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A Search for Thermal Isomerization of Olefins to Carbenes Thermal Generations of the Silicon-Nitrogen Double Bond

by

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A search for thermal isomerization of olefins to carbenes. Thermal generations of the silicon-nitrogen double bond

by

Xianping Zhang

Under the Supervision of Dr. Thomas J. Barton
Department of Chemistry
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Thermal isomerization of an olefin to a carbene is observed only in a few strained olefins. Attempts to observe a 1,2-silyl migration to form a carbene from a simple olefin were not successful. The olefins studied are stable at lower temperature and decomposed to smaller molecules at higher temperature probably via a radical process. The gas-phase thermal behavior of a series of organic and organosilicon compounds was studied by stirred-flow reactor (SFR) pyrolysis. Kinetic parameters were determined in the gas phase for various hydrocarbons and organosilicon compounds. The activation energies and log As of the compounds studied are in the normal range of olefinic cis-trans isomerization proceeding by a singlet biradical mechanism.

The substituent effect on the thermal isomerization of olefins was discussed. The substitution of phenyl, t-butyl, and trimethylsilyl groups on the double bond lowers the olefinic cis-trans isomerization energy.

A new reaction, gas-phase thermal isomerization of a silacyclobutene to silylallene, was discovered. The mechanism of the isomerization was studied by deuterium-labeling experiments.

Intermediates containing silicon-nitrogen double bonds were generated in the gas phase by β-elimination of trimethylmethoxysilane and retroene elimination of propene. The 1,2-silyl migration of silanimine to aminosilylene was observed. This is the first observation of a silanimine-to-aminosilylene isomerization. The aminosilylene formed was trapped by 1,3-butadiene and the structure of the trapping product was proven by comparison of its spectroscopic data with that of an authentic sample synthesized by an indepedent route. The isomerization of silanimine to aminosilylene by 2,3-allyl migration was not observed. Dimers of silanimine are formed in the absence of trapping reagents.

Different approaches to silicon-nitrogen double bond were also explored. Attempts to obtain evidence for silapyridine, an unknown compound, both theoretically and experimentally, were not successful.

A search for thermal isomerization of olefins to carbenes

Thermal generations of the silicon-nitrogen double bond

by

Xianping Zhang

A Dissertation Submitted to the

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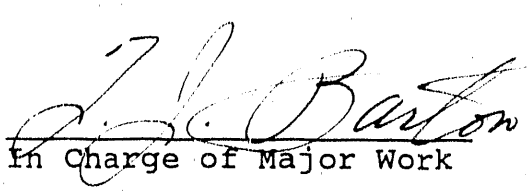

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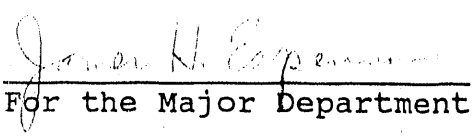

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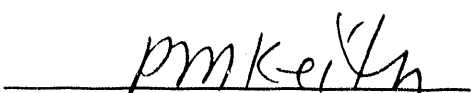


For the Graduate College

Iowa State University
Ames, Iowa

1990

TABLE OF CONTENTS

DEDICATION

To my parents, husband and son

INTRODUCTION

Two separate studies in organosilicon chemistry will be included in this thesis.

The first part of this thesis will search for the thermal isomerization of olefins to carbenes which is predicted to be a high energy process by calculations and has only been observed in a few strained olefins. The possibility of thermal isomerization of simple olefins to carbenes will be explored. Cis-trans isomerization of a double bond is believed to occur via a biradical transition state. The ability of silyl groups to stabilize carbenium ions and radicals at the β-position is well established. Substitution of a silyl group on the double bond of an olefin allows a potential intermediate which has a β-radical to the silyl group during the cis-trans isomerization. The effects of a trimethylsilyl group on this isomerization are the subject of this study.

The second part of this thesis will include the generation and chemistry of intermediates containing a silicon-nitrogen double bond. The isomerization of parent silanimine to the aminosilylene was calculated to be a high energy process. Attempts have been made to observe the isomerization experimentally by substituting different groups on the silanimine. New approaches to the silicon-nitrogen double bond will also be presented.

PART I.

A SEARCH FOR THERMAL ISOMERIZATION OF OLEFINS TO CARBENES

Literature Survey

The isomerization of an olefin to a carbene is a high energy process. Calculations of the activation energy of the rearrangement of ethylene to methylcarbene have been reported.[1,2] Recent calculations by Raghavachari et al.[1] estimate the activation energies of this rearrangement to be between 74.2 and 82.1 kcal/mol. Thermal rearrangement of an olefin to a carbene is a very rare reaction. However, photoreaction of various olefins with vacuum-UV radiation has been reported to occur via a carbene intermediate.

There are similar energies of the π,π^*, $(\pi,3s)$ Rydberg, and π,δ^*_{CH} singlet states of olefins.[3]

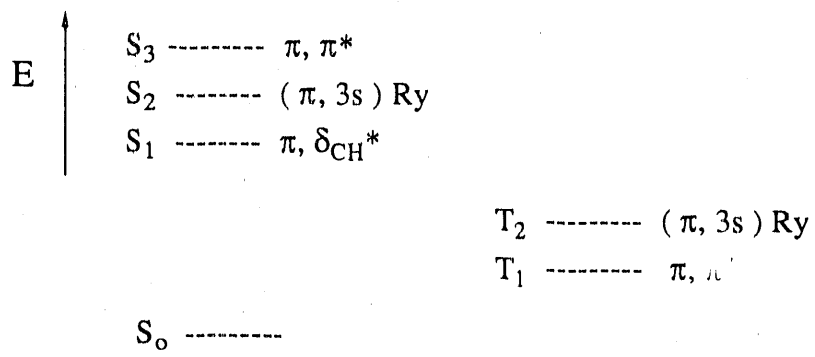
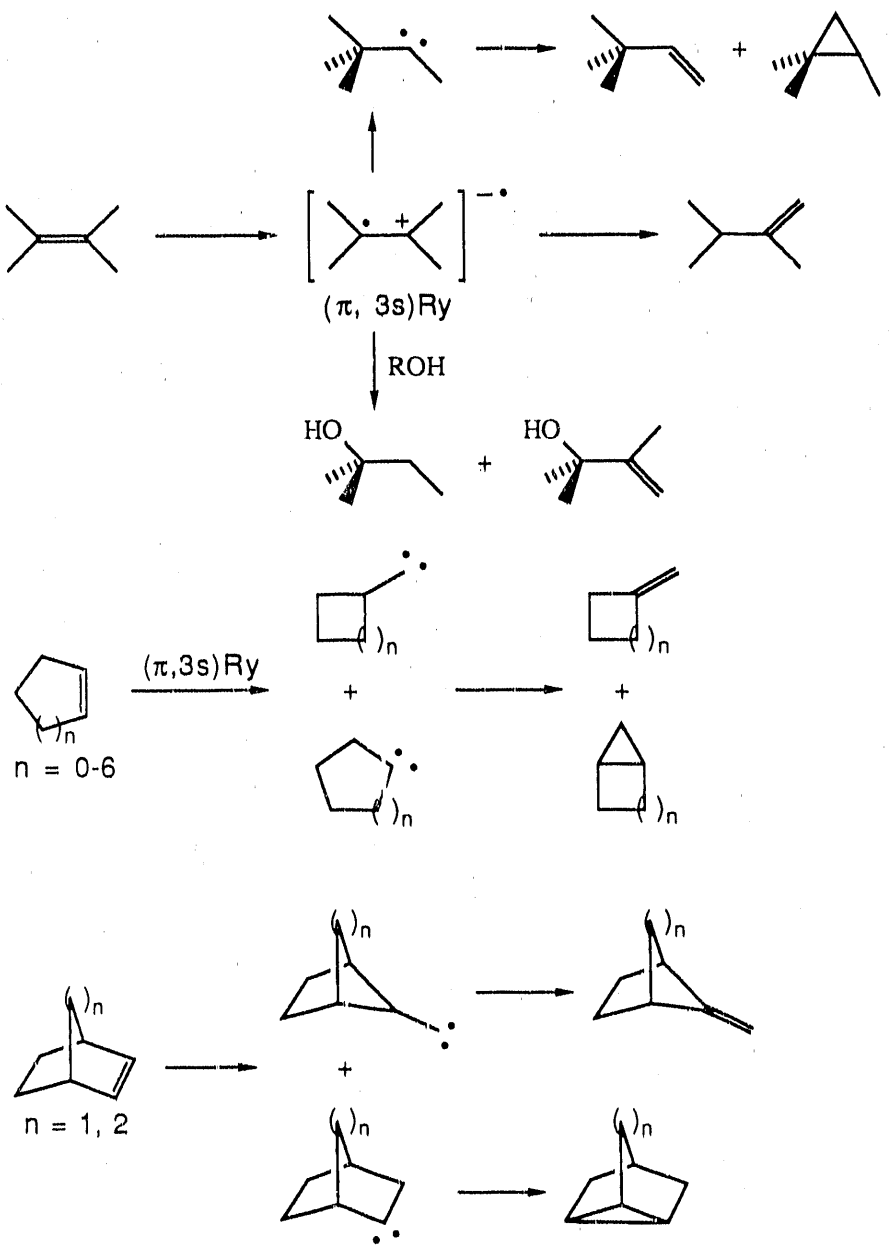


Figure 1. Electronic states of olefins[3]

A direct connection between the wavelength dependence and the quantum yield of fluorescence[4] of the alkene exists. With increasing wavelength of irradiation the chemical yield of the

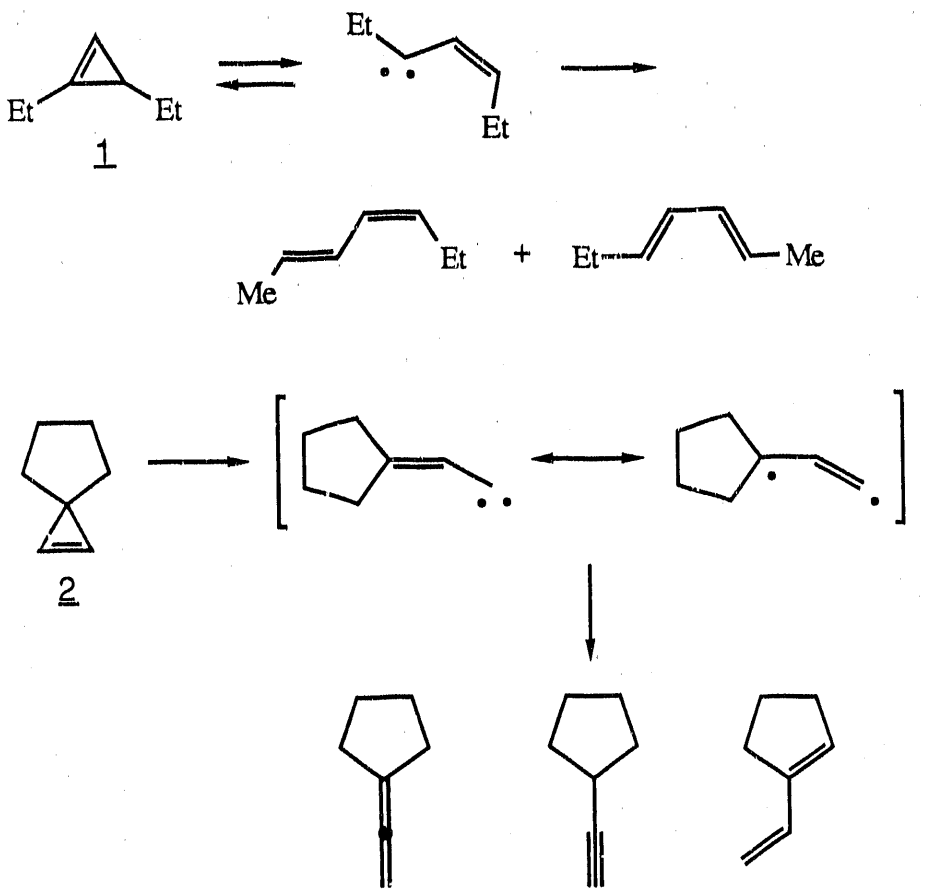
carbene products increases. This is a direct indication for the involvement of a Rydberg state as precursor to the intermediary carbene.

Photoreactions of substituted,[5] monocyclic,[6] and bicyclic olefins[7] are summarized in the following scheme:



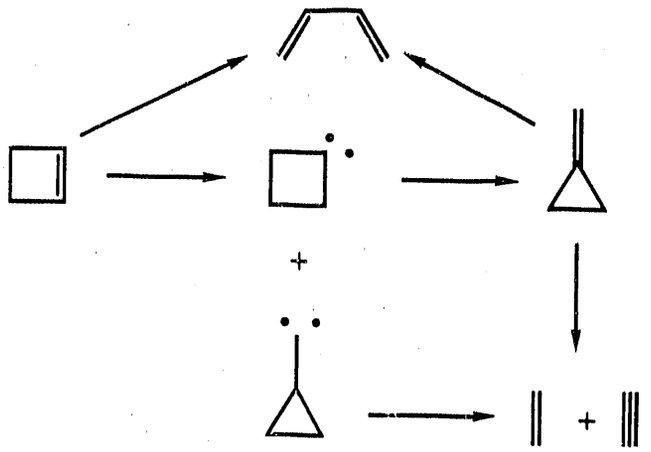
Only the products originating from the carbene intermediate are shown in this scheme. However, the positional isomerizations of olefins via π,π^* excited states are always in competition.

The 185 nm irradiation of cyclopropenes such as 1[8a] and 2[8b] provides evidence of cyclopropene-vinylcarbene rearrangement.

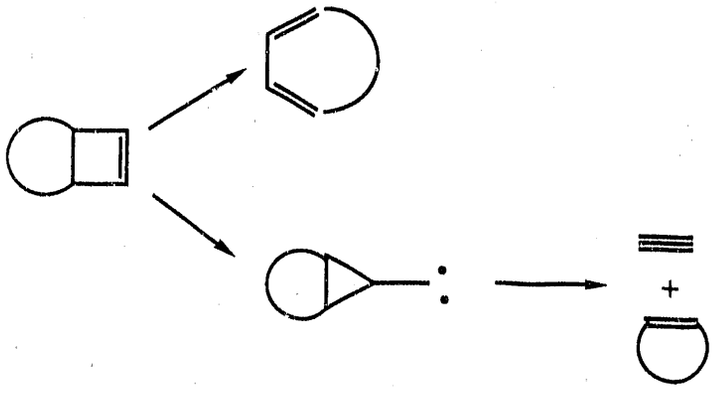


The photolysis of cyclobutene[9] and its substituted derivatives[10] provides important insights into the reaction

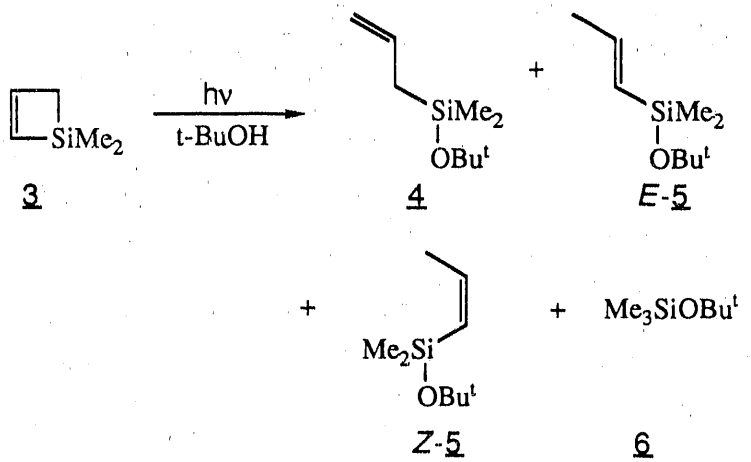
mechanisms. Photoreaction of a n-heptane solution of cyclobutene[9] at 185 nm yields 1,3-butadiene, methylenecyclopropane, ethylene, and acetylene. The minor products ethylene, acetylene, and methylenecyclopropane can be rationalized by the intermediacy of the carbenes, cyclopropylmethylidene and cyclobutylidene.



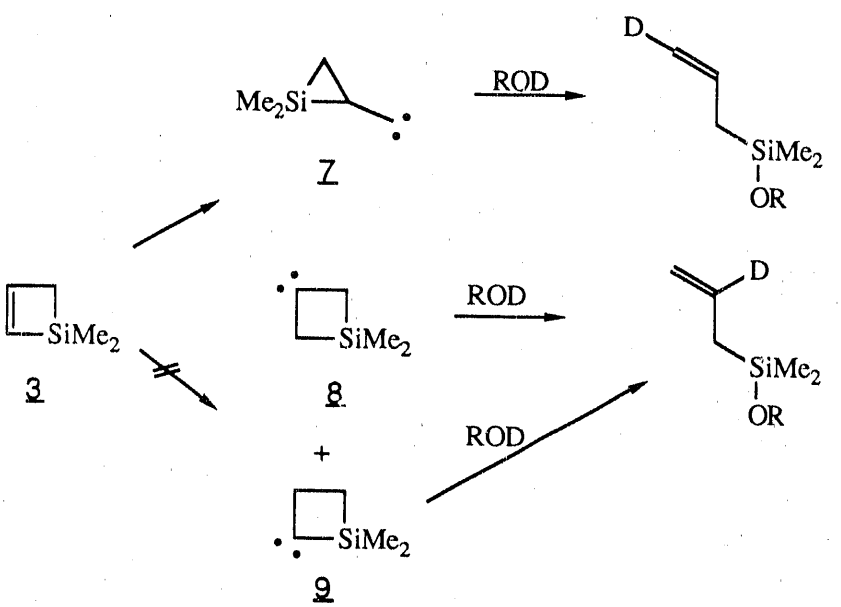
Irradiation of fused-ring cyclobutenes[11] gives rise to conjugated cyclic 1,3-dienes, cycloalkenes, and acetylene. No methylenecyclopropane products were detected.



Steimetz et al.[12] has studied the irradiation of 1,1-dimethyl-1-silacyclobut-2-ene 3 in t-butanol at 214 nm. Four primary products, t-butoxydimethyl(2-propenyl)silane 4, E- and Z-t-butoxydimethyl(1-propenyl)silane 5, and

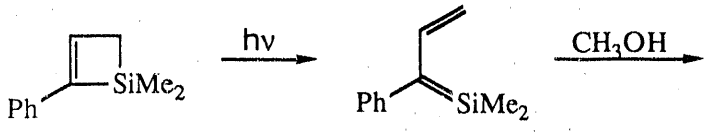


t-butoxytrimethylsilane 6 were isolated. The results are consistent with 1,1-dimethyl-1-sila-1,3-butadiene as the principal intermediate leading to products 4 and 5. Product 6 is ascribed to the trapping of silaethene, formed by the



decomposition of carbene 7. t-Butanol-trapped products corresponding to the carbene intermediates, 8, and 9 are not observed in the t-butanol-d_1 solution.

The earlier study[13] of the photolysis of 1,1-dimethyl-2-phenyl-1-silacyclobut-2-ene 10, the closest analogue of 3 studied previously, did not propose carbene intermediacy. In methanol, three solvent adducts, 11, E- and Z-12, were obtained. Dimethylmethoxy(1-phenyl-2-propenyl)silane 11 is believed to be the primary product and 12 could be the secondary photoproducts since it was also observed upon photolysis of 11.



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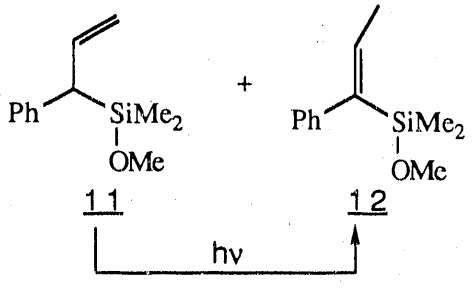
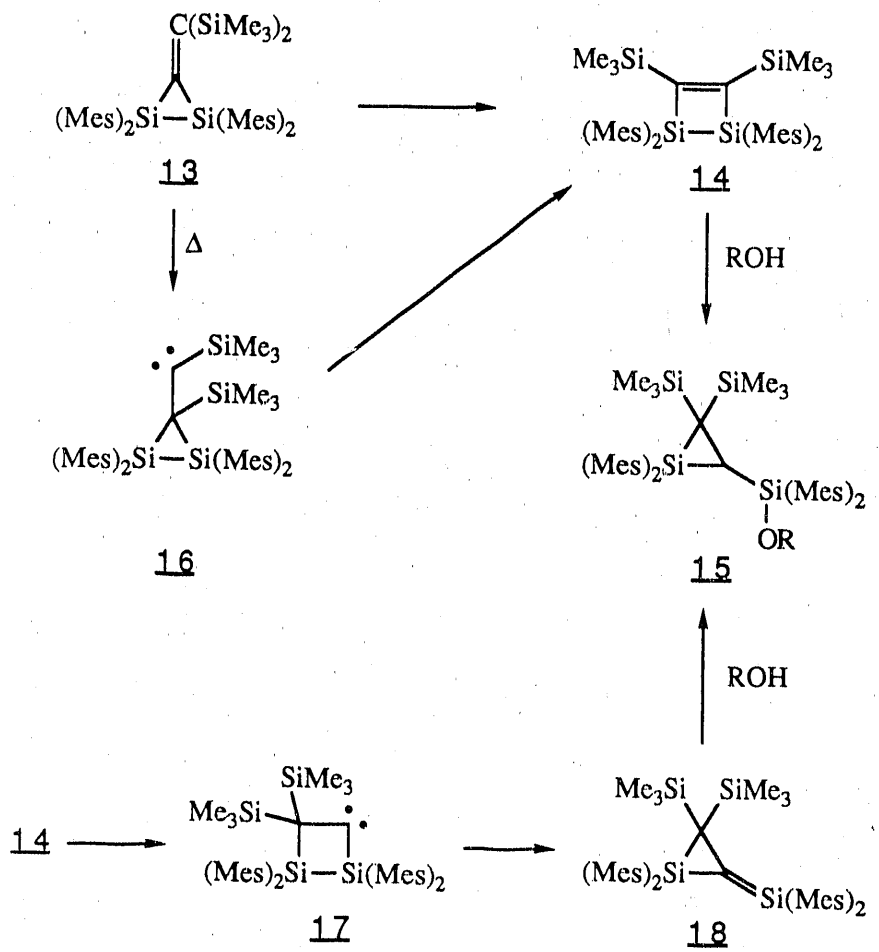


11 12

Thermal rearrangement of an olefin to a carbene was also observed in a few twisted olefins.

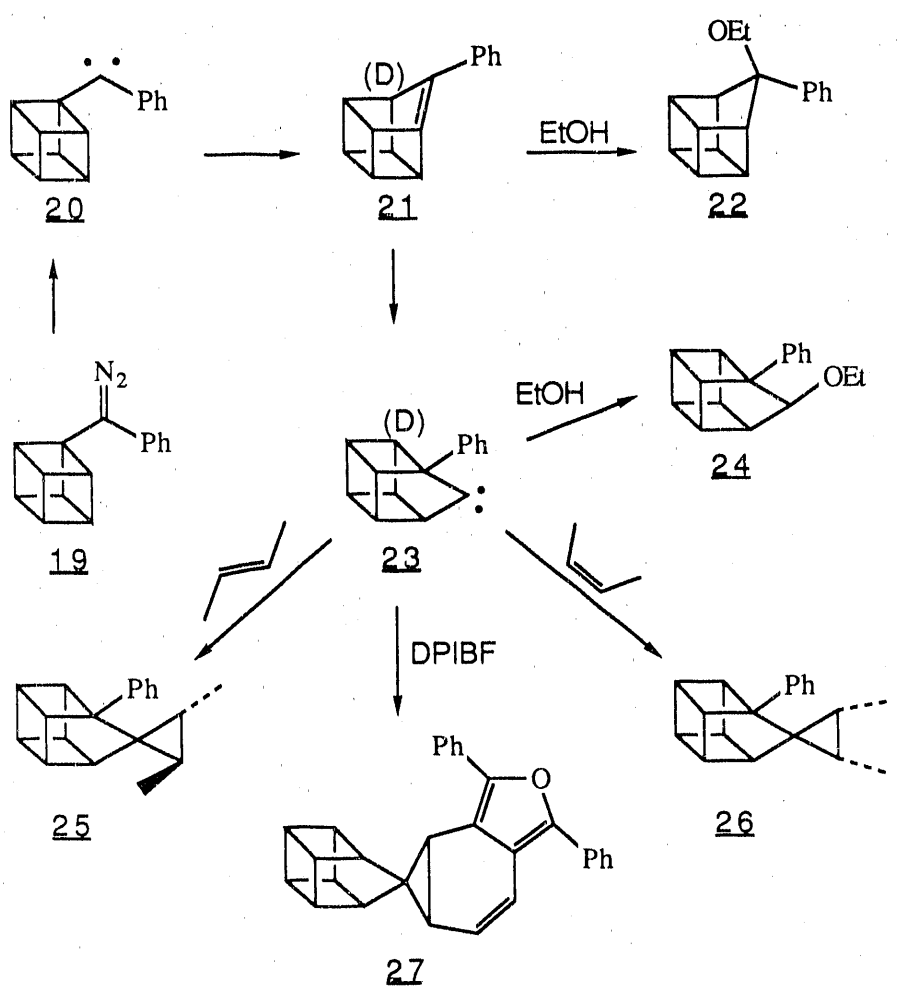
The stable disilacyclopropane 13 undergoes[14] ring enlargement to form 1,2-disilacyclobutene 14 on heating at 170°C. The mechanism of the transformation of 13 to 14

involving a carbene intermediate 16 was proposed by Barton.[15] The transformation of 14 to 15 could also take place via a carbene 17.

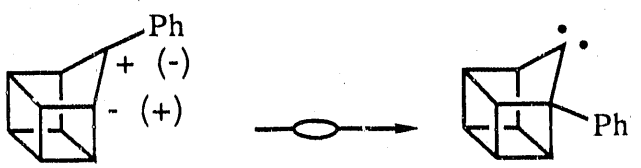


Eaton and Hoffman[16a] has reported an example of an olefin-to-carbene isomerization in the thermolysis or photolysis of cubylphenyldiazomethane 19. The very strained olefin 9-phenyl-1(9)-homocubene 21, formed from the 1,2-alkyl shift of cubylphenylcarbene 20, was trapped with ethanol to form 22. The homocubene 21 also underwent rearrangement to

1-phenyl-9-homocubylidene 23 via 1,2-alkyl migration of 23 instead of 1,2-phenyl migration, which was established by a deuterium-labeling experiment.[16b] Formation of 23 was proven by the trapping experiments with ethanol, trans- and cis-2-butene and 2,5-diphenylisobenzofuran to form corresponding cyclopropanohomocubane products 24, 25, 26, and 27, r. spectively. The retention of stereochemistry in adducts 25 and 26 indicates a singlet carbene in the transition state.

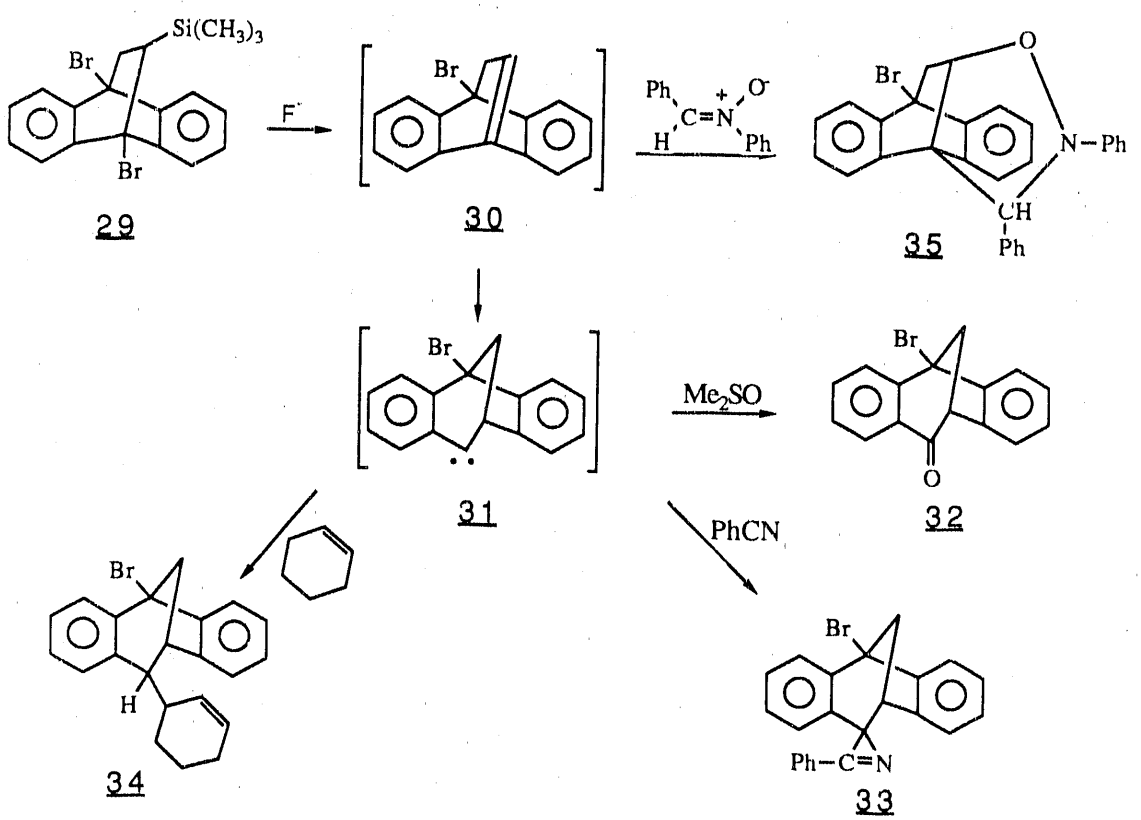


Calculations[17] show similar heats of formation for olefin 21 (201 kcal/mol) and carbene 23 (199 kcal/mol) and thus provide an explanation as to why the rearrangement from 21 to 23 is so easy. Another explanation is that the olefin 21 could be in a zwitterionic state 28 and undergo a "simple" Wagner-Meerwein shift to form the carbene 23.



28 23

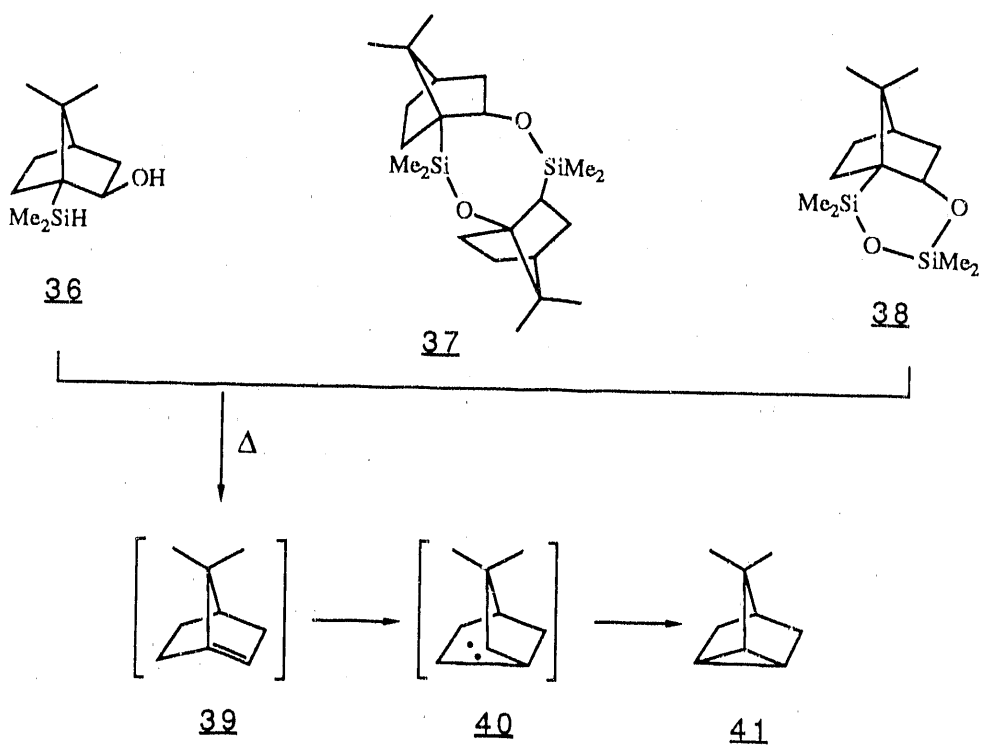
Chan and Massuda[18] observed the thermal generation of a carbene from a bicyclo[2,2,2] bridgehead alkene. Heating a



29 30 35 31 32 34 33

mixture of 29 and potassium fluoride in dimethyl sulfoxide affords 32, which was formed by the oxidation of the carbene intermediate 31 with dimethyl sulfoxide. The carbene intermediate could have arisen from the rearrangement of the expected bridgehead alkene 30. Trapping experiments verified the generation of both bridgehead olefin 30 and carbene 31.

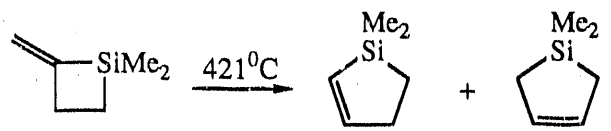
Another example of thermal isomerization of a strained bridgehead olefin to a carbene was studied by Barton and Yeh.[19] Thermal decompositions of compounds 36, 37, or 38 presumably afforded 7,7-dimethyl-1-norbornene 39 which underwent a 1,2-alkyl shift to give 2-norbornanylidene 40.



Nortricyclene 41, the isolated product, originated from γ-CH insertion in 40.

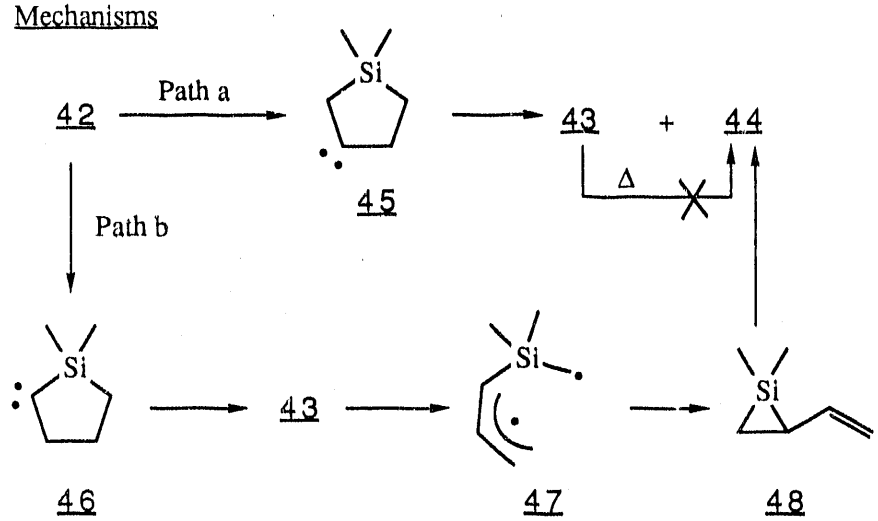
Pyrolysis of 42 at 421°C yields[20] the ring expansion products 43 and 44. This provides the first example where a 1,2-silyl shift was proposed to generate a carbene from an olefin.

Two possible mechanisms were proposed by Conlin et al.[20] for the transformation, each involving carbene intermediacy. Path a involves a β-silyl carbene intermediate, 45, formed from the vinylic silicon-carbon bond migration. Insertion of the carbene into adjacent methylene group gives the isomeric silacyclopentenes 43 and 44. Path b involves the vinylic



42 43 44

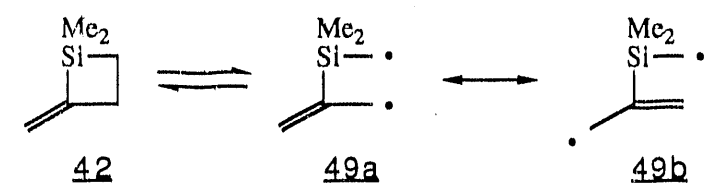
Mechanisms



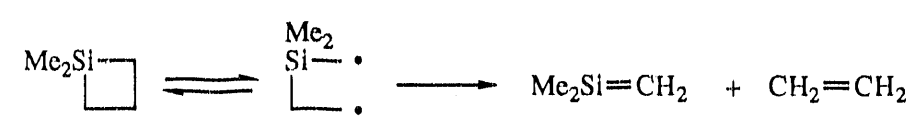
46 47 48

carbon-carbon bond migration to form the α-silyl carbene, 46, which can only give one silacyclopentene 43. The other isomer 44 could be produced from 43 via intermediate 47 and 48. However, Path b was ruled out by the fact that 43 does not isomerize under the experimental conditions.

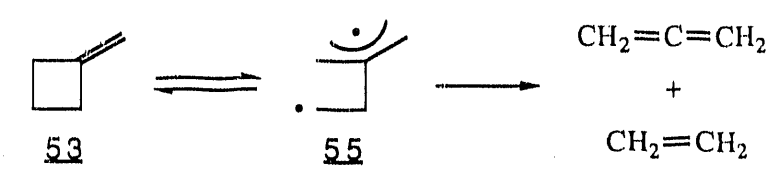
It is interesting to note that 42 does not undergo decomposition via a diradical intermediate 49. Silacyclobutanes are known to decompose by initial homolytic cleavage of one of carbon-carbon bonds.[21,22] Thermal decomposition of 50 to silene 51 is believed to proceed via a diradical intermediate 52. The activation energy of the decomposition is 63.8 kcal/mol and the log A is 15.8. It is known that radicals are stabilized by an α-double bond.[23] The cleavage of the vinyl-carbon bond in 42 should require less energy than



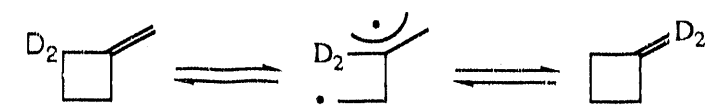
42 49a 49b



50 52 51



53 55



54 55-d_2 56

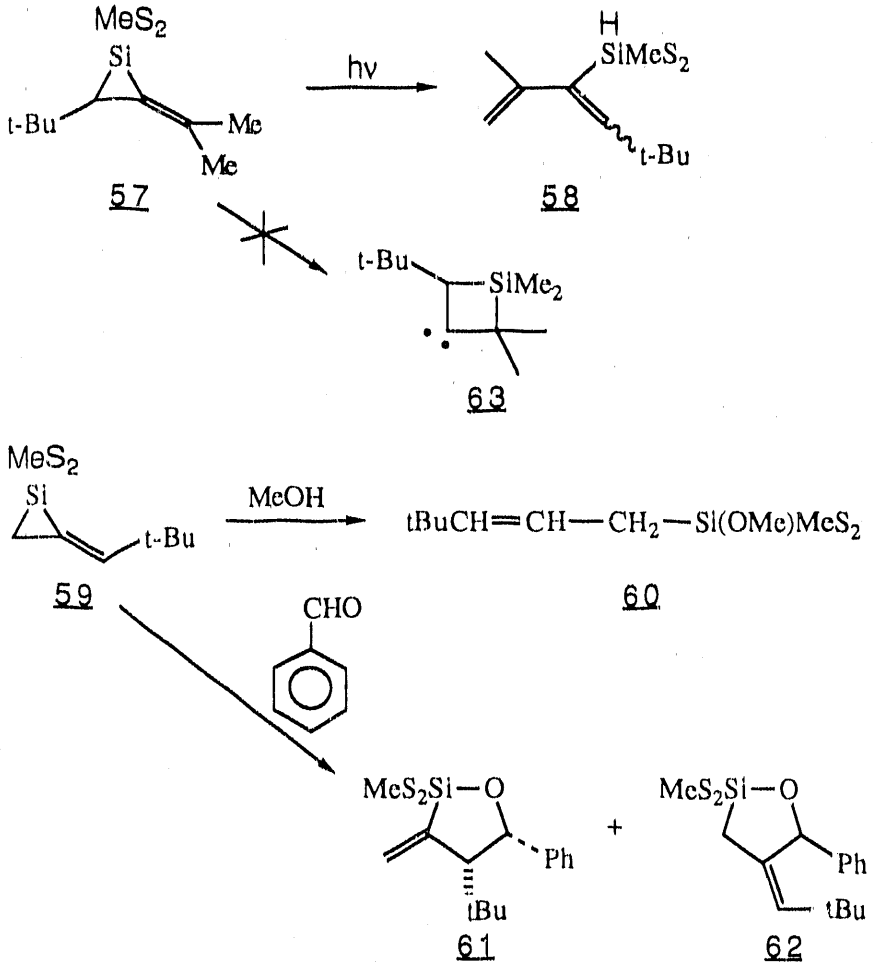
that in 50. However, the π-bond in 42 could be strained so that breaking the double bond to form the ring expansion products releases some strain and requires lower energy.

The thermal chemistry of the analogous methylenecyclobutane 53 is different from that of 42. No ring expansion products were observed for the thermal reaction of 53. The activation energy of the decomposition reaction of 53 to allene and ethylene was determined by Chesick[24] to be 63.3 kcal/mol (log A= 15.7), while E_a for the isomerization of deuterated methylenecyclobutane 54 to 56 is only 49.5 kcal/mol.[25] Doering and Gilbert[25] explain this difference by the cleavage of 53 to allene which requires twisting of diradical 55 with concomitant loss of resonance energy.

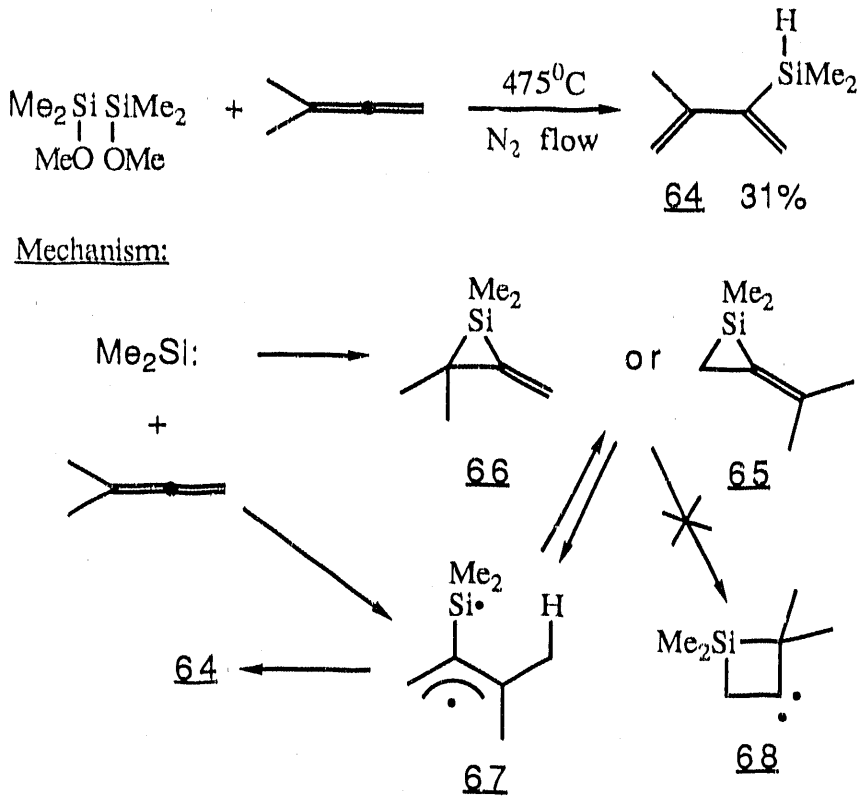
The strain ethalpies for three-, four-, five-, and six-membered saturated silacycles are reported to be 41.4, 24.7, 4.5, and 4.0 kcal/mol, respectively, and that for silacyclobutene ring to be 26.3 kcal/mol.[26] The strain energy lost by expanding a three- to a four-membered ring (~15 kcal/mol) is close to that of expanding a four- to a five-membered ring (~20 kcal/mol). Thus, it is reasonable that the methylenesilacyclopropanes would undergo ring expansion to yield silacyclobutenes.

Ando and Saso[27] synthesized the alkylidenesilacyclopropanes 57 and 59. Photolysis of 57 in cyclohexane with a low pressure mercury lamp gave 58 in 42% yield. Nucleophilic

reaction of 59 with methanol in benzene gave methoxysilane 60 quantitatively, and with benzaldehyde gave oxasilacyclopentanes, 61 and 62. There were no products found corresponding to generation of the ring expanded carbene 63.



Copyrolysis[28] of 1,2-dimethoxytetramethyldisilane and 3-methyl-1,2-butadiene yielded 2-dimethylsilyl-3-methyl-1,3-butadiene 64 in 32% yield. Again, the product formed can not be rationalized from a carbene intermediate.



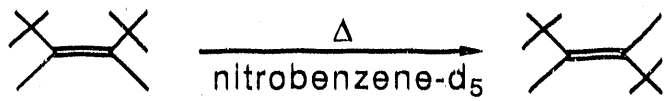
Thermal cis-trans isomerization of simple alkenes is a relatively old area of chemistry and has been reviewed.[29a,29b] Table 1 lists Arrhenius parameters for thermal cis-trans isomerization of substituted ethylenes reported in the literature.

Table 1. Arrhenius parameters[a] for olefin geometric isomerization

Reactants	log A(sec^{-1})	E_a (kcal/mol)	Method
cis-CHD=CHD	~13	~65	static
trans-CHD=$CHCH_3$	13.16	61.3±0.7	static
cis-CH_3CH=$CHCH_3$	13.78	62.8	static
	14.00	62.4	static
	13.6	62.0	static
	14.62	66.2	shock tube
cis-CHF=CHF	13.42	60.7	shock tube
cis-CHF=CHCl	13.24	58.3	shock tube
cis-CHCl=CHCl	12.8	56.0	shock tube
trans-CHCl=CHCl	12.7	55.3	shock tube
cis-CH_3CH=$CHCO_2CH_3$	13.2±0.3	57.8±1.5	static
cis-CH_3CH=CHCN	11.0±1	51.3±3.7	static
	13.2	58.1	shock tube
cis-C_6H_5CH=CHC_6H_5	12.8	42.3	static
cis-C_6H_5CH=CHCN	11.6	46.0	static
cis-C_6H_5CH=$CHCO_2CH_3$	11.5	41.6	static
cis-tBuCH=CHtBu [b]	/	54.4±0.7	
cis-tBu(Me)C=(Me)tBu [b]	14.4	40.4±1.7	solution

[a]Data from Ref. 29a. For original reports see Ref. Cited therein. [b]See Ref. 30.

Gano et al.[30] studied the thermal cis-trans isomerization of Z-2,2,3,4,5,5-hexamethyl-3-hexene 69 in solution at a temperature range of 195° to 225°C. The reverse



Z-69 E-69

isomerization from E-69 to Z-69 did not occur at temperatures below 225°C. The activation energy obtained by them is 40.4 ±1.7 kcal/mol and a log A of 14.4.

Results and Discussion

Theoretic and experimental results reveal that silyl groups stabilize free radicals and carbocation centers at the β-position (β-effect)[31a,b] and carbanions at the α-position (α-effect).[32] The β-effect is believed to take place by hyperconjugation of Si-C bond with the p orbital of the free radical or cation center. Thus this stabilization must be geometry dependent. Recent ab initio calculations by Weierschk et al.[31a] indicate that the 3-silapropyl cation, 71a, in the orthogonal conformation of the Si-C bond and the vacant p orbital is only 5 kcal/mol more stable than that of the analogous conformation of the n-propyl cation, 72a. On the other hand, the 3-silapropyl cation, 71b in the optimal conformation for Si-C hyperconjugation with the p-π orbital is 25.1 kcal/mol more stable than the analogous conformation of

the n-propyl cation, 72b. Lambert and Finzel[33a] measured the β-effect in solution to be 17.8 kcal/mol which is smaller than the calculated value.

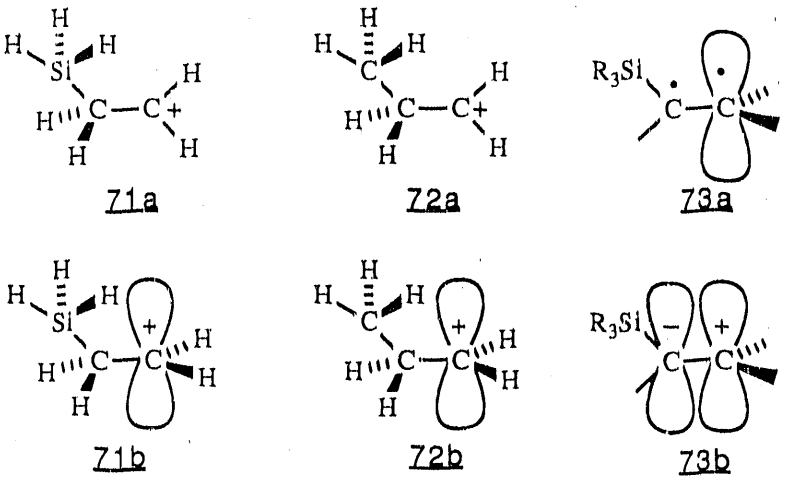


Figure 2. Geometry of radical and carbcation centers

The pathway for olefinic geometric isomerization seems simple, 180° rotation around the π bond via a perpendicular 1,2-biradical.[29b] However, the elucidation of the mechanisms has required a considerable amount of effort, and some aspects still remain unresolved. Magee et al.[34] proposed two alternative mechanisms for the cis and trans isomerization of olefins (Figure 3). One mechanism involves a crossing at point 'a' to the triplet state, followed by a crossing at 'b' back to the singlet state. This mechanism is expected to have a lower activation energy and smaller log A. Another suggests that the system can remain in the singlet state and attain its

position of maximum potential energy at an angle of twist of approximately 90°. This mechanism is expected to produce log A of 12~13 and activation energy E_a > 45 kcal/mol. Measurements of thermal cis-trans isomerization substantiate the second mechanism.[29a,35]

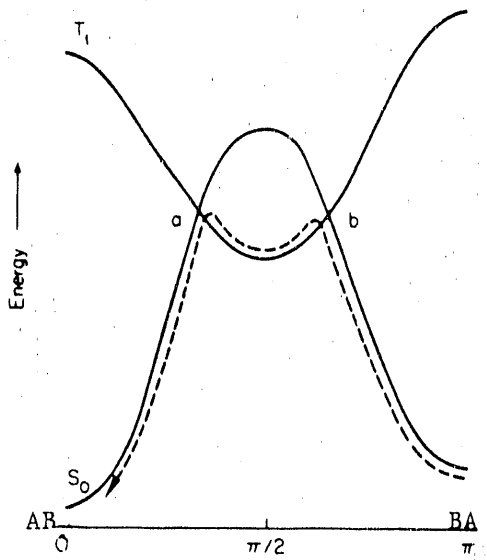


Figure 3. Schematic energy diagram of the singlet and triplet states of ethylene. AB at angle 0° and BA at 180°

The diradical intermediate 73 of a silyl substituted ethylene is in the same conformation as 71b. Thus, it may be stabilized by the β-effect of the silyl group. It is then reasoned that a silyl group substituted on the double bond of ethylene might stabilize the perpendicular 1,2-diradical and lower the activation energy of cis-trans isomerization.

All known examples of a thermal 1,2-shift along a C-C

dcuble bond to form a carbene intermediate come from molecules in which the double bond is already extremely twisted, which means that the two p-orbitals of the double bond are approaching a perpendicular relationship. Eaton and Hoffman[16a] suggested that the 1,2-alkyl migration in 21 might be via a zwitterion. In such a case the silyl group would stabilize the intermediate by both α- and β-effects in structure 73b. Thus, no matter which intermediate, diradical or zwitterion, the silyl group would be able to stabilize and lower the activation energy of a 1,2-silyl migration along the double bond to generate the carbene intermediate.

Kinetic data shown in Table 2 were obtained for the cis-trans isomerization of eight silyl- and carbon-substituted ethylenes in stirred-flow reactor (SFR) pyrolyses.

In order to confirm the reliability of the SFR system, the kinetic parameters of Z-2-butene were determined for comparison with those reported in the literature. The activation energy and log A (62.34 kcal/mol and 13.48) obtained are very close to those reported in the literature (see Table 1).

Cis-trans isomerization of 2-butene, 1-phenyl-1-propene, and 1-trimethylsilyl-1-propene is reversible.

$$Z\text{-}CH_3CH{=}CHR \underset{k_r}{\overset{k_f}{\rightleftharpoons}} E\text{-}CH_3CH{=}CHR$$

Table 2. Arrhenius parameters and the rate constants at 750 K for geometric isomerization of substituted ethylenes

#	R_1	R_2	R_3	log A	E_a kcal/mol	K_f 750 K
Z-74	CH_3	CH_3	H	13.48±0.19	62.34±0.78	2.07×10^{-5}
Z-75	CH_3	$SiMe_3$	H	13.01±0.14	56.00±0.34	4.90×10^{-4}
E-75	CH_3	H	$SiMe_3$	12.6	56.97	1.00×10^{-4}
Z-77	$SiMe_3$	$SiMe_3$	H	13.94±0.11	52.68±0.37	3.90×10^{-2}
Z-78	Ph	$SiMe_3$	H	14.29±0.08	53.00±0.29	7.04×10^{-2}
Z-79	Ph	CMe_3	H	14.79±0.07	54.90±0.26	6.25×10^{-2}
Z-80	Ph	CH_3	H	15.05±0.18	60.18±0.68	3.27×10^{-3}
E-80	Ph	H	CH_3	14.74±0.28	60.75±1.09	1.09×10^{-3}

Under the experimental conditions the cis isomer isomerized to trans and the trans goes back to cis. The reaction rates for cis to trans isomerization of Z-2-butene were obtained by the following equation:[36]

$$k_f = \frac{k_{ob}\ k_{eq}}{k_{eq} - \frac{[t]_f}{[c]_f}} \qquad (1)$$

K_{eq} = 1.31 was used, obtained by Rabinovitch and Michel.[37]

The K_{eq}s are not available for the cis-trans isomerization of 1-phenyl-1-propene and 1-trimethylsilyl-1-propene. Their reaction rates were calculated from the following equations:[36]

$$k_f = \frac{k_f' + k_r' \frac{[t]_f}{[c]_f}}{1 - \frac{[t]_f}{[c]_f} \cdot \frac{[c]_r}{[t]_r}} \qquad (2)$$

$$k_r = \frac{k_r' + k_f' \frac{[c]_r}{[t]_r}}{1 - \frac{[t]_f}{[c]_f} \cdot \frac{[c]_r}{[t]_r}} \qquad (3)$$

Where

K_f' ---Measured reaction rate from cis to trans isomerization;

K_r' ---Measured reaction rate from trans to cis isomerization;

$[t]_f$---Concentration of trans isomer measured for the cis

to trans isomerization;

$[t]_r$---Concentration of trans isomer measured for the trans to cis isomerization;

$[c]_f$---Concentration of cis isomer measured for the cis to trans isomerization;

$[c]_r$---Concentration of cis isomer measured for the trans to cis isomerization.

Z-1,2-Bis(trimethylsilyl)ethylene, Z-β-trimethylsilylstyrene, and Z-4,4-dimethyl-1-phenyl-1-butene do not undergo the reverse reaction under the experimental conditions. Therefore, the k's of cis-trans isomerization are the values of k_f'.

The activation energy of the cis to trans isomerization of Z-1-trimethylsilyl-1-propene is 6.3 kcal/mol lower than that of the Z-2-butene, and the activation energy of cis to trans isomerization of 1,2-bis(trimethylsilyl)ethylene is 9.7 kcal/mol lower than that of Z-2-butene. It is obvious from the numbers that the trimethylsilyl group indeed stabilizes the diradical transition state of the cis-trans isomerization of alkenes and lowers the energy barrier for the isomerization.

Attempts to determine the kinetic parameters of Z-t-butylmethylethylene were inconclusive due to decomposition at the onset of isomerization. The phenyl group lowers the E_a of cis-trans isomerization of an olefin (Table 1) so that

lower temperatures could be used to determine kinetic parameters for t-butyl substituted compounds for comparison. The kinetic parameters for four β-substituted styrenes were obtained. Comparing the data for cis-trans isomerization of

$$\text{Z-PhCH=CHR} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \text{E-PhCH=CHR}$$

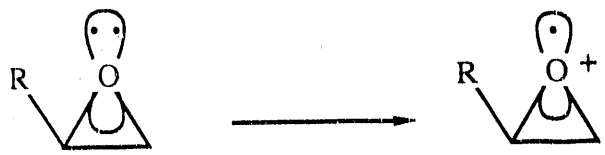
R = CH_3, CMe_3, $SiMe_3$, CH_3, (E- to Z-)

the β-substituted styrenes, it seems that there is little additional stabilization from a silyl group than from a t-butyl group. The stabilizations due to a β-trimethylsilyl group and a β-t-butyl group are 7.2 and 5.3 kcal/mol, respectively, compared with β-methylstyrene. The β-trimethylsilyl group lowers the activation energy of thermal cis-trans isomerization only 1.9 kcal/mol more than the t-butyl group.

The isomerization barrier of 1,2-bis-t-butylethylene 76 was measured by Roth[38] in the gas phase to be 54.4 kcal/mol which is in agreement with the predicted barrier, 53 kcal/mol.[30] The activation energy, obtained by SFR pyrolysis, of the cis-trans isomerization of Z-1,2-bis(trimethylsilyl)-ethylene is 52.7 kcal/mol, which is only 1.7 kcal/mol lower than that of 76.

The steric effect of a trimethylsilyl group is comparable with that of t-butyl. The results obtained by this research do not allow us to claim that the silyl group stabilizes the

biradical transition state in the cis-trans isomerization of simple olefins. Block et al.[31b] studied the β effect of silyl group by determining the first ionization potential of 82a and 82b. In compound 82a the Si-C bonds are nearly parallel to the heteroatom lone pair p orbital because of the ring strain. When 82 undergoes photoionization the lone pair p orbital becomes half-filled, which will be stabilized by β-effects of silyl group. However, from their experimental results, they concluded that a trimethylsilyl group adjacent to the half filled oxygen p-π orbital of an oxirane radical cation only provides a stabilization of 3.0 kcal/mol compared to a t-butyl group.



82 82'

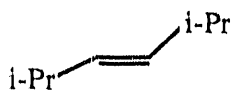
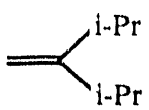
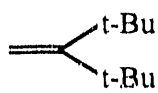
a R = $SiMe_3$ b R = CMe_3

There are no decomposition products in the temperature range in which kinetic data were obtained for all of the eight compounds in Table 2. Upon raising the reaction temperature decomposition products appeared. The major products are C_1-C_3 hydrocarbons which could not provide evidence of a carbene intermediate generated during the decomposition process.

To observe the 1,2-shift generating a carbene from an

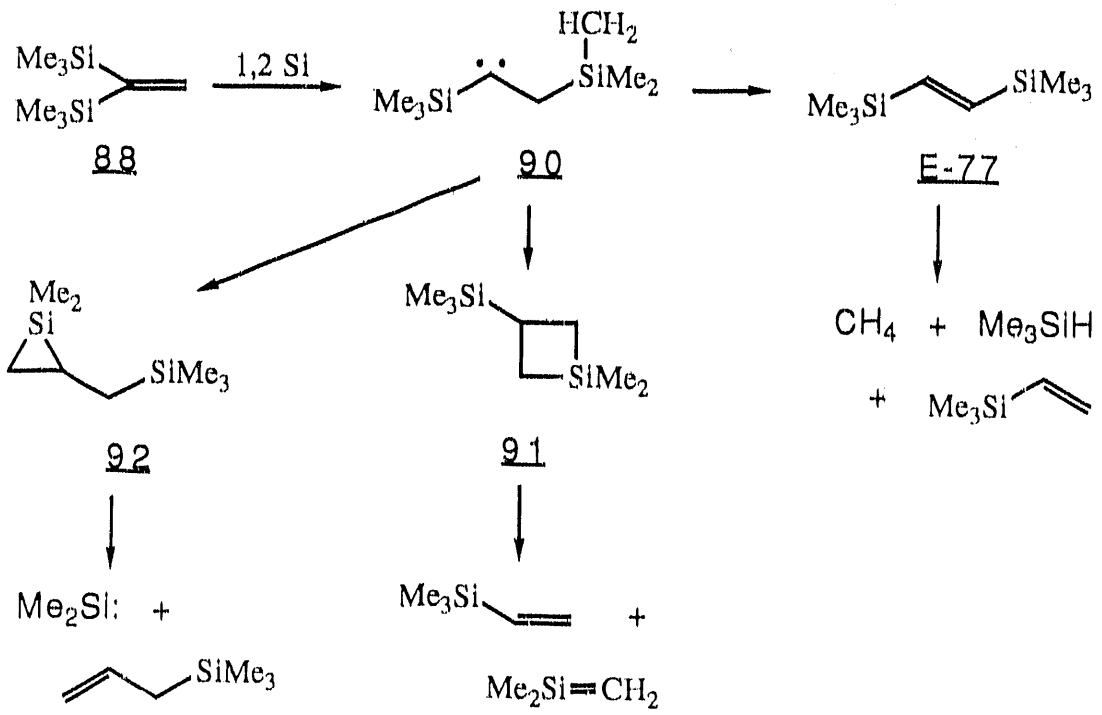
olefin, a "pre-strained" olefin would be the ideal structure. Calculations[39] show that the 1,1-disubstituted ethylenes are more strained than E-1,2-disubstituted ethylenes. The strain energy of 83 is 0.13 kcal/mol, 3.46 kcal/mol less than that of 84. When the substituents are t-butyl groups, the difference is 12.52 kcal/mol due to the larger steric effects of t-butyl versus iso-propyl groups. Constitutional isomerization of 1,1-disubstituted ethylene would release the strain energy.

Table 3. Strain energy of some disubstituted ethylenes

#	Ethylenes	Strain Energy (kcal/mol)
83		0.13
84		3.59
85		-0.47
86		12.05

SFR and flash vacuum pyrolysis were employed to study the thermal isomerization of 2-trimethylsilylpropene 87, 1,1-bis-(trimethylsilyl)ethylene 88, and α-trimethylsilylstyrene 89. 2-Trimethylsilylpropene decomposes at a very high temperature (~750°) to methane, propene and other products which were

unidentified by GC-MS. 1,1-Bis(trimethylsilyl)ethylene 88 partially decomposes at 700-800°C. Methane, trimethylsilane, and vinyltrimethylsilane are the major products. The mechanism leading to these products might be via a carbene intermediate.



1,2-Silyl migration of 88 would yield the carbene 90. This carbene could undergo α-C-H insertion to give E-1,2-bis-(trimethylsilyl)ethylene E-77, which was tested to decompose in the SFR conditions at 700°C to methane, trimethylsilane, and vinylmethylsilane as major products. However, E-77 was not detected in the reaction mixture even though it is stable enough to leave detectable amounts undecomposed under the experimental conditions if it would be formed. Another

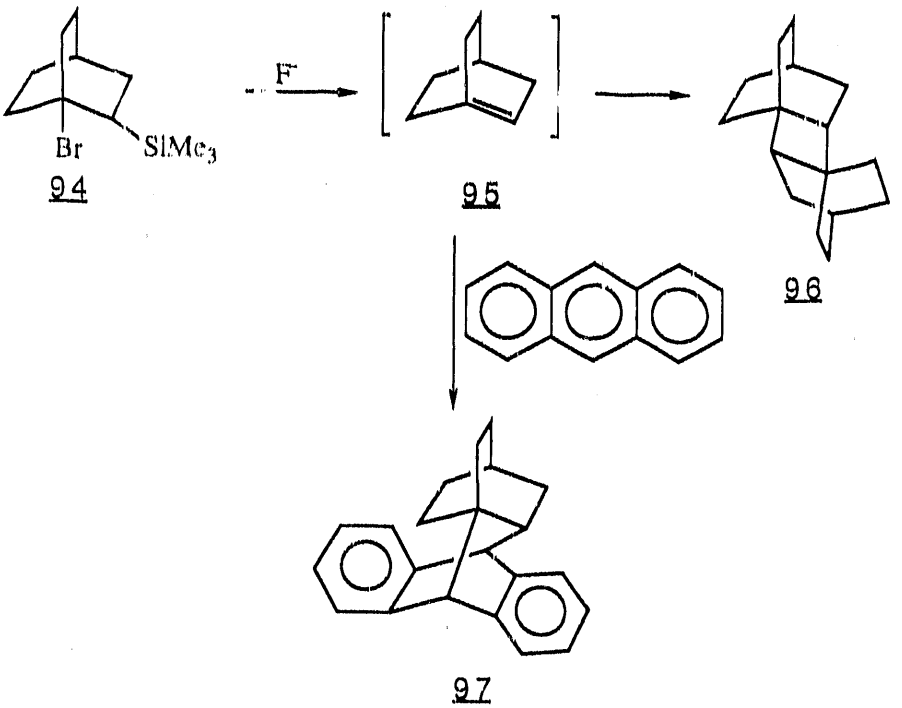
possibility is that the vinyltrimethylsilane came from the known decomposition of silacyclobutane 91, which formed from intramolecular C-H insertion of the carbene 90. The silacyclopropane 92 might be another intermediate derived from the carbene 90. However, 91 and allyltrimethylsilane were not detected from the reaction mixture. They should have been detected if formed.

Two major products along with undecomposed starting material were observed in SFR pyrolysis of α-trimethylsilyl-styrene at 800°C. One of the products was determined to be benzene via a mass spectrometer (MS) connected to the SFR. The other, with a longer retention time than the starting material, was not transferrable to the MS from the SFR. Flash vacuum pyrolysis of 89 was studied at 800°C with complete decomposition of starting material. The two major products were identified by GC-MS to be benzene and styrene; also a small amount of phenylacetylene was observed. No silicon-containing compounds were detected as volatile products in the liquid-N_2 trap.

It is most likely that high-energy radical processes dominate in the thermal decomposition of 1,1-disubstituted ethylenes.

Barton and Yeh[40] found that 94 smoothly produced bicyclo[2,2,2]oct-1-ene 95 upon treatment with $Me_4N^+F^-$. Intermediate 95 was trapped by anthracene or dimerized in the

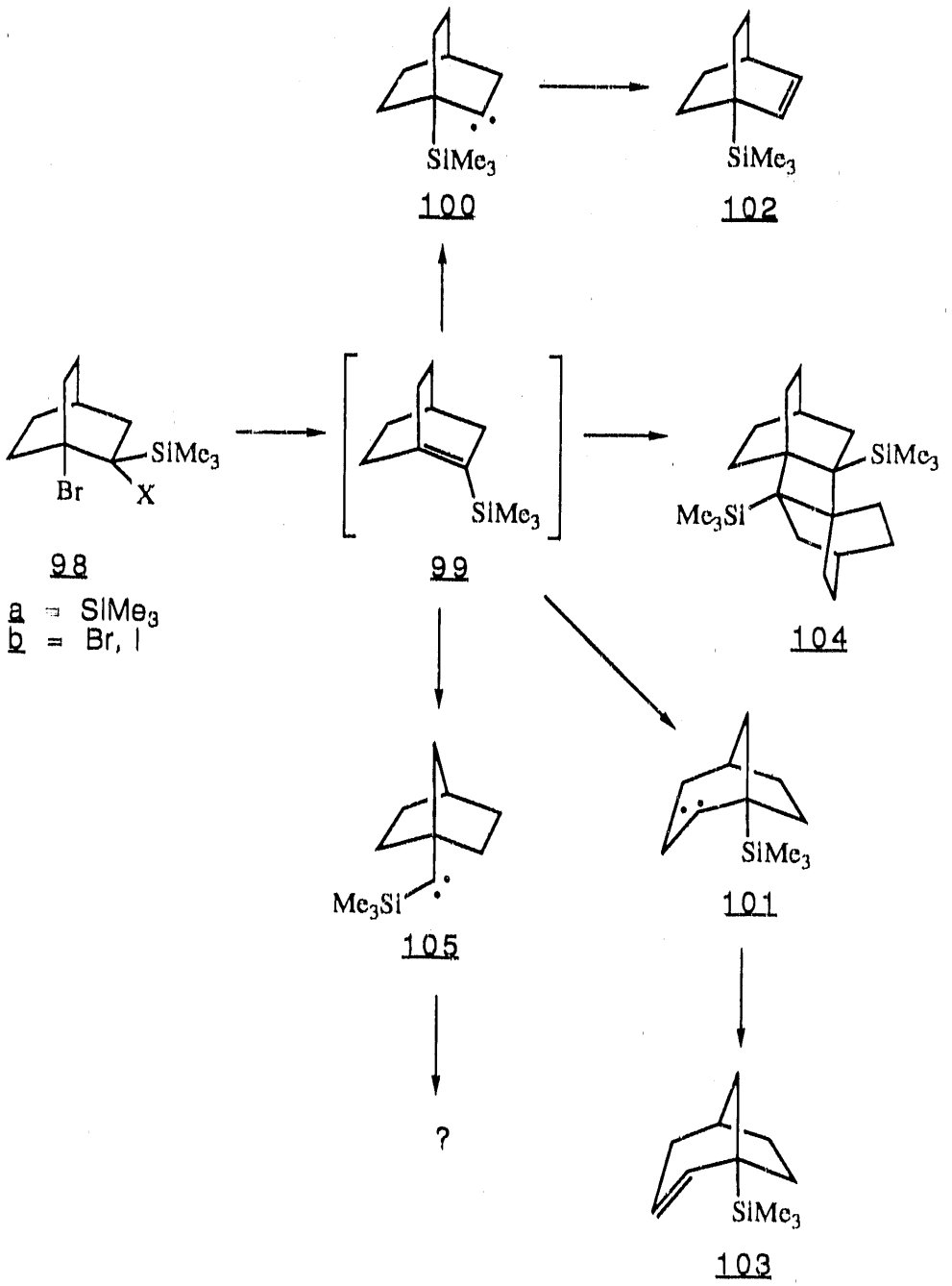
absence of trapping reagent to give mainly 97 or 96. The structures of 96 and 97 were determined by single-crystal x-ray diffraction.



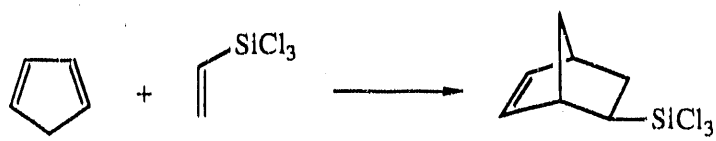
94 95 96 97

Molecule 98 was designed as the precursor to the silyl substituted bridgehead olefin 99. In the absence of trapping reagents 99 could dimerize to 104 in analogy to 95. Also there are three alternative ways for 99 to release its strain energy. It could undergo 1,2-silyl migration to form carbene 100, which leads to alkene 102, or 1,2-alkyl migration from either end of the carbon-carbon double bond to give carbenes 101 or 105.

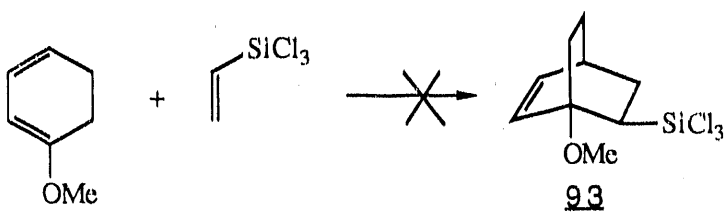
The synthesis of 98 turned out to be difficult. The Diels-Alder reaction has been used[41] to synthesize the


SiMe3
100
SiMe3
102
SiMe3
Br
X
98
a = SiMe3
b = Br, I
SiMe3
99
SiMe3
Me3Si
104
Me3Si
105
SiMe3
101
?
SiMe3
103

silyl-sustituted bicyclo[2,2,1]hept-2-ene. Vinyltrichlorosilane and cyclopentadiene react exothermically to give a near-quantitative yield of 5-trichlorosilylbicyclo[2,2,1]-hept-2-ene.[41]



However, the reaction of vinyltrichlorosilane and 1-methoxycyclohexa-1,3-diene in refluxing benzene or a sealed tube heated at ~150°C did not produce the desired product. Dimers of the diene are the the major products.



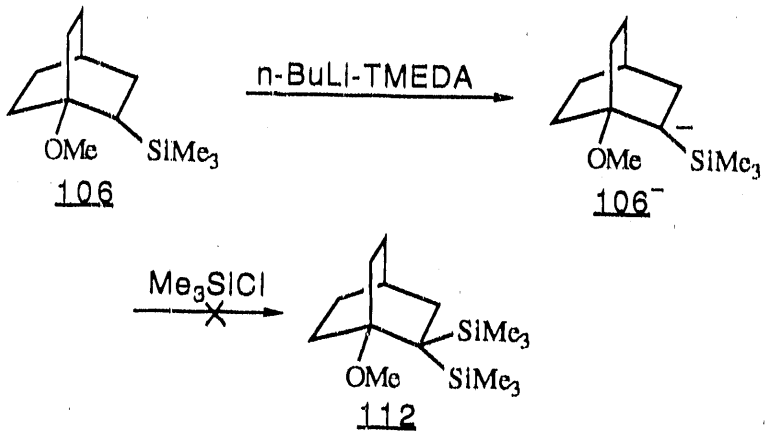
93

It is known that silyl groups stabilize α-anions so that $R_3SiCH_2^-$ are easy to form.[15]

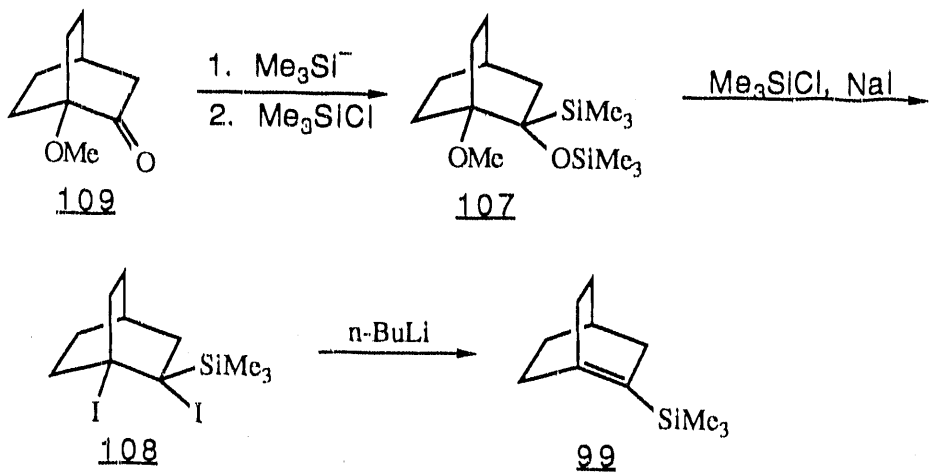
$$Me_4Si \xrightarrow[THF \quad R.T.]{\text{n-BuLi-TMEDA}} Me_3SiCH_2^-$$

If the known compound 106 is treated with n-BuLi-TMEDA under similar conditions as above, one would expect that the anion formed, when quenched with trimethylchlorosilane, would provide the bis(trimethylsilyl)-sustituted compound 112. However, when 106 and n-BuLi-TMEDA were stirred in THF at room temperature for 24 hours and quenched with trimethyl-

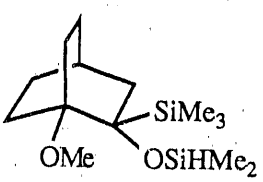
chlorosilane only starting material was recovered.



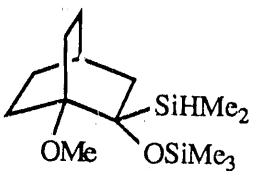
Silyl anions undergo smooth additions to a variety of organic electrophiles including ketones.[42a,b] This reaction could be used as the key step of another synthetic route to the precursor of bridgehead olefin 99. Reaction of trimethylsilyl anion[42b] with ketone 109, followed by the treatment with trimethylchlorosilane should produce the key product 107. Iodination of 107 under mild condition should yield diiodide 108.[43a] Reaction of 108 with n-BuLi could afford the bridgehead olefin 99.[43b]



Reaction of 109 with trimethylsilyl anion, followed by treatment of trimethylchlorosilane, instead of 107, gave



110

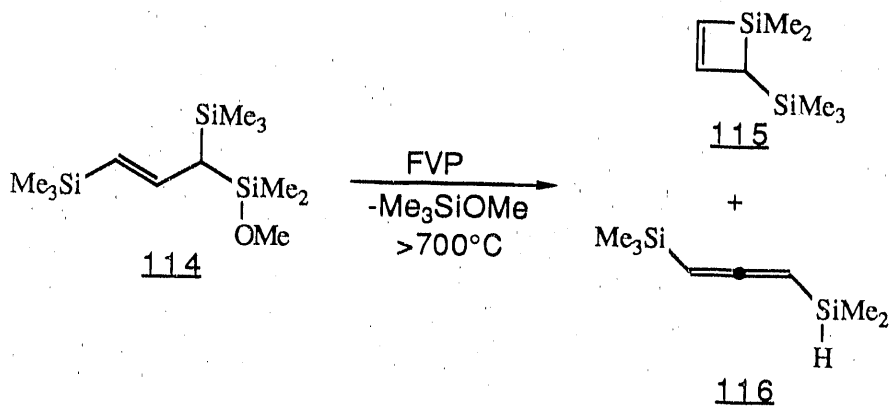


111

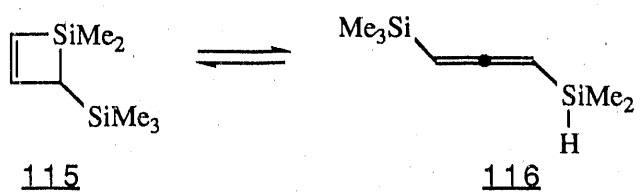
product 110 or 111, which were indistinguishable by ^{1}H NMR, in ~20% yield and ~60% starting material was recovered. The mechanism of the formation of 110 (or 111) is still a mystery.

Silacyclobutene 3 was used as a precursor to synthesize 1-aza-2-silahexa-3,5-diene[44a] (see second part of this thesis). However, it was produced as a mixture in low yield.[44b] Burns and Barton[45] found that pyrolysis of 1,3-bis(trimethylsilyl)-3-methoxydimethylsilylpropene 114 gives 4-trimethyl-3-dimethyl-3-silacyclobutene 115, a substituted silacyclobutene, in high yield. In using this method to synthesize 115, it was found that 115 was indeed the major product at lower pyrolysis temperature (~650°C) along with the unreacted 114. However, pyrolysis of 114 at higher temperatures (>700°C) affords an isomer of 115. The isomer was identified to be 1-dimethylsilyl-3-trimethylsilylallene 116 by ^{1}H, ^{13}C NMR, FTIR, and GC-MS spectra data.

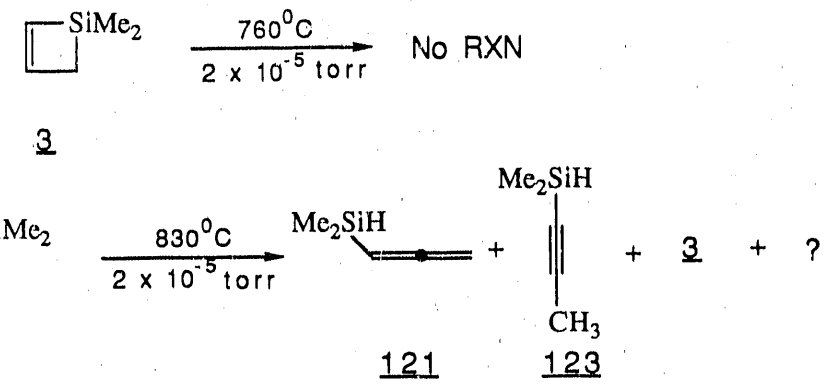
To study the origin of 116, flash vacuum pyrolysis (FVP) of pure 115 at 715°C (~10^{-4} torr) was conducted to give 57% of 115 and 11% of 116. This demonstrates that 116 originated



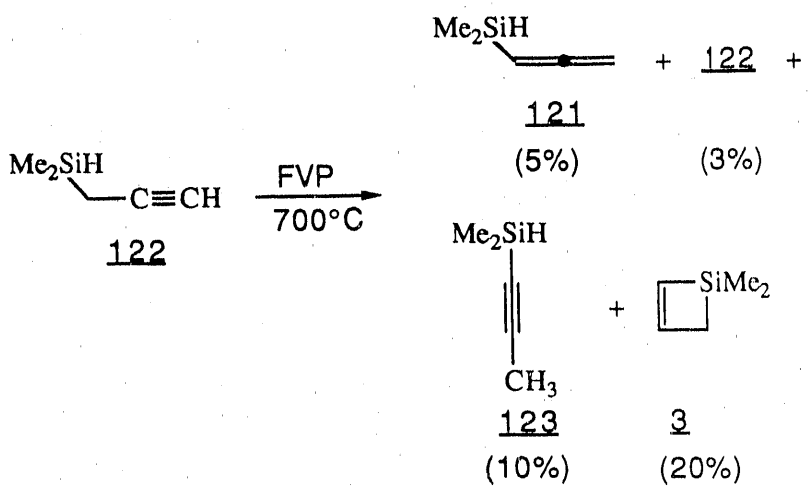
from 115. This is a new reaction of a silacyclobutene. Also, flash vacuum pyrolysis of 116 at 760° (~10^{-4} torr) gives 29.6% 115 and 12.2% 116 was recovered. Thus this remarkable reaction is reversible.



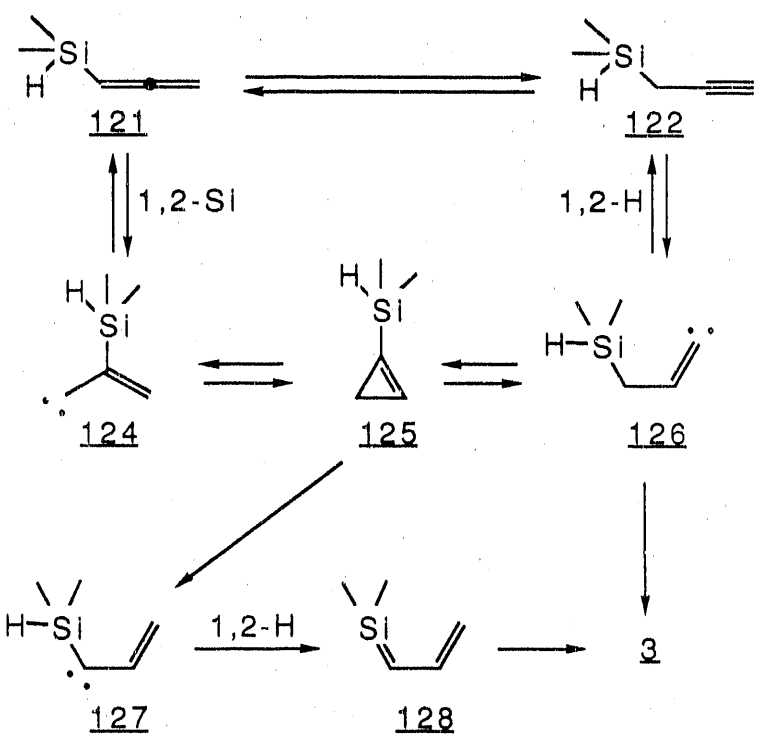
For comparison, flash vacuum pyrolysis of 3 was performed. At 760°C the starting material 3 was recovered and no detectable isomerization products were found by ^{1}H NMR and GC-FTIR. From the flash vacuum pyrolysis of 3 at 830°C, the starting material, 3, dimethylsilylallene, 121, and dimethylsilylpropyne were identified by GC-FTIR along with lots of unidentified decomposition products. Attempts were not made to isolate the products for further identification due to their similar retention times on the analytical GC.



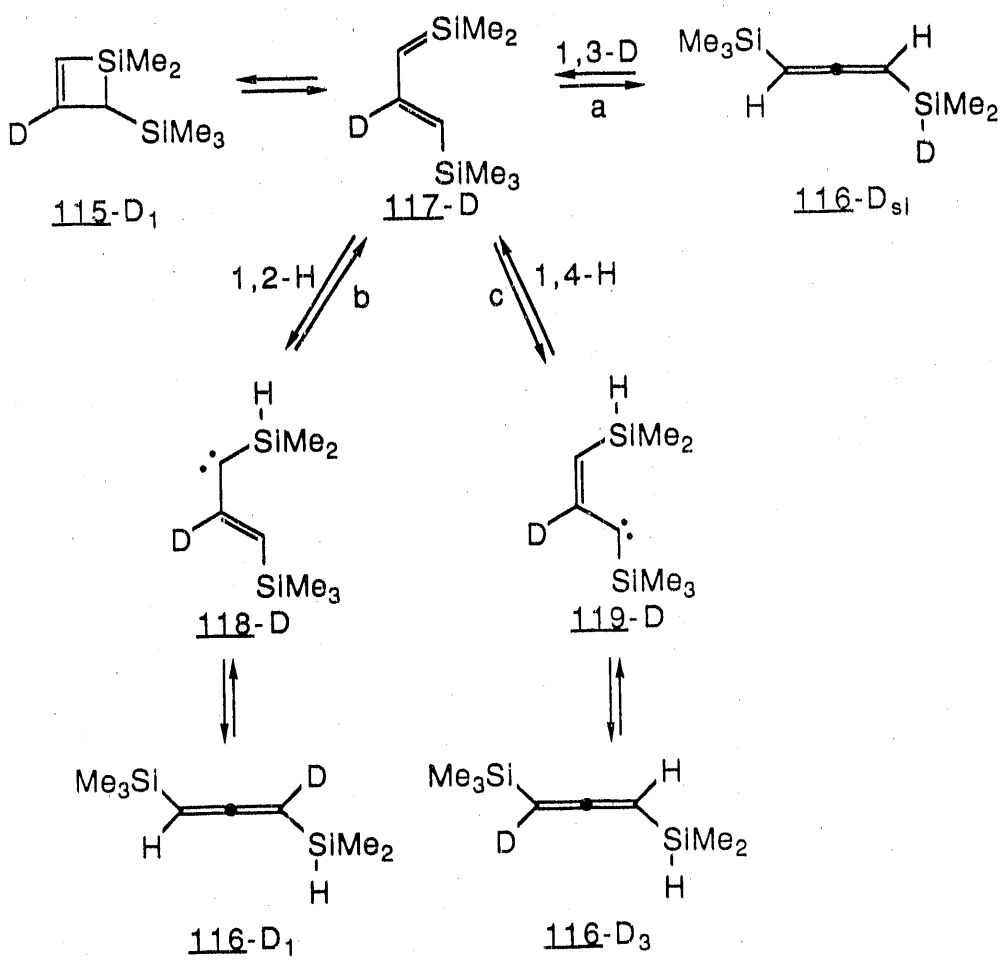
The thermal isomerization of dimethylsilylallene 121 was not studied. However, it, as a primary product, is proposed by Barton and Groh[46] to isomerize thermally to silacyclobutene 3. Flash vacuum pyrolysis of propargyldimethylsilane at 700°C affords dimethylsilylallene 121 (5%), the starting material 122 (3%), 1-dimethylsilylpropyne 123 (10%), and 3,3-dimethyl-3-silacyclobut-1-ene 3 (20%) as the major constituents. Because of the large number of intermediates one can write for a connecting energy surface between isomers



3 and 121-123 there exists a considerable number of mechanistic possibilities for the formation of a silacyclobutene. One of the possibilities is 1,2-silyl migration in 121 to sequentially produce vinylcarbene 124, cyclopropene 125, and vinylcarbene 127. This latter intermediate would be expected to isomerize to vinylsilene 128, a molecule that is known to close to 3. Such a pathway is supported by ab initio calculations[47] on allene-propyne isomerization which shows that propenylidene, cyclopropene, and vinylcarbene to be stable intermediates on the potential energy surface.



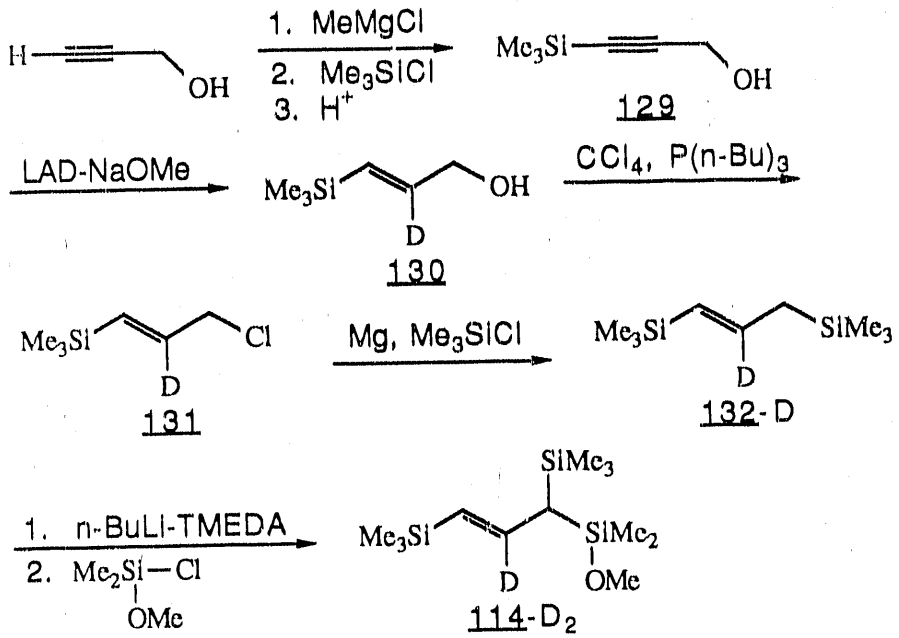
The mechanism for the isomerization of 115 to 116 could be much more simple. The ring opening of 115 to 4-trimethylsilyl1-silabuta-1,3-diene 117 has been proven by trapping experiments.[48a] In the gas phase, 117 could undergo a) 1,3-H migration to generate allene 116; b) 1,2-H migration to produce vinylcarbene 118, which undergoes C-H insertion to give the allene 116; c) 1,4-H migration of 117 to give another vinylcarbene 119 which would produce 116 by C-H insertion.



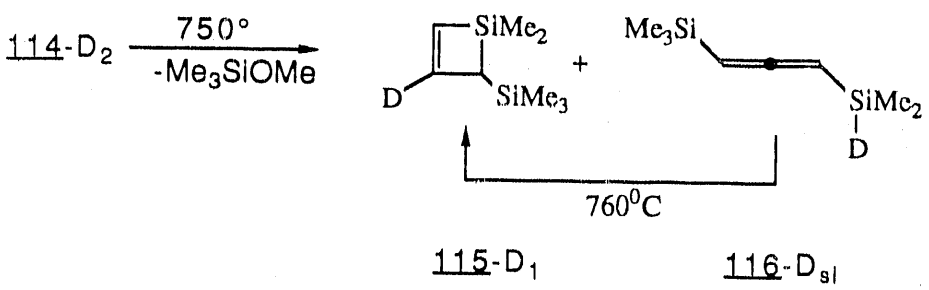
These mechanisms could be distinguished by deuterium labeling at C-1 of 115. Mechanism "a" would produce allene 116 with deuterium on the silicon. Mechanism "b" would produce allene 116 with deuterium on C-1, and mechanism "c" would produce allene 116 with deuterium on C-3.

1,3-Bis(trimethylsilyl)-3-dimethylmethoxysilyl-2-deuteropropene 114-D_2 was synthesized as a precursor of 115-D_1.

Reaction of propargyl alcohol with two equivalents of methylmagnesium chloride followed by quenching with trimethylchlorosilane and working up in acid condition yields 3-trimethylsilyl-2-propyl-1-ol 129. Reduction of the triple bond in 129 by lithium aluminium deuteride-sodium methoxide[49] gives 130 with deuterium on C-2. Chlorination of 130 by tributylphosphine in carbon tetrachloride at room temperature gives 1-trimethylsilyl-3-chloro-2-deuteropropene 131, which was transformed into 1,3-bis(trimethylsilyl)-2-deuteropropene 132-D by reaction of 131 with magnesium and trimethylchlorosilane. Treatment of 132-D with n-BuLi-TMEDA, and quenching the resulting anion with dichlorodimethylsilane gave 1,3-bis(trimethylsilyl)-3-dimethylchlorosilyl-2-deuteropropene 133. Methoxylation of 133 with methanol-pyridine was incomplete even after refluxing with excess methanol in THF. 114-D_2 was obtained by treatment of 132-D with n-BuLi-TMEDA followed by quenching with dimethylmethoxychlorosilane.



Flash vacuum pyrolysis of 114-D_2 at 750° (~10^{-5} torr) affords trimethylmethoxysilane, 115-D_1, and 116-D_{s1}. The positions of the deuterium in 115 and 116 were confirmed by ^1H, ^{13}C and ^2H NMR, and GC-FTIR. The formation of 116-D_{s1} is only consistent with the mechanism "a", 1,3-H migration of 117. And flash vacuum pyrolysis of 116-D_{s1} gives the silacyclobutene 115-D_1, which indicates that this remarkable



reverse reaction occurs via the 1,3-hydrogen migration of silabuta-1,3-diene 117. This is the second observation on a 1,3-hydrogen migration. The only experimental observation of 1,3-hydrogen migration was reported by Yeh et al.[50a] in a 1-silapropene system. Calculations by Bingham et al.[50b] predicted an activation energy of 49.2 kcal/mol for the 1,3-allylic hydrogen shift in propene.

Experimental

Routine proton and ^{13}carbon NMR spectra were obtained on a Nicolet NT-360 spectrometer. ^{2}H NMR spectra were recorded on a Varian VXR-300 spectrometer. All chemical shifts are reported as parts-per-million (δ-scale) using either benzene-d_6, chloroform-d or acetonitrile-d_3 as internal standards.

Infrared (IR) spectra were recorded on an IBM IR-90 series FTIR spectrometer. All bands were reported in reciprocal centimeters (cm^{-1}).

Exact mass measurement were obtained on a Krotos MS50 operating at 70 ev. Routine mass spectra were obtained on a Hewlett Packard 5790 GC mass-selective detector.

A Hewlett Packard 5790 gas chromatograph was used for determining the yields of pyrolysis experiments. Preparative GC was done either on a GOW-MAC series 550 or a Varian Aerograph series 1700 gas chromatograph. The column used will

be specified in experimental for synthesis of each compound. Reactions were generally carried out in oven dried glassware under an atmosphere of dry nitrogen or argon.

Flash vacuum pyrolysis experiments were performed by slowly distilling the compounds through a horizontal quartz tube hot zone packed with quartz chips. The pyrolysate was collected in a trap cooled by liquid nitrogen. The pressure behind the liquid nitrogen trap was 10^{-4} - 10^{-5} torr depending on the experiments. The flow pyrolysis experiments were performed by dripping the starting material through a vertical quartz tube packed with quartz chips under N_2 flow. The pyrolysate was collected into a trap at -78^{0}C.

The kinetic experiments were performed on a stirred flow reactor (SFR).[51]

The kinetic equations that are used in this type reactor can be described as following.[52]

For a unimolecular decomposition A to B in a flow system the balance for B can be written as:

$$kv[A] - u[B] = 0 \qquad (4)$$

Where: kv[A] -- the formation of B from A

u[B] -- the loss of B from the reactor

v -- volume of the reactor

u -- volumetric flow rate.

The rate constant for the formation of B can be obtained by rearranging equation (4):

$$k = \frac{u[B]}{v[A]} \qquad (5)$$

u/v is defined as $1/\tau$ and referred to as the residence time. Detemination of $1/\tau$ was described in the literature.[51] The Arrhenius parameters were determined by a plot of ln k vs 1/T in the usual fashion from the Arrhenius equation:

$$\ln k = \ln A - \frac{Ea}{RT}$$

The helium flow through the reactor was 60 ml/min. The reactor temperature was controlled to 0.1^0C by a Digi-Sense temperature controller. The pressure of the sample introduced was measured with a MKS Baratron transducer. The sample was introduced from a vacuum manifold to the reactor with the helium carrier gas. The products from the reactor were separated by a Varian 6000 gas chromatograph. The particular column employed was determined by the products. A splitter after the column directed a fraction of the eluent stream to a quadrapole mass spectrometer (VG-SX300). However, compounds which have not enough vapor pressure at room temperature could not be transferred into the mass spectrometer. Unimolecular reaction was maximized by using very low concentrations of the sample (~0.004%) in the reaction diluted by helium gas. A chart recorder and a Magnum XT/Mark 2 microcomputer were interfaced to the gas chromatograph. The appropriate programs

on the computer were used to measure the peak area of both reactant and products, calculate the k's and draw the Arrhenius plot. The purity of the compounds studied by SFR was in a range from 99.4 to 100 percent determined by analytical GC analysis.

Determination of Arrhenius parameters for Z-2-butene Z-74 to E-2-butene E-74

Approximately 0.1 torr of Z-74 was introduced into the reactor at the desired temperature. The data were collected by computer. The rate constants were determined over a temperature range of 617 to 677°C. The column used for separation of cis-trans isomer is 21' 20% $AgNO_3$ saturated ethylene glycol on chromasorb W.[53]

Table 4. Rate constants for Z-74 to E-74 isomerization

T°C	$kx10^2 sec^{-1}$	T	$kx10^2$	T	$kx10^2$
617.35	1.54	640.25	3.52	662.50	7.94
617.35	1.61	640.30	3.54	662.45	8.00
625.0	2.18	647.28	4.56	670.1	10.59
625.0	2.05	647.30	4.50	677.30	14.78
632.4	2.69	654.95	6.44	677.30	14.60

E_a 62.34 ±0.78 kcal/mol; log A 13.48 ±0.19; ΔH^* 60.50 ±0.78 kcal/mol; ΔS^* 1.09 ±0.85 eu; at T_{ave} =651.0°C for rxn order 1.000.

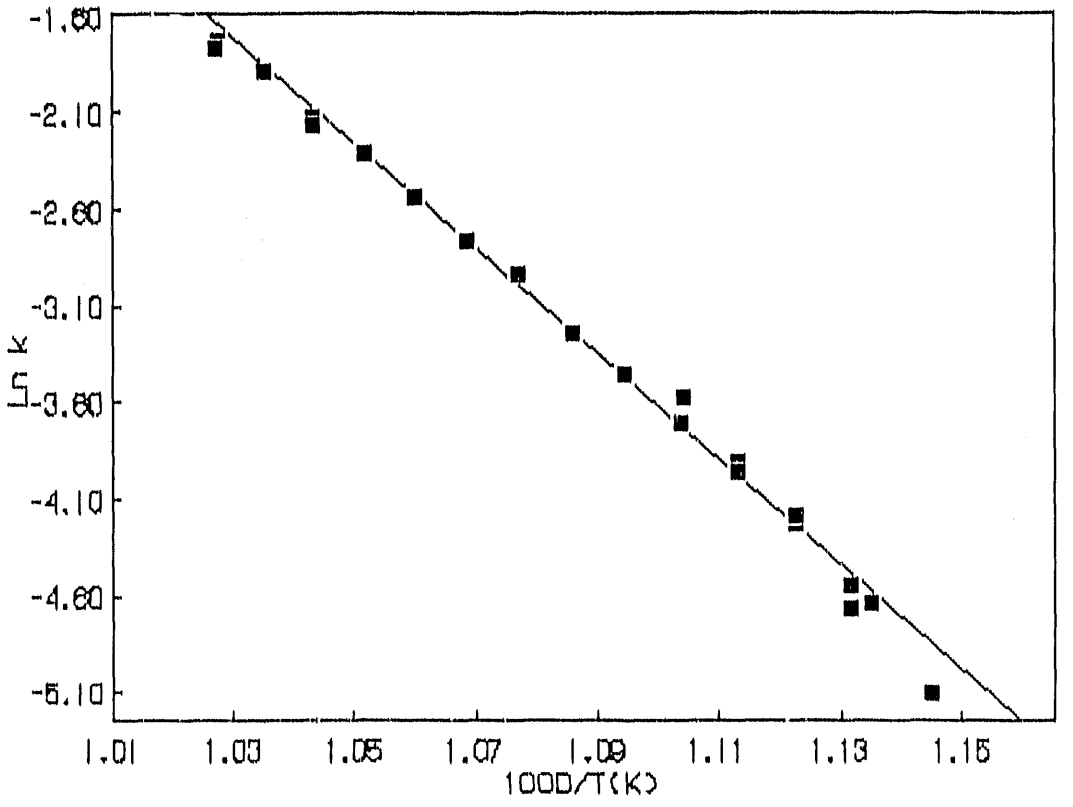


Figure 4. Arrhenius plot for Z-74 to E-74 isomerization

Synthesis of Z-and E-1-trimethylsilyl-1-propene 75

The literature[54a] procedure was used to synthesize Z- and E-75 in 56% yield. The cis and trans isomers were separated by preparative gas chromatograph with a 25' 20% SE 30 on Chrom W column.

Determination of Arrhenius parameters for cis-trans isomerization of 75

Approximately 0.1 torr of Z-75 was introduced into the reactor at the desired temperature. The data were collected by computer. The rate constants were determined over a temperature range of 550 to 610°C. The column used for separation of cis-trans isomers was 15' 15% dimethyl sulfolane on 60-80 mesh Firebrick at a temperature of 27°C.

Table 5. Rate constants for the Z-75 to E-75 isomerization

T (°C)	$kx10^2 sec^{-1}$	T	$kx10^2$	T	$kx10^2$
550.45	1.457	580.25	4.680	595.2	8.269
550.55	1.498	580.2	4.621	602.55	10.94
557.25	1.849	587.45	6.174	610.1	14.235
565.15	2.578	595.25	8.045	610.1	13.90
572.5	3.391				

E_a 56.00 ±0.55 kcal/mol; log A 13.00 ±0.14; ΔH^* 54.30 ±0.55 kcal/mol; ΔS^* -3.10 ±0.64 eu; at T_{ave} =582.4°C for rxn order 1.000.

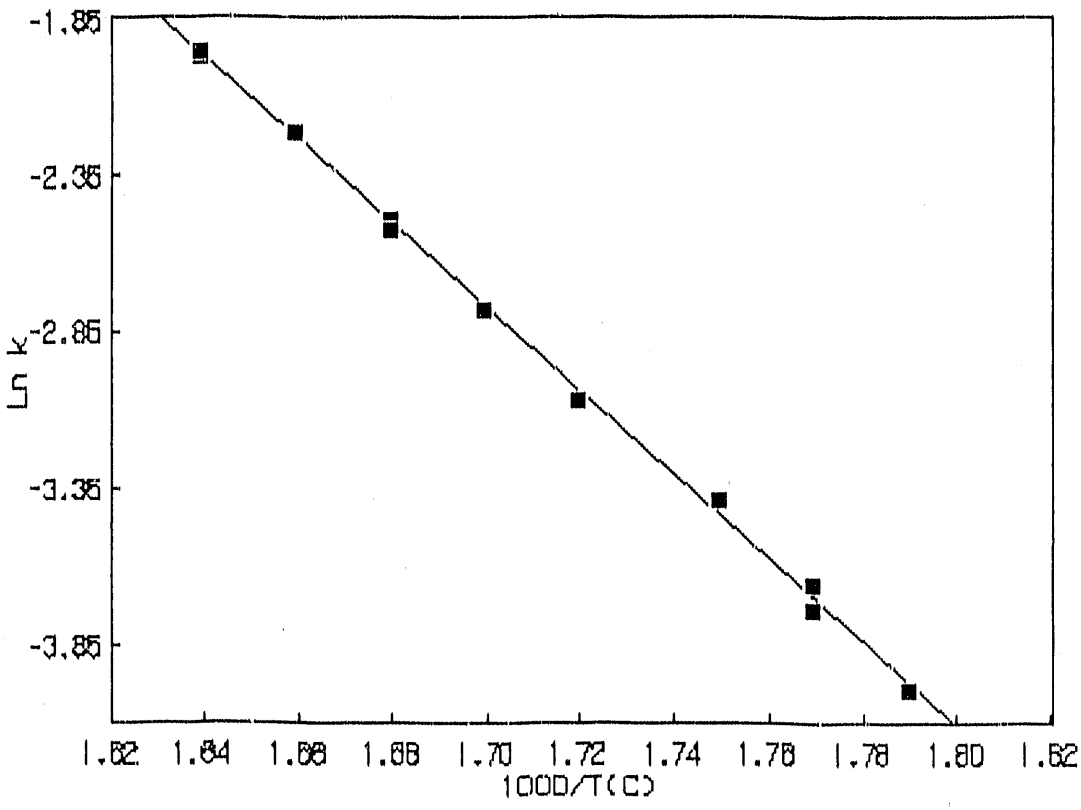


Figure 5. Arrhenius plot for Z-75 to E-75 isomerization

Table 6. Rate constants for the E-75 to Z-75 isomerization

T °C	k x 10^2 sec^{-1}	T	k x 10^2
565.0	0.640	587.45	1.537
572.55	1.013	595.25	2.018
580.2	1.211	602.6	2.695
		610.1	3.830

E_a 56.97 ±1.52 kcal/mol; log A 12.66 ±0.39; ΔH^* 55.25 ±1.52 kcal/mol; ΔS^* -4.72 ±1.76 eu; at T_{ave} =590.1°C for rxn order 1.000.

Synthesis of Z-1,2-bis(trimethylsilyl)ethylene[54b] Z-77

To a stirred solution of 1.7 g (10 mmol) bis(trimethylsilyl)acetylene in 20 ml dry THF cooled at 0°C was added 11 ml of BH_3 (1.0 M in THF). After stirring at 0°C for 1 hour, 5 ml glacial acetic acid was added slowly to the solution. The clear solution was stirred at room temperature for 24 hours and then neutralized by saturated aqueous $NaHCO_3$. The organic layer was separated and added 50 ml of pentane, the combined solution was washed by H_2O and brine, dried over Na_2SO_4. The solvent was removed by distillation. The product was trap-to-trap distilled and purified by preparatory GC on a 25' 15% SE-30-CW column.

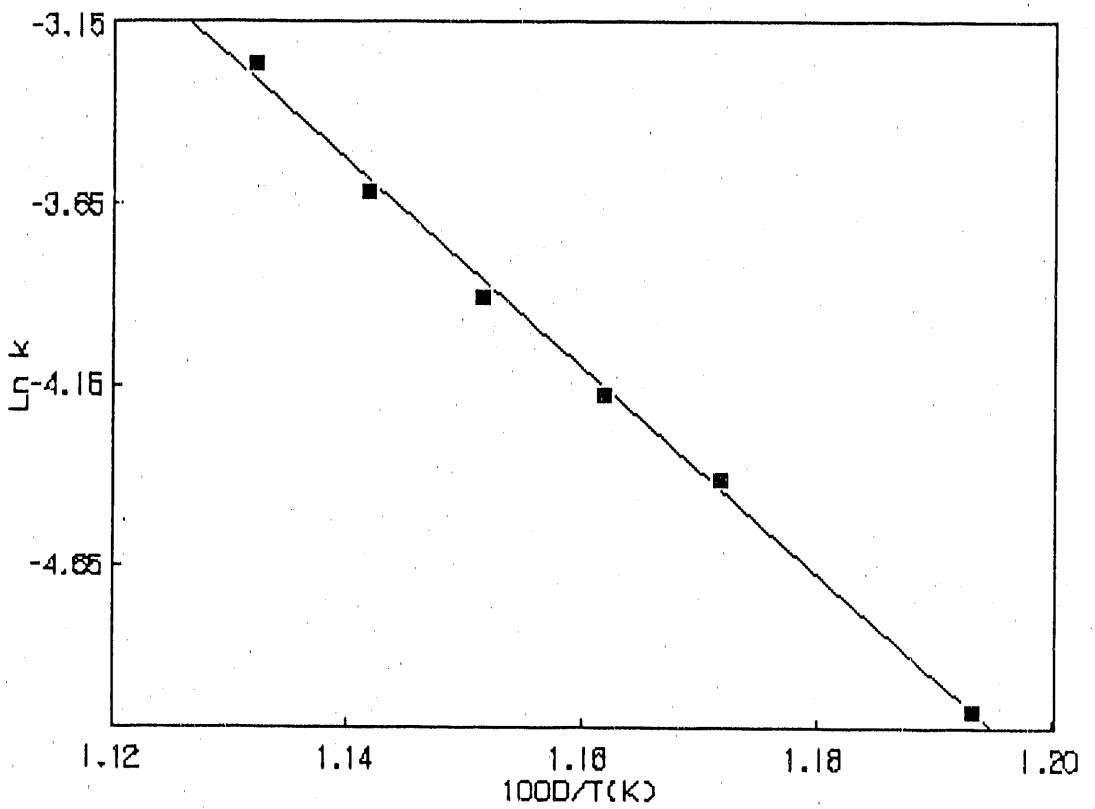


Figure 6. Arrhenius plot for E-75 to Z-75 isomerization

Determination of Arrhenius parameters for Z-77

Approximately 0.1 torr of Z-77 was introduced into the reactor at the desired temperature. The data were collected by computer. The rate constants were determined over a temperature range of 476 to 526°C. The column used for separation of cis-trans isomers was 5′ 15% SE-30-CW.

Table 7. Rate constants for Z-77 to E-77 isomerization

T°C	$kx10^2 sec^{-1}$	T°C	$kx10^2 sec^{-1}$	T°C	$kx10^2 sec^{-1}$
476.00	3.82	490.10	7.10	512.50	19.32
476.05	3.79	497.58	9.85	520.05	26.52
482.28	4.92	497.60	9.85	520.05	26.75
482.45	5.01	505.25	13.76	526.10	35.46
482.45	5.27	512.50	19.22	526.10	34.73

E_a 52.68 ±0.37 kcal/mol; log A 13.94 ±0.11; ΔH^* 51.14 ±0.37 kcal/mol; ΔS^* 1.37 ±0.48 eu; at T_{ave} =500.5°C for rxn order 1.000.

General procedure for synthesis of E-1,2-bis(trimethylsilyl)-ethylene[54b] E-77 and E-β-trimethylsilylstyrene[54c] E-78

A mixture of 0.47 g (5 mmol) of dimethylchlorosilane and 1 mg $H_2PtCl_6 \cdot 6\ H_2O$ was stirred in a ice bath for 10 min. To the mixture 5 mmol trimethylsilylacetylene or phenylacetylene was added and the mixture was stirred at 0°C for 10 min before

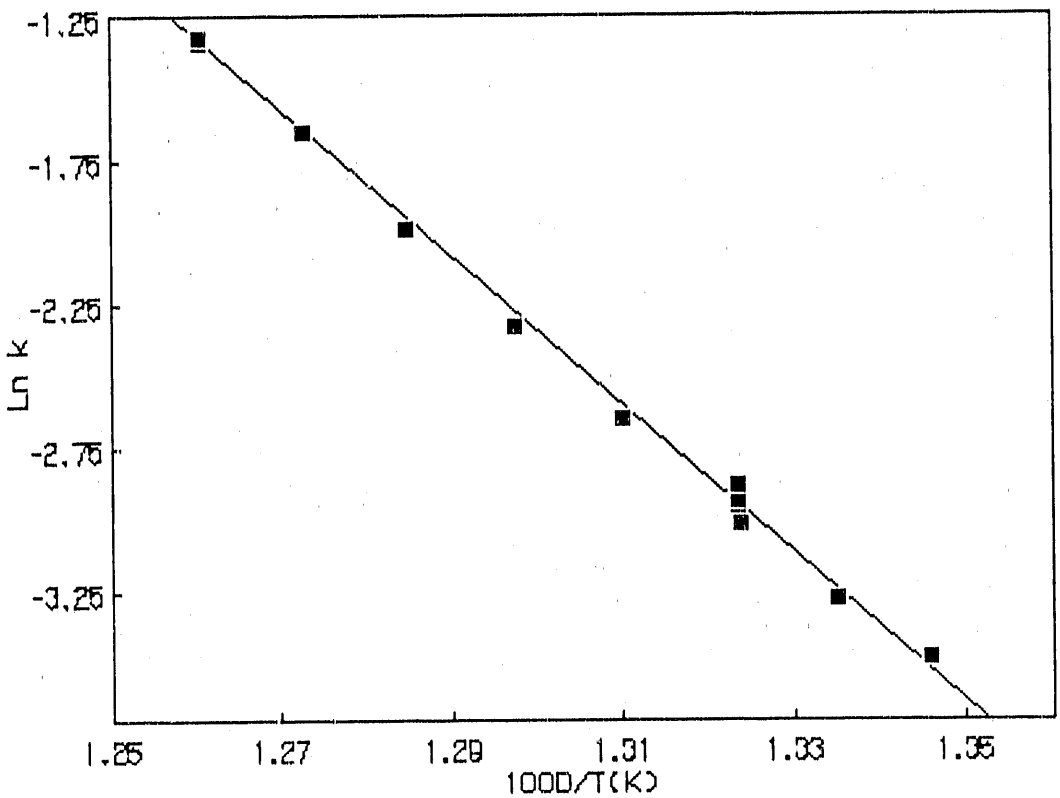


Figure 7. Arrhenius plot for Z-77 to E-77 isomerization

being allowed to slowly warm to room temperature. The mixture became dark green. After being stirred at room temperature for 18 hours, 1.83 ml MeMgCl (5 mmol, 3 M in THF) was added slowly. A yellow solid appeared during the addition. The mixture was stirred at room temperature for 2 hours. Trap-to-trap distillation gave the desired product E-77 or E-78 in ~100% yield.

SFR study of E-1,2-bis(trimethylsilyl)ethylene E-77

E-77 was stable in SFR condition up to ~650°C. At ~700°C, methane and trimethylsilane are the major products (~5% decomposition) with a small amount (<2%) of bis(trimethylsilyl)-acetylene.

Synthesis of Z-β-trimethylsilylstyrene[54c] Z-78

To a solution of 10 ml i-Bu_2AlH (10 mmol, 1 M in THF) in 10 ml heptane was added 0.85g (10 mmol) of 1-methylpyrrolidine at room temperature. After stirring the mixture for 2 min, 1.74 g (10 mmol) 1-phenyl-2-trimethylsilylacetylene was added. The mixture was stirred at 60°C for 15 hours, 100°C for 4 hours, and quenched with water. The organic layer was washed with water then brine, and the solvents were removed by simple distillation. The product Z-78 was obtained in 91% yield (1.6g). The product was further purified by preparatory GC in a 9′ 20% SE-30-CW column.

Determination of Arrhenius parameters for Z-78

Approximately 0.06 torr of Z-78 was introduced into the SFR reactor at the desired temperature. The data were collected by computer. The rate constants were determined over a temperature range of 470 to 527°C. The column used for separation of cis-trans isomers was 5′ 10% CW-20-M.

Table 8. Rate constants for Z-78 to E-78 isomerization

T°C	Kx10sec^{-1}	T°C	Kx10sec^{-1}	T°C	kx10sec^{-1}
470.0	0.516	491.0	1.329	512.5	3.524
470.0	0.510	491.0	1.329	520.15	4.912
477.0	0.728	498.0	1.832	520.1	4.923
477.0	0.729	505.0	2.537	527.08	6.678
484.0	0.988	505.0	2.501	527.05	6.710
484.05	0.964				

E_a 53.0 ±0.29 kcal/mol; log A 14.29 ±0.08; ΔH^* 51.47 ±0.29 kcal/mol; ΔS^* 2.984 ±0.38 eu; at T_{ave} =497.4°C for rxn order 1.000.

SFR study of E-β-trimethylsilylstyrene E-78

There was no reaction under SFR conditions below 650°C. At temperatures above 700°C, trimethylsilane and styrene were observed.

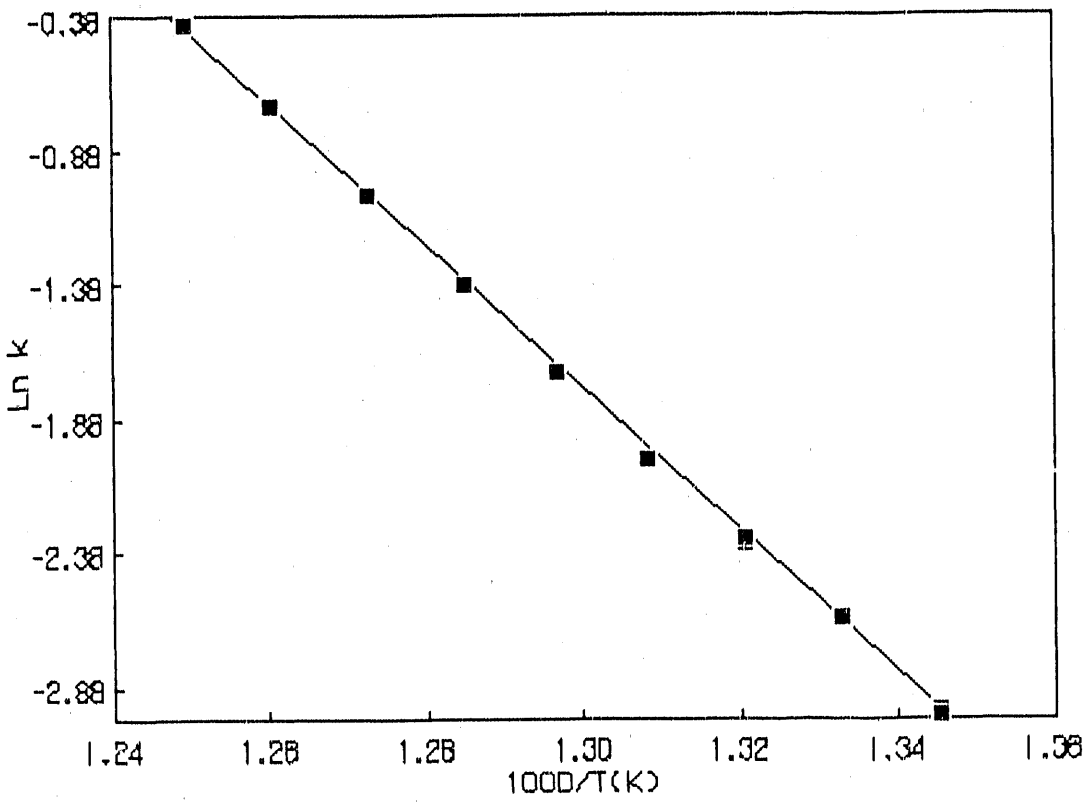


Figure 8. Arrhenius plot for Z-78 to E-78 isomerization

Synthesis of Z- and E-β-t-butylstyrene[54d] Z- and E-79

To a suspension of 5.83 g (15 mmol) benzyltriphenylphosphonium chloride in THF at -78°C under a N_2 atmosphere, 6.2 ml (15 mmol, 2.45 M in heptane) of n-BuLi was added. After the mixture was slowly warmed to room temperature (during 1 hour) the suspension had disappeared and the resulting solution was red. Trimethylacetaldehyde (1.29 g 15 mmol) was slowly dropped into the mixture at room temperature and refluxed overnight (oil bath 80°C). After the mixture cooled, 100 ml ether was added and the white solid was filtered. The ether was carefully removed by rotoevaporation until a white solid appeared. An additional 20 ml of ether was added with stirring and the solid was filtered. The filtrate was evaporated until the total volumn was about 10 ml. The crude product was passed through a silica gel column using Et_2O as the elutant. The solvent was removed and 0.81 g pure 79 was obtained as the mixture of cis and trans isomers in a ratio of 3:1 (34%). The cis and trans isomers were separated by preparatory GC on a 12′ 15% SE-30-CW column.

Determination of Arrhenius parameters for Z-β-t-butylstyrene Z-79

Approximately 0.06 torr of Z-79 was introduced into the reactor at the desired temperature. The data were collected by computer. The rate constants were determined over a temperature range of 470 to 527°C. The column used for separation of cis-trans isomers was 5' 10% CW-20-M. At the temperature range employed the trans isomer does not isomerize to the cis isomer.

Table 9. Rate constants for Z-79 to E-79 isomerization

T°C	Kx10sec^{-1}	T°C	Kx10sec^{-1}	T°C	Kx10sec^{-1}
470.0	0.454	491.96	1.262	512.90	3.376
470.05	0.449	498.9	1.831	520.05	4.716
477.4	0.641	498.9	1.777	520.05	4.595
484.85	0.919	505.98	2.437	527.0	6.410
484.85	0.914	512.98	3.389		

E_a 54.90 ±0.56 kcal/mol; log A 14.79 ±0.07; ΔH* 53.37 ±0.26 kcal/mol; ΔS* 5.279 ±0.34 eu; at T_{ave} =498.3°C for rxn order 1.000.

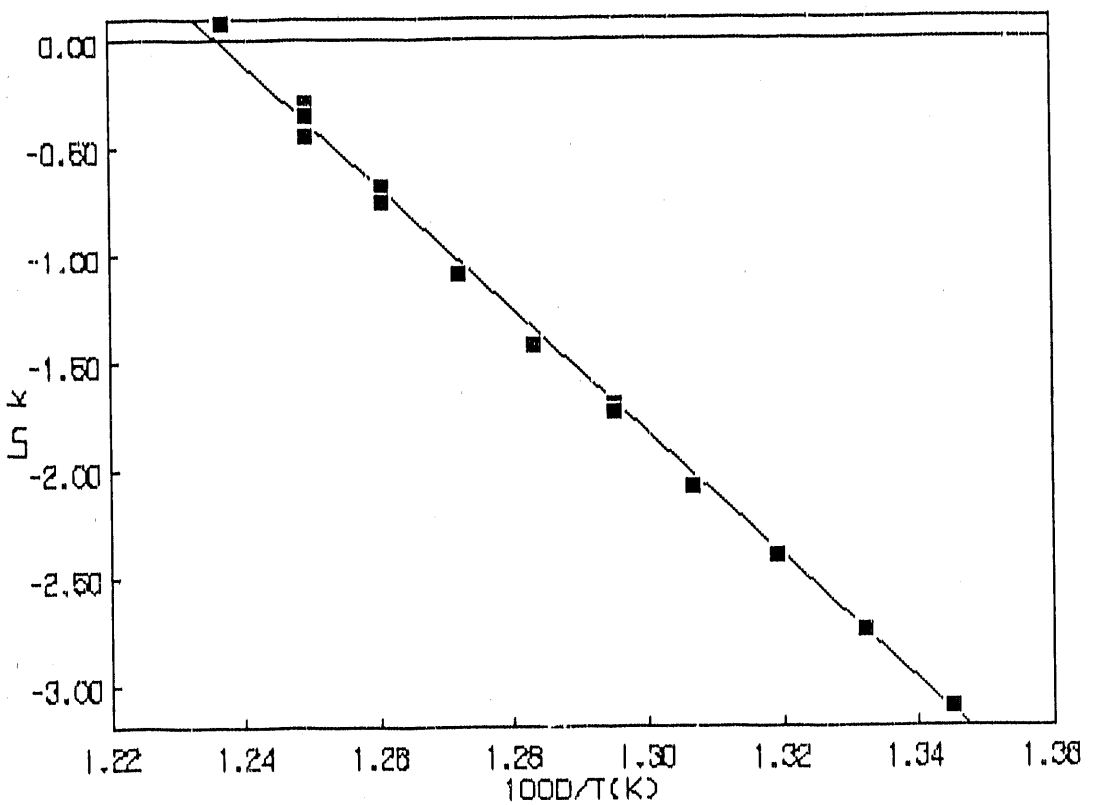


Figure 9. Arrhenius plot for Z-79 to E-79 isomerization

Determination of Arrhenius parameters for the cis-trans isomerization of 1-phenyl-1-propene 80

Approximately 0.07 torr of 80 was introduced into the reactor at the desired temperature. The data were collected by computer. The rate constants were determined over a temperature range of 540 to 590°C. The column used for separation of the cis-trans isomers was 5' 10% CW-20-M.

Table 10. Rate constants for Z-80 to E-80 isomerization

T°C	Kx10sec^{-1}	T°C	Kx10sec^{-1}	T°C	Kx10sec^{-1}
540.0	0.763	561.9	1.934	575.8	3.599
547.48	1.087	561.85	1.998	583.0	5.037
547.40	1.108	569.0	2.635	590.05	6.736
554.98	1.468	569.0	2.622	590.05	6.721
554.98	1.478	575.77	3.586		

E_a 60.18 ±0.68 kcal/mol; log A 15.05 ±0.18; ΔH^* 58.51 ±0.68 kcal/mol; ΔS^* 6.30 ±0.81 eu; at T_{ave}= 565.8°C for rxn order 1.000.

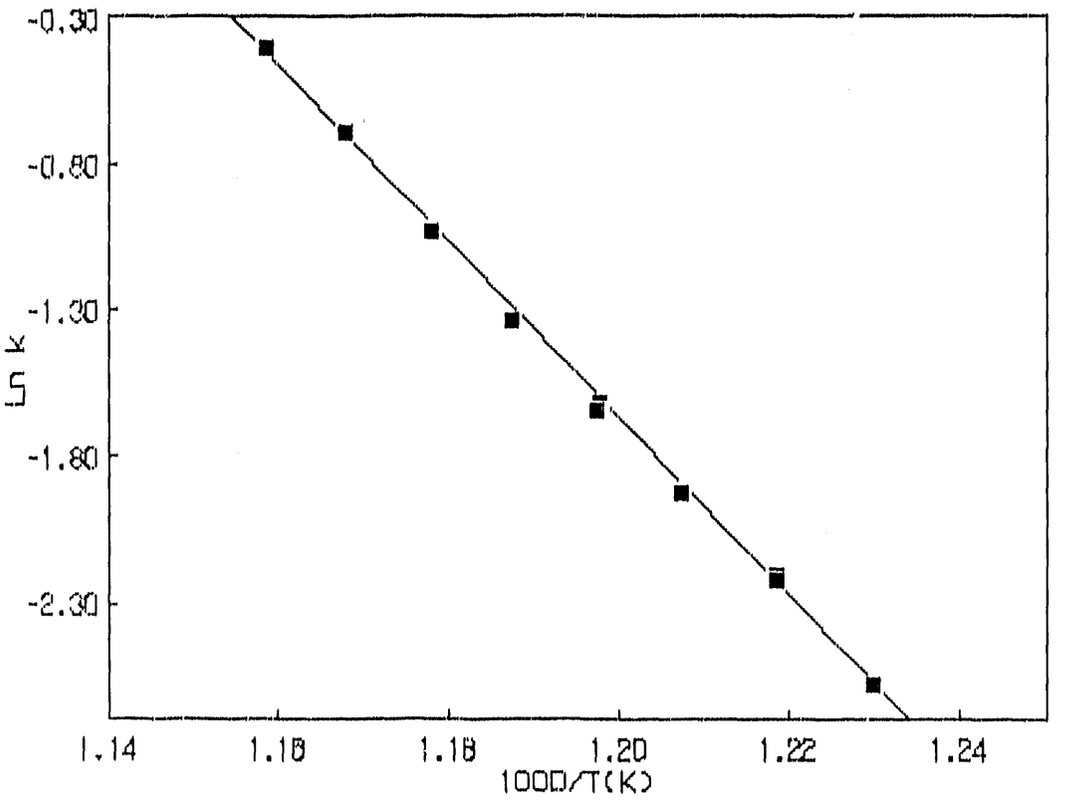


Figure 10. Arrhenius plot for Z-80 to E-80 isomerization

Table 11. Rate constants for E-80 to Z-80 isomerization

T°C	Kx10sec^{-1}	T°C	Kx10sec^{-1}	T°C	Kx10sec^{-1}
540.0	0.259	554.9	0.523	575.78	1.259
540.05	0.279	561.9	0.677	583.0	1.803
547.5	0.376	569.0	0.916	582.95	1.725
555.0	0.489	568.98	0.888	590.0	2.412

E_a 60.75 ±1.09 kcal/mol; log A 14.74 ±0.29; ΔH^* 59.09 ±1.09 kcal/mol; ΔS^* 4.89 ±1.3 eu; at T_{ave} =564.1°C for rxn order 1.000.

Synthesis of 2-trimethylsilyl-1-propene,[54e] 1,1-bis(trimethylsilyl)ethylene,[54b] and α-trimethylsilylstyrene[54f]

A three-necked round-bottom flask equipped with a mechanical stirrer, an additional funnel, a condenser with dry N_2 inlet and 0.36 g (15 mmol) magnesium. The system was dried by using a heat gun. Dibromoethane (0.3 ml) was added to initiate the reaction. The corresponding 1-R-1-bromoethylene (13.5 mmol) was added dropwise in a rate that kept the mixture at reflux. After completing the addition, the mixture was refluxed for 2 hours. After cooling to room temperature, 14 mmol trimethylchlorosilane in 2 ml of THF was added dropwise. The mixture was stirred at room temperature for 20 hours.

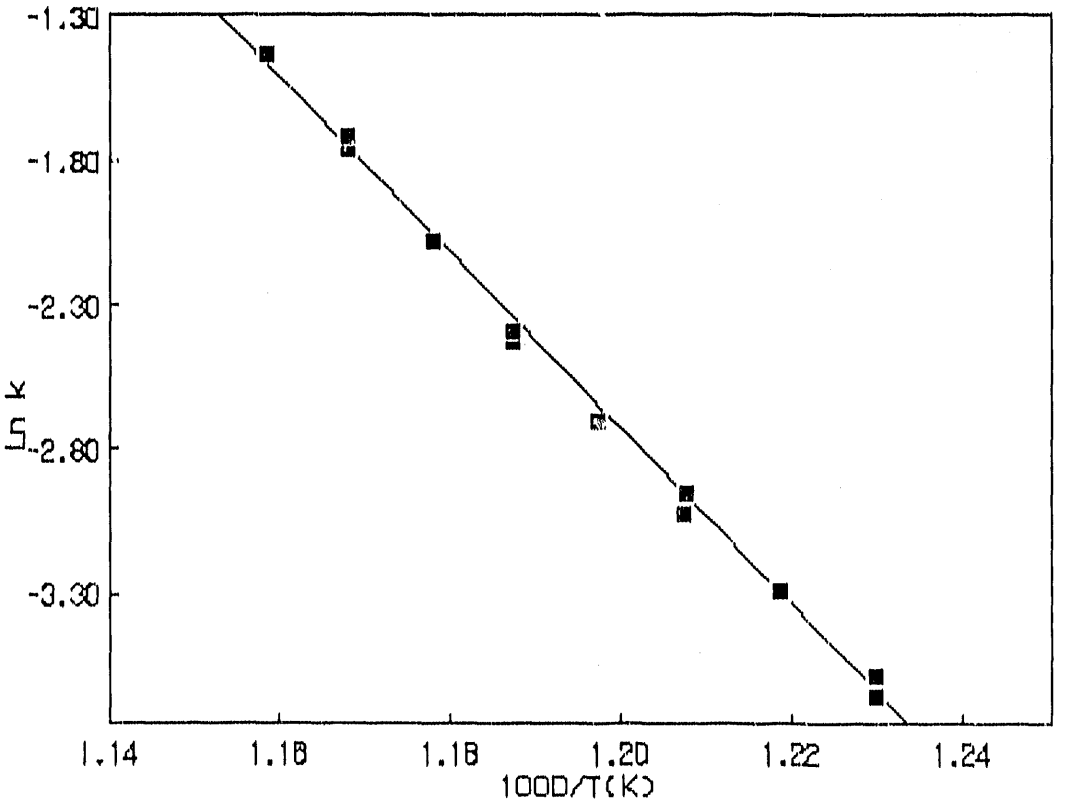


Figure 11. Arrhenius plot for E-80 to Z-80 isomerization

After washing with water and brine and removing the solvent the desired products were obtained in 20-60% yield. All three compounds were purified by preparatory GC on a 9' 20% SE-30-CW column.

Attempts to synthesize 1-methoxy-2-trichlorosilylbicyclo-[2,2,2]oct-5-ene 93

A mixture of 1.10 g (10 mmol) 1-methoxycyclohexa-1,4-diene and 3.24 g (20 mmol) vinyltrichlorosilane was refluxed in 20 ml benzene for 24 hours. Only vinyltrichlorosilane and dimers of the diene were identified by GCMS.

A mixture of 1-methoxycyclohexa-1,4-diene and 3-fold vinyltrichlorosilane was sealed in a K-max tube and heated at 150°C for 3 hours. Only vinylchlorosilane and dimers of the diene were identified by GCMS.

Attempts to synthesis of 1-methoxy-2,2-bis(trimethylsilyl)-bicyclo[2,2,2]octane 112

To a solution of 1.06 g (5 mmol) 1-methoxy-2-trimethylsilylbicyclo[2,2,2]octane 106 (synthesized by a known method[40]) in 10 ml dry THF at -78°C was added 0.58 g (5 mmol) TMEDA, followed by the addition of 2 ml (5 mmol, 2.5 M in heptane) n-BuLi. The mixture was allowed to warm to room temperature and then stirred for 24 hrs. To the mixture 0.66 g (5 mmol) trimethylchlorosilane was added. The mixture was stirred for additional 2 hrs. and quenched with saturated NH_4Cl solution. Starting material 106 was detected by GCMS.

Synthesis of 1-methoxy-2-trimethylsilyl-2-dimethylsiloxybicyclo[2,2,2]octane 110

To a solution of trimethylsilyllithium (prepared in situ by literature method[42b]) at 0°C, 228 mg (1.5 mmol) of ketone 109 in 1 ml of dry ether was added dropwise. The red color of the trimethylsilylanion faded during the addition. After stirring at 0°C for 5 min, the mixture was allowed to warm to room temperature and stirred for 30 min. Then cooled back to 0°C, 1.08 g (10 mmol) trimethylchlorosilane was added. The mixture was allowed to warm to room temperature and stirred for 1 hr. The mixture was washed with water to remove HMPA. The product 110 was purified by preparatory GC using a 11' 10% SE-30-CW column. It was characterized as follows: ^{1}H NMR ($CDCl_3$) 0.118 (s, 9 H, $SiMe_3$), 0.131 (d, 3 H, J=3.6, SiMe), 0.168 (d, 3 H, J=3.6, SiMe), 1.2-2.7 (m, 11 H), 3.218 (s, 3 H, MeO), 3.877 (heptet, 1 H, J=3.6, SiH). ^{13}C NMR ($CDCl_3$) -3.916, 3.285, 22.634, 24.915, 25.877, 26.967, 27.932, 41.645, 50.728, 77.699, 78.908. FTIR 2953, 2914, 2827, 2112, 1250, 1169, 1109, 1186, 901, 878, 839, 762. GCMS 271 M^+-CH_3 (0.66), 227 (9.80), 196 (14.75), 168 (100), 73 (78.60). Mass spectrum (Ammonia CI) 287.2 MH^+ (24.19), 273.2 (24.14), 272.2 MH^+-CH_3 (100), 255.2 (7.98), 180.1 (7.38), 164.1 (25.52), 148.1 (8.90), 139.1 (15.84), 106.0 (9.53). Exact mass: $C_{14}H_{30}Si_2O_2$ measured 286.17818, calculated 286.17844, error -0.9 ppm.

Synthesis of 3-trimethylsilyl-2-propyn-1-ol[54g] 129

To a solution of 3.36 g (60 mmol) propargyl alcohol in 150 ml dry ether cooled at 0°C was added slowly 40 ml (120 mmol, 3 M in ether) methylmagnesiumbromide. After the addition the mixture was allowed to warm to room temperature and stirred for 2 hrs. To the mixture, 13 g (120 mmol) of trimethylchlorosilane was added dropwise during 2 hrs. After completing the addition, the ether was distilled. The residue was heated at 100°C for 3 hrs. and cooled to room temperature, then 100 ml of ether was added. The complex was decomposed with 5% HCl. The ether extracts were combined and dried over sodium sulfide. After distilling the solvent, vacuum distillation of the residue yielded 4.6 g 129 (60%). The boiling point of 129 is 74-76°C/10-11 mmHg. It was characterized as follows: ^{1}H NMR ($CDCl_3$) 0.14 (s, 9 H, $SiMe_3$), 4.23 (s, 2 H, CH_2). GCMS 128 M^+ (0.23), 127 M^+-1 (0.23), 113 M^+-CH_3 (47.0), 85 (100), 75 (29.0), 73 (17.6), 61 (34.0).

Synthesis of 3-trimethylsilyl-2-deutero-2-propen-1-ol 130

A mixture of 0.84 g (20 mmol) lithium alumnium deuteride, 2.16 g (40 mmol) sodium methoxide and 1.28 g (10 mmol) 129 were refluxed in 200 ml THF for 3 hrs and quenched with saturated Na_2SO_4. The ether was distilled to give 2.55 g (95%) of pure 130. It was characterized as follows: ^{1}H NMR ($CDCl_3$) 0.04 (s, 9 H, $SiMe_3$), 1.43 (t, 1 H, J=4.5, CH_2), 4.13

(d, 2H, J=3.0, OH), 5.84-5.89 (m, 1 H, CH). GCMS 116 M^+-15 (38.5), 75 (100), 73 (56.3), 61 (36.8), 59 (27.7).

Synthesis of 1-trimethylsilyl-3-chloro-2-deutero-1-propene 131

To a solution of 2.62 g (20 mmol) 130 in 40 ml of CCl_4 was added slowly 5.1 g (25 mmol) tributylphosphine at room temperature. An exothermic reaction ensued, CCl_4 was removed by rotoevaporation and the residue was flashed through a silica gel packed column with hexanes as the elutant. After the solvent was removed, the remaining colorless liquid was 2.8 g (94%) of pure 131. It was characterized as follows: ^1H NMR ($CDCl_3$) 0.5 (s, 9 H, $SiMe_3$), 4.02 (s, broad, 2 H, CH_2Cl), 5.91-5.96 (m, 1 H, CH). GCMS 134 M^+-15 (66.3), 106 (15.0), 95 (36.8), 93 (100), 73 (24.3), 59 (21.4).

Synthesis of 1,3-bis(trimethylsilyl)-2-deutero-1-propene 132-D

To a mixture of 0.2 g (8 mmol, 40 mesh) magnesium dust and 1.08 g (10 mmol) trimethylchlorosilane in 10 ml THF was added slowly 1.0 g (6.7 mmol) 131. The mixture was stirred at 30°C overnight. After quenched with water and extracted with ether, the organic extracts were dried over Na_2SO_4. After distilling the solvent 1.0 g of pure 132-D was obtained as a colorless liquid in 80% yield. It was characterized as follows: ^1H NMR ($CDCl_3$) -0.01 (s, 9 H, $SiMe_3$), 0.03 (s, 9 H, $SiMe_3$), 1.61 (s, broad, 2 H, CH), 5.38-5.41 (m, 1 H, CH). ^{13}C NMR ($CDCl_3$) -1987, -0.949, 28.240, 127.858, 143.300 (t, J=91). FTIR 2955, 1585, 1400, 1248, 1146, 1049, 876, 829, 714, 689.

GCMS 187 M^+ (2.68), 172 M^+-CH_3 (5.34), 84 (12.4), 73 (100), 59 (6.61). Exact MS: $C_9H_{21}DSi_2$ measured 187.13214, calculated 187.13228, error -0.76 ppm.

Synthesis of 1,3-bis(trimethylsilyl)-3-dimethylmethoxsilyl-2-deutero-1-propene 114-D

To a stirred solution of 1.0 g (5.3 mmol) 132-D and 0.99 g (8.5 mmol) TMEDA in 10 ml ether at 0°C was slowly added 3.3 ml (8 mmol) n-BuLi. After the yellowish mixture was stirred at 0°C for 1.5 hr, 1.25 g (10 mmol) dimethylmethoxychlorosilane was added. The mixture was stirred at 0°C for 30 min, then at room temperature overnight. The solvent was removed and 5 ml pentane was added. The solid was filtered. The filtrate was purified by preparatory GC on a 9' 15% SE-30-CW column to obtain pure 114-D. It was characterized as follows: ^1H NMR ($CDCl_3$) 0.025 (s, 9 H, $SiMe_3$), 0.032 (s, 9 H, $SiMe_3$), 0.117 (s, 6 H, $SiMe_2$), 1.402 (b, 1 H, CH), 3.403 (s, 3 H, MeO), 5.366 (t, 1 H, J=2.4, CH). ^{13}C NMR ($CDCl_3$) -1.671, -1.445, -0.863, 32.553, 50.428, 128.438, 143.717 (m). FTIR 2955, 2899, 1570, 1404, 1249, 1094, 1043, 979, 690. GCMS 275 M^+ (4.28), 260 M^+-CH_3 (10.91), 170 (30.12), 156 (24.39), 89 (49.59), 73 (100), 59 (54.82), 45 (32.42).

Flash vacuum pyrolysis of 114-D

130 mg Compound 114-D (0.47 mmol) was distilled through the pyrolysis tube at 750°C ($\sim 10^{-4}$ torr). A yellowish pyrolysate was collected (108 mg, 83% mass recovery). The

pyrolysate contains trimethylmethoxysilane (70%), 4-trimethylsilyl-3,3-dimethyl-1-deutero-3-silacyclobutene 115-D_1 (47%) and 1-dimethylsilyl-3-trimethylsilylallene 116-D_{S1} (12.9%). The products were separated by preparatory GC on a 9' 15% SE-30-CW column. Product 115-D_1 was characterized as follows: ^{1}H NMR ($CDCl_3$) -0.036 (s, 9 H, $SiMe_3$), 0.277 (s, 3 H, SiMe), 0.290 (s, 3 H, SiMe), 1.174 (b, 1 H, CH), 6.045 (s, 1 H, CH). ^{2}H NMR ($CHCl_3$) 7.008 (s, 1 D). ^{13}C NMR ($CDCl_3$) -0.952, 0.712, 25.822, 137.673, 152.438 (m). GCFTIR 3050, 2963, 2908, 1482, 1258, 1142, 1018, 868, 841, 806, 748. GCMS 171 M^+ (12.80), 156 M^+-CH_3 (37.01), 96 (16.20), 73 (100), 59 (19.48), 43 (37.83). Exact MS: $C_8H_{17}DSi_2$, measured 171.10053, calculated 171.10098, error -2.6 ppm. Product 116-D_{S1} was characterized as follows: ^{1}H NMR ($CDCl_3$) 0.057 (s, 9 H, $SiMe_3$), 0.119 (s, 6 H, $SiMe_2$), 4.395 (d, 1 H, J=6.9, CH), 4.428 (d, 1 H, J=6.9, CH). ^{2}H NMR ($CHCl_3$) 4.134 (s, 1 D). ^{13}C NMR ($CDCl_3$) -3.627, -0.708, 69.201, 72.467, 211.558. GCFTIR 2966, 1917, 1547, 1423, 1258, 1142, 841, 702. GCMS 171 M^+ (6.68), 156 M^+-CH_3 (27.33), 96 (19.80), 73 (100), 60 (14.04), 59 (12.13), 45 (26.24). Exact MS: $C_8H_{17}DSi_2$, measured 171.10050, calculated 171.10098, error -2.8 ppm.

PART II.

THERMAL GENERATIONS OF THE SILICON-NITROGEN DOUBLE BOND

Literature Survey

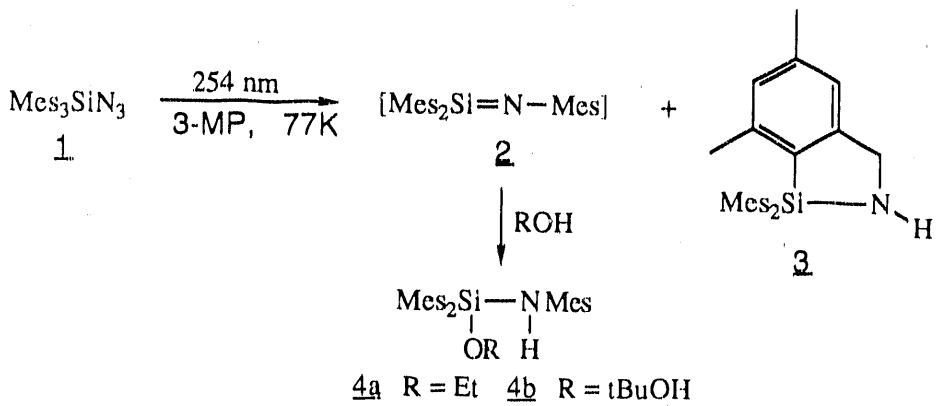
A complete literature survey about silanimines before 1987 was authored by Kinsley.[55] This part covers the literature of silanimines published since 1988.

Schleyer and Kost[56] calculated π bond energies for the double bond systems $H_2Y{=}XH_n$ (Y = C, Si; X= B; C; N; O; Al; Si; P; S) to compare the energies of double bonds of second row elements with carbon and silicon. They concluded that Si=X bonds are found to have significantly lower E_π energies than the corresponding C=X bonds. However when the electronegativity of the constituent elements is taken into consideration, second and first row π-bond energies are similar. The bond length of $H_2Si{=}NH$ is 1.573 A and E_π is 37.0 kcal/mol. The bond length of $H_2C{=}NH$ is 1.251 A and E_π is 80.8 kcal/mol.

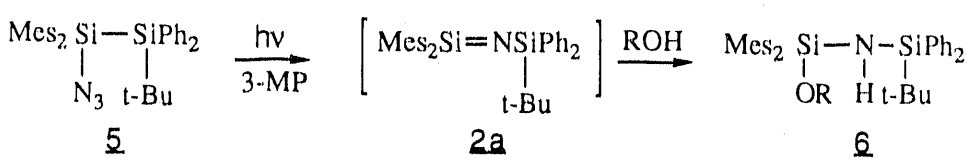
Pyrolysis or photolysis of silylazides are the usual routes to silanimines. Matrix-isolation was used to obtain the UV and IR spectrum of the reactive intermediate.[57-59]

Photolysis[57] of trimesitylazidosilane 1 in 3-methylpentane (3-MP) glass at 77 K or in 3-MP solution at -140°C, three new absorptions appear at 257, 296, and 444 nm in the UV-visible

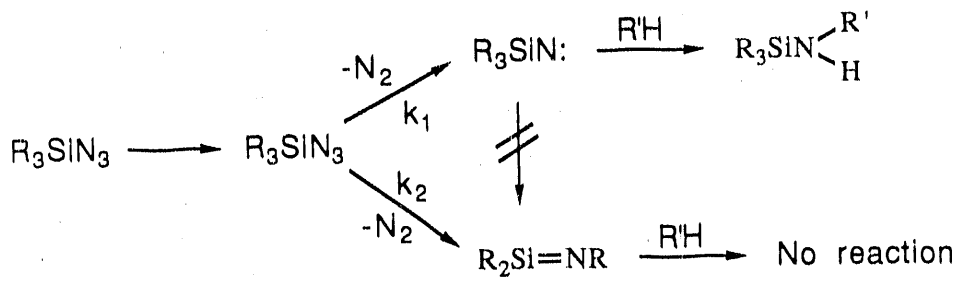
region. The ratio of intensity of 296 and 444 nm bands remained unchanged during photolysis of 1 and both bands disappeared when the resulting yellow glass was annealed, which led to assigning both bands to one product. The band at 257 nm was unaffected after annealing the glass. The structures of the products were determined by photolysis of 1 with EtOH or t-BuOH. The same three UV bands were formed, but those at 296 and 444 nm immediately disappeared on annealing. Two products 3 and 4 were isolated from the reaction mixture.



Based on this evidence, silanimine 2 was assigned as the species responsible for the 296 and 444 nm absorptions while the 257 nm band is due to the stable C-H insertion product 3. However, photolysis of $Mes_2SiN_3SiPh_2Bu^t$ 5[59] in 3-MP solution at temperature range from -140 to -125°C resulted in the formation of an orange solution. The orange color faded immediately upon addition of alcohols. Only one product 6 was

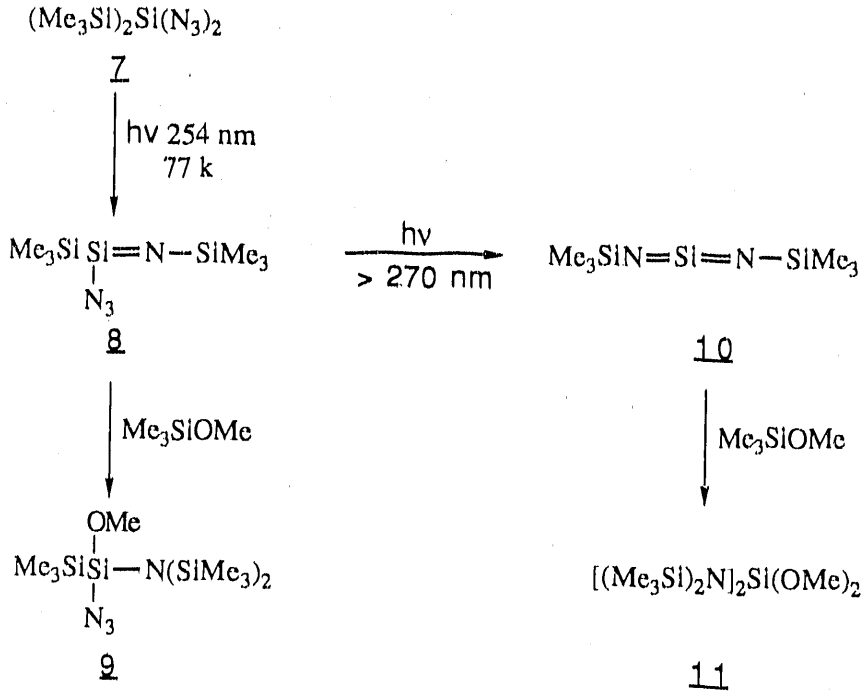


found. There is no observed product corresponding to C-H insertion of the nitrene to the methyl group of the mesityl group. The evidence agreed with the earlier explanation[60,61] that the photochemical generation of silanimine does not proceed via a nitrene intermediate. Instead, migration of an R group to nitrogen occurs simultaneously with loss of N_2. The replacement of Mes (R group) in compound 1 with a silyl substituent results in the more rapid formation of silanimine relative to nitrene.[58,59]



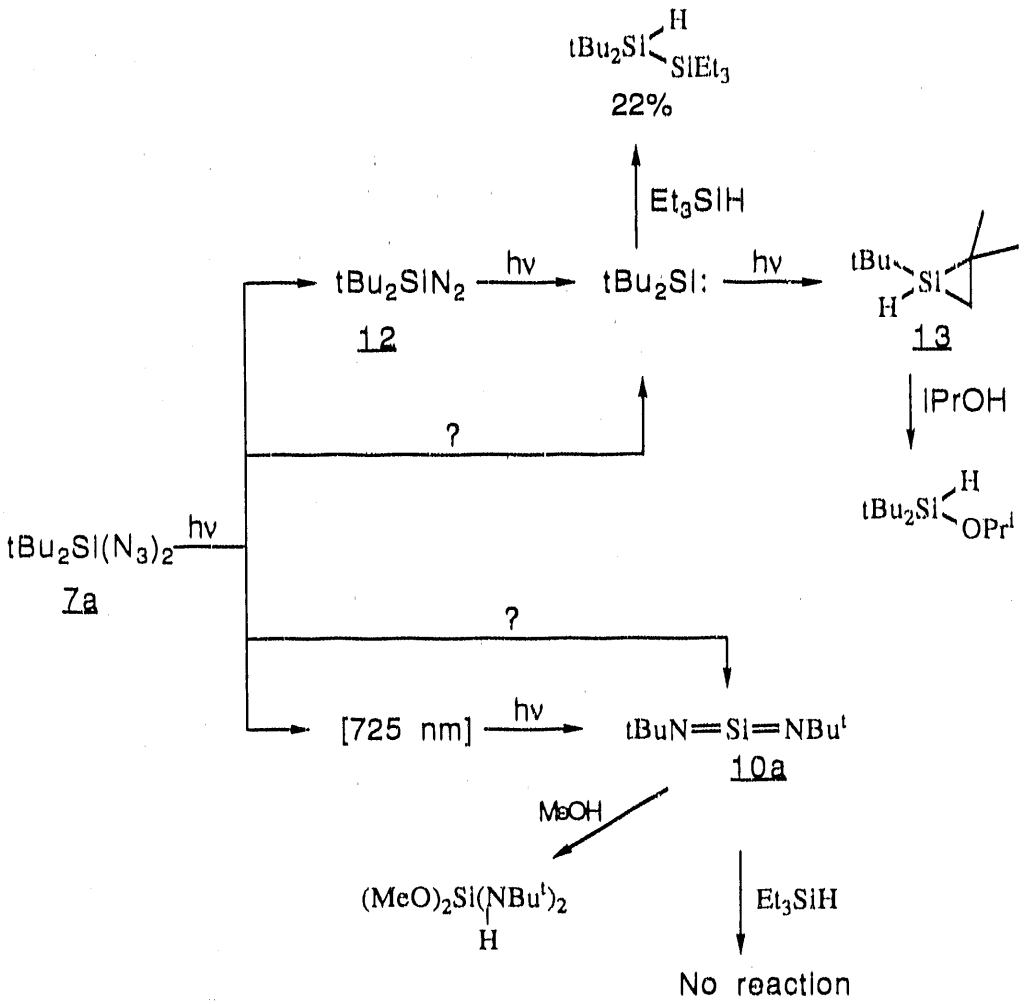
The first silicon analogue of a carbodiimide, bis(trimethylsilyl)silanediimine, 10, was generated by photolysis of matrix-isolated 2,2-diazidohexamethyltrisilane 7.[62]

Irradiation of 7 at 254 nm in glassy 3-MP at 77 K results in the appearance of two new bands in the UV at 214 and 324 nm. The two bands grow at different rates during irradiation indicating two new species are being generated. The structure of 8 and 10 were determined by trapping experiments. When 7 was irradiated at 77 K in a 3-MP glass in the presence of Me_3SiOMe, 9 and 11 are the only products observed after annealing the glass to room temperature.



During irradiation of di-t-butyldiazidosilane 7a,[63] four species were observed by UV spectroscopy, di-t-butylsilylene, silanediimine 10a, diazosilane 12, and an unknown compound having a visible absorption maximum at 725 nm.

The formation of di-t-butylsilylene was confirmed by its irradiation product silacyclopropane 13 and trapping experiments. Compound 13 is the first stable and isolable silacyclopropane containing a Si-H bond. This is also the first reported case of a photochemical C-H insertion by a silylene. Trapping experiments and the absorption maximum at 480 nm indicate that di-t-butylsilylene has a singlet ground

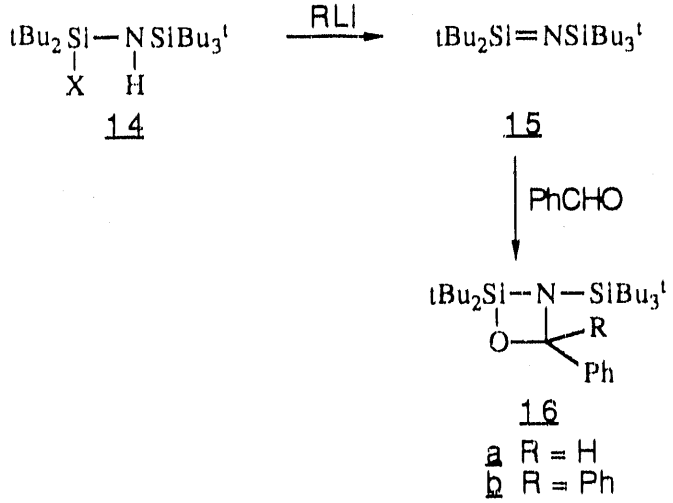


state. The assignment is supported by ESR measurements performed on matrices containing the silylene generated by the same precursor. Another product from the irradiation, matrix-isolated 10a, is characterized by UV absorption bands at 240 and 385 nm. UV and IR spectroscopic evidence and results of chemical trapping experiments demonstrate that this is a silicon analogue of carbodiimide, N,N'-di-t-butyl-silane-diimine which is formed in approximately 10% yield. However photolysis of $(t\text{-Bu})_2Si(N_3)_2$ 7a in pentane at ambient

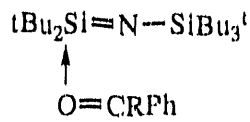
temperature in the presence of t-BuOH led to the formation of $(t\text{-BuO})_2Si(NHt\text{-Bu})_2$ and $t\text{-Bu}_2SiH(Ot\text{-Bu})$ in 80% and 10% yield, respectively. The alkoxysilane is believed to be the product of insertion of di-t-butylsilylene into the O-H bond of t-BuOH and $(t\text{-BuO})_2Si(NHt\text{-Bu})_2$ arises from the formal addition of two molecules of alcohol to 10a, although in this case the trapping undoubtedly occurs sequentially via an azidosilanimine intermediate 8.

$$\underline{7a} \xrightarrow{t\text{-BuOH}} \underset{80\%}{(t\text{-BuO})_2Si(NHBu^t)_2} + \underset{10\%}{t\text{-Bu}_2SiH(OBu^t)}$$

Silanimine reacts with non-enolizable ketones or aldehydes to form the polysiloxanes and imines.[64] It was postulated that the reaction proceeded via an intermediate oxaazasilacyclobutanes which was prepared recently by Wiberg et al.[65]



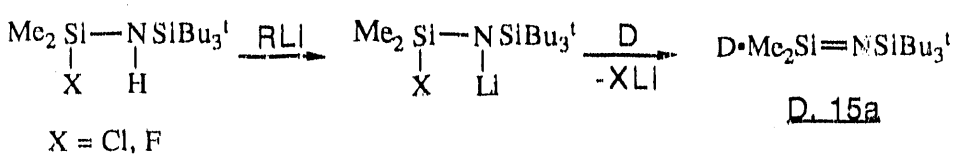
The sterically congested silanimine 15 generated from treatment of 14 with n-BuLi, reacted with benzaldehyde in pentane at -125°C to yield the crystalline 16. Reaction of 15 with benzophenone in diethyl ether yields a compound which was identified as 17b by x-ray structure analysis. Compound 17 is believed to be a potential precursor of 16 so that the evidence supports the two step mechanism with initial formation of a Si-O bond.



17

a R = H
b R = Ph

Wiberg and Schurz[66] found that silanimine $Me_2Si{=}NSi(t\text{-}Bu)_3$ 15a forms metastable adducts $D.Me_2Si{=}NSi(t\text{-}Bu)_3$. The adducts can serve as sources of 15a because they decompose thermally to give 15a and D.

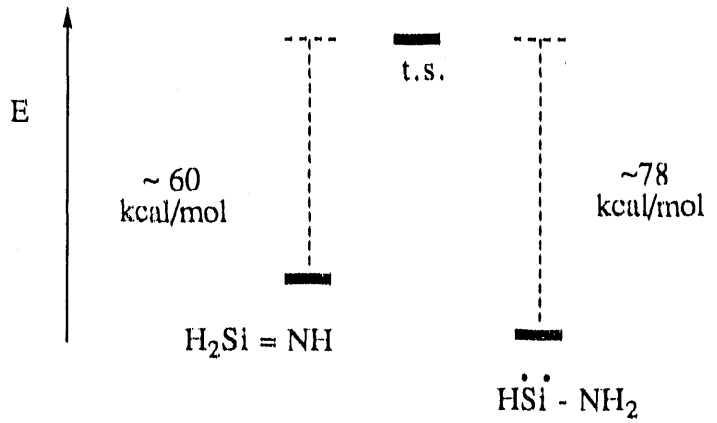


X = Cl, F

D = Et_2O, THF, NEt_3, NMe_2Et

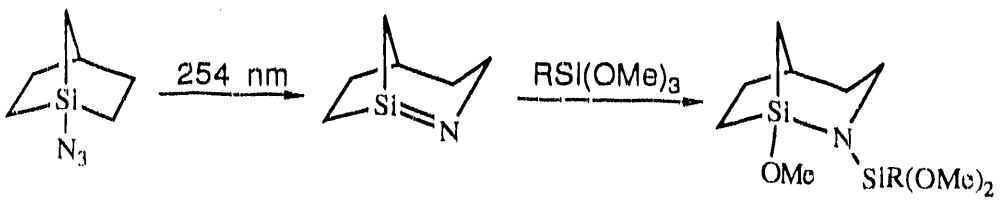
Results and Discussion

Calculations[67] suggest that the parent silanimine $H_2Si{=}NH$ is planar with Si-N bond length 1.576 A and SiNH bond angle of 129.5° and the back-donation of the nitrogen lone pair into the 3p orbital on silicon exists. The isomerization of silanimine to aminosilylene by a 1,2-hydrogen shift is calculated to be ~60 kcal/mol and the reverse reaction from aminosilylene to silanimine is calculated to be ~78 kcal/mol, very high barrier processes indeed.



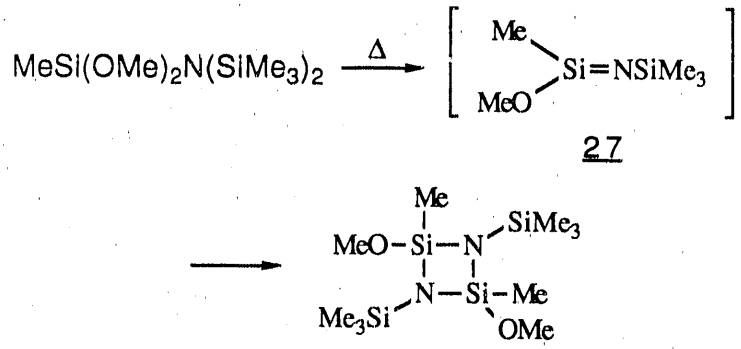
There are five methods known to generate silanimine.

1. The photolysis of azidosilanes is the most popular method used to generate silanimine. For example, when 1-azido-1-silabiclo[2,2,1]heptane is photolyzed[68] in the presence of triethoxysilane or trimethoxymethylsilane the



trapping products formally derived from the corresponding bridgehead silanimine are obtained.

2. β-Elimination of trimethylmethoxysilane was first used by Kazoura and Weber[69] to generate silanimine in the gas phase.



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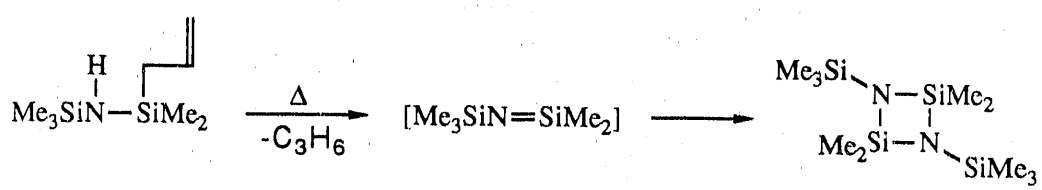
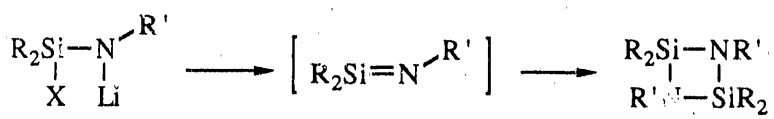
3. Retroene reaction was used by Barton's group to generate silanimine.[55]

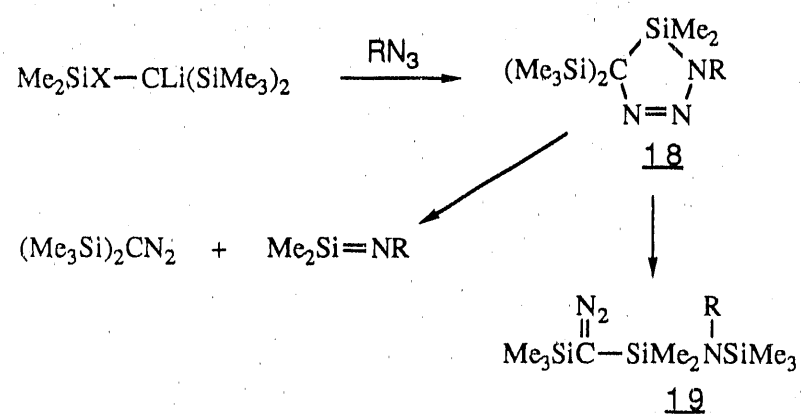


4. By elimination of LiX from lithium salts of aminohalosilanes[66,70] to generate silanimine which dimerize in the absen e of trapping agents.

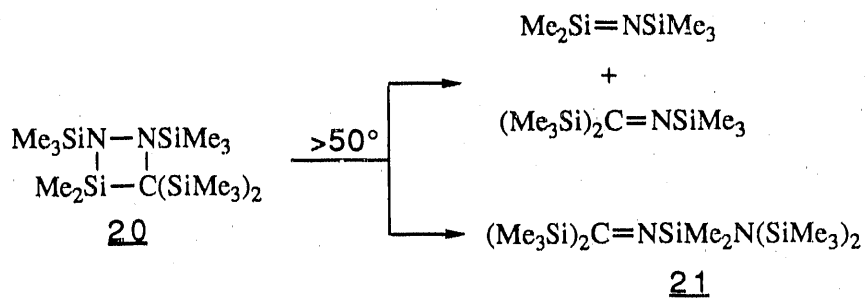


5. By cycloreversion reaction. Adduct 18, the 1,3-dipolar addition product of an azide to 1,1-dimethyl-2,2-

bis(trimethylsilyl)silane decomposes on heating to the diazo compound 19, silanimine, and bis(trimethylsilyl)diazomethane.



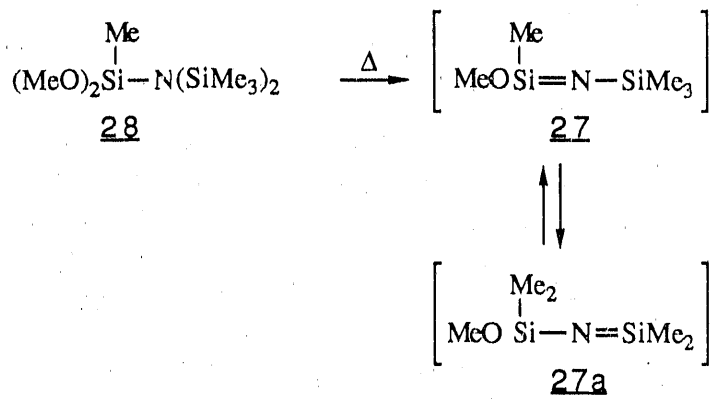
Thermal fragmentation of 20 is another example of a cycloreversion reaction leading to a silanimine which competes with a rearrangement of the adduct to 21.



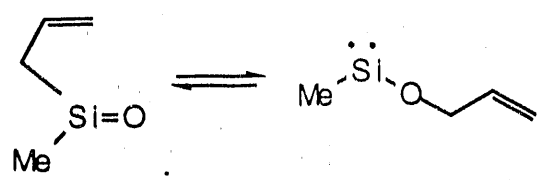
Generation of silanimines by β-elimination of trimethylmethoxysilane and the retroene reaction allowed the study of the chemistry of the reactive species in the gas phase. Other routes to generate silanimines in the gas phase were also explored by this author and will be presented later.

1,2-Elimination of trimethylmethoxysilane and retroene reaction have been successfully used to generate a number of doubly-bonded silicon intermiates.[44b,45,69,71,72] Kazoura and

Weber[69] have studied the thermal reaction of dimethoxymethylsilyl-bis(trimethylsilyl)amine in the gas phase and found that the reaction may be a facile way (albeit messy) to generate silanimine 27 giving another silanimine 27a. Twelve products were isolated from the pyrolysis of dimethoxymethylsilyl-bis-(trimethylsilyl)amine 28.

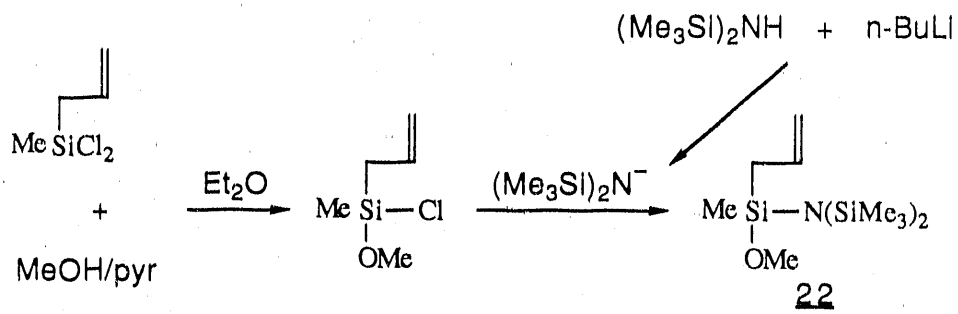


The allyl group has been used as migrating group for the alloxymethylsilylene-allylmethylsilanone isomerization.[73]



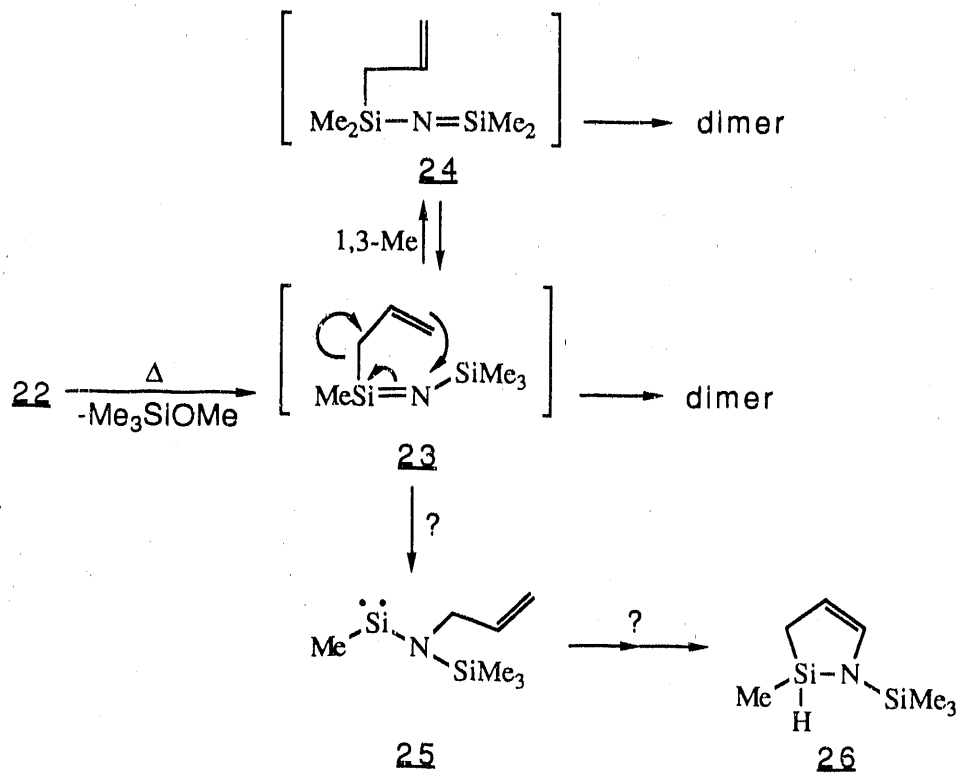
The silanimine-aminosilylene thermal isomerization may be accessible by substitution of the methoxy group in 27 with an allyl group.

Compound 22 was synthesized by the reaction of the lithium salt of hexamethyldisilazane and allylmethylmethoxychlorosilane in 35% overall yield. It was expected that compound 22 would undergo β-elimination losing trimethylmethoxysilane to



22

generate silanimine 23. The most reasonable fates for 23 are dimerization and 1,3-methyl migration to generate another silanimine 24 which would also dimerize. However, the allyl group in 23 could migrate from silicon to nitrogen to generate silylene 25. Although isomerization of silanimine to aminosilylene via a 1,2-hydrogen shift is calculated to be a high energy process,[67] the 2,3-allyl migration could undergo a concerted transition state which would lower the activation energy.



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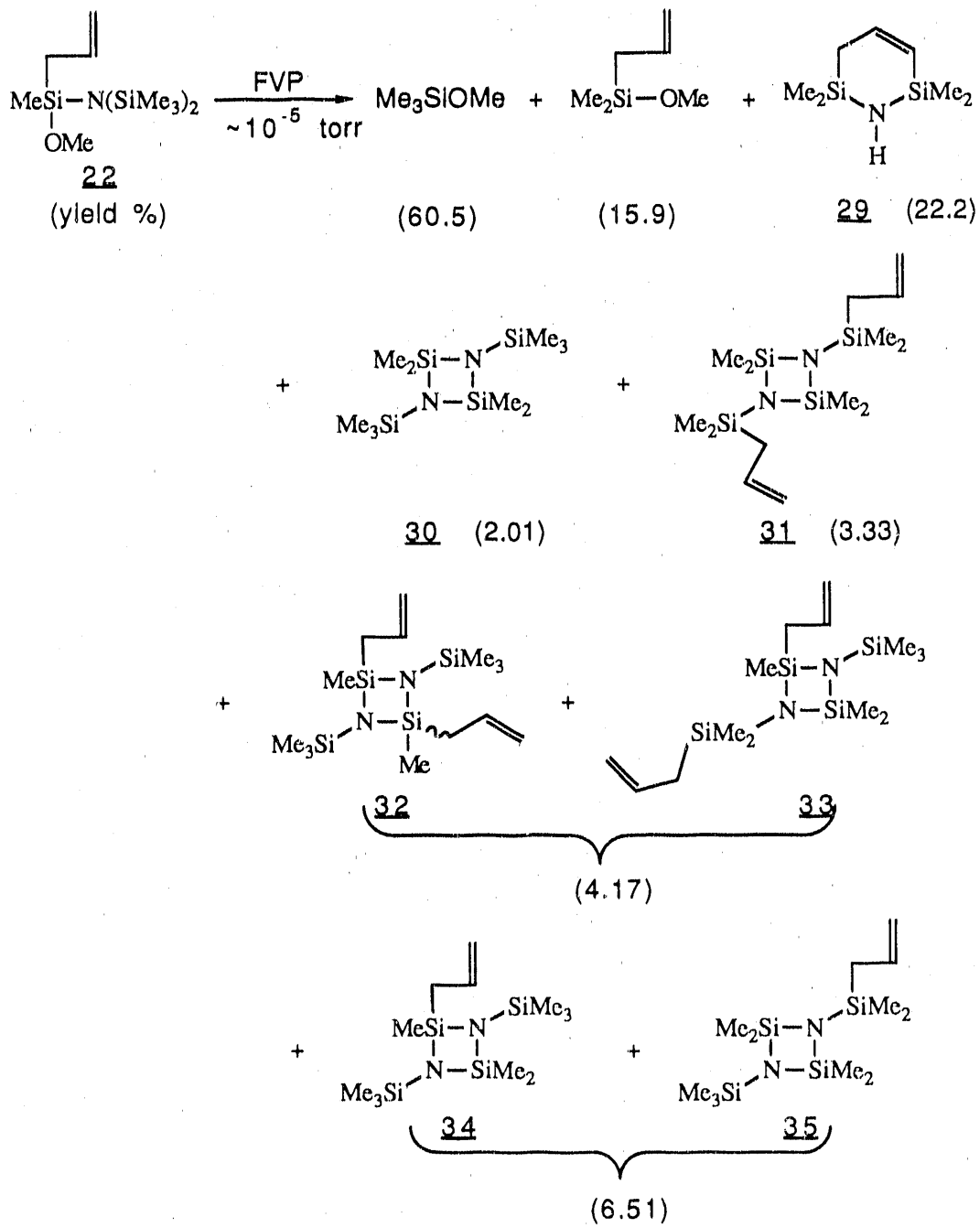
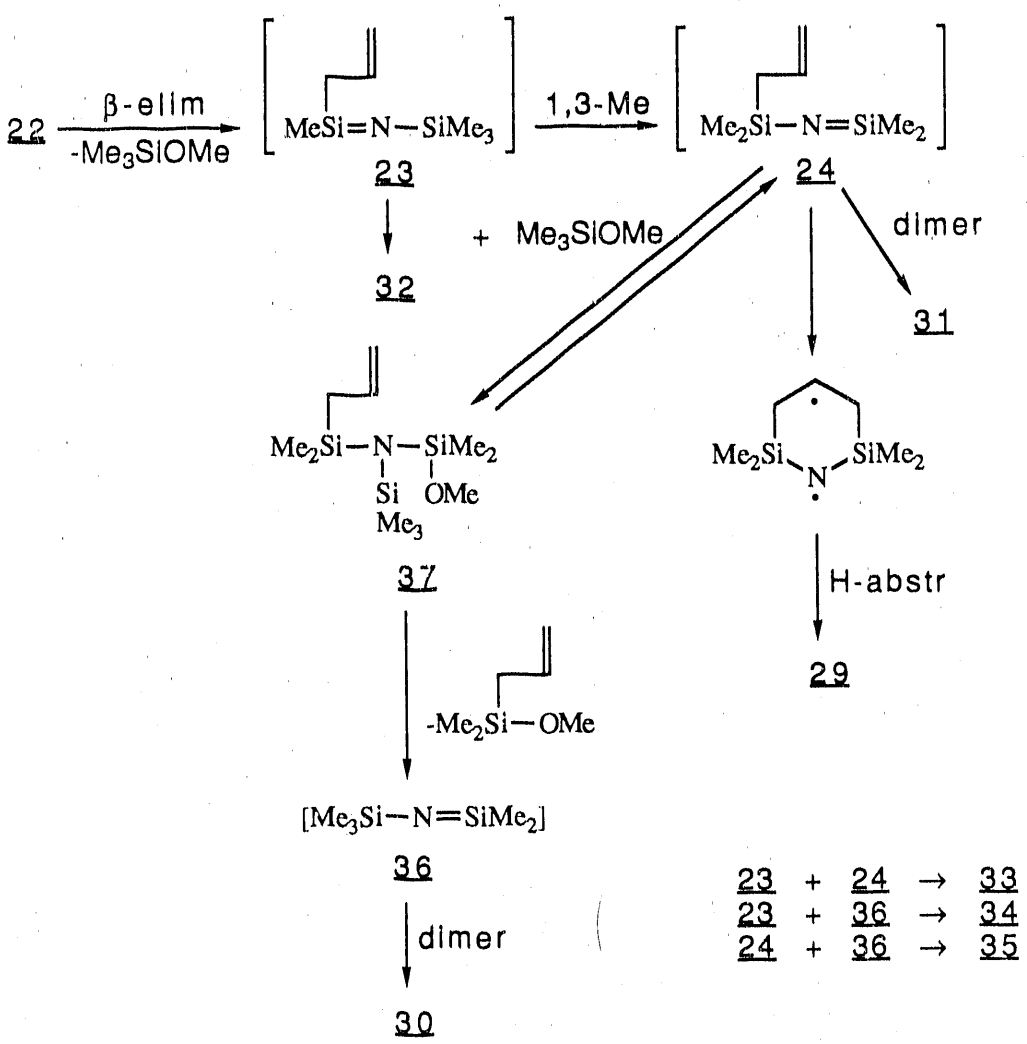
25

26

Flash vacuum pyrolysis of 22 was performed by slowly distilling 22 through a quartz chip-packed tube at 620°C (~10^{-5} torr). The starting material 22 was 100% converted with 73% mass recovery.

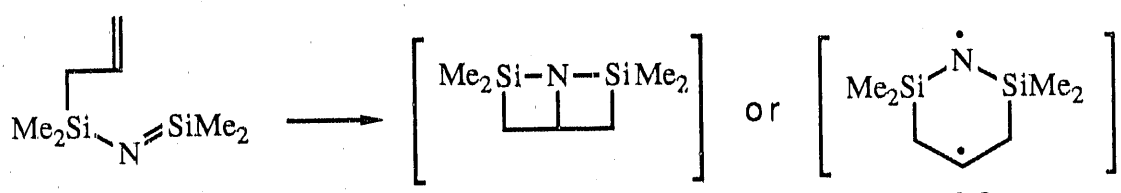


Beside the expected products, trimethylmethoxysilane and the dimers from silanimines 23 and 24, the unexpected products, 1,1,3,3-tetramethyl-1,3-disila-2-azacyclohex-4-ene 29, dimers 30, 34, and 35 also were identified. The reaction mechanism is proposed as the following:



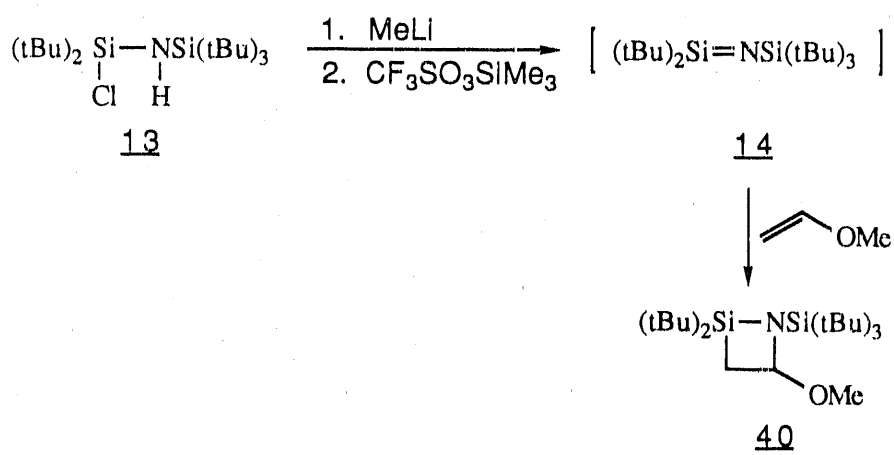
Compound 22 lost trimethylmethoxysilane upon heating to generate silanimine intermediate, 23, which can either dimerize to 32 or to undergo 1,3-methyl migration from one

silicon to another to generate a new silanimine 24. Silanimine 24 could dimerize with itself to produce 31, with 23 to produce 33, or could be trapped by trimethylsilane in the system to produce 37, which decomposes to allyldimethylmethoxysilane and a new silanimine 36. Dimers 30, 34, and 35 were derived from this silanimine. Compound 29 could be formed from 24 via either bicyclo[2,2,0] system 38 or biradical 39 intermediate.



38 39

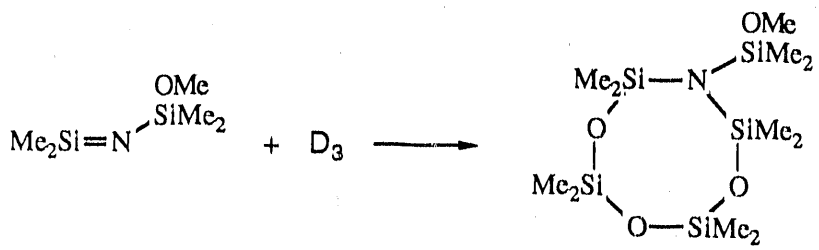
Olefins have been used to trap silanimines. Wiberg et al.[74] found that treating chlorosilane 13 with methyllithium followed by trimethylsilyltriflate yield the silanimine 14 which can be trapped by vinyl methyl ether to form 40. Thus, it is reasonable that the allyl group in 24 could



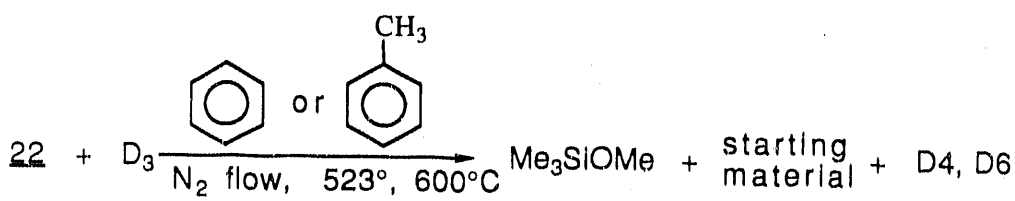
13 14 40

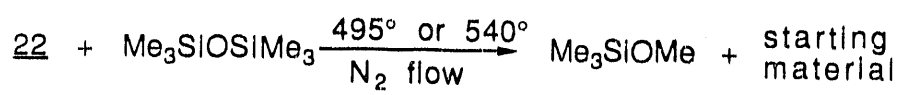
intramolecularly react with the silanimine. No further effort was made to elucidate the mechanism leading to 29.

Hexamethylcyclotrisiloxane (D_3) has been used as the trapping reagent for silanimines.[69] Trapping experiments by D_3 were performed to confirm the intermediacy of 23.

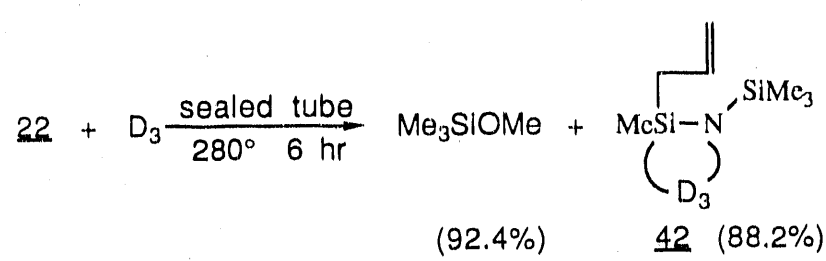


Copyrolysis of 22 with D_3 in benzene or hexamethyldisiloxane in N_2 flow pyrolysis was unsuccessful in trapping the silanimines 23 or 24 over a range of temperatures. Trimethylmethoxysilane was the only product identified by

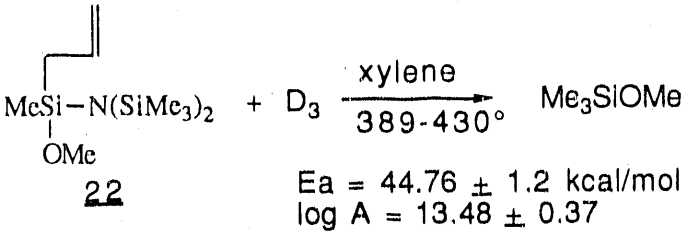




GC-MS. Compound 22 and three-fold of D_3 was sealed in a tube and heated at 280°C for six hours, the adducts of silanimine 22 and D_3, 42, and trimethylmethoxysilane were the only



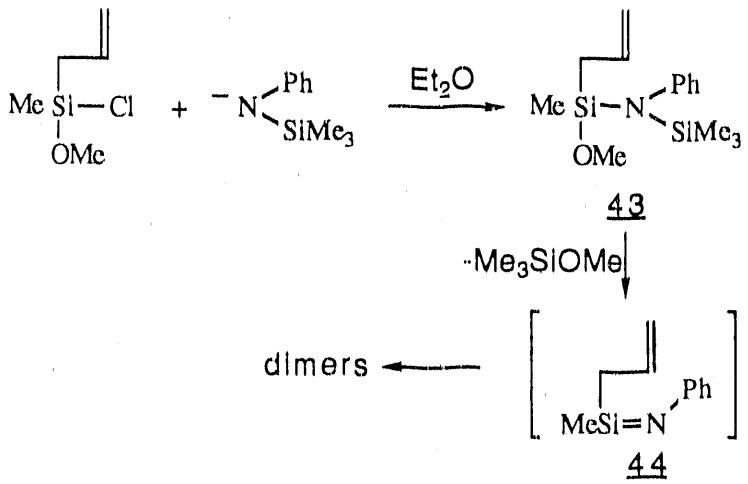
products formed according to GC-MS. Pyrolysis of 22 under SFR conditions at 430°C produced trimethylmethoxysilane, allyldimethylmethoxysilane, and dimers of the silanimines. However, unlike in the FVP experiment, 29 was not the major product in the SFR experiment. One explanation is that the formation of 29 requires activated silanimine 24* which deactivates by collision with the helium molecules under the SFR condition. The kinetic parameters were obtained under the SFR conditions by copyrolysis of 22 with five-fold of D_3 to prevent the reconsumption of the trimethylmethoxysilane formed to produce 37. Compound 22 does not have the minimum required vapor pressure needed for gas-phase injection into the SFR. Thus, it was dissolved with D_3 in xylene and injected by a syringe into the reaction vessel. Trimethylmethoxysilane and adduct 42 were the major products along with a trace amount of dimers. Allylmethylmethoxysilane was not observed from the GC trace indicating that the reconsumption of trimethylmethoxysilane was prevented. The rate constants were obtained by following trimethylmethoxy- silane formation. The activation energy obtained is 44.76 kcal/mol with a log A of 13.48.



22

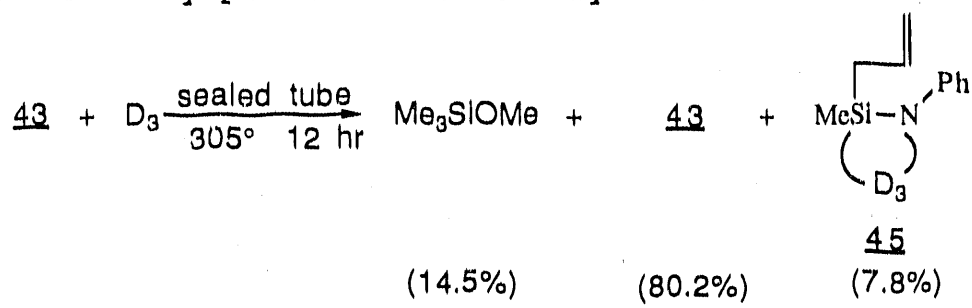
The 1,3-methyl sigmatropic rearrangement in silanimine 23 may be too facile to allow observation of the 2,3-allyl migration.

Compound 43 was synthesized in 47% yield. Flash vacuum pyrolysis of 43 would yield the silanimine 44 in which the 1,3-methyl sigmatropic rearrangement is prevented by replacing one trimethylsilyl group on nitrogen with a phenyl group.



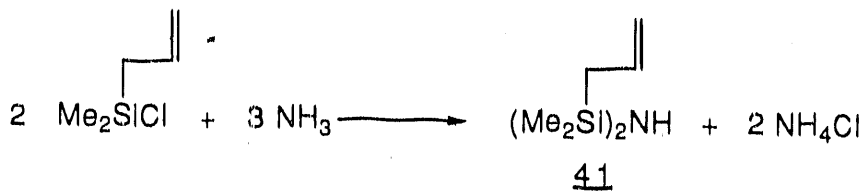
Flash vacuum pyrolysis of 43 was performed at 700°C ($\sim 10^{-5}$ torr). Two products were collected in a liquid nitrogen trap, trimethylmethoxysilane and a minor unidentified product. Also, a yellow solid condensed at the end of pyrolysis tube before reaching the liquid N_2 trap. It was collected and characterized by GC-MS and ^1H NMR spectroscopy. The solid was found to be a mixture of the cis and trans isomers of dimerized allylmethyl(N-phenyl)silanimine 44. The formation of silanimine 44 was also confirmed by the reaction of 43 with

D_3 in the sealed tube. Compound 43 and D_3 were heated in a sealed tube at 305°C for 12 hours. Trimethylmethoxysilane and 45 were the only products detected by GC-MS.

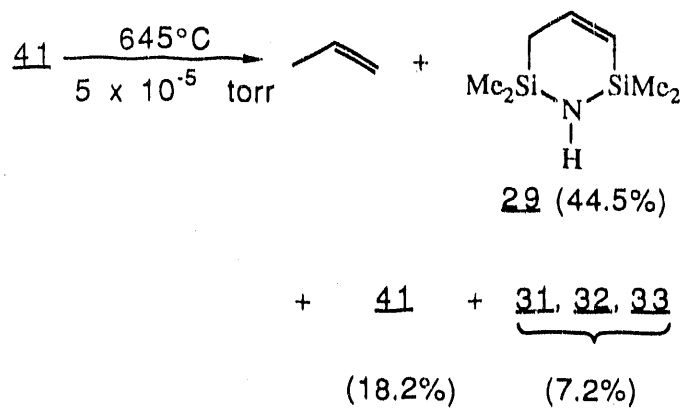


The retroene reaction of 41 was used to generate silanimine 24 for confirmation of the formation of 29 from 24.

Bubbling dry ammonia into a solution of allyldimethylchlorosilane in hexanes produces 41 as the major product in 73%



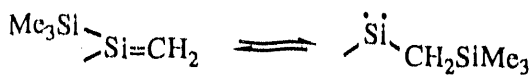
yield. Flash vacuum pyrolysis of 41 at 645°C (5 x 10^{-5} torr) affords propene, 29 (45%), and dimers of silanimine 31, 32, and 33 as the products with 18% starting meterial.



This leads to the conclusion that product 29 derives from the silanimine 24, generated by 1,3-methyl migration in 23 in the pyrolysis of 22. This also provides a good synthetic route to the previously unknown compound 29.

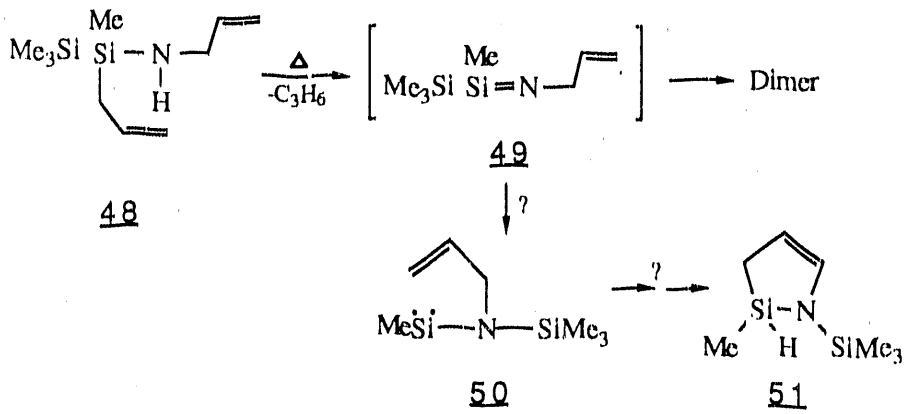
1,3-Diallyl-1,1,3,3-tetramethyldisilazane 41 was also studied in the SFR to obtain the kinetic parameters. The rate constant was obtained in temperature range of 490° - 555°C by following the formation of propene. The activation energy was 50.92 kcal/mol and log A 11.8 which indicated the formation of propene by a concerted retroene reaction with a six-member ring transition state.

Trimethylsilyl group migration was observed in the silene-silylene isomerization.[75] The trimethylsilyl group may be



able to provide a lower energy pathway for the silanimine-to-aminosilylene isomerization.

Compound 48 was synthesized. It was expected that pyrolysis of 48 would produce silanimine 49 via retroene



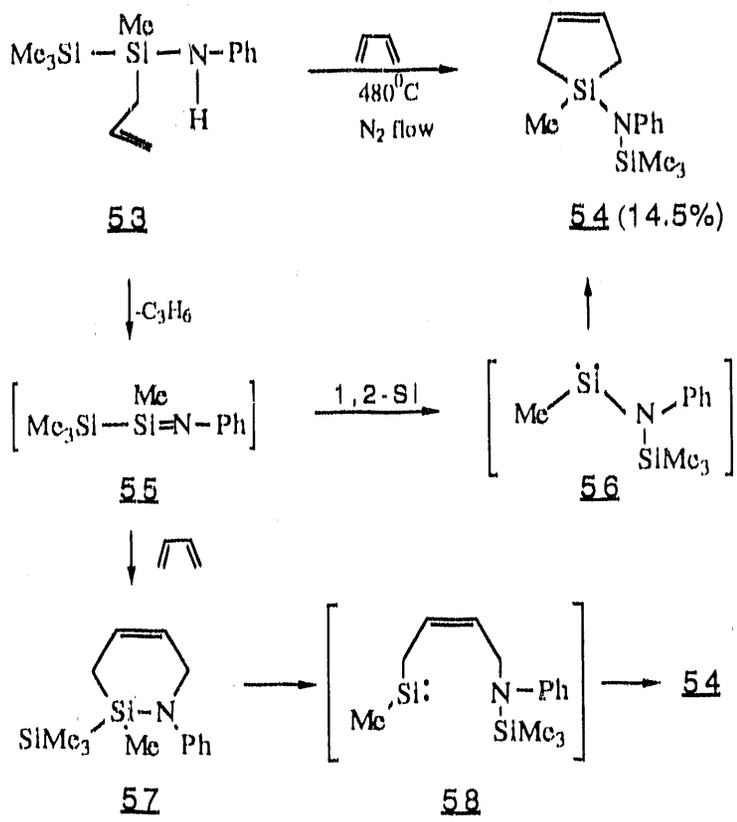
elimination of propene.

There are two likely fates for 49, dimerization and 1,2-trimethylsilyl migration to generate silylene 50. However, flash vacuum pyrolysis of 48 only gave N-allyltrimethylsilazane 52, methylsilacyclobutene and unidentifed products according to GCMS. In molecule 48 the retroene reaction did not compete with the α-elimination of silazane.

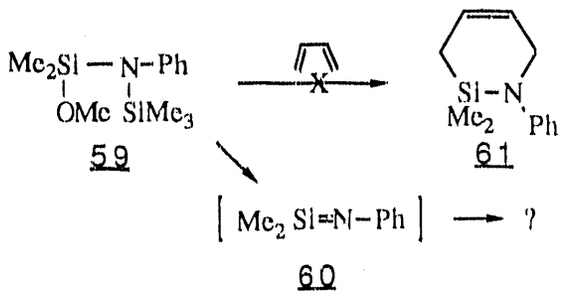
When a phenyl group was subsitituted on the nitrogen, the α-elimination of silazane from the molecule was much slower.[48b]

Compound 53 was synthesized and copyrolysized with 1,3-butadiene at 480°C. Adduct 54 was produced in 14.5% yield.

A possible mechanism for the conversion could be that the retroene reaction of 53 produced the silanimine 55. 1,2-Silyl migration of 55 yielded the aminosilylene 56 which was trapped by 1,3-butadiene to produce 54. However the arguement could be made that the silanimine generated was trapped by 1,3-butadiene before it isomerized to aminosilylene to produce 57. α-Elimination of silazane in 57 may give silylene 58 which would undergo C-N bond inserton to yield the isolated

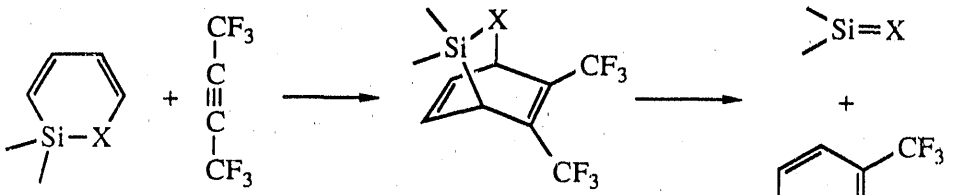


product 54. The latter mechanism can be ruled out by the fact that the silanimine 23 and 60 can not be trapped under the copyrolysis conditions by D_3 or 1,3-butadiene.



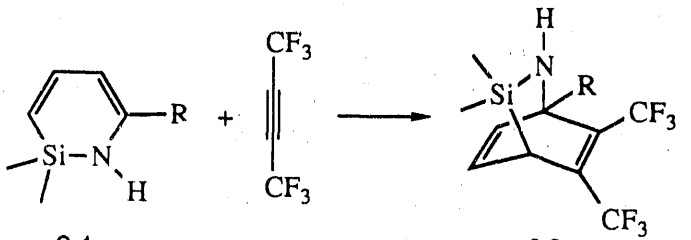
Two other potential synthetic routes were explored for generation of silanimines.

Silenes,[76] disilenes,[77] and silanones[78] have been successfully generated by thermally induced retrograde Diels-Alder reactions. It is expected that 7-aza-8-silabicyclo-

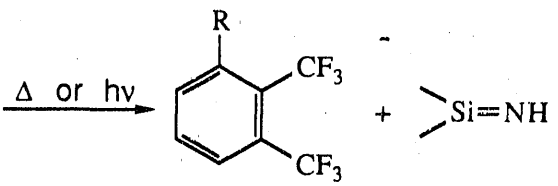


a: X = CH_2
b: X = O
c: X = $SiMe_2$

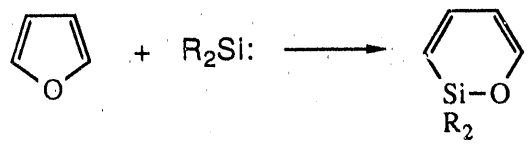
[2,2,2]octadiene ring system 63 might be used as precursor to generate silanimines. 1-Aza-2-silahexa-3,5-diene 64 may be used to synthesize the desired bicyclic ring system by reacting with a reactive acetylene.



64 63

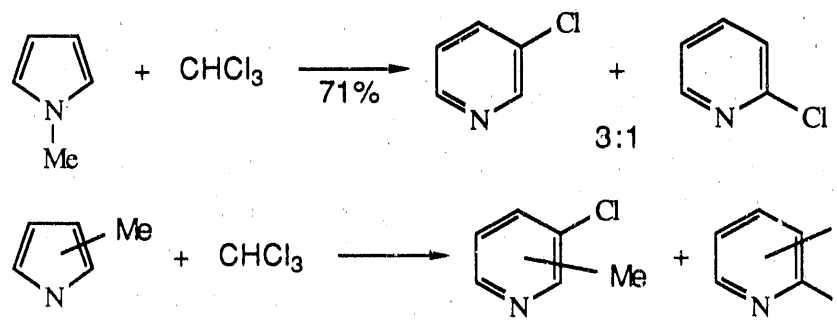


Synthesis of 64 was performed by several different routes. Furan reacts[79] with silylene to produce 1-oxa-2-silacyclohexa-3,5-diene 65.

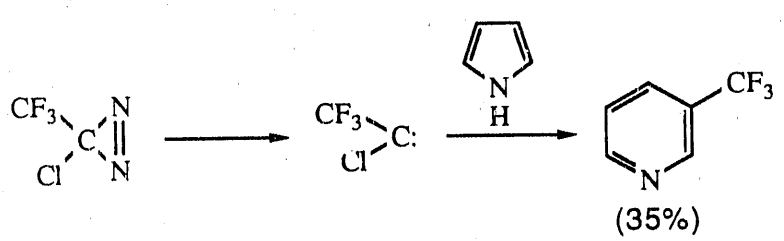


65

Chloroform reacts[80] with pyrrole and methylpyrroles at 550°C in the gas phase to give high yields of chloro- and chloromethylpyridines. The reaction may be via a carbene addition to the double bonds of pyrrole followed by the ring expansion.



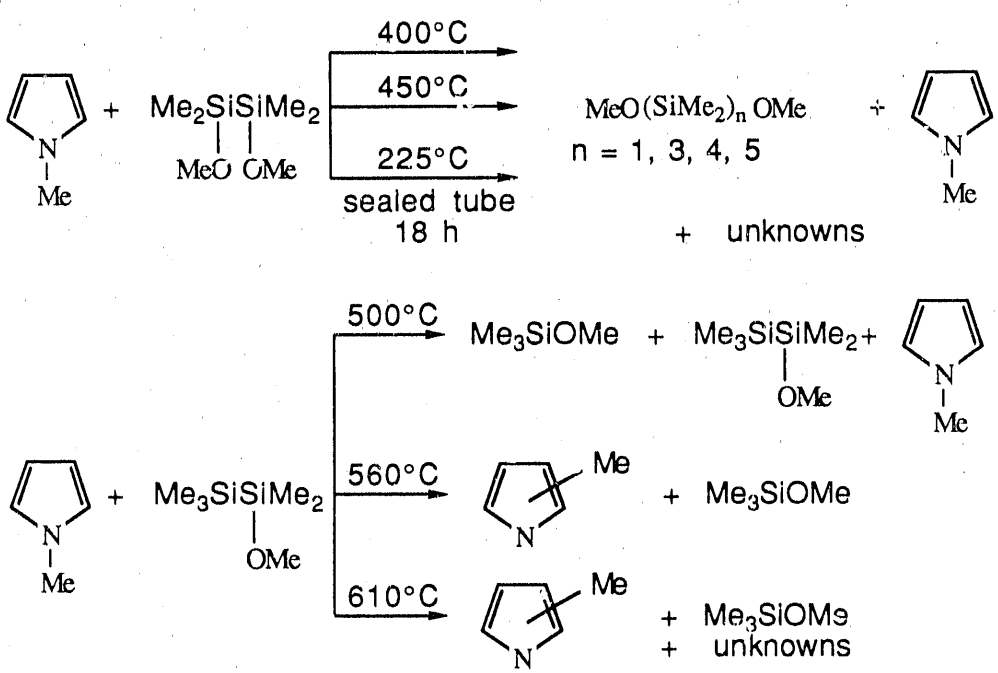
Chlorotrifluoromethyl carbene adds[81] to pyrrole to give 3-trifluoromethylpyridine.



Thus, similar reactions of 1-methyl pyrrole with silylene might give the desired compound 64.

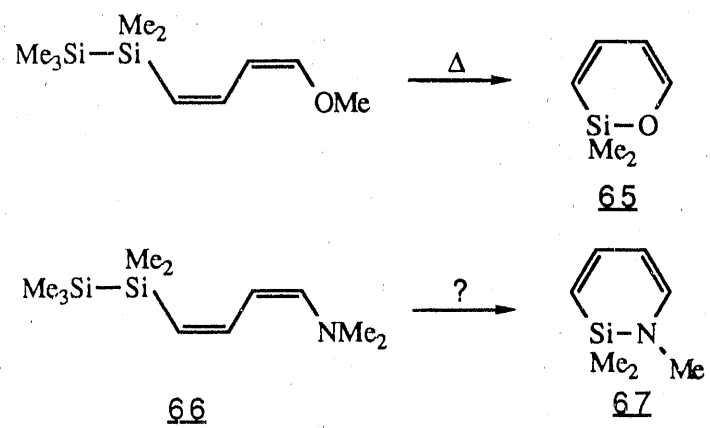
Copyrolysis of 1-methylpyrrole with tetramethyldimethoxy-disilane affords unreacted 1-methylpyrrole and products

corresponding to the dimethylsilylene insertion to dimethyldimethoxysilane. Tetramethyldimethoxydisilane was decomposed completely under the reaction conditions. No desired product, silylene addition to 1-methylpyrrole, was detected by GC-MS. It was suspected that the reaction temperature was not high enough for the addition of silylene to the double bonds of pyrrole. A higher reaction temperature was achieved by using pentamethylmethoxydisilane as the silylene precursor. The pyrolysis of $Me_3SiSiMe_2OMe$ and 1-methylpyrrole was performed at temperatures of 500°, 560°, and 610°C. At 500°C trimethylmethoxysilane was the only product identified by GC-MS along with the starting materials, pentamethylmethoxydisilane and 1-methylpyrrole. Above 560°C 1-methylpyrrole isomerized



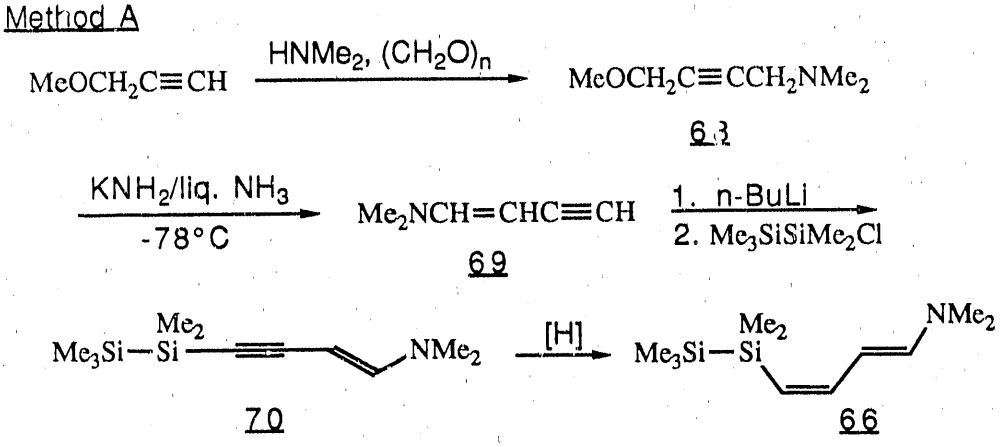
significantly to 2- and 3-methylpyrrole. No desired addition products were detected by GC-MS. Copyrolysis of 1-methylpyrrole with hexachlorodisilane at 500°C afforded unreacted 1-methylpyrrole, tetrachlorosilane and an unkown component plus a small amount of high molecular weight products. It was concluded that the silylene does not react with the pyrrole ring under the reaction conditions.

2,2-Dimethyl-1-oxa-2-silacyclohexa-3,5-diene 65, the oxygen analogue of 64, has been synthesized by flash vacuum pyrolysis of Z,Z-1-pentamethyldisilanyl-4-methoxy-1,3-butadiene.[78] Thus it was expected that the FVP of 1-pentamethyldisilanyl-4-(N,N-dimethylamino)-1,3-butadiene 66 would be a suitable synthetic route to the 1,2-azasilin ring system 67.



However, attempts to synthesize 66 by two different routes were not successful.

Method A



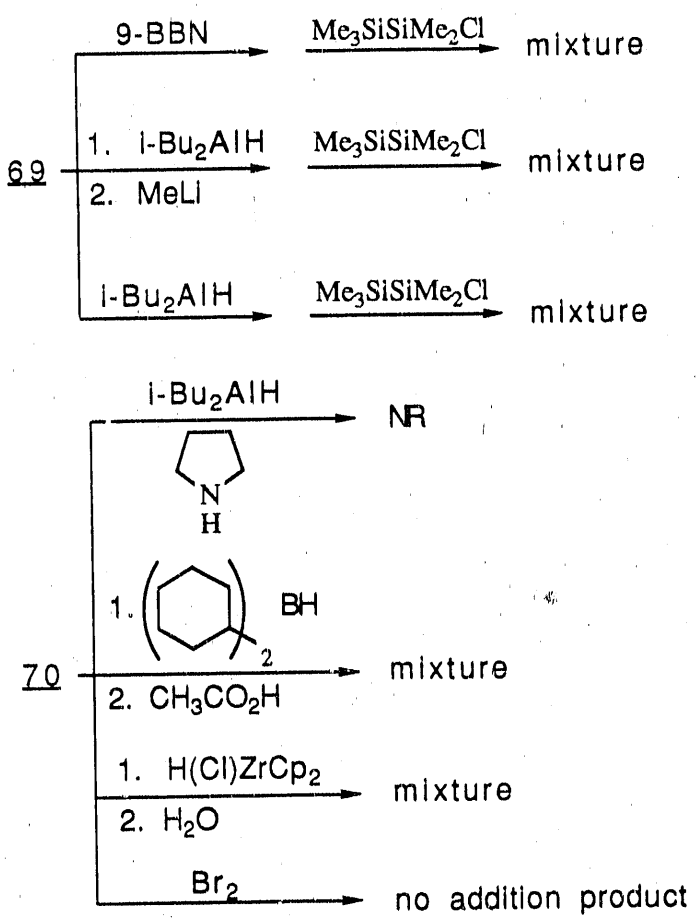
Compound 69 is known[82] and 66 and 70 are unknown.

Compound 70 was synthesized without problem but was difficult to purify due to its high boiling point and unstability even at 0°C. It was distilled at 0.5 mmHg at the bath temperature of 110°C.

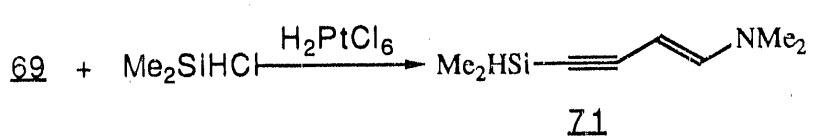
Several methods were tried to obtain the desired compound 66 from 69 and 70. Unfortunately, none of them succeeded.

Attempts to use organometallic hydride addition to the triple bond of 69 followed by quenching with pentamethyl-chlorodisilane produced a mixture in each case.

Diisobutylaluminumhydride and organoborane hydrides have been used for reduction of silylacetylenes to vinyl silanes with good yield.[83] However, DIBAL only gave recovered 70 and organoborane hydrides gave a mixture with complete consumption of 70.

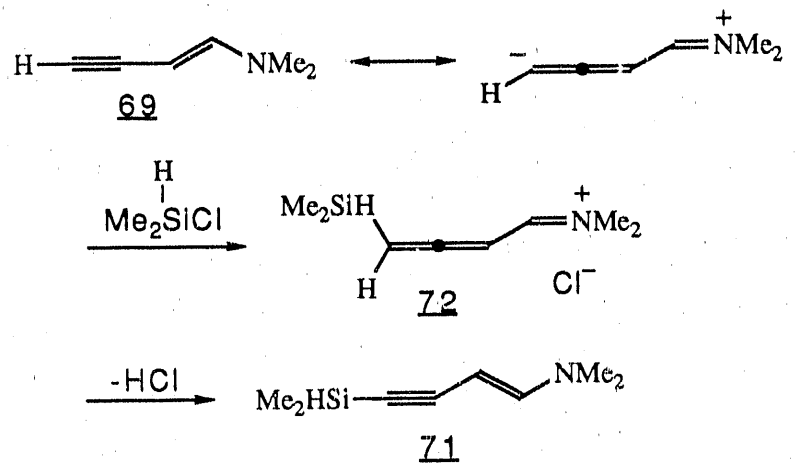


Another interesting reaction was that of hydrosilation of 69 with dimethylchlorosilane in the presence of tetrachloroplatinic acid as the catalyst, the only extractable product from ether was E-dimethylsilyl-4-(N,N-dimethylamino)-3-buten-1-yne 71 instead of the desired hydrosilation product. This reaction happened even in the absence of the catalyst.

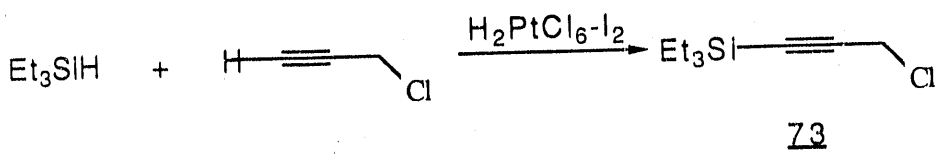


71

A possible mechanism is that dimethylchlorosilane reacts with the zwitterion form of 69 to form the salt 72, which loses hydrogen chloride to yield compound 71.



It is reported[84] that reaction of triethylsilane with propargyl chloride in the presence of H_2PtCl_6-I_2 as the catalyst yields dehydrogenation product 73 isolated in 61% yield. The catalyst is required in the reaction and no mechanism was discussed.



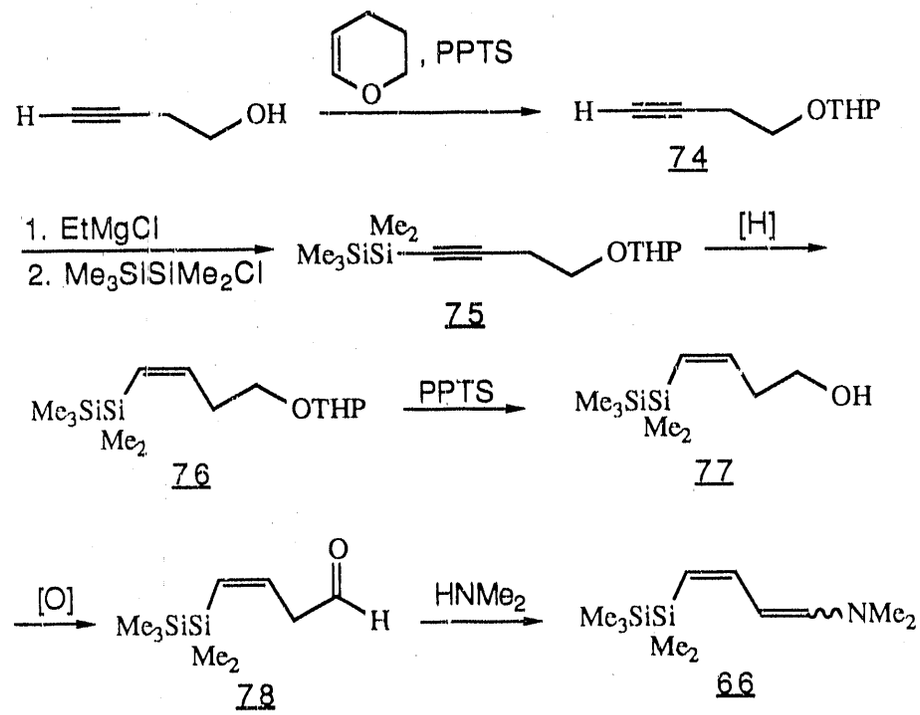
73

Since the triple bond in 70 could not be reduced, another synthetic route was designed for the synthesis of 66.

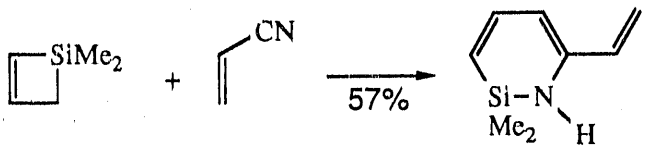
The protection of the hydroxyl group of 1-butyn-4-ol by dihydropyran went with high yield. The blocked 1-butyn-4-ol 74 was converted to the alkynyldisilane by reacting with ethylmagnesium chloride followed by quenching with

pentamethylchlorodisilane. Reduction of the triple bond of 75 to a double bond was not accomplished by DIBAL but produced similar results to those of Bernady et al.[85] who attempted to prepare an alkenylalanate reagent via hydroalumination of a blocked 1-octyn-3-ol. "This could not be accomplished in satisfactory yield." The reduction was achieved by hydroboration followed by the organoborane formed reacted with glacial acetic acid in 88% yield. Deprotection of 76 yielded the alcohol 77 which failed to be oxidized to the corresponding aldehyde by the commonly used oxidation reagents: PCC, Swain, and Collins reagents. Each of the reagents yielded a mixture without an appreciable amount of desired product.

Method B

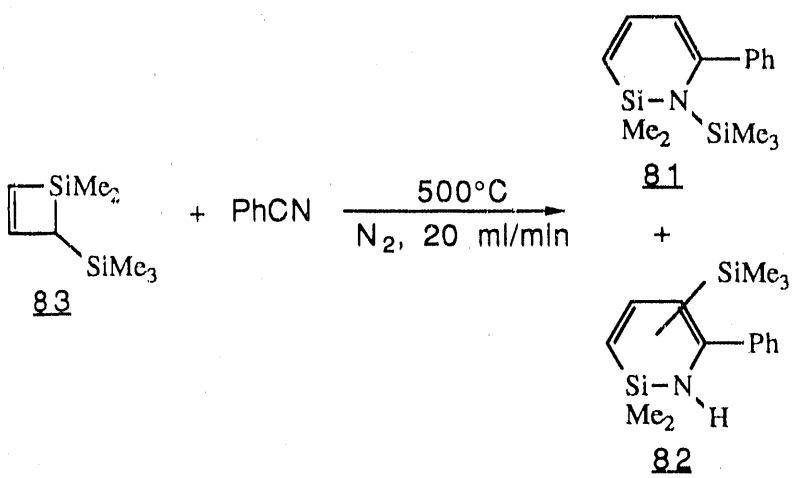


Conlin[44a] found that pyrolysis of 1,1-dimethylsila-cyclobutene 79 with acrylonitrile afforded 6-vinyl-2,2-dimethyl-1-aza-2-silacyclohexadiene 80. He suggested that the reaction undergoes [2+2] cycloaddition via the conjugated 1-silabutadiene intermediate formed from the silacyclobutene ring opening. It was surprising that the C≡N group instead of C=C reacted with 1-silabuta-1,3-diene.



79 80

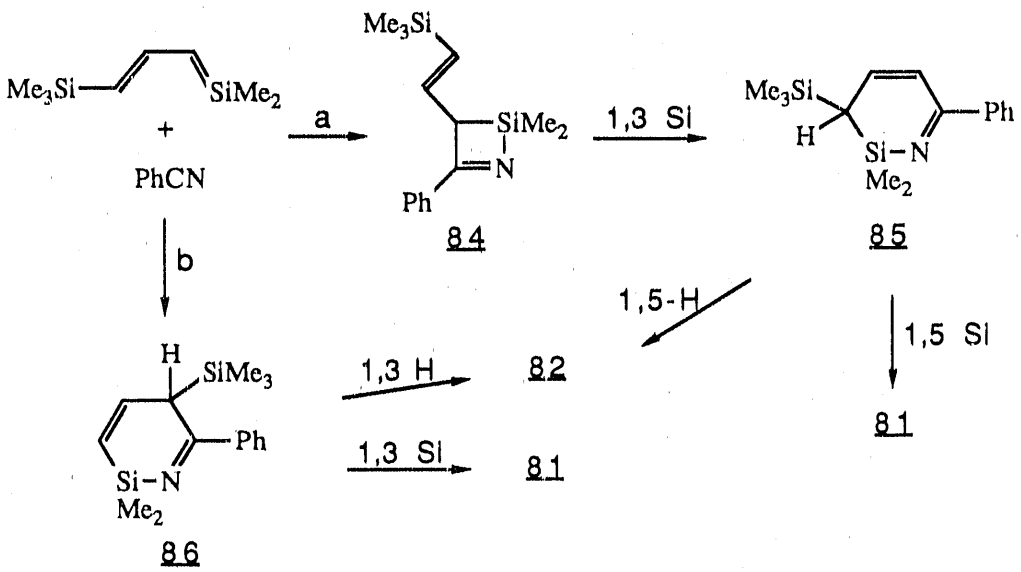
The desired substituted azasilacyclohexadiene 81 was synthesized by copyrolysis of 3-trimethylsilylsiletene 83 with benzonitrile at 500°C in N_2 flow pyrolysis. Two products 81 and 82 were separated in 7:1 ratio. Two pathways to the six-



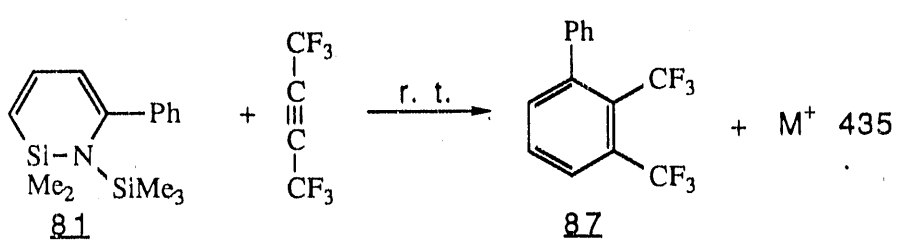
83 81 + 82

member ring are possible. [2+2] addition of the silene to C≡N bond forms the azasilacyclobutene 84 which undergoes 1,3-silyl

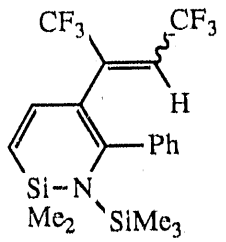
migration to form 85. 1,5-silyl migration of 85 will form 81 and 1,5-H migration affords 82. Another possibility is [4+2] addition of 1-silabutadiene with benzonitrile to give 86 which undergoes either 1,3-silyl or 1,3-H migration to form 81 or 82.



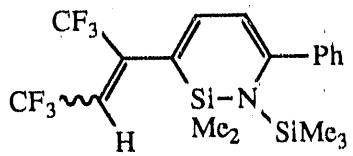
Compound 81 and hexafluorobut-2-yne were reacted in a sealed tube at room temperature for three days. Starting material 81 (~70%), product 87, and the adduct of 81 and



hexafluorobut-2-yne were isolated. The possible structures of the adduct were proposed to be 88 or 89 by GCMS, ^{1}H NMR and

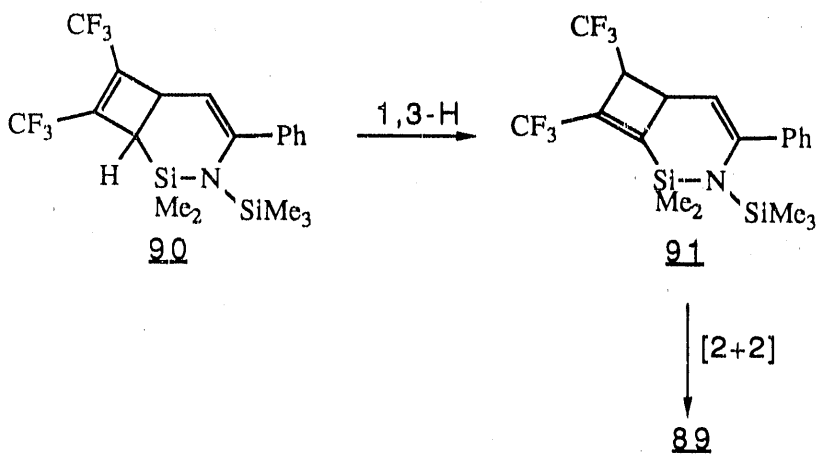


88



89

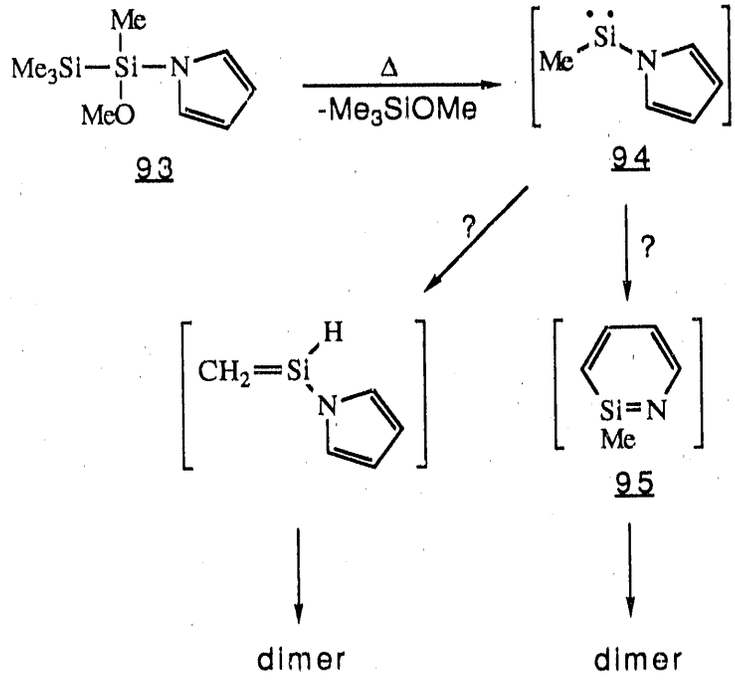
FTIR. A possible route to form 88 or 89 is [2+2] addition of 81 and hexafluorobutyne-2 affording 90 which undergoes 1,3-H migration to give 91 or [2+2] ring opening to give product 89. No evidence that silanimine was formed in the reaction was observed other than the formation of 87.



90 91 89

Although no silylene addition products were produced from copyrolysis of 1-methylpyrrole and silylene procursors, ring expansion of silylene 94 to form the silanimine 95 is still possible. It was expected that pyrolysis of 93 would give trimethylmethoxysilane and pyrrolylmethylsilylene 94. This silylene could undergo a 1,2-vinyl migration to give silapyridine 95. The silapyridine could dimerized or could be

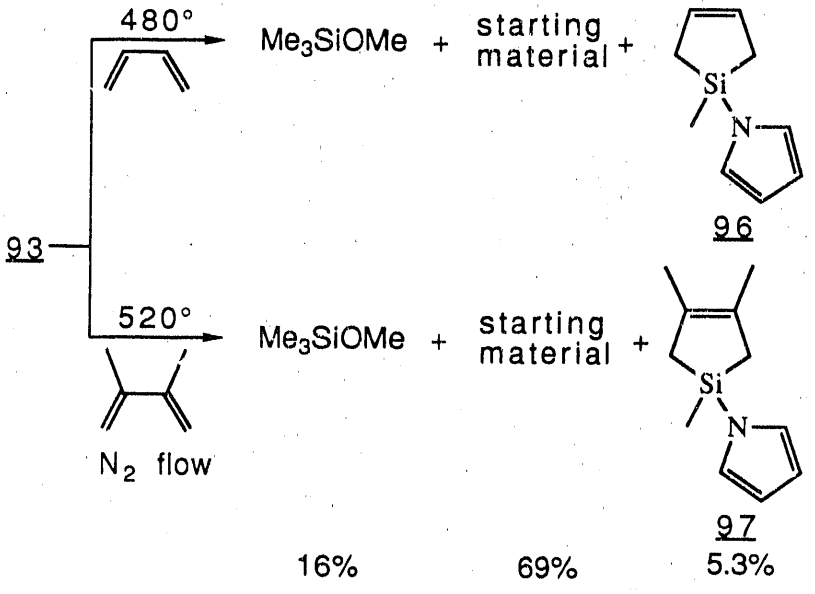
chemically trapped. From this, exciting chemistry could be revealed: First, to observe the isomerization of aminosilylene to silanimine; second, to generate silapyridine which is unknown both theoretically and experimentally.



Compound 93 was synthesized in 63% yield from the reaction of pyrrole anion with tetramethyl-1,1-dichlorodisilane followed by the treatment with methanol/pyridine. Distillation of 93 through a quartz tube packed with quartz-chips at 610°C afforded 90% trimethylmethoxysilane, trace amounts of unidentified volatile products, and yellow wax-like materials accumulated at the end of pyrolysis tube. ^{1}H NMR analysis of the wax reveals that it is a mixture of compounds with similar structures. There are only two groups

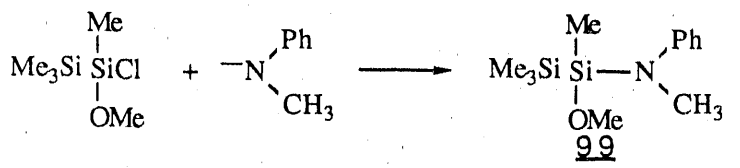
of hydrogens in two broad peaks (δ = 6-7 ppm and 0-1 ppm).

The formation of silylene 94 was confirmed by copyrolysis of 93 with 1,3-butadiene and 2,3-dimethyl-1,3-butadiene, which affords trimethylmethoxysilane and adducts 96 and 97, respectively.

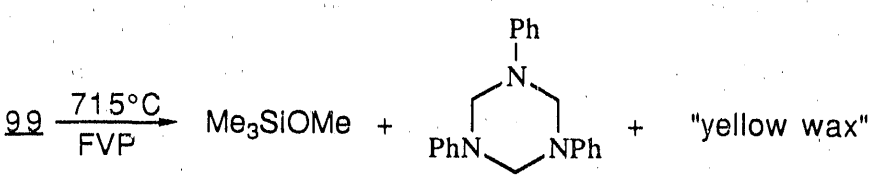


The conclusion from the experimental results is that the vinyl group on nitrogen does not migrate to the adjacent divalent silicon.

Compound 99 was synthesized by the reaction of lithium N-methylaniline and 1-methoxy-1-chlorotetramethyldisilane in 61% yield. Flash vacuum pyrolysis of 99 at 715°C gave trimethylmethoxysilane as the major volatile product, and trace amounts of others unidentified by GCMS. A white solid which was identified to be hexahydrotriphenyltriazine 100 was isolated by vacuum distilling all volatile products that were

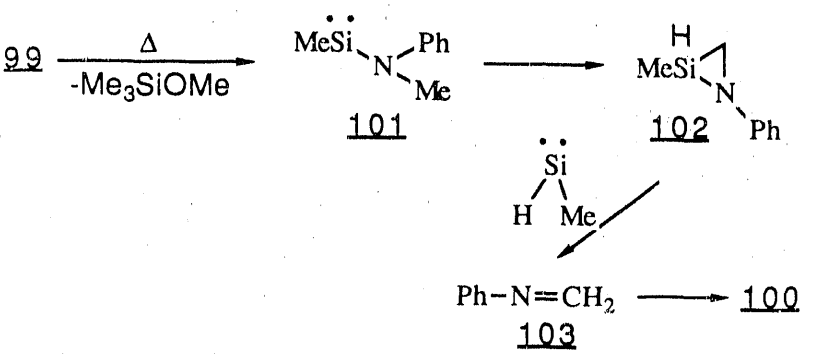


99



100

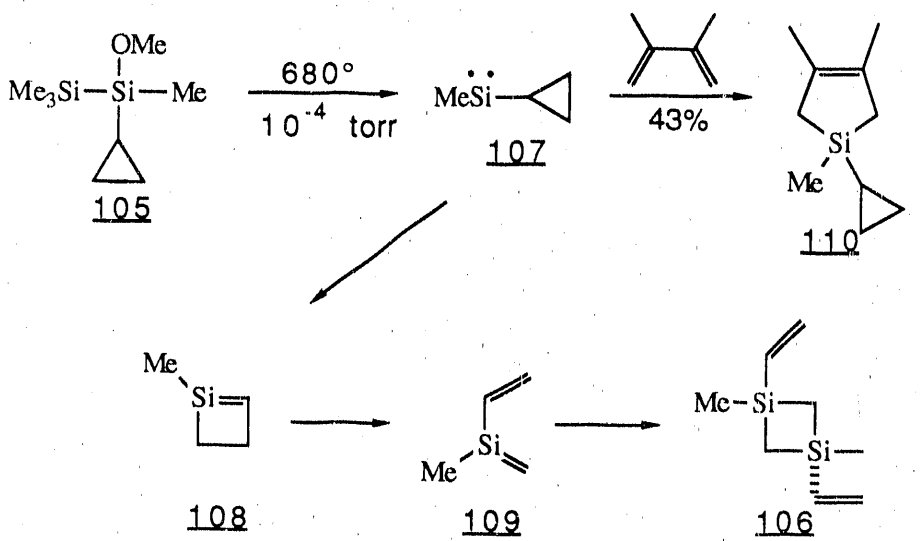
trapped. The yellow wax-like material accumulated at the end of pyrolysis tube was unidentifiable. A possible mechanism for the formation of 100 is that silylene 101 was generated from 99 by α-elimination of trimethylmethoxysilane. A C-H insertion of the silylene into N-methyl formed the silaaziridine 102 which lost a methylsilylene to form Ph-N=CH_2 103. Trimerization[86] of 103 yielded the hexahydrotriphenyl-triazine 100. However, the silylene intermediates could not be trapped by copyrolysis of 99 with 2,3-dimethyl-1,3-butadiene.



101 102 103 100

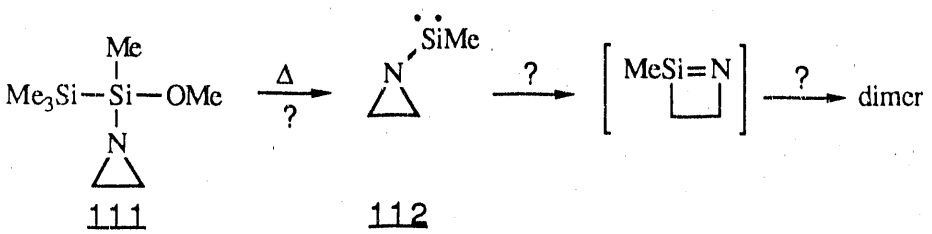
Barton et al.[87a] found that flash vacuum pyrolysis of 1-cyclopropyl-1-methoxytetramethyldisilane 105 at 680°C

yielded trimethylmethoxysilane and 1,3-dimethyl-1,3-divinyl-1,3-disilacyclo- butane 106.

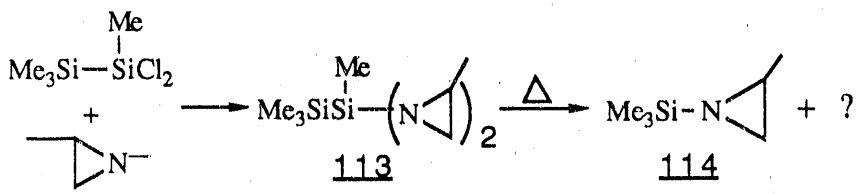


The likely mechanism involves α-elimination of trimethylmethoxysilane to form silylene 107, ring expansion of 107 to 1-methyl-1-silacyclobutene 108. Ring opening of 108 to vinylsilene 109 which undergoes the usual head to tail dimerization to form 106. Evidence that silylene 107 is indeed involved was obtained by the efficient trapping of 107 with 2,3-dimethylbutadiene yielding 110 in 43% yield.

Substitution of cyclopropyl ring in 105 with an ethylene-amine gave compound 111 which is analogues to 105.



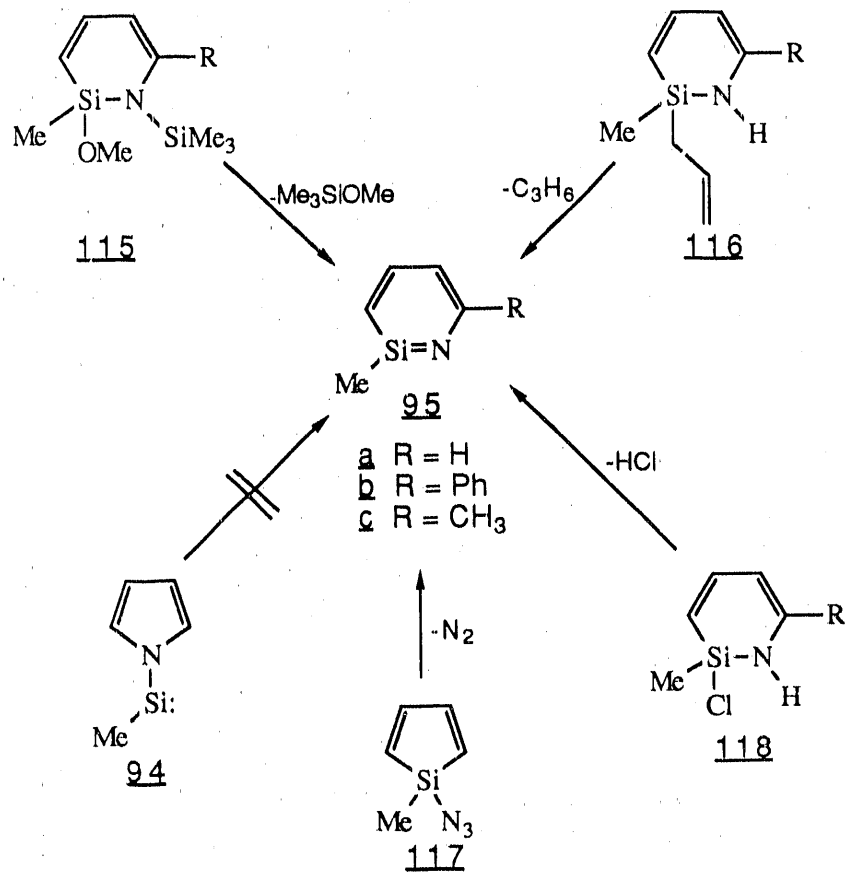
Compound 113 was synthesized in 22% yield by coupling of 2-methylaziridine anion with 1,1-dichlorotetremethyldisilane. Flash vacuum pyrolysis of 113 afforded propene, N-trimethylsilyl-2-methylaziridine 114, unreacted starting material 113 and unidentified products which are derived from 114. Copyrolysis of 113 with 2,3-dimethyl-1,3-butadiene in SFR afforded prop ne and N-trimethylsilyl-2-methylaziridine 114. The expected adduct of silylene and the trapping reagent was not observed by the mass spectrometer in the SFR system.



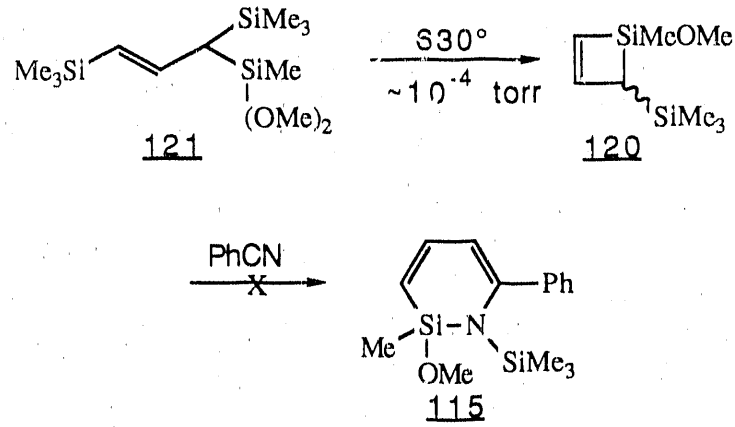
To confirm that the unidentified products arise from the decomposition of 114, it was synthesized and the same products were obtained under SFR condition with that of 113.

Silapyridine 95 and its analogues are not known either by theoretical calculation or experimental evidence. Obtaining evidence about this intriguing molecule was attempted experimentally.

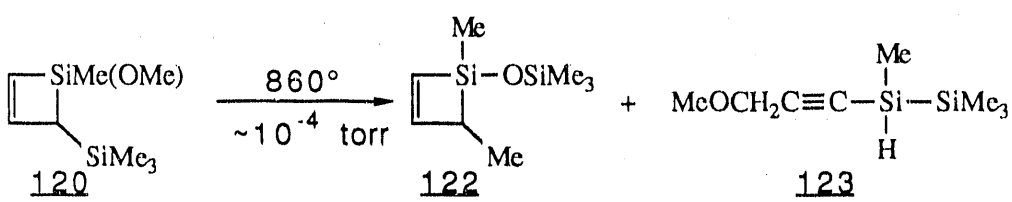
Several approches to the silapyridine could be visualized. β-Elimination of trimethylmethoxysilane or HCl, retroene elimination of propene and 1,2-alkyl shift from silicon to nitrene are known methods to generate silanimines. Those methods could be used to generate silapyridine, a new



silanimine. Aminosilylene does not isomerize to silanimine as indicated early and the routes from precursors 117 and 118 were not attempted. We synthesized compound 81 by copyrolysis of 83 and benzonitrile. One would anticipate that compound 115, an analogue of 81 could be obtained by the same synthetic route. Compound 120 was synthesized[45] by flash vacuum pyrolysis of 121 at 630°C. Copyrolysis of 120 with benzonitrile failed to give the desired compound 115. Trimethylmethoxysilane was the major product. The volatile

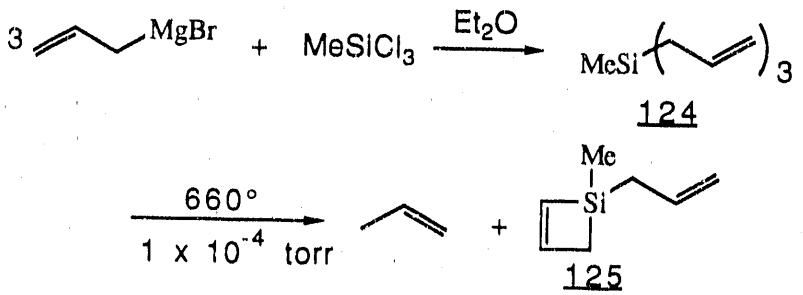


materials were vacuum distilled from the reaction mixture. ^{1}H NMR spectra of the yellow residue indicated a mixture and did not correspond to the dimers of silapyridine. Benzonitrile and 120 were heated in a sealed tube at 300°C for about 10 min. Starting material 120 was completely consumed. Trimethylmethoxysilane was the major product. There was a trace amount (<0.1% by GC) of product which had a molecular weight of 371 by GCMS corresponding to the adduct of silapyridine to the starting material 120. However, isolation of this product was not successful. Burns[88] found that pyrolysis of 120 at 860°C afforded two major products 122 and 123. Trimethylmethoxysilane was not the major product. The pyrolysate from copyrolysis of 120 with 2,3-dimethyl-1,3-butadiene contained only 2,3-dimethyl-1,3-butadiene and products

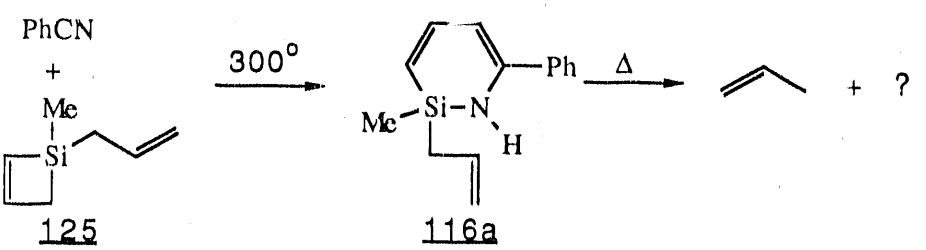


arising from it. The trapping adduct of silacyclobutadiene with 2,3-dimethyl-1,3-butadiene was not observed nor was trimethylmethoxysilane. His observations are different from ours from copyrolysis of 120 with benzonitrile, where trimethylmethoxysilane was the major product obtained. This may indicate that silapyridine was generated from 115 by extrusion of trimethylmethoxysilane. But its fate could not be determined.

Methyltriallylsilane 124 was prepared via the coupling of allylmagnesiumbromide with methyltrichlorosilane in 63% yield. Flash vacuum pyrolysis of 124 at 600°C (~10^{-4} torr) afforded

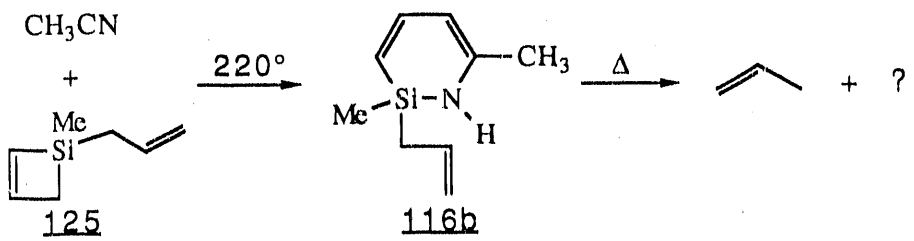


the desired allylmethylsiletene 125. Copyrolysis of 125 with benzonitrile at 400°C failed to produce the desired 116a. 2-Allylmethyl-6-phenyl-1-azasilacyclohexadiene 116a was synthesized by heating 125 with benzonitrile in a sealed tube



at 220°C for 2 hours. It was purified by preparatory GC. This may indicate that retroene reaction to generate silanimine requires higher temperature than β-elimination of trimethylmethoxysilane so that compound 116 is able to survive at the temperature at which it forms. Compound 116a had completely decomposed after heating in a sealed tube with dodecane at 300°C for 1 hour. Propene was formed. No silapyridine or its dimer was detected.

It is possible that with the phenyl substituent the dimers of silapyridine have too low a vapor pressure to be detected by GCMS. Methyl substituted compound 116b was synthesized by heating 125 with excess acetonitrile at 220°C for 70 min and purified by preparatory GC.



125 116b

Compound 116b completely decomposed at 600°C under SFR conditions. Propene was formed as the major product.

Distillation of 116b through a quartz tube packed with quartz-chips at 630°C (~10^{-5} torr) afforded propene and an orange solid in the liquid N_2 trap which would not dissolve in common solvents like benzene, chloroform, and acetonitrile. After washing the solid with benzene and vacuum dried, the

mass spectrum was obtained in a Kratos MS50 mass spectrometer. It did not correspond to the silapyridine dimer.

Heating 116b with excess D_3 in a sealed tube at 300°C for 2 hours afforded propene, D_4, D_5, and D_6 with complete decomposition of the 116b. Although a dark tar was observed in the reaction system, no adduct of silapyridine with D_3 was detected by GCMS and ^1H NMR.

Attempts to obtain evidence for generation of silapyridine by three silapyridine precursors were thus unsuccessful. More efforts should be made to obtain evidence for this interesting but elusive reactive intermediate.

Experimental

Instruments used in this section are the same as described in the first section of this thesis (see page 41).

General procedure for the condensation of chlorosilanes and amines

To a solution of 20 mmol amine in 50 ml dry Et_2O at -78°C was added dropwise 8.7 ml (20 mmol, 2.3 M in hexanes) n-BuLi. The mixture was stirred at -78°C for an additional 1 hr. and transferred into a solution of one equivelent of chlorosilane in 100 ml of dry Et_2O at -78°C. After the mixture was stirred for 10 min it was allowed to warm to room temperature and stirred overnight. The solid formed was filtered and solvent

was removed by simple distillation. The desired silazanes were purified by preparative GC.

Synthesis of allylmethylmethoxysilylbis(trimethylsilyl)trisilazane 22

The general procedure was used on a 50 mmol scale. After the solvent was distilled the remaining liquid was vacuum distilled at 70-75°C/1.4 mmHg. Product 22 (4.8 g) was obtained in 35% yield. It was further purified by preparatory GC using a 9' 15% SE-30-CW column. The product 22 was characterized as follows: ^{1}H NMR ($CDCl_3$) 0.20 (s, 3 H, SiMe), 0.26 (s, 18 H, $N(SiMe_3)_2$), 1.71 (dd, 2 H, J=8.1, 0.9, $SiCH_2$), 3.23 (s, 3 H, MeO), 4.95 (t, 1 H, J=0.9,CH), 4.96-5.01 (m, 1 H, CH), 5.78-5.95 (m, 1 H, CH). ^{13}C NMR ($CDCL_3$) 0.006, 4.994, 26.772, 49.626, 113.754, 134.478. FTIR 2955, 1632, 1418, 1254, 1092, 943, 906, 843, 675. GCMS 260 M^+-CH_3 (31.4), 234 (100), 130 (98.1), 100 (35.2), 73 (37.8), 59 (37.0). Exact Mass: (M^+-CH_3) $C_{10}H_{26}ONSi_3$, measured 260.13183, calculated 260.13223, error -1.52 ppm.

Flash vacuum pyrolysis of 22

Compound 22 (528 mg) was distilled at 25°C through a hot zone at 620°C (~10^{-5} torr). The clear pyrolysate (382 mg, 72.3% mass recovery) contained trimethylmethoxysilane (60.5%), allyldimethylmethoxysilane (15.9%), 2,2,6,6-tetramethyl-1-aza-2,6-disilacyclohex-3-ene 29 (22.2%), 1,3-bis(trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane 30 (2.01%), 1,3-bis(trime-

thylsilyl)-2-allyl-2,4,4-trimethylcyclodisilazane 34 and 1-allyldimethylsilyl-3-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane 35 (6.51%), 1,3-bis(allyldimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane 31 (3.33%), 1,3-bis(trimethylsilyl)-2,4-diallyl-2,4-dimethylcyclodisilazane 32 and 1-allyldimethylsilyltrimethylsilyl-2-allyl-2,4,4-trimethylcyclodisilazane 33 (4.17%). The products were separated by preparative GC with a 9' 15% SE-30-CW column. Allyldimethylmethoxysilane was characterized as follows: ^{1}H NMR ($CDCl_3$) 0.05 (s, 6 H, $SiMe_2$), 1.55 (dt, 2 H, J=8.1, 1.0, $SiCH_2$), 3.23 (s, 3 H, MeO), 4.91 (t, 1 H, J=0.9, CH), 4.93-4.98 (m, 1 H, CH), 5.72-5.88 (m, 1 H, CH). GCFTIR 3086, 2970, 2839, 1258, 1165, 1103, 933, 894, 841, 748. GCMS 130 M^+ (4.0), 115 M^+-CH_3 (10.8), 89 $M^+-C_3H_5$ (100), 59 (74.9). Product 29 was characterized as follows: ^{1}H NMR ($CDCl_3$), 0.05 (s, 6 H, $SiMe_2$), 0.14 (s, 6 H, $SiMe_2$), 1.38 (dd, 2 H, J=5.1, 1.2, $SiCH_2$), 5.66 (dd, 1 H, J=13.8, 1.2, SiCH), 6.83 (dt, 1 H, J= 13.8, 5.1,CH). FTIR 3402, 2955, 2899, 1589, 1250, 1157, 1126, 947, 903, 883, 806, 679. GCMS 171 M^+ (3.6), 156 M^+-CH_3 (100), 130 (15.0), 100 (22.0), 73 (20.5), 70 (24.9), 59 (17.8). Exact MS $C_7H_{17}Si_2N$, measured 171.09003, calculated 171.08996, error +0.4 ppm. Product 30 was characterized as follows: ^{1}H NMR ($CDCl_3$) 0.09 (s, 9 H, $SiMe_3$), 0.29 (s, 6 H, $SiMe_2$). GCMS 290 M^+ (1.9), 275 M^+-CH_3 (100), 187 (5.07), 130 (52.9), 100 (6.0), 73 (5.3). Product 31 was characterized as

follows: ^{1}H NMR ($CDCl_3$) 0.07 (s, 12 H, $SiMe_2$), 0.27 (s, 12 H, $SiMe_2$), 1.54 (dt, 4 H, J=8.1, 1.2$SiCH_2$), 4.91-5.00 (m, 4 H, CH_2), 5.76-5.93 (m, 2 H, CH). GCMS 301 M^+-C_3H_5 (100), 203 (16.2), 130 (78.0), 131 (18.6), 100 (8.7), 73 (14.6). Products 32 and 33 were inseparable under the conditions utilized. They were characterized as follows: ^{1}H NMR ($CDCl_3$) 0.08 (s, 6 H, $SiMe_2$), 0.09 (s, 9 H, $SiMe_3$), 0.25 (s, 3 H, SiMe), 0.30 (s, 6 H, $SiMe_2$), 1.54 (d, 1 H, J=8.1, CH), 1.56 (d, 1 H, J= 8.1, CH), 1.67 (d, 2 H, J=7.8, CH_2), 4.90-5.05 (m, 4 H, CH_2), 5.76-5.99 (m, 2 H, CH). GCMS 301 M^+-C_3H_5(100), 285 (9.6), 245 (7.1), 203 (15.6), 143 (19.5), 130 (33.5) 123 (16.8), 100 (8.5), 73 (14.5). Product 34 was characterized as follows: GCMS 301 M^+-CH_3(7.1), 275 M^+-C_3H_5 (100), 187 (4.7), 143 (15.6), 130 (25.0), 123 (10.4), 100 (5.9), 73 (6.4). Product 35 was characterized as follows: ^{1}H NMR ($CDCl_3$) 0.07 (s, 6 H, $SiMe_2$), 0.09 (s, 9 H, $SiMe_3$), 0.28 (s, 12 H, $SiMe_2$), 1.55 (dt, 2 H, J=7.8, 0.9, $SiCH_2$), 4.95-5.10 (m, 2 H, CH), 5.75-5.95 (m, 1 H, CH). GCMS 301 M^+-CH_3 (6.3), 275 M^+-C_3H_5 (100), 187 (5.3), 130 (43.1), 100 (5.5), 73 (6.6).

Copyrolysis of 22 with hexamethyldisiloxane

A solution of 22 and a 5-fold excess of hexamethyldisiloxane was added dropwise into a vertical pyrolysis tube heated at 540^{0}C with a N_2 flow of 20 ml/min. Trimethylmethoxysilane was the major product with more than 10 unidentified products. Approximately 50% of starting material, 22, was recovered.

Determination of Arrhenius parameters for decomposition of 22

Approximately 0.4 µl of a solution of 22 and a five-fold excess of D_3 in xylene was injected into the reactor by syringe. The data were collected by computer. The rate constants were determined by following the formation of trimethylmethoxysilane. The temparature range studied is 390 to 440°C. The products were separated by a 5' 15% SE-30-CW column.

Table 12. Rate constants for decomposition of 22

T°C	Kx10sec^{-1}	T°C	kx10sec^{-1}	T°C	kx10sec^{-1}
389.7	0.605	402.7	0.897	420.2	2.35
389.3	0.685	407.4	1.71	420.5	2.32
389.6	0.504	409.8	1.57	430.7	3.90
394.8	0.637	411.7	1.55	431.0	3.46
395.0	0.779	412.8	1.20	440.1	6.42
400.0	0.873	413.9	1.03	440.1	6.06
401.0	0.932				

E, 44.78 ±1.17 kcal/mol; log A 13.48 ±0.37; ΔH* 43.40 ±1.17 kcal/mol; ΔS* -0.48 ±1.7 eu at T_{ave}= 411.8°C for reaction order 1.000.

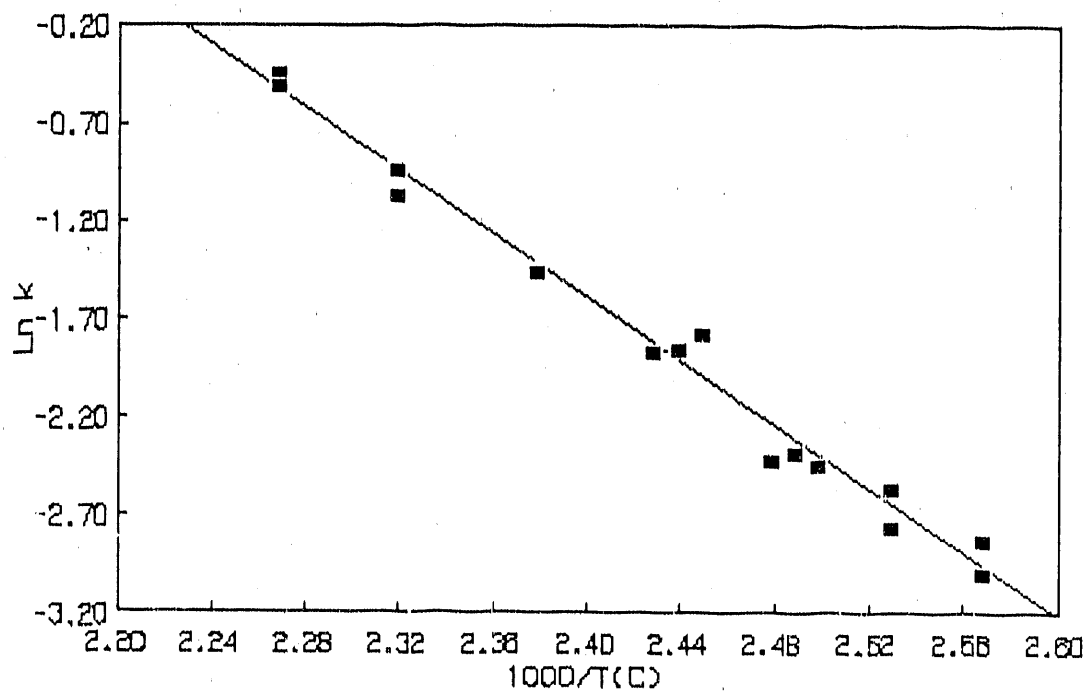


Figure 12. Arrhenius plot for decomposition of 22

Copyrolysis of 22 with D_3

A solution of 22 and a five-fold excess of D_3 in toluene was added dropwise into a vertical pyrolysis tube heated at 545°C with a N_2 flow of 20 ml/min. Trimethylmethoxysilane was the only product detected from GCMS.

Trapping of silanimine 23 by D_3 in a sealed tube

Compound 22 (157 mg) and 3.3 equivalents of D_3 were heated in a sealed tube at 284°C for six hrs. The starting material had decomposed completely. The yields were calculated by using a internal standard (nonane). The pyrolysate contained trimethylmethoxysilane (92.4%), and 7-trimethylsilyl-2-allyl-2,2,4,4,6,8,8-heptamethyl-1,3,5-trioxa-7-aza-2,4,6,8-tetrasilacyclooctane, 42, (88.2%). No other products were detected from GCMS. Product 42 was characterized as follows: ^{1}H NMR ($CDCl_3$) 0.19 (s, 6 H, SiMe), 0.20 (s, 12 H, $SiMe_3$, SiMe), 0.22(s, 3 H, SiMe), 0.34 (s, 3 H, SiMe), 0.35 (s, 3 H, SiMe), 0.36 (s, 3 H, SiMe), 1.82 (d, 2 H, J=8.1, $SiCH_2$), 4.95-5.06 (m, 2 H, CH_2), 5.84-6.02 (m, 1 H, CH). ^{13}C NMR ($CDCl_3$) 1.12, 1.22, 3.25, 4.90, 5.49, 5.53, 28.97, 114.1, 134.8. FTIR 2963, 1632, 1261, 1088, 1015, 918, 802. GCMS M^+ 393 (0.3), 378 M^+-CH_3 (34.6), 352 $M^+-C_3H_5$ (100), 264 (19.2), 73 (36.2). Exact MS $C_{13}H_{35}NO_3Si_5$ measured 393.14555, calculated 393.14634, error -2.0 ppm.

Synthesis of 1,3-diallyl-1,1,3,3-tetramethyldisilazane 41

To a 250 ml three-necked round-bottom flask equipped with a mechanical stirrer, gas in-outlet tube and reflux condenser was added 130 ml of dry hexanes and allyldimethylchlorosilane (20 mmol, 2.69 g). Dry ammonia was bubbled through the solution for 45 min with rapid stirring. White solid (NH_4Cl) was precipitated after ammonia bubbled in. The mixture was stirred for three hrs. at room temperature. The white solid was filtered with the help of celite. Solvent was removed by simple distillation. The yield of 41 was calculated by internal standard nonane to be 73%. It was characterized as follows: ^1H NMR ($CDCl_3$) 0.06 (s, 12 H, $SiMe_2$), 1.49 (dt, 2 H, J=5.1, 0.9, $SiCH_2$), 4.87-4.92 (m, 1 H, CH), 4.93-4.97 (m, 1 H, CH), 5.71-5.88 (m, 1 H, CH). ^{13}C NMR ($CDCl_3$) 0.366, 27.118, 112.860, 135.107. FTIR 3583, 2956, 1631, 1253, 1182, 1153, 1035, 929, 835, 811. GCMS M^+ 213 (0.5), 198 M^+-CH_3 (3.2), 172 $M^+-C_3H_5$ (79.2), 156 (25.6), 130 (100), 116 (27.9), 100 (27.6), 73 (42.6), 59 (41.6). Exact MS: $C_{10}H_{23}NSi_2$, measured 213.13733, calculated 213.13691, error +2.0 ppm.

Flash vacuum pyrolysis of 41

Compound 41 (80 mg) was distilled through the pyrolysis tube at 645°C (5×10^{-5} torr). Clear pyrolysate (71 mg) was collected in 89% mass recovery. (Internal standard: nonane). The pyrolysate contained 29 44.5%, starting material 41 18.2%, dimers 31, 32, 33 7.2%.

Determination of Arrhenius parameters for decomposition of 41

Approximately 0.1 torr 41 was introduced into the reactor. The data were collected by computer. The rate constants were determined by following the formation of propene. The temperature range studied was 490 to 555°C. The products were separated by a 5' 15% SE-30-CW column.

Table 13. Rate constants for decomposition of 41

T°C	$Kx10^2 sec^{-1}$	T°C	$Kx10^2 sec^{-1}$	T°C	$Kx10^2 sec^{-1}$
489.9	0.169	514.9	0.486	539.8	1.365
494.9	0.217	519.9	0.533	545.1	1.583
500.1	0.274	525.0	0.720	549.9	2.050
505.0	0.331	530.0	0.789	549.9	1.995
510.2	0.365	534.5	1.051		

E_a 50.92 ±0.55 kcal/mol; log A 11.80 ±0.15; ΔH^* 49.33 ±0.55 kcal/mol; ΔS^* -8.473 ±0.68 eu at T_{ave}= 528.1°C for reaction order 1.000.

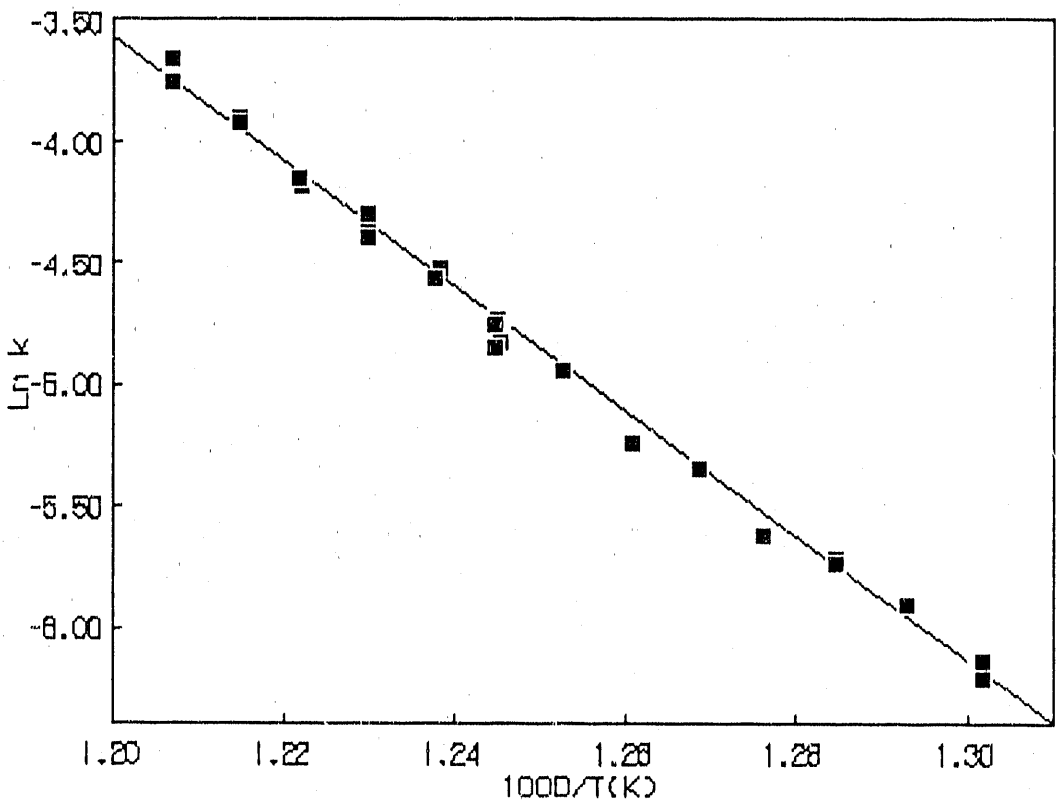


Figure 13. Arrhenius plot for decomposition of 41

Synthesis of N-phenyl-1-allyl-1-methoxy-1,3,3,3-tetramethyldisilazane, 43

Compound 43 was synthesized by the general procedure in 47% yield. It was characterized as follows: ^{1}H NMR (C_6D_6) 0.06 (s, 3 H, SiMe), 0.17 (s, 9 H, $SiMe_3$), 1.51-1.72 (m, 2 H, $SiCH_2$), 3.36 (s, 3 H, MeO), 4.82-4.98 (m, 2 H, CH_2), 5.70-5.87 (m, 1 H, CH), 6.90-7.12 (m, 5 H, Ph). GCMS 279 M^+ (0.8), 264 M^+-CH_3 (5.4), 238 $M^+-C_3H_5$ (100), 223 (34.8), 208 (39.7), 73 (10.4), 59 (19.4).

Flash vacuum pyrolysis of 43

Compound 43 (121 mg) was distilled through a quartz tube at 700°C. The pyrolysate collected, in a liquid N_2 trap, contained trimethylmethoxysilane (34.9%) and an unknown compound with M^+ 189. A yellow residue (43 mg) at the end of the pyrolysis tube was identified by GCMS to be a mixture of cis and trans isomer of 1,3-diphenyl-2,2-diallyl-2,2-dimethylcyclodisilazane, head-to-tail dimer of 44 (56.7%). It was characterized as follows: GCMS 350 M^+ (29.7), 309 $M^+-C_3H_5$ (100).

Trapping of silanimine, 44, by D_3 in a sealed tube

Compound 43 (80 mg) and a 5-fold excess of D_3 were heated in a sealed tube at 305°C for 12 hrs. After heating, the mixture contained D_3, D_4, D_6, trimethylmethoxysilane (14.52%), 6-allyl-7-phenyl-2, 2,4,4,6,8,8-heptamethyl-1,3,5-trioxa-7-aza-2,4,6,8-tetrasilacyclooctane, 45, (7.8%), starting

material, 43, (80.19%) (internal standard: nonane). Product 45 was characterized as follows: ^{1}H NMR ($CDCl_3$) 0.14 (s, 3 H, SiMe), 0.19 (s, 3 H, SiMe), 0.228 (s, 3 H, SiMe), 0.234 (s, 3 H, SiMe), 0.239 (s, 3 H, SiMe), 0.244 (s, 3 H, SiMe), 0.266 (s, 3 H, SiMe), 1.60-1.80 (m, 2 H, $SiCH_2$), 4.88-4.98 (m, 2 H, CH_2), 5.73-5.90 (m, 1 H, CH), 6.90-7.12 (m, 5 H, Ph). GCMS 382 M^+-CH_3 (5.5), 356 $M^+-C_3H_5$ (100), 268 (10.6), 73 (22.4).

Flash vacuum pyrolysis of 48

Compound 48 was distilled through a quartz tube heated at 530°C (5×10^{-5} torr). A clear pyrolysate was collected. N-Allyltrimethylsilane, 52, and methylsilacyclobutene were the major products.

Synthesis of (N-allyl)(trimethylsilyl)allylmethylsilazane, 48, and (N-phenyl)(trimethylsilyl)allylmethylsilazane, 53

To a solution of 20 mmol amine in 50 ml dry Et_2O at -78°C was added dropwise 8.7 ml n-BuLi (20 mmol, 2.3 M in hexanes). The mixture was stirred at -78°C for an additional 1 hr. and transferred into a solution of the 1,1-dichlorotetramethyl-silane in 100 ml of dry Et_2O at -78°C. After the mixture was stirred for 10 min. it was allowed to warm to room temperature and the LiCl formed was filtered. The filtrate was cooled to -78°C and one equivalent of allylmagnesiumchloride (2.0 M in THF) was added. After completing the addition the mixture was stirred at -78°C for 10 min. then allowed to warm to room temperature and stirred for 3 hrs. The solid formed was

removed by filtration and solvent was removed by simple distillation. The liquid residue contained mainly the silazane which was purified by preparatory GC on a 9' 15% SE-30-CW column. Compound 53 was characterized as follows: ^{1}H NMR ($CDCl_3$) 0.115 (s, 9 H, $SiMe_3$), 0.313 (s, 3 H, SiMe), 1.853 (t, 2 H, J=6.9, $SiCH_2$), 3.362 (s, 1 H, NH), 4.890 (d, 1 H, J=9.3, CH), 4.912 (d, 1 H, J=17.1, CH), 5.74-5.88 (m, 1 H, CH), 6.60-6.72 (m, 3 H, Ph) 7.11 (t, 2 H, J=7.8, Ph). ^{13}C NMR ($CDCl_3$) -3.040, -1.419, 23.555, 113.850, 116.180, 117.571, 128.089, 134.104, 147.622. FTIR 3383, 3076, 3040, 2953, 2893, 1620, 1603, 1499, 1475, 1383, 1294, 1246, 1153, 1030, 995, 895, 835, 750, 690. GCMS 249 M^+ (8.91), 251 M^++2 (0.74), 208 $M^+-C_3H_5$ (100), 192 (35.74), 150 (39.60), 134 (22.98), 120 (34.13), 73 (76.27). Exact MS: $C_{13}H_{23}NSi_2$, measured 249.13731, calculated 249.13691, error +1.61 ppm.

Copyrolysis of 53 and 1,3-butadiene

To a vertical pyrolysis tube at 480°C with a mixed flow of 1,3-butadiene (10 ml/min) and nitrogen (18 ml/min), 53 was added very slowly. The collected pyrolysate contained dimers of 1,3-butadiene and the adduct of silylene formed with 1,3-butadiene, 4-methyl-4-phenyl-trimethylsilylamino-4-sila-cyclopent-1-ene, 54. It was characterized as follows: ^{1}H NMR ($CDCl_3$) 0.045 (s, 9 H, $SiMe_3$), 0.182 (s, 3 H, SiMe), 1.135 (d, 2 H, J=17.4, $SiCH_2$), 1.278 (d, 2 H, J=17.4, $SiCH_2$), 5.773 (s, 2 H, CH), 6.853 (d, 2 H, J=7.8, Ph), 6.999 (t, 1 H, J=6.9,

Ph), 7.155 (t, 2 H, J=7.8, 7.2, Ph). ^{13}C NMR ($CDCl_3$) 0.694, 1.642, 18.774, 123.489, 128.636, 129.297, 130.559. FTIR 3016, 2954, 2891, 1606, 1593, 1483, 1252, 1219, 1099, 966, 901, 835, 714, 698, 619. GCMS 261 M^+ (63.1), 246 $M^+-C_3H_5$ (100), 218 (26.7), 192 (77.1), 73 (51.2). Exact MS: $C_{14}H_{23}NSi_2$, measured 261.13688, calculated 261.13691, error -0.1 ppm.

Copyrolysis of 1-methylpyrrole with silylene precursors

A mixture of a 10-fold excess of 1-methylpyrrole and silylene precursor (either tetramethyldimethoxydisilane, pentamethylmethoxydisilane, or hexachlorodisilane) was added dropwise into a vertical pyrolysis tube with a N_2 flow of 20 ml/min. The pyrolysate was collected in a cool trap at -78°C and then analyzed by GCMS.

Synthesis of 1-(N,N-dimethylamino)-4-methoxy-2-butyne[82] 68

A mixture of 3.57 g (120 mmol) dry paraformaldehyde and 3.76 g (84 mmol) dimethylamine in 10 ml THF was stirred at 0°C for 5 min. and at room temperature for 30 min. To the mixture 0.29 g (1.6 mmol) $Cu(AcO)_2$ was added followed by the addition of methylpropargyl ether (4.2 g, 60 mmol). A greenish yellow solid appeared. The mixture was gradually heated to 90°C in about 25 min and kept at 90°C until the greenish suspension changed to brown (about 40 min). The mixture was cooled to room temperature and 0.5 g KOH in 5 ml water was added. The organic layer was extracted with ether and dried over Na_2SO_4. The solvent was removed by rotory evaporater, the remaining

liquid contained 95% of 68 by GC, which was used for next reaction without further purification (6.7 g, 88%). Product 68 was characterized as follows: ^{1}H NMR ($CDCl_3$) 2.29 (s, 6 H, NMe_2), 3.29 (t, 2 H, J=1.8, NCH_2), 3.38 (s, 3 H, MeO) 4.13 (t, 2 H, J=1.8, OCH_2). GCMS 127 M^+ (20), 126 M^+-1 (24), 82 (40), 42 (100).

Synthesis of 1-(N,N-dimethylamino)but-2-en-3-yne[82] 69

To a 50 ml round-bottom flask charged with 6 ml liquid NH_3 and a catalytic amount of ferric nitrate at -78°C under N_2 atmosphere, small pieces of potassium (1.6 g, 41 mmol, cut and weighed under mineral oil) were added piece by piece (washed with dry hexanes before being added into the flask). To the solution of potassium amide in liquid NH_3 was added 2 g (16 mmol) 68 and the mixture was stirred for 2 additional hours. Then 1.8 g (32 mmol) solid ammonium chloride was added. The ammonia was evaporated by placing the flask in a water bath at 40°C. Extracted the residue with ether several times. The product 69 was distilled at 32-34°C/5 mmHg (1.36 g, 89%). It was characterized as follows: ^{1}H NMR ($CDCl_3$) 2.70 (d, 1 H, J=2.1, CH), 2.74 (s, 6 H, NMe_2), 4.026 (dd, 1 H, J=13.5, 1.8, CH), 6.677 (d, 1 H, J=13.8, CHN). GCMS 96 M^++1 (100), 95 M^+ (97.0).

Synthesis of 1-pentamethyldisilyl-4-dimethylaminobut-3-en-1-yne 70

To a solution of 0.4 g (4.2 mmol) 69 in 6 ml THF at 0°C, n-BuLi (4.2 mmol, 1.7 M in hexanes) was added dropwise. After the mixture was stirred at 0°C for 10 min 0.7 g (4.2 mmol) pentamethylchlorodisilane was added at 0°C. The mixture was stirred at 0°C for 10 min. then at room temperature for an additional 30 min. To the reaction mixture 3 ml of saturated ammonium chloride was slowly added. White solid was filtered out and the organic layer was washed with 3 ml brine and dried over Na_2SO_4. Removal of solvent by trap-to-trap vacuum distillation (0.2 mmHg, 110°C oil bath temperature) afforded 0.7 g 70 (74%). It was characterized as follows: ^1H NMR ($CDCl_3$) 0.08 (s, 9 H, $SiMe_3$), 0.14 (s, 6 H, $SiMe_2$), 2.68 (s, 6 H, NMe_2), 4.10 (d, 1 H, J=15, CH), 6.62 (d, 1 H J=15, CH). ^{13}C NMR ($CDCl_3$) -2.433, -2.053, 40.074, 74.406, 86.770, 109.256, 150.539. FTIR 3049, 2953, 2895, 2114, 1626, 1371, 1244, 1113, 835, 798, 764. GCMS 225 M^+ (22.4), 210 M^+-CH_3 (58.9), 184 (42.5), 152 (42.2), 94 (100), 73 (92.9), 59 (51.9). Exact MS: $C_{11}H_{23}NSi_2$, measured 225.13726, calculated 225.13691, error +1.55 ppm.

Attempted synthesis of 1-dimethylamino-1-pentamethyldisilyl-1,3-butadiene 66

a) To a solution of 60 mg (0.27 mmol) 70 in 0.5 ml THF was added 0.27 ml (0.27 mmol, 1 M in hexane) diisobutylaluminum

hydride (DIBAL). The mixture was heated at 60°C for 20 hr. After work up only starting material 70 was detected.

b) To a solution of 30 mg (0.18 mmol) cyclohexene in 0.4 ml THF was added 0.09 ml (0.09 mmol, 1 M in THF) borane. To the suspension of dicyclohexylborane, 20 mg (0.09 mmol) 70 was added and stirred at 0°C for 0.5 hr., then at room temperature for 4 hrs. To the reaction mixture 2 ml of glacial acetic acid was added and the mixture was stirred at room temperature for 2 hrs. The mixture was poured into ice water and the organic layer was washed with 20% aqueous sodium hydroxide, saturated $NaHCO_3$, and brine. Starting material 70 was completely consumed with no desired product.

c) To a suspension of 0.13 g $HZr(Cl)Cp_2$ in 0.2 ml dry benzene, compound 70 (93 mg, 0.4 mmol) was added at room temperature. After the mixture was stirred at room temperature for 8 hrs., 40°C for 12 hrs., GCMS showed that the mixture contained no starting material nor desired product.

d) To a solution of 100 mg (1.05 mmol) 69 in 0.2 ml heptane was added 1.05 ml DIBAL. The mixture was heated to 50°C for 2 hrs., then cooled at 0°C and 0.7 ml (1.05 mmol) MeLi was added. The mixture was quenched with 175 mg (1.05 mmol) pentamethylchlorodisilane. GCMS showed that the starting material 69 was completely consumed and showed no desired product in the mixture.

e) To a solution of 475 mg (5 mmol) 69 and one drop

chloroplatinic acid (10% in THF) in ether at 0°C, 480 mg (5 mmol) dimethylchlorosilane was added slowly. The reaction mixture turned to dark gum immediately. After warming to 45°C overnight the mixture was extracted with ether. One compound in the ether extract was identified as 1-(N,N-dimethylamino)-4-dimethylsilylbut-1-en-3-yne, 71. It was characterized as follows: ^{1}H NMR ($CDCl_3$) 0.18 (d, 6 H, J=4.0, $SiMe_2$), 2.70 (s, 6 H, NMe_2), 4.06 (db, 1 H, J=13.5, CH), 4.15 (heptet,d, 1 H, J=3.6, 0.6, SiH), 6.67 (d, 1 H, J=13.5, CH). GCMS 153 M^+ (55), 138 M^+-CH_3 (46), 113 (38), 110 (37), 95 (53), 94 M^+-Me_2SiH (100), 83 (18), 74 (23), 59 (26).

Synthesis of propargyl alcohol THP ether, 74

To a solution of 1.4 g (20 mmol) propargyl alcohol and dihydropyrane in 40 ml methylene chloride was added 19 mg p-toluenesulfonic acid monohydrate at 20°C and the mixture was maintained at 20°C for 1.5 hrs. It was then diluted with 60 ml ether and the mixture was washed with 12 ml saturated sodium bicarbonate followed by two portions of 12 ml brine. The organic phase was dried over $MgSO_4$. The solvent was removed by rotary evaporator. The residue was distilled at 48-55°C/1-1.5 mmHg to obtain 3.04 g 74 (99%).

Synthesis of 1-pentamethyldisilylpropargylalcohol THP ether, 75

To a solution of 1.01 g (6.56 mmol) 74 in 8 ml THF at 0°C was added 3 ml (6.56 mmol) n-BuLi. After the mixture was

stirred at 0°C for 15 min., one equivalent of pentamethylchlorodisilane was added. After the mixture was stirred at 0°C for 40 min. and at room temperature for 20 min. it was quenched with ammonium chloride, washed twice with saturated sodium chloride, and dried over sodium sulfate. After removal of solvent the product was purified by liquid chromatography. Eluent I (6:1 hexanes:cyclohexane) was used to get rid of impurity. Eluent II (10:1 hexanes:ethyl acetate) was used to elute the product 75 (84%). It was characterized as follows: FTIR 2956, 2900, 2162, 1246, 1038, 830, 800. GCMS 211 (8), 85 (100), 73 (70).

Reduction of 75 and synthesis of 1-petamethyldisilyl-1-buten-4-ol, 77

A mixture of cyclohexene (0.58 g, 7.0 mmol) and borane (3.5 mmol, 1 M in THF) were stirred in 3 ml THF at 0°C for one hr. To the mixture 1.0 g (3.5 mmol) 75 was added slowly. After stirring at 0°C for 30 min. and at room temperature for 4 hr, 2 ml glacial acetic acid was added to the mixture. The reaction mixture was stirred for an additional 2 hrs. then poured into ice water. The organic layer was washed with 20% aqueous sodium hydroxide, saturated $NaHCO_3$, and brine, and dried over Na_2SO_4. Product 76 was purified by liquid chromatography (4:1:1 hexanes:ethyl acetate:ether) (88%). Deprotection of 76 was accomplished by stirring 0.51 g (1.8 mmol) 76 and 0.05 g (0.18 mmol) pyridinium p-toluenesulfonate

(PPTS) in 15 ml ethanol at 55°C for three hrs. and at room temperature for 5 hrs. The solvent was removed and the residue was purified by liquid chromatograph (4:1:1 hexanes:ethylacetate:ether) to give product 77 (100%). It was characterized as follows: ^{1}H NMR ($CDCl_3$) 0.036 (s, 9 H, $SiMe_3$), 0.149 (s, 6 H, $SiMe_2$), 1.283 (t, 1 H, J=6.0, OH), 2.34 (q, 2 H, J=6.6, CH_2), 3.43 (t, 2 H, J=6.0, OCH_2), 5.64 (dd, 1 H, J=1.2, 13.8, CHSi), 6.27 (dt, 1 H, J=13.8, 6.6, CH). ^{13}C NMR ($CDCl_3$) -2.487, -2.100, 37.185, 62.272, 131.688, 143.788. FTIR 3327, 2950, 2893, 1603, 1408, 1244, 1046, 1025, 869, 833, 801, 768. Ammonia CI MH^+ 203 (10.73), 148 (100). Exact MS: (M^+-1) $C_9H_{21}OSi_2$, measured 201.11264, calculated 201.11310, error -2.27 ppm.

Preparation of PPTS

p-Toluenesulfonic acid monohydrate (11.4 g, 60 mmol) was slowly added to pyridine (23.7 g, 3.0 mmol) at room temperature. After stirring for 20 min. the excess pyridine was removed by a rotary evaporator at 60°C. The remaining colorless crystals were recrystallized from acetone giving 10 g white crystal with a melting point of 118-121°C (literature 120°C[89]) (63%).

Attempted synthesis of 4-pentamethyldisilyl-3-butenaldehyde, 78

a) Chromium trioxide was added[90] to a magnetically stirred solution of pyridine in 30 ml methylene chloride. The deep

burgundy solution was stirred for 15 min. at room temperature, then 0.3 g (1.48 mmol) 77 in 0.5 ml methylene chloride was added in one portion at 0°C. The mixture was stirred at 0°C for an additional 15 min then warmed to room temperature. The liquid was decanted from the residue, which was washed with 40 ml ether. The combined organic phase was washed with three 20 ml portions of 5% sodium hydroxide, 20 ml 5% aqueous HCl, 20 ml 5% $NaHCO_3$, and 20 ml saturated sodium chloride. The mixture obtained did not contain the desired aldehyde according to GCMS.

b) Under Ar gas a mixture of 5 ml dichloromethane and 0.56 g (4.4 mmol) oxalyl chloride was placed[91] in a 25-ml three-neck round-bottom flask equipped with a thermometer. dimethyl sulfoxide (0.75 g, 9.6 mmol), diluted with 1 ml methylene chloride, was added to the stirred oxalyl chloride solution at -50 to -60°C. The reaction mixture was stirred for 2 min. and 0.4 g (2 mmol) 77 in 2 ml methylene chloride was added within 5 min. The mixture was maintained at -50 to -60°C for 15 min. then 1.1 g (10 mmol) Et_3N was added. After stirring for 5 min. the reaction mixture was allowed to warm to room temperature. Water (10 ml) was added and the aqueous layer was reextracted with additional methylene chloride. The combined organic layer was sequentially washed with 1% HCl, 5% $NaHCO_3$ and brine. No desired product was detected by GCMS.

Synthesis of 1-trimethylsilyl-2,2-dimethyl-6-phenyl-1-aza-2-silahexa-3,5-diene, 81

3-Trimethylsilylsiletene 83 and a 10-fold excess of benzonitrile was added slowly into a vertical pyrolysis tube heated at 480°C with a nitrogen flow of 20 ml/min. Products 81 and 82 were the major products with a ratio about 7:1. Product 81 was characterized as follows: ^{1}H NMR ($CDCl_3$) -0.18 (s, 9 H, $SiMe_3$), 0.25 (s, 6 H, $SiMe_2$), 5.63 (d, 1 H, J=13.2, CH), 5.845 (d, 1 H, J=6.0, CH), 6.77 (dd, 1 H, J=13.2, 6.0, CH), 7.20-7.31 (m, 3 H, Ph), 7.35-7.41 (m, 2 H, Ph). ^{13}NMR ($CDCl_3$) -0.65, 3.53, 115.2, 121.0, 127.5, 127.6, 128.0, 140.7, 144.2, 148.0. FTIR 3059, 2981, 2951, 1585, 1572, 1521, 1487, 1321, 1258, 1070, 984, 962, 891, 847, 764, 700, 650. GCMS 273 M^+ (50.7), 258 M^+-CH_3 (100), 73 (83.2), 59 (16.5). Product 82 was characterized as follows: ^{1}H NMR ($CDCl_3$) 0.10 (s, 9 H, $SiMe_3$), 0.26 (s, 6 H, $SiMe_2$), 4.04 (broad 1 H, NH), 5.34 (dd, 1 H, J=6.3, 1.8, CH), 7.17 (d, 1 H, J=6.3, CH), 7.27-7.36 (m, 3 H, Ph), 7.41-7.47 (m, 2 H, Ph). FTIR 3400, 3061, 2953, 2894, 1597, 1512, 1491, 1389, 1243, 885, 837, 777, 762, 696. GCMS 273 M^+ (54.8), 258 M^+-CH_3 (100), 156 (63.1), 73 (32.9), 59 (11.9).

Reaction of 81 with hexafluorobut-2-yne

Compound 81 (79 mg) and a excess of hexafluorobut-2-yne was degassed and sealed in a tube and heated at 55-60°C for 15 days. Over 70% of the starting material had decomposed. Two

major products, 2,3-bistrifluoromethylbiphenyl 87 and an adduct 88 or 89 were isolated by preparative GC with a 4' 5% SE-30-CW column. Product 87 was characterized as follows: ^{1}H NMR ($CDCl_3$) 7.25-7.44 (m, 5 H, Ph), 7.51 (d 1 H, J=7.8, CH), 7.64 (t, 1 H, J=7.8, CH), 7.86 (d, 1 H, J=7.8, CH). GCMS 290 M^+ (100), 269 (13.1), 251 (11.6), 221 (14.4), 201 (53.0), 152 (11.7), 125 (29.5), 100 (10.3). Product 88 or 89 was characterized as follows: ^{1}H NMR ($CDCl_3$) -0.13 (s, 9 H, $SiMe_3$), 0.294 (s, 6 H, $SiMe_2$), 5.87 (d, 1 H, J=6.0, CH), 6.14 (dq, 1 H, J=7.5, 1.5, CH), 6.59 (d, 1 H, J=6.0, CH), 7.26-7.42 (m, 5 H, Ph). FTIR 3082, 2959, 1528, 1265, 1180, 1144, 839, 762, 698, 677, 652. MS 435 M^+ (21.1), 420 M^+-CH_3 (0.8), 176 (8.5), 77 (35.1), 73 (100), 59 (3.3). Exact MS: $C_{19}H_{23}NF_6Si_2$, measured 435.12653, calculated 435.12733, error -1.8 ppm.

Synthesis of 1-pyrrolyl-1-methoxy-1,2,2,2-tetramethyldisilane, 93

To a solution of 3.35 g (50 mmol) pyrrole in 25 ml dry ether at -78°C was added 22 ml of n-BuLi (50 mmol, 2.3 M in hexanes). The mixture was stirred at -78°C for 30 min. The yellowish milky mixture was slowly transferred to a solution of 9.3 g (50 mmol) 1,1-dichlorotetramethyldisilane in 50 ml ether at -78°C. The reaction mixture was stirred at -78°C for 10 min. then allowed to warm to room temperature and stirred overnight. To the stirred solution with a suspension of gray

solid, 150 ml hexanes was added and cooled to 0°C. A mixture of 20 ml methanol and 30 ml pyridine in 70 ml hexanes was added. The reaction mixture was then allowed to warm to room temperature and stirred at room temperature for additional 60 min. The top-layer, mainly solvent and product, was separated from the dark oily bottom layer. The solvent was removed by rotary evaporator and vacuum distilled at 59-63°C/0.8-1.2 mmHg to obtain 6.7 g 93 (63%). Also, about 1 g 1,1-dipyrrolyltetramethyldisilane was obtained. Product 93 was further purified by preparative GC with a 9' 15% SE-30-CW column. It was characterized as follows: ^{1}H NMR ($CDCl_3$) 0.14 (s, 9 H, $SiMe_3$), 0.50 (s, 3 H, SiMe), 3.40 (s, 3 H, MeO), 6.32 (t, 2 H, J=1.8, CH), 6.80 (t, 2 H, J=1.8, CH). ^{13}C NMR ($CDCl_3$) -2.588, -2.262, 50.807, 110.982, 122.847. GCFTIR 2962, 1470, 1257, 1198, 1080, 840, 784. GCMS 213 M^+ (32.0), 198 M^+-CH_3 (100), 182 (28.8), 168 (22.0), 140 (25.5), 73 (63.6), 59 (77.1). Exact MS: $C_9H_{19}ONSi_2$, measured 213.10067, calculated 213.10052, error +0.68 ppm.

Flash vacuum pyrolysis of 93

Compound 93 (400 mg) was distilled through a quartz tube heated at 610°C (1×10^{-4} torr). A yellowish pyrolysate (150 mg) was collected. Trimethylmethoxysilane was the major product. The yellow wax-like products that accumulated at the end of pyrolysis tube were washed out with deuterated benzene. ^{1}H NMR showed only two broad peaks at chemical shift of 6-7

and 0-1.5 ppm.

Copyrolysis of 93 and 1,3-butadiene

To a vertical pyrolysis quartz tube at 480°C with 1,3-butadiene as carrying gas at a flow of 15 ml/min, 93 was dripped very slowly. The pyrolysate collected by a trap at -78°C contained trimethylmethoxysilane, 93, dimers of 1,3-butadiene, and an adduct, 1-pyrrolyl-1-methyl-1-silacyclopent-3-ene 96. It was characterized as follows: GCMS 163 M^+ (100), 148 M^+-CH_3 (51.2), 97 (73.6), 96 (90.7), 94 (94.2), 67 (51.2).

Copyrolysis of 93 and 2,3-dimethyl-1,3-butadiene

A mixture of 93 (308 mg, 145 mmol) and a 10-fold excess of 2,3-dimethyl-1,3-butadiene was dripped slowly into a vertical pyrolysis tube at 520°C with a N_2 flow of 20 ml/min. The deep yellow pyrolysate (1.1 g, 74% mass recovery) contained trimethylmethoxysilane (52%, according decomposed starting material), 93 (31%), and adduct, 1-pyrrolyl-1,3,4-trimethyl-1-silacyclopent-3-ene 97 (17%). The products were separated on a preparative GC with a 9' 15% SE-30-CW column. Product 97 was characterized as follows: ^1H NMR ($CDCl_3$) 0.23 (s, 3 H, SiMe), 1.20-1.55 (m, 4 H, $SiCH_2$), 1.61 (t, 6 H, J=1.2, Me), 6.53 (t, 2 H, J=1.8, CH), 6.79 (t, 2 H, J=1.8, CH). GCFTIR 3128, 2982, 2920, 1565, 1423, 1189, 1083, 805, 730. GCMS 191 M^+ (100), 176 M^+-CH_3 (38.7), 123 (97.6), 109 (72.1), 67 (33.7).

Synthesis of 1-(N-methylanilino)-1-methoxy-1,2,2,2-tetramethyldisilane, 99

To a solution of 2.14 g (20 mmol) of N-methylaniline in 50 ml dry ether at -78°C was slowly added 8.7 ml (20 mmol) n-BuLi. White solid appeared during the addition. The mixture was stirred at -78°C for additional one hour after addition of n-BuLi, then transferred to a solution of 1,1-dichlorotetramethyldisilane in 100 ml dry ether at -78°C. After the anion solution was transferred the white solid disappeared. The mixture was stirred at -78°C for 10 min. then warmed to room temperature and stirred overnight. To the mixture at -78°C a solution of 0.64 g (20 mmol) methanol and 2.02 g (20 mmol) triethylamine in 20 ml dry ether was slowly added. The mixture was then warmed to room temperature and the solid was removed by filtration. The solvent was removed by rotary evaporator. The residue was mainly the desired product 99 (3.1 g, 61%). It was further purified by preparative GC on a 9' 15% SE-30 on 80-100 mesh chromosorb W column. It was characterized as follows: ^{1}H NMR ($CDCl_3$) 0.00 (s, 9 H, $SiMe_3$), 0.32 (s, 3 H, SiMe), 2.97 (s, 3 H, NMe), 3.45 (s, 3 H, MeO), 6.75-7.22 (m, 5 H, Ph). GCMS 253 M^+ (10.0), 238 M^+-CH_3 (53.8), 180 (82.7), 148 (21.8), 134 (35.2), 75 (72.3), 73 (75.3), 59 (100).

Flash vacuum pyrolysis of 99

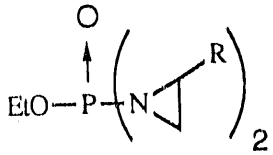
Compound 99 was distilled through a horizontal pyrolysis tube at 715°C (4×10^{-5} torr). Clear pyrolysate with white crystals were collected in the cold trap and yellow wax-like material accumulated at the exit of the pyrolysis tube. Analytical GC analysis showed five major components which were not identifiable by GCMS. Attempts to separate them by preparative GC were not successful. The clear pyrolysate contained mainly trimethylmethoxysilane. After the volatile products were removed by vacuum distillation, ^{1}H NMR and MS of the white solid showed that it was hexahydrotriphenyltriazine 100 (melting point 135-9°C).[86] It was characterized as follows: ^{1}H NMR ($CDCl_3$) 4.85 (s, 6 H, NCH_2N), 6.5-7.2 (m, 15 H, Ph). MS 315 M^+ (1.3), 210 (13.3), 105 (100), 77 (46.7).

Copyrolysis of 99 and 2,3-dimethyl-1,3-butadiene

A solution of 257 mg (1.02 mmol) 99 and a 10-fold (834 mg, 10.16 mmol) excess of 2,3-dimethyl-1,3-butadiene was added dropwise into a vertical pyrolysis tube at 490°C with a N_2 flow of 23 ml/min. The collected pyrolysate contained 99, trimethylmethoxysilane, N-methylaniline, and dimers of 2,3-dimethyl-1,3-butadiene. No adduct of silylene generated and 2,3-dimethyl-1,3-butadiene was detected by GCMS.

Synthesis of 1,1-bis(2-methylaziridinyl)tetramethyldisilane, 113

To a stirred solution of 0.57 g (10 mmol) aziridine in 15 ml ether at -78°C was added 5.5 ml (8.8 mmol, 1.6 M in ether) MeLi. The mixture was stirred at -78°C for 1 hr. To the aziridine anion solution 0.88 g (5 mmol) 1,1-dichlorotetramethyldisilane was slowly added at -78°C and stirred for 10 min. then warmed to room temperature. During the addition of the $Me_3SiSiMeCl_2$ The color of the mixture changed to yellow and a suspension developed. The mixture was stirred at room temperature for 1.5 hrs. The solid was removed by filtration and the solvent was removed by simple distillation. The product 113 was vacuum distilled at 70-74°C/0.5 mmHg (22%). It was characterized as follows: GCMS 228 M^+ (0.4), 227 M^+-1 (1.6), 213 (6.2), 171 (37.0) , 130 (100), 114 (42.4), 73 (95.0), 59 (59.5). ^1H NMR of 93 is very complex. The same result was obtained by Perlman and Bardos[92] on their synthesis of C-substituted phosphoraziridines 127.



127

Flash vacuum pyrolysis of 113

Compound 113 was distilled through a pyrolysis tube at 530°C (5×10^{-5} torr). All apparatus used was flame-dried

before using. The pyrolysate contained 113, propene, 1-trimethylsilyl-2-methylaziridine, 114, and decomposition products from 114.

Synthesis of 1,3-bis(trimethylsilyl)-3-dimethoxysilyl-propene,[45] 121

To a stirred solution of 1,3-bis(trimethylsilyl)propene (2.3 g, 12.4 mmol) in 25 ml ether at 0°C, was added 1.7 g (15 mmol) TMEDA followed by n-BuLi (16 mmol, 2.2 M in hexanes). After stirring at 0°C for 4.5 hrs., the anion was transferred to a mechanically stirred solution of trichloromethylsilane (6.5 g, 43.4 mmol) in 100 ml ether at 0°C and stirred for 20 min., then at room temperature for 50 min. To the mixture with white solid 150 ml hexanes was added followed by a solution of 4 ml methanol and 6 ml pyridine in 20 ml hexanes. After stirring for ~30 min. at room temperature the pyridium hydrochloride salt was removed via filtration. The filtrate was concentrated and 121 was distilled at 65-67°C/0.2 mmHg (1.85 g, 51%). It was characterized as follows: ^{1}H NMR ($CDCl_3$) -0.01 (s, 9 H, $SiMe_3$), 0.00 (s, 9 H, $SiMe_3$), 0.09 (s, 3 H, SiMe), 1.44 (d, 1 H, J=11.1, CH), 3.45 (s, 3 H, MeO), 3.46 (s, 3 H, MeO), 5.38 (d, 1 H, J=18, CH), 5.89 (dd, 1 H, J=18, 11.1, CH). GCMS 290 M^+ (30.7), 275 M^+-CH_3 (41.4), 186 (56.2), 171 (23.0), 143 (32.3), 117 (35.4), 75 (40.8), 73 (100), 59 (52.9).

Synthesis of 3-methyl-3-methoxy-4-trimethylsilyl-3-silacyclobutene,[45] 120

FVP of 121 through a pyrolysis tube at 610°C afforded 120 with undecomposed 121. The product was purified by preparative GC. It was characterized as follows: ^{1}H NMR ($CDCl_3$) -0.03, -0.07 (s, 9 H, $SiMe_3$), 0.298, 0.304 (s, 3 H, SiMe), 1.36 (d, 1 H, SiCH), 1.53 (d, 1 H, SiCH), 3.46, 3.50 (s, 3 H, MeO), 6.03 (dd, 1 H, J=7.8, 2.7, CH), 6.09 (d, 1 H, J=7.5, CH), 7.06-7.51 (m, 1 H, CH). GCMS 186 M^+ (18.8), 171 M^+-CH_3 (37.9), 143 (87.1), 117 (78.8), 89 (59.2), 73 (73.6), 59 (100).

Attempted synthesis of 1-trimethylsilyl-2-methyl-2-methoxy-1-aza-2-silacyclohexa-3,5-diene 95 and obtaining evidence for silapyridine, 95

Copyrolysis of 120 and a 5-fold excess of benzonitrile at 500°C with a N_2 flow of 20 ml/min affordeded benzonitrile and trimethylmethoxysilane as the major product. The volatile components of the pyrolysate were removed by vacuum distillation. ^{1}H NMR spectra of the yellow residue showed that it was a mixture and did not correspond to the dimers of silapyridine.

A 5-fold excess of benzonitrile and 120 were heated in a sealed tube at 300°C for 10 min. The starting material 120 had decomposed completely. Trimethylmethoxysilane was the major product. A trace amount of product corresponding to the

adduct of the generated silapyridine to 120 was detected by GCMS. However, it was not isolable by preparative GC.

Synthesis of triallylmethylsilane,[88] 124

A 2 L three-necked round bottom flask, equipped with a mechanical stirrer, a condenser and a pressure equilibrium additional funnel, was filled with 950 ml dry ether and 38.4 g (1.6 mol) magnesium. Allylbromide (181 g, 1.5 mol) was slowly added. After completing the addition, the mixture was stirred at room temperature for 30 min. Trichlorosilane (75 g, 0.5 mol) was added at a rate sufficiant to keep the mixture at a gentle reflux. After addition the slurry was refluxed for 2 hrs. The excess magnesium was removed by filtration. The filtrate was quenched with 200 ml of half-saturated NH_4Cl. The aqueous layer was extracted with 2-portions of 100 ml ether. The conbined organic layer was dried over $MgSO_4$. Vacuum distillation at 75°C/15 mmHg afforded 51.9 g 124 (63%). It was characterized as follows: ^1H NMR ($CDCl_3$) -0.03 (s, 3 H, SiMe), 1.54 (dt, 6 H, J=8.1, 0.9, $SiCH_2$), 4.81 (t, 3 H, J=0.9, CH), 4.83-4.89 (m, 3 H, CH), 5.65-5.83 (m, 3 H, CH). GCMS 166 M^+ (0.7), 125 $M^+-C_3H_5$ (23.4), 97 (100), 83 (46.4), 59 (14.1).

Synthesis of 3-allyl-3-methyl-3-silacyclobutene,[88] 125

Triallylmethylsilane 124 (2.52 g) was distilled through a pyrolysis tube at 660°C (2×10^{-4} torr). The yellow pyrolysate contained propene, allylmethylsilacyclobutene 124

and starting material. Distillation at 84-88°C/82 mmHg afforded 0.6 g 124 (23%). It was characterized as follows: ^{1}H NMR (C_6D_6) 0.21 (s, 3 H, SiMe), 1.46 (dd, 1 H, J=16.5, 1.8, CH), 1.57 (dd, 1 H, J=16.5, 1.8, CH), 1.65 (dd, 2 H, J=8.1, 0.9, CH), 4.86-4.97 (m, 2 H, CH_2), 5.68-5.86 (m, 1 H, CH), 6.19 (d, 1 H, J=7.5, CH), 7.05 (dt, 1 H, J=7.5, 1.8, CH). GCMS 124 M^+ (0.4), 109 M^+-CH_3 (12.9), 96 (56.3), 83 (100), 55 (54.4).

Synthesis of 2-allyl-2-methyl-6-phenyl-1-aza-2-silacyclohexa-3,5-diene, 116a

a) Copyrolysis of 124 and a 10-fold excess of benzonitrile in a vertical pyrolysis tube at 400-405°C with a N_2 flow of 18 ml/min afforded a deep yellow pyrolysate. Compound 124 had completely decomposed. No desired product was observed by GCMS.

b) Heating 124 and a 5-fold excess of benzonitrile in a sealed tube at 230°C for 1 hr. afforded 116a as major product. It was purified by preparative GC with a 4' 5% SE-30-CW column and was characterized as follows: ^{1}H NMR (C_6D_6) 0.19 (s, 3 H, SiMe), 1.60 (t, 2 H, J=6.9, $SiCH_2$), 3.83 (broad 1 H, NH), 4.80-5.03 (m, 2 H, CH_2), 5.36 (dd, 1 H, J=6.9, 1.8, CH), 5.53 (dd, 1 H, J=14.1, 1.8, CH), 5.68-5.84 (m, 2 H, CH), 7.05-7.12 (m, 3 H, Ph), 7.28-7.33 (m, 2 H, Ph). GCMS 227 M^+ (7.4), 186 $M^+-C_3H_5$(100), 108 (37.7), 93 (16.5), 82 (13.3), 77 (13.2).

Attempts to generate 3-methyl-6-phenylsilapyridine, 95b

Compound 116a and dodecane (as diluting reagent) were heated in a sealed tube at 300°C for 1 hr. 116a had completely decomposed and no silapyridine or its dimers were detectable by GCMS.

Synthesis of 2-allyl-2,6-dimethyl-1-aza-2-silacyclohexa-3,5-diene, 116b

Compound 124 and a 5-fold excess of acetonitrile in a sealed tube at 220°C for 1.5 hr. afforded 116b as major product with complete consumption of 124. Compound 116b was purified by preparative GC on a 4' 5% SE-30-CW column. It was characterized as follows: ^{1}H NMR (C_6D_6) 0.15 (s, 3 H, SiMe), 1.29 (m, 2 H, $SiCH_2$), 1.51 (s, 3 H, Me), 4.80 (dt, 1 H, J=6.0, 0.9, CH), 4.87-4.96 (m, 2 H, CH_2), 5.35 (dd, 1 H, J=12.1, 2.4, CH), 5.67-5.84 (m, 1 H, CH), 7.02 (dd, 1 H, J=14.1, 6.6, CH). GCMS 165 M^+ (12.3), 124 $M^+-C_3H_5$ (100), 96 (18.4).

Attempted generation 2,6-dimethylsilapyridine, 95c

a) Compound 116b was pyrolysized at 600°C under SFR conditions. Propene was the major product. A few higher boiling point products were observed in GC trace after starting material but were unable to be transferred into the mass spectrometer.

b) Flash vacuum pyrolysis of 116b at 627°C (5×10^{-5} torr) afforded an orange colored pyrolysate which contained a mixture by ^{1}H NMR analysis. There were a few crystals in the

trap which did not dissolve in benzene, or other common solvents. The crystals were washed by benzene and dried under reduced pressure. The mass spectrum of the solid did not correspond to dimer of silapyridine.

c) Heating 116b in a sealed tube at 285°C for 40 min. afforded starting material (90%) and propene as the only volatile product. An orange glass-like solid, the same as from procedure b, was also observed.

d) Heating 116b with a 3-fold excess of D_3 in a sealed tube at 300°C for 2 hrs. afforded propene, D_3, D_4, D_6 and a dark tar with complete decomposition of starting material.

CONCLUSIONS

An attempt was made to observe the effects of a silyl group on the olefin-carbene thermal isomerization and gas phase cis-trans isomerization was studied. This is the first experimental investigation on this subject.

Simple olefins do not undergo thermally induced 1,2-alkyl migration to form carbenes. No evidence was obtained that silyl substitution on the olefin would facilitate this olefin-carbene isomerization.

A trimethylsilyl group lowers the cis-trans isomerization activation energy by 6-7 kcal/mol compared with the methyl group, and an additional silyl group lowers it an additional 4 kcal/mol. Stabilization of 0.5-2 kcal/mol was found from a trimethylsilyl group compared with phenyl and t-butyl groups. The activation energies and log A's of compounds studied were in the normal range of olefinic cis-trans isomerization and consistent with the singlet mechanism.

The gas phase thermal isomerization of silacyclobutene and silylallene was discovered. The mechanism of the isomerization was studied. The deuterium-labeling experiments were consistent with a mechanism of 1,3-hydrogen shift of the intermediate silabuta-1,3-diene.

Silanimines were generated in gas phase. Head-to-tail dimerization was the main reaction in the absence of a trapping reagent. A allyl substituted on the silicon next to

the silicon-nitrogen double bond led to a rearrangement product, which is a new compound and can be obtained in high yield.

Under the conditions studied, trimethylsilylsilanimine isomerizes to aminosilylene and allylsilanimine does not. Attempts to generate silanimine by a 1,2-shift of aminosilylene and by retrograde Diels-Alder reaction were not successful. Evidence for generating silapyridine, a compound unknown both theoretically and experimentally, was not obtained.

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