Thermal isomerization and decomposition of ethynyldisilanes

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Thermal isomerization and decomposition of ethynyldisilanes

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Thermal isomerization and decomposition of ethynyldisilanes

by

Scott Allen Petrich

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For the Graduate College

Iowa State University
Ames, Iowa
1992
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The thermal isomerization and decomposition of ethynylpolysilanes is absent from the literature. However, ethynylsilane and its carbon analog, propyne, have been both experimentally and theoretically studied.

The literature began in 1960 when Wiberg and Bartley reported the thermal isomerization of cyclopropene to propyne. In 1975 two research groups individually reported the isomerization of allene to propyne. Both groups proposed a direct 1,3-hydrogen migration as the pathway. Walsh proposed in 1976 that cyclopropene was an intermediate in this isomerization. He also studied the isomerization of cyclopropene to propyne and observed a small amount of allene. Honjou et al. calculated the lowest energy pathway for the interconversion of allene, cyclopropene and propyne on the C_3H_4 singlet surface (Scheme 1). They determined the activation energy for the isomerization of allene to propyne to be 68.4 kcal per mole and for cyclopropene to propyne to be 41.5 kcal per mole. They proposed a series of 1,2-hydrogen shifts, after calculating the activation energy for a 1,3-hydrogen shift to be 95.6 kcal per mole. The most recent experimental work by Kakumoto et al. was in very good agreement with these
calculations. They obtained an activation energy of 68.1 kcal per mole and a log \( \text{A/s}^{-1} \) factor of 14.34 for the isomerization of allene to propyne.

Brown et al. have investigated the isomerization of terminal acetylenes by performing carbon-labelling experiments. Pyrolysis of \( ^{13}\text{C} \) - and \( ^{14}\text{C} \)-labelled acetylenes showed scrambling had occurred between the alkyne carbons. They proposed 1,2 shifts via vinylidene intermediates to obtain this scrambling (Scheme 2).

Scheme 2

\[ \begin{array}{c}
\text{R-CH} = \text{C} = \text{CH} \quad \text{R} \quad \text{H} \quad \text{C} = \text{C} \quad \text{R} \\
\text{C} = \text{C} \quad \text{H} \quad \text{C} = \text{C} \\
\text{H} \quad \text{C} = \text{C} \quad \text{H} \\
\text{R} = \text{phenyl, adamantyl, D} \\
* \text{denotes } ^{13}\text{C} \text{ or } ^{14}\text{C} \text{ label} \\
\end{array} \]
Kwart and Slutsky studied the isomerization of trimethylsilylallene to propargylsilane. They concluded the isomerization occurred via a 1,3-silyl shift with an activation energy of 50 kcal per mole. They also observed inversion of configuration on the silicon, when it was chiral, which supported a 1,3-silyl shift.

Barton and Groh studied the isomerization at higher temperatures and obtained a third isomer, 1 (Scheme 3). They proposed a mechanism involving 1,2-shifts which was in agreement with the calculations for the allene-propyne isomerization. They proposed that the inversion of configuration occurred during the 1,3-silyl shift.

Rogers et al. have reported shock tube experiments of the decomposition of ethynylsilane. They proposed the decomposition proceeded in four major pathways (Scheme 4): 1) α-elimination of hydrogen to form ethynylsilylene, 2) rearrangement to
silacyclopentane then extrusion of silylene to form acetylene, 3) rearrangement of the
silacyclopentane to vinyl silylene and 4) rearrangement of the silacyclopentane to
1-silacyclopropylidene which extruded elemental silicon to form ethylene.

Francisco et al. have calculated the activation energy for the decomposition of
ethynylsilane to acetylene\textsuperscript{10} to be 57 kcal per mole which was close to what Ring
determined experimentally to be 61.2 kcal per mole. Francisco proposed a silylvinylidene
intermediate via a 1,2-silyl shift (Scheme 5), which was determined to be 7 kcal per mole

\begin{equation}
\begin{aligned}
\text{Scheme 4} \\
\begin{array}{c}
H_2Si-\text{C}≡\text{CH} \\
\uparrow \\
\text{SiH}_2 \\
\downarrow \\
\text{Si} \\
\end{array}
\end{aligned}
\begin{array}{c}
\rightarrow 1 \\
\rightarrow 2 \\
\rightarrow 3 \\
\rightarrow 4 \\
\end{array}
\begin{aligned}
\rightarrow HSi-\text{C}≡\text{CH} + H_2 \\
\rightarrow \cdot\text{SiH}_2 + \text{HC}≡\text{CH} \\
\rightarrow \text{HSi} \cdot \text{C}≡\text{CH}_2 \\
\rightarrow \text{Si} + \text{H}_2\text{C}≡\text{CH}_2
\end{aligned}
\end{equation}

less than a hydrogen shift, followed by a 1,3-hydrogen shift via a four-membered
transition state. They did not report any calculations involving a silacyclopentane
Ishikawa et al. have calculated the pathway of isomerization of ethynylsilane to silacyclop propane via a diradical intermediate and reported an activation energy of 81 kcal per mole.

\[
\text{H}_3\text{Si} \equiv \text{C} \equiv \text{CH} \rightarrow \text{H}_2\text{Si}^* \rightarrow \text{H}_2\text{Si} \\
\]

Silacycloprenes have been proposed as intermediates in the trapping of silylenes with terminal acetylenes producing ethynylsilanes. Barton et al. proposed that if the silylene had a hydrogen or a silyl group, the initially formed silacyclopropene 2 rearranged to vinylsil ylene 3 via a 1,2 shift which was trapped again by acetylene to form vinylethynylsilane 4 (Scheme 6). If another good migrating group was on the silicon,
another 1,2 shift formed a divinylsilylene which was trapped by acetylene to form a divinylethynylsilane.

Silacycloprenes have been suggested as intermediates before by Barton et al. in the pyrolysis of 1-chloro-1-vinyltetramethyldisilane.\textsuperscript{14} An α-elimination of chlorotrimethylsilane afforded vinylsilylene 5 which isomerized to ethynylsilane 6 via a silacyclopropene. The silacyclopropene was formed by silylene insertion into a vinylic C-H bond.

\[
\begin{align*}
\text{Me}_3\text{Si-Si-Cl} & \rightarrow \text{Me}_3\text{Si-Si-Cl} \\
& \rightarrow \text{MeSi-Si}^* \rightarrow \text{H-SiMe}^* \rightarrow \text{HC≡C-SiH}_2
\end{align*}
\]

The thermal decomposition of stable silacycloprenes had been documented but was not well understood. Seyferth et al. were the first to study the thermal decomposition of a silacyclopropene.\textsuperscript{15} Silacyclopropene 7 was heated in benzene to 70-75°C and

\[
\begin{align*}
\text{Me}_3\text{Si} & \rightarrow \text{Me}_3\text{Si}^* \\
& \rightarrow \text{Me}_3\text{Si-C≡C-SiMe}_3
\end{align*}
\]

bis(trimethylsilyl)acetylene was the only volatile product formed in 20% yield. No trapping experiments were performed to trap the dimethylsilylene which was most likely extruded. Extrusion of silylene was also the result when silacycloprenone 8 was heated at 250°C for forty hours producing phenyl(trimethylsilyl)acetylene.\textsuperscript{16} Replacing a mesityl

\[
\begin{align*}
\text{Mes}_2 & \rightarrow \text{Mes}_2 \\
& \rightarrow \text{Ph-C≡C-SiMe}_3
\end{align*}
\]

Mes = 2,4,6-trimethylphenyl
group with a methyl group and heating to 250°C for thirty hours resulted in no volatile products. A similar result was observed when silacyclopene 9 was heated and no polymer was generated. However, silacycloprenes 10 and 11 rearranged via 1,2-silyl shifts to their respective disubstituted acetylenes in quantitative yields.

Ishikawa et al. have reported the photolysis of ethynylpolysilanes in which they observed a variety of products. Photolysis of ethynyltrisilane 12 in the presence of methanol afforded ethynylpentamethyldisilane and a trapped adduct 13 in 22 and 20% yield, respectively (Scheme 7). Irradiation in the absence of methanol resulted in a 10% yield of the disubstituted acetylene isomer as the only volatile product. The formation of...
dimethylsilylene was confirmed by trapping with diethylmethylsilane. The mechanism they proposed for the isomerization involved a 1,2-silyl shift to form diradical intermediate 14 which then ring-closed to form silacyclopene 15. Silacyclopene 15 rearranged to the isomer by a 1,2-hydrogen shift. Calculations were performed for the isomerization of the simplest ethynyltrisilane, and the energy of the proposed diradical intermediate was determined to be 85 kcal per mole higher than the starting ethynyltrisilane.

Photolysis of ethynyltrisilane 16 in the presence of methanol afforded an additional...
pair of products in 28% yield. These isomers corresponded to addition of methanol to silapropadiene intermediate 17 (Scheme 8). Irradiation in the absence of methanol yielded less than 6% of disubstituted acetylene isomer 18. A silapropadiene intermediate was calculated to be 30 kcal per mole higher than a silacyclopropene intermediate.

Photolysis of tris(trimethylsilyl)ethynylsilane 19 in the presence of methanol resulted in only a 5% yield of the silacyclopropene adduct 20 along with a 16% yield of hexamethyldisilane (Scheme 9). However, irradiation in the presence of diethylmethylsilane did not result in any formation of Si-H bond insertion product 21.
Scheme 9

\[
(Me_3Si)_3Si \equiv CH \quad 19
\]

\[
\text{hv} \quad \rightarrow \quad \text{polymeric substance}
\]

\[
Me_3SiSiCH + Me_3SiMe_3
\]

\[
\rightarrow \quad \text{Et}_2\text{MeSiH}
\]

\[
Me_3SiSiCH + Me_3SiMe_3
\]

\[
\rightarrow \quad \text{Et}_2\text{MeSiH}
\]

\[
Me_3SiSiCH + Me_3SiMe_3
\]
RESULTS AND DISCUSSION

Cyclopropene had been experimentally and theoretically determined to be an intermediate in the thermal isomerization between allene and propyne. Another intermediate involved in this isomerization was the vinylidene according to the calculations of Honjou et al.\(^4\) Brown et al. have also shown the importance of this intermediate\(^6\) in the thermal scrambling of the alkyne carbon atoms in terminal acetylenes. Will these same intermediates be important in the decomposition of ethynylsilanes?

Rogers et al. have reported the decomposition of ethynylsilane\(^9\) to be very complex based on the variety of products formed. Their proposed mechanism included a silacyclop propane intermediate but did not involve a vinylidene. Calculations by Francisco et al.\(^10\) involve a silylvinylidene as an intermediate but do not include a silacyclop propane. As was shown in the literature survey, the mechanism for the decomposition of ethynylsilane was not well understood. Previous work done in our group added to the confusion.

Pyrolysis of ethynyldimethylsilane, 50 by Power\(^20\) in a stirred-flow reactor at 650°C afforded acetylene and bis(dimethylsilyl)acetylene, 51. Acetylene was suggested to be an elimination product after extrusion of dimethylsilylene from silacyclop propane

\[
\text{Scheme 10}
\]

\[
\begin{aligned}
\text{Me}_2\text{Si}-\text{C}≡\text{CH} & \quad \text{Me}_2\text{Si}-\text{C}≡\text{C} & \quad \text{Me}_2\text{Si}: + \text{HC}≡\text{CH} \\
50 & \quad 52 & \quad \text{S.M.} \\
\downarrow & \quad 51 & \quad 53
\end{aligned}
\]
intermediate 52. The dimethylsilylene was trapped by the starting material to form silacyclopropene 53 which rearranged to bis(dimethylsilyl)acetylene, 51 (Scheme 10). The trapping of a silylene with acetylene to form an intermediate silacyclopropene which rearranged to a substituted acetylene was shown in the literature survey.

Power also determined through isotopic labelling that the two non-methyl hydrogens in ethynyldimethylsilane exchanged under flash vacuum pyrolysis conditions. At 800°C the mixture of isomers was 57:43 in favor of (deuteroethynyl)dimethylsilane, 54. The ratio never reached 50:50 at higher temperatures.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Me₂Si−C≡CD</th>
<th>H</th>
<th>H</th>
<th>D</th>
<th>Me₂Si=C=CHD</th>
<th>D</th>
</tr>
</thead>
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<tr>
<td>510</td>
<td>97%</td>
<td></td>
<td></td>
<td></td>
<td>3%</td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>89</td>
<td>11</td>
<td></td>
<td></td>
<td>19</td>
<td>43</td>
</tr>
<tr>
<td>750</td>
<td>81</td>
<td>11</td>
<td></td>
<td></td>
<td>19</td>
<td>43</td>
</tr>
<tr>
<td>800</td>
<td>57</td>
<td>11</td>
<td></td>
<td></td>
<td>19</td>
<td>43</td>
</tr>
</tbody>
</table>

These results were consistent with silacyclopropene 56 or silapropadiene 56A as an intermediate. If the exchange of the non-methyl hydrogens was due to extrusion of dimethylsilylene followed by trapping with acetylene, a 50:50 mixture should have been obtained. A mechanism involving a silacyclopropene or a silapropadiene intermediate would have a primary isotope effect, and the deuterium atom would not shift as fast as a hydrogen atom resulting in an equilibrium which was close to but not quite 50:50.

Another possible mechanism for the decomposition of ethynyldimethylsilane, 50,
involved a 1,2-hydrogen shift to form diradical intermediate 57 which ring-closed to obtain silacyclopropene intermediate 52. However, by comparing the energy of activation for this mechanism, which was calculated by Ishikawa et al. to be 81 kcal per mole, to those calculated for other mechanisms, the diradical intermediate was greater than 20 kcal per mole higher. For this reason a mechanism involving a diradical intermediate had been ruled out.

Francisco's mechanism via a four-centered transition state explained the extrusion of dimethylsilylene, but could not explain the exchange of the non-methyl hydrogens in ethynyldimethylsilane, so a four-centered transition state was ruled out.

The proposed mechanism (Scheme 11) for this decomposition involved a 1,2-silyl insertion or hydrogen shift to form silylvinyldene 58 which inserted into a Si-H bond to form silacyclopropene 52. This intermediate extruded silylene to form acetylene or rearranged back to the starting material via a 1,2-hydrogen shift.
We wanted to obtain the Arrhenius parameters for the isomerization and the extrusion of silylene in the pyrolysis of dimethylsilylacetylene. However, the decomposition temperatures were too high for accurate measurements.

The decomposition pathway proposed needed more evidence for the presence of the silacyclopropene. Once the existence of the silacyclopropene was established, more knowledge can be obtained about the thermochemistry of this intermediate in the gas phase.

To investigate this decomposition more thoroughly, we decided to replace the hydrogen on the silicon with a silyl group. Would silicon prove to be a more facile migrating group and would it result in isomerization or extrusion of silylene?

A flash vacuum pyrolysis of ethynyldisilane \( \text{59} \) at 550°C afforded trimethylsilylacetylene, \( \text{60} \), and two disubstituted acetylenes, \( \text{61} \) and \( \text{62} \), in 20, 53 and 24% yield, respectively.

\[
\begin{align*}
\text{Me}_3\text{Si} & - \text{Si} - \text{C} \equiv \text{CH} \quad \text{FVP} \quad 550^\circ \text{C} \quad \text{Me}_3\text{Si} - \text{C} \equiv \text{CH} + \text{Me}_3\text{Si} - \text{C} \equiv \text{C} - \text{SiMe}_2 \\
\text{59} & \quad \text{60}, 20\% \\
& + \text{Me}_3\text{Si} - \text{Si} - \text{C} \equiv \text{C} - \text{SiMe}_2 \\
& \quad \text{61}, 53\% \\
& \quad \text{62}, 24\%
\end{align*}
\]

From the products observed, it appeared that both pathways were followed. A possible mechanism (Scheme 12) explaining these results involved vinylidene \( \text{63} \) which was formed by a 1,2-hydrogen shift or a 1,2-disilanyl shift. Vinylidene \( \text{63} \) then inserted into the Si-Si bond to form silacyclopropene \( \text{64} \). The isomer \( \text{61} \) was formed by a 1,2-hydrogen shift, and the other two products, \( \text{60} \) and \( \text{62} \), were formed by the extrusion and trapping of the dimethylsilylene, respectively. Isomer \( \text{61} \) could also be formed by insertion of dimethylsilylene into trimethylsilylacetylene, \( \text{60} \). However, this was ruled out when a pyrolysis in a stirred-flow reactor with a 100:1 ratio of 2,3-dimethylbutadiene (a
silylene trap) to 59 resulted in no observable decrease in the amount of isomer 61 formed. From the amounts formed by the two different pathways, it appeared that the isomerization pathway was lower in energy than the extrusion of dimethylsilylene.

Another possible mechanism included a silapropadiene intermediate which replaced vinylidene intermediate 63. Silapropadienes have been shown to be intermediates in the photochemical decomposition of ethynyldisilanes as described in the literature survey. A silapropadiene intermediate, 65, was formed by a 1,3-silyl shift which then formed silacyclopropene 64 via a 1,2-hydrogen or silyl shift. Kwart and Slutsky have reported an activation energy of 50 kcal per mole for a 1,3-silyl shift to form an allene from propyne. Calculations performed by Ishikawa et al. have determined that a silapropadiene intermediate was 30 kcal per mole higher than a silacyclopropene.
intermediate. At this point a silapropadiene intermediate was not ruled out.

It was necessary before obtaining Arrhenius parameters to determine if an equilibrium existed between the two isomers, 59 and 61. Isomer 61 was isolated and pyrolyzed, but higher temperatures were needed to observe any decomposition. A flash vacuum pyrolysis of 61 at 750°C afforded trimethylsilylacetylene, 60, as the major product in 65% yield. No amount of isomer 59 was observed in the pyrolysate. However, at these high temperatures isomer 59 was unstable, so if the equilibrium did occur, it would not interfere with the kinetic studies.

The proposed mechanism for the decomposition of 61 involved a 1,2-silyl shift to vinylidene 66 which inserted into the Si-H bond to give the same silacyclopropene intermediate 64 as was proposed in the decomposition of 59 (Scheme 13). Another reason why ethynyldisilane 59 was not observed may be due to a 1,2-hydrogen shift on the silacyclopropene 64 being much faster than a 1,2-silyl shift.

A reason for the higher decomposition temperature may be due to a higher energy barrier for an intramolecular Si-H bond insertion than for an intramolecular Si-Si bond.
insertion. The decomposition temperatures were also higher for dimethylsilylacetylene 50, which also involved a vinylidene insertion into a Si-H bond. Another reason may be a 1,2-silyl shift taking more energy than a 1,2-hydrogen shift to form the vinylidene. If a silapropadiene intermediate was involved, a 1,3-hydrogen shift may take more energy than a 1,3-silicon shift. At this point no conclusions were made.

The isomer 61 was determined to be stable at the temperature range needed for the kinetic studies in the decomposition of ethynyldisilane 59. The Arrhenius parameters were obtained by gas-phase kinetic studies in a stirred-flow reactor with 2,3-dimethylbutadiene as the trapping agent for dimethylsilylene. The isomerization was determined to have a log (A/s⁻¹) of 12.3 and an activation energy of 44.3 kcal per mole (Figure 1). A log (A/s⁻¹) of 14.0 and an activation energy of 51.1 kcal per mole were determined for the elimination of dimethylsilylene (Figure 2). The energy of activation was higher for the extrusion of dimethylsilylene than isomerization, but entropy favored extrusion so both pathways became competitive.

In studying the proposed mechanism, was a terminal acetylene needed to observe isomerization and extrusion of silylene? By replacing the hydrogen with an alkyl group, only extrusion of dimethylsilylene should be observed because alkyl groups are poor migrating groups.

A flash vacuum pyrolysis of ethynyldisilane 67 at 650°C afforded 1-trimethylsilylbutyne, 68, as the major product in 80% yield with a small amount of dimethylsilylene dimers (9%). There was no isomer observed in the pyrolysate.

\[
\begin{array}{c}
\text{Me}_3\text{Si–Si–C≡C–Et} \quad \xrightarrow{\text{FVP}} \quad \text{Me}_3\text{Si–C≡C–Et} \quad + \quad \text{Me}_2\text{Si} \quad \text{dimers}
\end{array}
\]

\[
\begin{array}{c}
67 \quad \xrightarrow{650^\circ C} \quad 68, \quad 80\% \quad + \quad 9\%
\end{array}
\]

A hydrogen was needed for isomerization, but extrusion of silylene was still
Log $A = 12.3 \pm 0.3 \text{ s}^{-1}$

$E_{\text{act}} = 44.3 \pm 0.9 \text{ kcal/mol}$

Figure 1. Arrhenius plot for the isomerization of ethynylsilane 59 to disubstituted acetylene 61.
Figure 2. Arrhenius plot for the decomposition of ethynyldisilane 59 following trapped dimethylsilylene adduct 71

\[ \log A = 14.0 \pm 0.1 \text{ s}^{-1} \]

\[ E_{\text{act}} = 51.1 \pm 0.3 \text{ kcal/mol} \]
observed as shown by the silylene dimers and the eliminated product, 68. The proposed mechanism was still valid (Scheme 14). Vinylidene 69 was formed by a 1,2-disilanyl shift.

Scheme 14

![Scheme 14 diagram]

which inserted into the Si-Si bond to form silacyclopene 70. Since an alkyl group was a poor migrating group, the only available pathway was the extrusion of dimethylsilylene.

The Arrhenius parameters were obtained for the extrusion of silylene by following the formation of the eliminated product, 68, and the trapped silylene adduct, 71. The formation of the eliminated product, 68, had a log A of 12.6 s⁻¹ and an activation energy of 47.9 kcal per mole (Figure 3). Following the trapped silylene adduct 71, the log A was 12.0 s⁻¹ and the activation energy was 45.7 kcal per mole (Figure 4).

The higher decomposition temperatures indicated that more energy was needed for this decomposition rather than in the decomposition of ethynyldisilane 59. A reason for this may be due to the formation of the vinylidene in which more energy was needed for a disilanyl shift rather than a hydrogen shift.
Figure 3. Arrhenius plot for the decomposition of ethynyldisilane 67 following 1-trimethylsilyl-1-butyne, 68

\[
\begin{align*}
\log A &= 12.6 \pm 0.2 \text{ s}^{-1} \\
E_{\text{act}} &= 47.9 \pm 0.8 \text{ kcal/mol}
\end{align*}
\]
Figure 4. Arrhenius plot for the decomposition of ethynyldisilane 67 following trapped dimethylsilylene adduct 71

\[
\ln k(1/s) = -0.4 - 0.8 - 0.23 1.25 0.00/TCK
\]

\[
\log A = 12.0 \pm 0.2 \text{ s}^{-1}
\]

\[
E_{\text{act}} = 45.7 \pm 0.8 \text{ kcal/mol}
\]
It was decided to try to trap the vinylidene intermediate. Trapping of hydrogen substituted vinylidenes has not been reported in the literature, but trapping of alkyl substituted vinylidenes has been reported. Triethylsilane was used as the trapping reagent in solution, so a Si-H bond may be able to trap the vinylidene intramolecularly. It has already been proposed that the vinylidene inserted into the Si-H bond in the decomposition of dimethylsilylacetylene and disilyl-substituted acetylene. By moving the Si-H bond one more atom away, the energy needed for the insertion may be lowered by increasing the size of the ring. It would also form a disilacyclobutene.

Disilacyclobutenes with alkyl substituents on the vinyl carbons have been isolated and were known to be thermally stable.

A flash vacuum pyrolysis of ethynyl disilane at 550°C afforded dimethylsilylacetylene, bis(dimethylsilyl)acetylene, and disubstituted acetylene in 21, 40 and 23% yield, respectively (Scheme 15). There was no disilacyclobutene observed in the pyrolysate. The usual isomerization and decomposition products were obtained. Ethynylsilane was formed by insertion of dimethylsilylene into the starting...
material. Ethynylsilane 51 was formed by isomerization of the starting material or by insertion of dimethylsilylene into dimethylsilylacetylene, 50.

One more attempt was made to form a disilacyclobutene. By replacing the hydrogen bonded to the silicon with another silyl group, a more substituted disilacyclobutene would be formed which may stabilize the intermediate. From the results of previous decompositions, insertion into a Si-Si bond needed less energy than insertion into a Si-H bond. However, flash vacuum pyrolysis of ethynyltrisilane 74 resulted in isomerization and decomposition products with no disilacyclobutene observed (Scheme 16). The major product observed was isomerization of the starting material to

![Scheme 16](image)

ethynylsilane 62. The amount of this product could also be enhanced by insertion of dimethylsilylene into ethynylsilane 59 or by a loss of dimethylsilylene from ethynylsilane 75. Ethynylsilane 75 was formed by insertion of dimethylsilylene into the starting material. Ethynyltrisilane 59 was formed by a loss of dimethylsilylene from the starting material. Ethynyltrisilane 61 was formed by isomerization of ethynyltrisilane 59 and by a loss of dimethylsilylene from ethynylsilane 62. Intramolecular insertion of the vinylidene must be driven by entropy which favored the formation of a 3-membered ring rather than a 4-membered ring.

In the decomposition of 72, the formation of dimethylsilylacetylene, 50, could
come from two possible pathways. The first pathway involved the extrusion of
dimethylsilylene from silacyclopropene intermediate 76. The second pathway was an
α-elimination of dimethylsilylene of the starting material (Scheme 17).

Scheme 17

In reviewing the literature, Davidson et al. have reported the Arrhenius parameters
for an α-elimination of dimethylsilylene. The log (A/s⁻¹) was 13.1 and the activation
energy was 48.5 kcal per mole. By comparing these values with the parameters obtained

\[
\begin{align*}
\text{Me}_2\text{SiSiMe}_3 + & \rightarrow \text{Me}_2\text{Si}^+ + \text{Me}_3\text{SiH} \\
\log (A/s^{-1}) & = 13.1 \\
E_{\text{act}} (\text{kcal}) & = 48.5 \\
k_{450} (s^{-1}) & = 0.027
\end{align*}
\]

\[
\begin{align*}
\text{Me}_3\text{SiSiC=CEt} + & \rightarrow \text{Me}_2\text{Si}^+ + \text{Me}_3\text{SiSiC=CEt} \\
\log (A/s^{-1}) & = 12.0 \\
E_{\text{act}} (\text{kcal}) & = 45.7 \\
k_{450} (s^{-1}) & = 0.015
\end{align*}
\]

in the decomposition of ethynyldisilane 67, the rate constants at 450°C were within an
order of magnitude. The pathways may be competitive. To determine if the two
decomposition pathways were competitive, a compound needed to be pyrolyzed which
would yield two different sets of products depending on which pathway the decomposition
proceeded. Ethynyldisilane 77 would yield two different sets of products.

First, the Arrhenius parameters were determined for decomposition of a
trimethylsilyl substituted ethynylidisilane. The Arrhenius parameters may be different with a silyl group on the acetylene. Ethynylidisilane 78 was pyrolyzed in the stirred-flow reactor using 2,3-dimethylbutadiene as the silylene trapping agent. There was extrusion of dimethylsilylene as shown in the presence of eliminated product 79 and trapped dimethylsilylene adduct 71 (Scheme 20). The isomerization of the starting material was not observable since both migrating groups were trimethylsilyl groups. The Arrhenius parameters were obtained by following both products (Figures 5 and 6). By following the eliminated product 79, the log (A/s⁻¹) was 11.5 and the activation energy was 40.8 kcal per mole. By following trapped adduct 71, the activation energy was 40.3 kcal per mole and the log (A/s⁻¹) was 11.2. The rate constants increased but were still within an order of magnitude of the reported α-elimination. The increase in the rate may be due to a silyl
Figure 5. Arrhenius plot for the decomposition of ethynyldisilane 78 following bis(trimethylsilyl)acetylene, 79.

Log $A = 11.5 \pm 0.3 \text{ s}^{-1}$

$E_{\text{act}} = 40.8 \pm 1.1 \text{ kcal/mol}$
Figure 6. Arrhenius plot for the decomposition of ethnyldisilane 78 following dimethylsilylene trapped adduct 71
shift being faster than a disilyl shift in the formation of the vinylidene.

The pyrolysis of ethynylidisilane 77 afforded both sets of products. The decomposition via α-elimination was represented by trimethylsilane and trapped ethynylsilylene adduct 80. The decomposition via a silacyclopropene was represented by bis(trimethylsilyl)acetylene, 79, and trapped methylsilylene adduct 81 (Scheme 21). The α-elimination pathway was twice as fast as the silacyclopropene pathway. The Arrhenius parameters were obtained by following products 79, 80 and 81. Ethynylsilane 79 gave an activation energy of 41.4 kcal per mole and a log (A/s⁻¹) of 12.0. Formation of trapped adduct 80 occurred with a log (A/s⁻¹) of 13.5 and an activation energy of 45.2 kcal per mole. Formation of trapped adduct 81 occurred with a log (A/s⁻¹) of 12.5 and an activation energy of 43.0 kcal per mole (Figures 7, 8 and 9).

A second competition between α-elimination and decomposition via a silacyclopropene was set up by replacing the hydrogen with a methoxy group. An α-elimination was more facile with methoxy groups than hydrogen. A flow pyrolysis of
Figure 7. Arrhenius plot for the decomposition of ethynyldisilane 77 following bis(trimethylsilyl)acetylene, 79

\[ \ln k(1/s) = -\frac{E_{\text{act}}}{R} \left( \frac{1}{T(K)} \right) + A \]

where

- \( E_{\text{act}} = 41.4 \pm 0.8 \text{ kcal/mol} \)
- \( A = 12.0 \pm 0.2 \text{ s}^{-1} \)
Figure 8. Arrhenius plot for the decomposition of ethynyldisilane 77 following methylsilylene trapped adduct 81

\[
\log A = 12.5 \pm 0.3 \text{ s}^{-1} \\
E_{\text{act}} = 43.0 \pm 1.0 \text{ kcal/mol}
\]
Figure 9. Arrhenius plot for the decomposition of ethynyl disilane 77 following ethynylsilylene trapped adduct 80

Log $A = 13.5 \pm 0.4 \text{ s}^{-1}$

$E_{\text{act}} = 45.2 \pm 1.2 \text{ kcal/mol}$
trisilane 82 at 460°C also gave both sets of products. The α-elimination was represented

\[
\text{Me}_3\text{SiO} + \text{SiMe}^3 - \text{SiC} = \text{C} - \text{SiMe}^3 \rightarrow \text{Me}_3\text{SiO}\text{Me} + \text{SiMe}_3^3\text{SiC} = \text{C} - \text{SiMe}^3
\]

31% 80, 55%

Ome via

\[
\text{Me}_3\text{Si}-\text{SiC}-\text{C} = \text{C} - \text{SiMe}^3 \rightarrow \text{Me}_3\text{SiC}=\text{C} - \text{SiMe}^3 + \text{SiMe}^3\text{O} \text{Me}
\]

79, 8%

by methoxytrimethylsilane and trapped ethynylsilylene adduct 80 (55% yield). The silacyclop propane route was represented by trapped methoxysilylene adduct 83 (6%) and bis(trimethylsilyl)acetylene, 79, (8%). This time the α-elimination was nine times faster as determined from the product ratios.

What would happen if another trimethylsilyl group was added to the silicon bonded to the acetylene? In order to avoid isomerization, a methyl-substituted ethynyldisilane was studied first. A flow pyrolysis of propynyltrisilane 84 at 520°C

\[
\text{(Me}_3\text{Si)}_2\text{SiC} = \text{C} - \text{Me } \xrightarrow{\text{Flow}} \text{Me}_3\text{SiC}=\text{C} - \text{Me} + \text{Me}_3\text{SiSi}^+ 
\]

84 85, 42%

afforded 1-trimethylsilylpropyne, 85, and the trapped silylene adduct 86 in 42 and 25% yield, respectively. There was no isomerization observed. These were the only products
expected from the proposed mechanism.

When the methyl group was replaced by hydrogen, a much more complex pyrolysate was obtained. A flow pyrolysis of ethynyltrisilane 87 at 450°C afforded the isomer 77, bis(trimethylsilyl)acetylene, 79, and three different types of trapped silylene adducts, 80, 81 and 88.

\[
\text{(Me}_3\text{Si)}_2\text{Si-CH} \xrightarrow{450^\circ C} \begin{array}{c}
\text{Me} \\
\text{77, 20%}
\end{array} + \begin{array}{c}
\text{Me}_3\text{Si} \\
\text{79, 36%}
\end{array} + \begin{array}{c}
\text{Me} \\
\text{80, 16%}
\end{array} + \begin{array}{c}
\text{Me}_3\text{Si} \\
\text{81, 28%}
\end{array} + \begin{array}{c}
\text{Me} \\
\text{88, <10%}
\end{array}
\]

Scheme 22 shows a possible mechanistic route for this decomposition. The starting ethynyltrisilane 87 rearranged via a 1,2-hydrogen shift to the vinylidene which inserted into a Si-Si bond to form the first silacyclopene intermediate, 89. What was surprising was that there was no silylene extrusion observed from this intermediate. Silacyclopene 89 rearranged to the isomer 77 via another 1,2-hydrogen shift. From previous results, the decomposition of 77 was known to go through two different pathways. The first pathway was an α-elimination to form the trapped silylene adduct 80. The second pathway involved rearrangement of 77 to a second silacyclopene 90 by a 1,2-silyl shift to form a vinylidene which inserted into a Si-Si bond. Silacyclopene 90 extruded methylsilylene, which was trapped by 2,3-dimethylbutadiene to form trapped silylene adduct 81. The other product formed in this extrusion was bis(trimethylsilyl)acetylene, 79.
Scheme 22

\[ (\text{Me}_3\text{Si})_2\text{Si}-\text{C}≡\text{CH} \]

\[ \text{Me} \]

\[ 450^\circ\text{C} \]

\[ \text{Me}_3\text{Si} \]

\[ \text{Si} \]

\[ \text{Me} \]

\[ \text{Me}_3\text{Si} \]

\[ 89 \]

\[ \text{Me} \]

\[ \text{Si} \]

\[ \text{Me} \]

\[ \text{SiMe}_3 \]

\[ 91 \]

\[ \text{MeSi} \]

\[ \text{SiMe}_3 \]

\[ 88, <10\% \]

\[ \text{Me} \]

\[ \text{Si} \]

\[ \text{Me} \]

\[ \text{SiMe}_3 \]

\[ 79, 36\% \]

\[ \text{Me} \]

\[ \text{Si} \]

\[ \text{SiMe}_3 \]

\[ 80, 16\% \]

\[ \text{Me} \]

\[ \text{Si} \]

\[ \text{SiMe}_3 \]

\[ 81, 28\% \]
By looking at the product ratio between the two trapped silylene adducts, 80 and 81, the α-elimination product, 80, should have been the major product if the decomposition went exclusively through the isomer 77. Another decomposition pathway must have been present which also formed methylsilylene. The other decomposition pathway involved a 1,2-silyl shift of the first silacyclopropene 89 to form vinylsilylene 91 which inserted into the vinyl C-H bond forming silacyclopropene 90. This enhanced the amount of bis(trimethylsilyl)acetylene, 79, and trapped silylene adduct 81 formed. Further evidence was found for this pathway in small amounts of trapped silylene adducts 88 present in the pyrolysate. This mechanism also explained why no silylene was extruded by silacyclopropene 89. The 1,2-silyl shift was lower in energy than silylene extrusion from silacyclopropene.

There was literature precedent for the rearrangement of a silacyclopropene to a vinylsilylene. Barton et al. proposed a similar rearrangement in the pyrolysis of disilane 92 (Scheme 23).[^13] An α-elimination of trimethylsilane gave methylsilylene which was trapped by acetylene to form silacyclopropene 93. A 1,2-hydrogen shift resulted in vinylsilylene 94 which was trapped again by acetylene to form silacyclopropene 95. Silacyclopropene 95 did not have a good migrating group on the silicon, so it rearranged by a 1,2-hydrogen shift to form ethynylvinylsilane 96. This product was reported as the only one observed in 26% yield. They also reported examples of a silyl group migrating to form vinylsilylenes.

There was also literature precedent for silylene insertion into a vinylic C-H bond. Barton et al. proposed a similar insertion in the pyrolysis of vinyldisilane 97 (Scheme 24).[^14] An α-elimination of chlorotrimethylsilane afforded vinylsilylene 98 which rearranged to silacyclopropene 99 by a silylene insertion into the vinylic C-H bond. Silacyclopropene 99 rearranged to ethynylsilane 100 by a 1,2-hydrogen shift.
Scheme 23

\[
\begin{align*}
\text{Me}_3\text{Si-SiH}_2 &\xrightarrow{500^\circ\text{C}} \text{HSiMe} + \text{Me}_3\text{SiH} \\
&\xrightarrow{\text{HC}≡\text{CH}} \\
&\xrightarrow{1,2-\text{H}} \\
\text{C}=\text{C} &\rightarrow \text{C}=\text{CH}_2
\end{align*}
\]

Ethynylsilane 100 was reported as the only product observed in 12% yield.

Scheme 24

\[
\begin{align*}
\text{Me}_3\text{Si-SiCl} &\xrightarrow{800^\circ\text{C}} \text{MeSi}^\text{Cl} - \text{Me}_3\text{SiCl} \\
&\xrightarrow{\text{C-H insertion}} \\
&\xrightarrow{1,2-\text{H}} \\
\text{H} &\rightarrow \text{HC}≡\text{C-SiH}_2
\end{align*}
\]

With these examples from the literature, a question arose as to the existence of an initial silacyclopene. Based on the literature, the only product observed when a good migrating group was on the silicon was the trapped vinylsilylene. The mixture of products that were obtained in the pyrolysis of ethynyltrisilane 87 did not agree with these results.
Possibly the trapping reagent, 2,3-dimethylbutadiene, was not an efficient trap for vinylsilylenes. A flow pyrolysis of vinyldisilane 101 resulted in the trapped vinylsilylene adduct 102 (23% yield) and methoxytrimethylsilane (20% yield), so 2,3-dimethylbutadiene was a good trap for a vinylsilylene.

![Reaction equation](image)

A different route to the silacyclopropene intermediate was necessary to determine if it was still a possible intermediate. Pyrolysis of trisilane 103 would give methyl(trimethylsilyl)silylene by an α-elimination of trimethylsilane. This silylene can be trapped by trimethylsilylacetylene to form the same silacyclopropene intermediate 89 as in the decomposition of ethynyltrisilane 87.

![Reaction equation](image)

A flow pyrolysis of trisilane 103 in trimethylsilylacetylene at 500°C afforded another mixture of products very similar to those obtained in the pyrolysis of ethynyltrisilane 87 (Scheme 25). The major decomposition product was bis(trimethylsilyl)acetylene, 79, (37%) and only small amounts of the trapped silylene adducts 104 (7%), 105 (18%) and 106 (trace) were observed. The silylene trapped adduct 105 consisted of two trimethylsilylacetylenes. When methylsilylene was trapped, there was a hydrogen on the silicon in the silacyclopentene. This hydrogen shifted to the carbon to form a vinylsilylene which was trapped by another molecule of trimethylsilylacetylene. The other two trapped adducts, 104 and 106, only have one
Scheme 25

\[
\text{Me}_3\text{SiSiMe}_2\text{SiH} \overset{500^\circ\text{C}}{\longrightarrow} \text{Me}_3\text{SiSiMe} + \text{Me}_3\text{SiH}
\]

103

\[
\text{Me}_3\text{SiMe} \rightleftharpoons \text{Me}_3\text{Si}-\text{C} \equiv \text{CH}
\]

\[
\text{Me}_3\text{Si} \rightleftharpoons \text{H}
\]

89

\[
\text{Me}_3\text{Si}-\text{Si}-\text{C} \equiv \text{C}-\text{SiMe}_3
\]

77

\[
\text{Me}_3\text{SiSiMe} \rightleftharpoons \text{Me}_3\text{Si}-\text{C} \equiv \text{CH}
\]

90

\[
\text{Me}_3\text{SiSiMe} + \text{Me}_3\text{SiH}
\]

79, 37%

\[
\text{Me}_3\text{SiSiMe} \rightleftharpoons \text{Me}_3\text{Si}-\text{C} \equiv \text{CH}
\]

106, trace

\[
\text{Me}_3\text{SiH} + \text{Me}_3\text{Si}-\text{C} \equiv \text{C}-\text{SiMe}_3
\]

79, 37%

\[
2 \text{Me}_3\text{Si}-\text{C} \equiv \text{CH}
\]

104, 7%

\[
\text{Me}_3\text{SiSiMe} \rightleftharpoons \text{Me}_3\text{Si}-\text{C} \equiv \text{C}-\text{SiMe}_3
\]

105, 18%
trimethylsilylacetylene, because they did not have a good migrating group on the silacyclopene intermediate.

The difference between the silacycloprenes in the literature and the silacycloprenes in the decomposition of ethynylidisilanes was the substitution on the vinylic carbons. In the literature they were substituted with hydrogens and in the decomposition of ethynylidisilanes, at least one carbon was substituted with a trimethylsilyl group.

In the laboratory notebook of Stephanie Burns, whose work was reported in the literature, several small peaks in the gas chromatograph trace were not identified. With the better equipment now available in the lab, these peaks could be identified.

A similar pyrolysis was performed. Trisilane was pyrolyzed at 500°C in a flow of acetylene. The major product was the vinylsilylene trapped adduct (43%). The smaller peaks were identified and explained by the other decomposition pathways as shown in Scheme 26. The methyl(trimethylsilyl)silylene was trapped by acetylene to form silacyclopene. A 1,2-silyl shift formed vinylsilylene which was trapped by another molecule of acetylene to form trapped adduct. A 1,2-hydrogen shift on silacyclopene formed ethynylidisilane (5%). Formation of silacyclopene came from silylene insertion into a vinylic C-H bond of vinylsilylene or vinylidene insertion into a Si-Si bond of ethynylidisilane. Silacyclopene extruded methylsilylene which was trapped stepwise by two molecules of acetylene to form ethynylvinysilane (3%). Trimethylsilylacetylene (4%) was also formed in the extrusion of methylsilylene from silacyclopene. The last product identified was disubstituted acetylene (7%). This product came from a 1,2-hydrogen shift of silacyclopene or by trapping of methylsilylene by trimethylsilylacetylene. These results supported the presence of a silacyclopene intermediate in the thermal
decomposition of ethynyldisilanes.

To finish the ethynyldisilane series, another trimethylsilyl group was added to the silicon bonded to the acetylene. The decomposition temperature was lowered dramatically. A flow pyrolysis of ethynyltetrasilane 113 at 310°C afforded a similar mixture of products, but the ratios were different. The mechanism for this decomposition (Scheme 27) was a little different than previous decompositions. The major product was the isomer 114 which was formed by a 1,2-hydrogen shift on silacycloprenep 117. The
ratio between the α-elimination and the extrusion of silylene via silacyclopnone \( \text{118} \) was reversed. The amount of α-eliminated products formed, trimethylsilane and ethynlysilylene trapped adduct \( \text{115} \), was more than the products formed via silacyclopnone \( \text{118} \), bis(trimethylsilyl)acetylene, \( \text{79} \), and trimethylsilylsilylene trapped adduct \( \text{116} \). There was also no evidence for the existence of vinylsilylene \( \text{119} \). There was no trapped adduct observed in the pyrolysate, and the product distribution did not show any need for another decomposition pathway.

The pyrolysis of ethynyltetrasilane \( \text{113} \) in the stirred-flow reactor in the range between 290°C and 330°C afforded only one product which was not characterized. This product was probably isomer \( \text{114} \) based on retention time. From these results it appeared the decomposition was proceeding exclusively through isomer \( \text{114} \) without the vinylsilylene pathway competing.

At these low temperatures the decomposition could be done in solution. A sealed tube of ethynyltetrasilane \( \text{113} \) in deuterated benzene was heated at 200°C in the presence of triethylsilane. The only product observed was the trapped vinylsilylene adduct \( \text{120} \) in 67% yield. From this result the vinylsilylene was determined to be present in the
Scheme 27

\[(\text{Me}_3\text{Si})_3\text{Si} = \text{C} \equiv \text{CH} \]

\[\text{113} \rightarrow 310^\circ \text{C} \rightarrow \text{Me}_3\text{SiSiMe}_3\]

\[\text{Me}_3\text{Si} \quad \text{SiMe}_3\]

\[\text{Me}_3\text{Si} \quad \text{H} \quad ?\]

\[(\text{Me}_3\text{Si})_2\text{Si} = \text{C} \equiv \text{C} \equiv \text{SiMe}_3\]

\[\text{114}, 35\% \rightarrow \text{Me}_3\text{SiH} \quad 18\% \rightarrow \text{Me}_3\text{SiSiC} \equiv \text{C} \equiv \text{SiMe}_3\]

\[\text{Me}_3\text{SiSi} \quad \text{C} \equiv \text{C} \equiv \text{SiMe}_3\]

\[\text{115}, 28\% \rightarrow \text{Me}_3\text{SiH} + \text{Me}_3\text{Si} = \text{C} \equiv \text{C} \equiv \text{SiMe}_3\]

\[\text{Me}_3\text{SiH} + \text{Me}_3\text{Si} = \text{C} \equiv \text{C} \equiv \text{SiMe}_3\]

\[\text{79}, 13\% \rightarrow \text{Me}_3\text{SiSi} \quad \text{SiMe}_3\]

\[\text{Me}_3\text{SiSiH} + \text{Me}_3\text{Si} = \text{C} \equiv \text{C} \equiv \text{SiMe}_3\]

\[\text{116}, 6\% \rightarrow \text{Me}_3\text{Si} \quad \text{H} \quad ?\]
decomposition of ethynyltetrasilane 113. An explanation for this was that the isomerizations via silacycloprenes 117 and 118 were reversible and the vinylsilylene 119 was the only isomer that was trapped by triethylsilane.

A sealed tube of ethynyltetrasilane 113 in benzene was heated at 200°C without a trapping agent present. A mixture of products was obtained and analysis by GC/IR/MS. There was not enough sample to isolate the products. The major product was tris(trimethylsilyl)ethylene, 121, in less than 5% yield. Trace amounts of the other products were identified as the non-trapped products found in the flow pyrolysate. The major product is formally a hydrosilation adduct of two of the decomposition products, trimethylsilane and bis(trimethylsilyl)acetylene. To test this a sealed tube reaction was performed in which the two compounds were heated to 200°C. Only the starting materials, trimethylsilane and bis(trimethylsilyl)acetylene, 79, were left so no reaction was observed.

A possible mechanism for this decomposition (Scheme 28) was similar to what
Scheme 28

\[(\text{Me}_3\text{Si})_3\text{Si-} \equiv \text{CH}\]

113

\[
\begin{array}{c}
\text{Me}_3\text{Si} \\
\text{H} \\
\text{Me}_3\text{Si} \\
\end{array}
\]

117

310°C

\[
\begin{array}{c}
\text{Me}_3\text{Si} \\
\text{H} \\
\text{Me}_3\text{Si} \\
\end{array}
\]

118

\[
\begin{array}{c}
\text{Me}_3\text{Si} \\
\text{SiMe}_3 \\
\text{Me}_3\text{Si} \\
\end{array}
\]

114

\[
\begin{array}{c}
\text{Me}_3\text{Si} \\
\text{H} \\
\text{Me}_3\text{Si} \\
\end{array}
\]

119

\[
\begin{array}{c}
\text{Me}_3\text{Si} \\
\text{SiMe}_3 \\
\text{Me}_3\text{Si} \\
\end{array}
\]

118A

\[
\begin{array}{c}
\text{Me}_3\text{Si} \\
\text{C} \equiv \text{C} \\
\text{SiMe}_3 \\
\end{array}
\]

118B

\[
\begin{array}{c}
\text{Me}_3\text{Si} \\
\text{C} \equiv \text{C} \\
\text{SiMe}_3 \\
\end{array}
\]

122

\[
\begin{array}{c}
\text{Me}_3\text{Si} \\
\text{C} \equiv \text{C} \\
\text{SiMe}_3 \\
\end{array}
\]

121

\[
\begin{array}{c}
\text{H} \\
\text{Si} \\
\text{Me}_3\text{Si} \\
\end{array}
\]

\[
\begin{array}{c}
\text{Me}_3\text{Si} \\
\text{SiMe}_3 \\
\text{Me}_3\text{Si} \\
\end{array}
\]

\[
\begin{array}{c}
\text{Si} \\
\text{C} \equiv \text{C} \\
\text{SiMe}_3 \\
\end{array}
\]

\[
\begin{array}{c}
\text{Me}_3\text{Si} \\
\text{SiMe}_3 \\
\text{Me}_3\text{Si} \\
\end{array}
\]
Ring proposed in the decomposition of ethynylsilane. The decomposition pathways involving the formation of two products were not favored under the conditions of the sealed tube because of the high pressure. These pathways became less dominant and only a small amount of these products were observed. All of the isomerization pathways were reversible. The pathway which was not reversible was the extrusion of elemental silicon from the silacyclopropylidene intermediate 122. This pathway did not increase the pressure in the sealed tube and gradually bled off the equilibrium of the isomerizations.

After investigating the linear series of ethynyldisilanes, a question arose as to what would happen if the disilane was part of a ring? Would the triple bond isomerize into the ring or would some other decomposition pathway be more favorable? A flow pyrolysis of ethynylsilane 123 at 360°C afforded cyclooctyne 124, cycloheptyne 125 and trapped silylene adduct 81 in 69, 15 and 8% yield, respectively. Pyrolysis at 450°C afforded cycloheptyne 125 as the major product (53%), cyclooctyne 124 (34%) and trapped silylene adduct 81 (15%). Incorporation of the triple bond into the ring was observed, but how was cycloheptyne 125 formed? Did it come from the decomposition of cyclooctyne 124?

The proposed mechanism for the decomposition of 123 (Scheme 29) was
determined after cyclooctyne 124 was isolated and a flow pyrolysis at the same temperature resulted in no observable decomposition. This showed that the other products were not coming from the decomposition of cyclooctyne 124. The decomposition involved a 1,2-hydrogen shift followed by insertion into a Si-Si bond to form silacyclopropene 126. A 1,2-hydrogen shift formed the stable ring-expanded isomer, cyclooctyne 124. The pathway for the other products formed included a 1,2-silyl shift to form vinylsilylene 127 which inserted into a vinylic C-H bond to form the second silacyclopropene, 128. A 1,2-silyl shift formed cyclooctyne 124 and extrusion of methylsilylene formed cycloheptyne 125. In this mechanism no silacyclopropene was formed which had two methyl groups on the silicon in the three-membered ring which explained why no dimethylsilylene trapped adduct was observed.

Recently, Ando et al. have reported the synthesis and photochemistry of cyclic silylalkynes. Our research group has also synthesized cyclic silylalkynes and investigated the thermochemistry of some of the cyclic alkynes. A flow pyrolysis of cyclooctyne 129 at 530°C afforded cycloheptyne 130 (17.5%), cyclohexyne adduct 131A (7.5%), trapped adduct 131D (1.4%) and dimethylsilylene adduct 71 (57%). The
cyclohexyne adduct 131A was formed from aromatization of the Diels-Alder adduct of cyclohexyne 131 and 2,3-dimethylbutadiene. Trapped adduct 131D was formed by an extrusion of dimethylsilylene from cyclohexyne adduct 131A.

\[
\begin{align*}
\text{Me}_2\text{Si} - \text{SiMe}_2 + \text{Me}_2\text{Si} & \xrightarrow{\text{H}_2} \text{Me}_2\text{Si} - \text{SiMe}_2 \rightarrow \text{Me}_2\text{Si} - \text{SiMe}_2 \\
\text{Me}_2\text{Si} - \text{SiMe}_2 & \rightarrow \text{Me}_2\text{Si} - \text{SiMe}_2 \\
\text{Me}_2\text{Si} - \text{SiMe}_2 & \rightarrow \text{Me}_2\text{Si} - \text{SiMe}_2 \\
\end{align*}
\]

Cyclohexyne 131 had a molecular weight low enough to try the pyrolysis in a flash vacuum. A flash vacuum pyrolysis of cyclohexyne 131 at 690°C afforded a mixture of products which included three isomers that had a molecular weight equal to the starting material minus dimethylsilylene. All attempts made at isolating these isomers were unsuccessful.

A dimethylsilylene next to the triple bond was changed to a methylene. The synthesis of ethynylsilane 132 was achieved by coupling a dianion of allene with 1,5-dichlorodecamethylpentasilane. A flow pyrolysis of ethynylsilane 132 at 520°C afforded an isomeric exocyclic allene, 133, two ring-contracted isomers, 134 and 135, and dimethylsilylene trapped adduct 71. There appeared to be two different pathways competing (Scheme 30). The first pathway was isomerization to the exocyclic allene 133. This occurred by a 1,3-silicon shift or by a series of 1,2-silicon shifts. The 1,3-silicon shift...
formed allene 133 directly. The first 1,2-silicon shift formed cyclopropene 137 via vinylidene 136 which was followed by another 1,2-silicon shift to give the exocyclic allene 133. The second pathway was extrusion of dimethylsilylene. This pathway involved a 1,2-silicon shift of cyclooctyne 132 to form vinylidene 136 which inserted into a Si-Si bond to form silacyclopropene 138. Silacyclopropene 138 extruded dimethylsilylene to form cycloheptyne 135. The exocyclic allene 134 was formed by isomerization of cycloheptyne 135.

To demonstrate this, cycloheptyne 135 was synthesized by coupling a dianion of propyne with 1,4-dichlorooctamethyltetrasilane in 81% yield. A flow pyrolysis of

\[
\begin{align*}
\text{HC}≡\text{C}-\text{CH}_2\text{Br} & \quad \xrightarrow{1) \text{Mg}} \quad "\text{C}_3\text{H}_2\text{LiMgBr}" \quad \xrightarrow{2) n-\text{BuLi}} \quad \text{Me}_2\text{Si} \quad \xrightarrow{\text{Cl}(\text{Si} \equiv \text{Si})_2 \text{Cl}} \quad \text{Me}_2\text{Si}
\end{align*}
\]

81% yield
cycloheptyne \(135\) at \(520^\circ\text{C}\) in hexanes afforded exocyclic allene \(134\) as the major product with another isomer \(139\) present in a small amount. The mechanism for this
rearrangement also involved two possible pathways (Scheme 31). The first pathway was a 1,3-silicon shift to give the allene 134 directly. The other pathway involved 1,2-silicon shifts. The first shift gave cyclopropene 140 and the second shift formed allene 134.

Scheme 31

A comparison to linear isomerizations was needed to determine if there was any enhancement of isomerization due to the alkynes being in a ring. Linear propargyl silane 141 was pyrolyzed at 520°C in a flow pyrolysis and very little isomerization occurred.

This gave some evidence for relief of ring-strain as a driving force. However, a flash vacuum pyrolysis of propargyldisilane 142 at 650°C resulted in isomerization to

142

major isomer

144, 10%
allenylidisilane 143. Pyrolysis at 700°C afforded allenylsilane 144 (10% yield) which came from extrusion of dimethylsilylene. The mechanism for this decomposition (Scheme 32) involved isomerization of propargylidisilane 142 to allenylidisilane 143 via a 1,3-silicon shift. Vinylcarbene 145 was formed by a 1,2-silicon shift of allenylidisilane 143. This carbene then inserted into the Si-Si bond to form silacyclop propane 146 which extruded dimethylsilylene to form silylallene 144.

A synthesis of cycloheptyne 135 from allene was attempted (Scheme 33). It resulted in a 1:1 mixture of bicyclic allenes, 147 and 148. The bicyclic allene 147 crystallized out of a hexanes solution and a crystal structure was determined. The crystal structure (Figure 10) showed that the allene carbons were linear, and the allene was twisted 18 degrees toward planarity. This was unique since theoretical calculations have determined that allenes twist and bend at the same time to alleviate strain in the system.28
Bicyclic allene 147 is in a small category of allenes called "betweenallenes". There were only a few betweenallenes reported in the literature and betweenallene 147 with two seven-membered rings is by far the smallest to date. The smallest reported in the literature was [8.10] betweenallene 150. The size of the rings was limited by the synthetic route of treating dibromocyclopropane 149 with butyllithium to form the allene. Models showed that the smallest all-carbon betweenallene possible due to ring-strain would be a [5.5] betweenallene. There had also been reported [9.11] oxabetweenallene 152 which was synthesized by cyclization of cyclic allene 151. This was achieved by treating an alcoholic tosylate with a base under phase-transfer conditions.
Figure 10. X-ray crystal structure of betweenallene 147
betweenallene reported was symmetrical \([11.11]\) betweenallene 154.\(^31\) This was synthesized by treating vinylchloride 153 with activated zinc powder to form the allene by elimination of the methoxy group.

A better synthesis of the bicyclic allene 147 was achieved by starting from cycloheptyne 135 (Scheme 34). Addition of two equivalents of \(n\)-butyl lithium formed dianion intermediate 155. Quenching the dianion with 1,4-dichlorooctamethyldisilane resulted in a modest yield of betweenallene 147. No bicyclic isomer 148 was observed.

A flow pyrolysis of betweenallene 147 at 520°C in hexanes afforded a clean conversion to the exocyclic isomer 148. Three mechanisms were possible (Scheme 35).
The first pathway involved a 1,3-silicon shift of bicyclic allene 147 to form cycloheptyne 156 which rearranged to exocyclic allene 148 via a 1,3-silicon shift. The second pathway...
involved three 1,2-silicon shifts. The first shift formed cyclopropene 157 and a second shift formed cyclopropene 158. The third shift converted cyclopropene 158 to allené 148. The third pathway was a 1,3-dyatropic shift with two silyl groups migrating simultaneously.

A photolysis of bicyclic 147 resulted in the extrusion of dimethylsilylene but no other volatile products including ring-contracted products were observed.

\[
\text{Me}^2\text{Si} \quad \text{SiMe}_2
\]

\[
\begin{array}{c}
\text{C} = \text{C} = \text{C} \\
\text{Me}_2\text{Si} \\
\text{Me}_2\text{Si} \\
\end{array}
\xrightarrow{\text{hv}}
\begin{array}{c}
\text{Me}_2\text{Si} \quad \text{SiMe}_3 \\
\text{C}_2 \quad \text{Et} \\
\text{Me}_2\text{Si} \\
\end{array}
\]

A flow pyrolysis of cyclic allené 159 at 550°C resulted in isomerization to 160 and a small amount of cyclic allené 161. Cyclic allené 161 was stable at this temperature.

\[
\text{Me}_2\text{Si} \quad \text{SiMe}_2
\]

\[
\begin{array}{c}
\text{C} = \text{C} = \text{C} \\
\text{Me}_3\text{Si} \\
\text{Me}_3\text{Si} \\
\end{array}
\xrightarrow{550^\circ\text{C}}
\begin{array}{c}
\text{C} = \text{C} = \text{C} \\
\text{Me}_3\text{Si} \\
\text{Me}_3\text{Si} \\
\end{array}
\]

\[
\text{Me}_2\text{Si} \quad \text{SiMe}_2
\]

The first step of the proposed mechanism (Scheme 36) for the isomerization of 159 was a 1,2-silicon shift of the silicon in the ring or the trimethylsilyl group to form two different vinylcarbenes, 162 and 163. Carbene 163 only had the option of insertion into the \(\pi\)-bond of the vinyl group to form cyclopropene 164. Exocyclic carbene 162 had two options. The first option was insertion into the \(\pi\)-bond of the vinyl group to form
Scheme 36

Me₂Si - SiMe₂

Me₂Si

Me₃Si — SiMe₂
C = C = C
SiMe₃

1,2-Si

Me₃Si 159

Me₃Si
c = c
c = c
Me,Si

Me,Si

1,2-Si

Me₃Si — C* 162

SiMe₃

π-insert.

C
SiMe₃

Me₂Si

Me₂Si — SiMe₂
1,2-Si

Me₃Si

SiMe₃

π-insert.

C
Me₂Si

Me₂Si — SiMe₂
1,2-Si

Me₃Si

SiMe₃

π-insert.

C
Me₂Si

Me₂Si — SiMe₂
1,2-Si

Me₃Si

SiMe₃

π-insert.

C
Me₂Si

Me₂Si — SiMe₂
1,2-Si

Me₃Si

SiMe₃

π-insert.

C
Me₂Si

Me₂Si — SiMe₂
1,2-Si

Me₃Si

SiMe₃

π-insert.

C
Me₂Si

Me₂Si — SiMe₂
1,2-Si

Me₃Si

SiMe₃

π-insert.

C
Me₂Si

Me₂Si — SiMe₂
1,2-Si

Me₃Si

SiMe₃

π-insert.

C
Me₂Si

Me₂Si — SiMe₂
1,2-Si

Me₃Si

SiMe₃

π-insert.

C
Me₂Si

Me₂Si — SiMe₂
1,2-Si

Me₃Si

SiMe₃

π-insert.

C
Me₂Si

Me₂Si — SiMe₂
1,2-Si

Me₃Si

SiMe₃

π-insert.

C
Me₂Si

Me₂Si — SiMe₂
1,2-Si

Me₃Si

SiMe₃

π-insert.

C
Me₂Si

Me₂Si — SiMe₂
1,2-Si

Me₃Si

SiMe₃

π-insert.

C
Me₂Si

Me₂Si — SiMe₂
1,2-Si

Me₃Si

SiMe₃

π-insert.

C
Me₂Si

Me₂Si — SiMe₂
1,2-Si

Me₃Si

SiMe₃

π-insert.

C
Me₂Si

Me₂Si — SiMe₂
1,2-Si

Me₃Si

SiMe₃

π-insert.

C
Me₂Si

Me₂Si — SiMe₂
1,2-Si

Me₃Si

SiMe₃

π-insert.

C
Me₂Si

Me₂Si — SiMe₂
1,2-Si

Me₃Si

SiMe₃

π-insert.

C
Me₂Si

Me₂Si — SiMe₂
1,2-Si

Me₃Si

SiMe₃

π-insert.

C
Me₂Si

Me₂Si — SiMe₂
1,2-Si

Me₃Si

SiMe₃

π-insert.

C
Me₂Si

Me₂Si — SiMe₂
1,2-Si

Me₃Si

SiMe₃

π-insert.

C
Me₂Si

Me₂Si — SiMe₂
1,2-Si

Me₃Si

SiMe₃

π-insert.

C
Me₂Si

Me₂Si — SiMe₂
1,2-Si

Me₃Si

SiMe₃

π-insert.
cyclopropene 164. The second option for exocyclic carbene 162 was insertion into a Si-Si
bond to form silacyclopropane 165 which extruded dimethylsilylene to give cyclic allene
161. The cyclopropene 164 isomerized to two other possible cyclopropenes, 166 and 167, via a 1,2-silicon shift. Another 1,2-silicon shift of either cyclopropene formed exocyclic allene 160.

Another route for the formation of cyclic allene 161 could involve cycloalkyne 168 (Scheme 37). A 1,3-silicon shift on cyclic allene 159 formed cycloalkyne 168 which was followed by a 1,2-silicon shift to form vinylidene 169. This vinylidene inserted into a Si-Si bond to form silacyclopentene 170 which extruded dimethylsilylene to form cycloalkyne 171. A 1,3-silicon shift formed cyclic allene 161. This route was not favored due to the results in the decomposition of cyclic alkyne 135 where there was no loss of dimethylsilylene observed.
Scheme 37

\[ \text{Me}_2\text{Si} - \text{SiMe}_2 \]
\[ \text{Me}_2\text{Si} \]
\[ \text{SiMe}_2 \]
\[ \text{Me}_3\text{Si} \]
\[ \text{SiMe}_3 \]
\[ C = C = C \]
\[ \text{SiMe}_3 \]

1,3-Si

\[ \text{Me}_2\text{Si} \]
\[ \text{C} \]
\[ \text{Me}_2\text{Si} \]
\[ \text{C} \]
\[ \text{SiMe}_3 \]
\[ \text{SiMe}_2 \]
\[ \text{SiMe}_2 \]
\[ \text{SiMe}_3 \]

1,2-Si

\[ \text{Me}_2\text{Si} \]
\[ \text{Me}_2\text{Si} \]
\[ \text{C} = \text{C} = \text{C} \]
\[ \text{SiMe}_3 \]
\[ \text{SiMe}_3 \]
\[ \text{SiMe}_3 \]

Si-Si insert

\[ \text{Me} \]
\[ \text{Me} \]
\[ \text{C} = \text{C} \]
\[ \text{SiMe}_3 \]
\[ \text{SiMe}_3 \]
\[ \text{SiMe}_3 \]

\[ \text{Me}_2\text{Si} \]
\[ \text{Me}_2\text{Si} \]
\[ \text{C} \]
\[ \text{Me}_2\text{Si} \]
\[ \text{SiMe}_3 \]
\[ \text{SiMe}_3 \]

\[ \text{Me}_2\text{Si} \]
\[ \text{Me}_2\text{Si} \]
\[ \text{C} = \text{C} = \text{C} \]
\[ \text{SiMe}_3 \]
\[ \text{SiMe}_3 \]

1,3-Si

\[ \text{Me}_2\text{Si} \]
\[ \text{Me}_2\text{Si} \]
\[ \text{C} \]
\[ \text{SiMe}_3 \]
\[ \text{SiMe}_3 \]
\[ \text{SiMe}_3 \]

168

169

170

171

161
There is now one example of isomerization of the triple bond into the ring. It should be determined if this thermal isomerization can be extended to other systems such as alkynes, 172, 173 and 174. Alkyne 172 would be a logical step in the sequence and would be another possible route to cyclohexyne after extrusion of methylsilylene. Alkyne 173 could also form a cyclohexyne. This one would have an carbon atom in the ring which may cause the alkyne angle to be more bent than in systems already known. Alkyne 174 would set up a competition between extrusion of dimethylsilylene via an α-elimination and isomerization. This series of alkynes may show a trend by having different substituents on the silicon atom in the intermediate silacyclop propane.

Alkyne 175 would show a general approach to incorporation of the triple bond into the ring. All that would be needed to obtain this isomerization is a Si-Si bond next to the acetylene. Alkyne 175 would not extrude dimethylsilylene if the proposed mechanisms were correct. The only option for the silacyclopropene would be isomerization.

The mechanisms for the decomposition of the cyclic alkynes and allenes are not well understood. For a better understanding other cyclic alkynes and allenes need to be
synthesized and pyrolyzed. Cyclic alkyne 176 should afford the isomer 177 upon pyrolysis. The decomposition temperatures should also be compared to systems with good migrating groups in place of the methyl groups.

Cyclic allene 178 should be synthesized and pyrolyzed to determine if a vinyl carbene is an intermediate. If the carbene is involved, it should insert into a C-H bond to form diene 179. Isomerization to an exocyclic allene is not possible because a methyl group is a poor migrating group. Another cyclic allene which could be studied is allene 180 which would test the proposed mechanisms. This allene would not isomerize to an exocyclic allene because the alkyl group is a poor migrating group. Allene 180 does not
have an α-hydrogen so isomerization to a diene is not possible. The only pathway is extrusion of dimethylsilylene which would be another route to 1,2-cyclohexadienes.

In the pyrolysis of cyclic allenes why was alkyne 181 not observed? A 1,3-silyl shift would form this molecule directly from the allene. It should be synthesized to determine if cyclic allene 182 or cyclic alkyne 135R will be formed upon pyrolysis.

The exocyclic allenes also need to be studied under pyrolytic conditions. This has not been done. The photolysis of cyclic alkynes and allenes can also be done.

It was not clearly understood as to what happened in the attempted synthesis of betweenallene 147. A study of the metalation of these cyclic alkynes and allenes can be performed by coupling reactions with different halogenated compounds. The strain in these systems may favor different resonance structures than the linear systems. Examples of these systems may include cyclic alkyne 135 and cyclic allene 134. In this study will it be possible to synthesize hydrogen substituted cyclic allenes like cyclic allene 183?

The chemistry of betweenallenes has not been studied. The synthetic method used allows for many variations in the size of rings. Does the chemistry of the allene change
compared to linear allenes? The crystal structures of these betweenallenes need to be
determined to show how the allene alleviates the strain of being in two rings. The
pyrolysis and photolysis of these betweenallenes would also be interesting.

The chemistry of these cyclic allenes and alkynes should also be studied. Sakurai
et al. have examined the reaction of cyclic alkyne 184 and manganese carbonyl
compounds under photolytic conditions. They obtained vinylidene complexes, 185, with
a small amount of disilylketene 186. Some reactivity studies of cyclic alkyne 131 have
been done, but no reactivity studies have been done for the other cyclic alkynes or
cyclic allenes. The thermochemistry of the products similar to ketene 186 would also be
very interesting. It may be a route to cyclic alkynes containing an oxygen next to the
triple bond.
CONCLUSION

The isomerization and decomposition of ethynyldisilanes was found to be complex and probably involved a silacyclopropene intermediate. The mechanism for the formation of silacyclopropenes was not determined, but may involve a vinylidene or a silapropadiene. The two pathways can not be distinguished by what is known currently in the literature for these types of intermediates. As more is learned about the chemistry of silapropadienes, this problem may be solved.

The substitution on the silacyclopropene intermediate played an important role in determining which product was the major product in the pyrolysis of ethynyldisilanes. When the two vinylic carbons were substituted with hydrogens and there was a good migrating group on the silicon, the major product was the vinylsilylene as was shown in the trapping experiments using acetylene as the trapping reagent.

When one of the carbons was substituted with a trimethylsilyl group another pathway was competitive. A 1,2-hydrogen shift to form a disubstituted acetylene became the major pathway. When there was not a good migrating group on the silicon, the vinylsilylene was not formed. The disubstituted acetylene was the major product with elimination of silylene as a minor pathway. When both of the vinylic carbons were substituted with a trimethylsilyl group, the only decomposition was the extrusion of silylene.

The extrusion of silylene via a silacyclopropene competed with an α-elimination when both were possible as was the case in the pyrolysis of ethynyldisilanes 77 and 82. The Arrhenius parameters obtained also showed that these two pathways were competitive.

When the disilane was part of a ring, isomerization was the major pathway as shown in the pyrolysis of ethynyldisilane 123. The triple bond became incorporated into
the ring. The decomposition of cyclic alkynes was briefly studied. More work needs to be done to determine the decomposition mechanism, however, it appeared that the mechanism was similar to the acyclic disilanes.

The decomposition of cyclic propargylsilanes was much more difficult to understand. Isomerization to cyclic allenenes was the major pathway with extrusion of dimethylsilylene appearing for some decompositions. It depended on the system and several mechanisms were possible. The decomposition and isomerization of cyclic allenenes were also studied.

An X-ray structure was determined for [4.4] betweenallene 147. This was the smallest betweenallene synthesized. The structure showed no bend in the allene, and a twist of 18 degrees toward planarity. Table 1 shows the spectral data for the cyclic allenenes that have been synthesized and characterized. There was a noticeable trend in the infrared absorption for the allene. As the ring size decreased, the allene absorbed at smaller wave numbers. However, the resonance of the allene carbons in the $^{13}$C NMR showed no trend in relation to ring size. The x-ray structures showed the twist and bend do occur at the same time when the allene was in only one ring. The x-ray structure of the 1,2-cyclohexadiene also showed pyramidalization of the terminal carbons of the allene. When the allene was in two symmetrical rings, there was no bend, but more twist. More betweenallenenes need to be synthesized to determine if this is an exception or the rule. Will the allene bend when the betweenallene consists of two different size rings?

The work of this dissertation has increased the knowledge and understanding of silacyclop propane chemistry. It has also investigated the thermochemistry of cyclic alkynes and cyclic allenenes. Classes of compounds that were only thought of as intermediates are stable and isolable. There is an abundance of work which can be done in this area of chemistry.
Table 1. Summary of spectral data for cyclic allenes

<table>
<thead>
<tr>
<th>Structure</th>
<th>IR (cm(^{-1}))</th>
<th>(^{13})C NMR</th>
<th>Allene Twist</th>
<th>Allene Bend</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Me}_3\text{Si-C=C-SiMe}_3)</td>
<td>1870</td>
<td>203.6, 64.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(\text{Me}_2\text{Si-C=C-SiMe}_3) (^a)</td>
<td>1860</td>
<td>204.9, 63.9</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>(\text{Me}_2\text{Si-C=C-SiMe}_2)</td>
<td>1852</td>
<td>206.7, 62.1</td>
<td>18</td>
<td>0</td>
</tr>
<tr>
<td>(\text{Me}_3\text{Si-C=C-SiMe}_3) (^a)</td>
<td>1840</td>
<td>206.1, 63.2</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>(\text{Me}_2\text{Si-C=C-SiMe}_3) (^a)</td>
<td>207.6, 64.1</td>
<td>25</td>
<td>14</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) denotes compounds synthesized and characterized by Yi Pang.
EXPERIMENTAL

Instrumentation

High resolution $^1$H (300 Hz) and $^{13}$C NMR (75.5 Hz) spectra were recorded on a Nicolet NT-300 or Varian VXR-300 spectrometers. All chemical shifts are reported as parts per million from tetramethylsilane and taken in deuterated chloroform unless otherwise noted. Standard abbreviations are used to designate proton splitting. Mass spectra were recorded using a Hewlett Packard 5970B (GC/MS) operating at 70 eV and are reported as m/e (% relative intensity). Infrared (IR) spectra were recorded on an IBM 98 FT/IR spectrophotometer or a Hewlett Packard 5965A (GC/IR) and are reported as wave numbers ($\text{cm}^{-1}$).

Gas chromatographic (GC) analyses were performed on a Hewlett Packard 5790A using a 30 meter DB-5 capillary column. Preparative GC was performed on a Varian 920 or a GOW-MAC 550P using 15-25% SE-30 on chromasorb W packed columns. Column chromatography used silica as support and hexane as the eluting solvent. All solvents were distilled over calcium hydride.

A pulsed stirred-flow reactor (SFR) modeled after the design of Baldwin et al. was used for kinetic studies. The SFR was calibrated by following the well-established thermal isomerization of cyclopropane to propylene. The quartz sample chamber had a volume of 3 cm$^3$ and a $\tau$ of 2.39 s. The sample chamber was heated by an oven that was controlled by a Digi-Sense temperature controller. The SFR system used a 60 ml per minute flow of helium to sweep the sample through the reactor into a Varian 6000 GC fitted with a 30 meter DB-5 megabore column which had the option of diverting the separated products into a VG-SX300 quadrupole mass spectrometer for MS analysis. The GC (FID) signals were recorded on a Hewlett Packard 3390A integrator as well as a Magnum XT/Mark 2 microcomputer for determination of the reactant and product areas.
The response factors were determined for all the products and were included in the Arrhenius parameters which were obtained.

Procedures and Results

Purification of ethynyldisilane 59

An impure sample of 59 had been prepared by a previous group member. It was purified by isothermal preparative GC using a 9 ft column. The conditions were as follows: injector temperature 220°C, detector temperature 200°C, column temperature 130°C and flow rate 20 ml/min. Ethynyldisilane 59 was identified by spectra: $^1$H NMR 0.091 (s, 9H), 0.178 (s, 6H), 2.410 (s, 1H); FTIR 3294, 2957, 2899, 2029, 1406, 1248, 839, 804; GC/MS 156 (M$,^+$, 12), 141 (47), 83 (15), 73 (100), 45 (19), 43 (23). C$_7$H$_{10}$Si$_2$ measured m/z 156.07920, calculated 156.07906.

FVP of 59

After several trial runs in the SFR to determine the temperature needed to obtain approximately 50 percent decomposition, 0.270 g of 59 (1.7 mmol) was pyrolyzed in a vacuum at 550°C. A pyrolysate was collected with a 96% mass recovery by a liquid nitrogen trap. Three new peaks appeared in the GC trace. The first peak was formed in 20% yield and identified as trimethylsilylacetylene by GC/MS 98 (M$,^+$, 7), 83 (100), 67 (9), 55 (12), 53 (16). It also had the same retention time and MS as an authentic sample. The second peak was formed in 53% yield and identified as isomer 61. An attempt was made to collect the product by preparative GC, but it could not be separated from the starting material. This peak was identified by GC/MS 156 (M$,^+$, 18), 141 (100), 83 (14), 73 (85), 45 (11), 43 (19). It also had the same retention time and MS as an authentic sample. A mixture of the starting material and isomer 61 had one more peak in the IR at 2143 which suggested a Si-H bond in the isomer. A $^1$H NMR was taken of the mixture
and after removing the peaks of the starting material, three peaks remained: 0.140 (s, 9H), 0.200 (d, 6H, J=3.6 Hz), 4.095 (heptet, 1H, J=3.6 Hz). The third product was formed in 24% yield and isolated by preparative GC. It was identified as the insertion product, 62, by spectra: \(^1\)H NMR 0.082 (s, 9H), 0.159 (s, 6H), 0.194 (d, 6H, J=3.6 Hz), 4.075 (heptet, 1H, J=3.6 Hz); GC/IR 2957, 2897, 2141, 2100, 1248, 885, 837, 800; GC/MS 214 (M\(^+\), 16), 199 (28), 155 (43), 141 (34), 140 (27), 116 (40), 73 (100).

**Purification of isomer 61**

An impure sample of isomer 61 had been prepared by a previous group member. It was purified by isothermal preparative GC using a 9 ft column. The conditions were as follows: injector temperature 230°C, detector temperature 220°C, column temperature 135°C and flow rate 20 ml/min.

**FVP of isomer 61**

Pyrolysis in the SFR showed no decomposition at 500°C and only 9% decomposition at 550°C. More trials were made to determine the appropriate temperature for a flash vacuum pyrolysis. A flash vacuum pyrolysis of 0.103 g of isomer 61 (0.7 mmol) at 750°C resulted in 30% decomposition and a 90% mass recovery. The pyrolysate had one major peak other than starting material. This peak was formed in 65% yield and identified as trimethylsilylacetylene. The retention time and MS were the same as an authentic sample. The GC/IR spectrum was as follows: 3308, 2970, 2036, 1412, 1260, 852.

**Pyrolysis of 59 in SFR**

Ethynyldisilane 59 was pyrolyzed in the SFR from 400-520°C. A 0.1 torr sample
was mixed with 10 torr of 2,3-dimethylbutadiene before injection into the SFR. The formation of the isomer and the trapped adduct were followed.

**Flow pyrolysis of 59**

A mixture of 2 g of ethynyldisilane 59 (12 mmol) and 13.5 ml of 2,3-dimethylbutadiene (120 mmol) was pyrolyzed at 500°C in a flow of nitrogen (30 ml/min). A yellow pyrolysate was collected in an isopropanol-dry ice bath. The major products were trimethylsilylacetylene, 60, isomer 61 and silylene trapped adduct 71. Trapped adduct 71 was isolated by preparative GC (9 ft 25% SE-30, col. temp. 100°C) and identified by spectra: \( ^1H \text{ NMR} \) 0.091 (s, 6H), 1.265 (s, 4H), 1.648 (s, 6H); \( ^13\text{C} \text{ NMR} \) -1.76, 19.3, 25.5, 131; GC/IR 2891, 1257, 1172, 829; GC/MS 140 (M+, 44), 125 (100), 123 (21), 97 (26), 85 (20), 83 (18), 73 (11), 59 (63).

**Synthesis of ethynyldisilane 67**

A 20 ml solution of 2.17M \( n \)-butyl lithium (52 mmol) in hexanes was added to 100 ml of THF. The solution was cooled to -78°C and 1-butyne was bubbled through the solution for an hour. After allowing to warm to room temperature while stirring, the solution became colorless. An aliquot was taken and quenched with chlorotrimethylsilane. Analysis by GC/IR/MS showed that the sample contained butynyltrimethylsilane. It was cooled to -78°C again and 9 g of chloropentamethyldisilane (50 mmol) was added slowly via syringe to the colorless solution. The solution was allowed to warm to room temperature while stirring. It was washed several times with equal amounts of water and dried over sodium sulfate. The solvent was removed by rotavap leaving 9.2 g of a liquid containing 83% ethynyldisilane 67 (82% crude yield). It was further purified as needed by preparative GC (9 ft 25% SE-30, col. temp. 130-135°C).
Ethynyldisilane 67 was identified by spectra: $^1$H NMR 0.023 (s, 9H), 0.125 (s, 6H), 1.101 (t, 3H, J=7.5 Hz), 2.202 (q, 2H, J=7.5 Hz); $^{13}$C NMR -3.37, -2.81, 13.9, 14.0, 82, 111; GC/IR 2959, 2166, 1253, 835, 806; GC/MS 184 (M+, 22), 169 (30), 155 (25), 141 (25), 129 (18), 111 (90), 83 (34), 81 (11), 73 (100), 59 (12), 55 (11). C$_9$H$_{20}$Si$_2$ measured m/z 184.08184, calculated 184.11036.

**Synthesis of chloropentamethyldisilane**

A slurry containing 18 g of aluminum trichloride (137 mmol) and 28 ml of hexamethyldisilane (137 mmol) was prepared in a 3-neck 100 ml flask and fitted with a mechanical stirrer. By an addition funnel, 10 ml of acetylchloride (137 mmol) was added dropwise. The solution was kept below room temperature by an ice bath. A brown solution was obtained after addition was complete. The mixture was stirred overnight at room temperature. The volatile liquids were removed under vacuum and trapped in an isopropanol-dry ice bath. A clear liquid weighing 22.8 g and containing 85% chloropentamethyldisilane (80% crude yield) was collected. The product was identified by spectra: GC/MS 166 (M+, 1.7), 151 (1.9), 131 (2.2), 93 (48), 73 (100); GC/IR 2962, 1255, 837, 801.

**FVP of ethynyldisilane 67**

A flash vacuum pyrolysis of 0.285 g of 67 (1.5 mmol) at 650°C resulted in 70% decomposition with a 94% mass recovery. Four new peaks appeared in the GC trace. The products were isolated by preparative GC. However, the first two products could not be separated and were collected together. They were formed in a combined yield of 9% and identified as dimethylsilylene dimers by comparing spectra with the literature. Both peaks had similar spectra: GC/MS peak $^1$ 116 (M+, 79), 115 (22), 101 (100), 99 (25), 73
(32), 69 (15), 59 (30); peak #2 116 (M+, 79), 115 (16), 101 (100), 99 (25), 73 (36), 69 (16) 59 (31); GC/IR peak #1 2963, 2141, 1258, 958, 885, 823; peak #2 2968, 2126, 1257, 950, 884, 813; $^1$H NMR of mixture 0.172 (t, J=4.5 Hz), 0.255 (s), 0.332 (d, J=3.6 Hz), 0.335 (d, J=3.6 Hz), 4.422 (pentet, J=4.5 Hz), 4.618 (m, J=3.6 Hz) 4.678 (m, J=3.6 Hz). The third peak was formed in 80% yield and identified as 1-trimethylsilyl-1-butyne, 68, by spectra: $^1$H NMR 0.103 (s, 9H), 1.101 (t, 3H, J=7.5 Hz), 2.190 (q, 2H, J=7.5 Hz); $^{13}$C NMR 0.151, 13.5, 13.8, 83, 109; GC/IR 2967, 2907, 2173, 1316, 1258, 1075, 1038, 906, 847, 769; GC/MS 126 (M+, 11), 112 (11), 111 (100), 83 (24). The fourth product was formed in 2% yield and was not isolated. It was identified as an insertion product by spectra: GC/IR 2956, 2900, 2165, 1252, 837, 791; GC/MS 242 (M+, 6), 227 (20), 169 (31), 141 (30), 131 (12), 116 (52), 111 (24), 83 (21), 73 (100), 59 (15).

Pyrolysis of 67 in SFR

Ethynyldisilane 67 was pyrolyzed in the SFR from 450-560°C. A 0.1 torr sample of 67 was mixed with 3 torr of 2,3-dimethylbutadiene before injection into the SFR. The eliminated product, 1-trimethylsilyl-1-butyne, 68, and trapped silylene adduct 71 were followed.

Synthesis of 1,2-dichlorotetramethyldisilane

The procedure is the same as that described for chloropentamethyldisilane except for two equivalents of aluminum trichloride and acetylchloride were used. The product was identified by spectra: GC/IR 2970, 2905, 1918, 1723, 1404, 1258, 837, 792; GC/MS 188 (12), 186 (M+, 17), 151 (17), 95 (24), 93 (66), 73 (100), 65 (17), 63 (14), 58 (56).
Synthesis of ethynyldisilane 72

A 70 ml solution of 0.5M ethynyl magnesium bromide (35 mmol) in THF was added to 6.5 g of 1,2-dichlorotetramethyldisilane (35 mmol) in 10 ml of THF at -78°C. The solution was allowed to warm to room temperature and stirred overnight. It was then cooled to -78°C and 35 ml of 1.0M lithium aluminum hydride in diethyl ether was added slowly via syringe. As it was warming to room temperature, the solution turned from a brown to a milky brown color with a white solid precipitating out. After adding 50 ml of pentane, water was slowly added to quench the excess hydride. The solution was washed three times with water and dried over sodium sulfate. The solvent was removed by rotavap leaving a yellow liquid. The liquid was distilled at atmospheric pressure using a shortpath condenser with an oil bath temperature of 140°C. A clear liquid was collected which weighed 1.7 g and contained 76% ethynyldisilane 72 (26% yield) by GC analysis. It was purified as needed by preparative GC (9 ft 25% SE-30, col. temp. 130°C).

Ethynyldisilane 72 was identified by spectra: $^1$H NMR 0.161 (d, 6H, J=4.5 Hz), 0.229 (s, 6H), 2.44 (s, 1H), 3.67 (heptet, 1H, J=4.5 Hz); $^{13}$C NMR -6.99, -2.76, 88.6, 95.3; GC/IR 3306, 2966, 2156, 2039, 1334, 1265, 894. GC/MS 142 (M+, 3), 141 (7), 127 (100), 116 (14), 83 (40), 73 (63), 59 (12).

FVP of ethynyldisilane 72

After several trial runs in the SFR to determine an appropriate temperature, a flash vacuum pyrolysis of 0.326 g of 72 (2.3 mmol) at 550°C resulted in an 87% mass recovery. Three new peaks appeared in the GC trace. These peaks were identified by GC/IR/MS with no further characterization made. The first peak was formed in 21% yield and identified as dimethylsilylacetylene, 50: GC/MS 84 (M+, 29), 83 (30), 69 (100), 67 (16), 58 (77), 53 (48); GC/IR 3304, 2974, 2156, 2039, 1334, 1265, 894. The second peak was
formed in 40% yield and identified as an isomer, bis(dimethylsilylacetylene, 51: GC/MS 142 (M+, 1.4), 141 (8.5), 127 (100), 116 (13), 83 (32), 73 (99), 59 (15); GC/IR 2972, 2151, 1260, 877, 782. The third peak was formed in 23% yield and identified as insertion product 73: GC/MS 200 (M+, 9), 185 (28), 141 (44), 116 (39), 83 (14), 73 (100), 59 (18); GC/IR 2967, 2907, 2148, 2100, 1410, 1256, 888, 842, 811, 773.

Synthesis of ethynyltrisilane 74

An 8 ml solution of 3.0M methyl magnesium chloride (24 mmol) in THF was added slowly via syringe to 5 g of 1,3-dichlorohexamethyltrisilane (20 mmol) in 20 ml of THF at -78°C while stirring. The solution became gray with a suspended solid as it was allowed to warm to room temperature. An aliquot was taken and the salts were precipitated out with pentane. By GC analysis there was no starting material remaining and a new peak was present. The solution was then cooled to -78°C and 40 ml of 0.5M ethynyl magnesium bromide (20 mmol) in THF was added. After addition was complete, it was allowed to warm to room temperature. The solution had a yellowish-brown tint and was washed several times with water after pentane was added. It was dried over sodium sulfate, and the solvent was removed by rotavap leaving 5.15 g of a brown liquid containing 61% ethynyltrisilane 74 (73% crude yield). It was further purified as needed by preparative GC (5 ft 15% SE-30, col. temp. 110°C). The product was identified by spectra: 1H NMR 0.084 (s, 9H), 0.105 (s, 6H), 0.208 (s, 6H), 2.437 (s, 1H); GC/IR 3306, 2959, 2027, 1406, 1254, 792; GC/MS 214 (M+, 15), 199 (18), 155 (11), 141 (31), 131 (16), 116 (14), 110 (11), 83 (11), 73 (100).

Synthesis of 1,3-dichlorohexamethyltrisilane

A mixture of 11.05 g of 1,3-dihydridohexamethyltrisilane (50 mmol) and 0.02 g of
benzoylperoxide (0.08 mmol) was added to 60 ml of carbon tetrachloride. It was refluxed for about 12 hours. Analysis by GC/MS showed no starting material remained, and the major peak was the desired product. The solvent was removed by rotavap and 15.44 g of a yellow oil remained which contained 82% 1,3-dichlorohexamethyltrisilane (100% crude yield). The product was identified by spectra: GC/IR 2965, 2903, 1405, 1257, 840, 788; GC/MS 246 (0.9), 244 (M+, 1.3), 153 (23), 151 (57), 131 (12), 116 (39), 93 (14), 73 (100).

**FVP of ethynyltrisilane 74**

A flash vacuum pyrolysis of 0.125 g of 74 at 550°C resulted in a 100% mass recovery. The pyrolysate contained four new peaks which were identified by GC/IR/MS. The first and second peaks were ethynylidisilane 59 (11% yield) and its isomer 61 (10% yield), respectively. The third peak was an isomer, dimethylsilyl(pentamethyldisilanyl)-acetylene, 62, formed in 33% yield. It gave the following spectra: GC/IR 2964, 2904, 2148, 1255, 889, 841, 807, 772; GC/MS 214 (M+, 15), 199 (21), 155 (29), 141 (27), 116 (38), 73 (100). The fourth product was insertion product 75 formed in 23% yield. It gave the following spectra: GC/IR 2960, 2901, 2148, 1254, 889, 839, 789; GC/MS 272 (M+, 6.6), 257 (15), 199 (31), 183 (10), 116 (54), 73 (100).

**Synthesis of ethynylidisilanes 77 and 78**

A 12.6 ml solution of 3.0M methyl magnesium chloride (38 mmol) in THF was added dropwise via syringe to 3.7 g of trimethylsilylacetylene (38 mmol) in 40 ml of THF at room temperature. The solution began bubbling upon addition of the Grignard reagent. The flask was fitted with a reflux condenser and warmed to 50°C. After an hour the bubbling stopped, and the solution was cooled to -78°C.

Approximately half of the solution was transferred via cannula to 4.0 g of
1,1-dichlorotetramethyldisilane (21.5 mmol) in 10 ml of THF at -78°C. After allowing to warm to room temperature while stirring, 5 ml of 1.0M lithium aluminum hydride (5 mmol) in diethyl ether was added and allowed to stir for 2 hours. After pentane was added, the solution was washed several times with water and dried over sodium sulfate. The solvent was removed by rotavap leaving 6.0 g of a yellow oil containing 48% ethynyldisilane 77 (34% yield). It was further purified as needed by preparative GC (1 ft 25% SE-30, col. temp. 60°C). Ethynyldisilane 77 was identified by spectra: \(^1\)H NMR 0.136 (s, 18H), 0.215 (d, 3H, J=4.5 Hz), 3.843 (q, 1H, J=4.5 Hz); \(^{13}\)C NMR -7.510, -2.274, -0.144, 109, 118; GC/IR 2965, 2906, 2117, 1256, 861, 805, 770; GC/MS 214 (M+, 13), 199 (18), 155 (15), 141 (17), 140 (14), 126 (12), 116 (31), 73 (100). C\(_9\)H\(_{10}\)Si\(_2\) measured m/z 214.10242, calculated 214.10294.

The other half of the solution was kept at -78°C and 5.0 g of chloropentamethyl-disilane (30 mmol) was added slowly. The solution turned clear with a suspended white precipitate. It was allowed to warm to room temperature and stirred for two hours. After pentane was added, it was washed three times with water and dried over sodium sulfate. The solvent was removed by rotavap leaving 6.5 g of a clear liquid which was 72% ethynyldisilane 78 (78% yield). It was further purified as needed by preparative GC (9 ft 25% SE-30, col. temp. 150°C). Ethynldisilane 78 was identified by spectra: \(^1\)H NMR 0.149 (s, 6H), 0.125 (s, 9H), 0.075 (s, 9H); GC/IR 2963, 2903, 1406, 1255, 843, 807; GC/MS 228 (M+, 24), 213 (40), 155 (50), 140 (34), 125 (11), 97 (11), 73 (100). C\(_{10}\)H\(_{24}\)Si\(_3\) measured m/z 228.11878, calculated 228.11859.

**General procedure for the synthesis of 1,1-dichlorotetramethylidisilane**

A solution of pentane-washed lithium wire, cut into <1 inch pieces, in THF was prepared. The flask was fitted with a high-speed mechanical stirrer equipped with a wire
propeller and a reflux condenser. Chlorotrimethylsilane was added dropwise by an addition funnel with vigorous stirring. After an hour the addition was complete, and the solution turned a milky gray. Trichloromethylsilane was transferred to an addition funnel via cannula and slowly added to the solution. The ratio of lithium: trichloromethylsilane: chlorotrimethylsilane was 6:3:1. After two hours the addition was complete and the solution was stirred vigorously. The solution was brown after 36 hours and black after two days. After a week the solution was filtered through glass wool and then through celite. The solvent was removed by rotavap leaving a cloudy white solution. Pentane was added and the solution was washed three times with water and dried over sodium sulfate overnight. The pentane was removed by rotavap leaving a clear liquid. The tris(trimethylsilyl)methylsilane was distilled at 75-77°C head temperature at 0.4 torr. A white solid was collected.

The solid was dissolved in carbon tetrachloride and two equivalents of phosphorous pentachloride were added. The solution was heated to reflux using a heating mantle. After a week the solvent was removed by distillation at atmospheric pressure. The product was collected by vacuum distillation and purified by distillation at atmospheric pressure (head temperature 140°C). The product was identified by spectra: \(^1\)H NMR 0.227 (s, 9H), 0.792 (s, 3H); GC/IR 2958, 2901, 2049, 1252, 842; GC/MS 188 (0.8), 186 (M\(^+\), 1), 171 (1.5), 113 (6), 93 (9), 73 (100), 63 (15), 43 (24).

**Pyrolysis of 78 in SFR**

Ethynylsilane 78 was pyrolyzed in the SFR from 420-520°C. A 0.1 torr sample was mixed with 10 torr of 2,3-dimethylbutadiene before injection into the SFR. The formation of the eliminated product, 79, and silylene trapped adduct 71 were followed.
Flow pyrolysis of 77

A mixture of 0.100 g of ethynylsilane 77 (0.5 mmol) and 1.731 g of 2,3-dimethylbutadiene (21 mmol) was pyrolyzed at 450°C in a flow of nitrogen (30 ml/min). A yellow pyrolysate was collected in an isopropanol-dry ice bath. The major products were trimethylsilane (15%), bis(trimethylsilyl)acetylene, 79 (43%), methylsilylene trapped adduct 81, (15%) and α-elimination trapped adduct 80, (21%). The two trapped adducts were identified by comparing the GC/IR/MS spectra and retention times with authentic samples.

Synthesis of trapped adducts 80 and 81

A mixture of 2.88 g of 1,1,2,2-tetrachlorodimethylsilane (12.6 mmol) and 18 ml of 2,3-dimethylbutadiene (160 mmol) was pyrolyzed at 510°C in a flow of nitrogen. A brown pyrolysate was collected. The 2,3-dimethylbutadiene was removed by rotavap leaving a brown liquid, SP-29. The major product (38%), 1-chloro-1,3,4-trimethyl-1-silacyclopent-3-ene was identified by GC/IR/MS: GC/IR 2983, 2917, 1263, 1173, 814, 792; GC/MS 162 (27), 160 (79), 147 (29), 145 (84), 124 (58), 118 (38), 109 (100), 79 (38), 63 (66).

A solution of 1.48 g of SP-29 in 10 ml of diethyl ether was prepared. The solution turned from brown to yellow with a suspended white solid when 4 ml of 1.0M lithium aluminum hydride in diethyl ether was added. After allowing to stir for 30 minutes, the solution was cooled to 0°C and 5 ml of pentane were added. The solution was quenched with water and washed three times with water before drying over sodium sulfate. The solvent was removed by rotavap leaving 0.59 g of a brown liquid containing 55% methylsilylene trapped adduct 81, (70% crude yield). It was further purified by preparative GC (9 ft 25% SE-30, col. temp. 120°C). Trapped adduct 81 was identified by
spectra: $^1$H NMR 0.155 (d, 3H, J=3.3 Hz), 1.26 (d, 2H, J=18 Hz), 1.54 (d, 2H, J=18 Hz), 1.66 (s, 6H), 4.09 (octet, 1H, J=3.3 Hz); $^{13}$C NMR -4.72, 19.1, 22.8, 131; GC/IR 2899, 2132, 1172, 894, 817; GC/MS 126 (M+, 50), 125 (15), 111 (100), 109 (28), 95 (11), 83 (37), 71 (13), 69 (16), 59 (26).

A solution of trimethylsilylacetylide in THF was made by adding 4 ml of 3.0M methyl magnesium chloride (12 mmol) to 0.93 g of trimethylsilylacetylene (9.5 mmol) in 10 ml of THF at room temperature. The solution was heated to 50°C after the flask was fitted with a condenser. After one hour the bubbling stopped and the solution was cooled to -78°C. The solution was allowed to warm to room temperature after adding 1.67 g of SP-29. The solution was a sludge so pentane was added. It was washed four times with water and twice with a saturated sodium chloride solution. The solution was dried over sodium chloride, and the solvent was removed by rotavap leaving 4.2 g of a brown liquid containing 40% of the trapped adduct 80 in 75% yield. It was purified by preparative GC (9 ft 25% SE-30). Trapped adduct 80 was identified as the $\alpha$-elimination trapped adduct by spectra: $^1$H NMR 0.136 (s, 9H), 0.241 (s, 3H), 1.31 (d, 2H, J=17.4 Hz), 1.57 (d, 2H, J=17.4 Hz), 1.65 (s, 6H); GC/IR 2968, 2911, 1258, 1171, 827, 782, 765; GC/MS 222 (M+, 40), 207 (23), 124 (100), 109 (26), 83 (13), 73 (28).

**Pyrolysis of 77 in SFR**

Ethynyldisilane 77 was pyrolyzed in the SFR from 400-490°C. A 0.1 torr sample was mixed with 10 torr of 2,3-dimethylbutadiene before injection into the SFR. The formation of bis(trimethylsilyl)acetylene, 79, and the two silylene trapped adducts, 80 and 81 were followed.
Synthesis of ethynyl(disilane 82

A 6 ml solution of 3.0M methyl magnesium chloride (18 mmol) was added to 1.78 g of trimethylsilylacetylene (18 mmol) in 25 ml of THF at room temperature and allowed to stir. The flask was fitted with a reflux condenser and heated to 45°C for about an hour. The solution was cooled to -78°C and was added via cannula to 3.45 g of 1,1-dichlorotetramethyldisilane (18 mmol) in 10 ml of THF at -78°C. The solution was cloudy after addition. It was allowed to warm to room temperature. The solution became clear with a tint of yellow. It was cooled again to -78°C and 2 ml of a 1:1 mixture of methanol:pyridine (17 mmol) was added. A white solid formed immediately. It was warmed to room temperature and washed several times with water. The solution was dried over sodium sulfate, and the solvent was removed by rotavap leaving 13.4 g of a brown liquid containing 20% ethynyl(disilane 82 (12% crude yield). The product was purified as needed by preparative GC (5 ft 15% SE-30, col. temp. 130°C). Ethynyl(disilane 82 was identified by spectra: ¹H NMR 3.441 (s, 3H), 0.276 (s, 3H), 0.147 (s, 9H), 0.116 (s, 9H); GC/IR 2964, 2905, 2841, 1407, 1255, 1094, 847, 806, 786; GC/MS 244 (M⁺, 4), 229 (72), 171 (11), 155 (13), 141 (27), 131 (30), 97 (15), 73 (100), 59 (37).

Flow pyrolysis of ethynyl(disilane 82

A mixture of 0.072 g of ethynyl(disilane 82 in 1 ml of 2,3-dimethylbutadiene was pyrolyzed at 460°C in a flow of argon. A yellow pyrolysate was collected. The major products were methoxytrimethylsilane (31%), bis(trimethylsilyl)acetylene, 79 (8%), methoxymethylsilylene trapped adduct 83 (6%) and α-elimination trapped adduct 80, (55%). The methoxymethylsilylene trapped adduct 83 was identified by spectra: GC/IR 2896, 1448, 1396, 1259, 1172, 1102, 986, 837, 787; GC/MS 156 (M⁺,31), 141 (23),124 (53), 120 (15), 109 (21), 105 (33), 75 (13), 59 (100). The bis(trimethylsilyl)acetylene, 79,
methoxytrimethylsilane and trapped adduct 80 were identified by comparing the GC/IR/MS spectra and retention times with authentic samples.

**Synthesis of ethynyldisilane 84**

A solution of 0.44 g of propynyl lithium (9.6 mmol) and 20 ml of THF was cooled to -78°C and 2.0 g of 2-chloroheptamethyltrisilane (9.0 mmol) was added slowly. The solution was allowed to warm to room temperature while turning from yellow to orange. After pentane was added, the solution was washed five times with water and dried over sodium sulfate. The solvent was removed by rotavap leaving 2.1 g of a yellow liquid containing 16% ethynyldisilane 84 (17% yield). It was further purified by preparative GC (col. temp. 140°C). Ethynyldisilane 84 was identified by spectra: GC/IR 2958, 2901, 2170, 1408, 1252, 1019, 842, 787; GC/MS 228 (M+, 13), 213 (15), 179 (10), 155 (34), 125 (18), 116 (86), 101 (11), 97 (42), 73 (100), 69 (16), 67 (18).

**Synthesis of 2-chloroheptamethyltrisilane**

This procedure was the same as that for 1,1-dichlorotetramethyldisilane except for only one equivalent of phosphorous pentachloride was used. The product was identified by spectra: GC/IR 2960, 2901, 1403, 1254, 845, 784; GC/MS 226 (6), 224 (M+, 13), 209 (11), 131 (16), 116 (65), 101 (21), 73 (100).

**Flow pyrolysis of 84**

A mixture of 0.030 g of ethynyldisilane 84 (0.1 mmol) and 1.2 ml of 2,3-dimethylbutadiene (11 mmol) was pyrolyzed at 520°C in a flow of nitrogen. The two major products of a messy pyrolysate were identified by GC/IR/MS. The first product was identified as 1-trimethylsilylpropyne, 85 (42%): GC/IR 2967, 2182, 1258, 1026, 849,
769; GC/MS 112(M⁺, 12), 97 (100), 69 (16), 67 (9). The second product was identified as silylene trapped adduct 86 (25%): GC/IR 2956, 2923, 2889, 1253, 1169, 866, 835, 804; GC/MS 198 (M⁺, 40), 183 (40), 134 (31), 125 (86), 123 (36), 119 (75), 116 (26), 109 (30), 97 (18), 83 (17), 73 (100), 59 (65).

Synthesis of ethynyldisilane 87

A 55 ml solution of 0.5M ethynyl magnesium bromide (28 mmol) in THF was added to 2-chloroheptamethyltrisilane (18 mmol) at -78°C. The solution was warmed to room temperature and an aliquot was checked to see if any chlorosilane remained. If the chlorosilane was observed, more ethynyl Grignard was added. This was repeated until no chlorosilane was observed in the aliquot. Pentane was added and washed five times with water and dried over sodium sulfate. The solvent was removed by rotavap leaving a dark brown residue. A clear liquid (4.3 g) was obtained by vacuum distillation. The liquid contained 65% ethynyldisilane 87 (71% yield). It was purified as needed by preparative GC. Ethynyldisilane 87 was identified by spectra: GC/IR 3306, 2959, 2902, 2019, 1407, 1297, 1253, 842, 789; GC/MS 214 (M⁺, 13), 199 (17), 155 (12), 141 (17), 116 (44), 111 (12), 101 (10), 73 (100).

Flow pyrolysis of ethynyldisilane 87

A mixture of 0.160 g of ethynyldisilane 87 (0.8 mmol) and 2.5 ml of 2,3-dimethylbutadiene (22 mmol) was pyrolyzed at 450°C in a flow of nitrogen. The major products were identified by GC/IR/MS. The first product was formed in 20% yield and was identified as ethynyldisilane 77. The second product was formed in 36% yield and was identified as bis(trimethylsilyl)acetylene, 79. The third product was formed in 16% yield and identified as trapped adduct 80. The fourth product was formed in 28%
yield and identified as trapped adduct 81. There was another pair of products identified as trapped adducts 88 formed in a combined yield of <10%. Their GC/IR/MS spectra were similar: peak #1 GC/IR 2960, 2906, 1255, 1173, 843; GC/MS 296 (M+, 11), 281 (10), 255 (25), 254 (91), 126 (61), 125 (75), 116 (26), 111 (32), 73 (100), 59 (32); peak#2 GC/IR 2960, 2897, 1256, 1172, 1119, 891, 845, 769; GC/MS 296 (M+, 4.7), 281 (6.3), 255 (17), 254 (53), 126 (53), 125 (65), 116 (20), 111 (24), 73 (100), 59 (31).

Synthesis of disilane 101

A 40 ml solution of 0.5M vinyl magnesium bromide (20 mmol) in THF was added to 3.7 g of 1,1-dichlorotetramethyldisilane (20 mmol) in 40 ml of THF at -78°C. The solution remained brown after allowing to warm to room temperature. It was cooled again to -78°C and 2.4 ml of a 1:1 mixture of methanol: pyridine (20 mmol) was added. The solution was allowed to warm to room temperature while stirring. The solution was washed twice with a sodium bicarbonate solution after pentane was added. It was also washed with water twice and once with a saturated sodium chloride solution. It was dried over sodium sulfate, and the solvents were removed by rotavap. The major product was the desired disilane 101. A large impurity was also formed which was identified as 1,1-divinyltetramethyldisilane. The ratio was almost 1:1 between the two products. A 4:1 ratio was obtained by preparative GC (col. temp. 100°C). The desired product was identified by spectra: \(^1\)H NMR 0.084 (s, 9H), 0.227 (s, 3H), 3.407 (s, 3H), 5.72 (d of d, 1H, \(J_{AC}=19.8\) Hz, \(J_{BC}=3.9\) Hz), 6.00 (d of d, 1H, \(J_{AB}=14.4\) Hz, \(J_{BC}=3.9\) Hz), 6.16 (d of d, 1H, \(J_{AC}=19.8\) Hz, \(J_{AB}=14.4\) Hz); GC/IR 3056, 2958, 2903, 2839, 1404, 1253, 1094, 1009, 951, 838, 786; GC/MS 174 (M+, 15), 173 (17), 159 (54), 133 (42), 131 (39), 101 (36), 89 (40), 75 (34), 73 (70), 59 (100).
Flow pyrolysis of disilane 101

A mixture of 0.086 g of disilane 101 (0.5 mmol) and 2 ml of 2,3-dimethyl-butadiene (18 mmol) was pyrolyzed at 450°C in a flow of nitrogen. There were two major products in the GC analysis. The first product was methoxytrimethylsilane (20%). The other product was isolated by preparative GC and identified by spectra as trapped vinylsilylene adduct 102 (23%): \( ^1\)H NMR 0.170 (s, 3H), 1.28 (d, 2H, J=17.4 Hz), 1.415, 2H, J=17.4 Hz), 1.657 (s, 6H), 5.715 (d of d, 1H, J\(_{AC}\)=20.1 Hz, J\(_{BC}\)=4.2 Hz), 6.10 (d of d, 1H, J\(_{AB}\)=14.7 Hz, J\(_{BC}\)=4.2 Hz), 6.185 (d of d, 1H, J\(_{AB}\)=14.7 Hz, J\(_{AC}\)=20.1 Hz); GC/IR 3055, 2971, 2895, 1406, 1258, 1172, 820, 779; GC/MS 152 (M\(^+\), 82), 137 (53), 124 (53), 111 (56), 110 (62), 109 (100), 95 (51), 59 (64), 55 (45).

Synthesis of trisilane 103

A solution of 1.12 g of 2-chloroheptamethyltrisilane (5 mmol) and 15 ml of THF was cooled to -78°C. A 2 ml solution of 1M lithium aluminum hydride (2 mmol) in diethyl ether was added via syringe. The solution was allowed to warm to room temperature while stirring. After adding pentane, the solution was quenched with water and washed several times with more portions of water. It was dried over sodium sulfate, and the solvent was removed by rotavap leaving 1.3 g of a liquid containing 50% trisilane 103 (69% yield). It was purified as needed by preparative GC (col. temp. 130°C, 9 ft 15% SE-30). Ethynyldisilane 103 was identified by spectra: GC/IR 2958, 2901, 2070, 1253, 852, 792; GC/MS 190 (M\(^+\), 12), 175 (11), 116 (28), 102 (32), 101 (22), 73 (100), 59 (13).

Flow pyrolysis of 103 with trimethylsilylacetylene

A mixture of 0.099 g of trisilane 103 (0.5 mmol) and 2 ml of trimethylsilylacetylene (15 mmol) was pyrolyzed at 500°C in a flow of nitrogen. The
major products were identified by GC/IR/MS. The first product was identified as trimethylsilane: GC/IR 2965, 2126, 1421, 1261, 906. The second peak was formed in 37% yield and was identified as bis(trimethylsilyl)acetylene, 79. The third product was formed in 7% yield and identified as diethynylsilane 104: GC/IR 2969, 29 2172, 1259, 838, 779; GC/MS 238 (M+, 20), 223 (100), 183 (16), 155 (26), 140 (48), 125 (31), 73 (49). The fourth and fifth products were similar and formed in a combined 18% yield. They were identified as ethynylvinylsilane isomers 105: peak #1 GC/IR 2965, 2909, 2147, 1258, 839, 771; GC/MS 240 (M+, 11), 225 (65), 167 (23), 155 (27), 141 (37), 127 (22), 73 (100); peak #2 GC/IR 2966, 2143, 1258, 846, 770; GC/MS 240 (M+, 11), 225 (85), 167 (14), 155 (21), 141 (41), 127 (16), 73 (100). The final product was formed in only trace amounts. It was identified as ethynylvinylsilanes 106: GC/IR 2964, 2906, 2168, 1257, 846, 768; GC/MS 312 (M+, 2.1), 297 (6), 239 (9), 214 (29), 155 (19), 141 (14), 140 (13), 116 (13), 73 (100).

Flow pyrolysis of 103 in acetylene

A 3% solution of trisilane 103 (0.080 g, 0.4 mmol) in benzene was pyrolyzed at 500°C in a flow of acetylene (30 ml/min). The major products were identified by GC/IR/MS. The first product was identified as trimethylsilane. The second product was formed in 4% yield and identified as trimethylsilylacetylene: GC/IR 3308, 2970, 2909, 2036, 1333, 1260, 852, 769. The third peak was formed in 3% yield and identified as ethynylvinylsilane 96: GC/IR 3305, 3063, 2978, 2159, 2041, 1333, 1260, 852, 769. The fourth peak was formed in 5% yield and identified as ethynylidisilane 108: GC/IR 3308, 2968, 2147, 2037, 1335, 1261, 1054, 894, 850, 777; GC/MS 141 (M+-1, 10), 127 (100), 101 (12), 99 (18), 85 (11), 83 (11), 73 (14), 59 (11). The fifth product was formed in 7% yield and identified as ethynylsilane 111: GC/IR 2963, 2908, 2121, 1299, 1257, 989, 880,
800; GC/MS 142 (M*, 21), 127 (100), 99 (12). The last pair of products were formed in a combined 43% yield and were identified as the ethynylvinylsilane isomers: peak #1 GC/IR 3309, 2963, 2152, 2038, 1410, 1335, 1258, 1177, 1009, 845; GC/MS 153 (M+-15, 100), 127 (28), 125 (12), 113 (14), 85 (12), 83 (47), 73 (98), 69 (20), 59 (33), 53 (18); peak #2 GC/IR 3308, 2962, 2169, 2070, 2038, 1412, 1337, 1259, 843; GC/MS 153 (M+-15, 100), 127 (33), 125 (14), 113 (16), 85 (11), 83 (41), 73 (95), 69 (18), 59 (34), 53 (19).

**Synthesis of ethynyltetrasilane**

A 30 ml solution of 1.46M methyl lithium (43.8 mmol) in diethyl ether was added to a solution of 6.4 g of tetrakis(trimethylsilyl)silane (20 mmol) in 50 ml of THF at room temperature while stirring. After addition was complete the solution turned from opaque to having a tint of orange. It was allowed to stir overnight. The solution turned a gray color and an aliquot was quenched with acidic water. By GC/IR/MS the major peak was tris(trimethylsilyl)silane with very little starting material present. The solution was quenched with acidic water until the aqueous layer was no longer basic. It was washed five times with water and dried over sodium sulfate. The solvent was removed by rotavap leaving a yellow-tan liquid. Chloroform was added to the product and allowed to stand in light. After four days, the chloroform was removed by rotavap and 4.5 g of a yellow liquid (SP-22) remained which contained 33% chlorotris(trimethylsilyl)silane (25% yield).

A 10 ml solution of 0.5M ethynyl magnesium bromide (5 mmol) was added to 2.3 g of SP-22 in 10 ml of THF at -78°C. The solution was warmed to room temperature while stirring. The solvent was removed by rotavap. A clear liquid was collected in a trap-to-trap distillation. The liquid weighed 1.8 g and contained 31% ethynyltetrasilane (78% yield). It was further purified as needed by preparative GC (col. temp. 210°C). Ethynyltetrasilane was identified by spectra: ¹H NMR 0.178 (s, 27H), 2.254 (s, 1H);
Flow pyrolysis of ethynyltetrasilane 113

A mixture of 0.02 g of ethynyltetrasilane 113 (0.08 mmol) and 0.8 ml of 2,3-dimethylbutadiene (7 mmol) was pyrolyzed at 310°C in a flow of nitrogen. The products were identified by GC/IR/MS. The first product was formed in 18% yield and identified as trimethylsilane. The second product was bis(trimethylsilyl)acetylene, 79, formed in 13% yield. The third product was formed in 6% yield and was identified as trapped adduct 116 by spectra: GC/IR 2957, 2900, 2099, 1383, 1253, 1169, 984, 810; GC/MS 184 (M+, 30), 111 (16), 110 (100), 109 (24), 95 (48), 73 (59), 69 (12), 59 (17). The fourth product was formed in 35% yield and identified as the isomer 114 by spectra: GC/IR 2962, 2902, 2088, 1255, 848, 764; GC/MS 272 (M+, 5), 257 (37), 198 (27), 183 (76), 169 (12), 116 (15), 73 (100). The final product was formed in 28% yield and identified as trapped adduct 115 by spectra: GC/IR 2963, 2907, 1256, 1168, 854, 783; GC/MS 280 (M+, 21), 265 (12), 183 (14), 124 (100), 109 (14), 73 (53).

Pyrolysis of 113 in SFR

A 10% solution of ethynyltetrasilane 113 in benzene was injected into the SFR via syringe. The temperature of the pyrolysis ranged from 290-330°C. Only one peak other than starting material was observed in the GC trace. At higher temperatures more peaks were observed.

Sealed tube reaction of 113 in the presence of triethylsilane

A solution of 2% ethynyltetrasilane 113 and 20% triethylsilane in benzene was
degassed and sealed. It was heated to 200°C for 41 hours and opened after cooling. Only one major product was formed in 67% yield with very little starting material remaining. The product was isolated by preparative GC (1 ft 25% SE-30, col. temp. 100°C). It was identified as vinylsilylene trapped adduct 120 by spectra: ¹H NMR 0.045 (s, 9H), 0.129 (s, 9H), 0.134 (s, 9H), 0.708 (q, 6H, J=7.8 Hz), 0.942 (t, 9H, J=7.8 Hz), 3.800 (s, 1H), 7.273 (s, 1H); GC/IR 2960, 2890, 2090, 1252, 1008, 843; GC/MS 388 (M⁺, <1), 373 (3), 314 (17), 285 (25), 257 (46), 199 (22), 198 (32), 183 (25), 116 (20), 87 (24), 73 (100), 59 (47).

Sealed tube reaction of 113 without trap

A 10% solution of ethynyltetrasilane 113 in benzene was degassed and sealed in an NMR tube. It was heated to 200°C for 16 hrs. An ¹H NMR spectrum showed a much smaller acetylenic peak and many other peaks. The tube was opened and the products were identified by GC/IR/MS. There were many decomposition products as seen in the other pyrolyses of ethynyltetrasilane 113 with one exception. This peak was the major product (<5%) and identified as tris(trimethylsilyl)ethylene, 121, by spectra: GC/IR 2961, 2905, 1257, 847; GC/MS 244 (M⁺, 9), 229 (5), 171 (5), 156 (29), 155 (19), 141 (18), 73 (100). There was not enough sample to isolate the product.

Attempted hydrosilation of trimethylsilane and bis(trimethylsilylethylene)

A 7% solution of bis(trimethylsilyl)acetylene in benzene was degassed. A balloon of trimethylsilane was added to the tube to equalize pressure. The tube was sealed and heated to 200°C for 18 hours. The tube was opened and no peaks could be assigned to a hydrosilation product in the GC/IR/MS trace. Mostly starting material was left.
Synthesis of ethynylsilane 123

A solution of 2.01 g of dodecamethylecyclohexasilane (5.7 mmol) in 30 ml of carbon tetrachloride was cooled to -20°C. While the solution was stirring, 1.7 g of antimony pentachloride (5.7 mmol) was slowly added via syringe. The solution had a yellow tint. It was warmed to room temperature and a white solid precipitated. The solvent was removed by rotavap and pentane was added. The solid was removed by filtering. A 12 ml solution of 0.5M ethynyl magnesium bromide (6 mmol) in THF was added to the filtrate at -78°C and allowed to warm to room temperature while stirring for about an hour. The solution was washed several times with water and dried over sodium sulfate. The solvent was removed by rotavap leaving an oily yellow solid containing 60% ethynylsilane 123 (53% crude yield). The product was recrystallized from methanol to obtain a white solid whose melting point range was 205-210°C. Ethynylsilane 123 was identified by spectra: \(^1\)H NMR 2.457 (s, 1H), 0.234 (s, 3H), 0.211 (s, 6H), 0.159 (s, 6H), 0.142 (s, 6H), 0.116 (s, 3H), 0.101 (s, 6H), 0.097 (s, 3H); \(^13\)C NMR 96.6, 87.4, -5.81, -6.03, -6.11, -7.32; \(^29\)Si NMR -41.3, -41.7, -42.1, -58.7; GC/IR 3306, 2956, 2897, 2018, 1297, 1252, 802; GC/MS 358 (M\(^+\), 15), 344 (14), 343 (34), 299 (22), 286 (13), 285 (36), 270 (12), 269 (35), 241 (16), 227 (19), 129 (10), 73 (100), 59 (19). C\(_{13}\)H\(_{34}\)Si\(_{6}\) measured m/z 358.12690, calculated 358.12763.

Flow pyrolysis of ethynylsilane 123

A mixture of 0.139 g of 123 (0.4 mmol) in 2.0 ml of 2,3-dimethylbutadiene (20 mmol) was pyrolyzed at 360°C in a flow of argon. Three products were analyzed by GC/IR/MS. The major product was cyclooctyne 124 (69%) which was separated from the other peaks by column chromatography and identified by spectra: \(^1\)H NMR 3.969 (q, 1H, J=4.8 Hz), 0.242 (d, 3H, J=4.8 Hz), 0.211 (s, 3H), 0.163 (s, 3H), 0.143 (s, 3H), 0.140 (s, 3H);
$^{13}$C NMR 120, 114, -3.10, -3.17, -4.96, -5.00, -5.07, -5.16, -5.21, -6.16, -7.52; $^{29}$Si NMR 
-35.1, -37.8, -38.8, -39.5, -39.7, -57.8; GC/IR 2956, 2898, 2116, 1253, 881, 807; GC/MS 358 
(M$,^+$, 16), 343 (32), 299 (33), 285 (22), 269 (21), 241 (18), 227 (15), 202 (15), 125 (12), 73 
(100), 59 (17). The other products were cycloheptyne 125 (15%) and silylene trapped adduct 
81 (8%). Cycloheptyne 125 was identified by spectra: GC/IR 2958, 2899, 1253, 815, 771; 
GC/MS 314 (M$,^+$, 37), 301 (23), 300 (36), 299 (98), 243 (15), 242 (26), 241 (88), 183 (14), 
113 (10), 99 (13), 73 (100), 59 (16). These spectra also matched authentic samples.

**Flow pyrolysis of cyclooctyne 124**

A mixture of 0.075 g of cyclooctyne 124 in 1 ml of hexanes was pyrolyzed at 
360°C in a flow of argon. No decomposition was observed upon analysis by GC/IR/MS.

**FVP of cyclohexyne 131**

The sample of cyclohexyne 131 was obtained from a member of our research 
group. The sample was synthesized by adding 1,4-dichlorooctamethyltetrasilane to a 
solution of dilithioacetylide. The sample contained 50% cyclohexyne 131. Most of the 
impurities were non-volatile oligomers. A clear pyrolysate was collected in a flash 
vacuum pyrolysis of 2.5 g of this mixture at 690°C. Three new peaks appeared in the 
GC/IR/MS trace that had the same molecular weight. This molecular weight 
corresponded to a loss of dimethylsilylene from the starting material. These peaks had the 
following spectra: Peak #1: GC/IR 2971, 2912, 2140, 1355, 1259, 1097, 950, 886, 825; 
GC/MS 198 (M$,^+$, 20), 185 (12), 184 (26), 183 (100), 157 (13), 155 (17), 141 (18), 113 
(14), 99 (13), 85 (12), 83 (15), 81 (14), 73 (18), 69 (14), 59 (20); Peak #2: GC/IR 2970, 
2910, 2151, 2093, 1351, 1261, 1066, 948, 888, 833, 789; GC/MS 198 (M$,^+$, 20), 185 (18), 
184 (19), 183 (100), 157 (18), 155 (19), 141 (19), 129 (11), 125 (12), 113 (21), 99 (20), 97
(14), 85 (16), 83 (27), 81 (11), 73 (29), 69 (27), 67 (11), 59 (18); Peak #3: GC/IR 2967, 2907, 2149, 2094, 1408, 1355, 1258, 1038, 947, 840; GC/MS 198 (M+, 22), 185 (11), 184 (22), 83 (100), 157 (12), 155 (19), 141 (19), 113 (12), 99 (16), 85 (11), 83 (19), 81 (15), 73 (43), 69 (16), 59 (16). There were also two peaks that matched authentic samples of dimethylsilylene dimers and one peak that was equal to the starting material plus dimethylsilylene. It had the spectra: GC/IR 2958, 2899, 1405, 1253, 815, 771; GC/MS (M+, 314), 301 (19), 300 (31), 299 (83), 243 (12), 242 (21), 241 (68), 183 (12), 13 (10), 99 (13), 83 (12), 73 (100), 59 (16).

**Synthesis of ethynylsilane 132**

A 4 ml solution of 2.5M n-butyl lithium (10 mmol) in THF was added to 50 ml of THF and cooled to -78°C. Allene was bubbled through the solution. A dry-ice trap was fitted to the flask so allene would not escape. After about 30 minutes an aliquot was quenched with chlorotrimethylsilane. Analysis by GC showed no n-butyl lithium remaining. The solution was warmed to 10°C and argon was bubbled through the solution to remove any excess allene. Another 4 ml of the n-butyl lithium solution was added to the solution at -20°C and a 1:1 ratio of mono-: di-anion was observed upon quenching an aliquot. Another 4 ml of the n-butyl lithium solution was added, and the major peak was the dianion quenched product after quenching an aliquot. The solution was cooled to -20°C and 4.5 g of 1,5-dichlorodecamethylpentasilane (12 mmol) was slowly added via syringe. A brown solution was obtained after allowing the solution to warm to room temperature whole stirring. It was washed several times with water after pentane was added and dried over sodium sulfate. The solvent was removed by rotavap leaving 3.74 g of a brown liquid containing 67% cyclooctyne 132 (61% crude yield). The product was purified by column chromatography and identified by spectra: $^1$H NMR 1.59 (s, 2H), 0.146 (s, 6H), 0.139 (s,
6H), 0.131 (s, 6H), 0.112 (s, 6H), 0.108 (s, 6H); $^{13}$C NMR 111, 83.5, 7.79, -2.50, -2.62, -5.43, -5.89, -6.27; $^{29}$Si NMR -5.09, -35.49, -39.47, -39.87, -44.29; GC/IR 2956, 2897, 2144, 1404, 1254, 810, 776; GC/MS 328 (M+, 6), 315 (14), 314 (22), 313 (59), 256 (11), 255 (35), 241 (15), 197 (12), 113 (11), 99 (10), 73 (100), 599 (16).

Flow pyrolysis of 132

A mixture of 0.400 g of cyclooctyne 132 (1 mmol) in 2 ml of 2,3-dimethylbutadiene (20 mmol) was pyrolyzed at 520°C in a flow of argon. A yellow pyrolysate was collected. Analysis by GC/IR/MS showed a mixture of four products. The major product was isomer 133 (40% yield) which was separated, along with the starting material, from the other peaks by column chromatography. Isomer 133 was identified by spectra: $^{29}$Si NMR -20.49, -45.54, -49.84; GC/IR 2957, 2898, 1904, 1253, 867, 806, 773; GC/MS 328 (M+, 10), 315 (15), 314 (26), 313 (68), 256 (13), 255 (45), 241 (17), 227 (11), 197 (14), 171 (11), 129 (10), 113 (13), 99 (12), 73 (100), 59 (16); $^{13}$C NMR 209, 58.7 ($^1$H coupled spectrum showed the allene carbon at 58.7 as a triplet). The other products were identified by GC/IR/MS. The second product was cycloheptyne 135 (9% yield) and had the spectra: GC/IR 2957, 2900, 2126, 1405, 1254, 1121, 1025, 820, 776; GC/MS 270 (M+, 14), 256 (21), 255 (71), 227 (17), 211 (11), 197 (33), 113 (12), 99 (13), 73 (100), 59 (17). The third product was exocyclic isomer 134 (5% yield) and had the spectra: GC/IR 2959, 2899, 1907, 1544, 1405, 1252, 1168, 812, 769; GC/MS 270 (M+, 29), 257 (16), 256 (27), 255 (100), 227 (23), 211 (18), 197 (47), 113 (11), 73 (98), 59 (20). The final product was dimethylsilylene trapped adduct 71 (46% yield) and was identified by comparing GC/IR/MS spectra and retention time with an authentic sample.
Synthesis of α,ω-dihydridopolysilanes

Lithium wire, 75 g (10.8 mol), was cut into small pieces and added to 1.5 ml of THF and cooled to 0°C in a three-neck flask equipped with a high-speed motor and an addition funnel. A solution of 600 ml of chlorodimethylsilane (5.5 mol) and 400 ml of dichlorodimethylsilane (3.3 mol) was cooled to 0°C and slowly added to the lithium wire over a period of four hours. After the addition was complete, the solution was allowed to warm to room temperature overnight while stirring. The solution remained a gray color. After three days of stirring, the lithium wire disappeared and 700 ml of pentane was added. The solution was filtered and the solvent was removed by rotavap. The remaining yellow liquid was vacuum distilled through a 12” silver-lined column. Three fractions were collected. The first fraction was 38.1 g (92%) 1,3-dihydridohexamethyltrisilane (70-72°C / 40 mmHg). It was identified by spectra: $^1$H NMR 0.121 (s, 6H), 0.122 (d, 12H, J=4.5 Hz), 3.704 (septet, 2H, J=4.5 Hz); GC/IR 2961, 2903, 2094, 1413, 1254, 880, 839, 799; GC/MS 176 (M+, 6), 161 (13), 118 (16), 117 (77), 116 (98), 101 (25), 73 (100), 59 (36). The second fraction was 50.6 g (92%) 1,4-dihydridooctamethyltetrasilane (75-80°C / 5 mmHg). It was identified by spectra: $^1$H NMR 0.119 (s, 12H), 0.121 (d, 12H, J=4.5 Hz), 3.71 (septet, 2H, J=4.5 Hz); GC/IR 2959, 2901, 2092, 1410, 1253, 881, 837, 787; GC/MS 234 (M+, 15), 219 (11), 176 (19), 175 (77), 174 (50), 173 (27), 159 (25), 145 (15), 131 (16), 117 (45), 116 (83), 115 (20), 101 (43), 99 (13), 73 (100), 59 (34). The third fraction was 40.3 g (87%) 1,5-dihydridodecamethylpentasilane (82-84°C / 0.45 mmHg). It was identified by spectra: $^1$H NMR 0.148 (d, 12H, J=4.5 Hz), 0.155 (s, 18H0, 3.75 (septet, 2H, J=4.5 Hz); GC/IR 2959, 2901, 2090, 1409, 1253, 881, 837, 780; GC/MS 235 (18), 234 (30), 233 (M+-59, 100), 203 (11), 175 (32), 173 (20), 159 (51), 116 (28), 101 (19), 73 (69), 59 (22). The solution remaining was a mixture of α,ω-dihydridopolysilanes containing six to nine linear silicon atoms.
Synthesis of α,ω-dichloropolysilanes

The general procedure for converting hydridosilanes to chlorosilanes involves dissolving the hydridosilane in carbon tetrachloride and adding a catalytic amount of benzoyl peroxide. The solution is refluxed overnight and the carbon tetrachloride is removed by rotavap. A yellow oil is usually obtained in quantitative yields. The α,ω-dichloropolysilanes were identified by their spectra: 1,4-dichlorooctamethyltetrasilane, GC/IR 2963, 2902, 1917, 1405, 1257, 839, 782; GC/MS 289 (1.5), 287 (M+15, 1.8), 211 (36), 210 (18), 209 (84), 131 (60), 116 (21), 73 (100), 59 (13); 1,5-dichlorodecamethylpentasilane, GC/IR 2961, 2901, 1405, 1255, 838, 777; GC/MS 347 (5), 345 (M+15, 6), 270 (12), 269 (48), 268 (29), 267 (100), 211 (42), 210 (22), 209 (98), 173 (12), 159 (13), 131 (48), 116 (26), 73 (96), 59 (11).

Synthesis of cycloheptyne 135

A mechanical stirrer was fitted to a three-neck 100 ml round-bottom flask. A solution of 0.05 g of mercuric chloride and 0.8 g of magnesium turnings (32 mmol) in 50 ml of ether was prepared. The solution was stirred for about 30 minutes at room temperature and cooled to 0°C. About 0.3 ml of propargyl bromide was added and the solution became cloudy. After the addition of a total of 3.9 g of propargyl bromide (32 mmol), the solution was gray with magnesium turnings still present. The solution was stirred for another two hours until very little of the magnesium remained. A 20 ml solution of 1.6M n-butyllithium (32 mmol) was added at 0°C and the solution turned a light gray. It stirred for three hours at room temperature. The solution became yellow and contained a suspended white solid. The solution was cooled to 0°C and 9.9 g of 1,4-dichlorooctamethyltetrasilane (32 mmol) was added slowly. The solution turned orange after stirring overnight at room temperature. The solution was washed with acidic water several times and dried over sodium sulfate. The
solvent was removed by rotavap leaving 12.2 g of a brown liquid containing 57% cycloheptyne 135 (81% crude yield). It was purified as needed by column chromatography. Cycloheptyne 135 was identified by spectra: \(^1\)H NMR 1.63 (s, 2H), 0.146 (s, 6H), 0.176 (s, 12H), 0.197 (s, 6H); \(^{13}\)C NMR 111, 88.3, 7.93, -2.69, -2.72, -6.00, -7.01; GC/IR 2957, 2900, 2126, 1405, 1254, 1121, 1025, 820, 776; GC/MS 270 (M\(^+\)), 256 (21), 255 (71), 227 (17), 211 (11), 197 (33), 113 (12), 99 (13), 73 (100), 59 (17).\( \text{C}_{11}\text{H}_{26}\text{Si}_4 \) measured m/z 270.11043, calculated 270.11117.

**Flow pyrolysis of cycloheptyne 135**

A mixture of 0.314 g of cycloheptyne 135 in 2.5 ml of hexanes was pyrolyzed at 520°C in a flow of argon. A yellow pyrolysate was collected and analyzed by GC/IR/MS. The major product was exocyclic allene 134 (42% yield) and was identified by matching the spectra with those already obtained in the pyrolysis of cyclooctyne 132. Additional spectra was obtained by \(^{29}\)Si NMR -15.67, -46.03. A second isomer 139 (8% yield) was also formed, but was not characterized.

**Synthesis of propargyldisilane 142\(^{25}\)**

A solution of 0.05 g of mercuric chloride and 1.2 g of magnesium turnings (50 mmol) in 20 ml of diethyl ether was stirred for thirty minutes at room temperature and cooled to 0°C. A small amount of propargyl bromide was added in one portion to start the formation of the Grignard. The remaining propargyl bromide was slowly added over an hour. A total of 7.4 g of propargyl bromide (50 mmol) was added. The solution was stirred until very little magnesium was left and chloropentamethylsilane was slowly added at 0°C. The solution was washed several times with water and dried over sodium sulfate. The solvent was removed by rotavap leaving 6.90 g of a yellow oil containing
74% of a 4:1 ratio of propargyl:allenyl disilane (60% crude yield). The product was purified as needed by preparative GC (5 ft. column, 100°C col. temp.). The isomers were identified by spectra: Propargyl isomer 142: $^1$H NMR 1.799 (t, 1H, J=0.9 Hz), 1.490 (d, 2H, J=0.9 Hz), 0.107 (s, 6H), 0.088 (s, 9H); $^{13}$C NMR 82.8, 79.2, 4.67, -2.139, -4.418; Allenyl isomer 143: $^1$H NMR 4.838 (t, 1H, J=6.9 Hz), 4.259 (d, 2H, J=6.9 Hz), $^{13}$C NMR 212, 67.0, 66.7, -2.331, -3.834.

FVP of propargylsilane 142

A flash vacuum pyrolysis of 0.295 g of the 4:1 mixture of propargylsilane 142: allenylsilane 143 at 650°C resulted in almost complete isomerization upon analysis by GC/IR/MS to the allenylsilane 143 with 100% mass recovery. The pyrolysate was pyrolyzed at 700°C and resulted in 30% decomposition and a mass recovery of 76%. The products were analyzed by GC/IR/MS. The major product was a 1,1,3-trimethyl-1,3-disilacyclobutane (7%) and identified by spectra: GC/IR 2964, 2908, 2123, 1356, 1258, 946, 888, 832; GC/MS 130 (M+, 43), 116 (14), 115 (100), 73 (54), 59 (19). Three other products were not resolved in the trace but were identified as the dimethylsilylene dimers and trimethylsilyllallene, 144 (10%). The dimethylsilylene dimers separated but the trimethylsilyllallene overlapped both of them. The dimers were identified by an IR absorbance at 2141 and 2182 which matched authentic samples. The IR also showed an absorbance at 1931 which was assigned to the trimethylsilyllallene, 144. The mass spectrum had a peak at 114 which was assigned to the dimers and 112 which was assigned to the allene.

Flow pyrolysis of propargylsilane 141

A sample of propargylsilane 141 was prepared by a previous group member. A
mixture of 0.050 g of propargylsilane 141 in 1 ml of hexanes was pyrolyzed at 520°C in a flow of argon. The pyrolysate was analyzed by GC/IR/MS. Only a small amount of allenyl isomer 141i was observed in the trace.

**Attempted synthesis of cycloheptyne 135**

A synthesis of cycloheptyne 135 from allene was attempted but was not successful. Instead of cycloheptyne 135 being synthesized, two bicyclic isomers were obtained. Allene was bubbled through a solution of 10 mmol n-butyl lithium in THF at -30°C for 30 minutes. The solution was allowed to warm to room temperature while stirring. The solution became white and argon was bubbled through the solution for another hour. The solution was cooled to -30°C again and one more equivalent of n-butyl lithium was added. The solution was warmed again and turned a tan color. The 1,4-dichlorooctamethyl-tetrasilane (5.6 g, 18 mmol) was slowly added at -40°C and the solution turned a dark brown color. The solution was allowed to warm to room temperature while stirring for an hour. The solution was washed several times with water and dried over sodium sulfate. The solvent was removed by rotavap leaving a brown oily liquid. It was purified by column chromatography to obtain 1.21 g of a 1:1 mixture of bicyclic isomers 147 and 148 (26% yield). The fused-bicyclic isomer, 147, was crystallized out of solution by adding hexane. Clear needle-like crystals were obtained with a melting point range of 195-200°C. Allene 147 was identified by spectra: $^1$H NMR 0.224 (s, 12H), 0.171 (s, 12H), 0.161 (s, 12H), 0.095 (s, 12H); $^{13}$C NMR 206, 62.1, 0.550, -1.21, -5.20, -7.16; $^{29}$Si NMR -17.05, -40.33; GC/IR 2955, 2896, 1852, 1402, 1253, 890, 841, 809; GC/MS 500 ($M^+$, 12), 428 (10), 427 (21), 155 (11), 73 (100). $C_{14}H_{48}Si_8$ measured m/z 500.19046, calculated 500.19103. An X-ray crystal structure was also determined. The isomer 148 was identified by spectra: $^1$H NMR 0.153 (s, 24H), 0.128 (s, 24H); $^{13}$C NMR 198, 62.7,
Flow pyrolysis of bicyclic 147

A solution of 0.022 g of bicyclic 147 in 1 ml of hexanes was pyrolyzed at 520°C in a flow of argon. Another 1 ml of hexanes was used to clean the column. A clear pyrolysate was collected and analyzed on the GC/IR/MS. The solution now contained a 1:5 mixture of isomers 147:148. The isomer was the only product observed. The pyrolysate was pyrolyzed at 520°C and another 1 ml of hexanes washed the column. Now the ratio was 1:9 upon analysis by the GC/IR/MS. The products were identified by matching spectra with authentic samples.

Synthesis of bicyclic 147

A solution of 0.75 ml of 2.5M n-butyl lithium (2 mmol) in hexanes was slowly added to 0.16 g of cycloheptyne (0.6 mmol) in 25 ml of ether at -78°C. The solution turned yellow. Upon warming to room temperature, the solution turned orange. After an hour of stirring, an aliquot was taken and quenched with trimethylchlorosilane. The major peak was from a quenched dianion. The solution was cooled to -78°C and 0.3 g of 1,4-dichlorooctamethyltetrasilane (1 mmol) was slowly added. The solution turned brown. A solid formed when the solution was allowed to warm to room temperature. After two hours the solution was washed three times with water after adding hexanes and dried over sodium sulfate. The solvent was removed by rotavap leaving 0.46 g of a brown oil containing 20% bicyclic 147 (20% crude yield). The product was purified by column chromatography. Allene 147 was identified by matching spectra with an authentic sample.
Photolysis of bicyclic 147

A solution of 4 mg of bicyclic 147 in 2 ml of hexanes was degassed by bubbling argon through the solution for 20 minutes. A couple of drops of diethylsilane was added, and a balloon filled with argon was attached to the quartz tube. The solution was irradiated with a medium-pressure mercury Hanovia lamp for 450 minutes. Analysis by GC/IR/MS showed that a small amount of dimethylsilylene was trapped by the diethylsilane, but there were no other peaks in the trace other than the starting material.

Flow pyrolysis of cyclic allene 159

A sample of cyclic allene 159 was obtained from a group member. A solution of 0.044 g of cyclic allene 159 in 1 ml of hexanes was pyrolyzed at 550°C in a flow of argon. A clear pyrolysate was obtained and analyzed by GC/IR/MS. The major product was exocyclic isomer 160 (88%) and identified by spectra: GC/IR 2959, 2899, 1864, 1404, 1255, 893, 846, 810; GC/MS 414 (M+, 35), 399 (14), 343 (18), 342 (30), 341 (77), 283 (18), 229 (15), 185 (13), 171 (35),73 (100), 45 (19). The other product was cyclic allene 161 (12%) and was identified by spectra: GC/IR 2960, 2901, 1841, 1403, 1255, 1044, 886, 843; GC/MS 356 (M+, 20), 341 (19), 284 (34), 283 (100), 201 (10), 185 (10), 171 (22), 73 (60), 45 (11), 32 (54). This spectra was matched with an authentic sample.

Flow pyrolysis of cyclic allene 161

A sample of cyclic allene 161 was obtained from a group member. A solution of 0.275 g of cyclic allene 161 in 1 ml of hexanes was pyrolyzed at 520°C in a flow of argon. Analysis of the pyrolysate by GC/IR/MS showed no isomerization or decomposition.


27. Unpublished results of Yi Pang, Iowa State University.
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