

1987

# Mechanistic and kinetic investigations of thermally-induced [alpha]- and [beta]-eliminations of alkoxy silanes

Sukhamaya Bain  
Iowa State University

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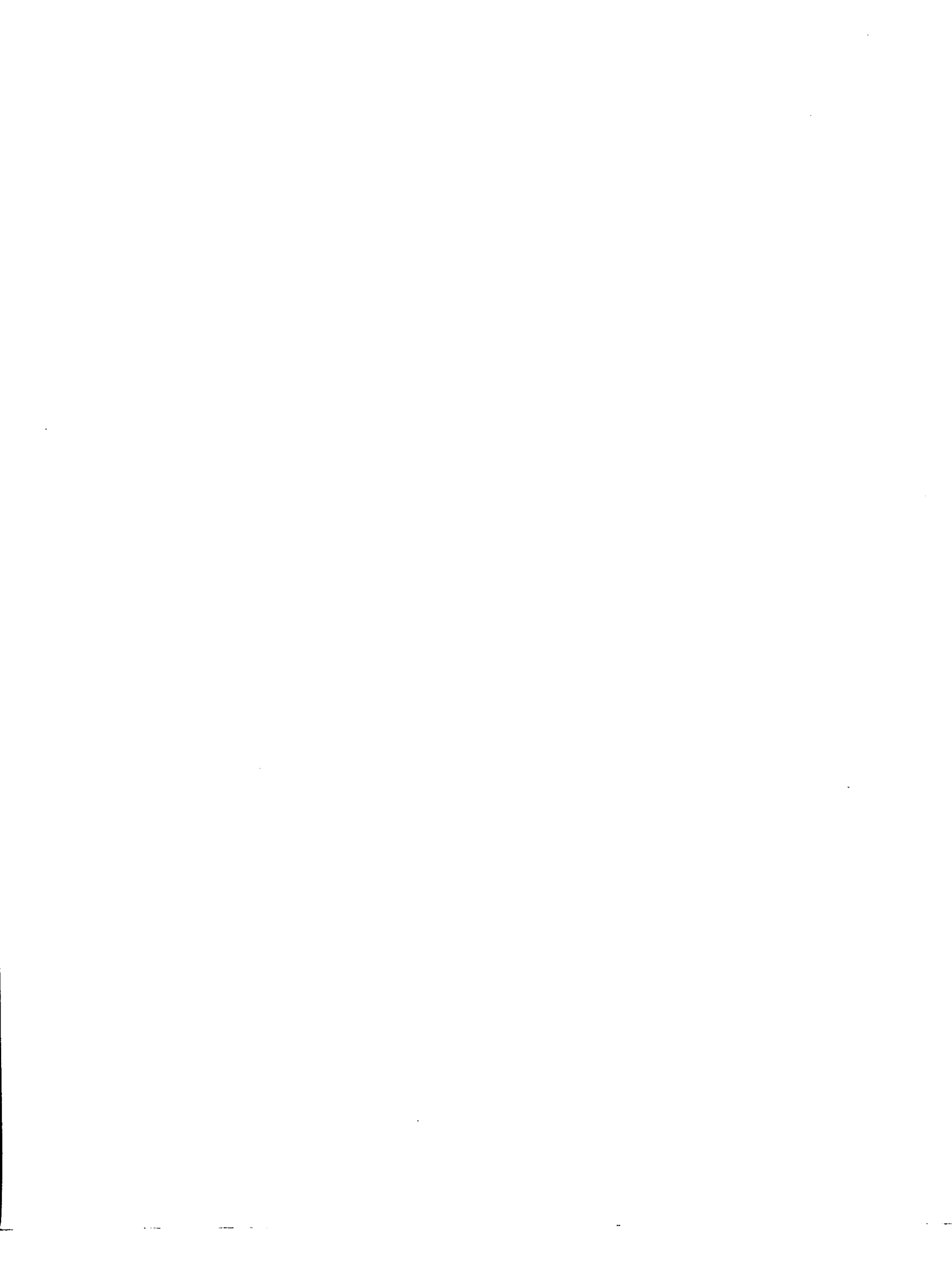
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**Mechanistic and kinetic investigations of thermally-induced  $\alpha$ -  
and  $\beta$ -eliminations of alkoxy silanes**

Bain, Sukhamaya, Ph.D.

Iowa State University, 1987

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Mechanistic and kinetic investigations of  
thermally-induced  $\alpha$ - and  $\beta$ -eliminations of alkoxysilanes

by

Sukhamaya Bain

A Dissertation Submitted to the  
Graduate Faculty in Partial Fulfillment of the  
Requirements for the Degree of  
DOCTOR OF PHILOSOPHY

Department: Chemistry  
Major: Organic Chemistry

Approved:

Signature was redacted for privacy.

~~In Charge of~~ Major Work

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For the Major Department

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For the Graduate College

Iowa State University  
Ames, Iowa

1987

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DEDICATION

To My Parents

Sreemati Laxmidevi Bain and Sree Phanindra Nath Bain



## I. INTRODUCTION

Since the discovery of  $\beta$ -elimination of oxidosilanes by Whitmore et al.<sup>1</sup> in 1947, this class of reactions, known as Peterson olefination,<sup>2</sup> has found numerous applications in organic synthesis. Fluoride ion<sup>3</sup> and high temperature conditions<sup>4,5</sup> have been employed for inducing  $\alpha$ - and  $\beta$ -eliminations of SiX (where X is an electronegative group) to generate carbenes and olefins respectively. Thermally induced  $\alpha$ - and  $\beta$ -eliminations of alkoxysilanes, to generate silylenes<sup>6</sup> and silenes<sup>7</sup> respectively, are two important reactions in the chemistry of organo-silicon reactive intermediates.

This dissertation will describe the scope and limitations of thermally induced  $\alpha$ - and  $\beta$ -eliminations of alkoxysilanes to generate carbenes, olefins, and silenes. Allenes have been generated by  $\beta$ -eliminations of hexamethyldisiloxane. An attempt to generate 1,1-dimethyl-1-silaallene from (1-trimethylsilyl)vinyl dimethylmethoxy-silane has led to the discovery that decomposition of vinyl dimethyl-alkoxysilanes generate dimethylsilanone via an unprecedented 1,5-migration of hydrogen. Dimethylsilanone has also been generated via retro-ene decompositions of allyloxydimethylsilanes. (1-Methoxy-ethenyl)pentamethyldisilane and (1-methoxyalkyl)pentamethyldisilanes have been found to extrude methoxypentamethyldisilane via an entropically favored  $\alpha$ -elimination to generate carbenes rather than extruding methoxytrimethylsilane via a thermodynamically favored  $\beta$ -elimination to generate silenes.

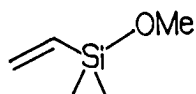
## II. NOMENCLATURE

The nomenclature used in this dissertation will, with the exceptions described below, follow the conventions set down by IUPAC.<sup>8</sup> Divalent silicon species will be named as derivatives of the parent silylene ( $:\text{SiH}_2$ ). Simple organosilicon compounds will be named as derivatives of silane ( $\text{SiH}_4$ ), while more complicated linear and cyclic systems will be named as sila-analogs of the corresponding carbon systems.

Examples:



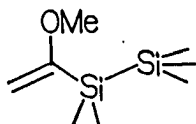
dimethylchlorosilane



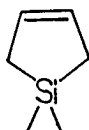
vinyltrimethylmethoxysilane



methoxytrimethylpentamethyldisilane



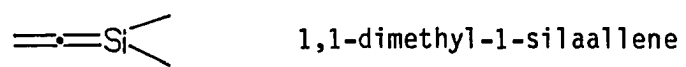
(1-methoxyethenyl)pentamethyldisilane



1,1-dimethyl-1-silacyclopent-3-ene

When referring to the general class of compounds containing isolated silicon-carbon double bonds, the term silene will be used. Compounds containing silicon in the  $\pi$ -framework of the 1,2-diene system will be named as derivatives of silaallenes.

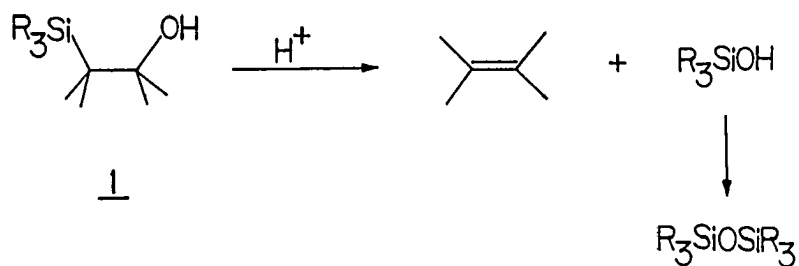
Examples:



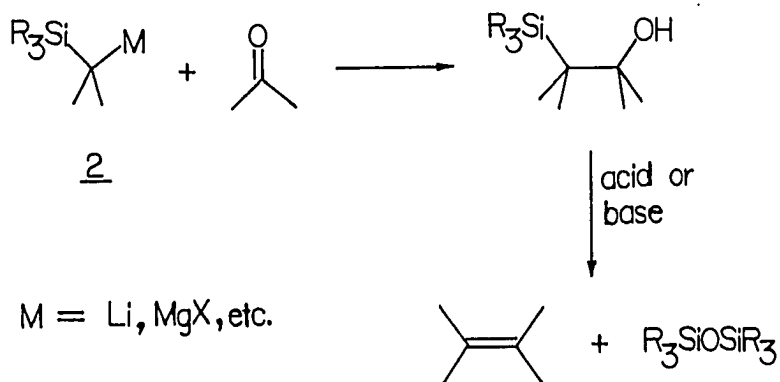
## III. HISTORICAL

A.  $\alpha$ - and  $\beta$ -Eliminations of SiX

Generation of unsaturated carbon and silicon compounds by  $\alpha$ - and  $\beta$ -eliminations of SiX (where X is an electronegative group) will be discussed in this section. In 1947, Whitmore et al.<sup>1</sup> discovered that  $\beta$ -hydroxysilanes underwent rapid conversion to olefins in presence of a catalytic amount of an acid.

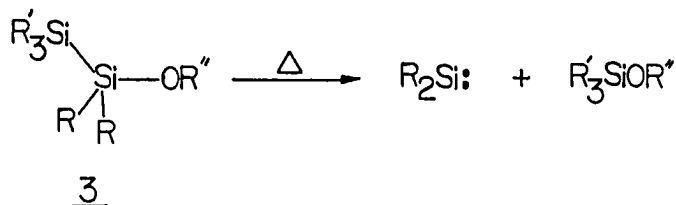


Easy accessibility to systems such as 1 via reactions of carbonyl compounds with  $\alpha$ -silyl organometallic species has made this elimination versatile<sup>2,9a-12</sup> for the synthesis of olefins.

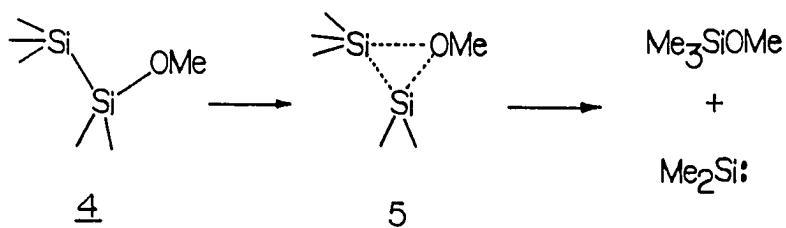


This type of  $\beta$ -elimination of oxidosilanes, known as Peterson olefination,<sup>8</sup> will not be discussed in any further details, as that would be beyond the scope of the subject matter of this dissertation.

Thermally-induced  $\alpha$ -elimination of alkoxy silanes from alkoxydisilanes has been one of the most widely used techniques for the generation of silylenes.<sup>6,13-15</sup> Discoverers of this technique, Atwell and Weyenberg,<sup>16</sup> also found that disilanes containing at least one alkoxy, halogen or hydrogen attached to silicon underwent thermal decomposition to generate silylenes.



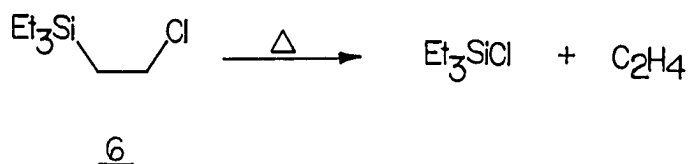
Davidson et al.<sup>17</sup> recently reported the kinetics of decomposition of several methoxydisilanes. The preexponential factors ( $\log A$ ) for these decompositions were approximately 12.5, suggesting silylene generation to involve three-centered transition states.<sup>18</sup> Generation of silylenes



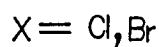
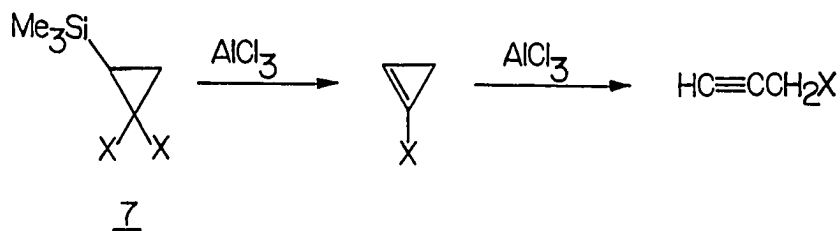
will not be discussed in any further details, rather the focus of discussion will be 1) generation of olefins by  $\beta$ -elimination of SiX, where X is not the OH of the conventional Peterson olefination, 2) generation of carbenes by  $\alpha$ -elimination of SiX, and 3) generation of silenes by  $\beta$ -elimination of SiX.

### 1. Generation of olefins

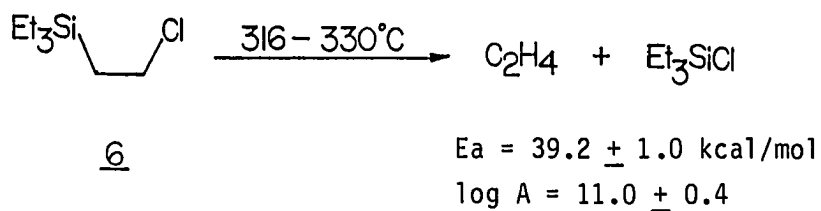
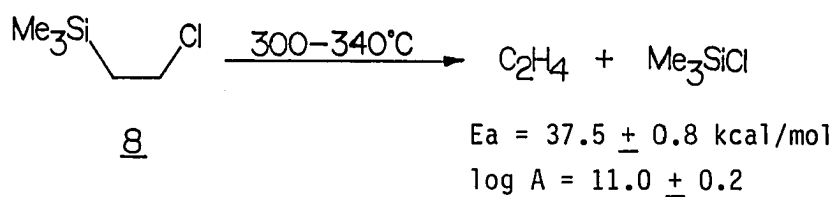
The lability of  $\beta$ -halosilanes toward elimination to form olefins and halosilanes has been known<sup>19-21</sup> for a long time. However, due to lack of efficient synthetic routes to the starting  $\beta$ -halosilanes, this reaction has not found versatile application in olefin synthesis. Sommer et al.<sup>4</sup> found that (2-chloroethyl)triethylsilane 6, when refluxed at atmospheric pressure, generated triethylchlorosilane and ethylene quantitatively.



$\beta$ -Eliminations of halosilanes from systems such as 6 have also been induced by Lewis acids,<sup>4</sup> Grignard reagents,<sup>22</sup> and alkoxides.<sup>23</sup> Seyferth and Julia<sup>24</sup> generated cyclopropenes via aluminum chloride induced eliminations of halosilanes from ( $\beta$ -halo)trimethylsilylcyclopropanes.

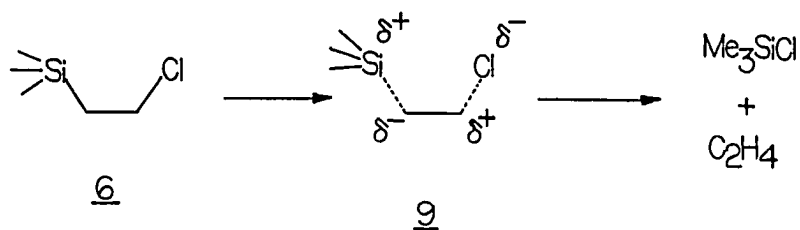


Davidson et al.<sup>25</sup> studied the kinetics of gas-phase thermal decomposition of (2-chloroethyl)trimethylsilane 8 and (2-chloroethyl)-triethylsilane 6. The decomposition rates for 6 and 8 were found to be

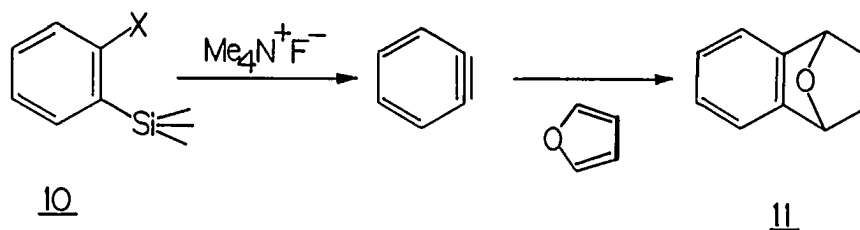


insensitive to surface to volume ratio and to added nitric oxide, indicating unimolecular reaction. Based on these Arrhenius parameters, obtained in such low temperature ranges, the authors suggested that the

decompositions of 6 and 8 involved four-centered transition states with some charge separation<sup>26</sup> as shown below.



Fluoride ion is well known to have high affinity towards silicon, and carbon-silicon bonds can be cleaved under very mild conditions by alkali-metal fluorides and tetraalkylammonium fluorides. Cunico and Dexheimer<sup>3,27</sup> first utilized this technique to synthesize acetylenes from both cis and trans 2-chloro silyl olefins. Benzyne was generated from ortho substituted trimethylsilylbenzenes.<sup>27</sup>

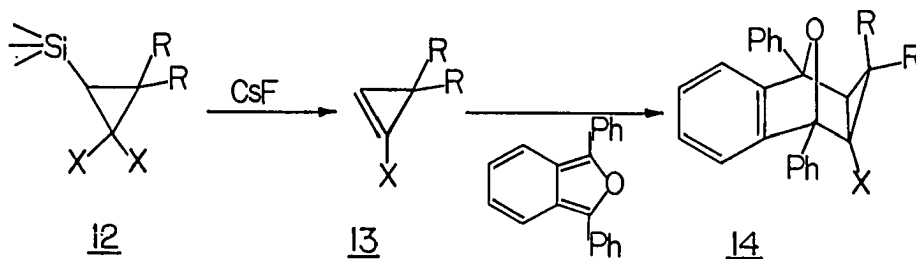


X = Cl, Br, OTs

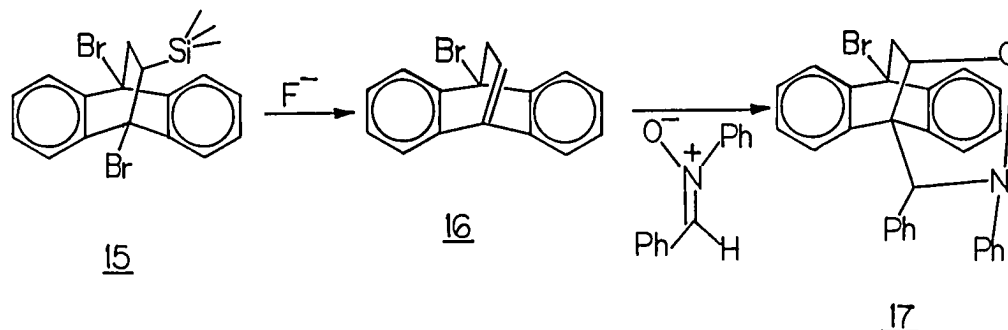
This mild technique to generate reactive olefins was utilized by several groups to generate cyclopropenes,<sup>28</sup> an anti-Bredt olefin,<sup>29</sup> and methylenecycloalkanes.<sup>30</sup> Chan and Massuda<sup>28</sup> were able to isolate or



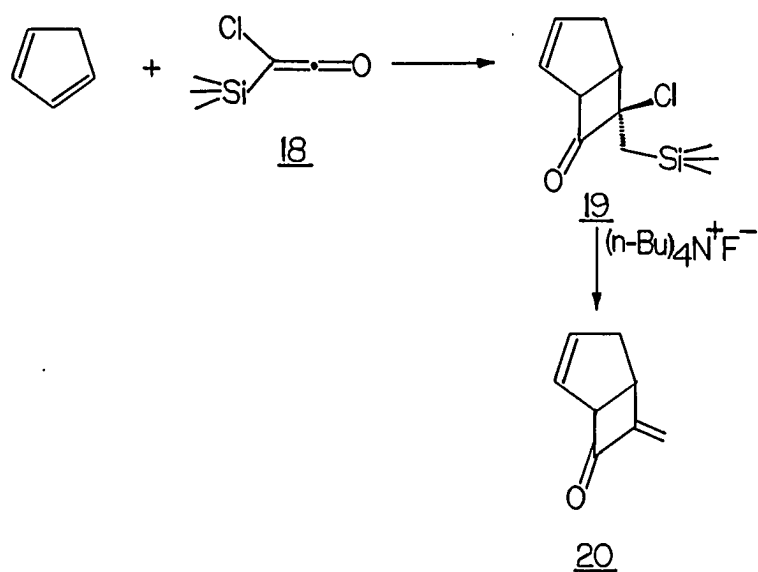
trap a variety of halogenocyclopropenes via fluoride-induced  $\beta$ -elimination of halosilanes.



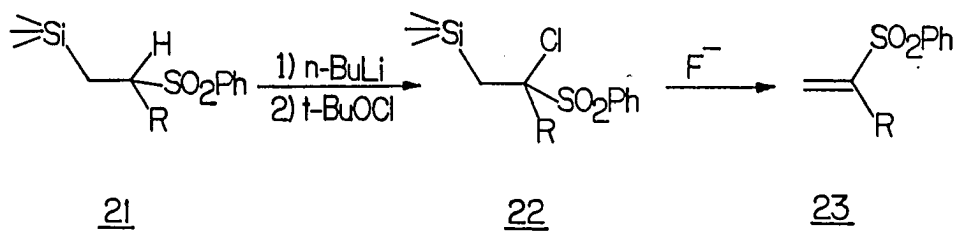
Chan and Massuda<sup>29</sup> also took advantage of this non acidic and non-basic conditions to generate bridgehead olefin **16**.



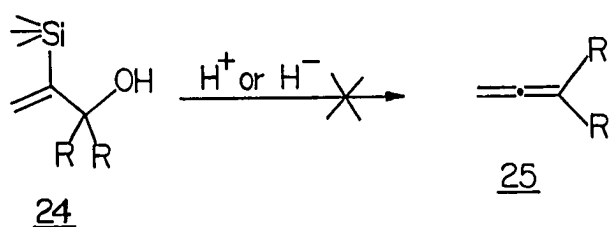
Paquette et al.<sup>30</sup> synthesized a variety of  $\alpha$ -methylene cyclic ketones via  $\beta$ -elimination of halosilanes.



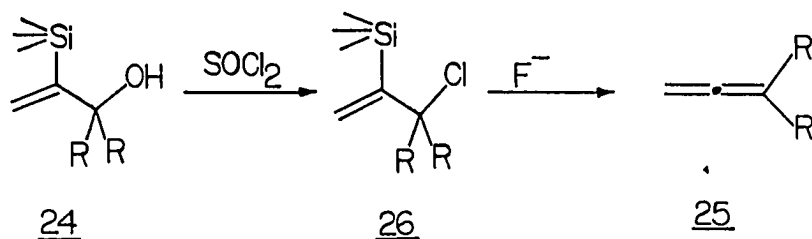
A variety of synthetically useful vinyl sulfones were synthesized by Hsiao and Shechter.<sup>31</sup>



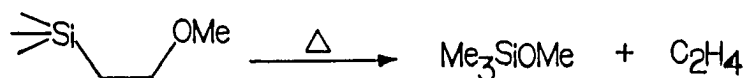
Chan et al.<sup>32,33</sup> were the first to try to generate allenes via Peterson reaction of alcohols 24. The alcohols 24 were found to be



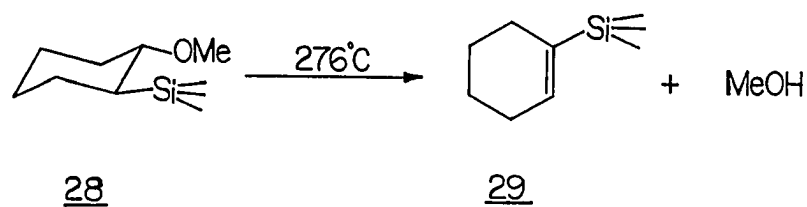
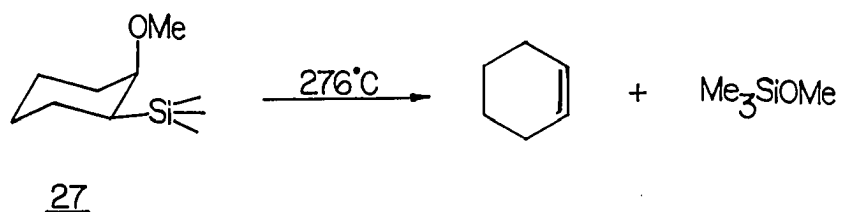
highly stable toward acids and bases, and did not generate allenes. Conversion of the alcohols to chloro compounds followed by fluoride induced elimination, however, led to smooth conversion to allenes.



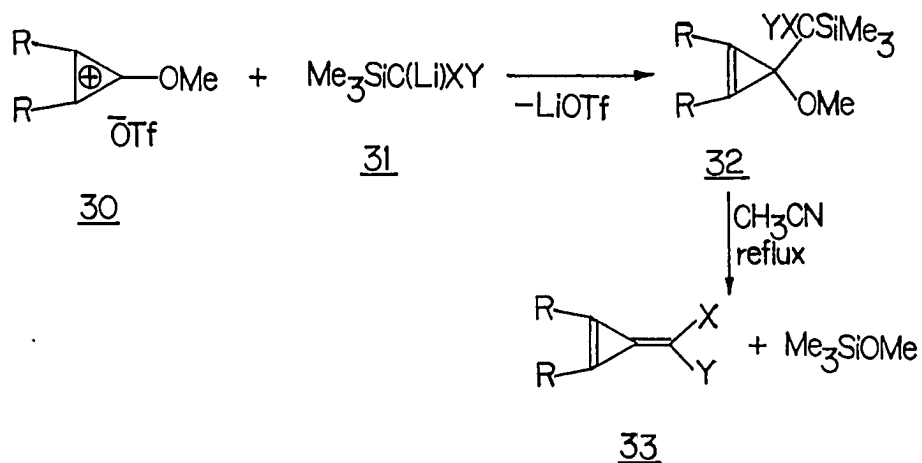
Relatively little work has been done on the  $\beta$ -elimination of alkoxy-silanes to generate olefins. This is most likely due to easier accessibility to olefins via a very similar technique, viz., Peterson olefination. In 1969, Musker and Larson<sup>34</sup> reported that (2-methoxyethyl)trimethylsilane underwent clean decomposition to ethylene and methoxytrimethylsilane, when heated to 276°C.



These authors also demonstrated that this reaction was a four-centered syn-elimination process. Thus (cis-2-methoxy)trimethylsilylcyclohexane 27 decomposed cleanly to cyclohexene and methoxytrimethylsilane, whereas the major process for the decomposition of (trans-2-methoxy)trimethylsilylcyclohexane 28 was found to be elimination of methanol to form 1-trimethylsilylcyclohexene 29.

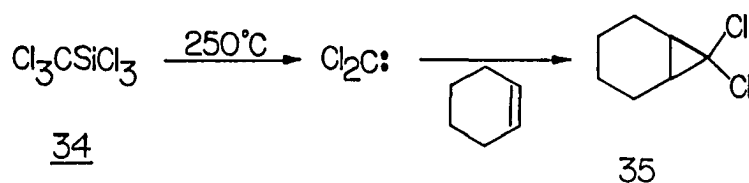


A variety of triafulvenes,<sup>35</sup> a class of theoretically interesting compounds, were synthesized by Schubert and Stang<sup>36</sup> under very mild conditions.

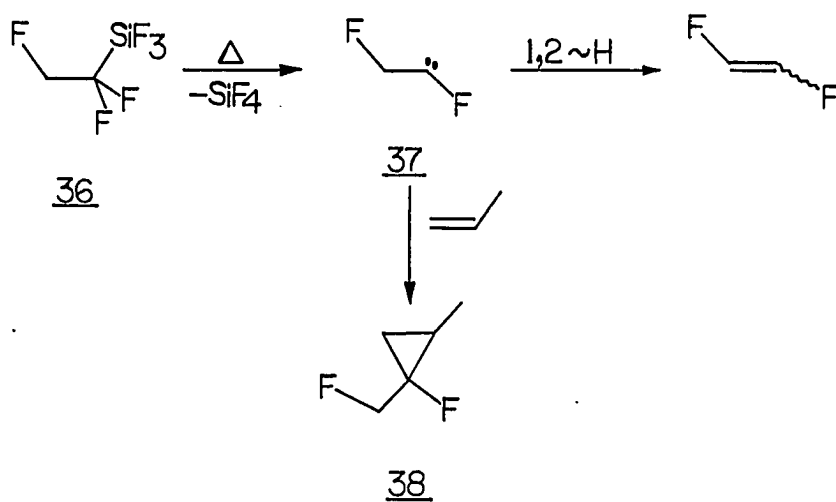


## 2. Generation of carbenes

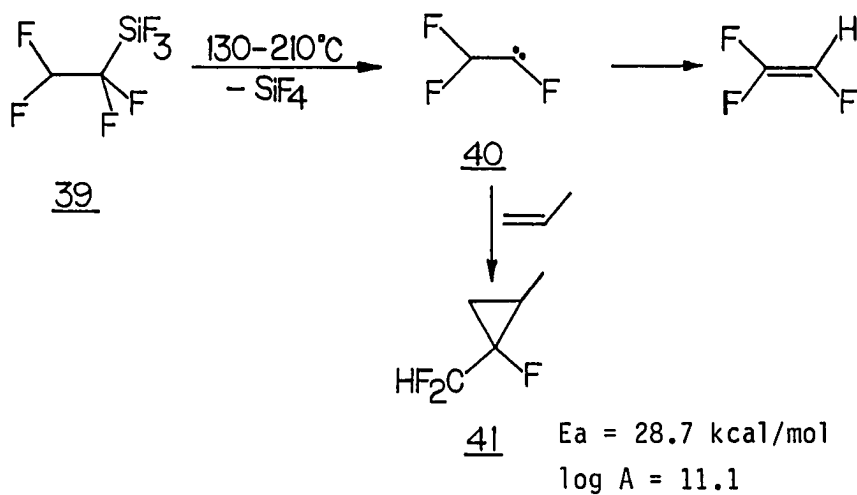
An extensive investigation of thermal decomposition of polyhalo- and perhalo-alkylsilanes by Haszeldine and his coworkers<sup>5,37-41</sup> led to the discovery that carbenes could be generated by thermally induced  $\alpha$ -elimination of halosilanes. Thus, thermolysis of (trichloromethyl)trichlorosilane 34 generated dichlorocarbene, which was trapped by cyclohexene.<sup>5</sup>

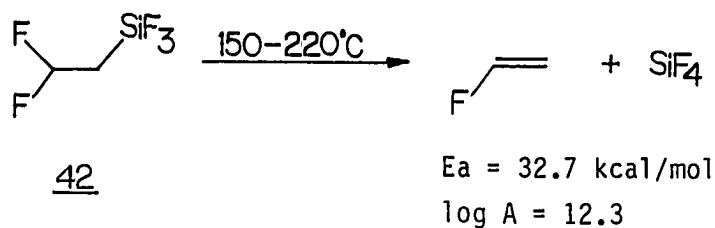


Formation of 1,2-difluoroethene from 36 was explained by the formation of carbene 37 followed by a 1,2-migration of hydrogen.<sup>38</sup>

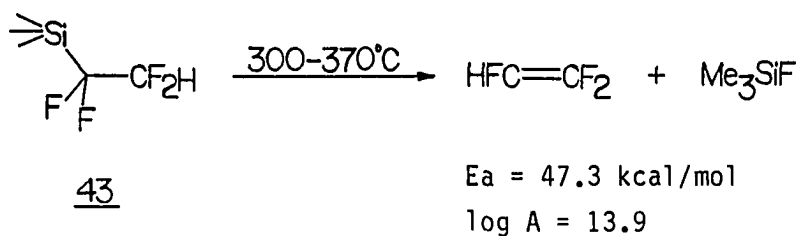


In an earlier kinetic investigation on the gas-phase thermal decomposition of 39 and 42, the Haszeldine group<sup>39</sup> found that the decompositions were first order with respect to substrate. However,

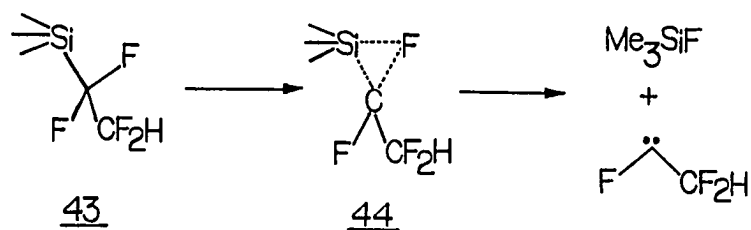




the low pre-exponential factor for the decomposition of 39 as compared to 42 suggests complex nature of at least one of these reactions, since a three-centered transition state is geometrically more favorable than a four-centered transition state. Two more recent reports by Haszeldine et al., however, disputed the earlier findings for 39. Reinvestigation<sup>40</sup> of the kinetics of decomposition of 39 in the temperature range of 140-200°C gave an activation energy of 32.9 kcal/mol, and an A-factor of  $\log A = 13.1$ . Replacement of the trifluorosilyl group by a trimethylsilyl group<sup>41</sup> increases the activation energy considerably, suggesting strengthening of the silicon-carbon bond by groups that donate electron density to silicon.

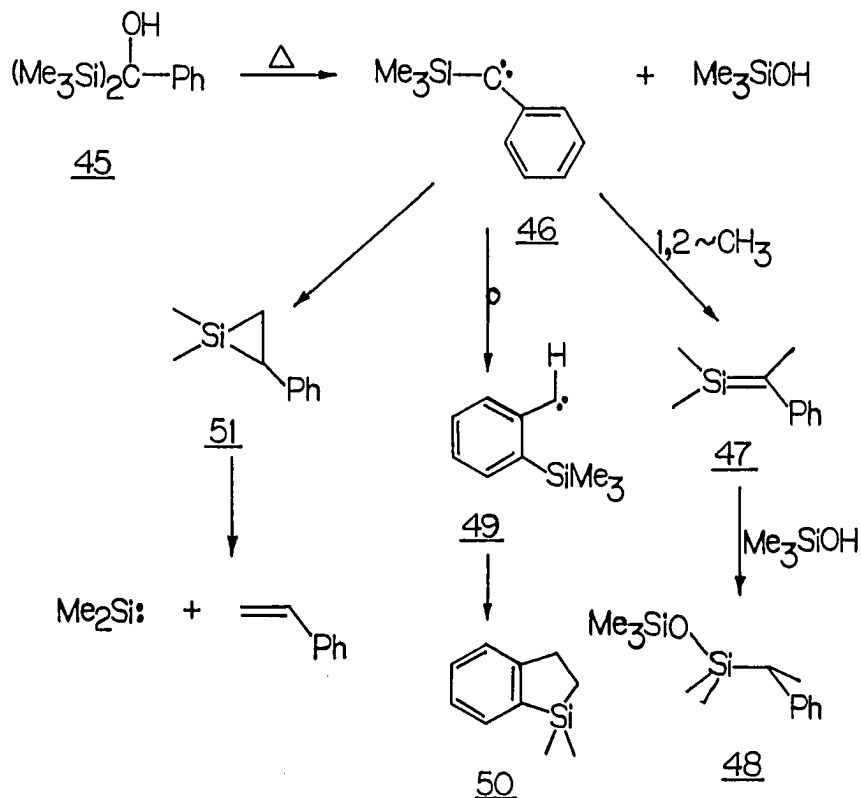


Based on these revised kinetic results, the authors suggested concerted three-centered transition states for the decomposition of 39 and 43.



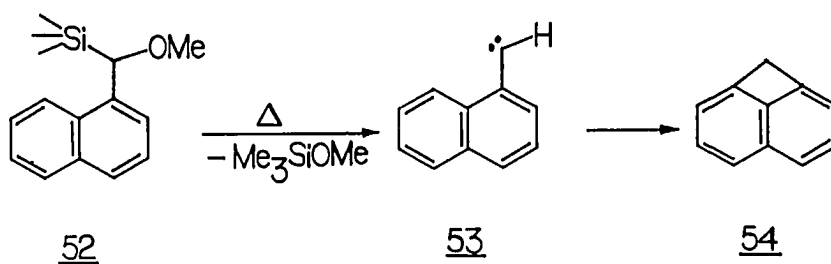
These results of Haszeldine et al. and the results of Davidson et al.<sup>25</sup> (vide infra) suggest that  $\alpha$ -elimination of halosilanes has an entropic favor (larger A-factor) over  $\beta$ -elimination of halosilanes.

Sekiguchi and Ando found that  $\alpha$ -elimination of silanols from 1,1-bis(trimethylsilyl)-1-alkanols such as 45 cleanly generated silylcarbenes under pyrolytic conditions.

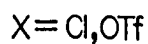
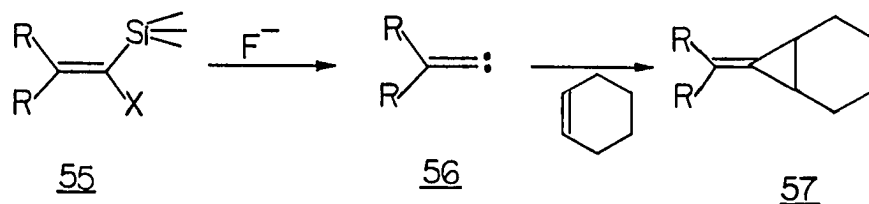




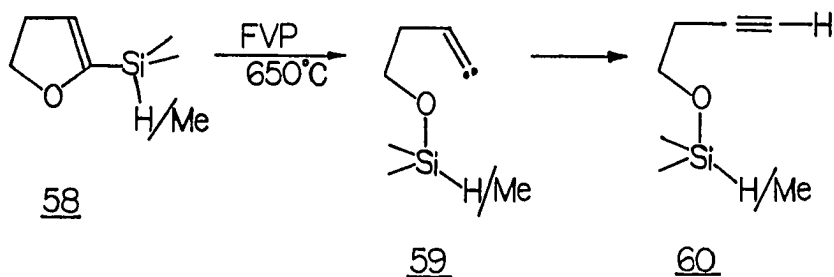
A variety of peri-methanoarenes were conveniently generated by Engler and Shechter<sup>43</sup> via thermally induced  $\alpha$ -elimination of methoxytrimethylsilane.



Strong affinity of fluoride ion toward silicon has been utilized by Cunico and Hans<sup>44</sup> for the generation of vinylidenes from ( $\alpha$ -halo)vinylsilanes. Stang and Fox<sup>45</sup> induced  $\alpha$ -elimination of silyltriflate by fluoride ion.

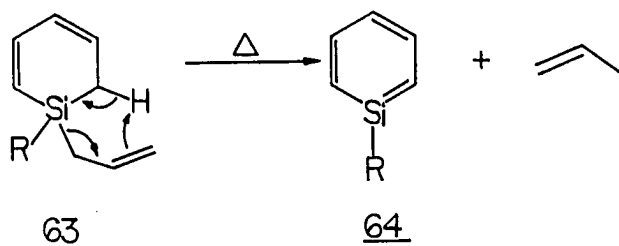
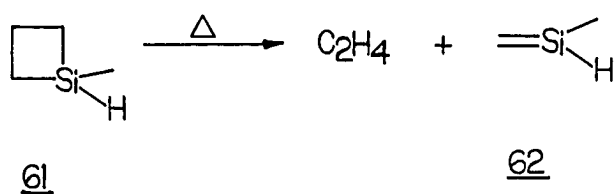


Vinylidines have also been generated under high temperature conditions. Thus, Barton and Groh<sup>46,47</sup> obtained acetylenes 60 from dihydrofurans 58 in good yields.

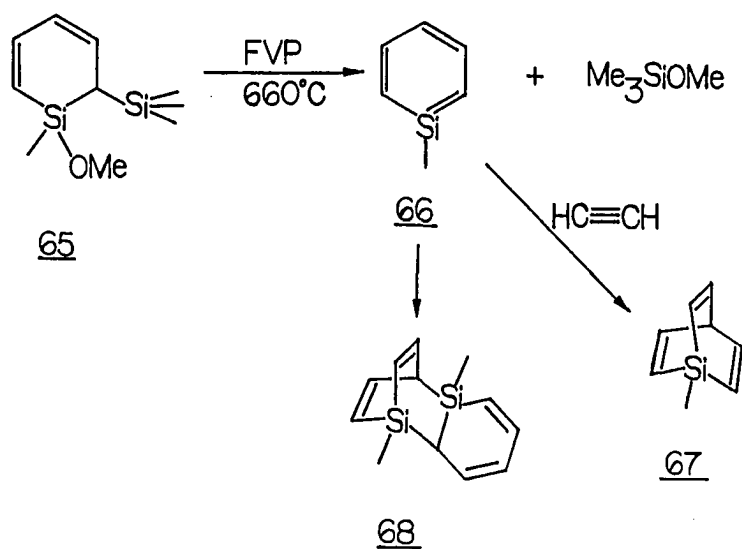


### 3. Generation of silenes

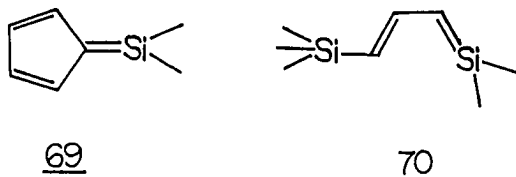
By far the most common routes to generating silenes have been thermal decomposition of silacyclobutanes, and retro-ene elimination of propene from allylsilanes.<sup>48-50</sup>  $\beta$ -Elimination of alkoxy-silanes to



generate silenes, first realized by Nametkin et al.,<sup>51</sup> has been found to be an efficient technique by Barton et al.<sup>7,52,53</sup> Thus, 1-silatoluene was conveniently generated by elimination of methoxytrimethylsilane from compound 65.<sup>53</sup>



Among other interesting silenes, generated using this technique were silafulvene **69**,<sup>7</sup> and silabutadiene **70**.<sup>52</sup>



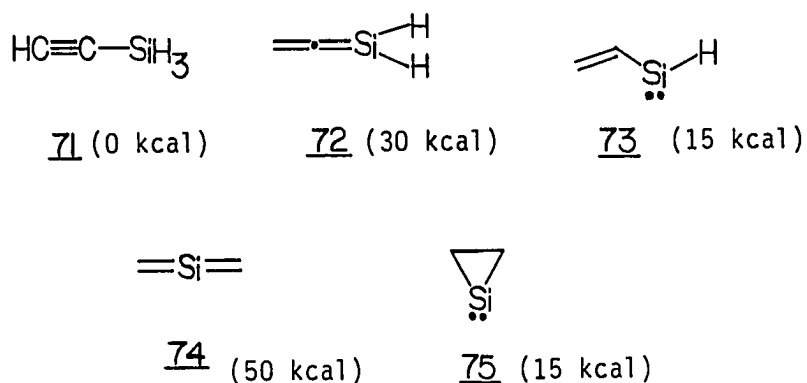
No kinetic investigation on the generation of silenes via  $\beta$ -elimination of alkoxy silanes has been found in the literature.

### B. Silaallenes

Since the pioneering work by Gusel'nikov and Flowers<sup>48</sup> presented evidence for the generation of a silicon-carbon double bond upon pyrolysis of 1,1-dimethylsilacyclobutane, a large volume of research has been done on this subject.<sup>49,50,54,55</sup> Several silenes have been

isolated and characterized.<sup>56-59</sup> A natural extension to this concept, generation of cumulated double bonds containing silicon has attracted attention of both theoreticians and experimentalists. However, the chemistry of silallenes is still in the infancy.

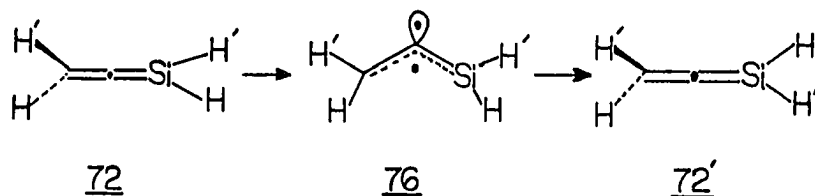
Several research groups have performed molecular orbital calculations on  $\text{SiC}_2\text{H}_4$ .<sup>60-63</sup> Silylacetylene 71 has been found to be the most stable isomer of  $\text{SiC}_2\text{H}_4$  at all the levels of theory thus far probed. Ab initio SCF calculations using a double zeta basis set,<sup>61</sup> a 6-31G\* basis set,<sup>62</sup> and a STO-3G basis set<sup>63</sup> arrived at similar conclusions that 1-silaallene 72 was about 30 kcal/mol higher in energy than silylacetylene 71. Vinylsilylene 73 was calculated to be about 15



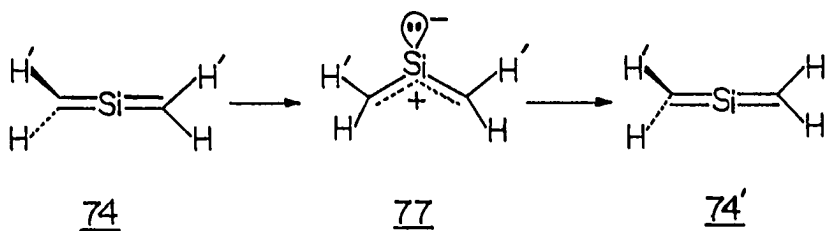
kcal/mol lower in energy than 1-silaallene 72, and silacyclopropylidene 75 was about 35 kcal/mol lower in energy than 2-silaallene 74. The greater stabilities of these silylene isomers (73 and 75) over the silene isomers (72 and 74) agree with the general trend of silicon to avoid multiple bonds.<sup>64,65</sup> 2-Silaallene 74 was calculated to be about 50 kcal/mol higher in energy than silylacetylene 71. The silicon-carbon

double bond lengths in 1-silaallene 72 (1.70 Å) and 2-silaallene 74 (1.70 Å) were calculated to be very close to the isolated silicon-carbon double bond in silene (1.71 Å).

MINDO/3 calculations by Dewar et al.<sup>66</sup> estimated the heat of formation (31.3 kcal/mol) and first ionization potential (9.17 eV) for 2-silaallene 74. Krogh-Jespersen<sup>67</sup> calculated the barriers to internal rotations of both 1-silaallene 72 and 2-silaallene 74 at an HF/6-31G\* level. The transition states for internal rotation in both 72 and 74 showed planer bent geometries. The transition state for 1-silaallene 72 was an open-shell singlet with one electron localized in a carbene type  $\sigma$  orbital and three electrons delocalized as in an allylic radical.

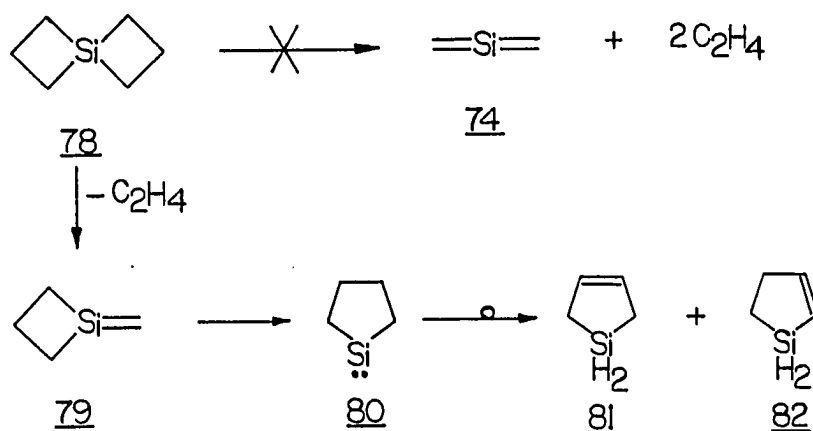


The barrier to rotation of 1-silaallene 72 was calculated to be 35 kcal/mol. Rotation of 2-silaallene 74 was predicted to involve a closed-shell singlet state possessing two electrons in a silylene type  $\sigma$  orbital and two delocalized  $\pi$  electrons. The barrier to rotation of 2-silaallene 74 was found to be 20 kcal/mol.

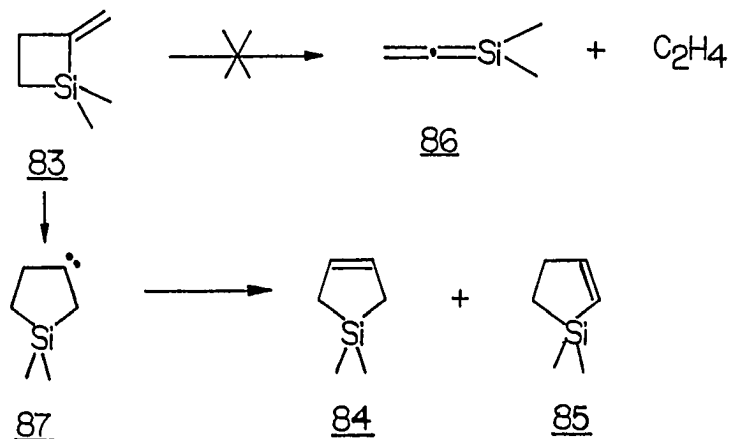


There have been no other calculations on the isomerization pathways for  $\text{SiC}_2\text{H}_4$  and judgments on the possibility of one isomer to convert to another must still depend on intuition.

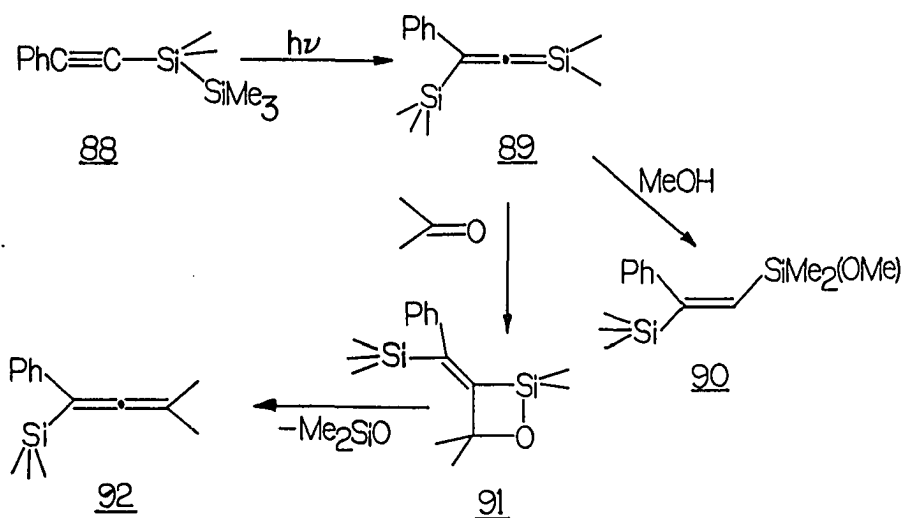
Two substrates that could be considered for the generation of silaallenes, by analogy with the pyrolysis of silacyclobutane to form silene and ethylene<sup>48</sup> (vide infra), have been found to give different chemistry. Pyrolysis of spirocyclic compound 78 by Barton et al.<sup>68</sup> did not indicate the formation of 2-silaallene 74.



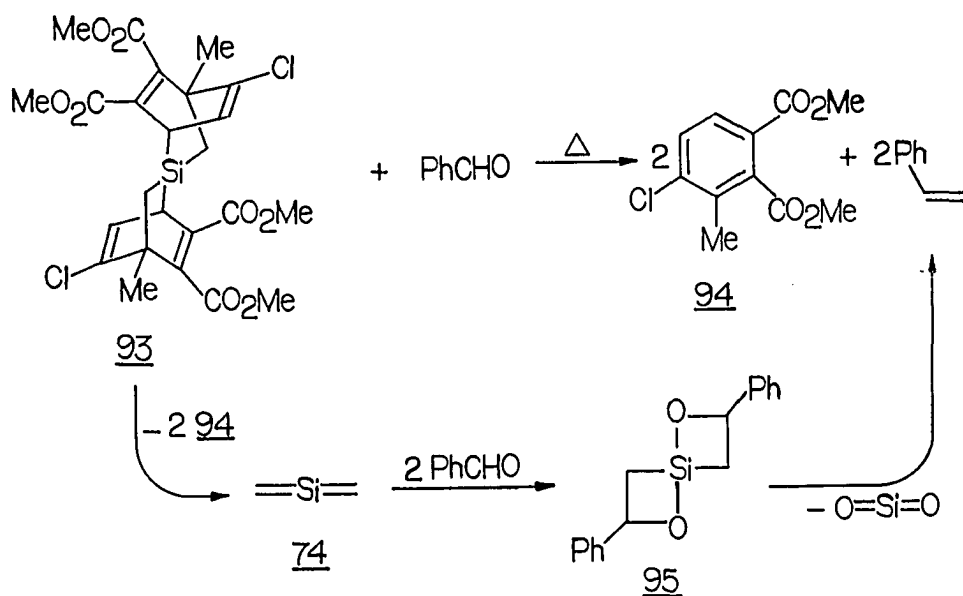
Pyrolysis of methylenesilacyclobutane 83 by Conlin et al.<sup>69</sup> formed silacyclopentenes 84 and 85 rather than the expected 1-silaallene 86.



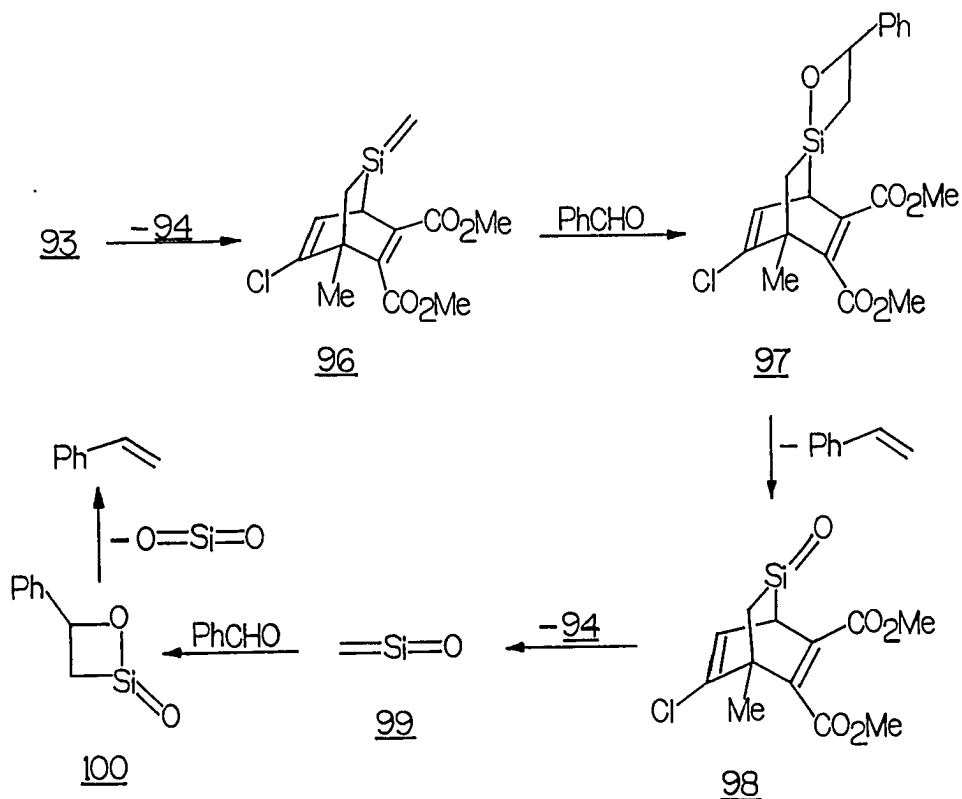
Ishikawa et al.<sup>63,70</sup> have demonstrated the formation of 1-silaallene 89 upon photolysis of ethynylsilane 88.



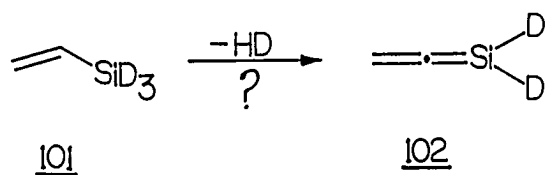
Bertrand et al.<sup>71</sup> reasonably considered the intermediary of 2-silaallene 74 when a coprolysis of spirocyclic silane 93 and benzaldehyde



was found to give two equivalents of styrene. These authors, however, considered an alternative mechanism involving generation silaketene 99 equally reasonable.

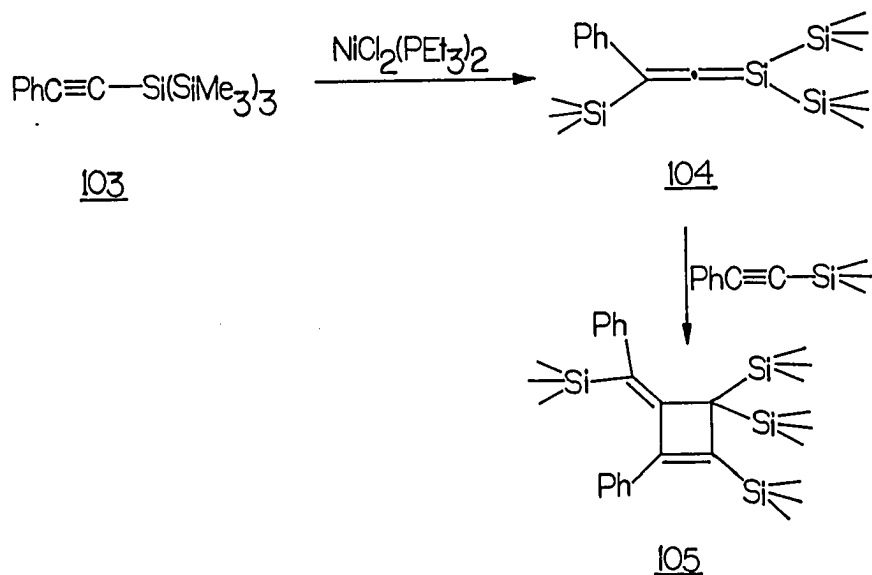


Based on the observation of HD in a shock-tube ( $\approx 1200\text{K}$ ) decomposition of trideuterovinylsilane 101, Rickborn et al.<sup>72</sup> assumed the formation of 1,1-dideutero-1-silaallene 102. However, they did not observe 102 or any of its oligomers.

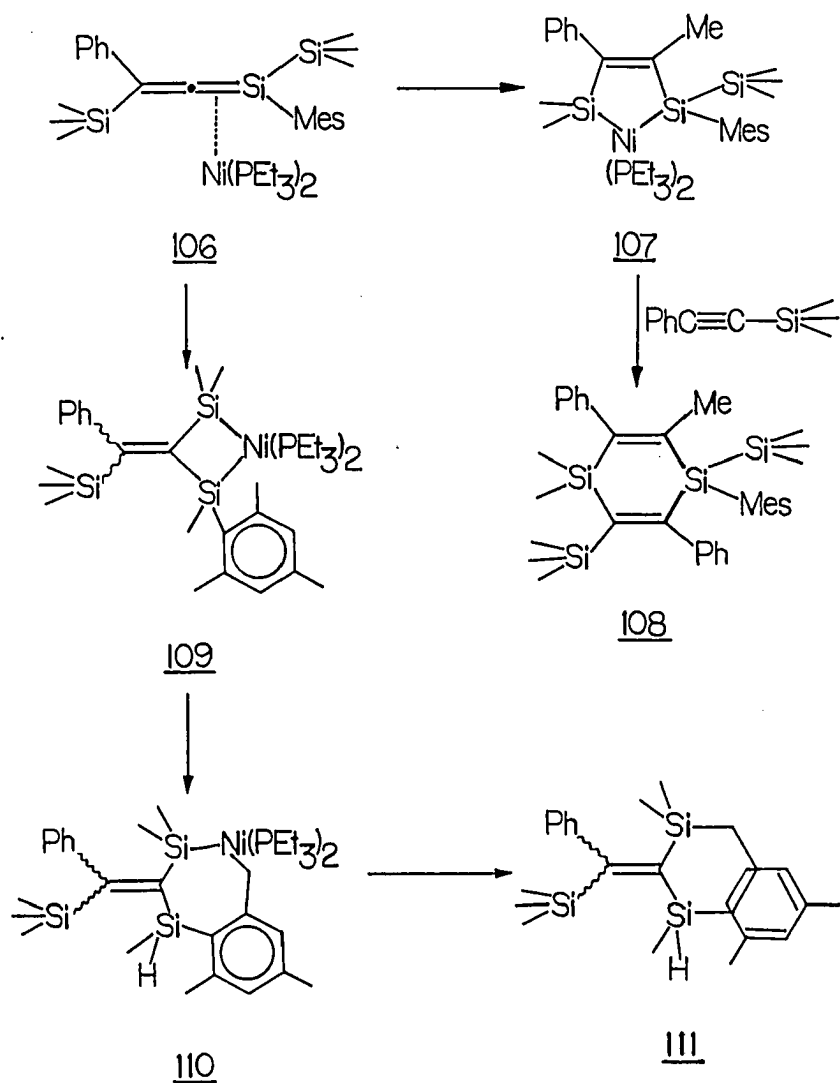




Ishikawa et al.<sup>73,74</sup> found that nickel(II) complexes were capable of isomerization of ethynylsilanes to silaallenes. Thus, 105 was obtained from 103 and phenyltrimethylsilylacetylene, as evidenced by the X-ray crystal structure determination of 105.



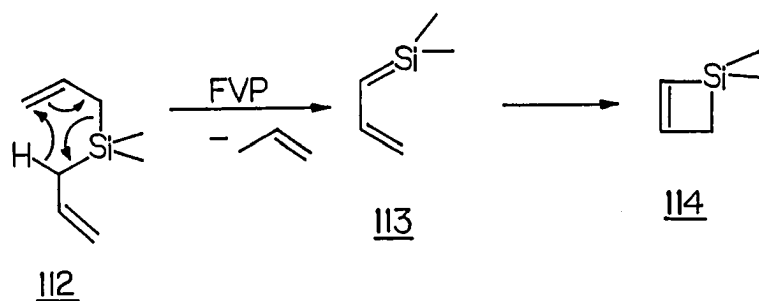
Recently Ishikawa et al.<sup>75</sup> found that the nickel-silaallene complex 106 underwent isomerization to 107 and 110.



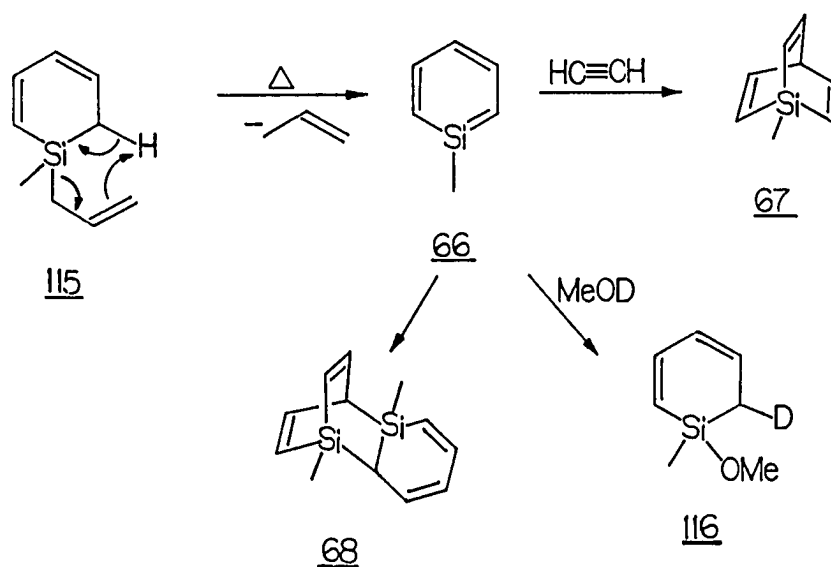
### C. Retro-ene Generation of $\pi$ -Bonded Silicon

Thermally induced retro-ene decomposition of allylsilanes has been found to be a very efficient technique for the generation of silenes. In 1978, Block and Revelle<sup>76</sup> found that diallyldimethylsilane 112, when

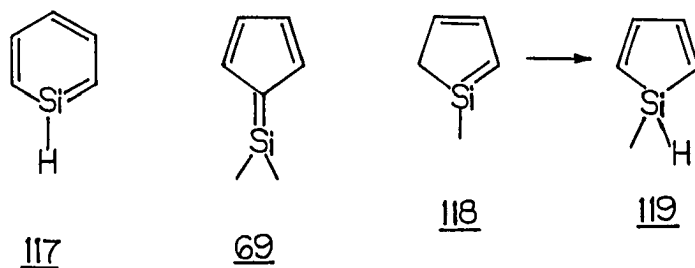
heated to 600°C under flash vacuum pyrolysis (FVP) conditions, formed dimethylsilacyclobutene 114, and they suggested a retro-ene mechanism.



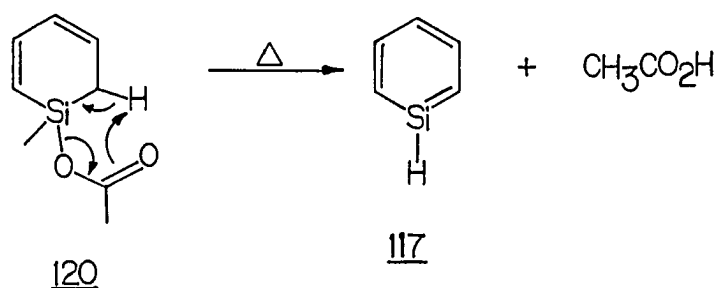
Since then several research groups have found this reaction useful, particularly in generating cyclic silenes. Barton and Burns,<sup>77</sup> and Kreil et al.<sup>78</sup> generated silatoluene 66 by pyrolysing allylsilacyclohexadiene 115.



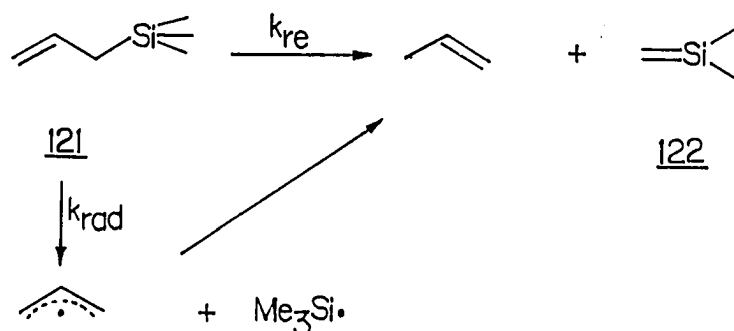
Using this technique, Solouki et al.<sup>79</sup> generated silabenzene 117, and Barton et al. generated silafulvene 69<sup>7</sup> and silacyclopentadiene 118.<sup>80</sup>



Silabenzene 117 was also generated via a retro-ene type decomposition of silylacetate 120 by Maier et al.<sup>81</sup>

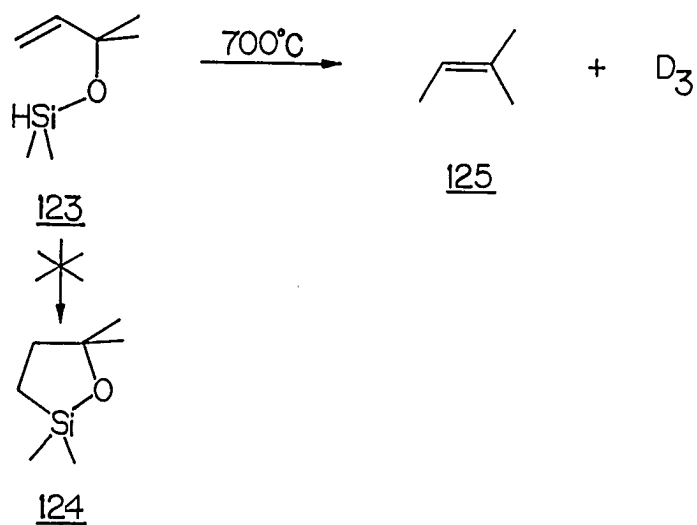


A detailed kinetic investigation on the thermal decomposition of allyltrimethylsilane 121 by Barton et al.<sup>82</sup> has led to the conclusion that 121 decomposes via two competitive pathways. The major pathway is a silicon-carbon bond homolysis to form allyl radical and trimethylsilyl radical, and the minor pathway is a concerted retro-ene process. The

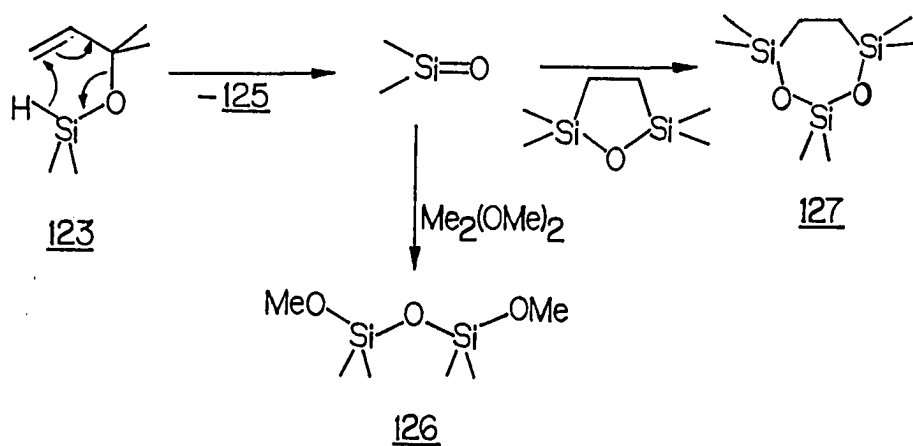


activation energy for the retro-ene process was found to be 55 kcal/mol, and the A factor was  $\log A = 11.6$ . A kinetic investigation on the thermal decomposition of diallyldimethylsilane 112 by Auner et al.<sup>83</sup> reveals that the major pathway was a retro-ene process. This has been attributed to the fact that an allylic carbon-hydrogen bond is weaker than a methyl carbon-hydrogen bond. The Arrhenius parameters for the decomposition of 112 were found to be  $E_a = 48$  kcal/mol, and  $\log A = 11.2$ .

There has been virtually no literature report on the retro-ene generation of  $\pi$ -bonds between silicon and atoms other than carbon. In an attempt to generate silatetrahydrofuran derivative 124 via intramolecular hydrosilation of 3-dimethylsiloxy-3-methyl-1-butene 123, Lane and Frye<sup>84</sup> obtained 2-methyl-2-butene 125 and hexamethylcyclotri-siloxane,  $\text{D}_3$ , when 123 was heated in a ketene lamp at 700°C.

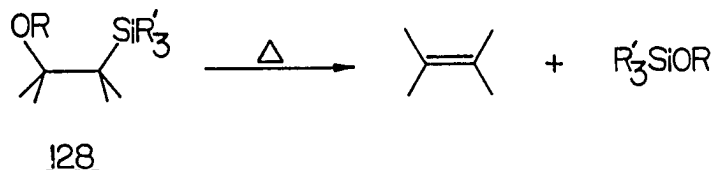


Decomposition of 123 in presence of known silanone traps revealed the formation of dimethylsilanone in the reaction. Although the authors did not suggest a mechanism for this reaction, this could be explained by a retro-ene process.

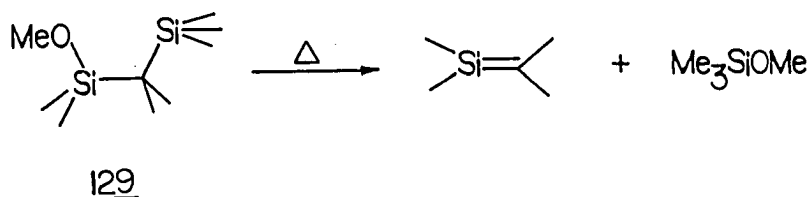


## IV. RESULTS AND DISCUSSION

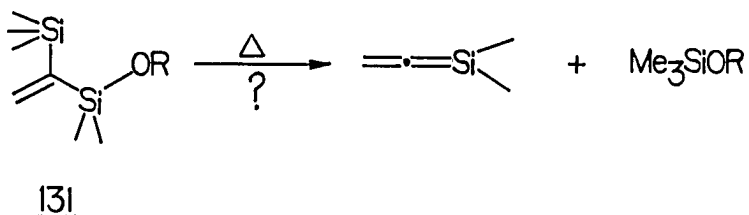
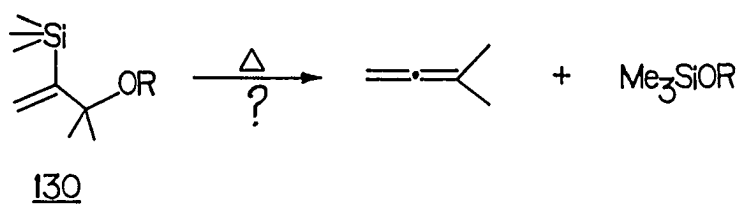
Thermal decomposition of  $\beta$ -alkoxysilanes such as 128 to generate olefins and alkoxy silanes is a conceptually simple reaction, and has been utilized in the generation of olefins.<sup>34,35</sup> This reaction,



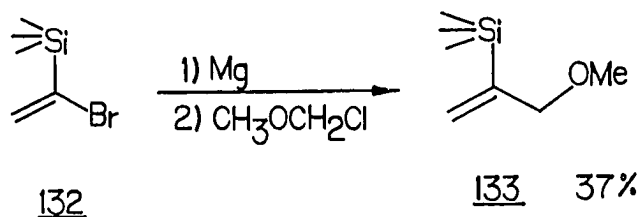
however, has not been used extensively due to lack of good general synthetic methods for 128, and due to easier accessibility to olefins via a very similar technique, viz., Peterson olefination.<sup>8</sup> However,  $\beta$ -elimination of alkoxy silanes to generate silenes<sup>7,51-53</sup> from system such as 129 has been a very useful reaction in the chemistry of organosilicon reactive intermediates.



Thus, it was quite intriguing to envision the generation of allenes and 1-silaallenes via  $\beta$ -elimination of alkoxy silanes from systems such as 130 and 131 respectively, where the eliminating silicon in the precursor is attached to a  $sp^2$  carbon rather than a  $sp^3$  carbon.

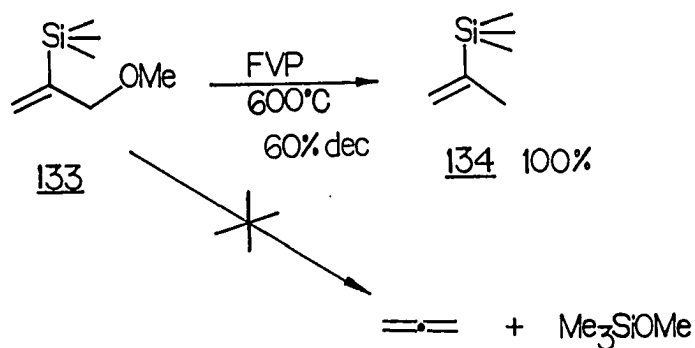


For the generation of allene, the potential precursor 1-methoxy-2-trimethylsilyl-2-propene 133 was synthesized in 37% yield by Grignard coupling of (1-bromoethyl)trimethylsilane 132<sup>85</sup> with chloromethyl methyl ether. However, when 133 was pyrolyzed under FVP conditions at

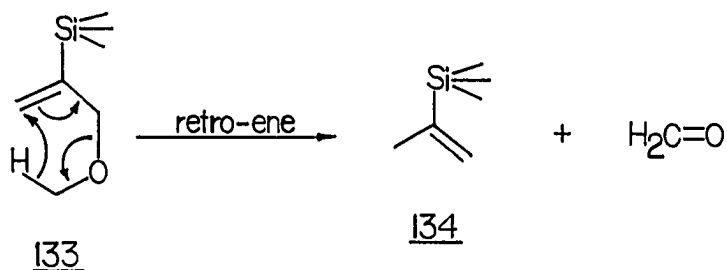


600°C, neither allene nor methoxytrimethylsilane was formed, instead isopropenyltrimethylsilane 134 was formed quantitatively.

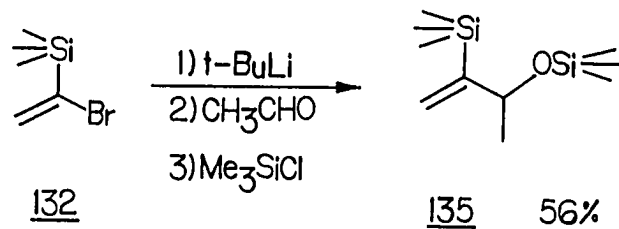




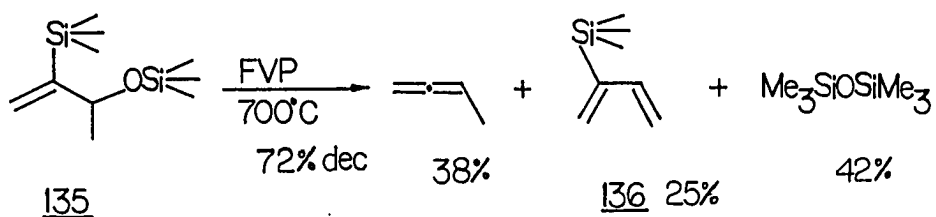
The most reasonable explanation for the formation of 134 from 133 would be a retro-ene elimination of formaldehyde.<sup>86</sup>



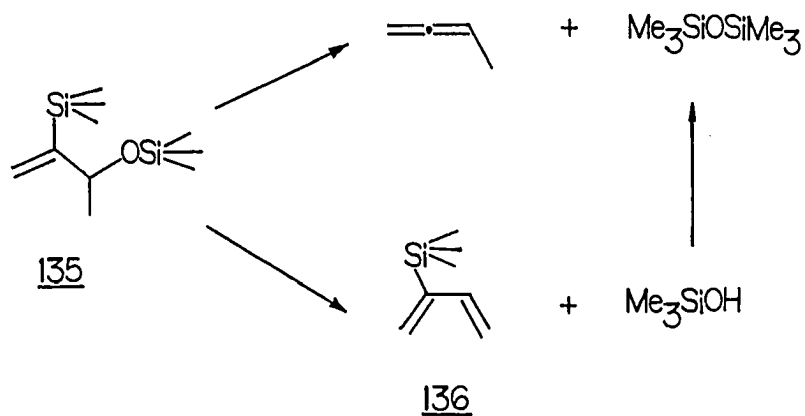
In order to avoid retro-ene type decomposition, replacement of methoxy group by trimethylsiloxy group was considered, and the precursor 2-trimethylsiloxy-3-trimethylsilyl-3-butene 135 was synthesized starting from (1-bromoethenyl)trimethylsilane 132. Flash vacuum pyrolysis of



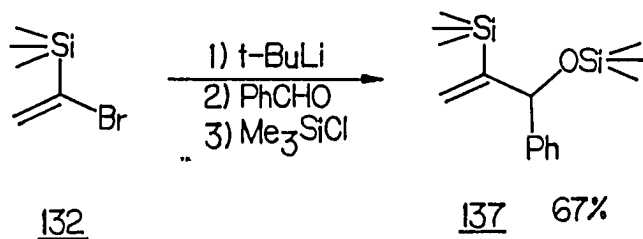
compound 135 afforded 1,2-butadiene (38%), 2-trimethylsilyl-1,3-butadiene 136 (25%) and hexamethyldisiloxane (42%).



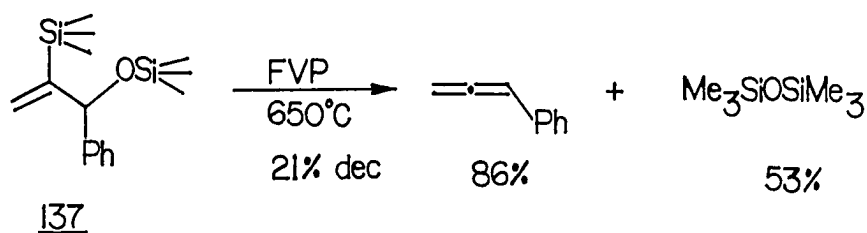
Formation of 1,2-butadiene indicates the desired  $\beta$ -elimination of hexamethyldisiloxane. However, formation of 136 seems to be the result of a  $\beta$ -elimination of trimethylsilanol, which would be expected to form hexamethyldisiloxane in the condensed phase.



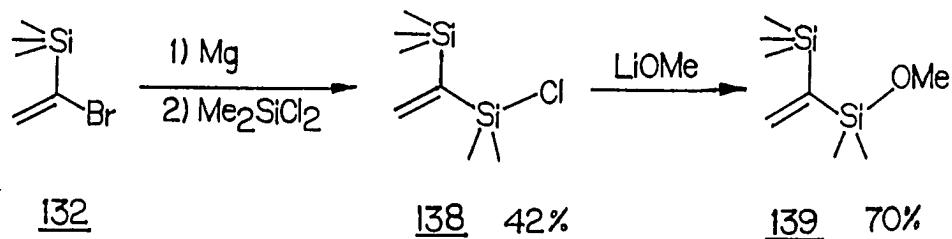
Compound 137 was considered likely to be a clean precursor to phenylallene, and was synthesized in an overall 67% isolated yield



starting from 132. Flash vacuum pyrolysis (FVP) of 137 indeed afforded phenylallene in high yields.



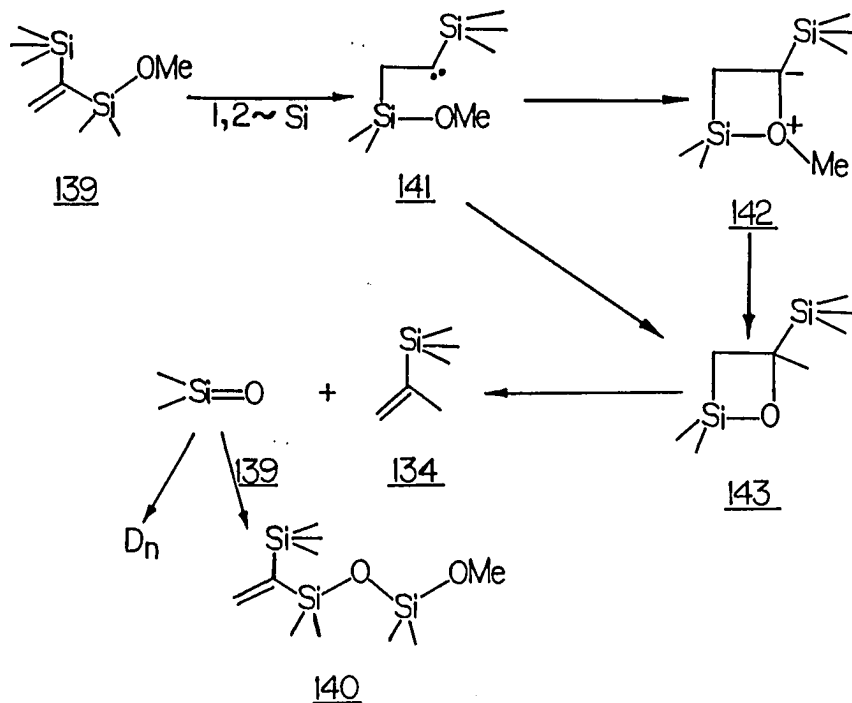
The major interest being in the generation of 1-silaallene, this clean formation of phenylallene prompted the synthesis of the potential 1-silaallene precursor 139 by Grignard coupling of (1-bromoethenyl)-trimethylsilane 132 with dimethyldichlorosilane followed by reaction with LiOMe. When compound 139 was pyrolyzed under FVP conditions at



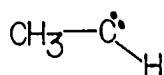
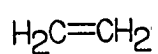
750-850°C, there was no indication of the generation of the desired 1,1-dimethyl-1-silaallene 86. The products were quite cleanly isopropenyltrimethylsilane 134, disiloxane 140, hexamethylcyclo-trisiloxane, D<sub>3</sub> and octamethylcyclo-tetracycloxane, D<sub>4</sub>.



Scheme I



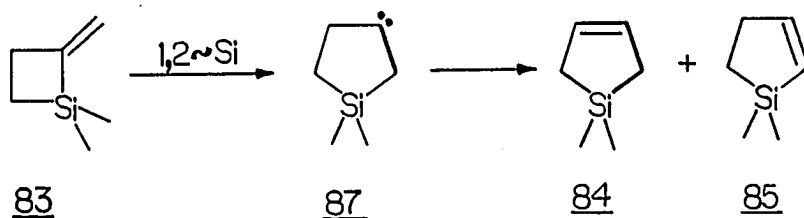
The isomerization of olefin 139 to carbene 141 should be expected to be a high energy process. For instance, a HF/6-31G\* calculation by Pople et al.<sup>87</sup> suggests that ethylidene is 77 kcal/mol higher in energy than ethylene, and is not an energy minimum. However, as compared to



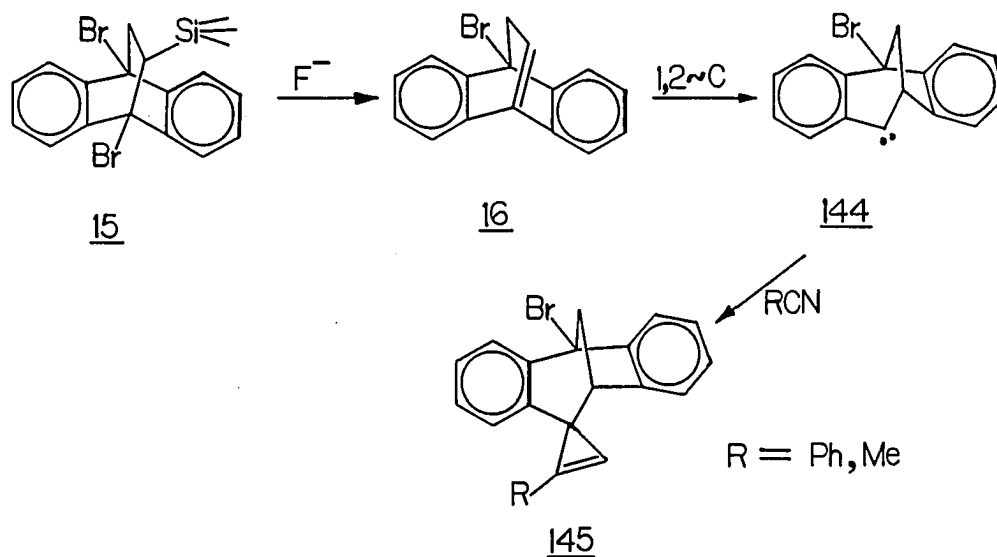
0 kcal/mol

77 kcal/mol

hydrogen, silicon is known to have an extremely high migratory aptitude in sigmatropic rearrangements,<sup>88</sup> and at least one report in the literature clearly suggests a 1,2-migration of silicon in a vinylsilane to form  $\beta$ -silylcarbene. Thus, Conlin et al.<sup>69</sup> obtained 84 and 85 upon pyrolysis of 83. There are at least two literature reports suggesting



1,2-migration of carbon for the isomerization of olefins to carbenes.<sup>29,89</sup> For example, Chan and Massuda<sup>29</sup> obtained compound 145 upon fluoride-induced debromosilation of 15 in presence of acetonitrile or benzonitrile.

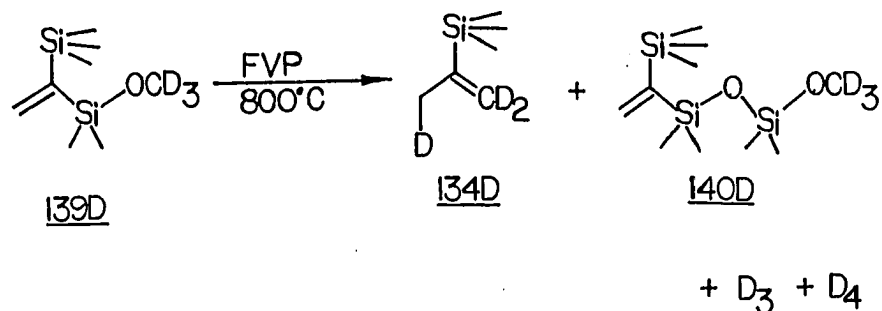


Another mechanistic possibility would be a loss of methyl radical from 139 to form siloxy radical 146, which can readd the methyl radical at its  $\pi$ -bond to form 1,4-biradical 147. Biradical 147 would be expected to break down to isopropenyltrimethylsilane 134 and dimethylsilanone directly, or indirectly via siloxetane 148 (Scheme II).



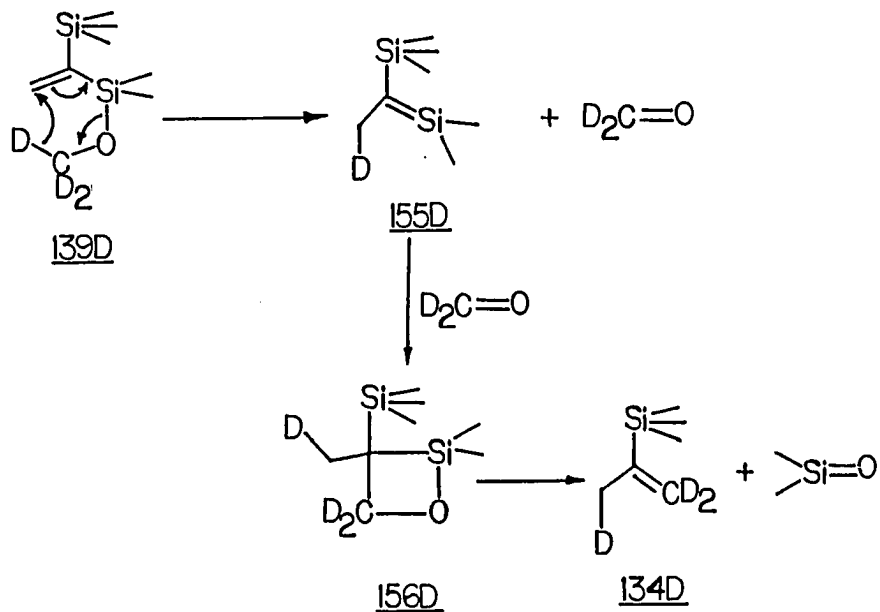






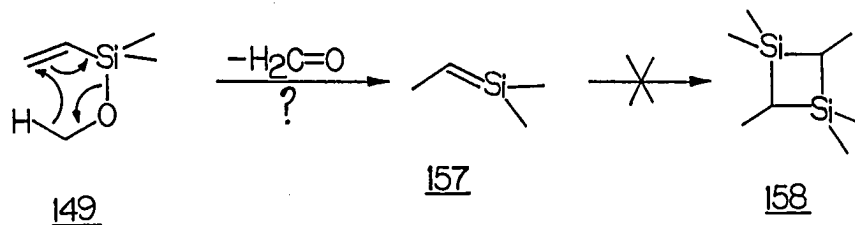
This deuterium labeling result and earlier observations can be explained by a mechanism involving a retro-ene cleavage, where the strongest bond in the molecule, Si-O, is broken to generate a silene and formaldehyde (Scheme III). Formaldehyde-D<sub>2</sub>, by reacting to the silene

Scheme III

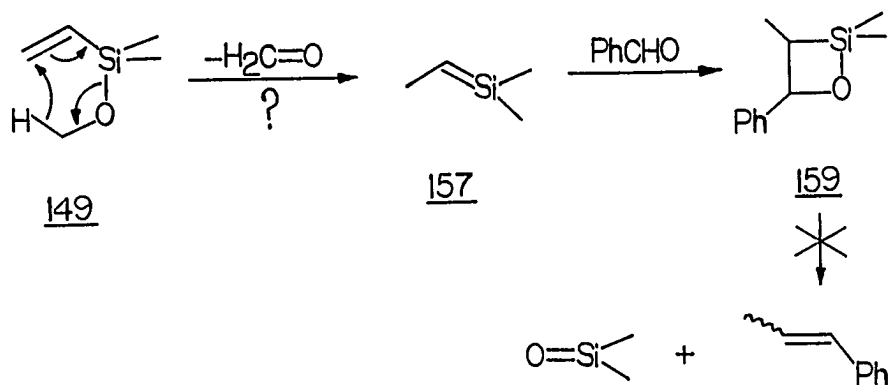


155D can form siloxetane 156D,<sup>49</sup> which would be expected to form the observed products. A common reaction of silenes in absence of added

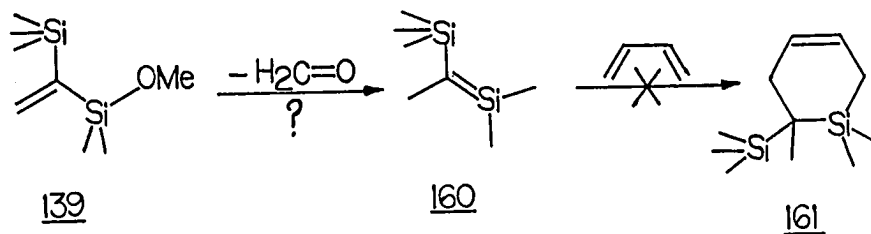
traps, head to tail dimerization,<sup>49</sup> however, was not observed in the preceding reactions.



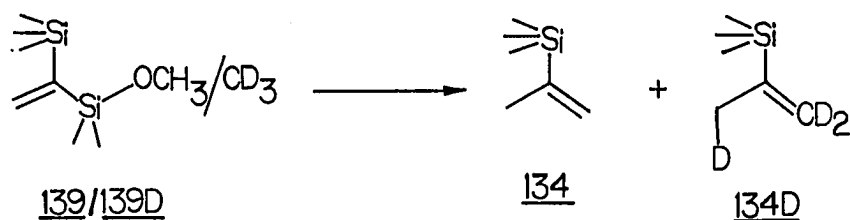
Two efforts were made to trap any silene that might be formed in these reactions. First, when **149** was copolyolyzed at  $720^\circ\text{C}$  with 12-fold excess of benzaldehyde in a nitrogen flow, there was no formation of 1-phenylpropene. Second, copolyolysis of **139** with excess of



1,3-butadiene at  $660^\circ\text{C}$  in a flow system did not produce any of the Diels-Alder adduct<sup>49</sup> **161**.

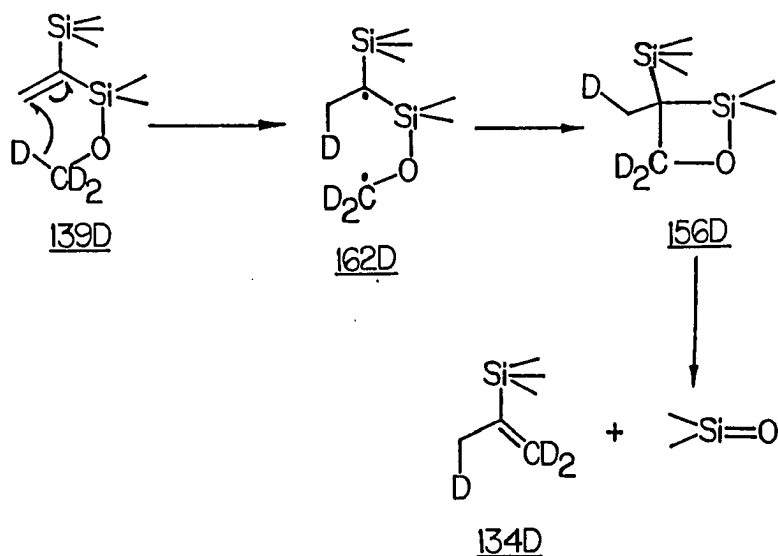


Unimolecularity of these reactions for the formation of dimethylsilanone, and no involvement of formaldehyde, were finally established by copyrolyzing a 1:1 mixture of 139 and 139D to obtain isopropenyltrimethylsilanes 134 and 134D exclusively. There was no mono- or dideutero isopropenyltrimethylsilane.

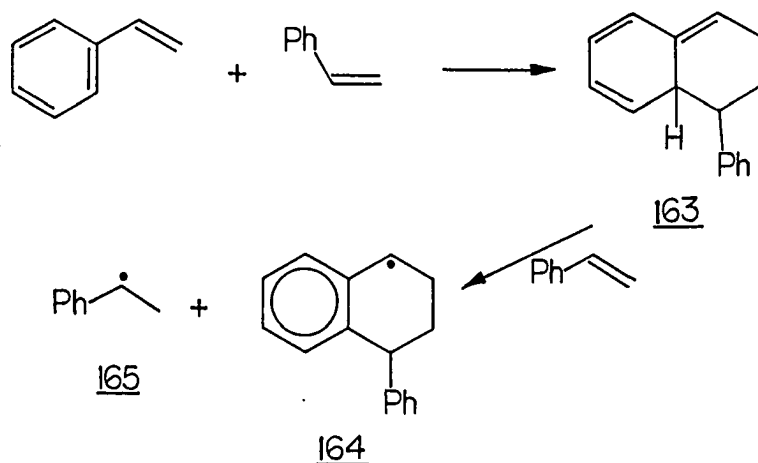


These results led to the conclusion that generation of dimethylsilanone from vinyl dimethylalkoxysilanes is initiated by a novel 1,5-migration of hydrogen.<sup>90</sup> Thus, the 1,5-migration of hydrogen in 139D generates diradical 162D which collapses to form siloxetane 156D

Scheme IV



leading to dimethylsilanone and 134D (Scheme IV). It should be noted here that this type of 1,5-hydrogen migration to form a 1,4-biradical is unprecedented in carbon chemistry. This can also be looked upon as an addition of a C-H single bond to an olefinic  $\pi$ -bond to form two radicals, which is a very uncommon reaction. The only known examples of such a reaction seem to be the uncatalyzed thermally-induced polymerization of styrene and its derivatives.<sup>91,92</sup> The initiation process for thermal polymerization of styrene is believed<sup>91</sup> to involve the formation of Diels-Alder dimer 163 followed by a homolytic transfer of a hydrogen from 163 to styrene, forming radicals 164 and 165.

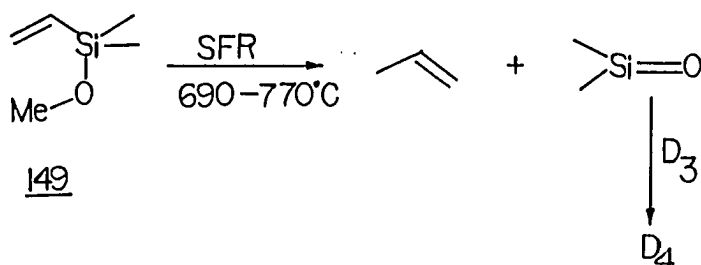


A 1,4-diradical such as 162D in an all carbon  $\sigma$ -framework would immediately break down to two olefinic fragments.<sup>93</sup> However, the strong Si-O bond is presumed to have stopped such a cleavage in 139D, instead the biradical closes to form siloxetane 156D.

The deuterium isotope effect for the decomposition of 139 and 139D was determined by measuring the rate constants for formation of 134 and

134D at 695°C in a pulsed, stirred-flow reactor (SFR).<sup>94</sup> A value of  $k_H/k_D = 1.34 \pm 0.08$ , seemingly low for a primary isotope effect, may be big enough at such a high temperature to support the mechanism of Scheme IV.

To understand this chemistry more clearly, a complete kinetic investigation was undertaken. Kinetics were performed in a pulsed stirred-flow reactor (SFR) designed after the system described by Baldwin et al.<sup>94</sup> (see experimental section). Decomposition of vinyl dimethylmethoxysilane 149 was studied kinetically at 690-770°C by measuring the first-order rate constants for formation of propene. Consumption of 149 by dimethylsilanone was avoided by using a 50-fold excess of  $D_3$ , which was found to be an efficient trap as neither  $D_3$  nor the product,  $D_4$ , decomposed significantly at the reaction condition.



A twenty-point Arrhenius plot ( $\ln k$  vs  $1000/T$ ) was almost a perfect straight line (Fig. 1), and gave an activation energy ( $E_a$ ) of  $66.9 \pm 0.4$  kcal/mol and an A-factor of  $\log A = 13.8 \pm 0.1$ , which corresponds to an entropy of activation ( $\Delta S^\ddagger$ ) of + 0.14 eu. This high activation energy is consistent with the formation of a high-energy species such as 1,4-diradical 162D. However, the value of A-factor is hard to comment on, as there was no model system with which to compare.

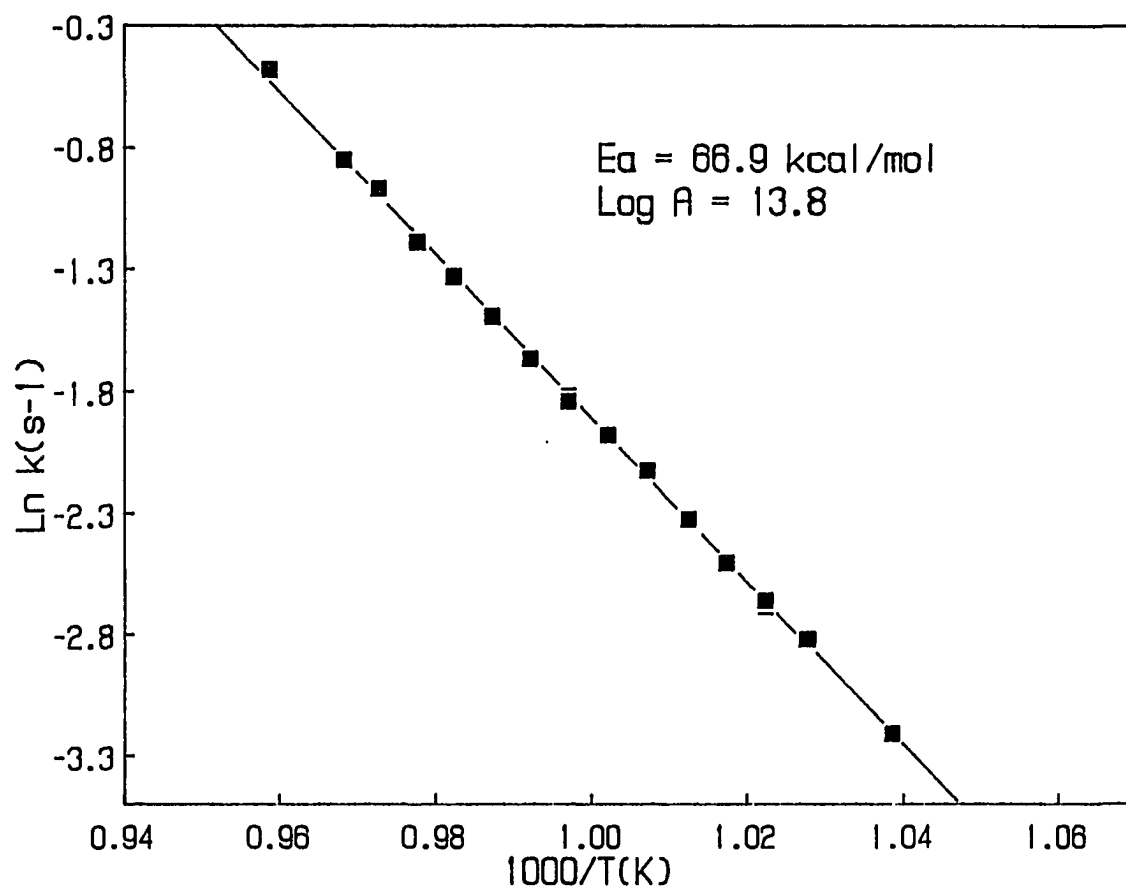
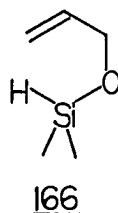
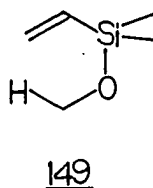
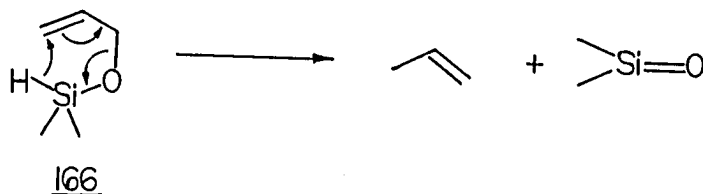


Figure 1. Arrhenius plot for the formation of propene from 149 in SFR

One model system that might have similar geometric requirements for decomposition as 149 would be allyloxydimethylsilane 166.



Allyloxydimethylsilane 166 was synthesized by reaction of allyl alcohol and dimethylchlorosilane in the presence of  $\text{CaH}_2$  as acid scavenger. Decomposition of 166 in the SFR was found to generate propene cleanly, and kinetics were determined by following the first-order rate constant for formation of propene in presence of a 50-fold excess of  $\text{D}_3$ . A twenty-point Arrhenius plot (Fig. 2) for the temperature range of 600-680°C gave an activation energy ( $E_a$ ) of  $54.6 \pm 0.5$  kcal/mol and  $\log A$  of  $12.6 \pm 0.1$ , corresponding to an entropy of activation ( $\Delta S^\ddagger$ ) of -5.2 eu. These big differences in activation energies as well as A-factors suggest that the transition states for decomposition of compounds 149 and 166 are not similar. The low A-factor for decomposition of allyloxydimethylsilane 166 is suggestive of a retro-ene type of six-centered transition state<sup>95</sup>. A homolytic



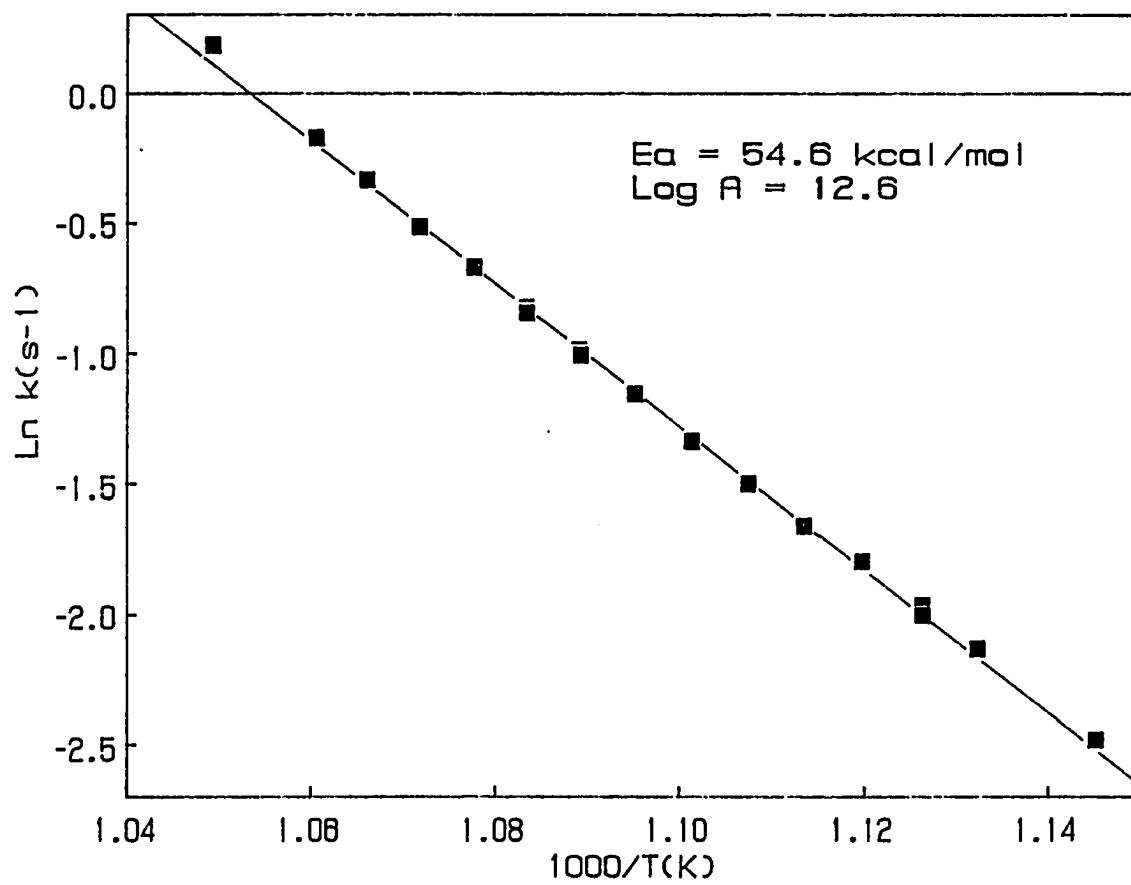
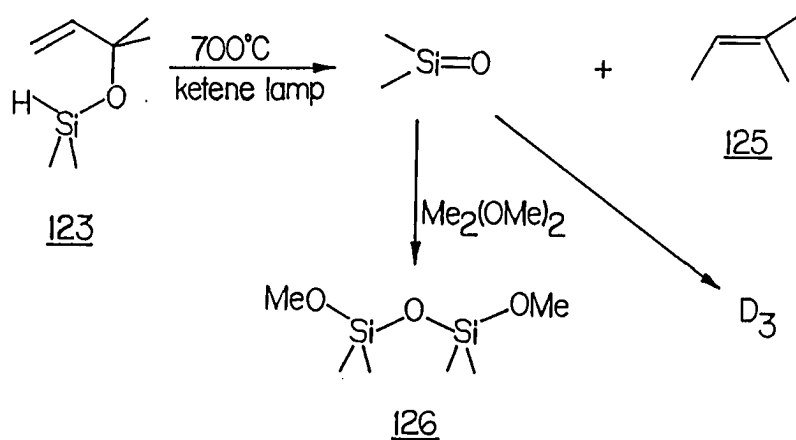


Figure 2. Arrhenius plot for the formation of propene from 166 in SFR

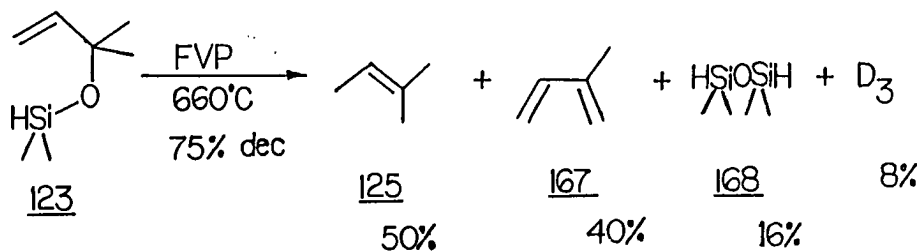


cleavage of the C-O bond in 166 to form allyl radical and dimethylsiloxy radical was ruled out based on the observations that i) allyloxy-trimethylsilane did not decompose even at 720°C in the SFR, and ii) 166, when pyrolyzed in the SFR at 640°C in the presence of a 20-fold excess of toluene-D<sub>8</sub>, there was no deuterium incorporation in propene.

This apparently simple retro-ene type of generation of silanone, has been virtually absent from the literature. In 1979, Lane and Frye<sup>84</sup> briefly reported the formation of 2-methyl-2-butene 125 and D<sub>3</sub> from pyrolytic decomposition of compound 123. Evidence for the formation of dimethylsilanone was obtained by copyrolysis of 123 with known silanone traps. No yields for the decomposition of 123 was reported, nor was

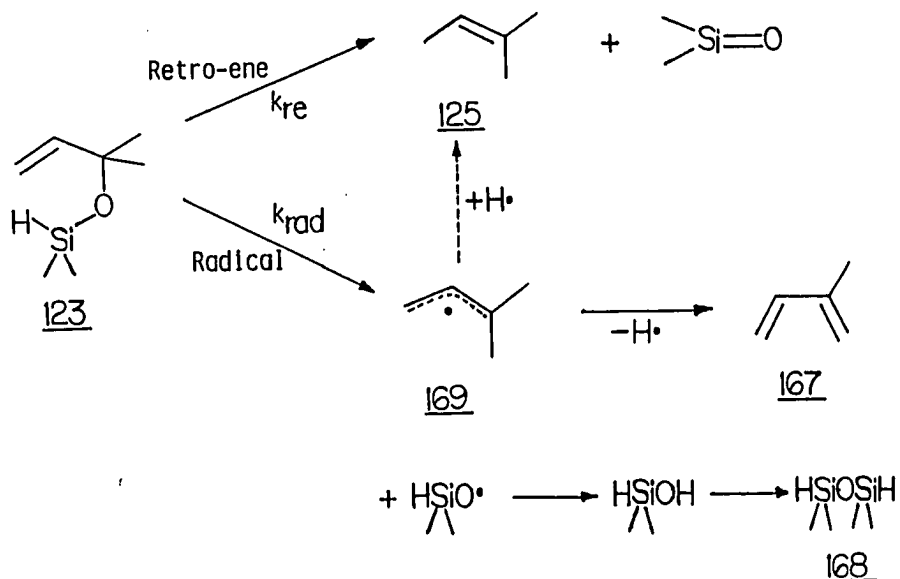


there any suggestion on the mechanism of formation of dimethylsilanone. So, a reinvestigation of this reaction was initiated. FVP of 123 at 660°C produced 2-methyl-2-butene 125 (50%) and D<sub>3</sub> (8%) along with substantial amounts of 2-methyl-1,3-butadiene 167 (40%) and sym-tetramethyldisiloxane 168 (16%).



Kinetics for the decomposition of 123 were determined by measuring the total rate constants of formation of 125 plus 167. A twenty-point Arrhenius plot (Fig. 3) in the temperature range of 500-580°C gave an activation energy of  $53.8 \pm 0.6$  kcal/mol and a  $\log A$  of  $13.9 \pm 0.2$ . This high A-factor coupled with the product distribution in the FVP clearly suggests two competitive pathways for the decomposition of 123. One involves a retro-ene generation of 2-methyl-2-butene and dimethylsilanone, and the other involves a homolytic cleavage to form

Scheme V



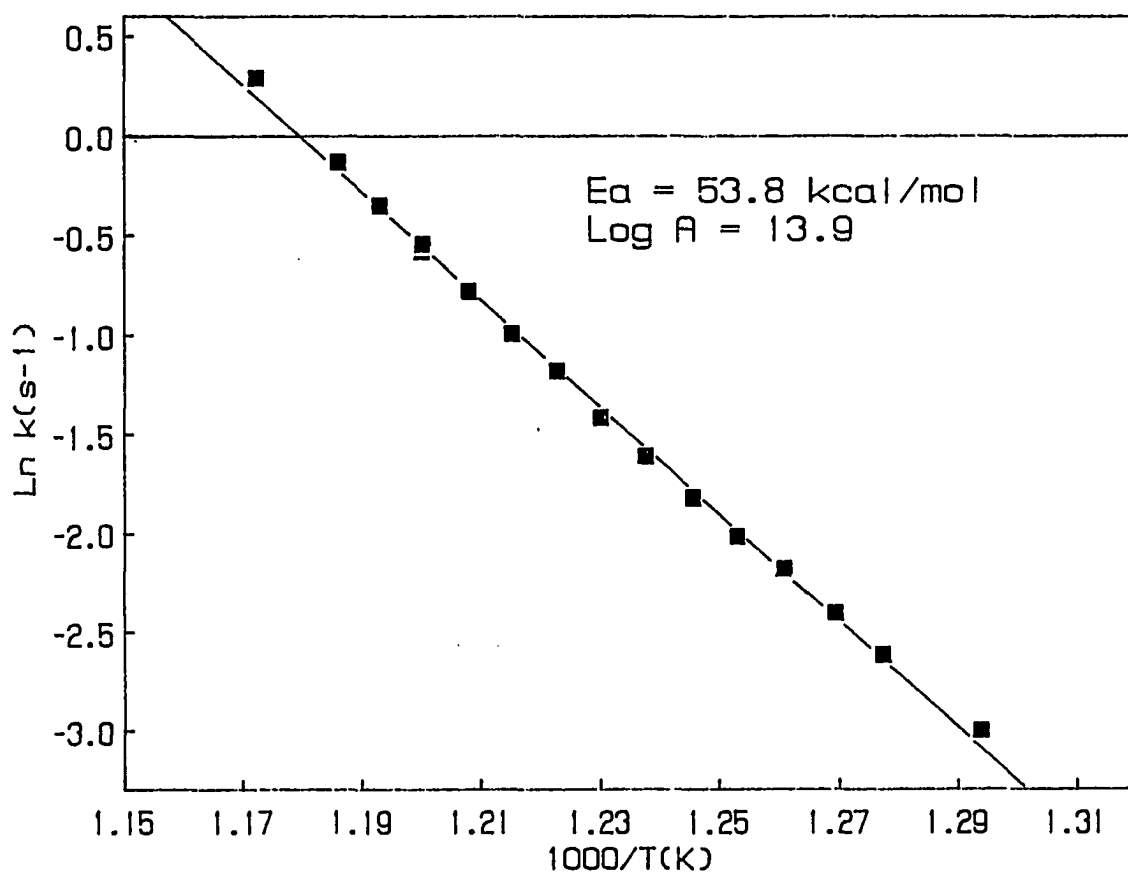


Figure 3. Arrhenius plot for the total formation of 125 plus 167 from 123 in SFR

the allylic tertiary radical 169 and dimethylsiloxy radical (Scheme V). The allylic radical 169 can abstract a hydrogen to form 125, or it can lose a hydrogen to form the conjugated system 167. The dimethylsiloxy radical can abstract a hydrogen to form dimethylsilanol which would be expected to form 168 in the condensed phase.

Attempts to intercept radical 169 by an excess of toluene-D<sub>8</sub> were unsuccessful. A 40-fold excess of toluene-D<sub>8</sub>, when copolyolyzed with 123 in a SFR at 550°C with a 60 ml/min flow of helium, did not incorporate deuterium in 125, nor did it suppress the formation of 167. This suggests that the allylic tertiary radical 169, if formed, loses a hydrogen to form the conjugated diene 167 much more readily than it can abstract a hydrogen to form 125. This result, coupled with the observation that 2-methyl-2-butene 125 itself did not form 167 at 550°C in the SFR, allowed kinetic separation of 125 and 167. Kinetics were determined in the temperature range of 545-590°C by following the first-order rate constants of formation of 125 and 167. The Arrhenius parameters for the formation of 125 (Fig. 4) were  $E_a = 51.6 \pm 0.7$  kcal/mol and  $\log A = 13.0 \pm 0.2$ , and those for the formation of 167 (Fig. 5) were  $E_a = 69.1 \pm 1.3$  kcal/mol and  $\log A = 17.2 \pm 0.3$ . These kinetic parameters again support the retro-ene pathway for the formation of 125 and the radical pathway for the formation of 167.

Returning to the generation of 1-silaallene,  $\beta$ -elimination of methoxytrimethylsilane from (1-methoxyethenyl)pentamethylidisilane 170 was considered. Although systems such as 129 have been found to be very

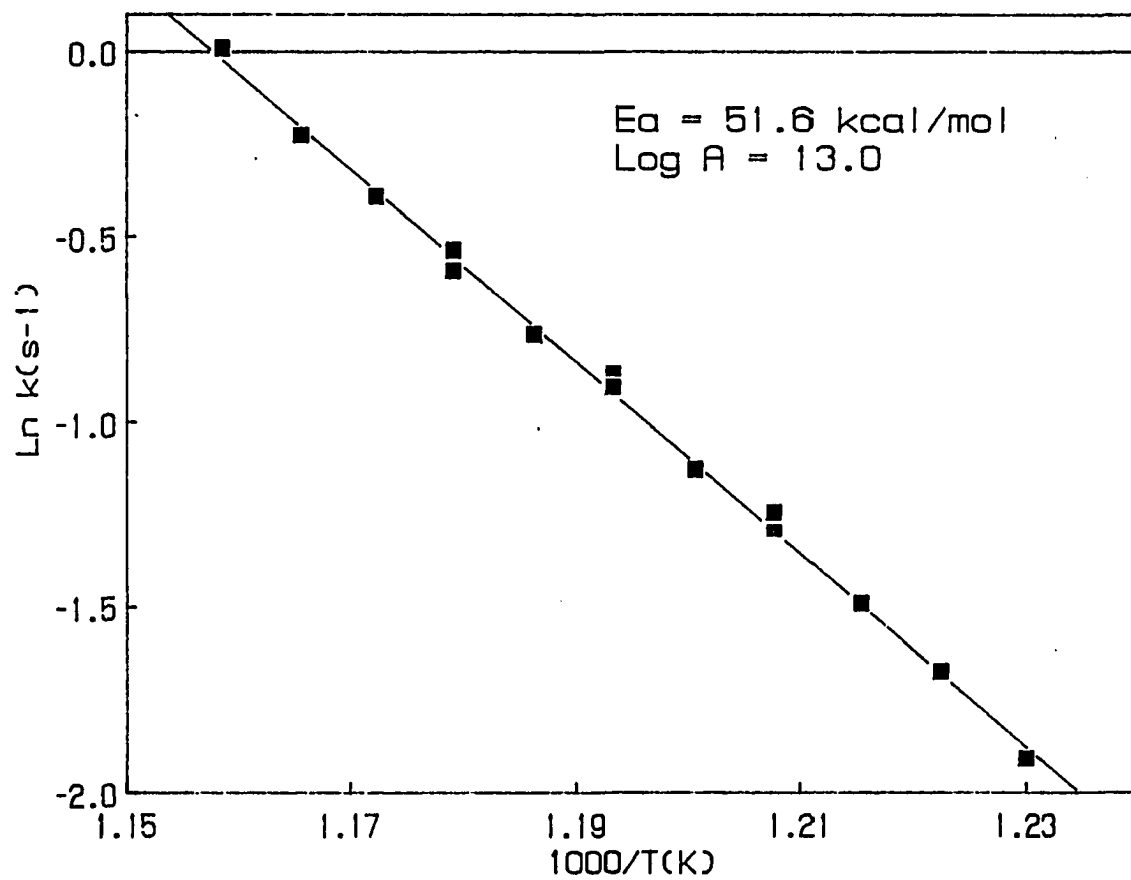


Figure 4. Arrhenius plot for the formation of 125 from 123 in SFR

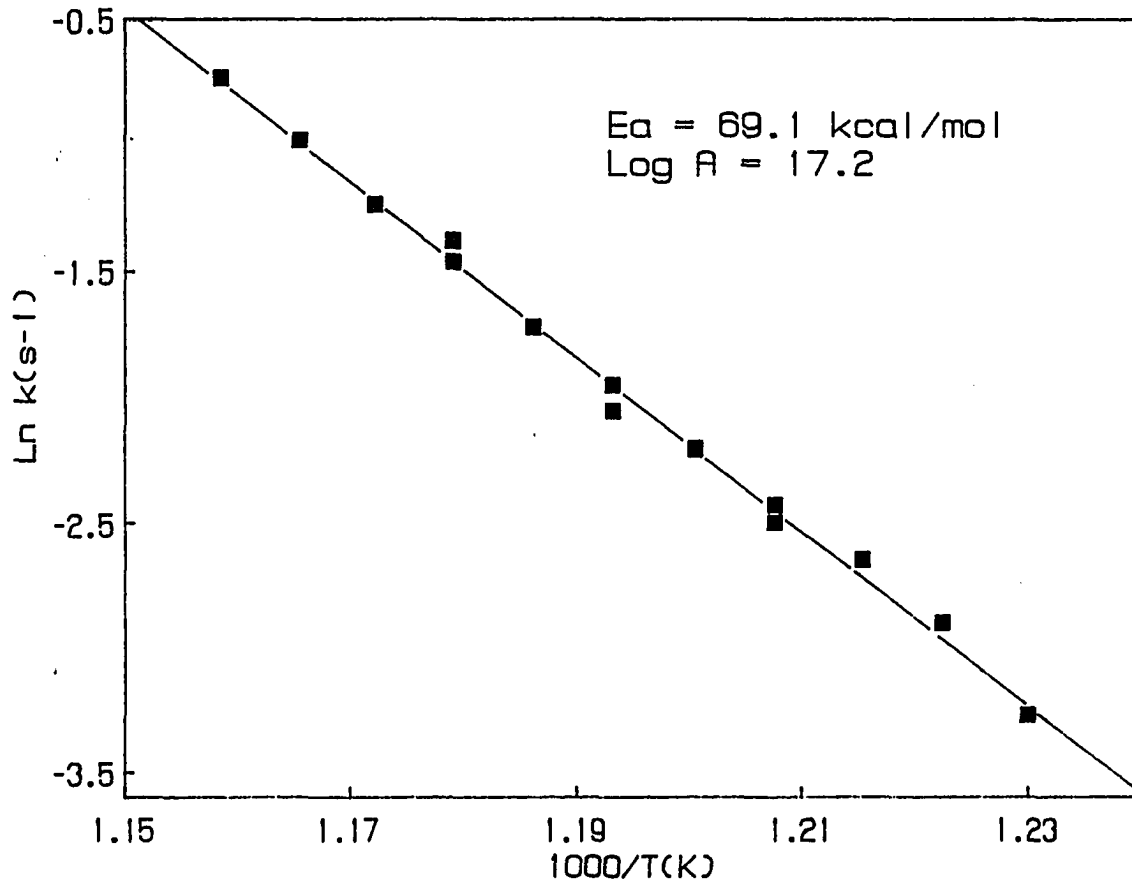
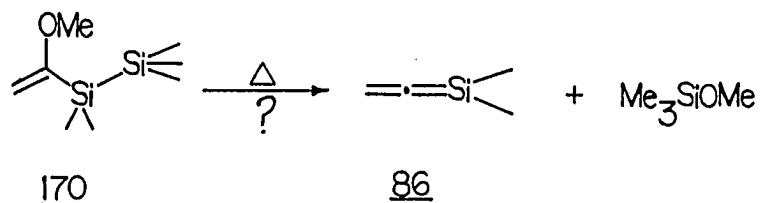
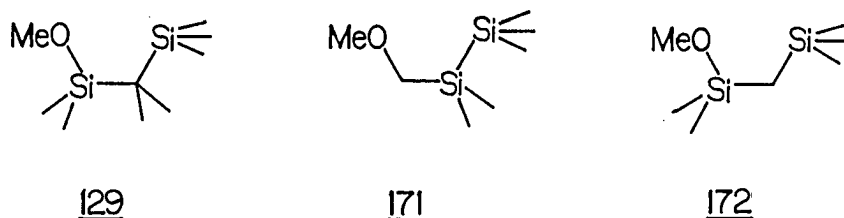


Figure 5. Arrhenius plot for the formation of 167 from 123 in SFR

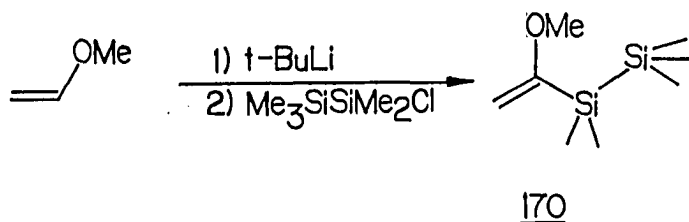


successful<sup>7</sup> in generating silenes, methoxymethylpentamethyldisilane 171 was found not to generate<sup>96</sup> 1,1-dimethylsilene via thermally induced  $\beta$ -elimination of methoxytrimethylsilane.

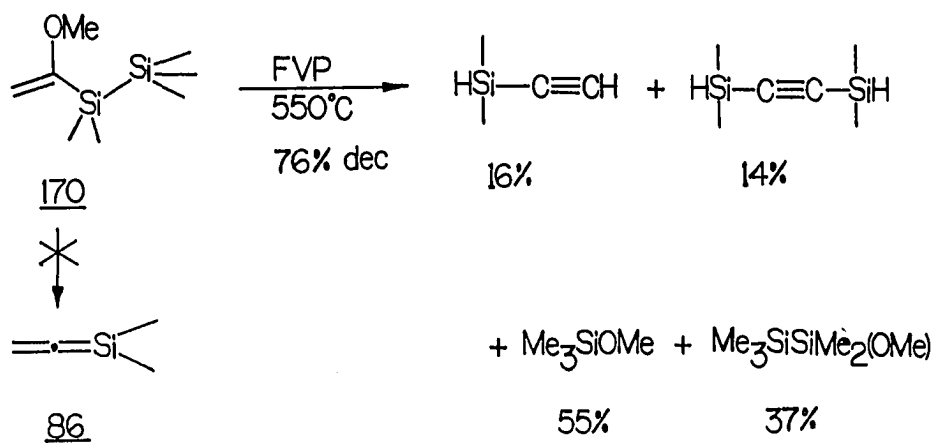


Examination of bond dissociation energies, however, indicates that 171 should be a much better candidate than 172 in generating 1,1-dimethylsilene. For 171, the bonds being broken are a silicon-silicon  $\sigma$  bond ( $D_{\text{Si-Si}} = 80.5$  kcal/mol) and a carbon-oxygen  $\sigma$  bond ( $D_{\text{C-O}} = 91.0$  kcal/mol), and the bonds being formed are a silicon-oxygen  $\sigma$  bond ( $D_{\text{Si-O}} = 128.0$  kcal/mol) and a silicon-carbon  $\pi$  bond ( $D_{\text{Si=C}} = 39.0$  kcal/mol).<sup>97</sup> Thus, formation of 1,1-dimethylsilene and methoxytrimethylsilane from 171 is endothermic by approximately 4.5 kcal/mol. For 172, a silicon-oxygen bond is both broken and formed, and so the bonds to be considered are the breaking of a silicon-carbon  $\sigma$  bond ( $D_{\text{Si-C}} = 89.4$  kcal/mol), and the formation of a silicon-carbon  $\pi$  bond ( $D_{\text{Si-C}} = 39.0$  kcal/mol). Thus, formation of 1,1-dimethylsilene and methoxytrimethylsilane from 172 is endothermic by about 50.4 kcal/mol.

Despite this high thermodynamic favor (46.9 kcal/mol) for 171 over 172, 172 was found to be a good generator of 1,1-dimethylsilene, whereas Burns<sup>96</sup> obtained only an intractable mixture when he pyrolyzed 171 under FVP conditions. This puzzling behavior, coupled with our desire to generate 1-silaallene, prompted the synthesis of 170 by coupling of chloropentamethyldisilane with  $\alpha$ -lithio methyl vinyl ether.<sup>98</sup>



Flash vacuum pyrolysis (FVP) of 170 at 550°C gave dimethylsilylacetylene (16%), bis-(dimethylsilyl)acetylene (14%), methoxytrimethylsilane (55%) and methoxypentamethyldisilane (37%).

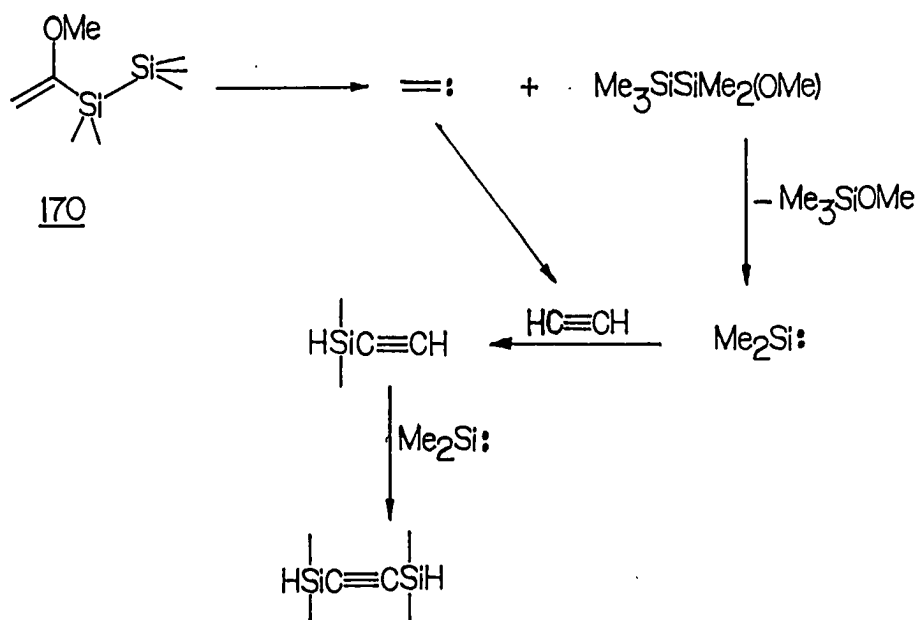


Although dimethylsilylacetylene is an isomer of the desired silaallene 86, there was no indication of the presence of dimer or trimer of 86 in the pyrolysate. This product distribution can be more satisfactorily

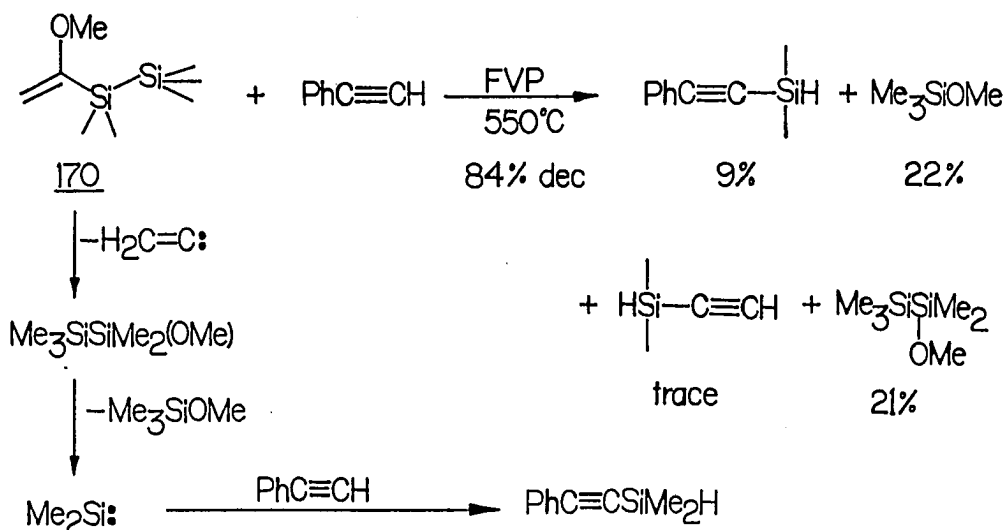


explained by an  $\alpha$ -elimination of methoxypentamethyldisilane from 170 to generate vinylidene. Methoxypentamethyldisilane would be expected<sup>6</sup> to form dimethylsilylene and methoxytrimethylsilylene under the reaction conditions. Isomerization of vinylidene to acetylene followed by addition of dimethylsilylene would produce both dimethylsilylacetylene and bis-(dimethylsilyl)acetylene (Scheme VI).

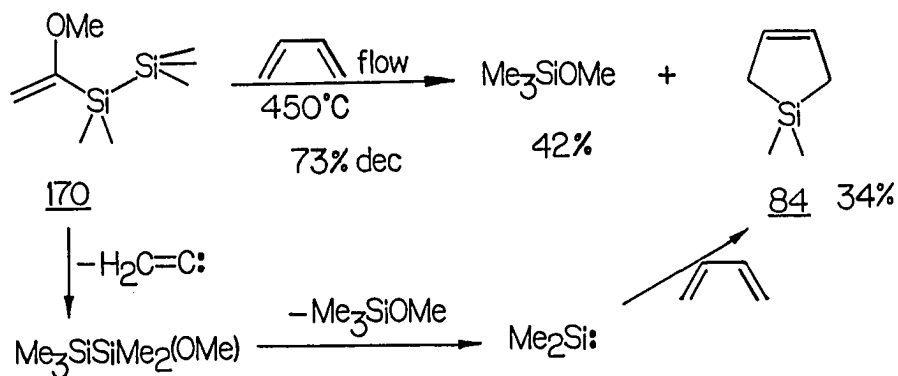
Scheme VI



To test this hypothesis, two reactions were carried out. First a 2:1 mixture of phenylacetylene and 170, when pyrolyzed under FVP conditions, formed dimethylsilylphenylacetylene. Second, when 170 was

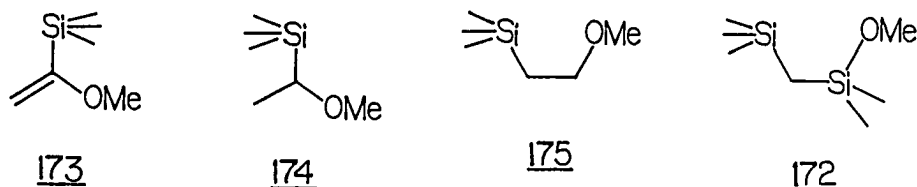


copolyolyzed with excess of 1,3-butadiene in a flow system at 450°C, dimethylsilylene was trapped by 1,3-butadiene to form 1,1-dimethyl-1-silacyclopent-3-ene 84. These results led to the conclusion that



thermal decomposition of 170 does indeed involve intermediacy of vinylidene as well as dimethylsilylene.

To understand this preference of  $\alpha$ -elimination over  $\beta$ -elimination, a kinetic investigation of simple model systems 173, 174, 175 and 172 was undertaken.



(1-Methoxyethenyl)trimethylsilane 173 was synthesized by the method of Soderquist and Hsu<sup>98</sup> and pyrolyzed under FVP conditions at 550°C to obtain cleanly methoxytrimethylsilane (89%). Kinetics for the decomposition of 173 were determined by using both stirred flow reactor (SFR) and low pressure pyrolysis (LPP)<sup>99</sup> techniques (see experimental section). By measuring the first-order rate constants for formation of methoxytrimethylsilane in the temperature range of 485-530°C in a SFR, an eleven-point Arrhenius plot (Fig. 6) was obtained. The Arrhenius parameters were found to be  $E_a = 50.4 \pm 1.0$  kcal/mol and  $\log A = 14.0 \pm 0.3$ . First-order rate constants for the decay of 173 in the temperature range of 403-462°C in a LPP apparatus were determined.<sup>100</sup> A fifteen-point Arrhenius plot (Fig. 7) gave an activation energy of  $49.3 \pm 0.7$  kcal/mol and an A factor of  $\log A = 13.6 \pm 0.2$ .

(1-Methoxyethyl)trimethylsilane 174 was synthesized by catalytic hydrogenation of 173 in 40% yield, and decomposition of 174 in a SFR gave, exclusively, ethylene and methoxytrimethylsilane. Kinetics for the decomposition of 174 were determined by both SFR and LPP techniques. First-order rate constants for the formation of methoxytrimethylsilane in a SFR in the temperature range of 524-579°C gave an Arrhenius plot (Fig. 8) with activation energy of  $52.6 \pm 0.4$  kcal/mol and an A-factor of  $\log A = 13.5 \pm 0.1$ . Kinetics in the LPP apparatus were determined in

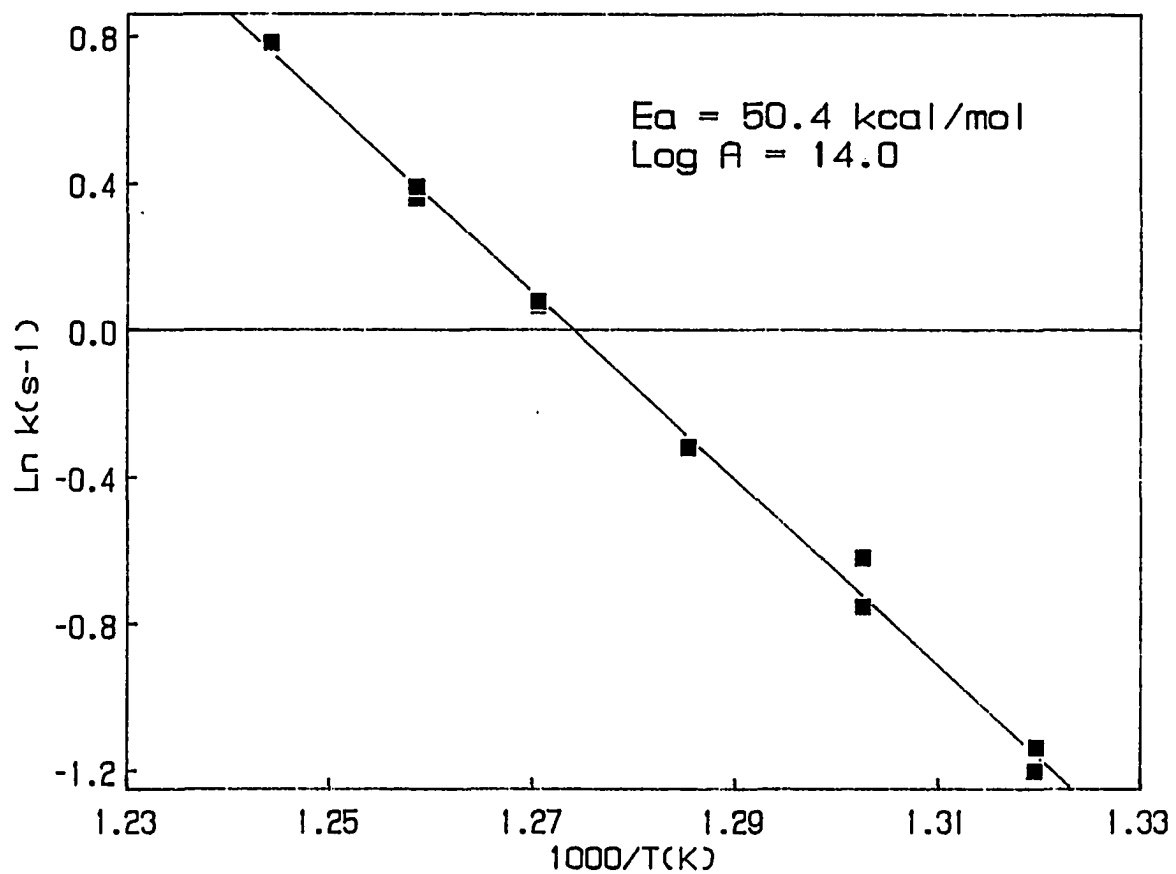


Figure 6. Arrhenius plot for the formation of  $\text{Me}_3\text{SiOMe}$  from 173 in SFR

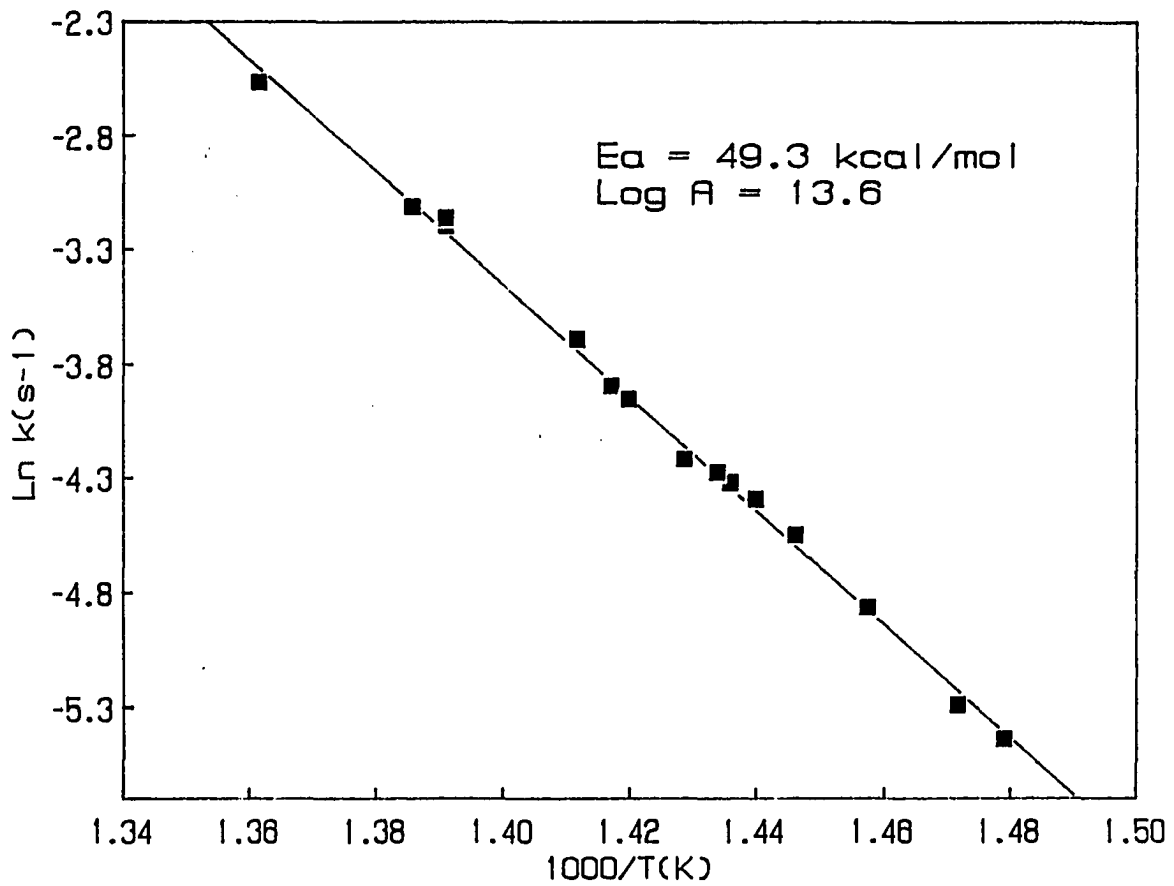


Figure 7. Arrhenius plot for the decay of 173 in LPP

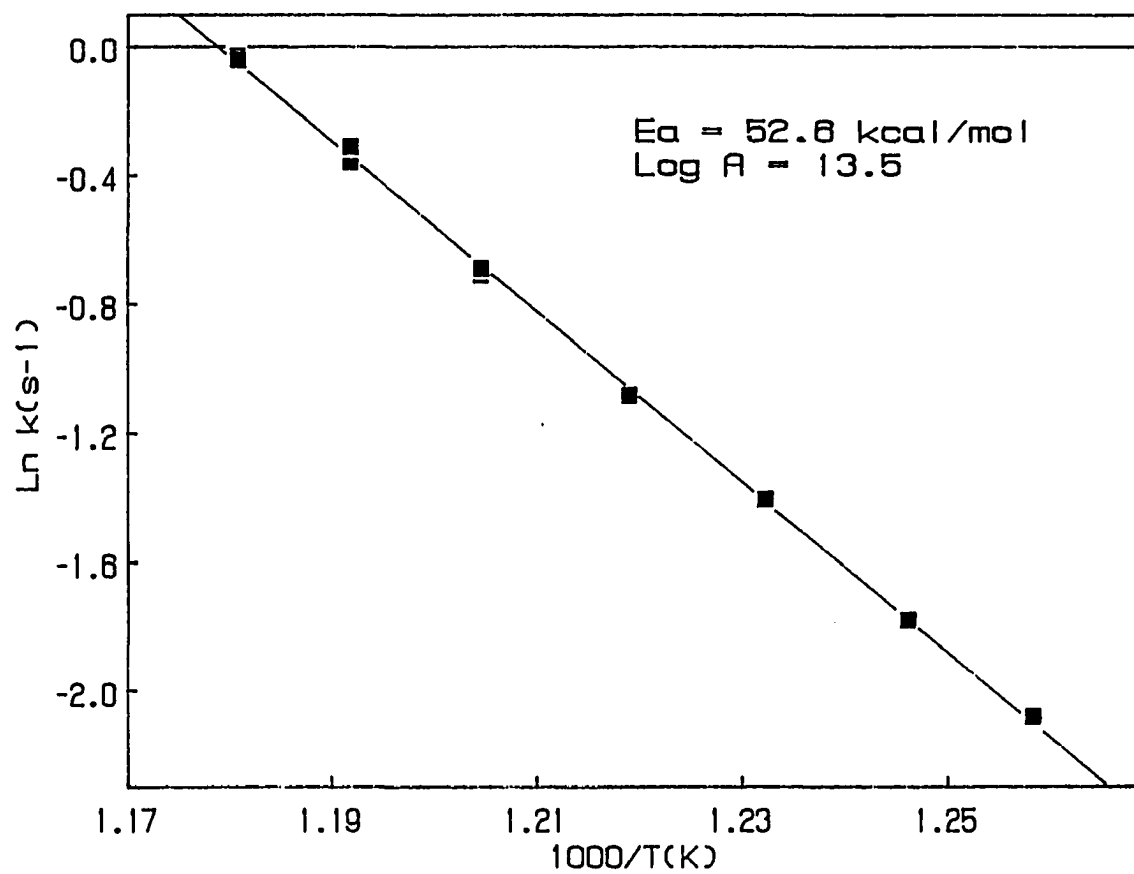


Figure 8. Arrhenius plot for the formation of  $\text{Me}_3\text{SiOMe}$  from 174 in SFR

the temperature range of 465-531°C by following the first-order rate constants of decay of 174 (Fig. 9). The activation energy ( $E_a = 52.0 \pm 0.6$  kcal/mol) and A-factor ( $\log A = 13.3 \pm 0.1$ ) were found to be very similar to those obtained by the SFR techniques.

These kinetic results (A-factors) for the decomposition of 173 and 174 clearly suggest three-centered<sup>18,40,41</sup> transition states for the decompositions of both 173 and 174.

(2-Methoxyethyl)trimethylsilane 175 was synthesized by the method of Pola et al.,<sup>101</sup> and was found to decompose cleanly to ethylene and methoxytrimethylsilane in a SFR. Kinetics were determined in the SFR by following the first-order rate constants of formation of methoxytrimethylsilane. A seventeen-point Arrhenius plot (Fig. 10) for the temperature range of 430-500°C, was almost a perfect straight line, and gave an activation energy ( $E_a$ ) of  $45.1 \pm 0.2$  kcal/mol and a  $\log A$  of  $12.7 \pm 0.1$ . An A-factor of  $\log A = 12.7$  is typical of a concerted four-centered transition state,<sup>18</sup> although the A-factors obtained by Davidson et al.<sup>25</sup> (vide infra) for the decompositions of (2-chloroethyl)trimethylsilane 8 and (2-chloromethyl)trimethylsilane 6 were 11.0. However, Davidson's data were obtained in very low temperature ranges, and the results were explained in terms of charge development in the transition state.

Compound 172 was synthesized by Grignard coupling of chloromethyltrimethylsilane with dimethyldichlorosilane followed by reaction with lithium methoxide. Pyrolysis of 172 in a SFR gave

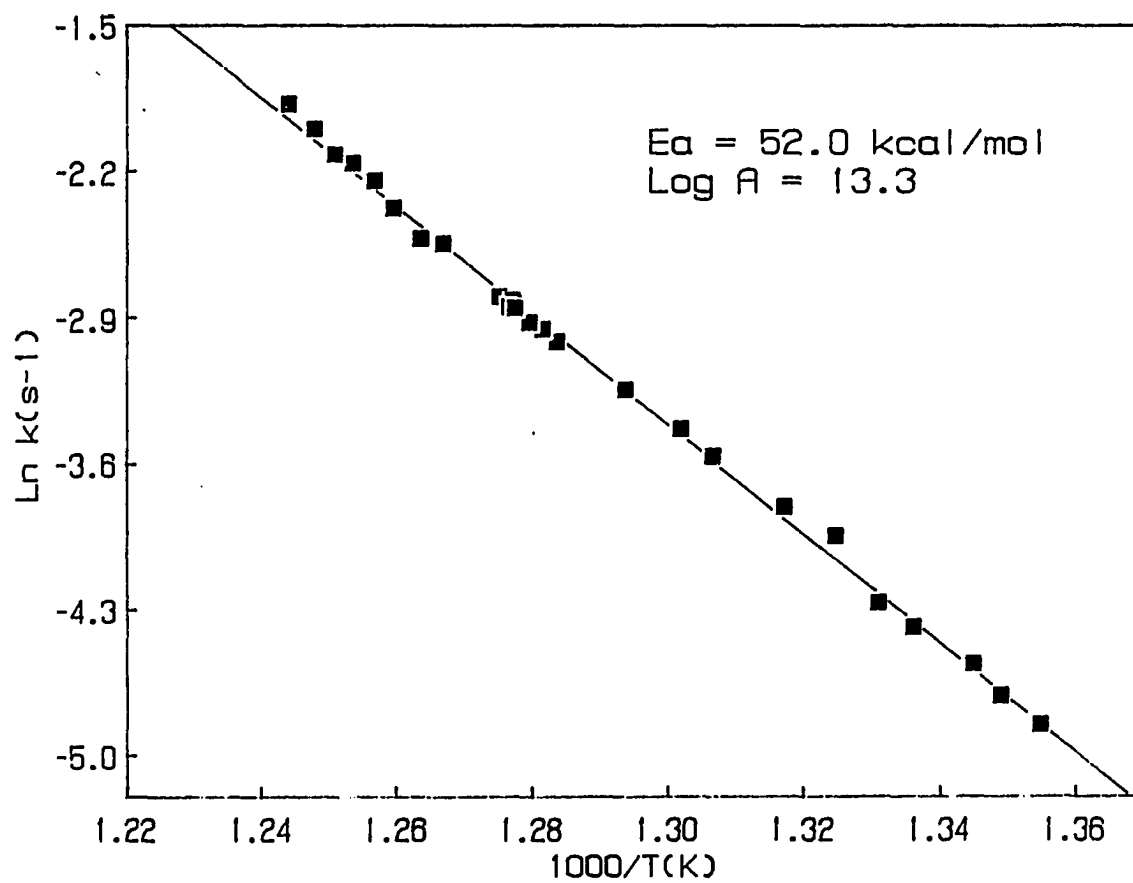


Figure 9. Arrhenius plot for the decay of 174 in LPP



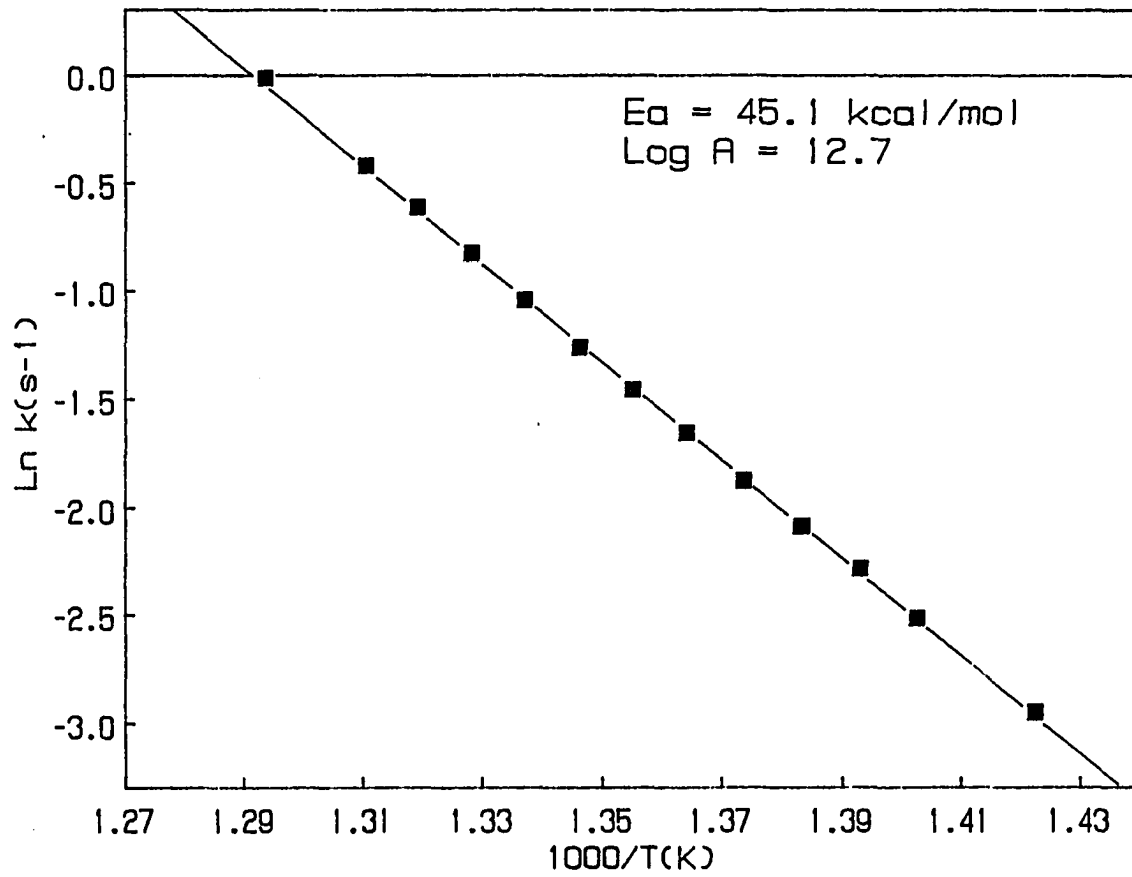


Figure 10. Arrhenius plot for the formation of  $\text{Me}_3\text{SiOMe}$  from 175 in SFR



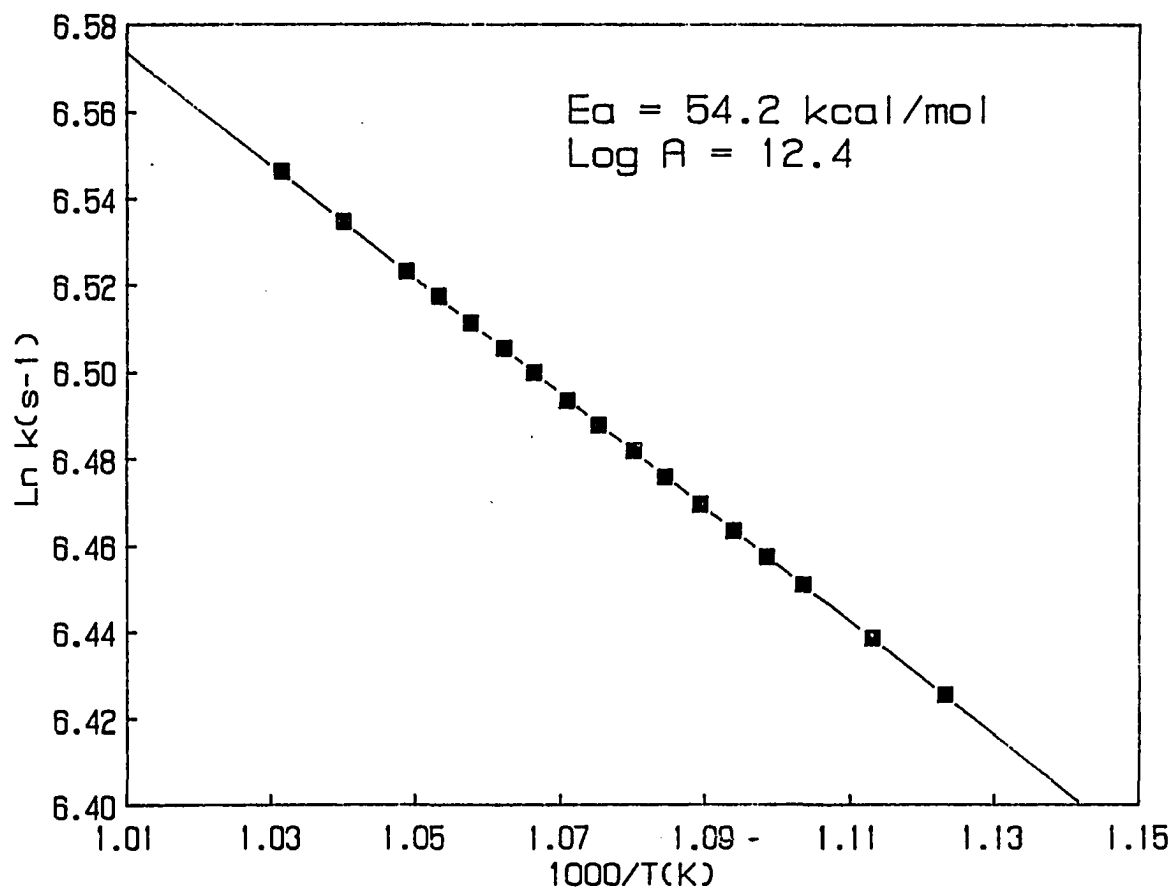


Figure 11. Arrhenius plot for the formation of  $\text{Me}_3\text{SiOMe}$  from 172 in SFR

Table 1. Arrhenius parameters for the decomposition of 173, 174, 175, and 172

Compound	Technique	Temp range °C	Ea (kcal/mol)	log A
<u>173</u>	SFR	485-530	50.4	14.0
	LPP	403-562	49.3	13.6
<u>174</u>	SFR	524-579	52.6	13.5
	LPP	465-531	52.0	13.3
<u>175</u>	SFR	430-500	45.1	12.7
<u>172</u>	SFR	618-697	54.2	12.4

Calculations based on these Arrhenius parameters give the rate constants ( $k$ ) and relative rate constants ( $k_{rel}$ ), as shown in Table 2, for the decomposition of 173, 174, 175, and 172 at 800K in the SFR. The results in Table 1 and Table 2 clearly show that the higher pre-exponential factors are the major contributors to the relative ease of  $\alpha$ -elimination of methoxytrimethylsilane from 173 and 174 over  $\beta$ -elimination of methoxytrimethylsilane from 175 and 172. This observation would be more apparent from the inspection of the entropy of activations ( $\Delta S^\ddagger$ ) at the mean temperatures of the experiments, and the relative values of pre-exponential factors, as shown in Table 3.

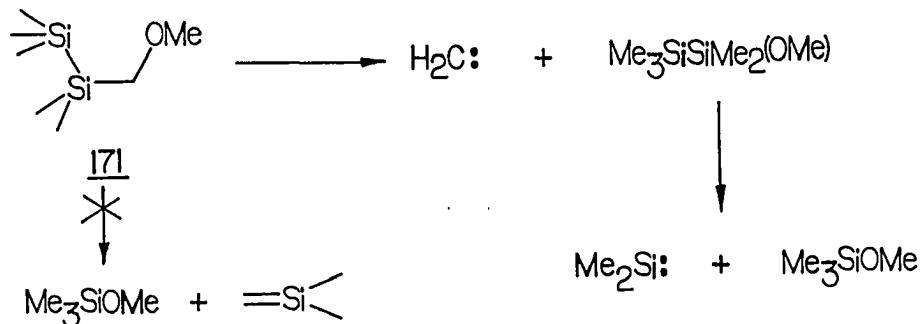
Table 2. Rate constants for decomposition of 173, 174, 175 and 172 at 800K

Compound	<u>173</u>	<u>174</u>	<u>175</u>	<u>172</u>
$k(s^{-1})$	1.70	0.135	2.39	0.00391
$k_{rel}$	435	34.5	611	1.00

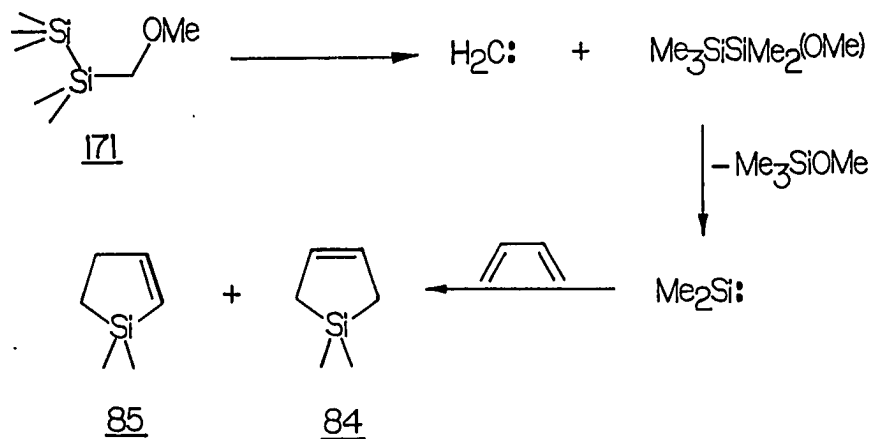
Table 3. Entropy factors for decomposition of 173, 174, 175 and 172

Compound	$\Delta S^\ddagger$	A	$A_{rel}$
<u>173</u>	1.80 $\pm$ 1.27	$1.00 \times 10^{14}$	39.8
<u>174</u>	-0.77 $\pm$ 0.49	$3.16 \times 10^{13}$	12.6
<u>175</u>	-6.08 $\pm$ 0.33	$5.01 \times 10^{12}$	2.00
<u>172</u>	-4.03 $\pm$ 0.29	$2.51 \times 10^{12}$	1.00

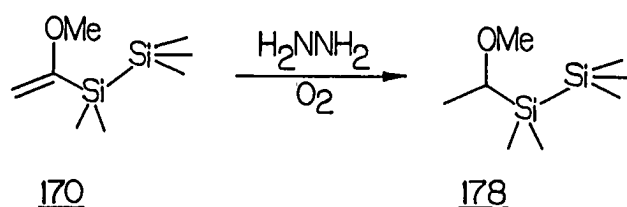
To reinvestigate Burns' work,<sup>96</sup> compound 171 was synthesized by the method of Kumada et al.<sup>102</sup> Flash vacuum pyrolysis of 171 at 750°C indeed gave a horrible mixture. However analysis by GCMS and GCIR showed the mixture to contain methoxytrimethylsilane as a major component. This may now be very clearly explained by an  $\alpha$ -elimination of methoxypentamethyldisilane to generate a very highly reactive species methylene, and methoxypentamethyldisilane. Methoxypentamethyldisilane, through a facile  $\alpha$ -elimination of methoxytrimethylsilane, would generate another highly reactive species, dimethylsilylene. It would be no surprise to obtain an intractable mixture from a reaction that generates two highly reactive species. Two efforts were made to clarify these



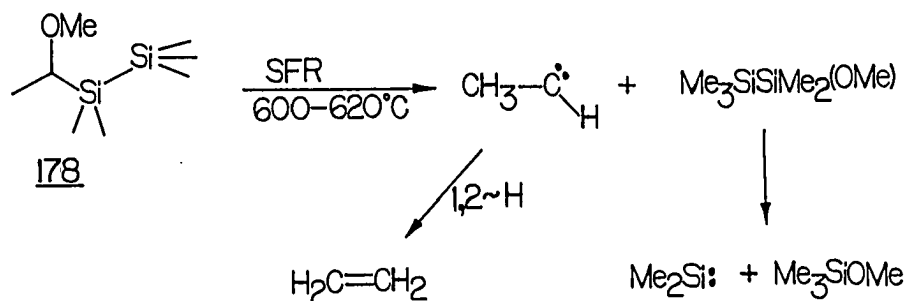
observations. First, compound 171 was copolylyzed with excess of 1,3-butadiene in a flow system at 620°C. The pyrolysate was still a mixture of many compounds as 1,3-butadiene also decomposed significantly under the reaction conditions. However GCMS analysis revealed the presence of methoxytrimethylsilane (19%), 1,1-dimethyl-1-silacyclopent-3-ene (8%), and 1,1-dimethyl-1-silacyclopent-2-ene (4%). 1,3-Butadiene is known to trap dimethylsilylene to form 84 and 85.<sup>103</sup> The second method to clarify this hypothesis of  $\alpha$ -elimination to generate carbene



involved synthesis of (1-methoxyethyl)pentamethyldisilane 178 by diimide reduction of 170.<sup>104</sup>



When compound 177 was pyrolyzed in a SFR at 600 and 620°C with a helium flow of 60 mL/min, GC trace of the product mixture gave a clean peak of ethylene (monitored by GCMS), as this was separated from all the other components. These product analyses and kinetic observations involving



170, 171, 172, 173, 174, 175, and 178 clearly point to the conclusion that systems such as 171 would undergo an entropically favored  $\alpha$ -elimination to generate carbenes, rather than a thermodynamically favored  $\beta$ -elimination to form silenes. An approximate quantitative thermodynamic favor for  $\beta$ -elimination of methoxytrimethylsilane from 171 can be estimated by examining the bond dissociation energies. It has already been calculated that formation of 1,1-dimethylsilene and methoxytrimethylsilane from 171 is endothermic by approximately 4.5 kcal/mol (vide infra). For the formation of ethylidene and methoxypentamethyldisilane, the bonds being broken are a silicon-carbon  $\sigma$  bond ( $D_{\text{Si-C}} = 89.4$  kcal/mol) and a carbon-oxygen  $\sigma$  bond ( $D_{\text{C-O}} = 91.0$  kcal/mol), and the bond that is formed is a silicon-oxygen  $\sigma$  bond ( $D_{\text{Si-O}} = 128.0$  kcal/mol). Thus,  $\alpha$ -elimination of methoxypentamethyldisilane from 171 is endothermic by approximately 60.4 kcal/mol, considering no energy release for the formation of ethylidene, as this has been found not to be a minimum in the energy surface of  $\text{C}_2\text{H}_4$ .<sup>87</sup>



## V. CONCLUSION

Through product analysis and kinetic investigations on a variety of model systems, a greater understanding of the scope and limitations of thermally-induced  $\alpha$ - and  $\beta$ -eliminations of alkoxysilanes to generate unsaturated carbon and silicon compounds has been accomplished.

Because of the availability of a much more facile retro-ene process to lose formaldehyde, 1-methoxy-2-trimethylsilyl-2-propene does not undergo a  $\beta$ -elimination of methoxytrimethylsilane to form allene. Replacement of the methoxy group by a siloxy group renders the retro-ene process unavailable, and  $\beta$ -elimination of hexamethyldisiloxane has been found to be a viable method for generation of allenes.

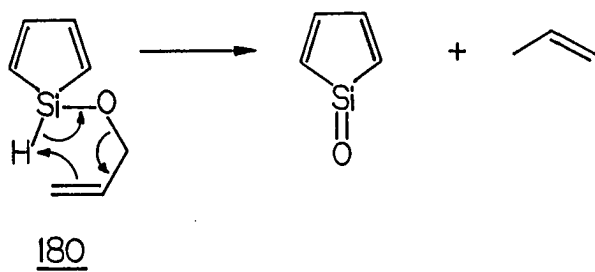
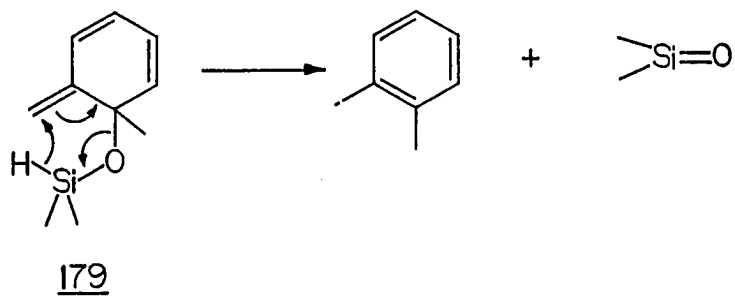
(1-Trimethylsilyl)vinyl dimethylmethoxysilane, upon flash vacuum pyrolysis, did not generate the desired 1,1-dimethyl-1-silaallene via a  $\beta$ -elimination of methoxytrimethylsilane, instead it underwent a surprising extrusion of dimethylsilanone. Mechanistic possibilities including an initial 1,2-migration of silicon to form a carbene, a homolytic loss of methyl group, and a retro-ene elimination of formaldehyde to generate a silene, have been ruled out based on product analysis, isotope labeling, and kinetic observations. These observations have led to the conclusion that vinyl dimethylalkoxysilanes generate dimethylsilanone via a novel homolytic 1,5-migration of hydrogen followed by closure of the resulting 1,4-biradical to form siloxetane.

(1-Methoxyethenyl)pentamethyldisilane has been found to undergo an  $\alpha$ -elimination of methoxypentamethyldisilane to form vinylidene,

rather than a much more thermodynamically favored  $\beta$ -elimination of methoxytrimethylsilane to form 1,1-dimethyl-1-silaallene. Kinetic investigations on a variety of model systems have led to the conclusion that this is due to an entropically more favored three-centered transition state in  $\alpha$ -elimination over a four-centered transition state in  $\beta$ -elimination.

Finally, allyloxydimethylsilane has been found to generate dimethylsilanone cleanly via a retro-ene elimination of propene. Substitution of the allylic position with two methyl groups has been found to lead to a competition between the retro-ene process and a homolytic process to form the highly stable 2-methyl-2-butenyl radical.

The results of these investigations on  $\alpha$ - and  $\beta$ -eliminations of alkoxysilanes could be used in the future for predicting the feasibility of a particular system to obtain the desired unsaturated carbon or silicon species. Although the thermal requirements for retro-ene decomposition of allyloxydimethylsilane to form dimethylsilanone are high, and substitution at allylic position gives rise to another competing reaction, this system could be made more viable by choosing appropriate substrates. Substrates (e.g., 179) that can form highly stable olefins, and substrates with weaker silicon-hydrogen bonds (e.g., 180), should be better precursors to silanones.



## VI. EXPERIMENTAL

## A. Instrumentation

1. General

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Nicolet model NT-300 spectrometer. A Bruker model WM-300 spectrometer was used for obtaining  $^2\text{H}$  NMR spectra. All chemical shifts are reported as parts-per-million ( $\delta$  scale) using either tetramethylsilane, benzene or chloroform as an internal standard. Infrared (IR) spectra were obtained on an IBM model IR/98 spectrometer. GCIR spectra were recorded on an IBM IR/98 spectrometer coupled with a HP5880A capillary GC. All bands are reported in reciprocal centimeters ( $\text{cm}^{-1}$ ). GCMS data were obtained at 70 eV on a HP5970 mass selective detector coupled with a HP5890 capillary GC. All signals are recorded in m/e percent relative intensities. Combustion analyses were performed by Desert Analytics, Tucson, Arizona.

Gas chromatographic (GC) analyses were performed on either a HP5890 or a HP5790 capillary GC. Unless otherwise specified, all GC yields were calculated from predetermined response factors and are based on the amount of starting material consumed. GC isolation on a preparative scale were performed on either a Varian-Aerograph series 1700 or a Varian-Aerograph model 920.

2. Kinetics

A pulsed, stirred-flow reactor (SFR) system, modeled after the description of Baldwin et al.<sup>94</sup> was routinely used for kinetic analyses.

The SFR system used a 60 ml/min flow of helium to sweep the material ( $\approx$  0.1 torr) through the reactor into a Varian 6000 GC which had the option of diverting the separated products, via a jet separator, into a VG SX-300 quadrupole mass spectrometer for MS analysis. The GC (FID) signals were recorded on a chart recorder as well as a Magnum XT/Mark 2 micro-computer (IBM-PC clone) for precise estimation of reactants and products.

For a brief description of the SFR system, a block diagram of the system is shown in Figure 12. In the sample storage line, reactants are stored in the gaseous form under vacuum. Sample from the storage line is transferred via a valve to the sample chamber where the pressure of the sample is measured by a pressure transducer. By a flow of an inert gas through the sample chamber, a pulse of sample is injected into the reaction vessel where the desired temperature and a "perfect mixing condition" are maintained. The reaction vessel is connected to a gas chromatograph where the various products are separated. The signals from the GC are fed into a chart recorder as well as a micro-computer for precise measurements of the various components. The pyrolysis products can also be diverted from the GC to a mass spectrometer for MS analysis.

The basic principle of the design is as follows: for a particular feed into the reaction vessel, the conversion depends on two factors. A higher reaction rate gives a higher conversion. A faster flow of mass through the reaction vessel lowers the conversion. The rate of mass flow is determined by the flow rate of the inert gas, the size of the

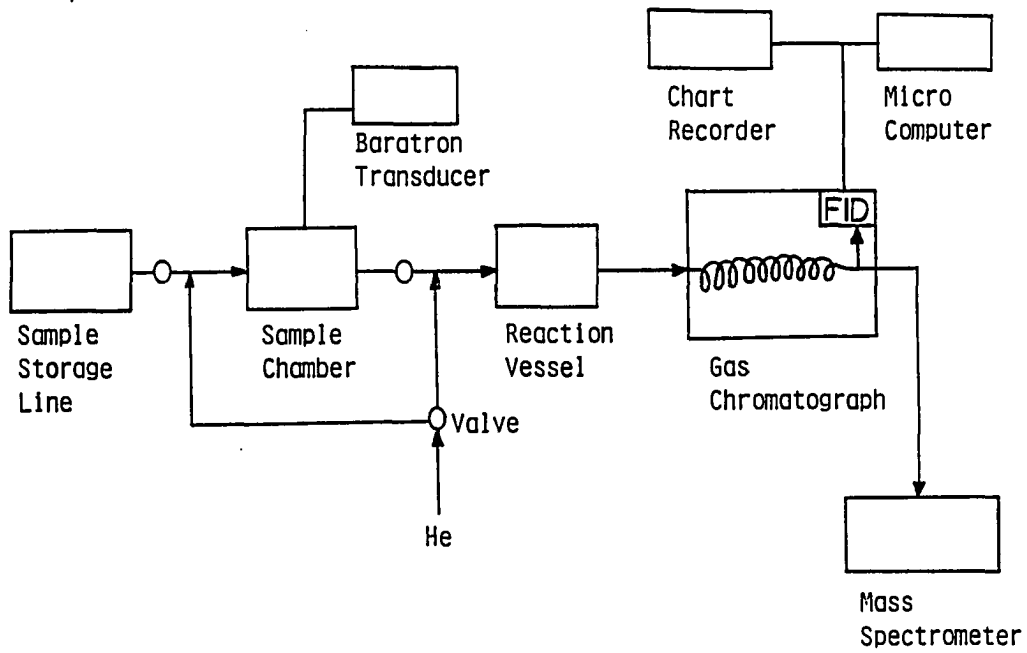


Figure 12. Pulsed stirred-flow reactor (SFR)

reaction vessel, and the difference between the room temperature and the temperature of the reaction vessel. If a "perfect mixing condition," i.e., a condition that allows all the reactant molecules to be subjected to the same reaction rate and flow rate, is maintained in the reaction vessel, one can mathematically relate the rate constant with the mass flow rate and the amount of product and reactant obtained at the outlet of the reaction vessel. A detailed discussion of the mathematics would be beyond the scope of this dissertation, and the interested readers are referred to the paper by Baldwin et al.<sup>94</sup>

A major advantage of the pulsed SFR system is that when a small pulse of reactant is dispersed in the reaction vessel with a huge excess of an inert gas, a condition for unimolecular gas-phase reaction devoid of surface reactions prevails.

Kinetics of decomposition of two compounds were also performed on a low pressure pyrolysis (LPP) system designed after that described by Davidson et al.<sup>99</sup> The heart of a LPP system is a reaction vessel where the desired temperature is maintained. A low pressure of sample ( $\approx 0.1$  torr) is introduced into the reaction vessel and decay of starting material or formation of product is monitored continuously by a mass spectrometer which is connected to the reaction vessel by a micro-capillary. The rate constant for decay of starting material or formation of a product is determined by a plot of mass spectral intensity of a selected peak versus time.

## B. Procedure and Results

1. Synthesis of (1-bromoethenyl)trimethylsilane 132

Compound 132 was prepared by the method of Boekman et al.<sup>85</sup> Thus, 90.4 g (0.904 mol) of vinyltrimethylsilane was cooled to -78 °C in a 1 L flask equipped with a mechanical stirrer, a condenser with a nitrogen inlet, and a pressure-equalizing addition funnel. Bromine (174 g, 1.09 mol) was added to the vigorously stirred liquid over a period of 1 h, and the flask was warmed to room temperature over 2 h. After stirring for 0.5 h, the reaction mixture was cooled by an ice-water bath, and 620 mL of diethylamine was added over a period of 2 h. The reaction mixture was then refluxed for 12 h, cooled to room temperature, and added to a mixture of 1 L of diethyl ether and 200 mL of water. The aqueous layer was discarded and the organic layer washed with 100 mL portions of ice-cold 10% aqueous HCl until the the aqueous extract remained acidic. The organic layer was then washed with 3 x 100 mL of water and 3 x 100 mL of saturated aqueous NaCl, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. Most of the ether was stripped by a rotary evaporator, and the residue fractionally distilled under vacuum using a 7 cm column packed with glass helices to obtain 88.5 g (0.494 mol, 55%) of pure 132 (bp 50-51 °C/60 torr, lit. bp 72-75 °C/120 torr). Compound 132 was characterized by GCMS 180 (6.9), 179 (1.0), 178 (M,7.3), 165 (28), 163 (27), 139 (100), 137 (100), 109 (16), 73 (28), and <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.18 (9 H, s), 6.16 (1 H, d, J = 2.0 Hz.), 6.25 (1 H, d, J = 2.0 Hz).



## 2. Synthesis of 1-methoxy-2-trimethylsilyl-2-propene 133

A 250 mL three-neck flask, equipped with a mechanical stirrer, a pressure-equalizing addition funnel, and a condenser with nitrogen inlet, was charged with 3.4 g (140 mmol) of magnesium turnings and 25 mL of THF. To the stirred suspension was added 0.4 mL of 1,2-dibromoethane to activate the magnesium. After the mixture warmed up, a solution of 8.9 g (50 mmol) of (1-bromoethenyl)trimethylsilane 132 in 25 mL of THF was added slowly to maintain a gentle reflux. After refluxing for an additional hour, the flask was cooled to 0 °C and a solution of 4.4 g (55 mmol) of chloromethyl methyl ether in 10 mL of THF was added slowly. The mixture was then stirred at room temperature for 24 h, and filtered through glass wool. The filtrate was added to 100 mL of water and 70 mL of pentane with stirring. The aqueous layer was discarded, and the organic layer washed with 5 x 25 mL of water and 3 x 25 mL of saturated NaCl, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and filtered. Fractional distillation under vacuum using a 7 cm column packed with glass helices gave 2.7 g (19 mmol, 37%) of pure 133: bp 53-54 °C/50 torr; GCMS 131 (1.1), 130 (3.2), 129 (M-15, 28), 89 (100), 73 (78), 59 (62), 45 (43), 43 (35); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.09 (9 H, s), 3.29 (3 H, s), 4.00 (2 H, m), 5.41 (1 H, m), 5.75 (1 H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ -1.57, 57.81, 76.85, 124.96, 148.95; and IR (neat) 3051 (w), 2957 (s), 2818 (s), 1452 (m), 1420 (m), 1410 (m), 1246 (s), 1190 (m), 1111 (m), 1092 (m), 935 (s), 858 (s), 760 (m), 692 (m) cm<sup>-1</sup>.

### 3. Flash vacuum pyrolysis (FVP) of 133

Compound 133 was pyrolyzed by distilling (25 °C,  $5 \times 10^{-4}$  torr) it through a horizontal quartz tube (length: 30 cm, OD: 0.6 cm) packed with quartz chips and heated to 600 °C. The pyrolysate was collected in a trap cooled with liquid nitrogen, and was found to contain isopropenyltrimethylsilane (134) (100%) along with 40% of unreacted starting 133. Compound 134 was identified by comparing its GCMS and  $^1\text{H}$  NMR spectrum with those of an authentic sample (vide supra).

### 4. Synthesis of 2-trimethylsiloxy-3-trimethylsilyl-3-butene 135

A 250 mL 3-neck flask, equipped with a magnetic stirrer, a nitrogen inlet, and septa, was charged with 2.6 g (14 mmol) of 132 and 50 mL of diethyl ether. After cooling to -78 °C, a solution of t-BuLi (9.5 mL, 1.7 M, 16 mmol) in pentane was added over a period of 10 min, and the mixture stirred at -78 °C for 2 h. Addition of acetaldehyde (0.80 g, 14 mmol) in 10 mL diethyl ether was followed by warming to room temperature and stirring for an additional 2 h. After cooling to -78 °C, 4.0 g (37 mmol) of trimethylchlorosilane and 10 mL of triethylamine was added, and the mixture allowed to warm up to room temperature. Stirring for 4 h was followed by addition of 50 mL of ice-cold water and 25 mL of pentane. The organic layer was washed with 4 x 25 mL of water and 3 x 25 mL of saturated NaCl, dried over  $\text{Na}_2\text{SO}_4$ , and filtered. Rotary evaporation to 10 mL was followed by fractional distillation using a 7 cm column packed with glass helices to afford 1.7 g (7.9 mmol, 56%) of pure 135: bp 51-53 °C/2.5 torr; GCMS 218 (0.3), 217 (0.9), 216 (M, 4.2), 201 (9.4), 149 (5.8), 148 (12), 147 (72), 117 (24), 73 (100), 66

(12), 45 (25);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.08 (9 H, s), 0.10 (9 H, s), 1.21 (3 H, d,  $J = 6.4$  Hz), 4.21 (1 H, m), 5.28 (1 H, m), 5.69 (1 H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -0.30, 0.15, 25.79, 73.02, 122.39, 156.75; IR (neat) 3055 (w), 2959 (s), 1252 (s), 1115 (m), 1086 (s), 978 (m), 891 (m), 839 (s), 748 (m), 690 (w)  $\text{cm}^{-1}$ .

#### 5. FVP of 135

Compound 135 was distilled (25 °C,  $5 \times 10^{-4}$  torr) through a horizontal quartz tube (length: 30 cm, OD: 1.6 cm) packed with quartz chips and heated to 700 °C. The pyrolysate was collected in a trap cooled with liquid nitrogen, and contained 28% of unreacted starting material. Products 1,2-butadiene (38%) and hexamethyldisiloxane (42%) were identified by comparing their GCMS with those of authentic samples. Product 2-trimethylsilyl-1,3-butadiene (25%) was characterized by GCMS 127 (0.7), 126 (M, 6.0), 113 (0.8), 112 (2.3), 111 (19), 85 (25), 73 (100), 59 (18), 45 (24), 43 (27) and  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.16 (9 H, s), 5.05 (1 H, d,  $J = 10.8$  Hz), 5.22 (1 H, d,  $J = 17.7$  Hz), 5.42 (1 H, d,  $J = 2.7$  Hz), 5.72 (1 H, d,  $J = 2.7$  Hz), 6.44 (1 H, d-d,  $J = 17.7$  Hz, 10.8 Hz).

#### 6. Synthesis of 1-trimethylsiloxy-1-phenyl-2-trimethylsilyl-2-propene 137

A 100 mL 3-neck flask, equipped with a magnetic stirrer, a nitrogen inlet, and septa, was charged with 2.5 g (14.0 mmol) of 132 and 15 mL of THF, and was cooled to -78 °C. To this stirred mixture was added 17 mL (1.7 M, 29 mmol) of t-BuLi solution in pentane over a period of 10 min. Stirring for 1 h was followed by addition of a solution of 3.1 g (29

mmol) of benzaldehyde in 10 mL THF and warming to room temperature. After stirring for 2 h, the mixture was cooled to  $-78\text{ }^{\circ}\text{C}$  and 5.0 g (46 mmol) of trimethylchlorosilane was added. After stirring for 2.5 h the mixture was treated with 50 mL of ice-cold water and 50 mL of pentane. The organic layer was washed with 3 x 25 mL of water and 3 x 25 mL of saturated NaCl, dried over  $\text{Na}_2\text{SO}_4$ , and filtered. Rotary evaporation was followed by fractional distillation using a 7 cm column packed with glass helices, to afford 2.6 g (9.4 mmol, 67%) of compound 137: bp  $87\text{--}90\text{ }^{\circ}\text{C}/0.3\text{ torr}$ ; GCMS 279 (2), 278 (M, 8), 181 (2), 180 (10), 179 (64), 149 (2), 148 (4), 147 (26), 116 (8), 115 (6), 73 (100), 45 (30);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -0.09 (9 H, s), 0.07 (9 H, s), 5.29 (1 H, s), 5.46 (1 H, d-d,  $J = 2.7\text{ Hz}, 1.3\text{ Hz}$ ), 5.81 (1 H, d-d,  $J = 2.7\text{ Hz}, 1.3\text{ Hz}$ ), 7.28 (5 H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -0.57, 0.16, 79.35, 124.24, 126.93, 127.86, 143.58, 154.91; IR (neat) 3063 (w), 3028 (w), 2957 (m), 1252 (s), 1088 (m), 1065 (s), 892 (m), 839 (s), 758 (m), 748 (m), 698 (m),  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{15}\text{H}_{26}\text{OSi}_2$ : C, 64.68; H, 9.41. Found: C, 65.02; H, 9.72.

#### 7. FVP of 137

Compound 137 was pyrolyzed by distilling ( $25\text{ }^{\circ}\text{C}$ ,  $2 \times 10^{-4}\text{ torr}$ ) it through a horizontal quartz tube (length: 30 cm, OD: 1.6 cm) packed with quartz chips and heated to  $650\text{ }^{\circ}\text{C}$ . The pyrolysate was collected in a trap cooled with liquid nitrogen and showed 21% of starting 137 to have decomposed. The products were exclusively hexamethyldisiloxane (53%) and phenylallene (86%). Hexamethyldisilane was identified by GCMS and phenylallene was identified by GCMS 117 (6.1), 116 (M, 64), 115 (100), 89 (16), 63 (20), 51 (15), 50 (13);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.14 (2 H,

d,  $J = 6.8$  Hz), 6.16 (1 H, t,  $J = 6.8$  Hz), 7.29 (5 H, m); and IR (neat) 3063 (w), 3032 (m), 1942 (s), 1597 (m), 1495 (s), 1458 (m), 1026 (m), 852 (s), 762 (s), 694 (s)  $\text{cm}^{-1}$ .

#### 8. Synthesis of (1-trimethylsilylethenyl)dimethylchlorosilane 138

A 250 mL 3-neck flask was charged with 3.5 g (144 mmol) of magnesium, 20.7 g (160 mmol) of dichlorodimethylsilane, and 40 mL of THF, and was equipped with a mechanical stirrer, a condenser with a nitrogen inlet, and a pressure-equalizing addition funnel. To the stirred suspension was added 0.3 mL of 1,2-dibromoethane to activate the magnesium. After the reaction mixture warmed up, a solution of 13.1 g (73.2 mmol) of (1-bromoethenyl)trimethylsilane 132 in 40 mL of THF was added slowly to maintain a gentle reflux. After the addition was complete, the reaction mixture was stirred at room temperature for 20 h, and then filtered and rotary evaporated to remove most of THF. About 50 mL of pentane was added to precipitate out the salt, and then filtered and rotary evaporated to obtain the crude product, which was distilled under vacuum using a 7 cm column packed with glass helices. The pure product 138, 5.9 g (30.7 mmol, 42%), boiled at 96-98 °C/65 torr, and was characterized by GCMS 179 (21), 178 (9), 177 (M-15, 54), 95 (9), 93 (23), 85 (8), 84 (44), 83 (100), 73 (71), 45 (43), 43 (52);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.42 (9 H, s), 0.49 (6 H, s), 6.38 (1 H, d,  $J = 4.4$  Hz), 6.46 (1 H, d,  $J = 4.4$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -0.35, 3.04, 148.8, 151.3; IR (neat) 3018 (w), 2961 (m), 1408 (m), 1254 (s), 1148 (m), 974 (m), 856 (s), 839 (s), 786 (m), 677 (w)  $\text{cm}^{-1}$  and Anal. Calcd for  $\text{C}_7\text{H}_{17}\text{ClSi}_2$ : C, 43.60; H, 8.89; found C, 43.26; H, 9.23.

### 9. Synthesis of (1-trimethylsilylethenyl)dimethylmethoxysilane 139

Lithium methoxide was prepared by adding a solution of n-BuLi (7.5 mL, 2.5 M, 19 mmol) in hexane to a solution of 2.5 mL of methanol in 30 mL THF at -78 °C and stirring the reaction mixture at room temperature for 2 h. A 100 mL flask, equipped with a magnetic stirrer and a nitrogen inlet, was charged with 20 mL of THF and 3.2 g (17 mmol) of compound 138, and was cooled to -78 °C. After addition of the lithium methoxide solution slowly via cannula, and stirring for 3 h, the flask was warmed up to room temperature. Trap to trap distillation was followed by removal of THF by distillation using a 17 cm vigreux column. The residue was distilled under vacuum using a 7 cm column packed with glass helices to afford 2.2 g (12 mmol, 70%) of pure 139: bp 43-44 °C/6 torr; GCMS 175 (5), 174 (12), 173 (M-15, 66), 91(4) 90 (8), 89 (100), 73 (37), 59 (62), 45 (26), 43 (23); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.09 (9 H, s), 0.17 (6 H, s), 3.37 (3 H, s), 6.33 (1 H, d, J = 5.2 Hz), 6.37 (1 H, d, J = 5.2 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ -1.52, -0.57, 50.26, 141.55, 153.16; IR (neat) 3011 (w), 2959 (s), 2930 (m), 2831 (m), 1408 (m), 1250 (s), 1150 (m), 1090 (s), 970 (m), 847 (s), 781 (m) cm<sup>-1</sup>. Anal. Calcd. for C<sub>8</sub>H<sub>20</sub>OSi<sub>2</sub>: C, 51.00; H, 10.70. Found C, 51.11; H, 10.98.

### 10. FVP of 139

Compound 139 was distilled (25 °C, 5 x 10<sup>-4</sup> torr) through a horizontal quartz tube (length: 30 cm, OD: 1.6 cm) packed with quartz chips and heated to 800 °C. The pyrolysate was collected in a trap cooled with liquid nitrogen. Isopropenyltrimethylsilane 134 (38%), and compound 140 (23%), were isolated by preparative GC, and D<sub>3</sub> 4%, D<sub>4</sub> (8%),

and 44% of starting 139 were detected by GC and GCMS of the crude pyrolysate. Isopropenyltrimethylsilane was identified by comparing its GCMS 114 (M, 4.2), 101 (1.9), 100 (4.3), 86 (10), 73 (100), 59 (24), and  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.06 (9 H, s), 1.80 (3 H, m), 5.22 (1 H, m), 5.52 (1 H, m), with an authentic sample.

Compound 140: GCMS 249 (2), 248 (4), 247 (M-15, 19), 165 (8), 164 (16), 163 (100), 143 (19), 133 (37), 89 (29), 73 (61), 59 (28);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.08 (6 H, s), 0.09 (9 H, s), 0.18 (6 H, s), 3.45 (3 H, s), 6.27 (1 H, d,  $J = 5.2$  Hz), 6.34 (1 H, d,  $J = 5.2$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -1.35, -0.50, 1.56, 49.83, 140.34, 154.50; IR (neat) 3009 (w), 2961 (m), 2930 (w), 2835 (w), 1409 (w), 1259 (s), 1096 (m), 1053 (s), 849 (s), 797 (m)  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{10}\text{H}_{26}\text{O}_2\text{Si}_3$ : C, 45.74; H, 9.98. Found C, 45.69; H, 10.42.

#### 11. FVP of vinyl dimethylmethoxysilane 149

Vinyl dimethylmethoxysilane was pyrolyzed by distilling (25 °C,  $6 \times 10^{-4}$  torr) it through a horizontal quartz tube (length: 30 cm, OD: 1.6 cm) packed with quartz chips and heated to 800 °C. The pyrolysate was collected in a trap cooled with liquid nitrogen. GC analysis of the pyrolysate showed propene (58%), disiloxane 150 (21%), and traces of  $\text{D}_3$  and  $\text{D}_4$  along with 80% of unreacted starting material. Propene was isolated in  $\text{CDCl}_3$  solvent, and characterized by GCMS as well as  $^1\text{H}$  NMR.

Compound 150: GCMS 177 (8), 176 (17), 175 (M-15, 100), 163 (15), 145 (60), 133 (34), 119 (14), 73 (18), 59 (31);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.07 (6 H, s), 0.16 (6 H, s), 3.44 (3 H, s), 5.73 (1 H, d-d,  $J = 20.1$  Hz, 4.2 Hz), 5.93 (1 H, d-d,  $J = 14.9$  Hz, 4.2 Hz), 6.12 (1 H, d-d,  $J = 20.1$  Hz,

14.9 Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -1.46, 0.19, 49.73, 131.77, 139.12; GCIR 3055 (w), 2966 (m), 2908 (w), 2843 (w), 1412 (w), 1261 (m), 1069 (s), 849 (m), 802 (s)  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_7\text{H}_{18}\text{O}_2\text{Si}_2$ : C, 44.16; H, 9.53. Found C, 44.37; H, 9.51.

## 12. FVP of vinyl dimethylethoxysilane 151

Vinyl dimethylethoxysilane was distilled (25 °C,  $7 \times 10^{-4}$  torr) through a horizontal quartz tube (length: 30 cm, OD: 1.6 cm) packed with quartz chips and heated to 800 °C. The pyrolysate was collected in a trap cooled with liquid nitrogen. Mixture of 2-butenes (35%), disiloxane 152 (11%), and disiloxane 153 (5%) were isolated by preparative GC, and unreacted starting 151 (54%),  $\text{D}_3$  (4%), and vinyl dimethyl silanol (17%) were detected by GC and GCMS of the crude pyrolysate. Mixture of cis- and trans-2-butenes was characterized by GCMS 57 (1.8), 56 (M, 41), 42 (4.1), 41 (100), 39 (58), and  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.57 (6 H, m), 5.43 (2 H, m). Disiloxane 152 was identified by GCMS 191 (9), 190 (19), 189 (M-15, 100), 163 (4), 162 (9), 161 (47), 145 (56), 133 (75), 119 (28), 75 (20), 73 (29), 59 (32);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.07 (6 H, s), 0.15 (6 H, s), 1.18 (3 H, t,  $J = 7.0$  Hz), 3.70 (2 H, q,  $J = 7.0$  Hz), 5.73 (1 H, d-d,  $J = 20.0$  Hz, 4.2 Hz), 5.95 (1 H, d-d,  $J = 14.9$  Hz, 4.2 Hz), 6.15 (1 H, d-d,  $J = 20.0$  Hz, 14.9 Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -0.85, 0.24, 18.41, 57.81, 131.74, 139.22; and GCIR 2966 (m), 1404 (w), 1261 (m), 1065 (s), 841 (m), 820 (s)  $\text{cm}^{-1}$ . Disiloxane 153 was characterized by GCMS 163 (7), 162 (13), 161 (M-15, 80), 135 (16), 134 (15), 133 (100), 119 (37), 75 (28), 73 (16), 61 (17), 60 (21), 45 (20);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.11 (6 H, s), 0.16 (6 H, s), 2.06 (1 H, s), 5.73 (1 H,



d-d,  $J = 20.0$  Hz, 4.2 Hz), 5.94 (1 H, d-d,  $J = 14.8$  Hz, 4.2 Hz), 6.15 (1 H, d-d,  $J = 20.0$  Hz, 14.8 Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.26, 0.49, 131.98, 139.12; and GCIR 2966 (w), 1265 (m), 1069 (s), 837 (m), 806 (s)  $\text{cm}^{-1}$ .

### 13. FVP of 1-butene

1-Butene was pyrolyzed by distilling (25 °C,  $5 \times 10^{-4}$  torr) it through a horizontal quartz tube (length: 30 cm, OD: 1.6 cm) packed with quartz chips and heated to 800 °C. The pyrolysate was collected in a trap cooled with liquid nitrogen and was found to be pure starting material by  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ).

### 14. Synthesis of vinyl dimethylphenoxy silane 154

A 100 mL flask, equipped with a magnetic stirrer and a nitrogen inlet, was charged with 2.5 g (27 mmol) of phenol, and 30 mL of triethylamine. To the stirred mixture was added 3.3 g (27 mmol) of vinyl dimethylchlorosilane slowly through a syringe. After stirring at room temperature for 40 h, 20 mL ether was added and the salts were filtered out. Rotary evaporation to 10 mL was followed by a further addition of 20 mL ether, which was followed by filtration and rotary evaporation to afford 6 mL of crude product. Fractional distillation under vacuum using a 15 cm Vigreux column gave 2.3 g (13 mmol, 50%) of pure 154: bp 80-82 °C/5.0 torr; GCMS 180 (1.5), 179 (5.4), 178 (M, 34), 165 (4.3), 164 (16), 163 (100), 151 (16), 137 (38), 104 (20), 77 (19), 59 (17);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.33 (6 H, s), 5.80 (1 H, d-d,  $J = 20.1$  Hz, 4.0 Hz), 5.90 (1 H, d-d,  $J = 13.8$  Hz, 4.0 Hz), 6.25 (1 H, d-d,  $J = 20.1$  Hz, 13.8 Hz), 6.90 (3 H, m), 7.21 (2 H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -1.49,

120.00, 121.45, 129.36, 133.83, 136.86, 155.06; and IR (neat) 3055 (w), 3040 (w), 2963 (m), 1597 (s), 1493 (s), 1408 (m), 1261 (s), 1252 (s), 1005 (m), 918 (s), 841 (s), 816 (s), 791 (s), 760 (s), 692 (s)  $\text{cm}^{-1}$ .

15. FVP of vinyl dimethylphenoxysilane 154

Compound 154 was distilled (25 °C,  $6 \times 10^{-4}$  torr) through a horizontal quartz tube (length: 30 cm, OD: 1.6 cm) packed with quartz chips and heated to 900 °C. The pyrolysate was collected in a trap cooled with liquid nitrogen, and was found to contain virtually GC-pure starting material.

16. Synthesis of 139D

Compound 139D was synthesized in 50% yield by following the same procedure as for the synthesis of 139, and was characterized by GCMS 178 (5.7), 177 (13), 176 (M-15, 75), 94 (3.6), 93 (8.1), 92 (100), 73 (29), 62 (15), 60 (36), 45 (18), 43 (16);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.09 (9 H, s), 0.18 (6 H, s), 6.34 (1 H, d,  $J = 5.3$  Hz), 6.38 (1 H, d,  $J = 5.3$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -1.51, -0.58, 141.67, 152.91, (OCD<sub>3</sub> carbon buried under baseline); and IR (neat) 3011 (w), 2959 (s), 2928 (m), 2222 (w), 2203 (w), 2064 (m), 1408 (m), 1250 (s), 1150 (m), 1126 (s), 1078 (s), 970 (m), 839 (s), 781 (s)  $\text{cm}^{-1}$ .

17. FVP of 139D

Compound 139D was distilled (25 °C,  $8 \times 10^{-4}$  torr) through a horizontal quartz tube (length: 30 cm, OD: 1.6 cm) packed with quartz chips and heated to 800 °C. The pyrolysate was collected in a trap cooled with liquid nitrogen. Compounds 134D and 140D were isolated by

preparative GC, and D<sub>3</sub> and D<sub>4</sub> were detected by GCMS of the crude pyrolysate. Identity of 134D was established by GCMS 117 (M, 4.1), 104 (1.8), 103 (5.2), 102 (51), 74 (100), 73 (34), 60 (20), 45 (25), 44 (20), 43 (37); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.06 (9 H, s), 1.78 (2 H, t, J = 2.1 Hz); and <sup>2</sup>H NMR (CDCl<sub>3</sub>) δ 1.81 (1 D, t, J = 2.1 Hz), 5.25 (1 D, s), 5.56 (1 D, s). Compound 140D was characterized by GCMS 252 (4), 251 (8), 250 (M-15, 31), 168 (7), 167 (15), 166 (100), 143 (13), 134 (21), 92 (17), 73 (28); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.07 (6 H, s), 0.09 (9 H, s), 0.17 (6 H, s), 6.27 (1 H, d, J = 5.2 Hz), 6.33 (1 H, d, J = 5.2 Hz); and <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ -1.35, -0.51, 1.55, 140.32, 154.53, (OCD<sub>3</sub> carbon buried under baseline).

#### 18. Copyrolysis of 149 and benzaldehyde

A mixture of 0.122 g (0.859 mmol) of 149 and 1.09 g (1.02 mmol) of benzaldehyde was pyrolyzed by dripping it with a syringe into a vertical quartz tube (length: 30 cm, OD: 1.6 cm) packed with quartz chips and heated to 720 °C. The pyrolysate was collected in a trap cooled to -78 °C and was found (GCMS) not to contain phenylpropene or any of its isomers.

#### 19. Copyrolysis of 139 and 1,3-butadiene

Compound 139 was pyrolyzed by dripping it with a syringe at a rate of 20 mg/min into a vertical quartz tube (length: 30 cm, OD: 1.6 cm) packed with quartz chips and heated to 660 °C, while a downward flow of 60 mL/min of 1,3-butadiene gas was maintained through the tube. The pyrolysate was a huge mixture of products, as 1,3-butadiene itself

decomposed. However GCMS analysis showed the pyrolysate not to contain even a trace of 161 or any of its isomers.

#### 20. Copyrolysis of 139 and 139D

A mixture of 83.4 mg (0.444 mmol) of 139 and 78.3 mg (0.410 mmol) of 139D was distilled (25 °C,  $5 \times 10^{-4}$  torr) through a horizontal quartz tube (length: 30 cm, OD: 1.6 cm) packed with quartz chips and heated to 800 °C. The pyrolysate was collected in a trap cooled with liquid nitrogen, and was analysed by GCMS. A low resolution MS (70 eV) quantitation for isopropenyltrimethylsilane in the range of m/e 113-120 (M) showed the following percent relative intensities: 113 (0.3), 114 (100), 115 (14), 116 (7.7), 117 (84), 118 (11), 119 (3.7), 120 (0.3). A low resolution MS (70 eV) quantitation for isopropenyltrimethylsilane in the range of m/e 98-105 (M-15) showed the following percent relative intensities: 98 (0.2), 99 (100), 100 (13), 101 (8.1), 102 (76), 103 (8.6), 104 (3.4), 105 (0.5).

#### 21. Determination of $k_H/k_D$ for the decomposition of 139 and 139D

Compounds 139 and 139D were pyrolyzed at 695 °C in an SFR (sample pressure: 0.04-0.06 torr) to determine the rate constants for the formation of 134 ( $k_H$ ) and 134D ( $k_D$ ) respectively. The results are summarized in Table 4.

#### 22. Kinetics of decomposition of 149

The first-order rate constants for formation of propene were determined by pyrolyzing 149 (sample pressure: 0.04-0.05 torr) at 590-770 °C in an SFR. The data, along with the results of a linear

Table 4.  $k_H/k_D$  for the decomposition of 139 and 139D in SFR

No of Obs	$k_H$ ( $s^{-1}$ )	Ave $k_H$ ( $s^{-1}$ )	$k_D$ ( $s^{-1}$ )	Ave $k_D$ ( $s^{-1}$ )	$k_H/k_D$
1	0.1437		0.1089		
2	0.1495		0.1157		
3	0.1526		0.1097		
		0.1486		0.1114	$1.34 \pm 0.08$

Table 5. Rate constants for the formation of propene from 149 in SFR

T ( $^{\circ}$ C)	k ( $s^{-1}$ )	T ( $^{\circ}$ C)	k ( $s^{-1}$ )	T ( $^{\circ}$ C)	k ( $s^{-1}$ )
730.2	0.1590	750.0	0.3025	735.0	0.1891
730.2	0.1623	760.0	0.4260	725.1	0.1383
720.0	0.1190	770.0	0.6179	714.9	0.0974
710.0	0.08163	755.2	0.3783	714.9	0.09652
700.1	0.05972	755.2	0.3722	705.1	0.06991
690.0	0.04054	745.2	0.2642	705.1	0.06797
740.0	0.2253	745.2	0.2672		

$\log A = 13.8 \pm 0.1 s^{-1}$ .       $E_a = 66.9 \pm 0.4$  kcal/mol.  
 $\Delta H^{\ddagger} = 64.9 \pm 0.1$  kcal/mol.       $\Delta S^{\ddagger} = 0.14 \pm 0.41$  eu at 730  $^{\circ}$ C.

least square calculation performed by a microcomputer, are summarized in Table 5.

### 23. Synthesis of allyloxydimethylsilane 166

A 100 mL 3-neck flask, equipped with a magnetic stirrer and a nitrogen inlet, was charged with 5.2 g (55 mmol) of dimethylchlorosilane, 3.2 g (76 mmol) of calcium hydride, and 40 mL of diethyl ether. After cooling the mixture to 0 °C, 2.1 g (36 mmol) of allyl alcohol was added dropwise through a syringe over a period of 5 min. The mixture was warmed up to room temperature and stirred for 24 h. Trap to trap distillation was followed by fractional distillation using a 17 cm Vigreux column to afford 1.9 g (17 mmol, 46%) of 166 (bp 87-90 °C, lit. bp 83-84 °C) which contained (by GC) a very small amount of allyl alcohol. Pure 166 was obtained by preparative GC and was characterized by GCMS 116 (M, 1.4), 115 (11), 101 (50), 99 (59), 75 (97), 61 (41), 59 (94), 45 (100), 43 (55), 41 (43) and  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.21 (6 H, d,  $J = 2.8$  Hz), 4.16 (2 H, m), 4.63 (1 H, hep,  $J = 2.8$  Hz), 5.09 (1 H, m), 5.21 (1 H, m), 5.91 (1 H, m).

### 24. Kinetics of decomposition of 166

The first-order rate constants for formation of propene were determined by pyrolyzing 166 at 600-680 °C in an SFR (sample pressure: 0.04-0.05 torr). The data, along with the results of a linear least square calculation performed by a microcomputer, are summarized in Table 6.

Table 6. Rate constants for the formation of propene from 166 in SFR

T (°C)	k (s <sup>-1</sup> )	T (°C)	k (s <sup>-1</sup> )	T (°C)	k (s <sup>-1</sup> )
630.0	0.2234	680.0	1.202	635.1	0.2633
630.0	0.2225	620.1	0.1655	645.0	0.3662
640.0	0.3154	610.2	0.1183	645.3	0.3719
650.2	0.4294	600.2	0.08342	655.0	0.5119
650.2	0.4377	615.0	0.1348	665.1	0.7151
660.1	0.5970	615.0	0.1397	665.1	0.7157
670.0	0.8405	625.1	0.1896		

$\log A = 12.6 \pm 0.1 \text{ s}^{-1}$ .	$E_a = 54.6 \pm 0.5 \text{ kcal/mol}$ .
$\Delta H^\ddagger = 52.8 \pm 0.5 \text{ kcal/mol}$ .	$\Delta S^\ddagger = -5.2 \pm 0.5 \text{ eu at } 640 \text{ }^\circ\text{C}$ .

## 25. Pyrolysis of allyloxytrimethylsilane

Allyloxytrimethylsilane was pyrolyzed at 650-720 °C in an SFR with a helium flow of 60 ml/min. There was no significant decomposition of allyloxytrimethylsilane, as evidenced by the GC trace of the material coming out of the reaction vessel.

## 26. Copyrolysis of 166 and toluene-D<sub>8</sub>

Copyrolysis of 166 (0.7 torr) and toluene-D<sub>8</sub> (15 torr) was performed in an SFR at 640°C. The MS of the propene peak obtained was identical to that obtained when 166 was pyrolyzed alone at the same reaction conditions.

### 27. Synthesis of 2-dimethylsiloxy-2-methyl-3-butene 123

A 100 mL three-neck flask, equipped with a magnetic stirrer, septa, and a nitrogen inlet, was charged with 30 mL of THF and 7.0 g (82 mmol) of 2-methyl-3-butene-2-ol. The stirred mixture was cooled to -78 °C and 23.5 mL (2.5 M, 59 mmol) of n-BuLi solution in hexane was added slowly with a syringe. After warming to room temperature in 1 h and stirring for an additional hour, the flask was cooled to -78 °C, and 5.8 g (61 mmol) of dimethylchlorosilane was added slowly. After warming to room temperature in 2 h and stirring for an additional hour, trap to trap distillation was followed by removal of solvent by distillation using a 17 cm Vigreux column. The crude product was fractionally distilled under vacuum using a 7 cm column packed with glass helices, to afford 4.6 g (32 mmol, 54%) of pure 123: bp 50-53 °C/98 torr (lit. bp 109 °C<sup>84</sup>); GCMS 144 (M, 0.2), 143 (0.3), 131 (1.2), 130 (3.3), 129 (29), 75 (100), 61 (28), 59 (23), 45 (20), and <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.17 (6 H, d, J = 2.7 Hz), 1.32 (6 H, s), 4.71 (1 H, hep, J = 2.7 Hz), 4.95 (1 H, d-d, J = 10.6 Hz, 1.0 Hz), 5.10 (1 H, d-d, J = 17.2 Hz, 1.0 Hz), 5.92 (1 H, d-d, J = 17.2 Hz, 10.7 Hz).

### 28. FVP of 123

Compound 123 was pyrolysed by distilling (25 °C, 5 x 10<sup>-4</sup> torr) it through a horizontal quartz tube (length: 30 cm, OD: 1.6 cm) packed with quartz chips and heated to 660 °C. The pyrolysate was collected in a trap cooled with liquid nitrogen. Products 2-methyl-1,3-butadiene 167 (40%), 2-methyl-butene 125 (50%), and sym-tetramethyldisiloxane 168 (16%), were isolated by preparative GC and characterized by comparing



their GCMS and  $^1\text{H}$  NMR spectra with those of authentic samples. Product  $\text{D}_3$  (8%), and 25% of undecomposed starting material were detected by GC and GCMS.

29. Kinetics of the total formation of 125 plus 167 from 123

The total rate constants for the formation of 125 plus 167 were determined by pyrolyzing 123 (sample pressure: 0.4-0.5 torr) at 500-580 °C in an SFR. The data, along with the results of a linear least square calculation, are summarized in Table 7.

30. Copyrolysis of 123 and toluene- $\text{D}_8$

Compound 123 (0.2 torr) and toluene- $\text{D}_8$  (8.1 torr) was copyrolyzed in an SFR at 550 °C. The GC trace of the product mixture, and that obtained from pyrolysis of 123 alone under the same conditions, showed identical ratios of 125 and 167. The MS of the 125-peak was identical to that obtained when 123 was pyrolyzed alone under the same conditions.

31. Pyrolysis of 125

Compound 125 was pyrolyzed at 550 °C in an SFR with a helium flow of 60 ml/min. The GC trace of the pyrolysate showed only starting material.

32. Kinetics of formation of 125 and 167 from 123

Compound 123 (sample pressure: 0.04-0.05 torr) was pyrolyzed at 545-590 °C in an SFR and the products 125 and 167 were separated by GC to measure the individual rate constants for formation of 125 and 167.

Table 7. Rate constants for the total formation of 125 plus 167 from 123 in SFR

T (°C)	k (s <sup>-1</sup> )	T (°C)	k (s <sup>-1</sup> )	T (°C)	k (s <sup>-1</sup> )
560.2	0.5802	529.9	0.1612	550.0	0.3752
520.1	0.1136	529.9	0.1624	555.0	0.4573
520.1	0.1139	535.1	0.1995	565.2	0.7035
500.1	0.0500	540.0	0.2425	570.2	0.8770
510.1	0.07303	540.0	0.2437	560.2	0.5546
515.0	0.009005	545.0	0.3086	580.2	1.336
525.1	0.1326	550.0	0.3706		

$\log A = 13.9 \pm 0.2 \text{ s}^{-1}$ .	$E_a = 53.8 \pm 0.6 \text{ kcal/mol}$ .
$\Delta H^\ddagger = 52.2 \pm 0.6 \text{ kcal/mol}$ .	$\Delta S^\ddagger = 0.91 \pm 0.73 \text{ eu at } 540 \text{ }^\circ\text{C}$ .

Table 8 summarizes the data and the results of a linear least square calculation for the Arrhenius plot for formation of 125, while Table 9 summarizes the data and the results of a linear least square calculation for the Arrhenius plot for formation of 167.

### 33. Synthesis of (1-methoxyethenyl)pentamethyldisilane 170

Compound 170 was synthesized by adding chloropentamethyl-disilane to a solution of  $\alpha$ -lithio methyl vinyl ether. Thus, 3.70 g (63.7 mmol) of methyl vinyl ether was dissolved in 30 mL of dry THF at  $-78 \text{ }^\circ\text{C}$  under an atmosphere of nitrogen in a 100 mL flask. A solution of t-BuLi (31.0 mL, 1.7 M, 52.7 mmol) in pentane was added to the stirred reaction

Table 8. Rate constants for the formation of 125 from 123 in SFR

T (°C)	k (s <sup>-1</sup> )	T (°C)	k (s <sup>-1</sup> )	T (°C)	k (s <sup>-1</sup> )
560.0	0.3241	585.0	0.7975	555.1	0.2877
570.1	0.4671	575.1	0.5854	555.1	0.2753
540.0	0.1485	575.1	0.5529	545.1	0.1876
580.1	0.6766	565.1	0.4035	549.9	0.2255
590.2	1.010	565.1	0.4179		

$\log A = 13.0 \pm 0.2 \text{ s}^{-1}$ .       $E_a = 51.6 \pm 0.7 \text{ kcal/mol}$ .  
 $\Delta H^\ddagger = 49.9 \pm 0.7 \text{ kcal/mol}$ .       $\Delta S^\ddagger = -2.9 \pm 0.9 \text{ eu at } 565 \text{ }^\circ\text{C}$ .

Table 9. Rate constants for the formation of 167 from 123 in SFR

T (°C)	k (s <sup>-1</sup> )	T (°C)	k (s <sup>-1</sup> )	T (°C)	k (s <sup>-1</sup> )
560.0	0.1103	585.0	0.3737	555.1	0.08217
570.1	0.1792	575.1	0.2506	555.1	0.08809
540.0	0.0378	575.1	0.2310	545.1	0.5458
580.1	0.2887	565.1	0.1414	549.9	0.07067
590.2	0.4821	565.1	0.1278		

$\log A = 17.2 \pm 0.3 \text{ s}^{-1}$ .       $E_a = 69.1 \pm 1.3 \text{ kcal/mol}$ .  
 $\Delta H^\ddagger = 67.4 \pm 1.3 \text{ kcal/mol}$ .       $\Delta S^\ddagger = 16.0 \pm 1.5 \text{ eu at } 565 \text{ }^\circ\text{C}$ .

mixture slowly with a syringe. After warming to 0 °C in 0.5 h, and stirring for another 0.5 h, the flask was cooled to -78 °C, and a solution of 7.70 g (46.1 mmol) of chloropentamethyldisilane in 10 mL THF was added slowly with a syringe. The reaction mixture was then warmed up to room temperature and stirred for 20 h. Trap to trap distillation was followed by fractional distillation under vacuum using a 12 cm column packed with glass helices to afford 5.9 g (31 mmol, 68%) of pure 170: bp 64-66 °C/20 torr; GCMS 187 (M-1, 0.8), 175 (1.8), 174 (4.3), 173 (23), 89 (100), 84 (43), 73 (92), 59 (79), 58 (40), 45 (47), 43 (33);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.05 (9 H, s), 0.14 (6 H, s), 3.49 (3 H, s), 4.22 (1 H, d,  $J = 2.0$  Hz), 4.60 (1 H, d,  $J = 2.0$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -4.91, -2.27, 54.09, 93.34, 170.64; IR (neat) 3096 (w), 2951 (s), 2897 (m), 1580 (m), 1246 (s), 1209 (s), 1040 (s), 891 (m), 835 (s), 800 (s), 764 (m), 729 (m)  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_8\text{H}_{20}\text{OSi}_2$ : C, 51.00; H, 10.70. Found C, 50.85; H, 10.97.

#### 34. FVP of 170

Compound 170 was distilled (25 °C,  $5 \times 10^{-4}$  torr) through a horizontal quartz tube (length: 30 cm, OD: 1.6 cm) packed with quartz chips and heated to 550 °C. The pyrolysate was collected in a trap cooled with liquid nitrogen. The products, methoxytrimethylsilane (55%), methoxypentamethyldisilane (37%), dimethylsilylacetylene 16%, bis(dimethylsilyl)acetylene (14%), along with 24% of undecomposed starting material, were isolated by preparative GC and characterized by GCMS, GCIR, and  $^1\text{H}$  NMR. Dimethylsilylacetylene:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.24 (6 H, d,  $J = 3.7$  Hz), 2.39 (1 H, s), 4.10 (1 H, hep,  $J = 3.7$  Hz); GCIR

3302 (w), 2974 (w), 2156 (m), 1265 (w), 895 (s), 679 (m)  $\text{cm}^{-1}$ .

Bis(dimethylsilyl)acetylene:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.23 (12 H, d,  $J = 3.7$  Hz), 4.10 (2 H, hep,  $J = 3.7$  Hz); GCIR 2970 (w), 2152 (m), 1261 (w), 876 (s), 849 (m), 783 (m)  $\text{cm}^{-1}$ .

### 35. Copyrolysis of 170 and 1,3-butadiene

Compound 170 was pyrolysed by dripping (10 mg/min) it with a syringe through a vertical quartz tube (length: 30 cm, OD: 1.6 cm) packed with quartz chips and heated to 450 °C. A 60 ml/min downward flow of 1,3-butadiene was maintained through the tube, and the copyrolysate was collected in a trap cooled with a dry-ice-isopropanol bath. Product 1,1-dimethyl-1-silacyclopent-3-ene 84 (34%) was isolated by preparative GC and characterized by GCMS 114 (1.2), 113 (2.8), 112 (M, 21), 99 (3.8), 98 (11), 97 (100), 58 (30), 43 (64);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.15 (6 H, s), 1.26 (4 H, d,  $J = 1.0$  Hz), 5.83 (2 H, q,  $J = 1.0$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -1.96, 17.89, 130.96; and IR (neat) 3020 (m), 2956 (m), 2901 (m), 1609 (m), 1250 (m), 1099 (s), 945 (w), 845 (s), 725 (m)  $\text{cm}^{-1}$ . Methoxytrimethylsilane (42%) and undecomposed starting 170 (27%) were detected by GC and GCMS. The amount of methoxypentamethyldisilane formed remained undetermined as the GC retention times of it and the huge amount of dimer of 1,3-butadiene formed were identical.

### 36. Copyrolysis of 170 and phenylacetylene

A mixture of 170 (92.3 mg, 0.491 mmol) and phenylacetylene (89.1 mg, 0.874 mmol) was pyrolysed by distilling (25 °C,  $5 \times 10^{-4}$  torr) it through a horizontal quartz tube (length: 30 cm, OD: 1.6 cm) packed

with quartz chips and heated to 550 °C. The pyrolysate was collected in a trap cooled with liquid nitrogen. Product phenyldimethylsilylacetylene (9%) was isolated by preparative GC, and characterized by GCMS 162 (1.2), 161 (5.2), 160 (30), 147 (5.2), 146 (15), 145 (100), 105 (14), 43 (36);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.30 (6 H, d,  $J = 3.7$  Hz), 4.25 (1 H, hep,  $J = 3.7$  Hz), 7.29 (3 H, m), 7.46 (2 H, m); GCIR 3067 (w), 2970 (w), 2149 (m), 1489 (w), 1265 (w), 891 (s), 756 (w), 694 (w)  $\text{cm}^{-1}$ . Methoxytrimethylsilane (22%), methoxypentamethyldisilane (21%), and undecomposed starting 170 (16%), were detected by GC, GCMS, and GCIR. Traces of dimethylsilylacetylene were also detected by GCMS.

### 37. Synthesis of (1-methoxyethenyl)trimethylsilane 173

Compound 173 was synthesized by following the method of Soderquist and Hsu.<sup>98</sup> Thus, methyl vinyl ether (11.8 g, 203 mmol) was dissolved in 150 mL of THF at -78 °C under nitrogen atmosphere in a 500 mL flask equipped with a magnetic stirrer and a nitrogen inlet. A solution of *t*-BuLi (63.9 mL, 1.7 M, 156 mmol) in pentane was added over a period of 15 min, and the mixture warmed up to 0 °C. After stirring at 0 °C for 0.5 h, the flask was cooled to -78 °C, and trimethylchlorosilane (17.0 g, 156 mmol) was added over a period of 5 min. Warming up to room temperature was followed by stirring for 15 h. Filtration and trap to trap distillation were followed by removal of solvent by distillation using a 17 cm Vigreux column. The crude product was then distilled under vacuum using a 12 cm column packed with glass helices to afford 10.4 g (80.0 mmol, 51%) of pure 173 (bp 54 °C/105 torr, lit. bp 102-104 °C/760 torr). Compound 173 was identified by GCMS 131 (0.3), 130 (M,

3.0), 117 (0.6), 116 (1.4), 115 (14), 89 (38), 73 (100), 59 (44), 45 (27), 43 (28);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.10 (9 H, s), 3.50 (3 H, s), 4.28 (1 H, d,  $J = 2.0$  Hz), 4.58 (1 H, d,  $J = 2.0$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -2.27, 54.13, 93.24, 170.70; and IR (neat) 3096 (w), 2959 (s), 2903 (m), 1591 (m), 1250 (s), 1219 (s), 1042 (s), 895 (s), 841 (s), 758 (s), 698 (m)  $\text{cm}^{-1}$ .

#### 38. FVP of 173

Compound 173 was distilled (25 °C,  $4 \times 10^{-4}$  torr) through a horizontal quartz tube (length: 30 cm, OD: 1.6 cm) packed with quartz chips and heated to 550 °C. The pyrolysate was collected in a trap cooled with liquid nitrogen. Product methoxytrimethylsilane (89%), and undecomposed starting material (26%) were detected by GC and GCMS of the crude pyrolysate.

#### 39. Kinetics of decomposition of 173 in the SFR

Compound 173 was pyrolyzed at 48-530 °C in an SFR (sample pressure: 1.0-1.1 torr), and the constants for formation of methoxytrimethylsilane were measured. The data and the results of a linear least square calculation are summarized in Table 10.

#### 40. Kinetics of decomposition of 173 in the LPP

The first-order rate constants for the decay of 173 at 403-462 °C were determined in an LPP (sample pressure: 0.30-0.35 torr) by following the decrease in intensities of  $m/e$  115 (M-15). The data,

along with the results of a linear least square calculation, are summarized in Table 11.

#### 41. Synthesis of (1-methoxyethyl)trimethylsilane 174

Compound 174 was prepared by catalytic hydrogenation of compound 173. Thus, 2.7 g (21 mmol) of (1-methoxyethenyl)trimethylsilane and 0.1 g of 5% palladium on charcoal were taken in a stainless steel bomb equipped with a magnetic stirrer. The bomb was charged with 600 psi of hydrogen, and the mixture stirred at room temperature for 6 days. Diethyl ether (15 mL) was added to the bomb, and the ethereal solution was then distilled trap to trap. Fractional distillation using a 15 cm column packed with glass helices gave 1.1 g (8.4 mmol, 40%) of GC-pure 174: bp 54-55 °C/125 torr; GCMS 119 (0.7), 118 (2.0), 117 (M-15, 19), 89 (27), 73 (100), 59 (40), 45 (28), 43 (22);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.00 (9 H, s), 1.19 (3 H, d,  $J = 7.3$  Hz), 2.90 (1 H, d,  $J = 7.3$  Hz), 3.32 (3 H, s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -3.85, 14.34, 58.20, 71.34; IR (neat) 2959 (s), 2901 (w), 2818 (m), 1248 (s), 1107 (m), 1078 (m), 864 (s), 839 (s), 754 (w)  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_6\text{H}_{16}\text{OSi}$ : C, 54.48; H, 12.19. Found C, 54.83; H, 12.54.

#### 42. Kinetics of decomposition of 174 in the SFR

The first-order rate constants for formation of methoxytrimethylsilane were determined by pyrolyzing 174 (sample pressure: 0.05-0.06 torr) at 524-579 °C in an SFR. The data, along with the results of a linear least square calculation, are shown in Table 12.



Table 10. Rate constants for the formation of Me<sub>3</sub>SiOMe from 173 in SFR

T (°C)	k (s <sup>-1</sup> )	T (°C)	k (s <sup>-1</sup> )	T (°C)	k (s <sup>-1</sup> )
505.0	0.7275	484.8	0.3218	521.6	1.429
494.8	0.5369	514.1	1.081	530.8	2.180
494.8	0.4714	514.1	1.067	530.8	2.178
484.9	0.3003	521.6	1.478		

$\log A = 14.0 \pm 0.3 \text{ s}^{-1}$ .       $E_a = 50.4 \pm 1.0 \text{ kcal/mol}$ .  
 $\Delta H^\ddagger = 48.9 \pm 1.0 \text{ kcal/mol}$ .       $\Delta S^\ddagger = 1.3 \text{ eu at } 509 \text{ }^\circ\text{C}$ .

Table 11. Rate constants for the decay of 173 in LPP

T (°C)	k (s <sup>-1</sup> )	T (°C)	k (s <sup>-1</sup> )	T (°C)	k (s <sup>-1</sup> )
446.0	0.0421	418.5	0.0106	431.3	0.0192
446.0	0.0408	421.5	0.0124	435.5	0.0250
427.0	0.0147	413.2	0.00770	432.7	0.0203
424.4	0.0139	406.5	0.00506	448.7	0.0443
423.5	0.0133	403.2	0.00435	461.6	0.0770

$\log A = 13.6 \pm 0.2 \text{ s}^{-1}$ .       $E_a = 49.3 \pm 0.7 \text{ kcal/mol}$ .  
 $\Delta H^\ddagger = 47.9 \pm 0.7 \text{ kcal/mol}$ .       $\Delta S^\ddagger = -0.08 \pm 1.0 \text{ eu at } 429 \text{ }^\circ\text{C}$ .

#### 43. Kinetics of decomposition of 174 in the LPP

The first order rate constants for the decay of 174 were determined by pyrolyzing 174 at 465-531 °C in an LPP (sample pressure: 0.22-0.37 torr), and following the decrease in intensities of m/e 117 (M-15). The data, along with the results of a linear least square calculation, are summarized in Table 13.

#### 44. Synthesis of (2-methoxyethyl)trimethylsilane 175

Compound 175 was synthesized by the method of Pola et al.<sup>101</sup> Thus, a 250 mL 3-neck flask, equipped with a mechanical stirrer, a condenser with a nitrogen inlet, and a pressure-equalizing addition funnel, was charged with 4.4 g (181 mmol) of magnesium turnings and 50 mL of diethyl ether. Addition of 0.3 mL of 1,2-dibromoethane was followed by addition of 12.8 g (104 mmol) of chloromethyltrimethylsilane in 50 mL ether to the stirred suspension. The mixture was refluxed for 7 hrs, and then cooled to room temperature. Addition of 7.4 g (91.8 mmol) of chloromethyl methyl ether was followed by stirring for 36 h. The mixture was then filtered through glass wool and added to 150 mL of water, and the organic layer washed with 5 x 40 mL of water and 3 x 40 mL of saturated NaCl, dried over Na<sub>2</sub>SO<sub>4</sub>, and filtered. Fractional distillation using a 7 cm column packed with glass helices gave 6.7 g (50.8 mmol, 55%) of pure 175: bp 52-53 °C/80 torr; GCMS 117 (M-15, 0.4), 91 (3.6), 90 (8.1), 89 (100), 73 (22), 59 (64), 45 (26), 43 (21); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ -0.01 (9 H, s), 0.91 (2 H, t, J = 8.1 Hz), 3.29 (3 H, s), 3.42 (2 H, t, J = 8.1 Hz); and IR (neat) 2955 (s), 2894 (m), 1250 (s), 111 (s), 939 (m), 928 (m), 860 (s), 835 (s) cm<sup>-1</sup>.

Table 12. Rate constants for the formation of  $\text{Me}_3\text{SiOMe}$  from 174 in SFR

T (°C)	k (s <sup>-1</sup> )	T (°C)	k (s <sup>-1</sup> )	T (°C)	k (s <sup>-1</sup> )
550.1	0.3402	568.9	0.6990	532.1	0.1688
550.1	0.3374	576.8	0.9625	532.2	0.1676
560.0	0.5011	576.8	0.9698	524.3	0.1247
560.0	0.4927	541.2	0.2458	524.3	0.1236
568.9	0.7329	541.2	0.2482		

$\log A = 13.5 \pm 0.1 \text{ s}^{-1}$ .       $E_a = 52.6 \pm 0.4 \text{ kcal/mol}$ .  
 $\Delta H^\ddagger = 50.9 \pm 0.4 \text{ kcal/mol}$ .       $\Delta S^\ddagger = -0.78 \pm 0.49 \text{ eu at } 550 \text{ }^\circ\text{C}$ .

Table 13. Rate constants for the decay of 174 in LPP

T (°C)	k (s <sup>-1</sup> )	T (°C)	k (s <sup>-1</sup> )	T (°C)	k (s <sup>-1</sup> )
530.8	0.1525	508.5	0.0535	486.3	0.0223
528.4	0.1355	507.4	0.0518	482.1	0.0194
526.5	0.1199	506.1	0.0490	478.4	0.0140
524.8	0.1148	510.4	0.0580	475.6	0.0125
522.8	0.1055	510.2	0.0598	470.6	0.0105
520.9	0.0925	511.3	0.0605	468.4	0.0090
518.4	0.0802	500.1	0.0388	465.2	0.0078
516.4	0.0780	495.2	0.0323		
509.9	0.0578	492.4	0.0282		

$\log A = 13.3 \pm 0.1 \text{ s}^{-1}$ .       $E_a = 52.0 \pm 0.5 \text{ kcal/mol}$ .  
 $\Delta H^\ddagger = 50.5 \pm 0.5 \text{ kcal/mol}$ .       $\Delta S^\ddagger = -1.6 \pm 0.68 \text{ eu at } 503 \text{ }^\circ\text{C}$ .

#### 45. Kinetics of decomposition of 175

The first-order rate constants for formation of methoxytrimethylsilane were determined by pyrolyzing 175 (sample pressure: 0.05-0.06 torr) at 430-500 °C in an SFR. The data, along with the result of a linear least square calculation performed by a microcomputer, are summarized in Table 14.

#### 46. Synthesis of (chlorodimethylsilyl)trimethylsilylmethane 176

A 100 mL flask, equipped with a mechanical stirrer, a pressure-equalizing addition funnel, and a condenser with nitrogen inlet, was charged with 4.2 g (173 mmol) of magnesium turnings and 30 mL of THF. To the stirred suspension was added 0.5 g of 1,2-dibromoethane to activate the magnesium. After the reaction warmed up, a solution of 9.5 g (77 mmol) of chloromethyltrimethylsilane in 30 mL THF was added slowly, the flask was heated to 70 °C, and stirred for 2 h. Addition of 20.0 g (155 mmol) of dimethyldichlorosilane was followed by stirring at 70 °C for 30 h. After cooling to room temperature, 50 mL of hexane was added, filtered, and distilled trap to trap. Fractional distillation using a 15 cm column packed with glass beads gave 6.6 g (37 mmol, 47%) of pure 176: bp 56-58 °C/20 torr; GCMS (70 eV) 167 (38), 166 (15), 165 (100), 149 (3), 145 (4), 129 (7), 95 (3), 93 (10), 73 (47), 59 (11), 45 (16), 43 (20);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.07 (9 H, s), 0.15 (2 H, s), 0.42 (6 H, s); and  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.08, 4.67, 7.88.

Table 14. Rate constants for the formation of Me<sub>3</sub>SiOMe from 175 in SFR

T (°C)	k (s <sup>-1</sup> )	T (°C)	k (s <sup>-1</sup> )	T (°C)	k (s <sup>-1</sup> )
500.2	0.9839	469.9	0.2838	450.0	0.1241
490.1	0.6566	469.9	0.2833	450.0	0.1231
485.1	0.5397	465.0	0.2338	445.0	0.1020
480.0	0.4335	460.1	0.1913	440.1	0.08123
480.0	0.4377	460.1	0.1913	430.0	0.05243
475.0	0.3536	455.0	0.1529		

$\log A = 12.7 \pm 0.1 \text{ s}^{-1}$ .	$E_a = 45.1 \pm 0.2 \text{ kcal/mol}$ .
$\Delta H^\ddagger = 43.7 \pm 0.2 \text{ kcal/mol}$ .	$\Delta S^\ddagger = -4.0 \pm 0.3 \text{ eu at } 465 \text{ }^\circ\text{C}$ .

47. Synthesis of (methoxydimethylsilyl)trimethylsilylmethane 172

Lithium methoxide was made by adding a solution of n-BuLi (8.2 mL, 2.5 M, 21 mmol) in hexane to a solution of methanol (1.0 g, 31 mmol) in 15 mL THF at -78 °C under nitrogen atmosphere. To this stirred solution was added 3.4 g (19 mmol) of 176 over a period of 10 min, and the mixture was stirred at -78 °C for 0.5 h and then warmed to room temperature. Trap to trap distillation was followed by fractional distillation using a 7 cm column packed with glass helices to afford 2.4 g (14 mmol, 73%) of compound 172: bp 54-55 °C/26 torr; GCMS 163 (7.5), 162 (16), 161 (M-15, 100), 131 (68), 115 (6.4), 89 (12), 73 (31), 59 (56), 45 (26), 43 (24); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ -0.14 (2 H, s), 0.02 (9 H, s),

0.10 (6 H, s), 3.38 (3 H, s); and  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.03, 1.13, 4.14, 49.94.

#### 48. Kinetics of decomposition of 172

The first-order rate constants for formation of methoxytrimethylsilane were determined by pyrolyzing 172 (sample pressure: 0.11-0.12 torr) at 618-697 °C in an SFR. The data and results of a linear least square calculation are summarized in Table 15.

#### 49. Synthesis of (methoxymethyl)pentamethyldisilane 171

Compound 171 was prepared by the method of Kumada et al.<sup>102</sup> Thus, a 250 mL flask, equipped with a mechanical stirrer, a pressure-equalizing addition funnel, and a condenser with nitrogen inlet, was charged with 3.1 g (128 mmol) of magnesium turnings, 0.2 g of  $\text{HgCl}_2$ , 50 mL of THF, and 6.55 g (39.2 mmol) of chloropentamethyldisilane. After cooling the stirred suspension to 0 °C, a solution of 13.2 g (106 mmol) of bromomethyl methyl ether in 50 mL THF was added. Stirring at room temperature for 18 h was followed by addition of 100 mL of diethyl ether. The mixture was then filtered, distilled trap to trap, and finally distilled under vacuum using a 12 cm column packed with glass helices to afford 2.2 g (32%) of pure 171 (bp 48-49 °C). Compound 171 was characterized GCMS 163 (0.7), 162 (1.7), 161 (M-15, 9.1), 133 (6.4), 132 (5.3), 131 (33), 89 (17), 75 (32), 73 (100), 72 (69), 59 (37), 45 (61), 43 (33);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.05 (9 H, s), 0.06 (6 H, s), 3.17 (2 H, s), 3.32 (3 H, s); and  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -5.70, -2.10, 63.25, 66.84.

Table 15. Rate constants for the formation of Me<sub>3</sub>SiOMe from 172 in SFR

T (°C)	k (s <sup>-1</sup> )	T (°C)	k (s <sup>-1</sup> )	T (°C)	k (s <sup>-1</sup> )
672.7	0.7168	660.8	0.4965	641.2	0.2680
672.6	0.7200	657.0	0.4368	633.3	0.2073
668.7	0.6598	657.01	0.4370	625.5	0.1618
676.7	0.8062	653.0	0.3856	617.5	0.1247
680.6	0.9254	649.1	0.3410	637.4	0.2369
680.6	0.9214	645.1	0.3030	688.7	1.188
664.9	0.5581	645.1	0.3045	696.6	1.526

$\log A = 12.4 \pm 0.1 \text{ s}^{-1}$ .	$E_a = 54.3 \pm 0.3 \text{ kcal/mol}$ .
$\Delta H^\ddagger = 52.4 \pm 0.3 \text{ kcal/mol}$ .	$\Delta S^\ddagger = 6.1 \pm 0.3 \text{ eu at } 658 \text{ }^\circ\text{C}$ .

50. FVP of 171

Compound 171 was pyrolyzed by distilling (25 °C, 8 x 10<sup>-4</sup> torr) it through a horizontal quartz tube (length: 30 cm, OD: 1.6 cm) packed with quartz chips and heated to 750 °C. The pyrolysate was collected in a trap cooled with liquid nitrogen and was found (by GC) to be a mixture of many products. GCMS and GCIR analyses showed the major component to be methoxytrimethylsilane.

51. Copyrolysis of 171 and 1,3-butadiene

Compound 171 was pyrolyzed by dripping it with a syringe at a rate of 25 mg/min into a 60 mL/min downward flow of 1,3-butadiene through a

quartz tube (length: 30 cm, OD: 1.6 cm) packed with quartz chips and heated to 620 °C. The pyrolysate was collected in a trap cooled at -78 °C, and was found to be a mixture of many components as 1,3-butadiene itself also decomposed and dimerized. GC and GCMS analyses showed methoxytrimethylsilane 19%, 84 (8%), 85 (4%) and unreacted starting 171 (11%).

## 52. Synthesis of (1-methoxyethyl)pentamethyldisilane 178

Compound 178 was synthesized by diimide reduction<sup>104</sup> of 170. Thus, 0.9 g (4.8 mmol) of 170 and 1.9 g (58 mmol) of hydrazine was taken up in 30 mL of methanol in a 100 mL flask equipped with a magnetic stirrer, and a condenser. A slow stream of pure oxygen was bubbled through the solution, while the mixture refluxed for 30 h at a bath temperature of 100 °C. The mixture (10 mL) was then cooled to 0 °C and stirred for an hour following addition of 5 mL of 0.1 N HCl. Diethyl ether (50 mL) was added, and the organic layer washed with 2 x 10 mL of water, dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. Removal of ether by distillation using a 17 cm vigreux column gave 0.3 g of crude 178, which was further purified by preparative GC.

(1-Methoxyethyl)pentamethyldisilane 178: GCMS 177 (0.4), 176 (0.8), 175 (M-15, 5.4), 148 (5.8), 131 (19), 89 (60), 86 (35), 73 (100), 59 (80), 58 (34), 45 (49), 43 (39); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.01 (3 H, s), 0.04 (3 H, s), 0.06 (9 H, s), 1.20 (3 H, d, J = 7.9 Hz), 3.05 (1 H, d, J = 7.3 Hz), 3.30 (3 H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ -6.13, -1.77, 15.18, 58.11, 71.25; IR (neat) 2951 (s), 2895 (m), 2818 (m), 1462 (w), 1398 (w), 1366 (w), 1244 (s), 1103 (s), 1076 (s), 870 (m), 833 (s), 797 (s), 760 (m), 690



(m), 615 (m)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_8\text{H}_{22}\text{OSi}_2$ : C, 50.46; H, 11.65.

Found C, 50.10; H, 11.95.

53. Pyrolysis of 178

Compound 178 was pyrolyzed at 600-620 °C in a SFR with a helium flow of 60 ml/min. The pyrolysate was a mixture of many compounds, as indicated by GC trace. However, the lone peak at a low retention time was found (GCMS) to be ethylene.

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