,4-disilacyclohexadiene formed in the gas phase reactions.

Kumada and co-workers [136] have since shown that direct σ -dimerization of a silacyclopentene can occur in the liquid phase.

Although these results demonstrate the possibility of σ -dimerization in the liquid phase, they in no way conflict with Barton's results. In contrast to Kumada's results, Conlin [87] reported that no 1,4-disilacyclohexadiene was formed in the sealed tube thermolysis of tetramethylsilacyclopentene. Only polymer was obtained.

The first clue that silylenes might add to alkynes to form 1:1 adducts was provided by Haas and Ring [46]. Ethynylsilane, a product arising from apparent C-H insertion, was isolated when silylene was generated in the presence of acetylene. The proposed mechanism involved formation of a silacyclopentene followed by Si-C bond rupture and hydrogen migration.

Conlin and Gaspar [87,86] reported that dimethylsilylene generated in the presence of propyne gave an ethynylsilane, presumably by a similar mechanism.

When dimethylsilylene was generated in the presence of 2-butyne, an internal acetylene, they obtained tetramethyl-1-silacycloprop-2-ene, the first silacyclopropene that was sufficiently stable for spectroscopic detection and for separation by gas chromatography.

Mild reaction conditions and avoidance of air and moisture allowed the preparation of this silacyclopropene which was characterized by proton NMR and mass spectroscopy and by its reaction with methanol.

In the year following Conlin's original work several other groups reported the preparation of other silacyclopropenes. Using very mild conditions, Seyferth and co-workers [3] were able to isolate 2,3-bis(trimethylsilyl)-1,1-dimethyl-1-silacyclopropene and completely characterize it by ^1H , ^{13}C , and ^{29}Si NMR spectroscopy.

Other silacyclopropenes have been prepared by Seyferth [81] using this same method.

Sakurai [5] and Kumada [4] both reported the photochemical generation of a silacyclopropene.

This silacyclopropene was characterized by proton NMR spectroscopy and by its reaction with methanol.

Ishikawa, Nakagawa, and Kumada [116] have prepared silacyclopropenes using photochemically generated trimethylsilylphenylsilylene.

Variations of product yields with time indicate that the silyl substituted acetylenes arise from photoisomerization of the silacyclopropenes. The silacyclopropenes were identified solely by their methanolysis products.

As evidenced by the many isolated products, silylenes generated in the presence of acetylenes can undergo a variety of reactions. The silylene may dimerize or it may add to the acetylene to form a silacyclopropene. The silylene dimer may rearrange to stable 1,3-disilacyclobutanes, or intermediates involved in the rearrangement may be trapped by acetylenes. The silylene dimer may undergo cycloaddition to the acetylene to form a 1,2-disilacyclobut-3-ene which can be isolated or which can react with a second acetylene to form a 1,4-disilacyclohexa-2,5-diene. The silacyclopropenes may undergo a specific σ -dimerization, or they may rearrange to silyl substituted acetylenes. This multiplicity of reaction paths not only leads to a variety of products, but makes the product distribution very sensitive to the reaction conditions. Although the sequence of elementary reactions has not been worked out for any set of reaction conditions under which disilacyclohexadienes are obtained, a number of the primary processes have been confirmed. Combined in the proper order, perhaps these processes will be able to explain the experimental observations.

4.0 SILACYCLOPROPENES

To date a number of silacyclopropenes have been prepared. The various methods employed for their production have been discussed in the preceeding section. Before examining the reactions that silacyclopropenes undergo, some of their physical properties will be presented.

Table 4a: Spectroscopic Data for Several Silacyclopropenes

SILACYCLOPROPENE	mass-spec parent peak (m/e)	NMR (TMS referece)		
		^1H (δ)	^{13}C (ppm)	^{29}Si (ppm)
[2]	112	0.15 (SiMe) 1.96 (CMe)	152.0 (C=C) 11.9 (C-CH ₃) $J_{\text{C-H}} = 125 \pm 2 \text{ Hz}$ -2.4 (Si-CH ₃) $J_{\text{C-H}} = 120 \pm 2 \text{ Hz}$
* [3]	228	0.19 (SiMe ₂) 0.30 (SiMe ₃)	189.6 (C=C) 0.4 (SiMe ₃) $J_{\text{C-H}} = 119 \text{ Hz}$ -2.2 (SiMe ₂) $J_{\text{C-H}} = 119 \text{ Hz}$	-106.2 (SiMe ₂) 8.5 (SiMe ₃)

*This silacyclopropene exhibits a band of medium intensity at 1505-1500 cm^{-1} in the IR. Three bands are exhibited in the UV region at 205nm ($\epsilon=3450$), 215nm ($\epsilon=2850$), and 345nm ($\epsilon=37$).

Table 4b: Spectroscopic Data for Several Silacyclopropenes
(continued)

SILACYCLOPROPENE	^1H (δ)	<u>NMR</u>	^{29}Si (ppm)
[6] 0.23 (SiMe_3) 0.30 (SiMe_2) [7] 0.32 (SiMe_3) 0.39 (SiMe_2)
[84]	-102.1 $\text{R} = \text{R}' = \text{SiMe}_2$ -91.9 $\text{R} = \text{SiMe}_3$; $\text{R}' = \text{CMe}_3$ -88.6 $\text{R} = \text{SiMe}_3$; $\text{R}' = \text{Me}$ -87.0 $\text{R} = \text{Me}$; $\text{R}' = \text{CMe}_3$	

The ^{29}Si NMR resonance frequencies are very characteristic for silacyclopropenes [3,81]. Cyclic and acyclic tetraalkylsilanes normally exhibit resonances between 5 ppm upfield and 20 ppm downfield from tetramethylsilane [117,118]. Silacyclopropanes are an exception; their ^{29}Si resonances occur between 50-55 ppm upfield from tetramethylsilane. Silacyclopropenes resonate even further upfield at 85-110 ppm atop the broad glass signal. Seyferth speculates that this high shielding may be due to the three-membered ring effect or to bonding involving participation of vacant 3d orbitals on Si.

4.1 STABILITY

None of these silacyclopropenes are stable to air. A 20% solution of tetramethyl-1-silacycloprop-2-ene is stable for weeks at room temperature in the absence of air and moisture [2]. When it is heated to 105°C polymer is formed within an hour. It did survive gas chromatography at 40°C on a 4' x 1/4" 15% SE-30 column using an all glass inlet and column. The peak was not collected but was routed into a mass spectrometer. The half-life in a benzene solution of 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silacycloprop-2-ene at 70-75°C is 60 hours [3]. Some bis(trimethylsilyl)-acetylene was formed in the course of the decomposition, but not in amounts comparable to the silacyclopropene consumed. It seems likely that there is more than one mode of decomposition. This silacyclopropene was isolated by preparative gas chromatography using a 3' x 1/4" 20% SE-30 column at 125°C. Using this same column both 1,1-dimethyl-2,3-bis(dimethylsilyl)-1-silacycloprop-2-ene and 1,1-dimethyl-2-trimethylsilyl-3-t-butyl-1-silacycloprop-2-ene have been isolated at column temperatures of 108°C and 125°C respectively [84].

The silacyclopropenes which result from the addition of phenyltrimethylsilylsilylene to 3-hexyne, 1-trimethylsilylpropyne, and 2,2,5,5-tetramethyl-3-hexyne could also be isolated by preparative gas chromatography [119]. However, attempts to isolate 1,2,3-tris-(trimethylsilyl)-1-phenyl-1-silacycloprop-2-ene using preparative gas chromatography (160°C) always afforded the rearranged product [bis(trimethylsilyl)phenylsilyl]trimethylsilylacetylene.

Interestingly, when a hexane solution of 1-trimethylsilyl-1-phenyl-2,3-di-t-butyl-1-silacycloprop-2-ene was exposed to air for 5 minutes, 30% of the silacyclopropene was recovered unchanged. These results suggest that the introduction of bulky groups to the silacyclopropene ring produces kinetically stable compounds.

4.2 REACTIONS WITH ALCOHOLS

The reaction of silacyclopropenes with alcohols to form alkoxyvinylsilanes is frequently cited as evidence for the existence of silacyclopropenes. Gaspar and Conlin [2,87] were the first to actually react a silacyclopropene with an alcohol. Methanolysis of tetramethylsilacyclopropene gave an 80% yeild of cis-1,2-dimethylvinyl-dimethyl-methoxysilane.

4.3 UNCATALYZED REACTIONS WITH CARBON-CARBON MULTIPLE BONDS

In 1977 Seyferth and co-workers [120,121] reported that reactive terminal olefins and acetylenes underwent novel two atom insertions into the silacyclopropene ring to form both ring-opened and ring-closed products. The following reactions were reported for the additions of styrene and α -methylstyrene.

2-Methyl-1,3-butadiene reacted with complete absence of regioselectivity giving a 50:50 mixture of the two cyclic products.

Gaspar and Conlin [2] reported that no reaction occurred between tetramethyl-1-silacycloprop-2-ene and cyclopentadiene when a 10% solution of tetramethylsila-cycloprop-2-ene was reacted with a five-fold excess of cyclopentadiene at room temperature for a week.

Seyferth and co-workers found that both ring insertion and ring opened products were obtained when 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silacycloprop-2-ene was reacted at room temperature with phenylacetylene [121] and with isopropenylacetylene [120]. When methylphenylacetylene was used no reaction occurred either at room temperature or at 70°C.

To explain the acyclic product formed from the reaction of phenylacetylene, Seyferth [121] initially proposed a mechanism involving electrophilic ring cleavage, i.e. attack of the phenylacetylene as a weak acid on the Si-C bond of the silacyclopropene. As more experiments were carried out, it became obvious that this suggestion was not applicable to the reactions of silacycloprenes with styrenes and 1,3-butadienes. As an alternative mechanism Seyferth [120] suggested a radical process involving the following types of intermediates.

Olefin and diene intermediate

Acetylene intermediate

These species, in which the radical centers are stabilized by phenyl, vinyl, or trimethylsilyl groups, can undergo intramolecular coupling to give a silacyclopentene (or a silacyclopentadiene in the case of alkyne addition). Or they can undergo hydrogen atom transfer from the CH_2 group (or CH group in the case of alkyne addition) adjacent to silicon to the β -radical center of the 1,2-bis(trimethylsilyl)vinyl group forming an acyclic product. The formation of both the trans- and the cis- α -styrylsilanes would be expected if the reaction of the silacyclopropene with styrene proceeded via the suggested intermediate; indeed, both isomers were formed when the reaction was actually carried out.

4.4. PALLADIUM CATALYZED REACTIONS WITH C-C MULTIPLE BONDS

Completely different products from those already discussed are obtained from the reactions of silacycloprenes with dienes and with acetylenes in the presence of a transition metal catalyst. Sakurai and co-workers [5]

reported the following reactions which were carried out at 75°C for 10-30 minutes. Yields varied between 30 and 50 percent.

Seyferth and co-workers [120,121] report the following palladium catalyzed reactions.

It is evident that the course of these reactions is dramatically affected by the structure of the acetylene. Both authors believe that a silapalladacyclobutene intermediate is involved.

The strained Si-C bonds of silacyclobutanes are known to undergo Pd complex-catalyzed cycloadditions with acetylenes [122].

The driving force of this reaction is apparently the ring strain of the silacyclobutane, since silacyclopentanes and other compounds with strain-free Si-C bonds do not react. The Si-C bonds in silacyclopropenes should be even more strained than the Si-C bonds in silacyclobutanes; therefore, silacyclopropenes should be more prone to Pd-catalyzed cycloadditions.

Once the silapalladacyclobutene intermediate is formed, it has several paths available to it for further reaction. Formation of C-9 may arise from insertion of the acetylene into the Si-Pd or the C-Pd bond of the silapalladacyclobutene followed by extrusion of the $\text{Pd}(\text{PPh}_3)_2$. In the presence of unreactive acetylenes such as diphenylacetylene the silapalladacyclobutene could react with another silacyclopropene to form the final product C-7. C-8 may be formed by the release of $\text{TMSC}\equiv\text{CTMS}$ from the silapalladacyclobutene to give a silylene-Pd complex. The silylene-Pd complex could then react with two molecules of acetylene to give the silacyclopentadiene product. These mechanisms are only speculative and are still under investigation.

4.5 REACTIONS WITH ALDEHYDES AND KETONES

Aldehydes and ketones undergo two atom insertions into the Si-C bond of silacyclopropenes. Conlin [87] reported that tetramethylsilacyclopropene reacted with acetone to yield only non-volatile compounds. However, his NMR data suggested that he had formed a 1-oxa-2-silacyclopent-3-ene although he never proved it.

Kumada and co-workers [4] were the first to actually report the formation of a 1-oxa-2-silacyclopent-3-ene from the addition of a ketone to a silacyclopropene. 1-Oxa-2-silacyclopent-3-enes were formed when (pentamethyl-disilanyl)phenylacetylene was photolyzed in the presence of acetone and when acetone was added to the reaction mixture after four hours of photolysis.

The allene was believed to arise from the intermediacy of a silicon-carbon double bonded species.

This route was postulated as a minor route which occurred simultaneously with the production of the silacyclopropene.

Sakurai and co-workers [5] used this same silacyclopropene to study the reactions with ketones. Products of the general structure 1-oxa-2-silacyclopent-3-enes were obtained, but reactions were quite different depending on the structure of the ketone. Aliphatic ketones such as acetone and cyclohexanone gave a mixture of 1-oxa-2-silacyclopent-3-enes only upon irradiation with a high pressure Hg arc lamp. No reaction occurred in the dark.

$\text{R} = \text{R} = \text{Me}$

$\text{R}^1 = \text{R}^2 = -(\text{CH}_2)_5-$

The yields of the 1-oxa-2-silacyclopent-3-enes varied from 30-60%, and the ratio of C-10 to C-11 varied from 6/1 to 2/1.

In contrast to the aliphatic ketones, fluorenone reacted with the silacyclopropene in the dark forming two 1-oxa-2-silacyclopent-3-enes in 42-51% yield (C-12 to C-13 was 1/3).

The reactivity of benzophenone was between that of fluorenone and that of the aliphatic ketones. A slow dark reaction occurred yielding 7.2% of C-14 and C-15 in the ratio 1/3 after 50 minutes of reaction. Upon irradiation through a Pyrex filter 42.4% of the 1-oxa-2-silacyclopent-3-enes (C-14/C-15=1/1.4) was obtained.

The photochemical cycloaddition of benzophenone was completely suppressed by the addition of piperylene; only the dark reaction was observed.

Seyferth and co-workers [120, 121] have also studied the reactions of a silacyclopentene with ketones and aldehydes. Two atom insertions of the carbonyl into the silacyclopentene occurred at room temperature when conjugated carbonyls were used.

<u>R</u>	<u>R'</u>
Ph	H
CH=CHMe	H
Me	CH=CH ₂
Me	CH=CMe ₂
Me	C CH
CF ₃	CF ₃

1,1-Dimethyl-2,3-bis(trimethylsilyl)-1-silacycloprop-2-ene did react with acetone and acetaldehyde in a benzene solution heated to 70°C for 18 hours to yield 14% and 26% of the respective 1-oxa-2-silacyclopent-3-enes. Upon irradiation, however, much higher yields were obtained. Other aliphatic carbonyl compounds were found to react with the silacyclopentene upon irradiation.

<u>R</u>	<u>R'</u>	<u>yield</u>
Me	Me	73%
Me	H	92%
—(CH ₂) ₅ —		73%
—(CH ₂) ₄ —		78%
Me	Et	57%
Me	CH ₂ COCH ₃	20%
H	CHMe ₂	28%
H	CMe ₃	33%

Seyferth suggests that the active species is the carbonyl compound in the excited ($n \longrightarrow \pi^*$) state. The $n \longrightarrow \pi^*$ triplet state is much less accessible for aliphatic carbonyls and explains why the aliphatic compounds need to be irradiated for reaction to take place. The authors suggest that these reactions are mechanistically akin to the formation of oxetanes by cycloaddition of carbonyl compounds to simple alkenes, dienes, and alkynes upon irradiation [123]. Thus a diradical intermediate

may be considered, but its existence has by no means been proven.

4.6 REACTIONS WITH DIPOLAR REAGENTS

Seyferth and co-workers [124] have investigated the reactions of a silacyclopropene with oxygen-containing dipolar reagents. These reaction are of particular interest, because dimethylsilanone ($\text{Me}_2\text{Si}=\text{O}$) appears to be an intermediate. A cyclic siloxane was produced when 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silacyclop-2-ene was reacted with dimethylsulfoxide.

Formation of these products can be rationalized by the following reaction scheme.

The dimethylsilanone was trapped with dimethyldimethoxysilane and hexamethylcyclotrisiloxane (D_3).

Dimethylsilanone is known to insert into the Si-O bonds of D_3 and of dimethyldimethoxysilane. However this is the first report of it inserting into the Si-C bond of a silacyclopentene.

Pyridine N-oxide and trimethylamine N-oxide also react with the silacyclopentene to give dimethylsilanone. When these reactions were carried out in the presence of dimethyldimethoxysilane, sym-tetramethyldimethoxydisiloxane was formed in 59% in the case of pyridine N-oxide, and in 32% in the reaction with trimethylamine N-oxide. The lower yield in the latter case was attributed to the poor solubility of the trimethylamine N-oxide in the reaction mixture.

The insertion of dimethylsilanone into the Si-C bonds of a silacyclopentene bears a formal similarity to the insertion of aldehydes and ketones into silacyclopentene rings. Despite this formal similarity, their mechanism may

very well be quite different. As discussed previously, a radical pathway was proposed for the insertion of aldehydes and ketones into silacyclopropenes. Keep in mind, however, that this mechanism is based on a very limited amount of evidence and is only speculative. So far, evidence suggests that species containing silicon-heteroatom double bonds are quite polar, i.e. $\overset{\delta+}{\text{R}_2\text{Si}}=\overset{\delta-}{\text{X}}$, and so the dimethylsilanone insertion may proceed via a polar, not a radical process.

Weber and co-workers [125,126] reported that dimethylsilylene deoxygenated dimethylsulfoxide giving dimethylsilanone which was trapped with D_3 . However, the possibility of silylene extrusion from the 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silacycloprop-2-ene prior to reaction with dimethylsulfoxide was ruled as unlikely. Under the reaction conditions the silacyclopropene used is resistant to silylene extrusion.

Seyferth and co-workers [127] have reported that the reaction of 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silacycloprop-2-ene with diazomethane produces a silacyclobutene.

Although no comment is made about the mechanism of the reaction, the analogous reaction with silacyclopropanes

is discussed. Presumably some analogies can be made between the two reactions. Hexamethylsilacyclopropane reacted with diazomethane to form 1,1,2,2,3,3-hexamethyl-1-silacyclobutane in 70% yield.

While the silacyclobutane formed is formally a product from CH_2 insertion into the silacyclopropane, this course of reaction is precluded, because under the reaction conditions diazomethane does not release CH_2 . It is more probable that the diazomethane is acting as a carbon nucleophile.

A similar mechanism may be invoked for the reaction with a silacyclopentene.

4.7 REACTION WITH SILYLENES

Seyferth and co-workers [81] have shown that dimethylsilylene can insert into the silacyclopriene ring yielding a disilacyclobutene. These reactions were discussed in Section 3.5 and will not be discussed further.

4.8 CATALYZED AND UNCATALYZED SELF-REACTIONS

Silacycloprienes can react with themselves. As previously mentioned in Section 3.5, Kumada [136] has shown that when heated in a sealed tube 1,1-dimethyl-2-phenyl-3-trimethylsilyl-1-silacyclopri-2-ene undergoes dimerization in high yield. Recall, however, that a 20% solution of tetramethyl-1-silacyclopri-2-ene heated at 105°C formed polymer within one hour [2,87]. Both Sakurai [5] and Kumada [128] have reported the following dimerization of 2-phenyl-3-trimethylsilyl-1,1-dimethyl-1-silacyclopri-2-ene in the presence of a transition metal catalyst. Mechanistic considerations were discussed in Section 4.4.

4.9 THEORETICAL CONSIDERATIONS

Although Volpin [1] was not the first to prepare a silacyclopropene, he was the first to predict their stability. He attributed this stability to the formation of a new type of aromatic system involving p-p-p or p-p-d conjugation, i.e. interaction of the 2p electrons of the carbon atoms and the 3d orbital of the silicon atom to form a more stable system, which could be expressed by $R_2Si^{\oplus} \begin{array}{c} R' \\ \diagup \\ \diagdown \\ R' \end{array}$. Recent theoretical calculations by P.R. Jones and D.D. White [129] support Volpin's predictions that the stability of the silacyclopropene ring system may be attributed to its pseudo-aromatic character. Using the CNDO/2 method which correctly predicted the structures of various substituted silacyclopropanes, restricting the bond lengths and bond angles so as to maintain C_{2v} symmetry, and maintaining tetrahedral bond angles and C-H bond lengths for the methyl groups, the following results were obtained.

Table 5: Theoretical Structure of Substituted Silacyclopropenes

R	X	C-C, Å	∠C-Si-C	C-Si	overlap population		
					%	C-C	%
H	H	1.369	43.3	0.9935	19.4	0.9810	21.1
F	H	1.377	43.8	1.0085	19.2	0.9608	21.4
Me	H	1.366	43.1	0.9867	18.8	0.9867	21.5
H	Me	1.397	44.1	0.9817	19.6	0.9122	19.9
Me	Me	1.393	43.8	0.9715	18.8	0.9200	20.2

These calculations predict a remarkably small average C-Si-C bond angle of 43.6° . The average C-C bond length $1.380 \text{ \AA}$ agrees exactly with the C-C bond length calculated for the aromatic cyclopropenyl cation. The nearly equivalent character for Si-C and C-C bonds suggests an aromatic type of π -electron delocalization. The main orbital on the Si contributing to this π -delocalization is the d-orbital of appropriate symmetry for bonding overlap with the π orbital of the carbon-carbon double bond.

In contrast to these CNDO/2 results, J.C. Barthelat, G. Trinquier, and G. Bertrand [130] using the SCF pseudopotential method, and M. Eckert-Maksic, K. Kovacevic, and Z.B. Maksic [131] using the iterative maximum overlap approximation (IMOA) method found that silacyclopropenes were not pseudo aromatic.

Table 6: CNDO/2 vs SCF and IMOA Calculations

		pseudopotential SCF	CNDO/2
Si-C $\text{\AA}$	1.84	
	C=C $\text{\AA}$	1.33	1.37
	Si-C overlap	0.80	0.99
	C=C overlap	1.22	0.98
	net atomic charge on Si	+0.24	+0.06
		IMOA	CNDO/2
Si-C $\text{\AA}$	1.795	
	C=C $\text{\AA}$	1.321	1.393
	C-Si-C angle	43.1°	43.6°
	Si-C-C angle	68.4°	

According to the SCF results the aromatic character of silacyclopentadiene would be very small although a certain $p\pi-d\pi$ overlap does exist between the silicon and carbon. These authors believe that the silacyclopentadiene would be more compatible to the model acetylene + silylene and that the discrepancy with the CNDO/2 results shows how much a CNDO/2 Hamiltonian can overestimate d atomic orbital participation.

The IMOA method predicts that the average p character and deviation angles are higher for the Si-C bonds than for the C-C bonds in the same silacarbycyclo. The Si-C bonds are highly strained and are, therefore, very reactive. These results are consistent with experimental observations (all reactions reported to date involve the Si-C bond, not the C-C bond) and are apparently a consequence of the relatively weak Si-C bond as reflected in the low overlap of the respective hybrid orbitals and shift of electron charge density to the outside of the ring where it is exposed to electrophilic attack.

Silacyclopentadienes and their reactions are just beginning to be explored and understood. Using mild reaction conditions and work-up procedures which exclude air and water, silacyclopentadienes can be isolated and characterized. These compounds undergo a variety of reactions, most of whose mechanisms have not been elucidated. However, a common characteristic of all the reactions studied so far is the attack by the reagent on the Si-C bond and not on the C-C double bond.

II. RESULTS AND DISCUSSION

Because tetramethyl-1-silacycloprop-2-ene is the least substituted silacyclopropene reported to date and, therefore, should be most reactive, it was fully characterized and its reactions with added substrates were studied. Tetramethylsilacyclopropene was characterized by its ^{29}Si and ^{13}C NMR spectra, two very important pieces of data that Conlin [2] failed to obtain. Reactions of tetramethylsilacyclopropene with added substrates included those with ketones, unsaturated hydrocarbons, nitriles, dipolar compounds, epoxides, and azobenzene. The reaction of tetramethylsilacyclopropene in the presence of a palladium catalyst was also studied. The substrates chosen all contained some form of unsaturation and most contained an oxygen or a nitrogen atom. The following general reaction scheme was proposed (specific mechanistic details will be given in the individual sections) in which 1:1 adducts were expected.

Silicon is known to form strong Si-O and Si-N bonds. Formation of such bonds along with the release of ring strain should be driving forces for these reactions. When the experiments were actually carried out the expected 1:1 adducts were not always obtained. The following sections discuss the products obtained and suggest possible mechanisms.

1.0 PREPARATION OF TETRAMETHYL-1-SILACYCLOPROP-2-ENE

Tetramethylsilacyclopropene was prepared by the flash vacuum pyrolysis of either sym-dimethoxytetramethyldisilane or sym-diethoxytetramethyldisilane in the presence of 2-butyne.

After the pyrolysis the entire reaction mixture was subjected to a trap-to-trap distillation on the vacuum line. Samples were then transferred to 4mm tubes which were sealed under vacuum. Because of the similar vapor pressures exhibited by the silicon compounds, pure tetramethyl-1-silacycloprop-2-ene could not be obtained. When sym-dimethoxytetramethyldisilane was used as the silylene source a 20% solution of the silacyclopropene in dimethoxydimethylsilane could be obtained after distillation. Using diethoxytetramethyldisilane as the silylene source increased the vapor pressure difference between the silacyclopropene and the monosilane, so samples of 40% silacyclopropene in diethoxydimethylsilane could be prepared by careful distillation. The disadvantage to using the sym-diethoxytetramethyldisilane precursor was that at

high (ca. 40%) concentrations of silacyclopentene, polymerization occurred. Even at -5°C polymerization occurred, albeit slowly. Both silylene precursors were used to make tetramethylsilacyclopentene.

2.0 SPECTROSCOPIC CHARACTERIZATION OF TETRAMETHYL-1-SILACYCLOPROP-2-ENE

Previous to Conlin's work [2] Seyferth [86] had shown that silacyclopentanes exhibited ^{29}Si chemical shifts between 50 and 55 ppm upfield from tetramethylsilane. By analogy one would expect silacyclopentenes to exhibit unusual ^{29}Si chemical shifts too. Although Conlin was unable to obtain the ^{29}Si spectrum of tetramethylsilacyclopentene, Seyferth was able to obtain the ^{29}Si spectra of several silacyclopentenes [3,81] and to show that they had characteristic ^{29}Si chemical shifts between 85 and 110 ppm upfield from tetramethylsilane. Because the silacyclopentene ring system exhibits such an unusual ^{29}Si chemical shift it was particularly important to obtain this datum to fully characterize tetramethyl-1-silacyclopent-2-ene.

2.1 Silicon-29 Nuclear Magnetic Resonance

The silicon-29 resonance frequency of tetramethylsilacyclopentene was determined to be 88.64 ppm upfield from tetramethylsilane, just on the edge of the glass peak. Because frequencies this far upfield are characteristic of the silacyclopentene ring system, this datum provides strong evidence in support of this ring system.

There are three major problems associated with obtaining silicon-29 NMR spectra. 1) Silicon-29 has a low natural abundance of 4.7%. 2) The magnetogyric ratio is negative; therefore, the nuclear Overhauser effect which causes an increase in ^{13}C peak areas as much as three fold in ^1H irradiated experiments is negative for ^{29}Si . This means that in ^1H irradiated experiments the ^{29}Si resonance lines may be greatly reduced in intensity, they may be nulled, or they may even be negative. 3) Silicon compounds have long spin-lattice relaxation times (T_1) and are easy to saturate. Usually the second and third problems are overcome by adding tris (acetylacetonato) chromium III $[\text{Cr}(\text{acac})_3]$ to the sample. $\text{Cr}(\text{acac})_3$ is a paramagnetic species and replaces the Si-H dipole-dipole and spin-rotation relaxation mechanisms by electron-nuclear dipole-dipole relaxation. Not only is the nuclear Overhauser effect eliminated, but there is a more complete relaxation between successive rf pulses (shorter T_1 's).

Unfortunately $\text{Cr}(\text{acac})_3$ would probably decompose the silacyclopentene and therefore was not added to the samples of tetramethylsilacyclopentene. However, the nuclear Overhauser effect was eliminated by gated decoupling of the hydrogens. The wide band ^1H decoupling power was turned on only during the periods of data acquisition; throughout the remaining time between ^{29}Si excitation pulses the decoupler was turned off. The long ^{29}Si T_1 's prevented

build-up of significant nuclear Overhauser effect during the brief ^1H irradiation periods, and yet the spectra were decoupled. The problem of long T_1 's still remained. Because of the long T_1 's, approximately 4200 pulses with a 45 degree pulse angle and an 8 second pulse delay were needed for each spectrum.

Sample manipulation problems included: 1) The sample could not be exposed to air or moisture. 2) The pyrolysis could be done on only a limited size and did not yield pure tetramethylsilacyclopropene [2]. 3) The silacyclopropene decomposed when heated. 4) A 10mm NMR tube had to be used. Filling and sealing a 10mm NMR tube was not at all practical. Instead several pyrolyses were done using sym-diethoxytetramethyldisilane so as to obtain as high a concentration of the silacyclopropene as possible, and the final samples from each pyrolysis were condensed into a 5mm NMR tube. The 5mm tube was nestled inside a 10mm NMR tube containing CDCl_3/TMS . Because of the silacyclopropene's thermal instability, especially when it was present in concentrations of ca. 40%, the sample was cooled to -5°C .

After the ^{29}Si NMR spectrum of tetramethyl-1-silacycloprop-2-ene was obtained, the sample was opened under vacuum, and methanol was added to the tube before it was resealed. Tetramethylsilacyclopropene is believed to undergo the following reaction with methanol.

As was expected, when the ^{29}Si NMR spectrum was obtained, the peak at -88.64 had been replaced by a new peak which corresponded to the chemical shift of C-16. However, the spectrum was more complicated than expected because of the following exchange reactions.

The chemical shifts assignments are shown below in Table 7.

Table 7: ^{29}Si Chemical Shifts (ppm from TMS)
of Tetramethylsilacyclopropene

$\text{Me}_2\text{Si} \begin{array}{c} \diagup \text{C-Me}^\dagger \\ \parallel \\ \diagdown \text{C-Me} \end{array}$	$\text{Me}_2\text{Si} \begin{array}{c} \diagup \text{C-Me}^{\dagger\dagger} \\ \parallel \\ \diagdown \text{C-Me} \end{array} + \text{MeOH}$	STRUCTURE
7.96	10.86	$[\text{Me}_2(\text{OMe})\text{Si}]_2$ $[\text{Me}_2(\text{OEt})\text{Si}]_2$
	7.63	$\text{Me}_2(\text{OMe})\text{Si}-\text{C}(\text{Me})=\text{CMeH}$
	4.94	$\text{Me}_2(\text{OEt})\text{Si}-\text{C}(\text{Me})=\text{CMeH}$
-2.59	-2.59	$\text{SiMe}_2(\text{OMe})_2$
	-4.44	$\text{SiMe}_2(\text{OMe})(\text{OEt})$
-6.23	-6.23	$\text{SiMe}_2(\text{OEt})_2$
-88.64		$\text{Me}_2\text{Si} \begin{array}{c} \diagup \text{C-Me} \\ \parallel \\ \diagdown \text{C-Me} \end{array}$

† ca 40% solution of tetramethylsilacyclopropene in $\text{SiMe}_2(\text{OEt})_2$

†† ca.40% solution of tetramethylsilacyclopropene in $\text{SiMe}_2(\text{OEt})_2$
with added MeOH

2.2 Carbon-13 Nuclear Magnetic Resonance

Using the same approach as was used to determine the ^{29}Si chemical shifts, the ^{13}C chemical shifts were obtained for tetramethylsilacyclopropene.

Comparing these values with those obtained by Seyferth for 2,3-bis(trimethylsilyl)-1,1-dimethyl-1-silacycloprop-2-ene,

we see that the major difference is the chemical shift of the ring carbons. This difference may be attributed to the presence of the trimethylsilyl groups. The chemical shift of the olefinic carbons of trans-diethylethylene is 130.4 ppm, whereas the chemical shift of the olefinic carbons of trans-bis(trimethylsilyl)ethylene is further downfield at 151 ppm. Further studies are necessary to determine exactly what effect the trimethylsilyl groups have on the chemical shift of the silacyclopropene ring carbons.

The final spectroscopic characterization of tetramethyl-silacyclopropene confirmed Conlin's assignment of a silacyclopropene ring structure. The distinctive ²⁹Si chemical shift leaves little doubt that tetramethyl-1-silacycloprop-2-ene is indeed the structure of the compound formed from the pyrolysis of dimethoxytetramethyldisilane in the presence of 2-butyne.

3.0 NATURE OF THE TETRAMETHYL-1-SILACYCLOPROP-2-ENE POLYMER

Both ^1H and ^{13}C NMR data suggest that tetramethyl-1-silacycloprop-2-ene polymerizes to form the following ring opened polymer.

^1H NMR (in benzene):

H^a 0.4 δ (broad s, 6H)

H^b 1.9 δ (broad s, 6H)

^{13}C NMR (in benzene):

C^1 2.84 ppm

C^2 21.80 ppm

C^3 149.15 ppm

4.0 ADDITION OF CARBONYL COMPOUNDS TO TETRAMETHYL-1-SILACYCLOPROP-2-ENE

Silacyclopropenes have been shown, during the course of this work, to react with aldehydes and ketones to form 1-oxa-2-silacyclopent-3-enes [4,5,120,121] (see section 4.5).

4.1 Addition of Fluorenone

Tetramethylsilacyclopropene reacted slowly with fluorenone at room temperature to form 2,2,3,4-tetramethyl-5-fluorenyl-1-oxa-2-silacyclopent-3-ene.

The product was characterized by its NMR, IR, mass spectrum, and elemental analysis.

melting poing: 149-152 C

NMR (in benzene):

H^a 0.38δ (s, 6H)

H^b 1.70δ (m, 3H)

H^c 1.10δ (m, 3H)

H 6.93-7.50δ (m, 8H)

Molecular models suggest that H^c is positioned over the aromatic ring so that it is shielded by the ring current.

IR: 1620(m), 1248(s), 1042(s), 890(s), 840(m), 780(m), 760(m), 740(s)

Mass spectrum: 292(parent), 277(base), 238, 224, 203

Elemental analysis: 77.60% C, 7.44% H, 9.70% Si
(calculated: 78.03% C, 6.89% H, 9.60% Si)

4.2 Addition of Acetone

The addition of acetone to tetramethylsilacyclopentene gave unreliable results. In some experiments a 1-oxa-2-silacyclopent-3-ene was formed; in other experiments no 1-oxa-2-silacyclopent-3-ene was isolated; and in one experiment there was no reaction.

In most experiments at least some of the acetone adduct was formed. The length of time needed for reaction at room temperature varied from a few minutes to several days. One sample showed little change even after being heated at 45°C for 11 hours. This same sample still showed no change after being irradiated for one and a half hours in a Pyrex tube using a medium pressure mercury lamp.

The acetone adduct was isolated by preparative gas chromatography using a 10' x 1/4" 15% DC-200 on 40/50 ABS Anakrom column with an oven temperature of 87°C. The adduct was identified by its NMR and mass spectrum as 2,2,3,4,5,5-hexamethyl-1-oxa-2-silacyclopent-3-ene.

NMR (in benzene):	H ^a	0.16δ	(s, 6H)
	H ^b	1.26δ	(s, 6H)
	H ^c	1.50δ 1.56δ	(m, 3H) (m, 3H)

Mass spectrum: m/e=155 (base: P-15). It is not surprising that the parent peak (m/e=170) was absent from the mass spectrum. tert-Butoxytrimethylsilane exhibits no parent peak [128] in its mass spectrum, rather a peak at m/e=131 (P-15) is seen.

4.3 Discussion

Tetramethylsilacyclopropene exhibited behavior typical of other silacyclopropenes when it was reacted with fluorenone. Acetone proved to be a slightly different story. Typically, silacyclopropenes have been found to undergo a slow reaction or no reaction when they are reacted with aliphatic ketones in the dark [5,120,121]. Upon irradiation high yields of the 1-oxa-2-silacyclopent-3-enes are obtained [5,120,121]. In several cases tetramethylsilacyclopropene did react slowly with acetone. Approximately three days were needed in some experiments for complete disappearance of tetramethylsilacyclopropene; 2,2,3,4,5,5-hexamethyl-1-oxa-2-silacyclopent-3-ene was the isolated product. In one case the silacyclopropene and acetone did not even react after heating at 45°C for 11 hours and photolyzing for one and a half hours in a Pyrex tube. This behavior was similar to what would be expected from the behavior of other silacyclopropenes. The reason the sample failed to react even after photolysis may have been because it was in a Pyrex tube and not a quartz tube.

Some reactions of tetramethylsilacyclopropene and acetone exhibited unexpected behavior. Some reactions took place rapidly to give good yields of 2,2,3,4,5,5-hexamethyl-1-oxa-2-silacyclopent-3-ene, while others gave only trace amounts of the adduct, and some gave none of the 1-oxa-2-silacyclopent-3-ene. In all cases the silacyclopropene underwent decomposition. NMR data indicated that

ring-opening had occurred. The singlet corresponding to the vinylmethyls of the silacyclopropene disappeared, and a broad singlet appeared slightly upfield but still in the vinylmethyl region suggesting that tetramethylsilacyclopropene polymer had formed.

This erratic behavior in the presence of acetone suggests that more than just a simple addition is occurring. Perhaps an intermediate is being formed which is reactive toward tetramethylsilacyclopropene and induces polymerization. One might envision a diradical intermediate as suggested by Seyferth [121].

Another possible explanation is the presence of trace impurities in the acetone despite the great care that was taken to purify it. These impurities may compete with acetone for the silacyclopropene, or they may catalyze the decomposition of the silacyclopropene. If the reaction with impurity is a chain process this would explain why only traces of the impurity are needed to decompose the silacyclopropene.

5.0 ADDITION OF UNSATURATED HYDROCARBONS TO TETRAMETHYL-1-SILACYCLOPROPENE

To date no substrates have been successfully added to the carbon-carbon double bond of silacyclopropenes. Conlin has shown that tetramethylsilacyclopropene does not react with cyclopentadiene [87] but prefers to react with itself to form polymer. Seyferth [120,121] found that 2,3-bis(trimethylsilyl)-1,1-dimethyl-1-silacycloprop-2-ene reacts with styrene and phenylacetylene to form both ring-opened and ring-closed 1:1 adducts (see section 4.3). Since tetramethylsilacyclopropene is less hindered sterically than any other silacyclopropene thus far prepared, it was reacted with styrene and phenylacetylene to determine its reactions. In the hope of a reaction occurring at the carbon-carbon double bond of tetramethyl-1-silacycloprop-2-ene, it was also reacted with tetracyanoethylene, a more reactive olefin.

5.1 Addition of Styrene

When styrene was added to the tetramethylsilacyclopropene no reaction occurred at room temperature. After heating at 55°C for 83 hours approximately half the silacyclopropene had decomposed. None of the expected products were isolated.

As the silacyclopentadiene NMR peaks disappeared two broad peaks appeared at 1.9 δ and 0.4 δ which were presumably due to an oligomer of the tetramethylsilacyclopentadiene.

5.2 Addition of Phenylacetylene

In the presence of an excess of phenylacetylene, tetramethylsilacyclopentadiene slowly polymerized and formed an unexpected product. After 48 hours at room temperature, half the silacyclopentadiene had decomposed. Samples containing tetramethylsilacyclopentadiene in similar concentrations, but with no added phenylacetylene, were stable for months at room temperature. After a week at room temperature two layers had formed - a bottom congealed layer and a top fluid layer. Evaporation of the volatiles left a white solid which exhibited two broad peaks in its NMR spectrum at 1.9 δ and 0.4 δ in a ratio 1:1 and two sharp singlets at 1.74 δ and 0.06 δ in a ratio 1:1. The two broad peaks are presumably due to an oligomer of the silacyclopentadiene. The two sharp peaks were identified as arising from octamethyl-1,4-disilacyclohexa-2,5-diene.

The ratio of polymer to disilacyclohexadiene was determined to be 19 to 4. None of the expected phenylacetylene adducts were detected.

5.3 Addition of Tetracyanoethylene

An exothermic reaction occurred when the tetramethylsilacyclopropene containing product fraction was added to the TCNE, and the solution and TCNE particles immediately turned black. An NMR taken approximately 24 hours after mixing indicated the presence of tetramethylsilacyclopropene. Further study suggested that it was the dimethoxydimethylsilane and the dimethoxytetramethyldisilane which were reacting with the TCNE and causing the black solution.

This reaction was not investigated further.

5.4 Discussion

In no case did the tetramethylsilacyclopropene behave as expected (see section 4.3). No conclusions can be drawn concerning the reaction of the silacyclopropene with TCNE because of the interfering reaction of the methoxysilanes with TCNE. In the presence of phenylacetylene an unexpected product, octamethyl-1,4-disilacyclohexa-2,5-diene, was formed along with polymer. These results suggest that again more than just a simple addition is occurring. The phenylacetylene may be adding to tetramethylsilacyclopropene to form the following ionic intermediate (I-1) which can react with the remaining silacyclopropene and induce polymerizations.

Formation of the disilacyclohexadiene may occur via a S_N2 type of displacement on silicon, or by an addition-elimination mechanism. Seyferth has suggested that 2,3-bis(trimethylsilyl)-1-silacycloprop-2-ene reacts with phenylacetylene via a diradical intermediate (see section 4.3). However, the formation of the disilacyclohexadiene in the case of tetramethyl-1-silacycloprop-2-ene argues in favor of an ionic intermediate (I-1) rather than a diradical intermediate.

It is not difficult to rationalize the polymerization of tetramethylsilacyclopropene in the presence of styrene with heating. Even in the absence of styrene, one would expect polymerization to occur upon heating. It is important to note that there was no evidence that any octamethyl-1,4-disilacyclohexa-2,5-diene was formed. This suggests that the polymerization is occurring via a different mechanism than in the phenylacetylene reaction. In this case diradical intermediates may indeed be involved.

6.0 ADDITION OF NITRILES TO TETRAMETHYL-1-SILACYCLOPROP-2-ENE

Because some silacyclopropenes have been found to react with carbon-carbon multiple bonds, it was of interest to see if tetramethylsilacyclopropene would react with carbon-nitrogen triple bonds. Seyferth [120] had reported the addition of benzaldehyde methylimine to hexamethylsilacyclopropane,

and it was hoped that tetramethylsilacyclopropene would undergo a similar reaction with carbon-nitrogen triple bonds.

6.1 Addition of Acetonitrile

The reaction of acetonitrile with tetramethylsilacyclopropene is just as puzzling as the reaction with acetone. The only isolated product has been tentatively assigned the following structure based on NMR data.

The yield of adduct varied considerably. The adduct was formed quantitatively in several experimental trials. In most trials, however, it was formed in small amounts.

Perhaps a similar reaction mechanism can be invoked for the addition of acetonitrile to tetramethylsilacyclopropene. There are some similarities between the reactions of silacycloprenes and sila olefins.

Perhaps these similarities carry over to the reactions of silacycloprenes with acetonitrile.

There was no evidence of the $\text{C}\equiv\text{N}$ bond inserting into the Si-C bond of tetramethylsilacyclopropene.

To eliminate the possibility of the nitrile acting as a weak acid, *t*-butylcyanide was used. If the $\text{C}\equiv\text{N}$ bond inserted into the silacyclopropene ring the following product would be expected.

However, no evidence was obtained for this type of product. Again polymer was formed, suggesting that an intermediate was produced that reacted with the silacyclopropene, causing polymerization.

7.0 ADDITION OF DIPOLAR COMPOUNDS TO TETRAMETHYLSILACYCLOPROPENE

The addition of dipolar reagents to tetramethylsilacyclopropene was of interest because of the possibility of a variety of new reactions occurring. Methyl isocyanate and phenyl azide were chosen because they did not have to be prepared in situ and because they did not contain substituents which might react with the silacyclopropene.

7.1 Addition of Methyl Isocyanate

Tetramethylsilacyclopropene reacted slowly with methyl isocyanate to form octamethyl-1,4-disilacyclohexa-2,5-diene and silacyclopropene polymer in a ratio of 3.0:1.7. The IR, NMR, and mass spectra of the octamethyl-1,4-disilacyclohexa-2,5-diene were identical with those of the independently synthesized compound [94].

NMR (in CCl_4):

H^a 0.068 δ (s, 12H)

H^b 1.748 δ (s, 12H)

IR: 1220(s), 944(m), 820(s), 755(s), 736(m)

Mass spectrum: parent 224
base (P-15) 209

7.2 Addition of Phenyl Azide

Tetramethylsilacyclopropene reacted with phenyl azide to form octamethyl-1,4-disilacyclohexa-2,5-diene and silacyclopropene polymer in a ration of 1.0 to 2.8. The octamethyl-1,4-disilacyclohexa-2,5-diene was identified by its NMR spectrum and by a comparison with the authentic compound of its retention times on three different gas chromatographic columns.

7.3 Discussion

None of the expected products were isolated from the reaction of tetramethylsilacyclopropene with methyl isocyanate.

There was no evidence of any 2-butyne being formed which would indicate the intermediacy of an azasilacyclobutene. Rather, what was isolated was a totally unexpected product, octamethyl-1,4-disilacyclohexa-2,5-diene. The isolation of the disilacyclohexadiene along with silacyclopropene polymer suggests the following reaction scheme.

Either of the two resonance forms of methyl isocyanate could rationalize the reaction with the silacyclopentene; however, only one has been illustrated.

These same products were formed when phenyl azide was added to tetramethylsilacyclopentene suggesting a similar type of intermediate. None of the expected products were isolated.

In this case, however, a trace of 2-butyne was formed suggesting that a small amount of the tetramethylsilacyclopentadiene added to phenyl azide via route a. The formation of a disilacyclohexadiene along with silacyclopentadiene polymer suggests the following reaction scheme:

It is important to keep in mind that these reactions are not done with pure tetramethylsilacyclopropene but with 20% solutions of tetramethylsilacyclopropene in $\text{SiMe}_2(\text{OMe})_2$ with 5% other compounds (dimethoxytetramethyldisilane, 1,1-dimethyl-1,3-disilacyclobutane, 1,3-dimethyl-1,3-disilacyclobutane, and 1,1,3-trimethyl-1,3-disilacyclobutane). These other silicon compounds may interfere with the reaction. There is some evidence that this may be the case with the phenyl azide addition; the NMR spectrum of the heavier components of the reaction mixture indicated the presence of a series of "new" peaks between 0.5 δ and 0.0 δ due to various methyl groups attached to silicon. It is also important to remember that only 15 mg of tetramethylsilacyclopropene is available for reaction. Therefore, any compounds formed in low yields might go undetected. Since most of the proposed products are unknown compounds, we can only speculate on their stability. They might be decomposing before they can be detected.

8.0 ADDITION OF EPOXIDES TO TETRAMETHYL-1-SILACYCLOPROP-2-ENE

Epoxides were chosen as one type of compound to react with tetramethylsilacyclopropene because of the affinity silicon has for oxygen, and because ring opening of the epoxide would lead to a further release of energy.

8.1 Addition of Ethylene Oxide

Tetramethylsilacyclopropene reacted with ethylene oxide to form octamethyl-1,4-disilacyclohexa-2,5-diene and silacyclopropene polymer in a ratio of 1 to 11. The disilacyclohexadiene was identified from its NMR spectrum and by a comparison with the authentic compound of its retention times on three different gas chromatographic columns.

8.2 Addition of Tetraphenylethylene Oxide

When tetraphenylethylene oxide was added to tetramethylsilacyclopropene only silacyclopropene polymer was formed.

8.3 Discussion

The predominant product isolated from the reaction of tetramethylsilacyclopropene with both epoxides is the silacyclopropene polymer. Again none of the expected products were detected.

The formation of polymer suggests that an intermediate is being formed which can react with tetramethylsilacyclopropene and induce polymerization. Based on the formation of some octamethyl-1,4-disilacyclohexa-2,5-diene, an ionic polymerization is more likely than a radical polymerization. A growing ionic chain fragments more easily to the disilacyclohexadiene by "biting back on itself". A similar type of reaction scheme as shown in section 7.3 might be envisioned.

9.0 ADDITION OF AZOBENZENE TO TETRAMETHYLSILACYCLOPROPENE

It was of interest to see if the N=N bond of azobenzene would insert into the Si-C bond of tetramethylsilacyclopentene. When tetramethylsilacyclopentene was reacted with azobenzene octamethyl-1,4-disilacyclohexa-2,5-diene and silacyclopentene polymer were formed in a ratio of 1.0 to 4.4. The disilacyclohexadiene was identified by its NMR spectrum and from a comparison with the authentic compound of its retention times on three different gas chromatographic columns.

9.1 Discussion

Again none of the expected products were obtained from the reaction of tetramethylsilacyclopropene with azobenzene.

As was the case with the previously discussed reactions, an intermediate seems to be formed which can react with tetramethylsilacyclopropene and induce polymerization. Formation of the disilacyclohexadiene suggests that nucleophilic addition rather than a free radical process initiates polymerization.

10.0 ADDITION OF TRIMETHYLAMINE TO TETRAMETHYL-1-SILACYCLOPROP-2-ENE

The ionic polymerization mechanisms proposed in the previous sections gain further support from the reaction of trimethylamine with tetramethylsilacyclopentene. The silacyclopentene can undergo ring opening via nucleophilic

11.0 PALLADIUM CATALYZED REACTIONS OF TETRAMETHYL-1-SILACYCLOPROP-2-ENE

Upon heating, solutions of tetramethylsilacyclopropene yielded silacyclopropene polymer; there was no evidence for the formation of any dimer. It was of interest to see if the presence of a transition metal catalyst would alter the course of the reaction.

11.1 Palladium Catalyzed Self Reaction

In the presence of catalytic amounts of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ tetramethylsilacyclopropene undergoes a clean high yield reaction to form octamethyl-1,4-disilacyclohexa-2,5-diene. The silacyclohexadiene was characterized by its melting point, NMR, IR, and mass spectra, which were identical to those of the authentic compound.

11.2 Palladium Catalyzed Reaction in the Presence of Added Acetylenes

In the presence of excess 2-butyne, methylacetylene, or phenylacetylene and a catalytic amount of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, tetramethylsilacyclopropene exclusively underwent dimerization to form octamethyl-1,4-disilacyclohexa-2,5-diene.

11.3 Discussion

Seyferth, Kumada, and Sakurai have all shown that in the presence of a palladium catalyst silacyclopropenes undergo dimerization (see sections 4.4 and 4.8). However, both Sakurai and Seyferth report that in the presence of added acetylenes disilacyclohexadienes are not necessarily formed (see section 4.4). If a silapalladacyclobutene is an intermediate in this reaction, as postulated, it appears that in the case of tetramethylsilacyclopropene, the silacyclopropene is more reactive than the added acetylenes toward the silapalladacyclobutene intermediate. Formation of the disilacyclohexadiene without appreciable polymerization is evidence for the operation of a different mechanism in the reaction of silacyclopropene with palladium catalyst from that with the other reagents discussed.

12.0 PHOTOLYSIS OF TETRAMETHYLSILACYCLOPROPENE

When a 30% solution of tetramethylsilacyclopentadiene in dimethoxydimethylsilane was irradiated for 166 hours with a medium pressure mercury lamp, the silacyclopentadiene disappeared and 2-butyne appeared in comparable yield. When a different sample was photolyzed for 45 hours the decrease in the amount of tetramethylsilacyclopentadiene was approximately four times larger than the corresponding increase in the 2-butyne. Formation of a broad NMR peak at 1.8δ suggested that the silacyclopentadiene had polymerized. The appearance of 2-butyne along with the disappearance of the silacyclopentadiene suggested that tetramethylsilacyclopentadiene was extruding dimethylsilylene and generating 2-butyne. The SiMe_2 that was extruded was trapped by $\text{Me}_3\text{Si-H}$.

The pentamethyldisilane was identified by its mass spectrum. After photolysis the reaction mixture was gas chromatographed on a 12' x 1/8" SF96 column. The peaks were then routed into a mass spectrometer (Figures 3, 4, and 5).

Figure 3: Reconstructed Gas Chromatographic Trace of Tetramethyl-1-silacycloprop-2-ene Reaction Mixture After Photolysis in the Presence of Trimethylsilane (from gc-ms spectrometer).

Gas chromatographic-mass spectral analysis of tetramethyl-1-silacycloprop-2-ene reaction mixture after photolysis in the presence of trimethylsilane

Figure 4: Authentic $\text{Me}_5\text{Si}_2\text{H}$
Mass Spectrum

Figure 5: Sampling 1449-1447
Mass Spectrum

Although the mass spectrum shown in Figure 5 has lost most of its fine structure because of the background subtraction process, the large peaks correspond nicely to the large peaks in the authentic spectrum (Figure 4).

When a low pressure mercury lamp was used, the tetramethylsilacyclopropene decomposed within 6 hours forming a white solid. There was no increase in the concentration of the 2-butyne. The NMR spectrum exhibited two broad bands centered at 1.7 δ and 0.4 δ suggesting that the tetramethylsilacyclopropene had polymerized.

12.1 Discussion

The experimental results suggest that tetramethylsilacyclopentene extrudes SiMe_2 , which has been trapped with Me_3SiH , and generates 2-butyne upon photolysis with a medium pressure mercury lamp. The amount of 2-butyne formed is less than the amount of silacyclopentene decomposed, suggesting that tetramethylsilacyclopentene is also decomposing via a route other than SiMe_2 extrusion. Both Sakurai [5] and Kumada [4] reported that 1,1-dimethyl-2-phenyl-3-trimethylsilyl-1-silacyclopent-2-ene photochemically extruded SiMe_2 which was trapped with Et_3SiH .

Sakurai reported a quantitative yield whereas Kumada reported a 12% yield of the alkyne.

13.0 INVESTIGATION OF THE POSSIBILITY OF TETRAMETHYL-1-SILACYCLOPROP-2-ENE DIMERIZATION IN THE GAS PHASE

Although Conlin [15] reported that 20% solutions of tetramethyl-1-silacycloprop-2-ene polymerized on heating, he had not demonstrated that tetramethylsilacyclopropene did not dimerize in the gas phase. To investigate this possibility further a pyrolysis of dimethoxytetramethyldisilane in the presence of 2-butyne to form the silacyclopropene was carried out. After the pyrolysis the products trapped below the oven (see experimental section for more detail) were transferred to another part of the vacuum line, and the oven and trap were removed from the vacuum line. The oven and trap were rinsed with benzene; the benzene was removed using rotary evaporation; and an NMR spectrum was obtained. The NMR spectrum indicated the absence of any octamethyl-1,4-disilacyclohexa-2,5-diene.

14.0 CONCLUSION

The final spectroscopic characterization of tetramethylsilacyclopropene confirmed the presence of the silacyclopropene ring structure. As the reactions of this silacyclopropene were studied it soon became evident that it was behaving differently than the more highly substituted silacyclopropenes. All of the reactions did however, involve the Si-C bond and not the C=C bond in accord with theoretical calculations. [117,130,131]. The formation of polymer and in some cases octamethyl-1,4-disilacyclohexa-2,5-diene suggests that

in the presence of added substrates an intermediate is being formed which can induce polymerization. The polymerization seems to follow more than one route, possibly anionic and free radical, with the former producing some octamethyl-1,4-disilacyclohexa-2,5-diene by cleavage. At this time, however, the suggested mechanisms are only speculative. Further studies are needed to fully elucidate them.

15.0 INVESTIGATION OF THE REACTION OF SiMe_2 WITH METHYLACETYLENE

R.T. Conlin [8] has shown that pyrolysis of sym-dimethoxytetramethyldisilane in the presence of propyne forms dimethyl-1-propynylsilane.

The suggested mechanism involved formation of a silacyclopropene followed by rearrangement.

Methanol trapping experiments were used to probe the mechanism of formation of dimethyl-1-propynylsilane. If the reaction was proceeding via a silacyclopropene intermediate, the methanol should react with it to form a methoxyvinylsilane.

If the reaction was not proceeding via a silacyclopropene intermediate, then no matter how much MeOH was added some dimethyl-1-propynylsilane would still be formed (unless the intermediate, even though it was not a silacyclopropene, was being trapped by MeOH).

The vacuum flow pyrolysis of diethoxytetramethyldisilane in the presence of propyne and methanol yielded only the methoxyvinylsilane. This suggests that the dimethyl-1-propynylsilane was formed from the rearrangement of a silacyclopropene. The methoxyvinylsilane was characterized by NMR spectroscopy. A full characterization has not been completed.

NMR: H^{a} 5.56 δ (m, 2H)
 H^{b} 3.36 δ (s, 3H)
 H^{c} 1.96 δ (m, 3H)
 H^{d} 0.36 δ (s, 6H)

To see if the silacyclopropene was surviving the oven temperatures, methanol was condensed into the liquid nitrogen cooled trap just below the oven. Both dimethyl-1-propynylsilane and the methoxyvinylsilane were isolated in a ratio of ca. 6:1, suggesting that some of the silacyclopropene produced was indeed surviving past the oven. These results suggest that trimethylsilacyclopropene may be surviving long enough to study its chemistry. Methanol trapping experiments with the methanol located further away from the oven will determine how long the silacyclopropene is surviving.

16.0 INVESTIGATION OF A POSSIBLE MECHANISM FOR THE PHOTOCHEMICAL GENERATION OF A SILACYCLOPROPENE FROM ALKYNYLDISILANES

Sakurai [7] and Kumada [6] both report preparation of the following photochemically generated silacyclopropene.

A possible mechanism for this reaction involves radical intermediates.

To test this mechanism (dimethylsilyl)-t-butylacetylene was photolyzed in the presence of radical producers (i.e. di-t-butylperoxide, dibenzoylperoxide, and azobisisobutyronitrile (AIBN)). Using di-t-butylperoxide as the radical source the following reactions were proposed.

When di-t-butylperoxide was used as the radical initiator, photolysis with either a low pressure mercury lamp or a medium pressure mercury lamp gave the same results. The starting silane had decomposed after 27 hours of irradiation. NMR analysis indicated the development of a broad peak in the Si-CH₃ region; however, no peaks were present which would indicate the presence of vinyl hydrogens. Gas chromatographic analysis on a 6' x 1/4" 10% silicon oil column at 65°C indicated the absence of any new products. The (dimethylsilyl)-t-butylacetylene was unaffected when photolyzed in the presence of dibenzoylperoxide or AIBN.

Recent studies cast doubt on the proposed mechanism. In a review article Ishikawa [131] discusses the photolysis of some organopolysilanes. Trapping experiments with MeOD suggest that aryl-disilanes isomerize to Si-C double bonded intermediates.

A similar mechanism involving a 1,3-trimethylsily migration was proposed for the photochemical rearrangement of alkenyldisilanes.

<u>R¹</u>	<u>R²</u>	<u>R³</u>
Ph	H	Me
Me	H	Ph
Me	Ph	Me

This evidence suggests that the rearrangement of alkynyldisilanes probably does not involve radical intermediates, but rather an initial 1,3-trimethylsilyl migration. Kumada and co-workers [6] have reported evidence for the existence of the silapropadiene which would result from the photolysis of phenyl(pentamethyldisilanyl)acetylene.

The authors suggest that the silacyclopropene and the silapropadiene are formed simultaneously by two different routes. However, no evidence is presented in support of there being two different routes.

Recently these same authors [132] reported that irradiation of trimethylsilyl(1,1-diphenyltrimethyldisilanyl)acetylene in benzene gave 1,1,2,2-tetraphenyl-3,4-[bis(trimethylsilyl)-methylene]-1,2-disilacyclobutane which was isolated in 18% yield after recrystallization.

The formation of the 1,2-disilacyclobutane was explained in terms of a head-to-head dimerization of a transiently formed silapropadiene.

In view of the previously reported photochemical rearrangement of phenyl(pentamethyldisilanyl)acetylene to a silacyclopropene, one would expect trimethylsilyl(1,1-diphenyltrimethyldisilanyl)acetylene to undergo a similar reaction.

However, Kumada does not report the formation of any silacyclopropene. One explanation for the absence of any silacyclopropene would be that the silacyclopropene formed is rearranging to the starting material. Addition of a trapping agent such as acetone could be used to investigate the possibility of silacyclopropene formation. The presence of a silacyclopropene would be indicated by the formation of a 1-oxa-2-silacyclopent-3-ene.

Perhaps the presence of the two phenyl groups on the silicon of the silapropadiene confers some stability to the silapropadiene so that it has a long enough lifetime to dimerize. The silapropadiene postulated in the photolysis of phenyl(pentamethyldisilanyl)acetylene was not reported to form dimers.

Ishakawa, Nakagawa, and Kumada [116] recently reported that silacyclopropenes can undergo photochemical isomerizations to silyl-substituted acetylenes.

The reverse of this reaction is very similar to the photochemical generation of a silacyclopropene from phenyl(penta-methyldisilanyl)acetylene [6,7].

The photochemical rearrangement of phenyl(pentamethyldisilanyl)acetylene to form a silacyclopropene is not completely understood. Perhaps the silapropadiene is the precursor of the silacyclopropene. Or perhaps the silacyclopropene comes directly from the disilanylacetylene via a 1,2-trimethylsilyl shift. Very recently, Sakurai [135] has successfully trapped silyl radicals from the photolysis of arylidisilanes. Thus, one of the primary steps in the photolysis of arylidisilanes is the generation of silyl radicals.

Therefore, the involvement of the radical intermediates in the formation of silacyclopropenes cannot be entirely discounted.

III EXPERIMENTAL

General Instrumentation:

Proton magnetic resonance spectra were recorded on a Varian A-60 spectrometer and on a Hitachi Perkin-Elmer R-24B 60 MHz NMR spectrometer. Silicon-29 and carbon-13 magnetic resonance spectra were recorded on a JEOL JNM-FX-100 FT NMR spectrometer. Infrared spectra were obtained using a Perkin-Elmer Model 457 grating spectrophotometer. Ultraviolet spectra were determined using an Applied Physics Corporation Model Cary 14 double beam spectrometer. Mass spectra were recorded on a Varian M-66 spectrometer, calibrated internally against perfluoroalkane.

Materials used:

2-Butyne: Pfaltz and Bauer. The following arrangement was used.

Figure 6: 2-Butyne Distillation Arrangement

Sodium was added to the round bottom flask before it was attached to the line. The round bottom flask was then evacuated and ca. 10 ml of butyne was added and degassed three times. The butyne was allowed to sit over the Na for 24 hours and then was trap-to-trap distilled using three baths held at -35°C (PhBr slush), -50°C (PhCl slush), and -196°C (liquid nitrogen). Trap-to-trap distillations allow for the separation of compounds according to their vapor pressures. Figure 6 shows the positions of the baths on the traps. The stopcocks were opened to allow the butyne to pass through the traps as a gas. The butyne passed through the -35°C and -50°C baths and was frozen out in the -196°C trap. Any "heavy" impurities would have condensed in the -35°C or -50°C baths. As the distillation proceeded solid butyne would form a plug in the -196°C trap. The liquid nitrogen bath would then be lowered slightly, and the plug would be warmed until it moved further into the trap. After the distillation was completed the -196°C trap was isolated, and the butyne was allowed to warm to room temperature. It was then transferred to a storage tube.

Methylacetylene: Matheson Company. The gas cylinder of methylacetylene was attached to the vacuum line, and the methylacetylene was carefully distilled onto the line using the following apparatus.

Figure 7: Methylacetylene Distillation Arrangement

The methylacetylene was condensed in the liquid nitrogen cooled trap. Any "heavy" impurities were stopped in the -78°C bath.

Fluorenone: Eastman. The material was distilled under high vacuum ($115^{\circ}\text{C}/100$ microns Hg) and then recrystallized from benzene: hexane.

Acetone: Taylor Chemical Company, spectroquality 99 mole %. The material was dried over K_2CO_3 and then carefully distilled from KMnO_4 .

Styrene: Eastman, 98% pure. The material was washed with 5% NaOH to remove the inhibitors, washed twice with water, dried over MgSO_4 and distilled at reduced pressure ($52^{\circ}\text{C}/19\text{mm}$ Hg). To keep it from polymerizing it was stored at -78°C .

Tetracyanoethylene: Eastman. CAUTION: TCNE SLOWLY HYDROLYZES TO HCN AT ROOM TEMPERATURE. The material was recrystallized in nine times its weight of chlorobenzene.

The crystals were washed with cold chlorobenzene and dried by suction filtration (An inverted funnel was used to direct a flow of dry N_2 over the crystals). All operations were carried out in the hood.

Phenylacetylene: Aldrich 98%. The material was vacuum distilled using a 5" column packed with glass helices (70-71°C/ 50mm Hg).

Acetonitrile: Fisher 99%. The material was stored over $CaCl_2$. The $CaCl_2$ was filtered off and calcium hydride was added. The solution was stirred for several hours until no more H_2 was evolved. The calcium hydride was filtered off and a small amount of P_2O_5 was added. The CH_3CN was distilled from the P_2O_5 (b.p. 82°C) at atmospheric pressure.

t-Butylcyanide: Aldrich. This material was purified using the same procedure as was used to purify acetonitrile.

Di-t-butylperoxide: Matheson Coleman and Bell. This material was distilled at reduced pressure (52°C/ 68mm Hg).

Triethylamine: Aldrich. This material was stored over NaOH pellets and distilled prior to each use.

Cyclohexane: Fisher. This material was stored over Na and distilled prior to each use.

Trimethylchlorosilane: Fisher. This material was distilled prior to each use.

Dimethylchlorosilane: Petrarch. This material was used directly from the bottle. For the synthesis of

$(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{C}-\text{Si}(\text{CH}_3)_2\text{H}$ it was trap-to-trap distilled on the vacuum line using -35°C , -50°C , and -196°C baths (see purification of 2-butyne for the procedure).

Trimethyl Orthoformate: Fisher. This material was distilled from calcium hydride.

Trimethylsilane: Petrarch. This material was freshly distilled on the vacuum line before each use. See Methylacetylene for apparatus. (bp $6.7^\circ\text{C}/760\text{mm Hg}$)

$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$: Alfa Ventron 99%. This material was used directly from the bottle.

Methyl Isocyanate: Aldrich. The material was purified by a trap-to-trap distillation on the vacuum line using baths at room temperature, -10°C , and liquid N_2 (see Figure 6 for apparatus).

Ethylene Oxide: Fisher. The material was purified by distilling it from NaOH via a trap-to-trap distillation on the vacuum line using baths at -35°C , -50°C , and liquid nitrogen (see Figure 6 for apparatus).

Tetraphenylethylene Oxide: A methylene chloride solution containing excess perbenzoic acid and 3g (10^{-2} moles) tetraphenylethylene was placed in a Nalgene bottle equipped with a magnetic stirring bar. The solution was stirred for 2-1/2 weeks at 0°C . Then it was extracted 4 times with 30 ml of water or until the aqueous layer had a pH of 5. The aqueous layers were combined and extracted with 20 ml of CH_2Cl_2 . The organic layers were combined, dried over MgSO_4 , and removed using the rotary evaporator.

The crystals which were obtained were recrystallized from hot ethyl acetate to give 2.16 g (69% yield) of fine white needles which melted at 206-207°C.

Azobenzene: Pfaltz and Bauer. This material was purified by column chromatography on an alumina column using 1:4 benzene: petroleum ether as the eluting solvent. After the eluting solvent was evaporated the material was recrystallized from hexane. All operations were carried out in the dark to avoid trans⇌cis isomerization.

t-Butylacetylene: Pfaltz and Bauer. This material was trap-to-trap distilled on the vacuum line using -35°C, -50°C, and -196°C baths (see purification of 2-butyne for the procedure).

sym-Dichlorotetramethyldisilane: This material was synthesized by the method of Barton and Banasiak [134]. A 100 g. (1.06 moles) sample of Me_2SiClH , boiling chips, and a drop of Hg were placed in a quartz vessel equipped with a condenser and N_2 inlet and outlet. N_2 was bubbled through the solution for 45 minutes, and then a low pressure Hg lamp was turned on. The sample was photolyzed for 96 hours and then vacuum distilled to give 37.2 g. (38%) of the dichlorotetramethyldisilane, which was collected between 68-80°C at 54mm Hg.

sym-Dimethoxytetramethyldisilane: This material was synthesized by the method of Barton and Banasiak [134]. A 37.2 g. (0.2 moles) sample of sym-dichlorotetramethyldisilane

was added to 110ml (1 mole) of trimethyl orthoformate in a 250 ml round bottom flask equipped with a condenser and drying tube. The reaction mixture was stirred at 60°C overnight. An atmospheric distillation was used to remove the low boiling components, and then a vacuum distillation was carried out to give 26.9 g. (70%) of sym-dimethoxytetramethyldisilane, isolated as the fraction boiling at 65-68°C/ 33mm Hg.

sym-Diethoxytetramethyldisilane: This material was synthesized using a modified version of the procedure of Hengge and Waldhor [133]. A 500 ml flask containing 33.2 g. (0.18 moles) of sym-dichlorotetramethyldisilane in 100ml of cyclohexane was externally cooled in an ice bath. To this mixture a solution of 18.4 g. (0.4 moles) dried ethanol and 40.0 g. (0.4 moles) triethylamine in 100 ml cyclohexane was added dropwise. After stirring at room temperature overnight and then refluxing for one hour, the reaction mixture was filtered to remove triethylamine hydrochloride. The cyclohexane solvent was removed by fractional distillation, and the remaining mixture was distilled to yield 14.7 g. (40%) of sym-dimethoxytetramethyldisilane, b.p. 86-87°C/ 38mm Hg.

Hexamethyldisilane: A 4 g. sample of Na and a 15 g. sample of K were cut up and placed in a 500 ml round bottom flask equipped with a glass-coated magnetic stirring bar and a stopcock. The round bottom flask was attached to a

vacuum line and evacuated. After checking to make sure there were no leaks, the flask was heated with a heat gun until the Na and K melted to form an alloy. A large magnet outside the flask was used to move the stirring bar to obtain thorough mixing. Several milliliters of degassed Me_3SiCl were condensed into the flask. The flask, remaining open to the manometer, was allowed to warm to room temperature with stirring. If the pressure went up too quickly the flask was immediately cooled with liquid N_2 and evacuated; then it was warmed to room temperature again. The Me_3SiCl reacted exothermically with the Na/K turning it into a black porous solid at which time stirring stopped. The Me_3SiCl was added in 10 ml portions until all 50 ml had been added making sure there was no pressure build up. The Me_3SiCl sat over the Na/K for 3 days. The volatiles were then condensed into a trap on the vacuum line. Approximately 4 hours were needed to remove all the volatiles from the flask. An atmospheric distillation removed any unreacted Me_3SiCl . The fraction boiling between $110\text{--}111^\circ\text{C}$ containing $\text{Me}_3\text{SiSiMe}_3$ and 5% $\text{Me}_3\text{SiOSiMe}_3$ was washed once with concentrated H_2SO_4 and then 3 times with H_2O . It was dried over MgSO_4 and subjected to an atmospheric distillation to yield 21.9 g. (75%) hexamethyldisilane boiling at 110°C .

Dimethylsilyl-t-butylacetylene: The following arrangement was used in the preparation of this compound.

Figure 8: Arrangement for Preparation of Dimethylsilyl-t-butylacetylene

A solution of 5.35 g. (0.07 moles) of t-butylacetylene in ca. 100 ml of Et_2O was added to the 250 ml flask which was cooled to -20°C by a CCl_4 /liquid N_2 slush bath. 39 ml (0.07 moles) of 1.8M MeLi in Et_2O was transferred to the 50 ml dropping funnel and added dropwise to the alkyne solution. Bubbles of CH_4 were produced. After the MeLi addition the reaction mixture was stirred for 20 minutes and then transferred to the 200 ml dropping funnel. The transfer was made using a double pointed hollow needle. One end was stuck through the

septum on the vacuum adapter. The hose between the two flasks was clamped shut and the N_2 flow was increased until the solution began to transfer. The CCl_4 /liquid N_2 slush bath was transferred to the 500 ml flask and 6.58 g. (0.07 moles) of Me_2SiClH in 100 ml Et_2O was added to the flask. The $(Me)_3CC\equiv CLi$ solution was added dropwise with vigorous stirring to the $SiMe_2ClH$ solution. The bath was allowed to warm to room temperature overnight. The ether solution was decanted, and the salts were washed with Et_2O several times. All ether fractions were combined and distilled at atmospheric pressure to remove Et_2O , *t*-butylacetylene, and Me_2SiClH . The remaining 25 ml were transferred to a small flask and vacuum distilled. 5.3 g. (54%) of the dimethylsilyl-*t*-butylacetylene were isolated. b.p. 56-58°C (60 mm Hg). NMR: 0.12δ(d, 6H, $SiMe_2$), 1.15δ(s, 9H, Me_3C), 4.18δ(m, 1H, SiH).

Phenyl Azide: This compound was prepared using the procedure in Organic Synthesis, Collective Volume 3, page 710.

Pentamethylmethoxydisilane: This compound was a by-product from the preparation of sym-dimethoxytetramethyldisilane prepared by the methods of Ishikawa, Kumada, and Sakurai [132] and Hengge and Waldhor [133]. In a 250 ml flask fitted with a 30 cm Vigreux column was placed 16.7 g (0.114 mmoles) of hexamethyldisilane, 101.2 g. (0.92 moles) of trimethylchlorosilane, and 0.5 g of anhydrous aluminum chloride. The mixture was stirred mechanically and brought to reflux. After 15 ml of tetramethylsilane

had been collected, the temperature of the flask was then raised until 60 ml of trimethylchlorosilane was collected. The remaining reaction mixture was fractionally distilled at reduced pressure to yield 12.0 g (57%) pentamethylchlorodisilane b.p. 58°C/ 40 mm Hg. The pentamethylchlorodisilane (0.08 moles) was dissolved in 100 ml of cyclohexane in a 500 ml flask which was externally cooled with an ice bath. To this mixture a solution of 17 ml (0.43 moles) of absolute methanol and 17 g (0.19 moles) of triethylamine in 100 ml cyclohexane was added dropwise. After stirring at room temperature for 5 hours and refluxing for an additional 3 hours, the reaction mixture was filtered to remove the triethylamine hydrochloride. The excess cyclohexane was removed by fractional distillation and the remaining solution was distilled under vacuum (b.p. 40-41°C/ 14 mm Hg) to yield 10.3 g. of pentamethylmethoxydisilane (80%).

Pentamethyldisilane: A 3-necked 25 ml round bottom flask was equipped with a condenser, an addition funnel, N₂ inlet, and a stirring bar. A 0.2 g (.005m) sample of lithium aluminum hydride in n-butyl ether was added to the flask. After 1.6 ml (.0074m) pentamethylmethoxydisilane in n-butylether was added dropwise the reaction mixture was heated for 2 hours at 120°C. After cooling to room temperature the reaction mixture was poured into ice water, extrated twice with ether, and dried over Na₂SO₄. The reaction mixture was distilled to remove the ether and then was separated using a 5' x 1/4" DC-200 gas chromatographic

column at 75°C. No yield was calculated because only enough for an analytical sample was desired. NMR: 0.23 δ (s,9H), 0.26 δ (d,6H), 3.80 δ (m,1H).

Octamethyl-1,4-disilacyclohexa-2,5-diene: This material was prepared using a method developed by Atwell and Weyenberg [96]. A 1.62 ml (9mm) sample of sym-tetramethyldimethoxydisilane and a 0.9 ml (13mm) sample of 2-butyne were sealed under vacuum in a thick-walled tube. The tube was placed into a metal cylinder (with vent holes) to contain it if it exploded. The reaction mixture was heated in an oven at 225°C for 18 hours. After cooling to room temperature, and then to liquid nitrogen temperature, the tube was broken open and the volatiles were removed using a rotary-evaporator. The crystals were recrystallized from EtOH yielding 135.9 mg (13% yield). Mp. 76-77.5°C; NMR (in CCl₄): 0.06 δ SiMe(s,12H), 1.74 δ C-Me (s, 12H); IR: 1220(s), 944(m), 820(s), 755(s), 736(m); Mass Spec: 224 parent, 209 base (P-15).

Pyrolysis of Dimethoxytetramethyldisilane (or Diethoxytetramethyldisilane) in the Presence of 2-Butyne (or Propyne):

The thermal decomposition of dimethoxytetramethyldisilane was achieved through techniques commonly used for flash vacuum pyrolysis [39]. The hot zone was constructed by winding approximately 15 feet of 26 gauge nichrome wire around a quartz tube of 10 mm i.d. and 12 cm. length. The nichrome wire was insulated from the quartz and the atmosphere with asbestos ribbon. The design of the pyrolysis apparatus allowed the disilane vapor to flow into the hot

zone at a rate that was nearly independent of the flow rate of the added trapping agent. Temperatures in the hot zone were measured by a Chromel P-Alumel thermocouple placed between the outer surface of the tube and the asbestos ribbon. Typically the hot zone was maintained at 650°C.

Disilane vapors were passed through the hot zone at a rate of ca. 200mg./hour (0.20 ml./hour) in the presence of a 10-fold excess of alkyne (flow rate: 1.2 ml./hour). The flow rates of both the disilane and the alkyne were monitored by ball type flow meters. The storage tube containing the 2-butyne was cooled to 0°C to facilitate maintenance of the proper flow rate. Propyne was cooled to -45°C using a chlorobenzene slush bath. Products were condensed at -196°C within 2 cm. of the hot zone.

Figure 9: Flash Vacuum Pyrolysis Arrangement

After the pyrolysis the oven was cooled down, and the products were transferred to another part of the vacuum line for trap-to-trap distillation. The following bath temperatures were used.

<u>Trapping Agent</u>	<u>Temperature of baths (°C)</u>		
	A	B	C
2-Butyne	-35 (PhBr slush)	-50 (PhCl slush)	-196 (liquid N ₂)
Propyne	-50 (PhCl slush)	-78 (dry ice/acetone)	-196 (liquid N ₂)

Figure 10: Trap-to-trap Distillation

The distillation removed the alkyne. As the distillation proceeded trap C became plugged, and the -196°C bath was lowered to move the plug further down into the trap. After the distillation was completed trap C was isolated and all products remaining in flask A were moved to trap B. To accomplish this transfer, the slush baths were removed from A and B, and a -196°C bath was placed on B. Once the transfer had been made, trap B was isolated and allowed to warm to room temperature. Flask A was removed from the vacuum line

and replaced by a collection tube. After the collection tube was degassed, it was cooled to -196°C and the contents of trap B were condensed into the tube. The tube was sealed off using a gas/oxygen torch.

Figure 11:
Collection Tube

The sealed 3 mm. tubes were placed inside 5 mm. NMR tubes and spectra were recorded directly from collected samples. The liquid collected (2-butyne) in trap C was moved to a storage bulb and later purified for re-use. This procedure afforded 10-40% solutions of tetramethylsilacyclopropene in dialkoxymethylsilane with 5% other compounds.

^{29}Si Spectrum of Tetramethyl-1-silacycloprop-2-ene:

A JEOL JNM-FX-100FT-NMR spectrometer was used to obtain ^{29}Si spectra. For tetramethylsilacyclopropene ca. 4200 cycles of a 45° pulse with an 8 second pulse delay were needed to obtain each spectrum. To obtain a large enough sample for ^{29}Si NMR 12 hours of pyrolyses were done. After every two and one-half hours of pyrolysis, the oven was cooled and products were transferred to a

round bottom flask attached to the vacuum line. After every 2 transfers to the round bottom flask (i.e., 5 hours of pyrolysis), the products were trap-to-trap distilled and transferred to a collection tube which was then sealed. The collection tube was constructed from a 5 mm. high-quality NMR tube which had been attached to a length of 5 mm. pyrex tubing. To condense in successive product fractions the tube was attached to the line via a breaking tube, the breaking tube was degassed, the collection tube was cooled with a -196°C bath and broken open, and the next product fraction was condensed in.

Before inserting the tubing into the breaking tube, a score was made with a glass file ca. 3 cm. from the seal. The tube was inserted such that the scored mark was just above the top of the glass tube (see Figure 12). The tube was broken in the typical fashion. After the final collection of product had been made, the 5 mm. Pyrex tube

was sealed as close to the NMR tube as possible. The 5 mm. tube was positioned in a 10 mm. high-quality NMR tube using vortex plugs which had been drilled out to fit the 5 mm. tube. CDCl_3 and SiMe_4 were put inside the 10 mm. tube. To keep the sample from thermally decomposing ^{29}Si NMR spectra were run at -5°C . Between runs the sample was stored in liquid nitrogen.

Figure 13:
NMR Tube Arrangement used
to obtain ^{29}Si NMR Spectra

After the ^{29}Si spectrum was obtained the tube was attached to the vacuum line using the breaking tube; it was broken open under vacuum, and MeOH was added before the tube was resealed. The ^{29}Si NMR spectrum was then obtained on this solution in which the tetramethylsilacyclopropene had been converted into 2-methoxy-2,3-dimethyl-1-silapent-3-ene. A comparison of the peaks allowed for the chemical shift assignment of the silacyclopropene (see Section 6.2).

^{13}C Spectrum of Tetramethyl-1-silacycloprop-2-ene:

A JEOL JNM-FX-100FT-NMR was used to obtain ^{13}C spectra. For tetramethylsilacyclopropene 6040 cycles of a 20° pulse with an 4 second pulse delay were needed to obtain each spectrum. The same procedure was used to obtain ^{13}C

spectra as was used to obtain ^{29}Si spectra. The peak assignments are shown below.

Basic Procedure for Adding Substrates to Tetramethylsilacyclopentene: The tetramethylsilacyclopentene was prepared using the previously described vacuum flow pyrolysis techniques. After the pyrolysis was complete, the products were trap-to-trap distilled. The final product fraction was condensed under vacuum into a collection tube containing the substrate. The tube was then sealed and removed from the vacuum line.

Addition of Fluorenone to Tetramethylsilacyclopentene: The final product fraction containing the silacyclopentene from a 105 minute pyrolysis was condensed into a tube containing 20 mg. of purified fluorenone. After 12 hours at room temperature the solution had turned from yellow to clear. The

tube was broken on the vacuum line, and the volatiles were removed leaving a white solid. The solid was column chromatographed on an alumina column using benzene:hexane (1:1) as the eluting solvent. After the solvent was evaporated, a white solid melting at 149-152°C was isolated and identified as 2,2,3,4-tetramethyl-5-fluorenyl-1-oxa-2-silacyclopent-3-ene. NMR: 0.38 δ (s, 6H, SiMe), 1.10 δ (m, 3H, C=C-Me), 1.70 δ (m, 3H, Si-C(Me)=C), 6.93-7.50 δ (m, 8H, aromatic Hs). IR: 1620 (m), 1248 (s), 1042 (s), 890 (s), 840 (m), 780 (m), 760 (m), 740 (s). Mass spec: 292 (parent), 277 (base). Elemental analysis: Found: 77.60% C, 7.44% H, 9.70% Si (calculated: 78.03% C, 6.89% H, 9.60% Si).

Addition of Acetone to Tetramethylsilacyclopentene:

The tetramethylsilacyclopentene product fraction was condensed into a tube containing purified acetone. The disappearance of the silacyclopentene was monitored by NMR. After all the silacyclopentene was gone, the tube was broken open, and the contents were gas chromatographed on a 10' x 1/4" 15% DC-200 on 40/50 ABS Anakrom column with an oven temperature of 87°C. The peak that appeared just after MeOMe₂SiSiMe₂OMe was identified as 2,2,3,4,5,5-hexamethyl-1-oxa-2-silacyclopent-3-ene. NMR: 0.16 δ (s, 6H, SiMe), 1.26 δ (s, 6H, CMe), 1.50 δ (m, 3H, MeC=C), 1.56 δ (m, 3H, C=CMe). Mass spec: 155 (base: P-15).

Addition of Styrene to Tetramethylsilacyclopentene:

The product fraction from a 90 minute pyrolysis was condensed into a tube containing 20 μ l of styrene. After 6

days at room temperature no reaction had occurred. The tube was heated in an oil bath at 55°C for 83 hours. NMR spectroscopy was used to follow the disappearance of the tetramethylsilacyclopropene. New peaks formed at 1.9 δ and 0.4 δ in the NMR spectrum indicating formation of a tetramethylsilacyclopropene polymer.

Addition of Tetracyanoethylene to Tetramethylsilacyclopropene:

The product fraction from a 75 minute pyrolysis was condensed into a tube containing 18 mg. of TCNE. Upon warming to room temperature the solution immediately turned black. This "black" reaction was caused by $\text{SiMe}_2(\text{OMe})_2$ and $\text{MeOMe}_2\text{Si-SiMe}_2\text{OMe}$ reacting with TCNE. Test reactions were done by adding Me_6Si_2 , $\text{Me}_3\text{SiOSiMe}_3$, and $\text{MeOMe}_2\text{SiSiMe}_2\text{OMe}$ to small amounts of TCNE in vials. Only the $\text{MeOMe}_2\text{SiSiMe}_2\text{OMe}$ reacted, turning the solution black.

Addition of Phenylacetylene to Tetramethylsilacyclopropene:

The product fraction from a 150 minute pyrolysis was added to a tube containing 30 μl of phenylacetylene. After a week at room temperature two layers had formed - a top fluid layer and a bottom congealed layer. The sample was broken open on the vacuum line, and the volatiles were removed. The whitish-clear solid which remained exhibited two broad peaks in its NMR spectrum at 0.4 δ and 1.9 δ in the ratio 1:1. The solid was identified as a polymer of the silacyclopropene.

Addition of Acetonitrile to Tetramethylsilacyclopropene:

The product fraction from a 90 minute pyrolysis was condensed

into a tube containing 20 μ l of CH_3CN . After 12 hours at room temperature, the tube was broken open, and its contents were gas chromatographed on a 5' x 1/4" 15% DC-200 on 40/50 Anakrom column at 90°C. The peak appearing just before $\text{MeOMe}_2\text{SiSiMe}_2\text{OMe}$ was identified as cis-5-cyano-3,4,4-trimethyl-4-sila-2-pentene. NMR: 0.3 δ (s, 6H, SiMe), 1.7-1.8 δ (m, 8H, $\text{H}_2\text{CSi-CMe=CMe}$), 5.8-6.2 δ (m, 1H, C=CH).

Addition of t-Butylcyanide to Tetramethylsilacyclopropene:

The product fraction from a pyrolysis was added to an evacuated tube containing 15 μ l of t-butylcyanide. The tube was sealed under vacuum. After 4 days at room temperature NMR spectroscopy indicated that all the tetramethylsilacyclopropene had decomposed. A white solid had formed, but no new peaks were evident on the NMR spectrum. Gas chromatography on a 5 x 1/4" DC-200 on 40/50 ABS Anakrom column at 82°C indicated the absence of any products.

Addition of Methyl Isocyanate to Tetramethylsilacyclopropene:

The product fraction from a 3 hour pyrolysis was condensed into a tube containing 30 μ l $\text{H}_3\text{C-N=C=O}$. After 10 days the tube was broken on the vacuum line and the volatiles were removed. The nonvolatiles were separated on a 10' x 1/4" DC-200 gas chromatographic column at 130°C. The peak with a retention time of 40.8 minutes was identified as octamethyl-1,4-disilacyclohexa-2,5-diene by its mp. 76-77.5°C; NMR (in CCl_4): 0.06 δ SiMe(s, 12H), 1.74 δ

C-Me(s,12H); IR: 1220(s), 944(m), 820(s), 755(s), 736(m);

Mass spec: parent 224; base (P-15) 209.

Addition of Phenyl Azide to Tetramethylsilacyclopentene:

The product fraction from a 3 hour pyrolysis was condensed into a tube containing 30 μ l of PhN₃. After 4 days the tube was broken on the vacuum line and the volatiles were removed. An NMR spectrum of the nonvolatiles suggested the presence of octamethyl-1,4-disilacyclohex-2,5-diene and polymeric tetramethylsilacyclopentene. The disilacyclohexadiene was identified by a comparison of its retention times on 3 gas chromatographic columns (10' x 1/8" DC-200 140° oven, 10' x 1/8" OV-17 140° oven, and 10' x 1/8" Apiezon L 140° oven) with the retention times of the authentic compound. On all three columns the retention times of the synthesized and the authentic compound were identical.

Addition of Ethylene Oxide to Tetramethylsilacyclopentene:

The product fraction from a 2 hour pyrolysis was condensed into a tube containing 30 μ l of ethylene oxide. After 3 days the tube was broken open and the volatiles were removed, An NMR spectrum of the nonvolatiles indicated the presence of silacyclopentene polymer and octamethyl-1,4-disilacyclohexa-2,5-diene. The disilacyclohexadiene was identified by gas chromatographic analysis (see phenyl azide addition).

Addition of Tetraphenylethylene Oxide to Tetramethylsilacyclopentene: The product fraction from a 90 minute pyrolysis was condensed into a tube containing tetraphenyl-

ethylene oxide. The reaction, as followed by NMR, was complete after 2 weeks. The only product identified was the silacyclopropene polymer.

Addition of Azobenzene to Tetramethylsilacyclopropene:

The product fraction from a 3 hour pyrolysis was condensed into a tube containing azobenzene. After 4 days the tube was broken open on the vacuum line, and the volatiles were removed. The nonvolatiles were separated by preparative thin layer chromatography using silica gel plates with benzene as the eluting solvent. The band with $rf=.89$ was identified as the silacyclopropene polymer and octamethyl-1,4-disilacyclohexa-2,5-diene. The disilacyclohexadiene was identified by its NMR spectrum and by gas chromatographic analysis (see phenyl azide addition).

Reactions of Tetramethylsilacyclopropene in the Presence of $\text{PdCl}_2(\text{PPh}_3)_2$:

The product fraction from a 3 hour pyrolysis was condensed into a tube containing a catalytic amount of $\text{PdCl}_2(\text{PPh}_3)_2$. After 3 days the tube was broken open on the vacuum line and the volatiles were removed. NMR spectroscopy indicated that the product was octamethyl-1,4-disilacyclohexa-2,5-diene. The disilacyclohexadiene was purified using column chromatography. A disposable pipette filled with silica gel was used as the column, and benzene was used as the eluting solvent. The benzene was evaporated and the crystals were recrystallized from EtOH. The mp: $76-77.5^\circ\text{C}$ uncorrected;

NMR: 0.06 δ (s, 12H) 1.74 δ (s, 12H); IR: 1220(s), 944(m), 820(s), 755(s), 736(m); and Mass spec: parent 224; base (P-15) 209 were identical with those of the authentic compound.

Reactions of Tetramethylsilacyclopentene in the Presence of Alkynes and a Catalytic Amount of $\text{PdCl}_2(\text{PPh}_3)_2$: The product fraction from a 3 hour pyrolysis was condensed into a tube containing a catalytic amount of $\text{PdCl}_2(\text{PPh}_3)_2$ and an excess of alkyne (either 2-butyne, phenylacetylene, or methylacetylene). After 3 days the tube was broken on the vacuum line and the volatiles were removed. NMR spectroscopy indicated that octamethyl-1,4-disilacyclohexa-2,5-diene had formed. See the "Reactions of Tetramethylsilacyclopentene in the Presence of $\text{PdCl}_2(\text{PPh}_3)_2$ " for the purification and identification of the disilacyclohexadiene.

Photolysis of Tetramethylsilacyclopentene: A 90 minute pyrolysis was followed by a careful trap-to-trap distillation to make sure all of the 2-butyne was distilled off. The final product sample was collected in a 3 mm. quartz tube which was sealed under vacuum. The sample was photolyzed using a medium pressure lamp. At various time intervals the photolysis was stopped, and the sample was analyzed by NMR spectroscopy.

Photolysis of Tetramethylsilacyclopentene in the Presence of Me_3SiH : A sample of tetramethylsilacyclopentene from a 90 minute pyrolysis was condensed into a 3 mm. quartz tube containing Me_3SiH . The volume of $\text{Me}_2\text{Si}(\text{OMe})_2$ to Me_3SiH was ca. 1:1. The sample was photolyzed using

a Hanovia medium pressure 450-W Hg arc lamp, and analyzed by NMR spectroscopy and gas chromatography/mass spectroscopy.

Pyrolysis of $\text{MeOMe}_2\text{SiSiMe}_2\text{OMe}$ in the Presence of Propyne and Methanol: The pyrolysis was carried out in the usual manner with one modification. The butyne storage tube was replaced by the following piece of apparatus.

Figure 14:
Propyne/Methanol
Storage Tube

Flow rates were followed by monitoring liquid volumes remaining in the storage cylinders. There were problems in maintaining proper flow rates; therefore, the slush bath on the propyne was varied from -45°C to -78°C in an attempt to regulate the flow rates. After trap-to-trap distillation of the reaction mixture, the final product fraction was sealed under vacuum in a tube and removed from the vacuum line. After NMR analysis the tube was broken open and subjected to gas chromatographic analysis on a 10' x 1/4" 15% DC-200 on ABS Anakrom column at 82°C . The product was isolated, and identified by its NMR spectrum.

NMR: 0.3 δ (s, 6H, SiMe),
 1.9 δ (m, 3H, C=CMe)
 3.3 δ (s, 3H, OMe)
 5.5 δ (m, 2H, C=CH)

Reactions of (Dimethylsilyl)-t-butylacetylene with

Radical Sources: The acetylene and radical source (di-t-butylperoxide, dibenzoylperoxide, or AIBN) were put in a 3 mm. quartz tube and degassed on the vacuum line. The sealed tubes were photolyzed using a low pressure Hg lamp. Analysis was done by NMR spectroscopy.

Figure 15: ^1H NMR Spectrum of a Reaction Mixture Containing Tetramethyl-1-silacycloprop-2-ene

Figure 16: ^1H NMR Spectrum of a Reaction Mixture Containing
Tetramethyl-1-silacycloprop-2-ene (Expanded: 0-200 Hz)

Figure 17: ^{29}Si NMR Spectrum of a Reaction Mixture Containing Tetramethyl-1-silacycloprop-2-ene

Figure 18: ^{29}Si NMR Spectrum of a Reaction Mixture Containing Tetramethyl-1-silacycloprop-2-ene to which Methanol had been Added

Figure 19: ^{13}C NMR Spectrum of a Reaction Mixture Containing Tetramethyl-1-silacycloprop-2-ene

Figure 20: ^{13}C NMR Spectrum of a Reaction Mixture Containing Tetramethyl-1-silacycloprop-2-ene to which Methanol had been Added

Figure 21: ^1H NMR Spectrum of Polymeric Tetramethyl-1-silacycloprop-2-ene in C_6D_6
(Some ethoxymethyl disilanes are also present)

Figure 22: ^{13}C NMR Spectrum of Polymeric Tetramethyl-1-silacycloprop-2-ene in C_6D_6

Figure 23: ^1H NMR Spectrum of 2,2,3,4-Tetramethyl-5-fluorenyl-1-oxa-2-silacyclopent-3-ene in CCl_4 (TMS reference)

Figure 24: IR Spectrum of 2,2,3,4-Tetramethyl-5-fluorenyl-1-oxa-2-silacyclopent-3-ene

Figure 25a: Mass spectrum of 2,2,3,4-Tetramethyl-5-fluorenyl-1-oxa-2-silacyclopent-3-ene
(continued on next page)

Figure 25b: Mass Spectrum of 2,2,3,4-Tetramethyl-5-fluorenyl-1-oxa-2-silacyclopent-3-ene
(continued)

Figure 26: ^1H NMR Spectrum of 2,2,3,4,5,5-Hexamethyl-1-oxa-2-silacyclopent-3-ene in C_6D_6

Figure 27: Mass Spectrum of 2,2,3,4,5,5-Hexamethyl-1-oxa-2-silacyclopent-3-ene

Figure 28: ^1H NMR Spectrum of 1-Cyano-2,2,3-trimethyl-2-sila-3-pentene
in C_6D_6

Figure 29: ^1H NMR Spectrum of Octamethyl-1,4-disilacyclohexa-2,5-diene with Benzene as a Reference

Figure 30: IR Spectrum of 1,1,2,3,4,4,5,6-Octamethyl-1,4-disilacyclohexa-2,5-diene

Figure 31: Mass Spectrum of 1,1,2,3,4,4,5,6-Octamethyl-1,4-disilacyclohexa-2,5-diene

Figure 32: ^1H NMR Spectrum of 2,3-Dimethyl-3-methoxy-3-sila-1-butene and/or 4-Methyl-4-methoxy-4-sila-trans-2-pentene from the Addition of Methanol to 1,1,2-Trimethyl-1-silacycloprop-2-ene in C_6D_6

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APPENDIX

DISPROPORTIONATION OF TRIMETHYLSILYL RADICALS TO A SILA OLEFIN IN THE LIQUID PHASE

1.0 INTRODUCTION

Until very recently the disproportionation of trimethylsilyl radicals to the sila olefin, 2-methyl-2-silapropene, was considered to be a minor process compared to radical recombination [1]. Prompted by the high ratio of disproportionation to recombination, $k_{\text{disp}}/k_{\text{recomb}} = 0.48$ found in the gas phase by Tokach and Koob [2], we have reexamined the self-reactions of trimethylsilyl radicals in solution.

In 1972 Gaspar, Haizlip, and Choo [3] reported that the rate of decay of trimethylsilyl radicals generated by the photolysis of tert-butyl peroxide in solutions of trimethylsilane was a rapid process second order in the concentration of $\text{Me}_3\text{Si}\cdot$:

Based on the observation that hexamethyldisilane and tert-butyl alcohol were the only products at the short reaction times of the kinetic studies, radical recombination was believed to be the exclusive mode of self-reaction for trimethylsilyl radicals. Upon extended photolysis, however, a third product, tert-butoxytrimethylsilane, was formed. This product was believed to arise from secondary reactions, and its source was not fully investigated at that time. Attack of tert-butoxy radical on hexamethyldisilane was, however, ruled out as the

mechanism for the formation of tert-butoxytrimethylsilane. We now believe that most of the tert-butoxytrimethylsilane is formed by trapping of the disproportionation product by tert-butyl alcohol.

A series of simple experiments has demonstrated that tert-butoxytrimethylsilane is an early product when a trapping reagent is present and is formed from the addition of alcohol to sila olefin. Several alternative mechanisms have been ruled out.

2.0 RESULTS AND DISCUSSION

In the presence of excess tert-butyl alcohol the product ratio of $\text{Me}_3\text{COSiMe}_3/\text{Me}_3\text{SiSiMe}_3 = 0.18 \pm .08$ remained constant with irradiation time.

Table A-1: Product Ratio vs. Irradiation Time

Irradiation Time (hours)	$\text{Me}_3\text{SiOCMe}_3/\text{Me}_3\text{SiSiMe}_3$
2/3	0.14
1	0.17
1-1/2	0.16
2	0.13
3	0.26
4-1/2	0.21

Samples contained 25 μl $\text{Me}_3\text{COOCMe}_3$, 40 μl Me_3COH , and 30 μl Me_3SiH

The product ratio was not affected by changes in the ratio of Me_3SiH to di-tert-butyl peroxide nor by variations in the light intensity.

Table A-2: Product Ratios vs Initial Concentrations and Irradiation Intensity

$\text{Me}_3\text{SiH}/\text{Me}_3\text{COOCMe}_3$	$\text{Me}_3\text{SiOCMe}_3/\text{Me}_3\text{SiSiMe}_3$
4:1	$0.16 \pm .010$
2:1	$0.17 \pm .005$
1:1	$0.17 \pm .015$
1:2	$0.14 \pm .010$

% Transmission	$\text{Me}_3\text{SiOCMe}_3/\text{Me}_3\text{SiSiMe}_3$
100.	$0.21 \pm .030$
63.2	$0.28 \pm .030$
43.9	$0.26 \pm .015$
21.7	$0.25 \pm .030$

That 2-methyl-2-silapropene was being trapped was demonstrated by the use of Me_3COD either generated in situ from Me_3SiD or added in excess.

Formation of the monodeuterated tert-butoxytrimethylsilane was established by ^1H NMR and mass spectroscopy.

Table A-3: % Deuterium Incorporation for tert-Butoxytrimethylsilane

Reaction	%D in $\text{Me}_3\text{SiOCMe}_3^*$	% Reaction
$\text{Me}_3\text{SiD} + \text{Me}_3\text{COOCMe}_3$	22 ± 1.4	90
	54 ± 0.6	49
	26 ± 1.7	62
	31 ± 0.7	15
$\text{SiMe}_3\text{H} + \text{Me}_3\text{COOCMe}_3 + \text{Me}_3\text{COD}$	$37^\dagger \pm 1.7$	92
	43 ± 1.2	38
	43 ± 1.3	37

*Corrected for fact that mass spectrum shows no parent peak but rather (P-15) peak and for

$$\frac{\text{loss of } \text{CD}_3}{\text{loss of } \text{CH}_3} = 4$$

† Also corrected for Me_3COD being only 52% deuterated initially.

There is a scatter of the quantitative results between 0.2 and 0.5 deuterons incorporated per molecule. Thus, the labeling experiments do not exclude contributions from additional sources of tert-butoxytrimethylsilane. Four sources have been considered.

(1) Attack by tert-butoxy radicals on hexamethyldisilane

has been rendered unlikely by the absence of either product when tert-butoxy radicals were generated in hexamethyldisilane [3].

(2) Induced decomposition of tert-butyl peroxide can also

be ruled out as a source of tert-butoxytrimethylsilane

since the presence of tert-butyl alcohol is required for its formation. Irradiation of mixtures of tert-butylperoxide trimethylsilane, and methanol yields methoxytrimethylsilane and hexmethyldisilane as products with only traces of tert-butoxytrimethylsilane. Control experiments showed that the exchange of alkoxy groups did not occur for the product methoxytrimethylsilane nor for the recovered tert-butylperoxide.

Thus, the alkoxysilane arises from reaction of a silicon-containing intermediate with an alcohol.

(3) A third possibility is that the trimethylsilyl radical itself reacts with an alcohol molecule to form an alkoxysilane via an unconventional radical complex that could act as a hydrogen atom donor in a chain process [4].

A very low yield (<2%) of hydrogen speaks against this process.

(4) A remaining possibility is that trimethylsilane is reacting directly with the alcohol to form tert-butoxytrimethylsilane. Solutions of trimethylsilane and tert-butyl alcohol do not form tert-butoxytrimethylsilane in the dark or during short irradiation times (<2 hours). At longer (>20 hours) irradiation times tert-butoxytrimethylsilane is formed. When methanol is the alcohol used trimethylmethoxysilane is formed after 2 hours of irradiation. When MeOD is used mass spectral results indicate no deuterium incorporation in the product trimethylmethoxysilane. These findings may account for the low deuterium incorporation for methoxytrimethylsilane when solutions of trimethylsilane, tert-butyl peroxide, and deuterio methanol are irradiated.

Table A-4: % Deuterium Incorporation for Methoxytrimethylsilane

% deuterium incorporation in Me_3SiOMe	% decomposition
7.5 ± 1.5	43
2.0 ± 0.2	71
0.1 ± 0.8	89
2.2 ± 1.4	100

Since positive evidence for the formation of $\text{CH}_2=\text{SiMe}_2$ is given by the trapping experiments with deuterated tert-butyl alcohol, we believe that the disproportionation of trimethylsilane in solution is established. The observed product ratio of $\text{Me}_3\text{COSiMe}_3/\text{Me}_3\text{SiSiMe}_3 = 0.2$ is insensitive

to variations of alcohol concentrations above 10 mole percent and thus may be equated with the ratio of bimolecular rate constants for disproportionation and recombination of trimethylsilyl radicals*. Since the recombination rate is nearly at the diffusion controlled limit [3] the disproportionation is astonishingly rapid [5], perhaps owing to stabilization of the transition state by the incipient C-Si π bond. Facile disproportionation of trimethylsilyl radicals may therefore be taken as indirect evidence for substantial π bonding in the sila olefin.

A point of interest is that an increase in the yield of $\text{Me}_3\text{COSiMe}_3$ at long irradiation times (>12 hours) and a concomitant decrease in the yield of $\text{Me}_3\text{SiSiMe}_3$ is observed.

* 0.2 represents an upper limit, since the amount of deuterium incorporated from Me_3COD is only ca. 0.4. A lower limit is $(0.2) \cdot (0.4) = 0.08$.

Figure A-1: Product Concentration vs Hours of Photolysis

Trapping experiments with labelled alcohol indicate that photolysis of hexamethyldisilane is another route to 2-methyl-2-silapropene.

Table A-5: % Deuterium Incorporation for Methoxytrimethylsilane

% deuterium in $\text{Me}_3\text{SiOCMe}_3$
(corrected for Me_3COD being 53% deuterated)

85 ± 1.3
 96 ± 0.8

This has also been observed by Boudjouk and Koob in the gas phase [6], but a much shorter wavelength light was employed.

3.0 EXPERIMENTAL

General Instrumentation:

Proton magnetic resonance spectra were recorded on a Hitachi Perkin-Elmer R-24B 60 MHz NMR spectrometer. Mass spectra were recorded on a Varian M-66 spectrometer, calibrated internally against perfluoroalkane.

Materials Used:

Diethyl ether: Fisher. This material was distilled from sodium prior to each use. bp $34^\circ\text{C}/760\text{mm Hg}$.

tert-Butyl alcohol: Fisher. This material was dried over MgSO_4 and then distilled from calcium hydride. bp $82^\circ\text{C}/760\text{mm Hg}$.

10-Deutero tert-butyl alcohol: Aldrich. This material was used directly from a freshly opened bottle.

Methyl alcohol-d: Aldrich. 99.5+ atom %. This material was used directly from a freshly opened bottle.

Di-n-butyl ether: Fisher. This material was distilled from sodium prior to each use. b.p. $142^\circ\text{C}/760\text{mm Hg}$.

Trimethylchlorosilane: Fisher. This material was distilled prior to each use. b.p. $58-60^\circ\text{C}/760\text{mm Hg}$.

Lithium aluminum deuteride: Aldrich. This material was used directly from the bottle.

Di-tert-butylperoxide: Fisher. This material was distilled under reduced pressure prior to each use. b.p. $52^\circ\text{C}/68\text{ mm Hg}$.

Trimethylsilane. Petrarch. The gas cylinder was attached to the vacuum line, and the trimethylsilane was carefully distilled into a trap cooled with liquid N_2 .

Methanol: Fisher. This material was dried with magnesium and freshly distilled prior to each use. b.p. $65^\circ\text{C}/760\text{ mm Hg}$. See The Chemist's Companion for the procedure.

General Procedure for the Generation of Trimethylsilyl Radicals: In a typical experiment the samples to be photolyzed were prepared in the following manner. A $25\text{ }\mu\text{l}$ sample of di-tert-butyl peroxide and a $40\text{ }\mu\text{l}$ sample of tert-butylalcohol were syringed into a 3 mm OD quartz tube. The tube was attached to the vacuum line and degassed three times. Approximately $30\text{ }\mu\text{l}$ of trimethylsilane

was condensed into the tube which was then sealed under vacuum. The tubes were irradiated with a Hanovia medium-pressure 450-W mercury arc lamp. The apparatus shown in Figure A-2 was used to rotate the samples to insure equal irradiation.

Figure A-2: Apparatus Used for Rotating Samples During Irradiation

After being irradiated the tubes were cooled with liquid nitrogen and broken open. Care was taken to avoid bumping as the solution was warming to room temperature. The solution was then injected with a pre-cooled microsyringe onto a 30' x 1/4" 20% silicone oil SF96 column with an oven temperature of 75°C.

Synthesis of Deuterated tert-Butyl Alcohol: A 3.5g sample of potassium-tert-butoxide was dried in a 3-necked round bottom flask by heating it under vacuum (1mm Hg) at 150°C for 2 hours. After allowing the potassium-tert-butoxide to cool to room temperature, N₂ was admitted to the flask and dry ether was added to make a slurry. An addition funnel containing 0.4 ml D₂O in 10 ml of ether

was fitted to the round bottom flask and the solution was added dropwise. Excess ether was removed by an atmospheric distillation. The flask was then attached to the vacuum line, and the remaining volatiles were removed. A series of small samples were collected from the vacuum line and checked by NMR until the samples no longer contained any ether. Because ether has a higher vapor pressure than the alcohol the ether can be selectively removed. The final tert-butyl alcohol samples were 66% deuterated.

Synthesis of Deuterio-trimethylsilane: A 1.1 ml sample of SiMe_3Cl (8×10^{-3} mole) and 15 ml di-n-butyl ether were placed in a 50 ml 3-necked round bottom flask which was equipped with a stopper and a bent side arm tube containing lithium aluminium deuteride (LAD) (0.2g., 4.2×10^{-3} moles). A stirring bar was put into the flask which was then attached to the vacuum line and degassed 4 times. With stirring the LAD was carefully added by rotating the side arm 180° and gently tapping it. The round bottom flask was open to a manometer but closed to the pump allowing for observation of pressure changes. The reaction mixture was stirred for 3 hours, and then 3 ml of the volatiles were condensed into another trap and subjected to a trap-to-trap distillation using -35°C , -75°C , and liquid N_2 traps. The NMR spectrum showed that the liquid in the final trap was Me_3SiD . NMR (in CCl_4): 0.03 δ (s, 9H) mass spectrum: (parent-15) 73.

Preparation of $\text{Me}_3\text{SiOC}(\text{CD}_3)_3$: A 25 ml 3-necked round bottom flask was equipped with a stirring bar, N_2 inlet, condenser, N_2 outlet, and a septum. After flushing with N_2 , the N_2 was shut off. A mercury trap was attached to the N_2 outlet so air couldn't back up into the system. Using a syringe, 5 ml of ether, 0.5 ml 10-deutero-tert-butanol, and 0.8 ml NEt_3 were introduced into the round bottom flask. A 0.6 ml sample of Me_3SiCl was added last. After sitting overnight the flask was attached to the vacuum line and all volatiles were removed. The volatiles were removed from the vacuum line in 2 fractions. The second fraction, enriched in $\text{Me}_3\text{SiO}(\text{CD}_3)_3$, was separated into its components using a 30' 20% SF96 gas chromatographic column at 79°C . Mass spectrum: (parent-18) 137; (parent-15) 140; NMR (in benzene): 0.30δ (s,9H)

Preparation of tert-Butoxytrimethylsilane: This compound was prepared using the same procedure as was used to prepare $\text{Me}_3\text{SiO}(\text{CD}_3)_3$ except Me_3COH was used instead of $(\text{D}_3\text{C})_3\text{COD}$. The mass spectrum was identical with that reported in the literature [7]. NMR (in benzene): 0.3δ (s,9H), 1.32δ (s,9H)

Preparation of Methoxytrimethylsilane: This compound was prepared using the same procedure as was used to prepare $\text{Me}_3\text{SiO}(\text{CD}_3)_3$ except 0.2 ml MeOH was used in place of $\text{HO}(\text{CD}_3)_3$. NMR: 0.08δ (s,9H), 3.3δ (s,3H).

Procedure for Hydrogen Analysis: Quartz tubes of the following design were used.

Figure A-2: Quartz Collection Tube

In a typical experiment 100 μl of di-tert-butyl peroxide was added to the tube using a syringe. The apparatus was then attached to the vacuum line and degassed. After 200 μl of trimethylsilane were condensed into the tube, it was sealed under vacuum at position A. The tube was then irradiated for 5 hours using a Hanovia medium-pressure 450-W Hg arc lamp. Afterwards the 3 mm portion of the tubing was placed in a liquid N_2 bath to freeze out the condensables, and the tube was sealed at position B. The 1.8 cm quartz tubing was broken in the inlet chamber of a gas chromatograph and the gaseous products analyzed on a 10' x 1/4" molecular sieve 5Å column (40-60 mesh) at room temperature. These chromatographic conditions were chosen in order to detect hydrogen. The carrier gas employed was argon.

Calculation of Deuterium Incorporation: The percent deuterium incorporation was determined from mass spectral analysis. The peaks at (P-15) and (P-14) were expanded, and their heights were measured. The calculations are shown in Table A-6.

Table A-6: Peak Height Measurements for
 $\text{Me}_3\text{SiD} + \text{Me}_3\text{COOCMe}_3 \xrightarrow{h\nu}$

Trial	Peak height in centimeters*	
	m/e=131	m/e=132
1	20.4 ± 1.28	7.1 ± 0.83
2	15.9 ± 1.25	20.9 ± 1.82
3	17.8 ± 0.28	9.3 ± 0.62
4	14.0 ± 3.28	6.0 ± 1.47

*average of 10 scans

The mass spectrum of $\text{Me}_3\text{SiOC}(\text{CD}_3)_3$ indicates that loss of CD_3 /loss of $\text{CH}_3 = 4/1$. Therefore, CH_2D would be lost from $(\text{CH}_2\text{D})\text{Me}_2\text{SiOCMe}_3$ $1/15 = (1/5 \times 1/3)$ the time, and it would not get counted as a deuterated product. The peak height due to deuterium incorporation (D) in the tri-methyl-tert-butoxysilane is:

$$D = (1/15)(m/e=131) + (m/e=132) - [(m/e=131)(11.86\%)]$$

The 11.86% is the percent of naturally occurring isotopes that would have m/e=132.

$$\text{DI} = \% \text{ deuterium incorporation} = \frac{D}{(m/e=131) + (m/e=132)} \times 100$$

Table A-7: Peak Height Measurements for
 $\text{SiMe}_3\text{H} + \text{Me}_2\text{COOCMe}_3 + \text{Me}_3\text{COD} \longrightarrow$
 and $\text{Me}_3\text{SiSiMe}_3 + \text{Me}_3\text{COD} \longrightarrow$

Trial	Peak height in centimeters*	
	m/e=131	m/e=132
$\text{SiMe}_3\text{H} + \text{Me}_2\text{COOCMe}_3 + \text{Me}_3\text{COD} \xrightarrow{h\nu}$		
1	7.4 ± 1.11	2.3 ± 0.29
2	19.1 ± 1.15	6.9 ± 0.53
3	5.3 ± 0.95	1.9 ± 0.23
$\text{Me}_3\text{SiSiMe}_3 + \text{Me}_3\text{COD} \xrightarrow{h\nu}$		
1†	16.7 ± 0.27	21.8 ± 0.46
2	14.5 ± 2.26	16.6 ± 2.62

*Average of 10 scans

† Me_3COD was 64% deuterated

The percent deuterium incorporation was calculated as shown above with the added correction that the Me_3COD was only 53% deuterated.

$$\% \text{ deuterium incorporation} = \frac{DI \cdot (100)}{53}$$

Table A-8: Peak Height Measurements for
 $\text{Me}_3\text{SiH} + \text{Me}_3\text{COOCMe}_3 + \text{MeOD} \xrightarrow{h\nu}$

Trial	Height of peak in Centimeters*	
	m/e=89	m/e=90
1	4.0 $\pm$ 0.29	0.7 $\pm$ 0.08
2	15.7 $\pm$ 0.02	1.7 $\pm$ 0.23
3	12.8 $\pm$ 0.33	1.1 $\pm$ 0.05
4	13.5 $\pm$ 0.23	1.5 $\pm$ 0.04

*average of ten scans

The peak height due to deuterium incorporation (D'') in the trimethylmethoxysilane is:

$$D'' = (m/e=90) - [(m/e=89)(8.52\%)]$$

The 8.52% is the percent of naturally occurring isotopes that would have m/e=90.

$$\% \text{ deuterium incorporation} = \frac{D''}{(m/e=89)+(m/e=90)} \times 100$$

4.0 BIBLIOGRAPHY

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