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Catalytic dehydrogenation condensation of silyl hydrides and amines: thermal decomposition of silazanes and polysilazanes

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Catalytic dehydrogenative condensation of silyl hydrides and amines. Thermal decomposition of silazanes and polysilazanes

Kinsley, Kermit K., Ph.D.

Iowa State University, 1988

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Catalytic dehydrogenation condensation of silyl hydrides and amines. Thermal decomposition of silazanes and polysilazanes

by

Kermit K. Kinsley

A Dissertation Submitted to the
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For the Graduate College

Iowa State University
Ames, Iowa

1988

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DEDICATION

To Virg and Melissa

NOMENCLATURE

Simple organosilicon compounds will be named as derivatives of silane. Organosilicon compounds with silicon nitrogen bonds will be named silazanes, with disilazane meaning two silicon atoms bonded to one nitrogen, trisilazane three silicon atoms bonded to a single nitrogen.

Examples:

Me_2SiClH	dimethylchlorosilane
Me_3SiN_3	trimethylazidosilane
$(Me_2HSi)_2N\text{-}H$	1,1,3,3-tetramethyldisilazane
$(Me_3Si)_3N$	tris(trimethylsilyl)trisilazane

When referring to reactive intermediates with multiple bonds to silicon the following system will be used.

Examples:

$Me_2Si{=}CH_2$	1,1-dimethylsilene
$Me_2Si{=}O$	1,1-dimethylsilanone
$Me_3Si{=}N\text{-}SiMe_3$	1,1-dimethyl-3-trimethylsilylsilanimine

SECTION I. CATALYTIC DEHYDROGENATIVE CONDENSATION OF SILYL HYDRIDES AND AMINES

INTRODUCTION

The synthesis of silicon nitrogen bonds is most generally accomplished by the condensation of silyl chlorides with amines/ammonia.[1] A few examples exist of condensing silyl hydrides and amines but no conditions exist which are both mild and general.

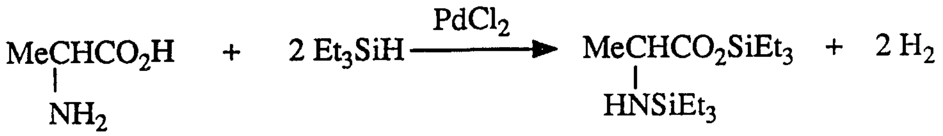
This section of the thesis will be devoted to developing the catalytic dehydrogenative condensation of silyl hydrides and amines.

LITERATURE SURVEY

The synthesis of silicon nitrogen bonds is most generally accomplished by the condensation of an amine with a chlorosilane.[1] This reaction is usually accomplished at room temperature unless bulky substrates are present.

$$\mathrm{PrEtPhSiCl} + \mathrm{MeC_6H_4NH_2} \longrightarrow \mathrm{PrEtPhSiNHC_6H_4Me}$$

The corresponding reaction between silyl hydrides and amines can not be accomplished unless a catalyst is employed. The first example of such a reaction was reported by Birkofer[2] in which palladium chloride was used as the catalyst. The first silane is attached to the oxygen while



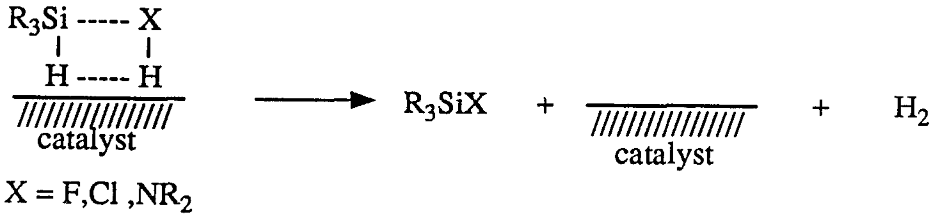
$$\underset{\displaystyle \mathrm{NH_2}}{\mathrm{MeCHCO_2H}} + 2\,\mathrm{Et_3SiH} \xrightarrow{\mathrm{PdCl_2}} \underset{\displaystyle \mathrm{HNSiEt_3}}{\mathrm{MeCHCO_2SiEt_3}} + 2\,\mathrm{H_2}$$

the second equivalent of triethylsilane reacts with the amine hydrogen. A number of amino acids were studied and the reaction was quite general for amino acids. Saam and Speier[3] studied the reaction of primary and secondary allyl amines with silyl hydrides in the presence of chloroplatinic acid. They observed the formation of hydrogen but were unable to characterize the organic products.

Sommer and Citron[4a] have studied the use of metal-supported catalysts to form bonds between silicon and electronegative elements such as nitrogen, florine, chlorine and sulfur. The results are summarized in Table 1. A number of other catalysts were employed but did not facilitate the desired reactions. The use of less hindered silanes was studied as well and a number of catalysts were found to catalyze halogenation of silyl hydrides in very good yields, e.g.,

$$\underset{\underline{2}}{Et_3SiH} + HCl \xrightarrow{Ru/C\ or\ Pt/C} \underset{\underset{100\ \%}{\underline{3}}}{Et_3SiCl} + H_2$$

The mechanism for these reactions is not understood. The results are particularly difficult to rationalize when inversion had occurred at the chiral silicon. In these

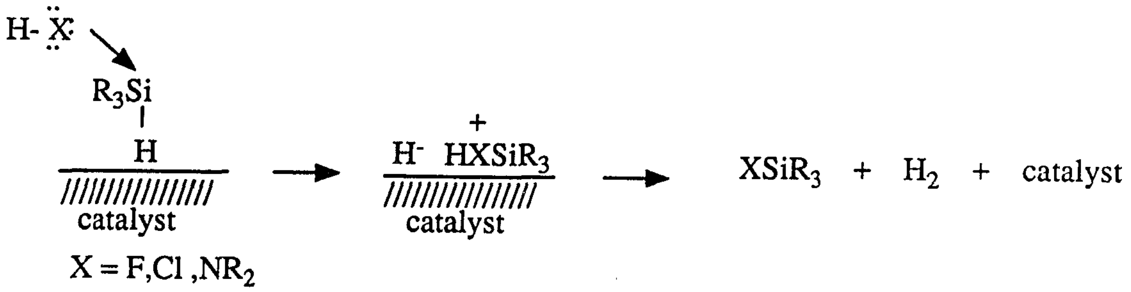


cases a four centered mechanism does not explain the results because this mechanism demands that stereochemistry be retained in the product. The mechanism in these cases may involve a nucleophilic attack by the electronegative element on the silane which is bonded to the catalyst.

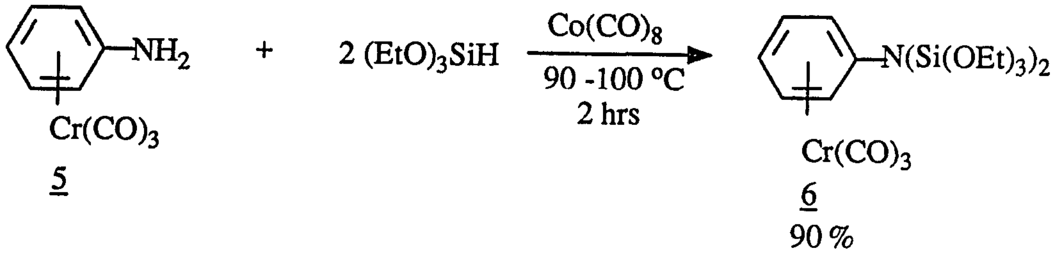
Table 1. $R_3SiH^a + HX \xrightarrow{\text{catalyst}} R_3Si\text{-}X + H_2$

Reagent	Catalyst	Product	Enantiometric excess	Yield
pyrrolidine	5% Pd/Al_2O_3	(+) $R_3Si\text{-}NR$	100	87%
isobutylamine	10% Pd/C	(±) $R_3Si\text{-}NR$	0	76%
HF	5% Pd/C	(+) R_3SiF	38	58%
HCl	5% Pd/Al_2O_3	(−) R_3SiCl	64	95%
H_2S	5% Pd/Al_2O_3	(+) R_3SiSH	68	11%

[a] The silane was optically active α naphthylphenylmethylsilane.[4b]



Magomedou and Shkol'nik[5a] have studied the silylation of various amines with dicobalt octacarbonyl. A number of different amines were used and it was found that less basic amines were most useful. No rationale for this effect was given by the authors. The author's silating agent was restricted to triethoxysilane. The reactions studied are given below. The authors postulate the following series of



$$\underset{\underline{7}}{PhNH_2} + 2\ (EtO)_3SiH \xrightarrow[\text{90 -100 °C, 2 hrs}]{Co(CO)_8} \underset{\underset{60\ \%}{\underline{8}}}{PhN(Si(OEt)_3)_2}$$

$$\underset{\underline{9}}{i\text{-}BuNH_2} + 2\ (EtO)_3SiH \xrightarrow[\text{90 -100 °C, 10 hrs}]{Co(CO)_8} \underset{\underset{40\ \%}{\underline{10}}}{i\text{-}BuN(Si(OEt)_3)_2}$$

reactions to account for the formation of the observed products. This report provides a good alternative to the

$$Co_2(CO)_8 + (EtO)_3SiH \longrightarrow \underset{\underline{11}}{HCo(CO)_4} + \underset{\underline{12}}{(EtO)_3SiCo(CO)_4}$$

$$\underset{\underline{11}}{HCo(CO)_4} + (EtO)_3SiH \longrightarrow \underset{\underline{12}}{(EtO)_3SiCo(CO)_4} + H_2$$

$$2\ \underset{\underline{12}}{(EtO)_3SiCo(CO)_4} + RNH_2 \longrightarrow \underset{\underline{13}}{RN(Si(OEt)_3)_2} + 2HCo(CO)_4$$

use of chloroalkoxysilanes in the synthesis of alkoxysilazanes. The problem arises because alkoxychlorosilanes have been shown to undergo disproportionation very readily.[5b]

$$2\ \underset{\underline{14}}{\mathrm{MeSiHCl(OEt)}} \xrightarrow[\text{room temp}]{} \mathrm{MeSiHCl_2} \quad + \quad \mathrm{MeSiH(OEt)_2}$$

Andrianov et al.[6] have studied the use of a large number of catalysts to form silicon nitrogen bonds between aniline derivatives and silyl hydrides. The reactions are often very complex with many products in poor yields. An example is given below. The isolation of such large amounts of triethylchlorosilane is a bit puzzling since the catalyst, the only chlorine source in the reaction mixture, was present in quantities significantly less than the yields obtained for the chlorosilane. The isolation of large amounts of hexaethylsilane suggest that a free radical process is involved.

$$\underset{\underline{2}}{\mathrm{Et_3SiH}} \ + \ \mathrm{PhNH_2} \xrightarrow[\substack{\mathrm{PhH} \\ 60\ ^{\circ}\mathrm{C} \\ 5\ \text{days}}]{\mathrm{(Ph_3P)_3RuCl}} \underset{\substack{\underline{3} \\ 19\ \%}}{\mathrm{Et_3SiCl}} \ + \ \underset{11\ \%}{\mathrm{Et_3SiSiEt_3}} \ + \ \underset{61\ \%}{\mathrm{PhNHSiEt_3}}$$

Tables 2 and 3 summarize the data reported by Andrianov et al.[6]

Koetzsch et al.[7] have found that the use of very clean nickel, platinum or palladium surfaces can catalyze the condensation of amines and silyl hydrides. An example is

Table 2. $Et_3SiH + PhCH_2NHPh \longrightarrow PhCH_2N(SiEt_3)Ph$

Catalyst	Chlorosilane	$Et_3SiSiEt_3$	Silazane
$TaCl_5$	16.1	3.4	0
$WOCl_4$	17.2	3.1	54.5
$K_2[IrCl_6]$	26.2	11.5	13.2
$[(C_8H_{17})_3NH]_2[PdCl_4]$	19.5	20.2	0[a]
$(Ph_3P)_3RuCl$	trace	6.5	0

[a] Toluene and aniline in yields of 19.1% and 11.1% were observed in the product mixture.

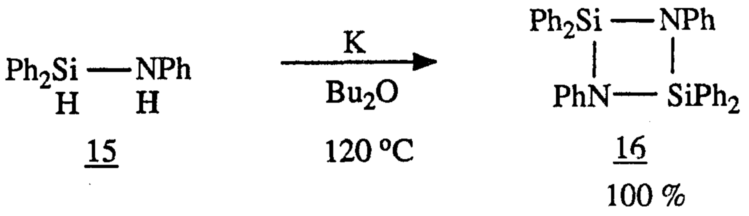
Table 3. $Et_3SiH + PhNH_2 \longrightarrow PhNHSiEt_3$

Catalyst	Chlorosilane	$Et_3SiSiEt_3$	Silazane
$WOCl_4$	33.4	13.6	1.5
$K_2[IrCl_6]$	11.0	12.6	45.0
$[(C_8H_{17})_3NH]_2[PdCl_4]$	15.3	37.8	7.8
$(Ph_3P)_3RuCl$	10.3	11.1	61.0

given below. The temperatures needed to catalyze the reaction are quite high.

$$2\,Me_3SiH + NH_3 \xrightarrow[120-170\,^{\circ}C]{Ni,Pt\ or\ Pd} (Me_3Si)_2NH + 2\,H_2$$

A number of groups[8] have found that alkali metals or their salts are capable of promoting silazane bond formation when exposed to silyl hydrides and amines. The initial discovery in this area was made by Fink[8] in 1964. The alkali metal that was used by Fink was potassium. An example is noted here and the yields in all cases studied are uniformly high.



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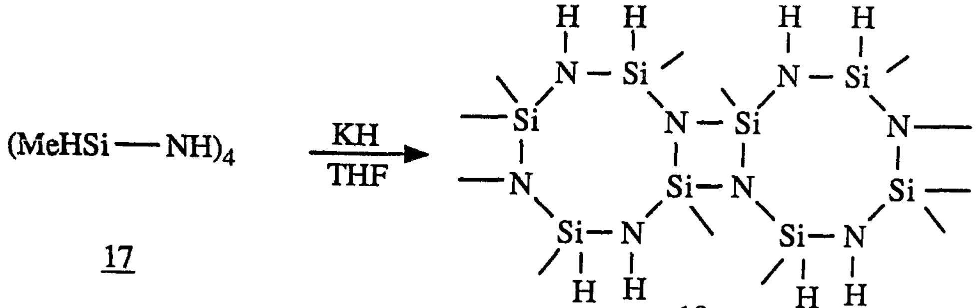
16

Seyferth and Wiseman[9a,b] have reported that this method can be used to prepare polysilazanes. They found that if one treats the ammonolysis product of methyldichlorosilane 17, with potassium hydride one can isolate polysilazanes with sheet like structures. The sheet also extend in two dimensions to a limited extent.



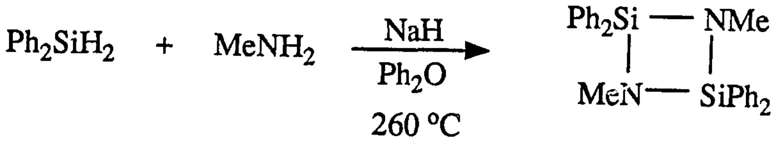
17

18

99 %

$\overline{M}_n = 1180$

Peake[10] has reported the reaction of diorganosilanes and primary amines in the presence of catalytic amounts of bases such as sodium hydride or sodium amide. It is interesting



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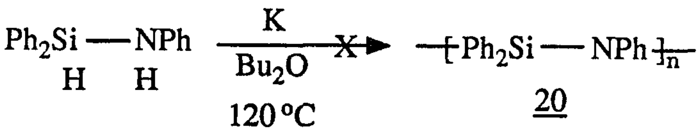
to note that in the work of Fink[8] and Peake[10] no linear oligomers or polymers were reported since it is conceivable in both cases that linear structures would be possible products.



$$\underset{H}{Ph_2Si}-\underset{H}{NPh} \cancel{\xrightarrow[\substack{Bu_2O\\120\,^{\circ}C}]{K}} -\!\!\left[Ph_2Si-NPh\right]_n-$$

20

$$Ph_2SiH_2 + MeNH_2 \cancel{\xrightarrow[\substack{Ph_2O\\260\,^{\circ}C}]{NaH}} -\!\!\left[Ph_2Si-NMe\right]_n-$$

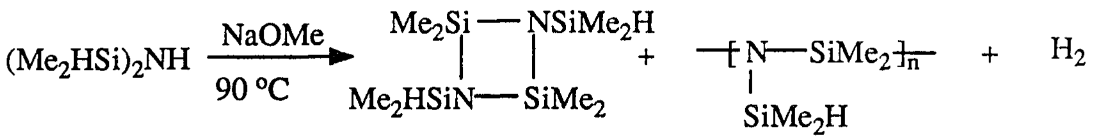
21

Two groups, that of Hagenmuller and Pouchard[11a] and Rustad and Jolly[11b] have found that silane and ammonia are immediately condensed to form a polysilazane when exposed to

$$SiH_4 + NH_3 \xrightarrow[-77\,^{\circ}C]{NaNH_2} \underset{\underline{22}}{Si(NH_2)} + \underset{100\,\%}{H_2}$$

potassium or sodium amide. In these reports no characterization of the polymer was attempted.

Andrianov et al.[12a] have found that potassium or sodium methoxide are useful catalysts for the synthesis of silazanes from silyl hydrides with amine functional groups. In this report polymeric material was also isolated but not characterized.

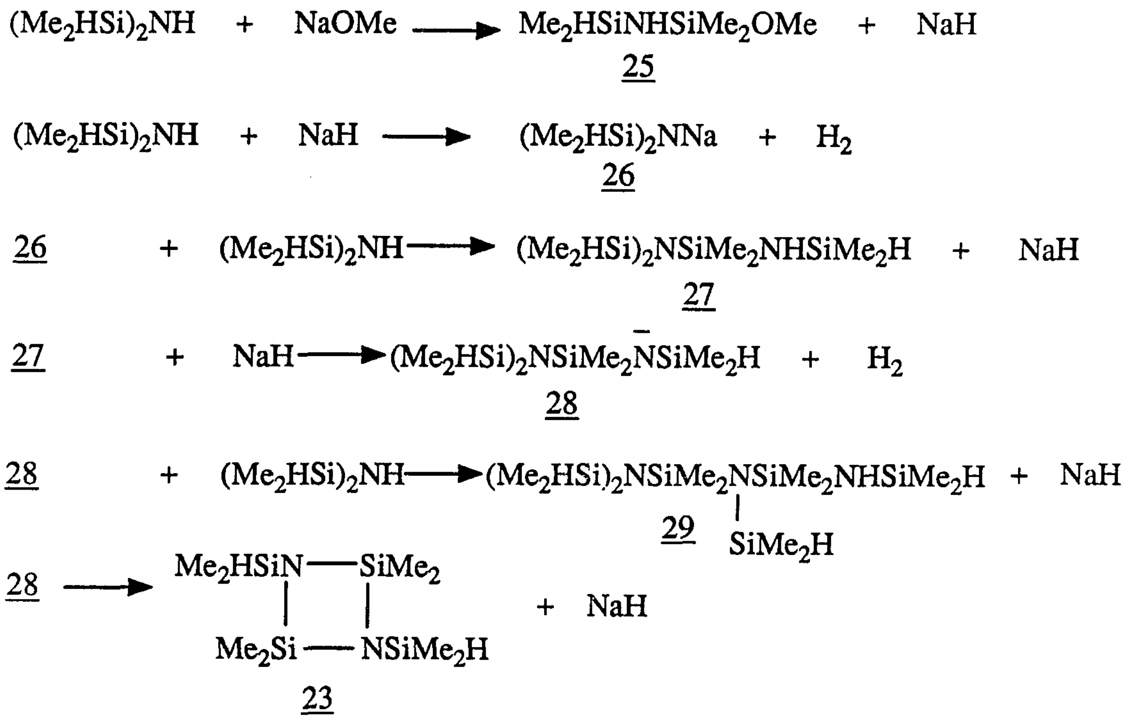


23 55 %

24 20 %

96 %

The mechanism postulated by Andrianov et al.[12a] is ionic in nature, involving a series of S_N2 substitutions on the silyl hydride functional group. This mechanism is initiated by the formation of sodium hydride as the basic species. The first step involves deprotonation followed by nucleophilic attack of the sodium amide formed on the silyl hydride functional group of another molecule of 1,1,3,3-tetramethyldisilazane. The linear diaminosilane 28 can then either react with an additional molecule of 1,1,3,3-tetramethyldisilazane to produce a linear polysilazane 29 or it can react intramolecularly to produce the cyclodisilazane 23.



$$(Me_2HSi)_2NH + NaOMe \longrightarrow \underset{\underline{25}}{Me_2HSiNHSiMe_2OMe} + NaH$$

$$(Me_2HSi)_2NH + NaH \longrightarrow \underset{\underline{26}}{(Me_2HSi)_2NNa} + H_2$$

$$\underline{26} + (Me_2HSi)_2NH \longrightarrow \underset{\underline{27}}{(Me_2HSi)_2NSiMe_2NHSiMe_2H} + NaH$$

$$\underline{27} + NaH \longrightarrow \underset{\underline{28}}{(Me_2HSi)_2NSiMe_2\bar{N}SiMe_2H} + H_2$$

$$\underline{28} + (Me_2HSi)_2NH \longrightarrow \underset{\underline{29}}{(Me_2HSi)_2NSiMe_2N(SiMe_2H)SiMe_2NHSiMe_2H} + NaH$$

$$\underline{28} \longrightarrow \underline{23} + NaH$$

Interestingly when the active hydrogen on nitrogen is replaced with a methyl group polymerization occurs also. Dimethylsilane is also produced in this reaction. The mechanism for this process is far from clear.

$$2\,(Me_2HSi)_2NMe \xrightarrow{KOMe} Me_2HSi[NMeSiMe_2]_2H + Me_2SiH_2$$

30 31

These same authors[12b,c] later report that another reaction is also operative under these conditions. The important reaction involves disproportionation of 1,1,3,3-tetramethyldisilazane 32 to the corresponding trisilazane 33 and monosilazane 34. 1,1-Dimethylsilazane 34

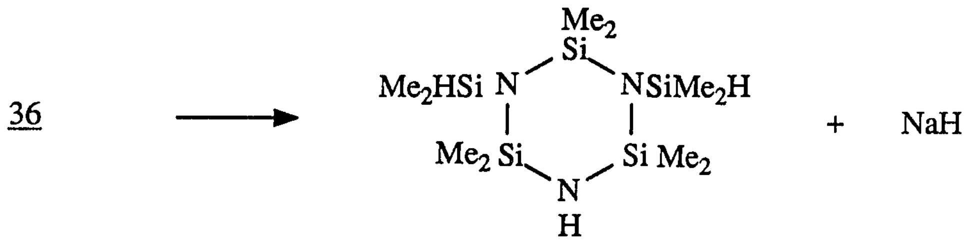
$$2(Me_2HSi)_2NH \longrightarrow (Me_2HSi)_3N + Me_2HSiNH_2$$

32 33 34

then reacts with the anionic intermediates present in the mixture, specifically 28, to produce the additionally observed cyclotrisilazane 37. The mechanism is outlined below. The yield of this material is not stated nor is there any mention of isolating any of the tris(dimethylsilyl)amine.

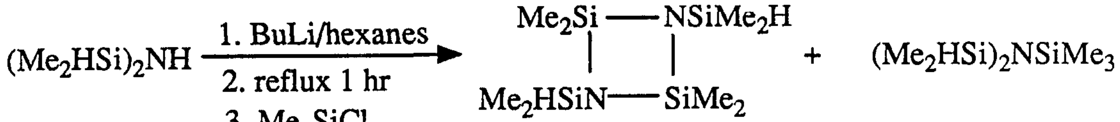
$$\underline{28} + \underline{34} \longrightarrow \underset{\underline{35}}{Me_2HSiN(SiMe_2H)SiMe_2N(SiMe_2H)SiMe_2NH_2} + NaH$$

$$\underline{35} + NaH \longrightarrow \underset{\underline{36}}{Me_2HSiN(SiMe_2H)SiMe_2N(SiMe_2H)SiMe_2\overline{N}H}$$



37

Wiseman et al.[13] has found that when 1,1,3,3-tetramethyldisilazane is treated with butyllithium the formation of silazane bonds from silicon hydrogen bonds and nitrogen hydrogen bonds is possible under certain circumstances. The following reaction is representative of the conditions

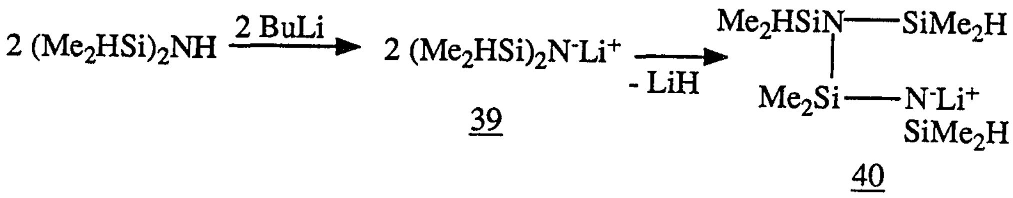


23 83 %

38 17 %

required to produce the cyclodisilazane 23. The authors found that when the reaction was performed in polar solvents such as tetrahydrofuran the only product isolated was 38, which results from a nucleophilic substitution of the amide anion on the chlorosilane functionality.

The authors consider two different mechanisms for the formation of the cyclodisilazane. The first is an entirely ionic mechanism which involves a series of nucleophilic substitutions. This mechanism was originally proposed by Andrianov et al.[12a] and later postulated by Breed and Wiley[14] in a related paper. Wiseman et al.[13] were able to demonstrate that the ionic intermediate 40 does indeed produce the observed cyclodisilazane under these conditions. But no evidence was obtained for the first nucleophilic substitution reaction that produces 40.



$$2\,(Me_2HSi)_2NH \xrightarrow{2\,BuLi} \underset{\underline{39}}{2\,(Me_2HSi)_2N^-Li^+} \xrightarrow[-\,LiH]{} \underset{\underline{40}}{\begin{array}{l} Me_2HSiN\text{—}SiMe_2H \\ \quad\;\; | \\ Me_2Si\text{—}N^-Li^+ \\ \qquad\quad SiMe_2H \end{array}}$$

$$\underline{40} \xrightarrow{-\,LiH} \underline{23}$$

The second mechanism involves a silanimine intermediate. This type of mechanism was originally proposed by Klingebiel et al.[15] in their studies of the decomposition of an amidoflorosilane. The first step involves the usual metal

$$\underset{\underline{39}}{(Me_2HSi)_2N^-Li^+} \xrightarrow{-\,LiH} \underset{\underline{42}}{[\,Me_2HSiN{=\!=}SiMe_2]} \longrightarrow \underline{23}$$

hydrogen exchange of butyl lithium with the amine hydrogen in 1,1,3,3-tetramethyldisilazane. This lithiated species 39 then loses LiH in a β elimination reaction to produce 1,1-dimethyl-2-dimethylsilylsilanimine 42. This intermediate then dimerizes in the usual fashion. Wiseman et al.[13] attempted to trap the silanimine but were not successful and the trapping agent was recovered in quantitative yield.

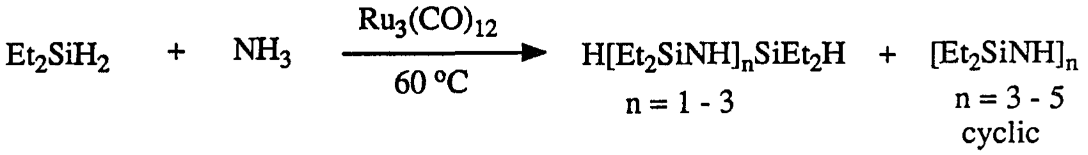
One puzzling aspect is the involvement of the chlorotrimethylsilane used as the quenching agent. Neither mechanism requires its involvement but when it is not added to the mixture no cyclodisilazane is isolated. One other type of quenching agent was used, namely t-butylchloride, which yields the same type of reaction. In this case the quenching product is the starting material.

$$(Me_2HSi)_2NH \xrightarrow[\substack{2.\ \text{reflux 1 hr} \\ 3.\ Me_3CCl}]{1.\ \text{BuLi/hexanes}} \underset{74\ \%}{\underline{23}} \quad + \quad \underset{6\ \%}{(Me_2HSi)_2NH} \quad + \quad Me_2C{=}CH_2$$

Blum and Laine[16a] have reported that triruthenium dodecacarbonyl is capable of oligomerizing polyhydriosilanes and ammonia. Two reactions were initially studied. The product mixture consisted of cyclic and linear oligomers.

$$(Me_2HSi)_2NH \quad + \quad NH_3 \quad \xrightarrow[60\ ^{\circ}C]{Ru_3(CO)_{12}} \quad \underset{\underline{43}}{[\,Me_2SiNH]_n}$$

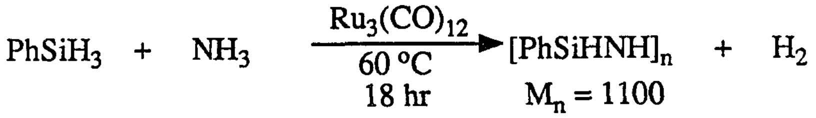
The yield of nonvolatile oligomers was 20% with a molecular weight average of 1000-2000 daltons. When diethylsilane was used as the silyl hydride the molecular weights were quite low.[16b]



$$Et_2SiH_2 + NH_3 \xrightarrow[60\,^{\circ}C]{Ru_3(CO)_{12}} \underset{n = 1-3}{H[Et_2SiNH]_nSiEt_2H} + \underset{\substack{n = 3-5 \\ \text{cyclic}}}{[Et_2SiNH]_n}$$

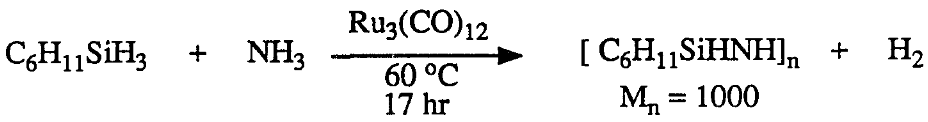
44 45

Later Laine et al.[16c] reported the use of hexylsilane and phenylsilane as the polyhydriosilanes. The initial polymers were linear in nature with no cross linking. When additional ammonia was added to the polymers and the temperature increased cross linking had occurred to a limited extent.



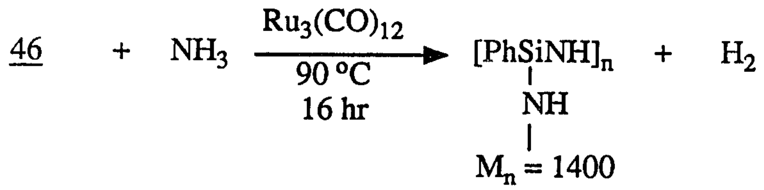
$$PhSiH_3 + NH_3 \xrightarrow[\substack{60\,^{\circ}C \\ 18\text{ hr}}]{Ru_3(CO)_{12}} \underset{M_n = 1100}{[PhSiHNH]_n} + H_2$$

46

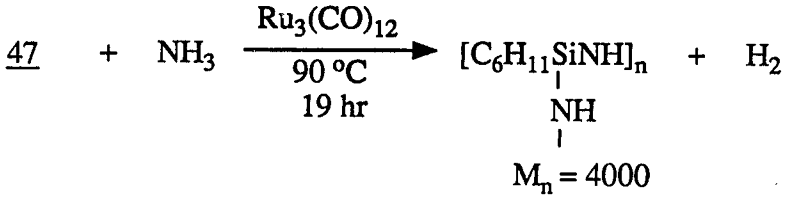


$$C_6H_{11}SiH_3 + NH_3 \xrightarrow[\substack{60\,^{\circ}C \\ 17\text{ hr}}]{Ru_3(CO)_{12}} \underset{M_n = 1000}{[C_6H_{11}SiHNH]_n} + H_2$$

47



$$\underline{46} \quad + \quad NH_3 \xrightarrow[\substack{90\,^{\circ}C\\ 16\ hr}]{Ru_3(CO)_{12}} [Ph\underset{\substack{|\\ NH\\ |\\ M_n = 1400}}{Si}NH]_n \quad + \quad H_2$$



$$\underline{47} \quad + \quad NH_3 \xrightarrow[\substack{90\,^{\circ}C\\ 19\ hr}]{Ru_3(CO)_{12}} [C_6H_{11}\underset{\substack{|\\ NH\\ |\\ M_n = 4000}}{Si}NH]_n \quad + \quad H_2$$

A significant increase in molecular weight was realized when the following polymer was subjected to these conditions. The resulting polymer had a molecular weight average of 50,000 daltons but it had molecules with molecular weights as high as 500,000 daltons. This is the first example of such high molecular weight polysilazanes. This report also contains results in the synthesis of polysiloxazanes from siloxanes and ammonia or amines. Cross

$$\underset{\underline{48}}{MeNH[H_2SiNMe]_nH} \xrightarrow[\substack{90\,^{\circ}C\\ 20\ hr}]{Ru_3(CO)_{12}} \text{cross linked}$$

$$(Me_2HSi)_2O \quad + \quad NH_3 \xrightarrow{Ru_3(CO)_{12}} \underset{\substack{\underline{49}\\ M_n = 5000 - 7000}}{H[Me_2SiOSiMe_2NH]_nH}$$

$$[MeHSiO]_4 \quad + \quad NH_3 \xrightarrow{Ru_3(CO)_{12}} \underset{\substack{\underline{50}\\ M_n = 1200 - 1500}}{[MeSiO(NH)_{0.5}]_x[MeSiNO]_y}$$

linked polymers can be obtained if cyclic siloxanes are used.

RESULTS AND DISCUSSION

The synthesis of polysilazanes is achieved by one of the following methods. The first method involves the very efficient reaction of a silyl chloride and ammonia or a secondary amine. This method suffers from the formation of ammonium chloride which is difficult to remove if the polymer is not soluble in organic solvents. In the case cited below, the polymer is soluble in ether below -30°C but

$$H_2SiCl_2 \quad + \quad NH_3 \xrightarrow[-30\,^{\circ}C]{Et_2O} [H_2SiNH]_x \cdot [(H_2Si)_{1.5}N]_y \quad + \quad NH_4Cl$$

becomes insoluble after standing at 0°C, making removal of the ammonium chloride difficult at best.[17a,b] The work of Verbeek and Winter et al.[18a,b] are examples of use of a secondary amine as the nitrogen source. The initially

$$MeSiCl_3 \quad + \quad MeNH_2 \longrightarrow MeSi(NHMe)_3 \quad + \quad 3\,MeNH_2 \cdot HCl$$

prepared polymers were crosslinked to a higher molecular weight resin <u>51</u> by heating to 520°C. These resins, although

$$MeSi(NHMe)_3 \xrightarrow{520\,^{\circ}C} \underset{\underline{51}}{\text{resin}}$$

soluble, were not characterized in the original patents, but were later characterized by Penn et al.[18c]

The second method of preparing polysilazanes involves the redistribution reaction between silazanes and silylchlorides. Legrow et al.[19] have prepared polysilazanes by the following reactions. These steps are speculated to

$$HSiCl_3 + (Me_3Si)_2NH \xrightarrow{\Delta} \underset{\underline{52}}{Me_3SiNHSiHCl_2} + Me_3SiCl$$

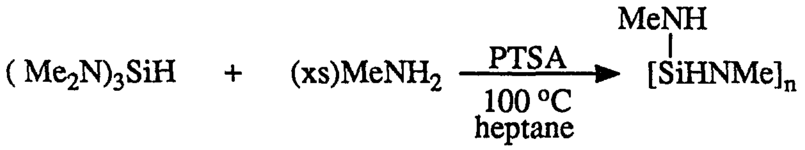
$$\underline{52} + (Me_3Si)_2NH \xrightarrow{\Delta} \underset{\underline{53}}{(Me_3SiNH)_2SiHCl} + Me_3SiCl$$

$$2\ \underline{53} \xrightarrow{\Delta} \underset{\underline{54}}{(Me_3SiNHSiHCl)_2NH}$$

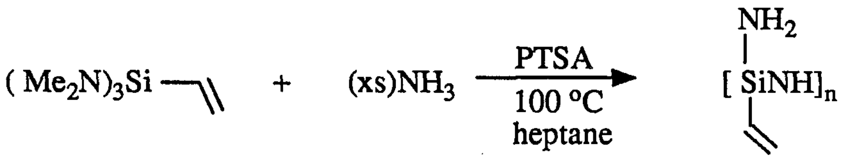
occur. The tetrasilazane <u>54</u> can then undergo additional redistribution reactions to produce polysilazanes. An additional example is from two patents by Gaul.[20a,b] These involve the use of dichlorosilanes or 1,2 dichlorodisilanes and hexamethyldisilazane.

$$(Me_3Si)_2NH + ClSiMe_2SiMe_2Cl \xrightarrow{\Delta} \underset{M_n = 3100}{[NHSiMe_2SiMe_2]_n} + Me_3SiCl$$

The third method of preparing polysilazanes involves the transamination and condensation of aminosilanes with ammonia or primary amines.[20c] A large number of catalysts such as



$$(Me_2N)_3SiH + (xs)MeNH_2 \xrightarrow[\substack{100\ ^{\circ}C \\ heptane}]{PTSA} [\overset{MeNH}{\overset{|}{Si}}HNMe]_n$$



organic acids, inorganic acids and CO_2 will facilitate this redistribution reaction.

The goal of this research is to find catalysts that would facilitate the condensation of silyl hydrides and nontertiary amines. The model reaction which was used involved triethylsilane and N-methylbutylamine. These

$$Et_3SiH + n\text{-}BuMeNH \xrightarrow[solvent]{catalyst} \underset{\underline{55}}{Et_3SiNBuMe} + H_2$$

reactants were chosen to place high steric demands upon the catalyst in hopes that bulky substituents would mimic a growing polymer. If this reaction could be catalyzed it would solve the problem of the large losses of material which was discussed previously. The catalyzed reaction may also lead to higher molecular weight material which would be more useful in the final pyrolysis to silicon nitride.

Two types of catalysts were studied to see if they would facilitate the condensation of triethylsilane and

N-methylbutylamine. They include catalysts which activate silyl hydrides such as chloroplatinic acid[21] and tris(triphenylphosphine)rodium(I)chloride.[22]

$$\text{1-pentene} \quad + \quad \mathrm{MeHSiCl_2} \quad \xrightarrow[100\ ^\circ\mathrm{C}]{\mathrm{H_2PtCl_6 \cdot 6\,H_2O}} \quad \text{n-}\mathrm{C_5H_{11}SiMeCl_2}$$

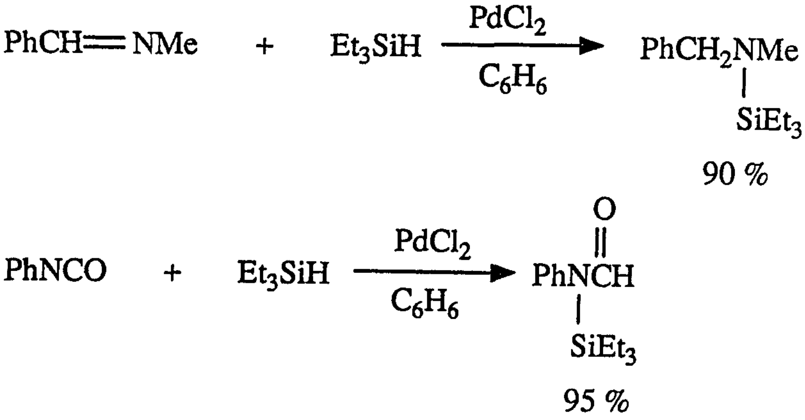
$$\mathrm{ArPhSiH_2} \quad + \quad \mathrm{MeOH} \quad \xrightarrow{\mathrm{(Ph_3P)RhCl}} \quad \mathrm{ArPhSiHOMe} \quad + \quad \mathrm{H_2}$$

Table 4 contains a summary of the catalysts that were used. The most notable feature of the catalysts that were tried is that most show no activity in condensing silyl hydrides and amines. The two exceptions were palladium chloride and ruthenium dodecacarbonyl. The later catalyst has been used by Blum and Laine[16a] to be effective in the synthesis of polysilazanes. This report by Blum and Laine[16a] was published midway through our own studies in this area. A number of other metal carbonyls were used by Blum and Laine[16a] with varying degrees of success. The most notable difference between the conditions employed by Blum and Laine and those presented in this work is that Blum and Laine[16a] used no solvent in a pressurized vessel while our results are entirely solution phase reactions at atmospheric pressure. The temperatures are also very different. Blum and Laine[16a] used temperatures up to 180°C while these results have a maximum temperature of 80°C.

Table 4. $Et_3SiH + HNBuMe \xrightarrow[Ph\text{-}H]{catalyst} \underset{\underline{55}}{Et_3SiNBuMe} + H_2$

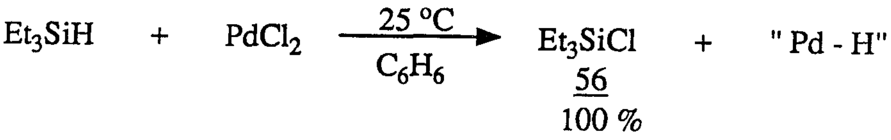
Catalyst	Time (hrs)	% Yield
$PdCl_2$	4	84
$NiCl_2$	3	0
$H_2PtCl_6 \cdot H_2O$	3	0
$RhCl(PPh_3)_3$	24	0
$PtCl_2$	24	14
Pd^0	20	0
$Pd(OAc)_2$	22	0
$Ru_3(CO)_{12}$	4	>95
Pt/C	22	0
$[RhCl(1,5)\text{-}C_8H_{12}$	8	<5
$Rh(C_5H_7O_2)(CO)_2$	7	0
$PdCl_2(PPh_3)_2$	7	0
$[Ru(OAc)_2]_2$	20	0
$CrCl_3$	2	0
$Ru(C_5H_7O_2)_3$	20	0
Raney Nickel	20	0

The use of palladium chloride was suggested by two reports by Ojima et al.[23a] and Ojima and Inaba[23b]. These two reports show that palladium chloride is useful in catalyzing the hydrosilation of imines and isocyanates. Neither of these reports contain any comment on what the actual catalyst is in this system. It was thought that the actual catalyst may not be $PdCl_2$ but some other form of palladium metal. When the silane is added to a benzene solution of $PdCl_2$ a vigorous exotherm results. In this reaction hydrogen is not evolved in this step and one can isolate a quantitative yield of triethylchlorosilane.



$$PhCH{=}NMe + Et_3SiH \xrightarrow[C_6H_6]{PdCl_2} \underset{90\ \%}{\underset{SiEt_3}{PhCH_2NMe}}$$

$$PhNCO + Et_3SiH \xrightarrow[C_6H_6]{PdCl_2} \underset{95\ \%}{\underset{SiEt_3}{PhN\overset{O}{C}H}}$$



$$Et_3SiH + PdCl_2 \xrightarrow[C_6H_6]{25\ ^{\circ}C} \underset{100\ \%}{\underset{\underline{56}}{Et_3SiCl}} + \text{"Pd-H"}$$

One possible mechanism to account for the observed activity of $PdCl_2$ in this reaction is outlined below. In

$$\begin{aligned}
&Et_3SiH + PdCl_2 \longrightarrow \underset{\underline{56}}{Et_3SiCl} + \text{"Pd - H"}\\
&Et_3SiCl + HNBuMe \longrightarrow \underline{55} + HCl\\
&\text{"Pd - H"} + HCl \longrightarrow PdCl + H_2\\
&Et_3SiH + PdCl \longrightarrow \underset{\underline{56}}{Et_3SiCl} + HCl
\end{aligned}$$

this mechanism the metal serves as a chlorine transfer agent. This mechanism is discounted because firstly the chlorosilane and the amine do not condense as effectively under these conditions as was observed when palladium chloride is used in the condensation of silyl hydrides and amines. The second observation that discounts this mechanism is that the palladium residue will also catalyze the condensation of silyl hydrides and amines. In this case the chlorine is removed as triethylchlorosilane from the Pd residue.

$$\underline{56} + HNBuMe \xrightarrow[\substack{C_6H_6\\ \text{reflux}}]{Et_3N} \underset{\substack{\underline{55}\\ 26\ \%}}{Et_3SiNBuMe} + Et_3N\bullet HCl$$

$$Et_3SiH + HNBuMe \xrightarrow[\substack{C_6H_6\\ \text{reflux}\\ 4\ \text{hr}}]{\text{"Pd - H"}} \underset{\substack{\underline{55}\\ 95\ \%}}{Et_3SiNBuMe} + H_2$$

The next area of study involved the use of polyfunctional silylhydrides to see if these catalysts could be used to prepare polysilazanes. Table 5 summarizes the results of condensing diethylsilane with N-methylbutylamine. When diethylsilane is used as the silyl hydride $PdCl_2$ is clearly the superior catalyst, of some concern is the lower yield and increased reaction time. The monosubstituted silane $\underline{58}$ can be observed as the first formed product. This

$$\mathrm{Et_2SiH_2} \quad + \quad \mathrm{HNBuMe} \xrightarrow[\substack{\mathrm{C_6H_6} \\ \mathrm{reflux}}]{\mathrm{catalyst}} \underset{\underline{58}}{\mathrm{Et_2SiHNBuMe}} \xrightarrow[\mathrm{HNBuMe}]{\mathrm{catalyst}} \underset{\underline{57}}{\mathrm{Et_2Si(NBuMe)_2}}$$

initial reaction is complete in 2-3 hours. The second substitution on diethylsilane could be slowed by a number of factors including the higher steric demands of the second substitution of the amine.

Polyfunctional amines were also used to determine if the polymerization could be extended through the nitrogen. This data, with n-butylamine as the polyfunctional amine, is summarized in Table 6.

This data is a bit troubling because it indicates that the second amine hydrogen can not be condensed with a silyl hydride. Factors that may account for this are the higher steric demands of the second condensation, particularly in the case where $PdCl_2$ is used as the catalyst and the lower

Table 5.

$$\mathrm{Et_2SiH_2 + HNBuMe \xrightarrow[\text{Ph-H}\\ \text{reflux}]{\text{catalyst}} \underset{\underline{57}}{Et_3Si(NBuMe)_2} + H_2}$$

Catalyst	Time (hrs)	% Yield
$PdCl_2$	20	56
$Ru_3(CO)_{12}$	44	15

Table 6.

$$\mathrm{Et_3SiH + H_2NBu \xrightarrow[\text{Ph-H}\\ \text{reflux}]{\text{catalyst}} \underset{\underline{59}}{Et_3SiNHBu} + H_2}$$

Catalyst	Time (hrs)	% Yield
$PdCl_2$	3	74
$Ru_3(CO)_{12}$	20	35

basicity of the amine hydrogen in the monosubstituted product.

In order to determine if the basicity of the amine had any effect on the activity of the catalysts an amine which has a much lower basicity, aniline, was used. These data are summarized in Table 7. The use of aniline as the amine component shows that the basicity is very important in the condensation of silyl hydrides and amines, particularly when palladium chloride is used as the catalyst while the basicity of the amine component has little effect when ruthenium dodecacarbonyl is used as the catalyst.

The inability of these catalysts to prepare disilazanes from triethylsilane and n-butylamine makes their use in the synthesis of polysilazanes somewhat suspect. In order to circumvent this problem hydrazines were used as the amine component. The data in Table 8 show that hydrazines work very poorly in this reaction. In fact when ruthenium dodecarbonyl was used as the catalyst no 1,2 disilylhydrazine 61 was observed after extended reaction time, while when palladium chloride was used as the catalyst the yields were disappointingly low.

In order to determine what may be the ideal solvent a brief survey of solvents was undertaken. Tables 9 and 10 show these results.

Table 7. $\mathrm{Et_3SiH} + \mathrm{PhNH_2} \xrightarrow[\text{Ph-H reflux}]{\text{catalyst}} \underset{\underline{60}}{\mathrm{Et_3SiNHPh}} + \mathrm{H_2}$

Catalyst	Time (hrs)	% Yield
$PdCl_2$	3	36
$Ru_3(CO)_{12}$	3	86
$Ru(PPh_3)Cl$	120	61[a]

[a] Data taken from reference 6.

Table 8. $\mathrm{Et_3SiH} + \mathrm{H_2NNH_2} \xrightarrow[\text{Ph-H reflux}]{\text{catalyst}} \underset{\underline{61}}{\mathrm{Et_3SiNHNHSiEt_3}} + \mathrm{H_2}$

Catalyst	Time (hrs)	% Yield
$PdCl_2$	20	39
$Ru_3(CO)_{12}$	44	0

Table 9. $Et_3SiH + HNBuMe \xrightarrow[\text{solvent reflux}]{PdCl_2} \underline{55} + H_2$

Solvent	Time (hrs)	% Yield
Benzene	3	84
THF	2	28[a,b]
Hexane	21	21
Chloroform	3	0[c]

[a] After 2 hr 10% of silane had reacted with THF.

[b] Yield uncorrected for unconsumed starting silane.

[c] Formation of triethylsilylchloride was observed.

Table 10. $Et_3SiH + HNBuMe \xrightarrow[\text{solvent reflux}]{Ru_3(CO)_{12}} \underline{55} + H_2$

Solvent	Time (hrs)	% Yield
Benzene	3	95
THF	21	<10
Hexane	21	12
Chloroform	3	0

The results in Tables 9 and 10 show that benzene is the most useful solvent employed. When palladium chloride was used as the catalyst two solvents proved to be particularly poor choices.

The use of tetrahydrofuran as the solvent resulted in an additional product being formed. This product resulted from

$$\mathrm{Et_3SiH} \quad + \quad \mathrm{HNBuMe} \xrightarrow[\substack{\mathrm{THF}\\ \mathrm{reflux}\\ 2\ \mathrm{hr}}]{\mathrm{PdCl_2}} \underset{28\ \%}{\underline{55}} \quad + \quad \underset{\substack{\underline{62}\\ 10\ \%}}{\mathrm{Et_3SiOBu}}$$

the hydrosilation of the carbon oxygen bond in tetrahydrofuran. English and Sommer[24] have observed similar reactions with nickel metal as the catalyst.

$$\mathrm{Et_3SiH} \quad + \quad \mathrm{THF} \xrightarrow[\mathrm{reflux}]{\mathrm{Raney\ Ni}} \underset{\substack{\underline{62}\\ 56\ \%}}{\mathrm{Et_3SiOBu}}$$

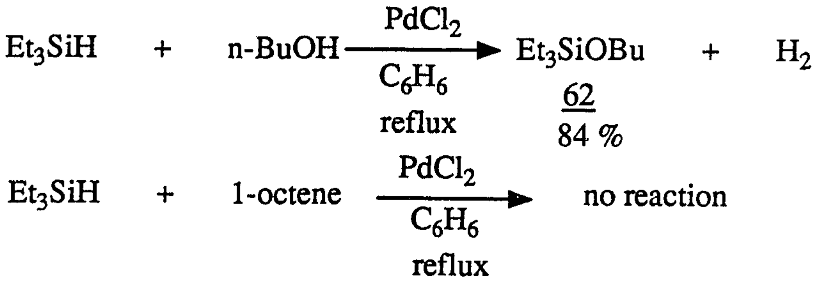
Table 9 also shows that chloroform is also not a good choice of solvents when palladium chloride was used as the catalyst. In this case triethylchlorosilane was isolated as the major product. The mechanism for the formation of this product is outlined below. The initiation step that

$$\mathrm{Et_3Si\bullet} \quad + \quad \mathrm{CHCl_3} \longrightarrow \mathrm{Et_3SiCl} \quad + \quad \mathrm{\bullet CHCl_2}$$

$$\mathrm{\bullet CHCl_2} \quad + \quad \mathrm{Et_3SiH} \longrightarrow \mathrm{Et_3Si\bullet} \quad + \quad \mathrm{CH_2Cl_2}$$

produces the silyl radicals is uncertain. The ability of chlorine containing solvents to trap silyl radicals has been demonstrated in a number of cases.[25] Attempts to observe radical products in other solvents, i.e., benzene, were not successful.

Two other condensations were attempted with the palladium chloride catalyst. The first being the



$$Et_3SiH + n\text{-}BuOH \xrightarrow[C_6H_6 \text{ reflux}]{PdCl_2} \underset{84\ \%}{\underset{\underline{62}}{Et_3SiOBu}} + H_2$$

$$Et_3SiH + 1\text{-octene} \xrightarrow[C_6H_6 \text{ reflux}]{PdCl_2} \text{no reaction}$$

condensation of silyl hydrides and alcohols, as indicated the catalyst is quite successful is performing this condensation.[26] Attempts at using palladium chloride as a hydrosilation catalyst were not successful. Ruthenium dodecacarbonyl has been shown to be useful as a hydrosilation catalyst.[27]

The synthesis of polymeric silazanes was undertaken using the catalytic dehydrogenation of silyl hydrides and ammonia. There was some question what temperature would be required to produce the desired reaction. The monomer studies suggested that elevated temperatures may be required

$$\mathrm{Et_3SiH} \quad + \quad \mathrm{HNBuMe} \xrightarrow[\substack{\mathrm{PdCl_2} \\ \text{or } \mathrm{Ru_3(CO)_{12}}}]{25\ ^\circ\mathrm{C}} \text{no reaction}$$

to produce polysilazanes. The condensation of diethylsilane with ammonia was undertaken at room temperature to determine if these conditions would produce polysilazanes. The experiments were performed by bubbling dry ammonia through a benzene solution of the silane and the catalyst. In the case when palladium chloride was used as the catalyst, polysilazanes were produced in 85% yield with a molecular weight of 300. When ruthenium dodecacarbonyl was used as the catalyst no polysilazanes were formed under these conditions. This result clearly indicates that lower temperatures can be used when palladium chloride is utilized as the catalyst.

$$\mathrm{Et_2SiH_2} \quad + \quad \mathrm{NH_3} \xrightarrow[\substack{\mathrm{C_6H_6} \\ 25\ ^\circ\mathrm{C}}]{\mathrm{PdCl_2}} \underset{\substack{85\ \% \\ \text{M= 300 daltons}}}{[\mathrm{Et_2SiNH}]_n}$$

$$\mathrm{Et_2SiH_2} \quad + \quad \mathrm{NH_3} \xrightarrow[\substack{\mathrm{C_6H_6} \\ 25\ ^\circ\mathrm{C}}]{\mathrm{Ru_3(CO)_{12}}} \text{no reaction}$$

The polysilazanes produced in the above reaction consisted of mainly low molecular weight linear oligomers as well as cyclic oligomers. The infrared spectrum of the product mixture contained a sharp N-H stretch at 3393 cm^{-1}

along with a weak peak at 3410 cm^{-1}. The spectrum also had an N-H bending vibration at 1590 cm^{-1} which is characteristic of primary amines. The infrared spectrum contained no peaks in the range of 2250-2100 cm^{-1} which indicates that silicon hydride functionalities are not present. The lack of these bonds precludes treatment of this polymer with potassium hydride to increase the molecular weight.

The low molecular weight of the product mixture can be understood in terms of two factors. The first factor is the lack of a stoichometric mixture of diethylsilane and ammonia. If the reactants are not present in a one to one ratio the end groups tend to be capped with the reagent in excess.[28] This factor is very difficult to control using this technique. Since the rate of reaction is not known, the proper rate of ammonia addition could only be approximated. The second factor that lowers the molecular weight is the use of slightly bulky organic groups on the silane that tend to increase cyclization.

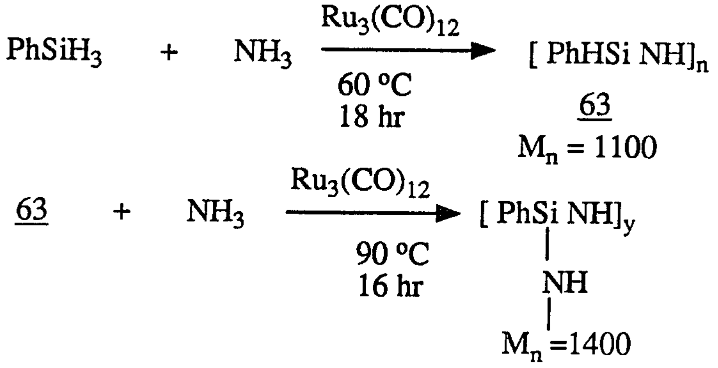
The use of another monomer was sought to help reduce the second factor in particular. Tetramethyldisilazane was chosen as the monomer that would help limit the production of cyclic oligomers. Condensation of tetramethyldisilazane with ammonia was studied using palladium chloride as the catalyst. Again ruthenium dodecacarbonyl was not active in condensing tetramethyldisilazane and ammonia. The molecular

$$(\mathrm{Me_2HSi})_2\mathrm{NH} + \mathrm{NH_3} \xrightarrow[\mathrm{C_6H_6}\ \ 25\ ^{\circ}\mathrm{C}]{\mathrm{PdCl_2}} [\mathrm{Me_2SiNH}]_n \quad M = 400 \text{ daltons}$$

weight was increased slightly but certainly not a significant degree.

The second modification that was undertaken was to vary the addition rate of ammonia. The rate of addition of ammonia had a significant impact on the molecular weights of the polysilazanes produced. These data are summarized in Table 11.

One technique that has been used to prepare polysilazanes that are useful for silicon nitride synthesis is to prepare a linear polymer, then crosslink the polymer to higher molecular weight material. An example from the work of Laine et al.[16c] is given below.



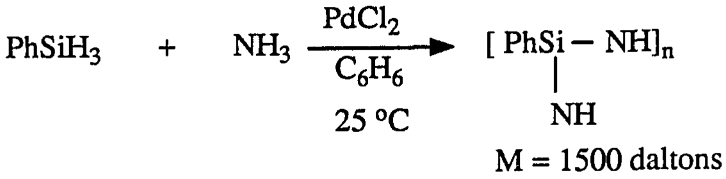
$$\mathrm{PhSiH_3} + \mathrm{NH_3} \xrightarrow[60\ ^{\circ}\mathrm{C},\ 18\ \mathrm{hr}]{\mathrm{Ru_3(CO)_{12}}} [\mathrm{PhHSi\,NH}]_n \quad \underline{63} \quad M_n = 1100$$

$$\underline{63} + \mathrm{NH_3} \xrightarrow[90\ ^{\circ}\mathrm{C},\ 16\ \mathrm{hr}]{\mathrm{Ru_3(CO)_{12}}} [\mathrm{PhSi}(-\mathrm{NH}-)\mathrm{NH}]_y \quad M_n = 1400$$

Table 11. $(Me_2HS_1)_2NH + NH_3 \xrightarrow[C_6H_6 \\ 25\,^\circ C]{PdCl_2} [Me_2SiNH]_n$

Rate of NH_3 addition	Molecular Weight
4.3 ml/min	800
11.0 ml/min	600
23.0 ml/min	400

The use of palladium chloride in the condensation of phenylsilane and ammonia indicates that at room temperature all of the silyl hydride functionalities were consumed at room temperature. This is evident by no Si-H stretches in the infrared spectrum. The material produced by this



$$PhSiH_3 + NH_3 \xrightarrow[C_6H_6 \\ 25\,^\circ C]{PdCl_2} [\underset{\underset{NH}{|}}{PhSi}-NH]_n$$

M = 1500 daltons

reaction has a slightly higher molecular weight than that produced by Laine et al.[16c]

CONCLUSIONS

In conclusion the synthesis of silazanes can be accomplished by the condensation of silyl hydrides and amines or ammonia. Two catalysts were found to facilitate the reaction at 80°C, namely palladium chloride and ruthenium dodecacarbonyl. Both catalysts produce diaminosilanes when diethylsilane is condensed with N-methylbutylamine. The synthesis of disilazanes was not possible under these conditions when butylamine was condensed with triethylsilane.

The synthesis of polysilazanes was possible at room temperature only when palladium chloride is used as the catalyst. The rate of ammonia addition to the solution is very important.

A number of areas warrant further study. Measuring the amount of ammonia introduced to the reaction mixture is obviously a problem. The use of a pressurized vessel is one possible solution to this problem. Related to this problem is the turnover frequency of the catalyst. If one knew the rate of ammonia uptake the rate of ammonia addition could be modified to introduce a stoichometric amount of ammonia.

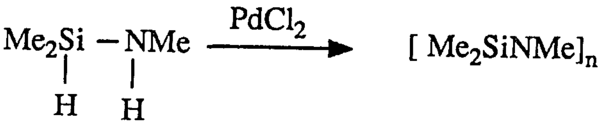
The use of different silanes and amines could be studied to see what effect they have on the polymer properties. The monomer studies indicated that the use of primary amines may not be possible since only silazanes and no disilazanes were produced. Increasing the temperture by doing the reaction

$$Et_3SiH + BuNH_2 \xrightarrow{PdCl_2} \underset{\underset{74\ \%}{\underline{59}}}{Et_3SiNHBu} + \underset{0\ \%}{(Et_3Si)_2NBu}$$

in a pressurized vessel may allow the synthesis of disilazanes by this method. If this works the use of an exact 1:1 ratio of silane to amine would be possible which would increase the molecular weight of the polysilazanes produced. An example of such a reaction is given below.

$$(Me_2HSi)_2NH + MeNH_2 \xrightarrow{PdCl_2} [Me_2SiNHSiMe_2NHMe]_n$$

The ultimate solution to the problem of stoichometry is the synthesis of molecules which have both the Si-H and N-H functionalities within the same molecule.



$$\underset{H}{Me_2Si} - \underset{H}{NMe} \xrightarrow{PdCl_2} [Me_2SiNMe]_n$$

Nonorganic silanes are also of interest in the synthesis of polysilazanes. The advantage of using these materials is that no carbon or chlorine impurities would be introduced. The solubilities of such polymers may be very low but could

$$\mathrm{SiH_4} + \mathrm{NH_3} \xrightarrow{\mathrm{PdCl_2}} \text{cross linked Si N polymer}$$

64

be increased by the use of primary amines as the amine component. In this case carbon impurities such as silicon carbide or carbon would be minimized since the N-C bond is the most likely bond to cleave in the pyrolysis step.

EXPERIMENTAL

Proton and carbon NMR spectra were obtained on a Nicolet NT-300 spectrometer. All chemical shifts are reported in parts per million from tetramethylsilane using $CHCl_3$ as an internal standard.

Routine mass spectra were obtained on a Hewlett Packard 5970 GCMS operating at 70 eV. Exact mass measurements were recorded on a Kratos MS 50 operating at 70 eV.

Infrared data were obtained on an IBM IR-90 series FTIR spectrometer. Elemental analyses were performed by Desert Analytics, Tucson, Arizona.

Gas chromatographic (GC) data were obtained on a Hewlett Packard 5970 gas chromatograph equipped with a 25 m x .25 mm capillary column coated with dimethylsilicone. All yields were determined by GC using internal standards and predetermined response factors. Preparative GC was done on a GOW-MAC Series 550P gas chromatograph fitted with a 5 ft. x 1/4 in. column that was packed with 20% SE 30 on Chromosorb W. Molecular weights were determined on a Perkin Elmer 601 liquid chromatograph fitted with four styrasel columns with a size exclusion range of 500 Å to 10^6Å. The solvent used was THF with polystyrene standards.

All liquid reagents except hydrazine and chloroform were distilled fro calcium hydride to remove any water. Hydrazine was distilled from potassium hydroxide under reduced pressure and chloroform was distilled from phosphorus pentaoxide. Palladium chloride was obtained from Alfa Products, ruthenium dodecacarbonyl was obtained from Aldrich Chemical Company and all other catalysts were obtained from Englehard. All reactions were carried out in oven dried glassware under an atmosphere of dry nitrogen.

Condensation of triethylsilane and N-methylbutylamine

An oven-dried flask was fitted with a reflux condenser, an inlet septum and a magnetic stir bar. The flask was flushed with dry nitrogen and 5 mole % catalyst was added. To the flask was added 3 ml of dry benzene followed by triethylsilane (0.47 g, 0.0040 moles) along with 3 ml of benzene. The mixture was stirred for 15 minutes. N-methylbutylamine (0.35 g, 0.0040 moles) was then added in one portion. At this time an additional 4 ml of benzene was added. The mixture was allowed to reflux for the time indicated in Table 4. The benzene was removed by trap to trap distillation at reduced pressure (0.1 torr). The product was isolated by preparative gas chromatography. N-methyl-N-butyl-1,1,1-triethylsilazane had the following spectral properties. ^{1}H NMR δ (300 MHz, $CDCl_3$) δ 0.530 (q, J = 8.0 Hz, 6 H); 0.88-0.91 (two overlapping triplets centered at 0.894 and 0.904 ppm, J = 7.0 and 8.0 Hz respectively, 12 H); 1.240 (m, 2 H); 1.370 (m, 2 H); 2.443 (s, 3 H); 2.664 (t, J = 7.0 Hz, 2 H). ^{13}C NMR (75 MHz,

$CDCl_3$) δ 4.439, 7.341, 14.201, 20.342, 31.894, 35.064, 50.708. IR (neat) ν 2876, 2766, 1458, 1169, 1003, 737 cm^{-1}. Mass spectrum 201 (8.0) M^+; 172 (48.0) M^+ -29; 158 (100) M^+ -43. Exact mass for $C_{11}H_{27}NSi$ (M^+) calculated 201.19129 measured 201.19099. Elemental analysis for $C_{11}H_{27}NSi$ calculated 65.59% C, 13.51% H, 6.95% N, measured 65.55% C, 13.62% H, 6.95% N.

Reaction of triethylsilane and palladium chloride

To an oven-dried 3 neck flask equipped with a stir bar, a reflux condensor and an inlet septum was added palladium chloride (0.60 g, 0.0034 moles) and 5 ml of dry benzene. Triethylsilane (1.52 g, 0.013 moles) was added over 15 minutes followed by 5 ml of dry benzene. The solution was stirred for 1/2 hour at room temperature. Triethylchlorosilane was observed in 100% yield.

Use of "Pd" residue in condensation of triethylsilane and N-methylbutylamine

To an oven-dried flask which was fitted with a reflux condensor, a stir bar and an inlet septum was added palladium chloride (8 mg) and 3 ml of dry benzene. To this solution was added triethylsilane (0.364 g, 0.0031 moles) and 3 ml of benzene. N-methylbutylamine (0.273 g, 0.0031) was then added to the flask and the mixture refluxed for 4 hours. At this time the mixture was cooled to room temperature and the liquid decanted from the black residue. The flask was recharged with the above amounts of triethylsilane and N-methylbutylamine and 10 ml of dry benzene. The mixture was refluxed for 3 hours. N-methyl-N-butyl-1,1,1,triethylsilazane was formed in 95% yield.

Reaction of triethylchlorosilane and N-methylbutylamine

To an oven-dried flask which was fitted with a reflux condensor, a stir bar and an inlet septum was added 4 ml of dry benzene and triethylchlorosilane (0.90 g, 0.0060 moles) and triethylamine (0.60 g, 0.0060 moles). To this solution was added N-methylbutylamine (0.44 g, 0.0050 moles). The solution was refluxed for 3 hours. The yield of N-methyl-N-butyl-1,1,1-trisilazane was 26%.

Condensation of diethylsilane and N-methylbutylamine

An oven-dried flask was fitted with a reflux condenser, an inlet septum and a magnetic stir bar. The flask was flushed with dry nitrogen and 5 mole % catalyst was added. To the flask was added 3 ml of dry benzene followed by diethylsilane (0.34 g, 0.0039 moles) along with 3 ml of benzene. The solution was allowed to stir for 15 minutes. N-methylbutylamine (0.70 g, 0.0080 moles) was added in one portion followed by 4 ml of benzene. The solution was refluxed for the time indicated in Table 5. The benzene was removed by trap to trap distillation and the product isolated by preparative gas chromatography. The 1,1-bis(N-methyl-N-butyl)-1,1-diethylsilazane had the following spectral properties. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.574 (q, J = 8.0 Hz, 4 H): 0.87-0.90 (two overlapping triplets centered at 0.880 and 0.894 ppm, J = 7.0 and 8.0 Hz respectively, 12 H); 1.249 (m, 4 H); 1.386 (m, 4 H); 2.418 (s, 6 H); 2.656 (t, J = 7.0 Hz, 4 H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 4.198, 7.273, 14.256, 20.427, 31.764, 34.545, 50.158. IR (neat) ν 2957, 2876, 2862, 1460, 1173, 1005, 727 cm^{-1}. Mass spectrum 258 (9.0) M^+; 229 (21.0) $M^+ -C_2H_5$; 215 (50.0) $M^+ -C_3H_7$; 172 (100) M^+ - NMeBu. Exact mass for $C_{14}H_{34}N_2Si$ (M^+) calculatled 258.2491, measured 258.2494. Elemental analysis for $C_{14}H_{34}N_2Si$ calculated 65.08% C, 13.25% H, 10.83% N, measured 64.92% C, 13.24% H, 10.80% N.

Condensation of triethylsilane and butylamine

An oven-dried flask was fitted with a reflux condenser, an inlet septum and a magnetic stir bar. The flask was flushed with dry nitrogen and 5 mole % catalyst was added. To the flask was added 3 ml of dry benzene followed by triethylsilane (0.59 g, 0.0051 moles) along with 3 ml of benzene. The mixture was stirred for 15 minutes. Butylamine (0.18 g, 0.0025 moles) was then added in one portion followed by 4 ml of benzene. The mixture was refluxed for the time indicated in Table 6. The benzene was removed by trap to trap distillation at reduced pressure and the product isolated by preparative gas chromatography. The N-butyl-1,1,1-triethylsilazane had the following spectral properties. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.500 (q, J = 8.0 Hz, 6 H); 0.87-0.930 (two overlapping triplets centered at 0.888 and 0.921 ppm, J = 7.0 and 8.0 Hz, respectively, 12 H); 1.339 (m, 4 H); 2.164 (s, 1 H); 2.688 (q, J = 6.9 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 4.906, 7.240, 14.034, 20.111, 37.833, 41.885. IR (neat) ν 3408 (s), 2955, 2910, 1458, 1119, 1003, 731 cm^{-1}. Mass spectrum 187 (6.3) M^+; 158 (100) $M^+ -C_2H_5$; 144 (27.0) $M^+ -C_3H_7$. Exact mass for $C_{10}H_{25}NSi$ M^+ calculated 187.1756, measured 187.1759. Elemental analysis for $C_{10}H_{25}NSi$ calculated 64.09% C, 13.45% H, 7.47% N, measured 64.10% C, 13.66% H, 7.18% N. No disilazane products were observed.

Condensation of aniline and triethylsilane with $PdCl_2$ as a catalyst

To an oven-dried flask which was fitted with a reflux condenser, a stir bar and an inlet septum was added palladium chloride and 3 ml of benzene. To this solution was added triethylsilane (0.73 g, 0.0063 moles) over 15 minutes. At this time 3 ml of benzene was added followed by aniline (0.57 g, 0.0063 moles) and 4 ml of benzene. The solution was refluxed for 3 hours. The yield of N-phenyl-1,1,1-triethylsilazane was 36%. The product was isolated by filtration through celite and distillation of benzene away from the product. The product had the following spectral properties. ^1H NMR (300 MHz, $CDCl_3$) δ 0.746 (q, J = 7.4 Hz, 6 H); 0.967 (t, J = 7.4 Hz, 9 H); 3.400 (s, broad, 1 H); 6.800 (m, 5 H). ^{13} C NMR (75 Hz, $CDCl_3$) δ 4.760, 7.070, 116.100, 117.390, 129.200. IR (neat) ν 3418, 3047, 2963, 2893, 1604, 1496, 1380, 1288, 887, 725 cm^{-1}. Mass spectrum 207 (29.8) M^+; 178 (100) M^+ -29; 150 (64.6); 122 (69.9); 120 (61.9); 79 (30.0); 77 (26.9). Exact mass for $C_{12}H_{21}NSi$ (M^+) calculated 207.14433 measured 207.14386, for $C_{10}H_{16}NSi$ (M^+ $-C_2H_5$) calculated 178.10520 measured 178.10451.

Condensation of aniline and triethylsilane with ruthenium dodecacarbonyl as catalyst

To an oven-dried flask which was fitted with a reflux condenser, a stir bar and an inlet septum was added a catalytic amount of ruthenium dodecacarbonyl and 4 ml of benzene. To this solution was added triethylsilane (0.73 g, 0.0063 moles) then aniline (0.57 g, 0.0063 moles). To this mixture was added 6 ml of dry benzene and the solution was refluxed for 3 hours. The yield of N-phenyl-1,1,1-trimethylsilazane was 86%.

Condensation of triethylsilane and hydrazine with palladium chloride as the catalyst

To an oven-dried flask fitted with a reflux condenser, stir bar and an inlet septum was added a catalytic amount of palladium chlorideand 3 ml of benzene. To this solution was added triethylsilane (1.16 g, 0.010 moles) over 15 minutes. Hydrazine (0.16 g, 0.0050 moles) was then added to the solution which was refluxed for 20 hours. The product was isolated by filtration through celite and distillation of benzene away from the product. Final purification was performed by preparative gas chromatography (25% SE 30 on Chrom. W., 5'). The 1,2(bistriethylsilyl)hydrazine had the following spectral features. ^1H NMR (300 MHz, $CDCl_3$) δ 0.533 (q, J = 8.0 Hz, 12 H); 0.926 (t, J = 8.0 Hz, 18 H); 2.322 (s, broad, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 3.569, 7.201. IR (neat) ν 3335 (s), 2910, 2875, 1458, 1415, 1238, 1076, 1016, 815, 725. Mass spectrum 260 (88) M^+; 231 (36) M^+ -29; 173 (29); 160 (48); 145 (28); 87 (65); 59 (100). Exact mass for $C_{12}H_{32}N_2Si_2$ (M^+) calculated 260.21041, measured 260.21043, for $C_{10}H_{27}N_2Si_2$ (M^+ $-C_2H_5$) calculated 231.17129, measured 231.17104.

Condensation of triethylsilane and hydrazine with ruthenium dodecacarbonyl as the catalyst

To an oven-dried flask fitted with a reflux condenser, a stir bar and an inlet septum was added a catalytic amount of ruthenium dodecacarbonyl and 4 ml of benzene. Triethylsilane (1.16 g, 0.010 moles) was then added followed by hydrazine (0.16 g, 0.005 moles). The solution was refluxed for 44 hours. No product was seen by gas chromatography.

Condensation of triethylsilane and N-methylbutylamine using tetrahydrofuran as the solvent and $PdCl_2$ as catalyst

An oven-dried flask was fitted with a reflux condenser, an inlet septum and a stir bar. The flask was flushed with nitrogen and 5 mole % $PdCl_2$ was added. To the flask was added 3 ml of dry hexanes and triethylsilane (0.37 g, 0.0032 moles) followed by 3 ml of hexanes. The solution was allowed to stir for 15 minutes. N-methylbutylamine (0.28 g, 0.0032 moles) was then added in one portion followed by 4 ml of hexanes. The mixture was refluxed for 2 hours. The gas chromatography yield of N-methyl-N-butyl 1,1,1-triethylsilazane 55 was 28% (Table 9).

Condensation of triethylsilane and N-methylbutylamine using hexanes (Skelly B) as the solvent and $PdCl_2$ as catalyst

An oven-dried flask was fitted with a reflux condenser, an inlet septum and a stir bar. The flask was flushed with nitrogen and 5 mole % $PdCl_2$ was added. To the flask was added 3 ml of dry hexanes and triethylsilane (0.37 g, 0.0032 moles) followed by 3 ml of hexanes. The solution was allowed to stir for 15 minutes. N-methylbutylamine (0.28 g, 0.0032 moles) was then added in one portion followed by 4 ml of hexanes. The mixture was refluxed for 21 hours. The gas chromatography yield of N-methyl-N-butyl 1,1,1,triethylsilazane 55 was 21% (Table 9).

Condensation of triethylsilane and N-methylbutylamine using chloroform as the solvent and $PdCl_2$ as catalyst

An oven-dried flask was fitted with a reflux condenser, an inlet septum and a stir bar. The flask was flushed with nitrogen and 5 mole % $PdCl_2$ was added. To the flask was added 3 ml of dry hexanes and triethylsilane (0.37 g, 0.0032 moles) followed by 3 ml of hexanes. The solution was allowed to stir for 15 minutes. N-methylbutylamine (0.28 g, 0.0032 moles) was then added in one portion followed by 4 ml of hexanes. The mixture was refluxed for 3 hours. The gas chromatography yield of N-methyl-N-butyl 1,1,1,triethylsilazane 55 was 0%. The isolated product was triethylchlorosilane (Table 9).

Condensation of triethylsilane and N-methylbutylamine using tetrahydrofuran as the solvent and $Ru_3(CO)_{12}$ as catalyst

An oven-dried flask was fitted with a reflux condenser, an inlet septum and a stir bar. The flask was flushed with nitrogen and 5 mole % $Ru_3(CO)_{12}$ was added. to the flask was added 3 ml of dry hexanes and triethylsilane (0.37 g, 0.0032 moles) followed by 3 ml of hexanes. The solution was allowed to stir for 15 minutes. N-methylbutylamine (0.28 g, 0.0032 moles) was then added in one portion followed by 4 ml of hexanes. The mixture was refluxed for 21 hours. The gas chromatography yield of N-methyl-N-butyl 1,1,1,triethylsilazane 55 was < 10% (Table 10).

Condensation of triethylsilane and N-methylbutylamine using hexanes (Skelly B) as the solvent and $Ru_3(CO)_{12}$ as catalyst

An oven-dried flask was fitted with a reflux condenser, an inlet septum and a stir bar. The flask was flushed with nitrogen and 5 mole % $Ru_3(CO)_{12}$ was added. To the flask was added 3 ml of dry hexanes and triethylsilane (0.37 g, 0.0032 moles) followed by 3 ml of hexanes. The solution was allowed to stir for 15 minutes. N-methylbutylamine (0.28 g, 0.0032 moles) was then added in one portion followed by 4 ml of hexanes. The mixture was refluxed for 21 hours. The gas chromatography yield of N-methyl-N-butyl 1,1,1,triethylsilazane 55 was 12% (Table 10).

Condensation of triethylsilane and N-methylbutylamine using chloroform as the solvent and $Ru_3(CO)_{12}$ as catalyst

An oven-dried flask was fitted with a reflux condenser, an inlet septum and a stir bar. The flask was flushed with nitrogen and 5 mole % $Ru_3(CO)_{12}$ was added. To the flask was added 3 ml of dry hexanes and triethylsilane (0.37 g, 0.0032 moles) followed by 3 ml of hexanes. The solution was allowed to stir for 15 minutes. N-methylbutylamine (0.28 g, 0.0032 moles) was then added in one portion followed by 4 ml of hexanes. The mixture was refluxed for 3 hours. The gas chromatography yield of N-methyl-N-butyl 1,1,1,triethylsilazane 55 was 0% (Table 10).

Condensation of triethylsilane and n-butanol

To an oven-dried flask which was fittee with a reflux condenser, a stir bar and an inlet septum was added a catalytic amount of palladium chloride. To this flask was added 3 ml of benzene followed by triethylsilane (0.36 g, 0.0032 moles). To this solution was added 3 ml of benzene followed by n-butanol (0.29 g, 0.0032 moles), 4 ml of benzene was then added to the solution. The solution was refluxed for 3 hours. The 1,1,1-triethylsilylbutoxysilane was isolated by filtration through celite and removal of the benzene by distillation. The gas chromatographic yield of the product was 82%. The product had the following spectral properties. ^{1}H NMR (300 MHz, $CDCl_3$) 0.587 (q, J = 8.0 Hz, 6 H); 0.90-0.95 (two overlapping triplets with coupling constants 7.1 Hz and 8.0 Hz, respectively, 12 H); 1.343 (m, 2 H); 1.496 (m, 2 H); 3.594 (+, J = 6.7 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 4.618, 6.828, 13.972, 19.115, 35.190, 62.767. IR (neat) ν 2958, 1460, 1415, 1384, 1238, 1149, 1120, 1099, 1039, 1006, 983, 781, 744 cm^{-1}. Mass spectrum

159 (100) M^+ -29; 131 (28); 103 (32); 75 (99); 59 (34). Exact mass calculated for $C_{10}H_{24}OSi$ 188.15965, measured 188.15940. Elemental analysis for $C_{10}H_{24}OSi$ calculated 63.76% C, 12.84% H, measured 64.05% C, 13.09% H.

Attempted reaction of triethylsilane and 1-octene

To an oven-dried flask fitted with a reflux condenser, stir bar and an inlet septum was added a catalytic amount of $PdCl_2$ and 4 ml of dry benzene. To this was added triethylsilane (0.73 g, 0.0063 moles) and 3 ml of benzene. The solution was allowed to stir for 15 minutes then the 1-octene (0.56 g, 0.0050 moles) was added in one portion. The solution was allowed to reflux for 18 hours after which only starting material remained.

Condensation of diethylsilane and ammonia

To a flask fitted with a gas inlet which was connected to a tank of annhydrous ammonia, an inlet septum and a stir bar was added ~ 100 ml of dry benzene and a catalytic amount of palladium chloride or ruthenium dodecacarbonyl. To this was added diethylsilane (2.05 g, 0.023 moles) over 15 minutes. The ammonia was bubbled through the solution over 3 hours. The palladium catalyst was removed by filtration through celite. The volatiles were removed by trap to trap distillation at 0.1 torr. The viscous oil (1.97 g, 85%) that remained had a molecular weight of 500 daltons. The infrared spectrum had the following adsorbances: 3410, 3393 (strong), 2953, 2910, 1590, 1458, 1414, 1236, 1169, 1059, 1009, 974, 918, 841, 781, 723 cm^{-1}. The ruthenium dodecacarbonyl did not produce any polymeric or oligomeric silazanes.

Condensation of tetramethyldisilazane and ammonia

The procedure was exactly as in the condensation of diethylsilane and ammonia. The tetramethyldisilazane (4.6 g, 0.034 moles) was added to 150 ml of dry benzene. The flow of ammonia was varied by a Cole Parmer flow meter which was connected to the ammonia tank by tygon tubing. The polymer molecular weights varied with the flow rate of ammonia as indicated in Table 11. The typical yield of isolated material was 60%.

Condensation of phenylsilane and ammonia

The procedure was exactly as in the condensation of diethylsilane and ammonia. The phenylsilane (2.60 g, 0.024 moles) was added to 150 ml of benzene. The molecular weight of the polymer was 1500. The polymer mixture had the following infrared bonds: 3391, 3076, 2957, 2914, 1630, 1420, 1380, 1254, 1167, 1036, 993, 930, 843, 797, 731 cm^{-1}.

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SECTION II. THERMAL DECOMPOSITION OF SILAZANES AND POLYSILAZANES

INTRODUCTION

The use of polysilazanes in the synthesis of silicon nitride is a fairly recent development. One problem with polysilazanes as silicon nitride precursors is that with these polymers large amounts of silicon carbide and carbon can be formed along with silicon nitride.

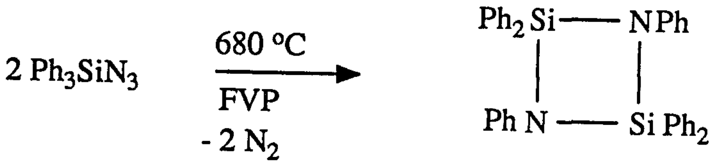
No studies exist in the literature in which a functional group was purposefully introduced into the polysilazane to increase its reactivity which could minimize the carbon based impurities. Monomers have been used in this study to serve as model polysilazanes. The decomposition of these monomers have been used to indicate what types of reactive intermediates may be involved in the synthesis of silicon nitride.

LITERATURE SURVEY

The most general route to silanimines involves the pyrolysis or photolysis of silylazides. Silyl azides are generally prepared by the aluminum chloride catalyzed addition of the azide anion to a chlorosilane.[1,2,3,4] This route is the most widely used method to prepare silylazides.

$$\underset{\underline{1}}{Ph_3SiCl} + NaN_3 \xrightarrow[THF]{AlCl_3} \underset{\underset{90\ \%}{\underline{2}}}{Ph_3SiN_3} + NaCl$$

When azidotriphenylsilane $\underline{2}$ was pyrolyzed in a flash system at 680°C Reichle[5] observed the formation of a perphenylated cyclodisilazane. The mechanism postulated by Reichle for the formation of hexaphenylcyclodisilazane $\underline{3}$ is illustrated here. The intermediacy of a silanimine was very speculative, based entirely on the observed product. Reichle was also quite bold in invoking a silicon nitrogen



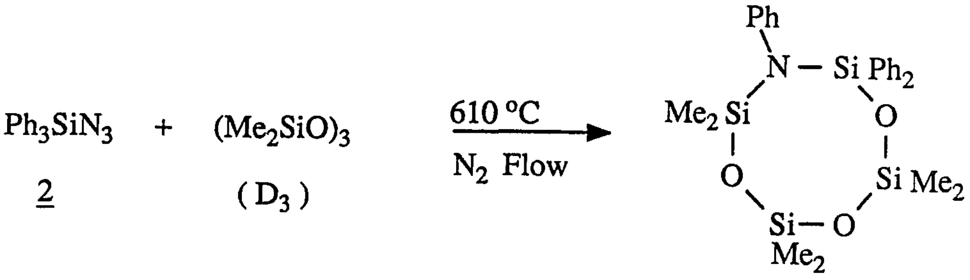
$\underline{2}$ $\underline{3}$

47 %

$$\underset{\underline{2}}{Ph_3SiN_3} \xrightarrow[-N_2]{} \underset{\underline{4}}{[\overset{+}{Ph_2Si} - \overset{-}{N}Ph]} \xrightarrow{+\underline{4}} \underline{3}$$

double bond since many researchers at that time thought that multiple bonds to silicon were impossible.[6] Patil and Rao[7] reported a similar study.

Parker and Sommer[8a] performed the pyrolysis of azidosilanes in the presence of various trapping agents in hopes of obtaining additional evidence for the intermediacy of silanimines in the pyrolysis of azidosilanes. The first trap that was used was hexamethylcyclotrisiloxane (D_3). The



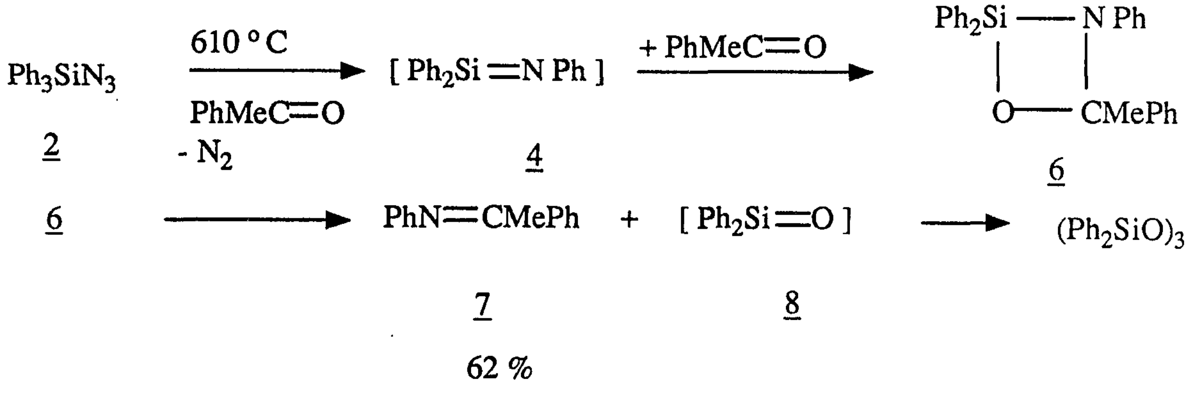
5

25 %

eight membered heterocycle 5 was formed in 25% yield. The ability of D_3 to trap intermediates with multiple bonds to silicon had been demonstrated in earlier work by Golino et al.[8b] The isolation of 5 was then taken as additional evidence that silanimines are intermediates in the pyrolysis of azidosilanes.

In a unique trapping experiment Parker and Sommer[8a] were able to generate siloxanes in the pyrolysis of silyazides. The traps employed were ketones, most notably acetophenone.

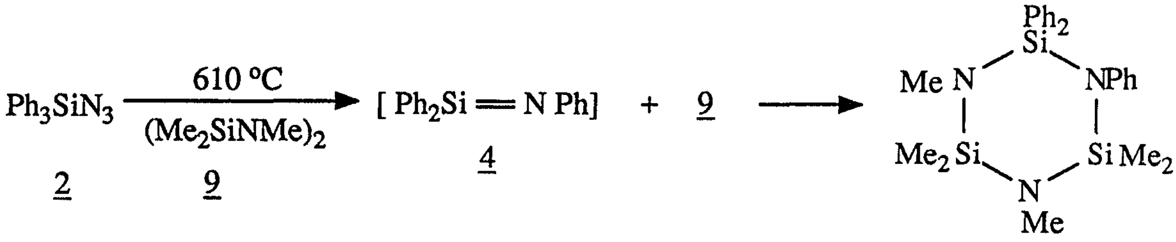
When triphenylazidosilane was pyrolyzed in the presence of acetophenone, hexaphenyltrisiloxane and the N-phenylimine



were formed as major products. The experiment involves trapping of the silanimine with acetophenone. This generates a unique heterocycle 6 which decomposes under the reaction conditions to the N-phenylimine 7 and diphenylsilanone 8. The silanone is then isolated as hexaphenyltrisiloxane.

The authors[8] were also able to trap the silanimine with a strained silicon nitrogen bond. The trapping agent is hexamethylcyclodisilazane. This is the only example in the literature of trapping silanimines with a silicon nitrogen bond.

An interesting study by Bock and Dammel[9] suggests that a triple bond between silicon and nitrogen may be possible.



10

31 %

The starting material for the study was prepared by a redistribution reaction of phenyltrichlorosilane and trimethylazidosilane.

$$PhSiCl_3 \quad + \quad 3\,Me_3SiN_3 \quad \xrightarrow{AlCl_3} \quad PhSi(N_3)_3 \quad + \quad 3\,Me_3SiCl$$

11

The experiment involves a continuous pyrolysis of 11 while following the photoelectron spectra of the gases formed. The triazidosilane was found to be completely decomposed at 827°C. Complete decomposition of 11 was needed to prevent interference from the peaks present in the starting material. In connection with this study a

$$PhSi(N_3) \quad \xrightarrow{827\ ^{\circ}C} \quad Ph\overset{+}{N}\equiv\overset{-}{Si} \quad + \quad 4\,N_2$$

11 12

semiempirical calculation was performed to predict what spectrum would be obtained if the silicon nitrogen triple bonded species were present. These calculations suggest that the intermediate 12 with a terminal silicon would be more stable than the intermediate with a terminal nitrogen 13. The heats of formation for the parent system have been

$$\mathrm{Ph}\overset{+}{\mathrm{N}}\equiv\overset{-}{\mathrm{Si}} \qquad\qquad \mathrm{PhSi}\equiv\mathrm{N}$$

12 13

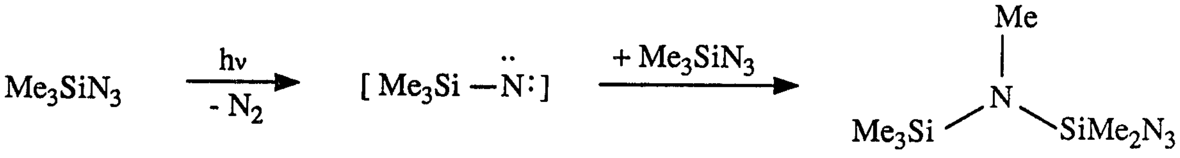
$$\Delta H_f^{MNDO} = 20.3 \text{ Kcal/mole} \qquad\qquad \Delta H_f^{MNDO} = 116.0 \text{ Kcal/mole}$$

calculated by Murrell et al.[10a,b] and Preuss et al.[10c] These calculations suggest that the silaisocyanide would be more stable by 89.0 kcal/mole and 68.0 kcal/mole respectively.

The pyrolysis of silylazides as a means of generating silanimines is somewhat limited. The major problem is that the product mixtures can be very complex. This is especially profound when nonaromatic substituents are attached to silicon. The intermediacy of a discreet nitrene 14 intermediate is also open to speculation. No studies to date have answered this question when a thermal means of generating the silanimine from azidosilanes is used.

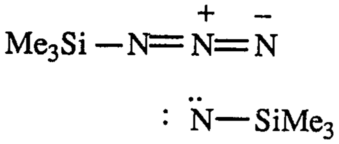
$$\underset{\underline{2}}{\mathrm{Ph_3SiN_3}} \xrightarrow{-\mathrm{N_2}} \underset{\underline{14}}{[\mathrm{Ph_3Si}-\ddot{\mathrm{N}}\!:]} \xrightarrow{1,2\ \mathrm{Ph}} \underset{\underline{4}}{[\mathrm{Ph_2Si}=\mathrm{N\,Ph}]} \xrightarrow{+\underline{4}} \underline{3}$$

In contrast to the thermal decomposition of silylazides as a means of generating silanimines, photolytic decomposition has received a large amount of study. Klein and Connolly[11] were the first to study the photolysis of silylazides. This study involved photolysis of silylazides at varying degrees of conversion. The product mixture is quite complex but 15 was shown to be the primary photoproduct. The mechanism postulated by Klein and Connolly is outlined below. Although Klein and Connolly are



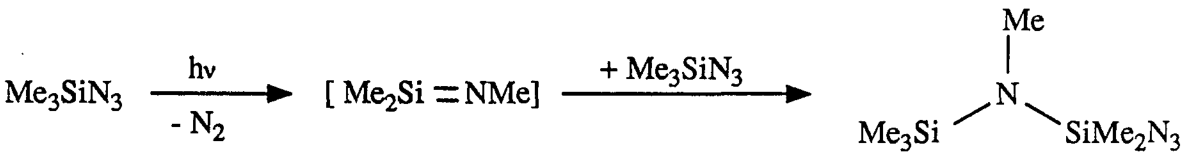
15

not entirely convinced that a nitrene is involved no other intermediate is postulated. The authors speculate that the nitrene is complexed to the azide present in the reaction mixture. Of interest is the lack of any consideration by



16

Klein and Connolly of a multiple bond between silicon and nitrogen as was postulated by Reichle[5] in his original work on the thermolysis of silylazides. The intermediacy of a silanimine is also consistent with all the data presented by Klein and Connolly.

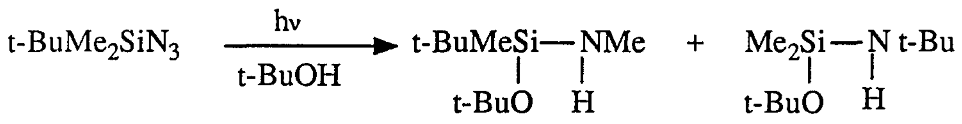


15

Parker and Sommer[12] have studied the photolysis of silylazides in the presence of trapping agents such as alcohols and siloxanes. In the cases where alcohols were used as trapping agents the experiments were limited to the use of bulky silylazides and bulky alcohols such as tertiary butanol. This limitation was necessary due to the reaction of less bulky substrates with the azidosilane.

$$Me_3SiN_3 + MeOH \longrightarrow Me_3SiOMe + HN_3$$

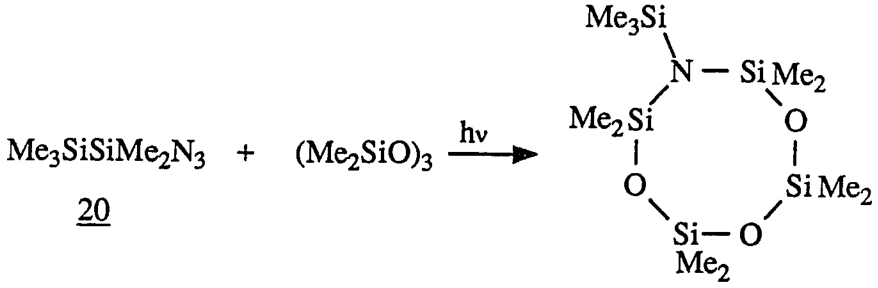
When t-butanol was used as the trapping agent the siloxanes were formed in fairly low yield. The use of



17 18 19

38 % 16 %

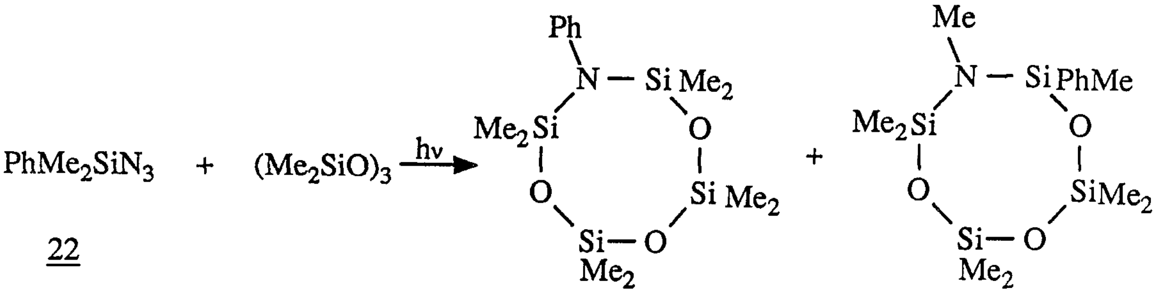
hexamethylcyclotrisiloxane showed that the migratory aptitude of the group on silicon was most important in determining which silanimine was formed. This is illustrated in two experiments, the photolysis of pentamethylazidodisilane 20 and the photolysis of dimethylphenylazidosilane 22.



20

21

28 %



22

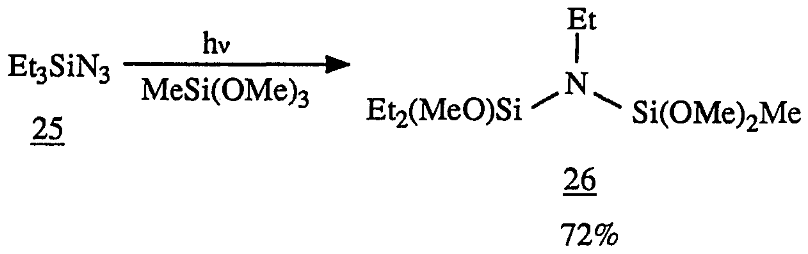
23

10 %

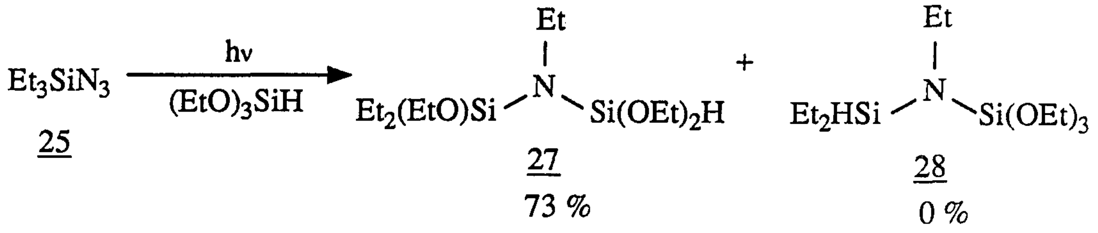
24

13 %

Elsheikh et al.[13] found that methoxysilanes serve as more efficient traps of silanimines than alcohols or siloxanes in the photolysis of silylazides. The yield in the case below is more than double any case cited previously.

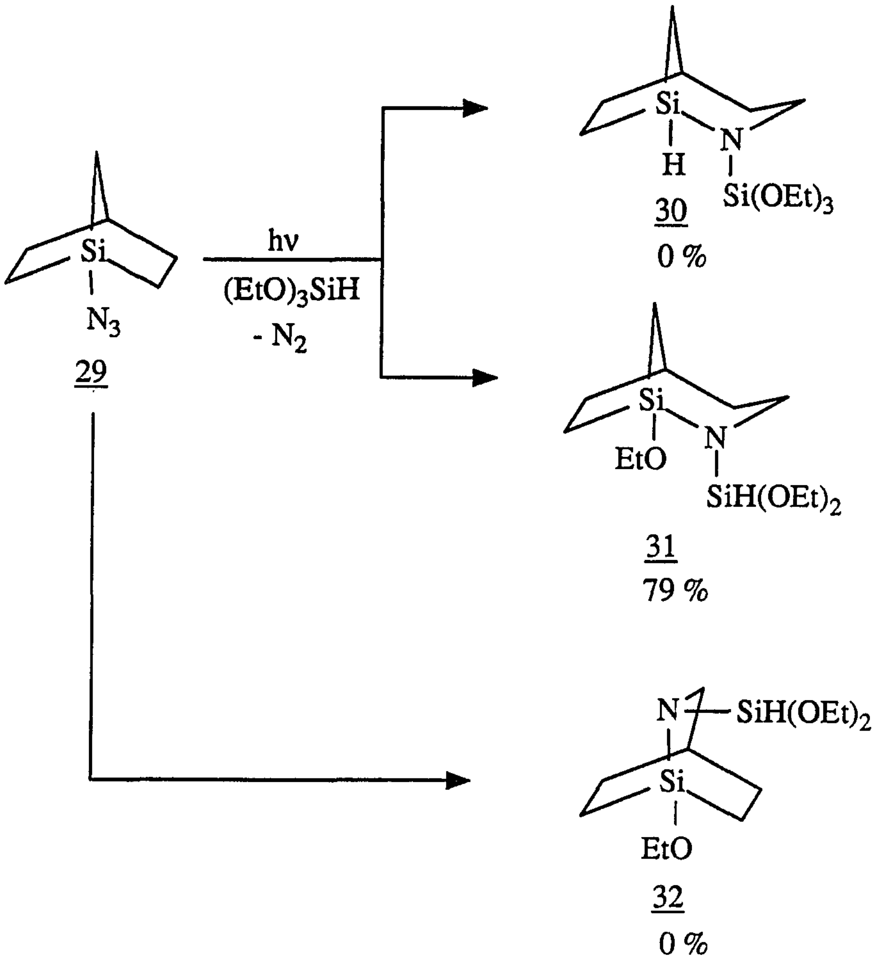


In order to determine if silanimines had a biradical or dipolar nature Elseikh et al.[13] have studied the photolysis of triethylazidosilane in the presence of triethoxysilane. This trap can conceivably react with both, diradical and dipolar intermediates. The product 27 observed was only

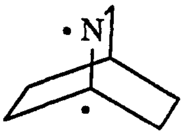


that which had arisen by addition of a silicon oxygen bond across the unsaturated linkage of the silanimine.

In order to try to make the silanimine have a biradical nature Elseikh and Sommer[14a] photolyzed compound 29. No product 30 that resulted from the addition of a silicon hydride bond across the unsaturated linkage was observed.



Additional evidence to support the dipolar nature of silanimines is obtained by the observation that no products 32 resulting from the migration of the one bridge in 29 were observed. The following intermediate 32a has been shown to contain no multiple bonding between carbon and nitrogen and exists as a triplet biradical.[14b]



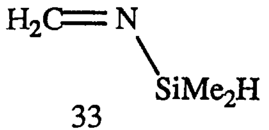
32a

Since the synthesis of azidosilanes was accomplished in 1962, a number of attempts have been made to observe silanimines by matrix techniques. Ogilvie and Cradock[15] recorded the infrared spectra of a species generated in the photolysis of azidosilane. The bands observed were compared with the data obtained in the photolysis of hydrogen isocyanide. The proposed structure for the product was that of silylisocyanide. This assignment is consistent with the

$$\overset{-}{\mathrm{Si}}\equiv\overset{+}{\mathrm{N}}\mathrm{H}$$

ab-initio calculations of Preuss et al.[10c] and Murrell et al.[10b] which suggest that the silylisocyanide structure is more stable by 68 kcal/mole and 90 kcal/mole respectively.

The photolysis of trimethylazidosilane in a matrix has been studied by two groups. The infrared spectrum of the product was very complex. In the original work of Ogilvie[16a] no mention was made of Si-H stretches in the spectrum. In contrast, Perutz[16b] observes a complex pattern of bands in the range of 2140-2130 cm^{-1}. The reports are in agreement that the strong band at 1670 cm^{-1} is not arising from a silanimine. The two most likely structures 33 and 34 are noted below. No mechanistic rationale is given by the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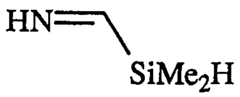
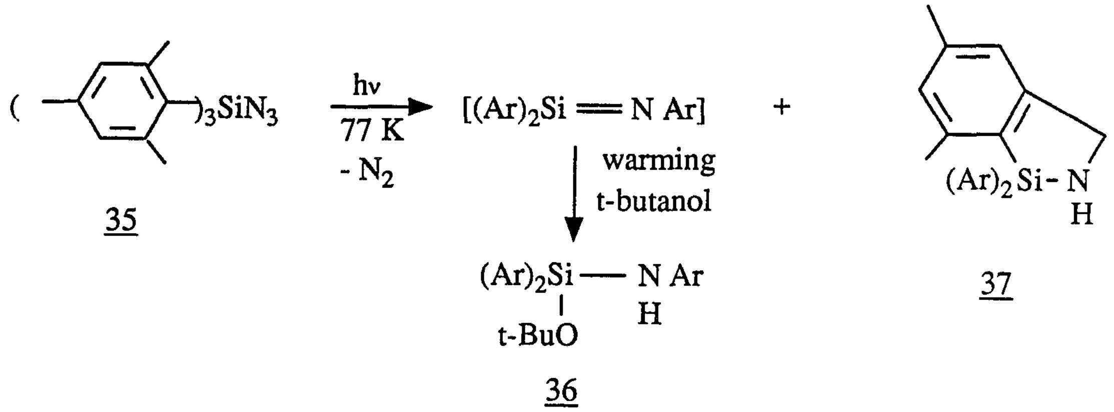

34

authors other than to speculate that these structures arise by a secondary photolysis.

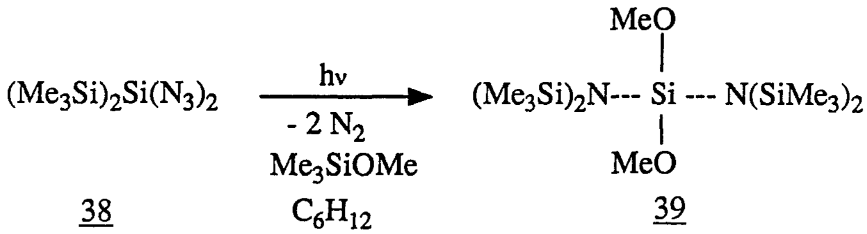
Two groups have reported the photolysis of trimesitylazido silane 35 in a frozen matrix.[17a,b] Two bands at 296



nm and 444 nm in the ultraviolet visible spectrum grew in at the same rate. A third band at 257 nm grew into the spectrum at a different rate. This indicates that most likely the bands at 296 nm and 244 nm result from the same product while the band at 257 nm results from a different product. The bands at 296 nm and 244 nm disappeared upon warming the sample to room temperature while the band at 257 nm did not disappear upon warm up.

The photolysis was also performed in the presence of t-butanol at 77 K. Identical bands were observed in this experiment but upon warm up two products were isolated, the t-butoxysilazane 36 and 37. The band at 257 nm was assigned to 37 by an independent method, while the bands at 244 nm and 296 nm are assigned to the n-π* transition and the π-π* transition in silanimine 9.

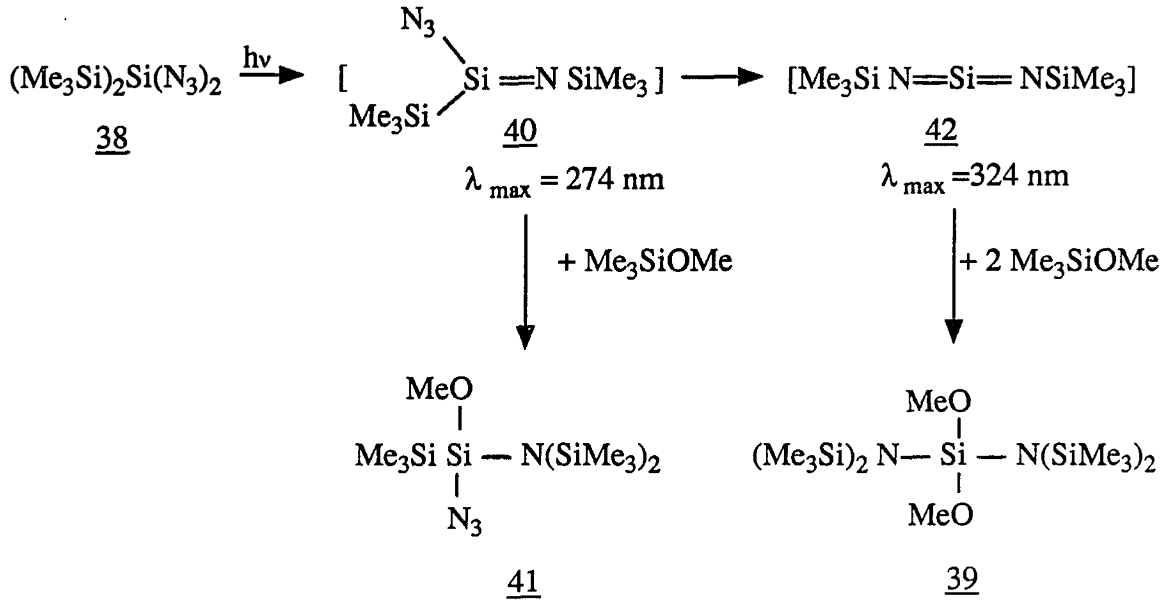
Zigler et al.[18] has also studied the photolysis of a diazidosilane in solution and in a matrix. When compound



$$(Me_3Si)_2Si(N_3)_2 \xrightarrow[\substack{-2\,N_2 \\ Me_3SiOMe \\ C_6H_{12}}]{h\nu} (Me_3Si)_2N\text{---}\overset{\displaystyle MeO}{\underset{\displaystyle MeO}{Si}}\text{---}N(SiMe_3)_2$$

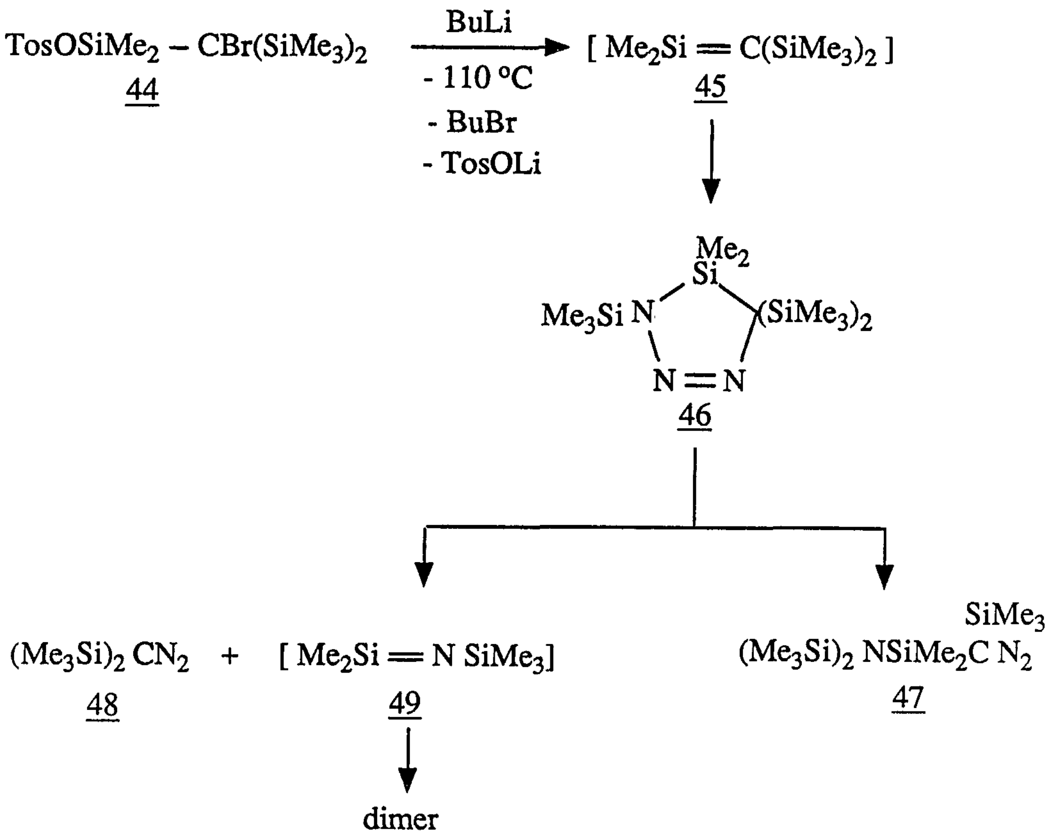
38 39

38 was irradiated in cyclohexane solution the only product observed was 39. The irradiation of 38 in a matrix showed two peaks in the ultraviolet spectrum. These two bands at 274 nm and 324 nm grew into the spectrum at different rates, suggesting that they arise from different intermediates. The authors suggest the following mechanism. The ratio of



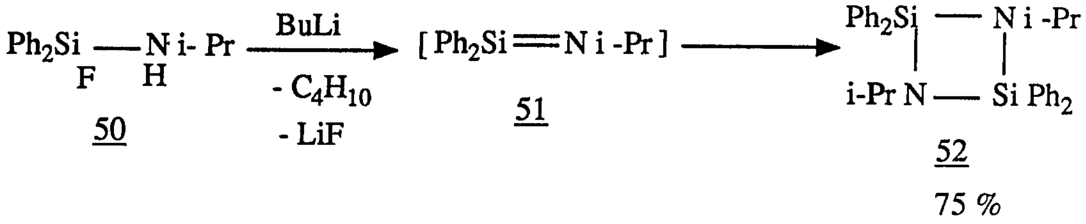
39 to 41 increases with increasing irradiation with 254 nm light. When the sample was irradiated at 270 nm after the initial 254 nm irradiation the band at 324 nm increased in intensity while the band at 274 nm decreased. Also supporting the assignment that 324 nm results from the silanediimine is a plot of the absorbance at 324 nm versus the moles of 39 produced. The plot in this case is linear suggesting again that 42 is the intermediate involved in the formation of 39.

A relatively mild means of generating silanimines was reported by Wiberg and Preiner.[19] This involves the metal

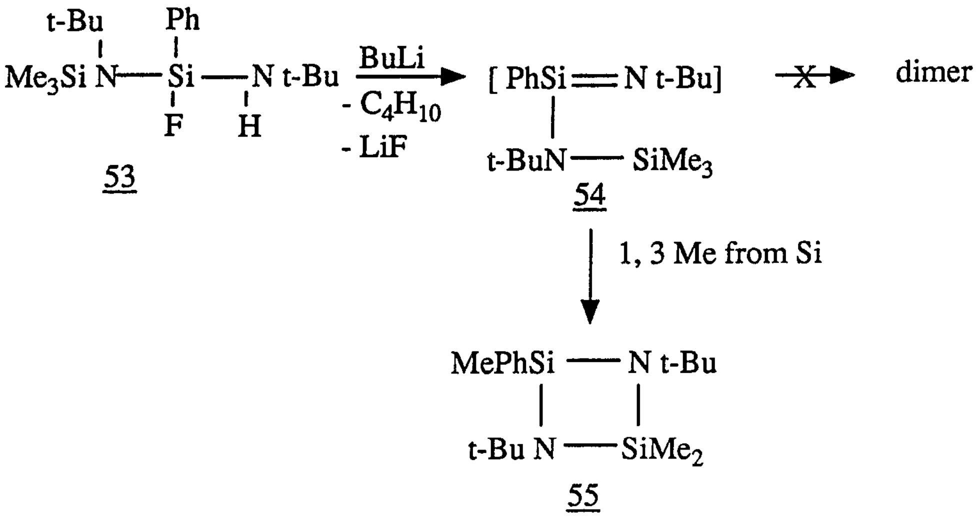


halogen exchange of 44 with butyl lithium followed by loss of lithium tosylate. This reaction produces silene 45 which in the presence of trimethylsilylazide reacts in 3+2 cycloaddition manner to produce hetercycle 46. This compound is not stable and undergoes two reactions. The first reaction is formally a 1,3 silyl shift to generate the ring open product 47 while the second reaction is a 3+2 cycloreversion which produces 48 and silanimine 49.

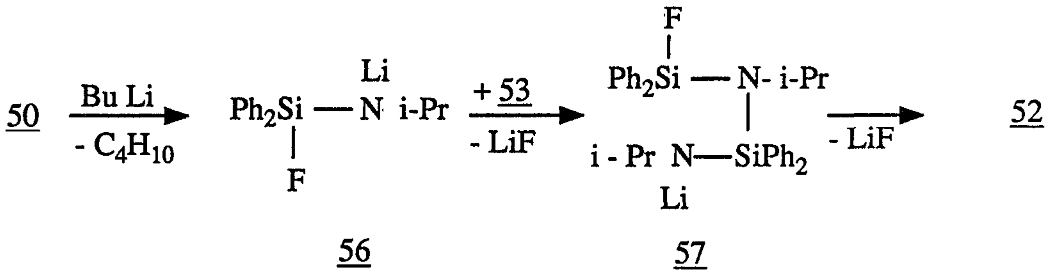
Klingebiel et al.[20a] have studied the reaction of butyl lithium and aminoflorosilanes. The authors in this report contend that silanimines are involved as the reactive intermediates. No attempts at trapping the intermediate



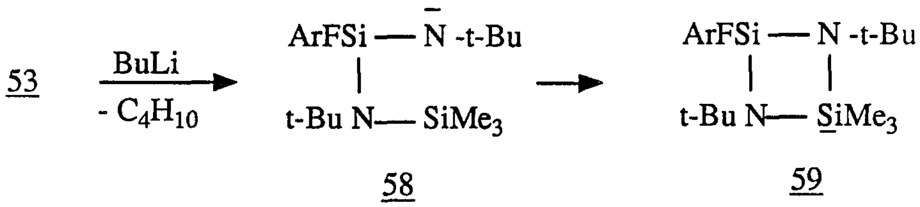
were reported. Klingebiel and Meller[20b] have also studied this reaction using diaminosilanes. The reaction in this

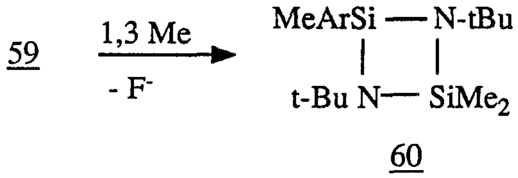


case 54 undergoes an unusual 1,3 shift of a methyl anion to produce the unsymmetrical cyclodisilazane 55 in 88% yield. The intermediacy of a silanimine is not demanded in these reactions. An entirely ionic mechanism can also accommodate all of the observations. Nucleophilic displacement of

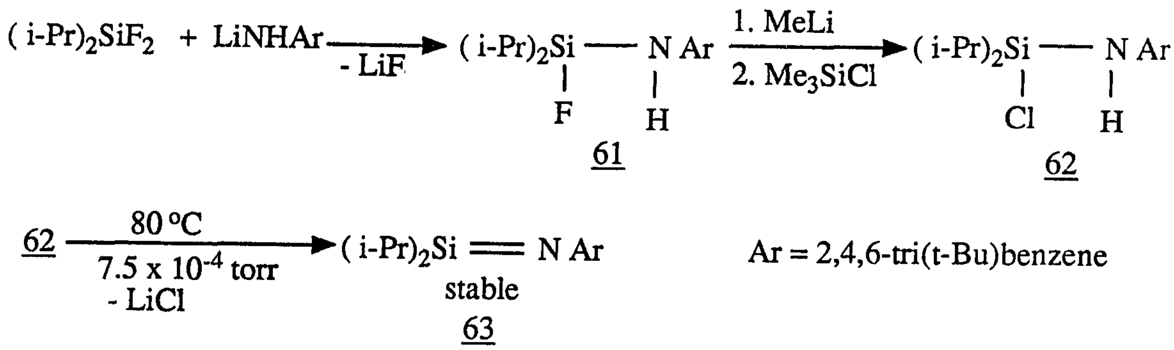


florine by the amide anion 56 in an intermolecular fashion produces intermediate 57 which can lose LiF to generate the observed cyclodisilazane 52. Likewise a similar mechanism can be written for the reaction of butyl lithium and diaminoflorosilane 53. In this case a petavalent silicon 59 is involved.

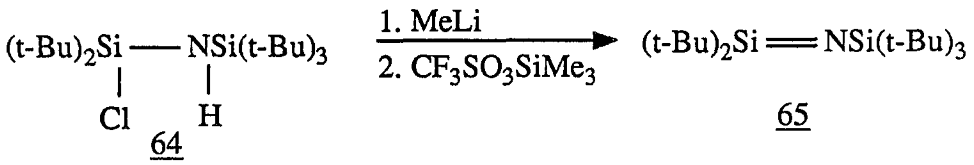


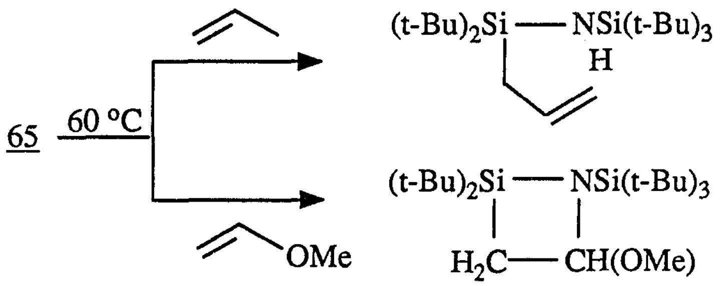


Two groups have studied the β elimination of lithium chloride from amidochlorosilanes to generate silanimines. Hesse and Klingebiel[21a] have developed a four step method to stable silanimines using this reaction. In this case the



silanimine 63 was fully characterized at ambient conditions. Wiberg et al.[21b] has found that treating chlorosilane 64 with methyl lithium followed by trimethylsilyltriflate





yields the silanimine 65 at room temperature. The silanimine 65 in this case was trapped by vinylmethylether or propene.

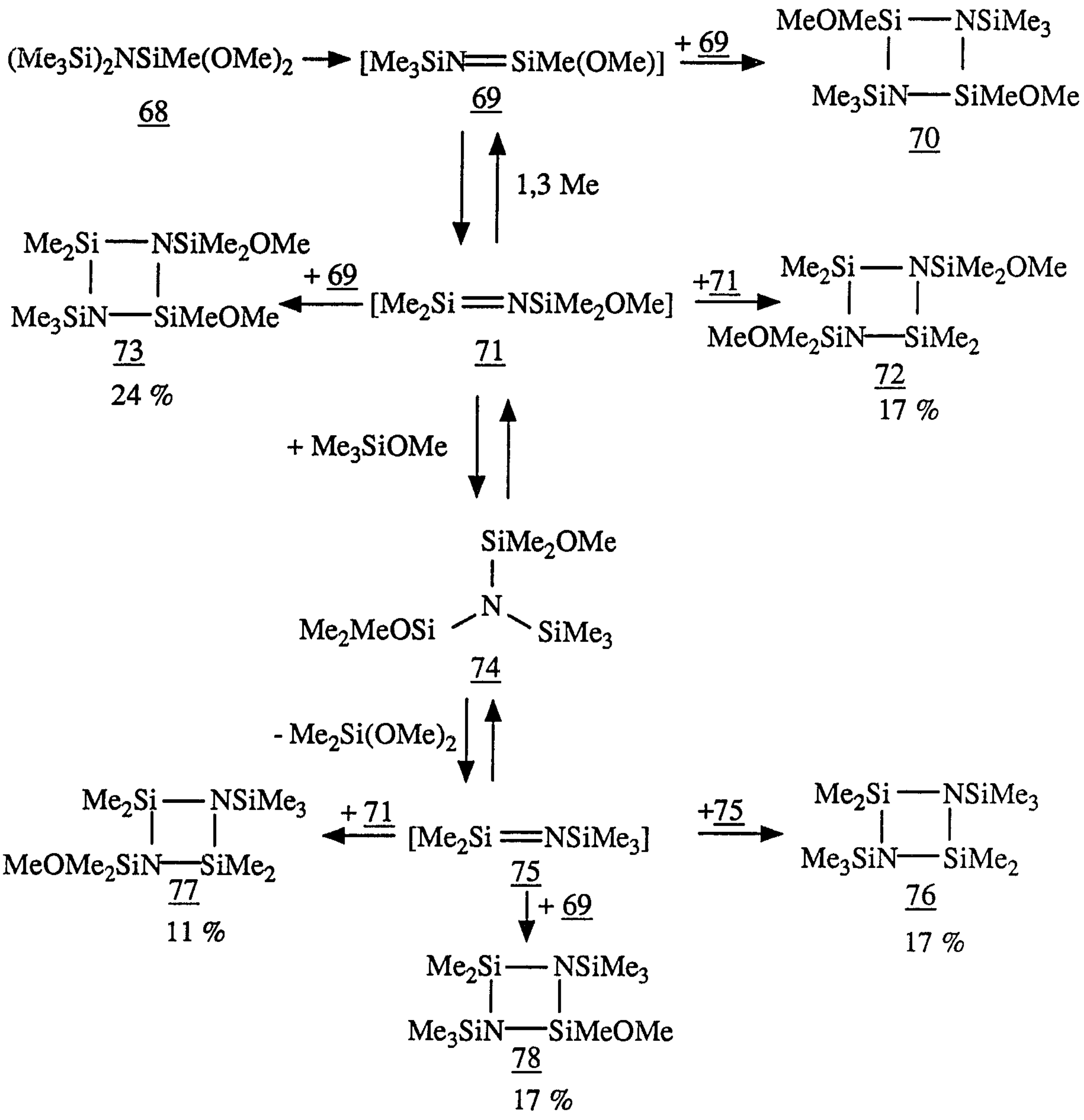
Wiberg et al.[21c] have prepared a stable silanimine by the addition of a silyl anion to azidochlorosilane 66. The

$$\underset{\underline{66}}{(t\text{-Bu})_2SiN_3Cl} \quad + \quad (t\text{-Bu})_3SiNa \xrightarrow[\substack{-\,NaCl \\ -\,N_2}]{-\,78\ ^{o}C} \underset{\substack{\underline{\text{stable}} \\ \underline{65}}}{(t\text{-Bu})_2Si{=}NSi(t\text{-Bu})_3}$$

X-ray analyses of 65 shows it to have a linear Si-N-Si framework with silicon nitrogen bond lengths of 1.568 Å and 1.695 Å. The later bond length is well within the range of bond lengths found in typical silicon nitrogen single bonds. The former bond length is assigned to the silicon nitrogen double bond. Complete characterization of 65 was obtained.

Kazoura and Weber[22a] have studied the β elimination of methoxysilanes from trisilazanes in the gas phase. Although a large number of products were observed the mechanistic interpretation is quite simple. The complexity of the reaction arises from the rearrangement of the initial silanimine produced. The main reactions are outlined below.

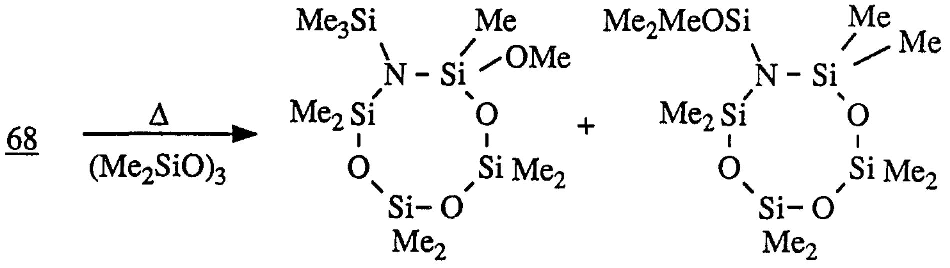
The initial step involves β elimination of methoxytrimethylsilane from 68. This produces silanimine 69 which dimerized to cis and trans cyclodisilazanes 70 in low yields. Alternatively 69 can undergo a 1,3 methyl shift to produce 71. This silanimine then dimerizes to 72 in 17% yield or reacts with 69 to produce 73 in 24% yield. Since the readdition of methoxytrimethylsilane to 71 is possible another trisilazane is produced 74. This can then eliminate dimethoxydimethylsilane and produce 75. This can then


(Me3Si)2NSiMe(OMe)2
68
[Me3SiN=SiMe(OMe)]
69
+ 69
MeOMeSi—NSiMe3
Me3SiN—SiMeOMe
70
1,3 Me
Me2Si—NSiMe2OMe
Me3SiN—SiMeOMe
73
24 %
+ 69
[Me2Si=NSiMe2OMe]
71
+71
Me2Si—NSiMe2OMe
MeOMe2SiN—SiMe2
72
17 %
+ Me3SiOMe
SiMe2OMe
N
Me2MeOSi
SiMe3
74
- Me2Si(OMe)2
Me2Si—NSiMe3
MeOMe2SiN—SiMe2
77
11 %
+ 71
[Me2Si=NSiMe3]
75
+75
Me2Si—NSiMe3
Me3SiN—SiMe2
76
17 %
+ 69
Me2Si—NSiMe3
Me3SiN—SiMeOMe
78
17 %

dimerize to produce 76 in 17% yield. Silanimine 75 can also react with 71 to produce 77 in 11% yield or react with 69 to produce 78 in 17% yield.

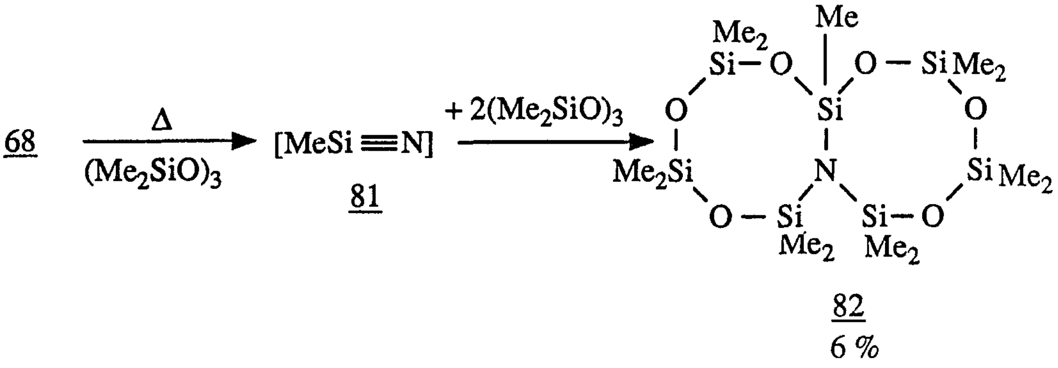
A number of other products are also formed in the reaction but the yields are all less than 3%. These products have arisen by similar mechanisms.

Kazoura and Weber[22b] have also studied this reaction in the presence of hexamethylcyclotrisiloxane. The results show that even in the presence of a trapping agent the silanimine undergoes a 1,3-methyl shift. Also formed in 6% yield was a product 82 that formally had arisen from the trapping of a silicon nitrogen triple bonded intermediate. More likely than the formation of 81 is that 79 lost

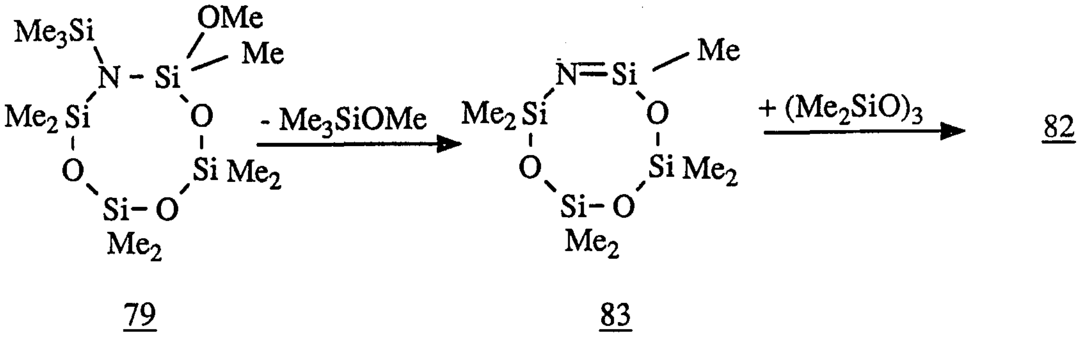


79 40 %

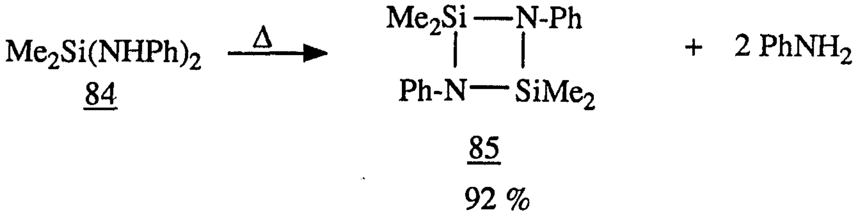
80 19 %



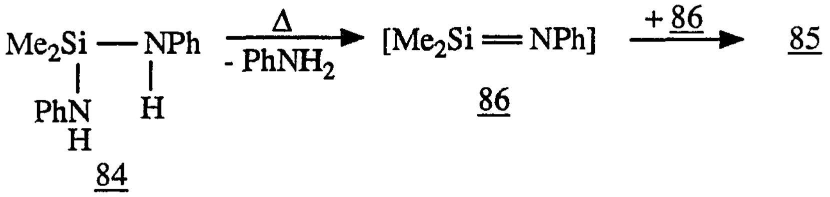
methoxytrimethylsilane to generate 83 which is trapped by hexamethylcyclotrisiloxane to produce 82.



In 1964 Fink[23] suggested that silanimines may be intermediates in the solution phase pyrolysis of diaminosilanes. Two possible mechanisms were postulated to

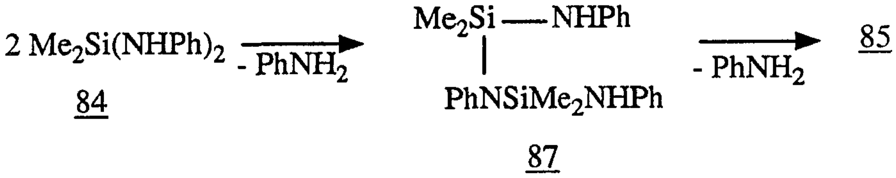


account for the formation of cyclodisilazane <u>85</u>. The first mechanism postulated by Fink was the β elimination of aniline. The second involves a series of transilylations.



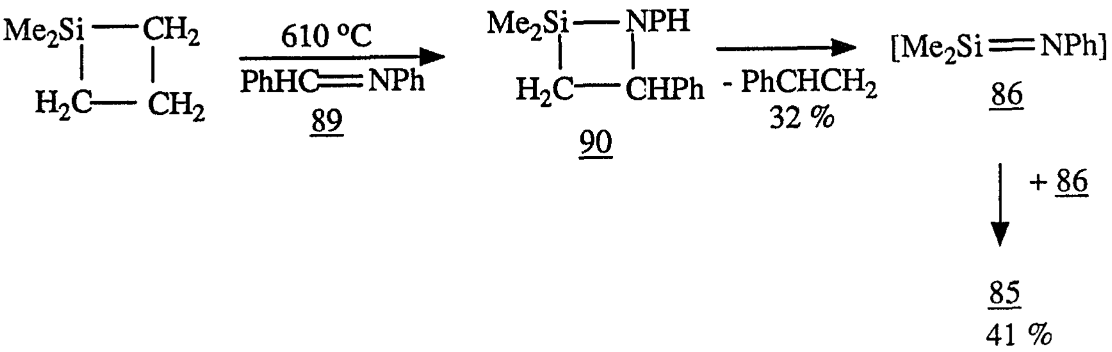
$$\underset{\underline{84}}{\mathrm{Me_2Si(NHPh)NHPh}} \xrightarrow[-\,\mathrm{PhNH_2}]{\Delta} \underset{\underline{86}}{[\mathrm{Me_2Si{=}NPh}]} \xrightarrow{+\,\underline{86}} \underline{85}$$

This type of exchange reaction is well precedented in the literature and is most likely the mechanism by which <u>85</u> is formed under these conditions.



$$\underset{\underline{84}}{2\,\mathrm{Me_2Si(NHPh)_2}} \xrightarrow[-\,\mathrm{PhNH_2}]{} \underset{\underline{87}}{\mathrm{PhNHMe_2Si{-}N(Ph)SiMe_2NHPh}} \xrightarrow[-\,\mathrm{PhNH_2}]{} \underline{85}$$

Golino et al.[24a] have used the thermal generation of silenes from 1,1-dimethylsilacyclobutane as a route to silanimines by performing the pyrolysis in the presence of an imine. The use of a silacyclobutane is a well precedented means of generating silenes.[24b] In this case the silene reacts with the imine <u>89</u> present to form the intermediate heterocycle <u>90</u>. This heterocycle <u>90</u> is not



isolated but decomposes to styrene and silanimine 86 which undergoes the usual dimerization of these intermediates and is isolated as the cyclodisilazane 85.

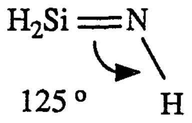
The theoretical study of silanimines has received very little attention. Luke et al.[25a] and Truong and Gordon[25b] have reported that the aminosilylene isomer is 18-20 kcal/mole lower in energy than the parent silanimine. The energy of activation in the isomerization of the imine to the silylene is calculated by Truong and Gordon to be 78 kcal/mole.

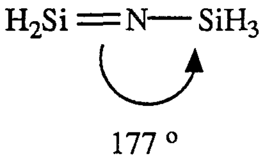
The bond lengths that are predicted in both studies mentioned above indicate that in aminosilylene the silicon nitrogen bond has some double bond character. The predicted bond length for a normal single bond between silicon and nitrogen is 1.726 Å but the calculated value for aminosilylene is 1.708 Å. This double bond character is also noted in the large rotational barrier of the silicon nitrogen bond in aminosilylene (27 kcal/mole).[25b] The donation of the lone pair of electrons on nitrogen into the vacant p orbital of the silylene is most likely the origin of the double bond character.

The parent silanimine is reported to have a π bond strength of 37 kcal/mole.[25b] The silicon nitrogen bond length is 1.576 Å. The Si-N-R bond angles are highly dependent upon the R group. If the group is hydrogen this angle is 125°, but if the group is a silyl group the bond angle becomes 175.6°. The linearization of the Si-N-Si bond angle was observed by Wiberg et al.[21c] in the X-ray structure of 67. Both Wiberg et al.[21c] and Schleyer and Stout[25c] attribute this linearization to electronic effects.

$(t\text{-}Bu)_2Si{=}NSi(t\text{-}Bu)_3$

67





Reichle[5] was the first to suggest that silanimines have a polar nature while later Elsheikh and Sommer[14a] demonstrated that silanimines behave like polar intermediates by their experiments using triethoxysilane as a trapping agent. The calculations of Luke et al.[25a] suggest that the nitrogen in silanimine bears nearly a full negative charge while the silicon has a full positive charge.

The theoretical study of a triple bond between silicon and nitrogen was prompted by a report that silylnitrile or silylisocyanide may be responsible for certain microwave spectral lines in outer space.[26] Three groups[10a,b,c,25a] have performed calculations at the ab-initio level. The calculations suggest that the silylisocyanide is more stable by 68-90 kcal/mole. The studies also suggest a linear arrangement of the atoms in both species with very similar bond lengths. Preuss et al.[10c] conclude that neither silylnitrile or silylisocyanide are a likely source of the spectral lines observed by Lovas.[26]

RESULTS AND DISCUSSION

The primary purpose of this section relates to some of the problems of using organopolysilazanes in the synthesis of silicon nitride (Si_3N_4). Until very recently the use of organopolysilazanes as Si_3N_4 precursors was an area of little study.[27a,b] The principal means of producing bulk Si_3N_4 powder are outlined in the following reactions.[28,29,30a,b,31]

$$SiCl_4 + NH_3(l) \longrightarrow Si\ N \text{ polymer} \xrightarrow{\Delta} Si_3N_4$$

$$3\,SiO_2 + 2\,N_2 + 6\,C \xrightarrow{\Delta} Si_3N_4 + 6\,CO$$

$$3\,Si + 2\,N_2 \xrightarrow{\Delta} Si_3N_4$$

$$3\,SiH_4 + 4\,NH_3 \xrightarrow{\Delta} Si_3N_4 + 12\,H_2$$

Each of these techniques has various advantages and disadvantages. A common disadvantage to each of these techniques is the inability to produce anything other than bulk Si_3N_4 powder. In order to get this material in a useful form additional processing must be done. Organopolysilazanes potentially could be used as Si_3N_4 precursors which could be poured and molded into the desired shape, particularly if shrinkage could be minimized.

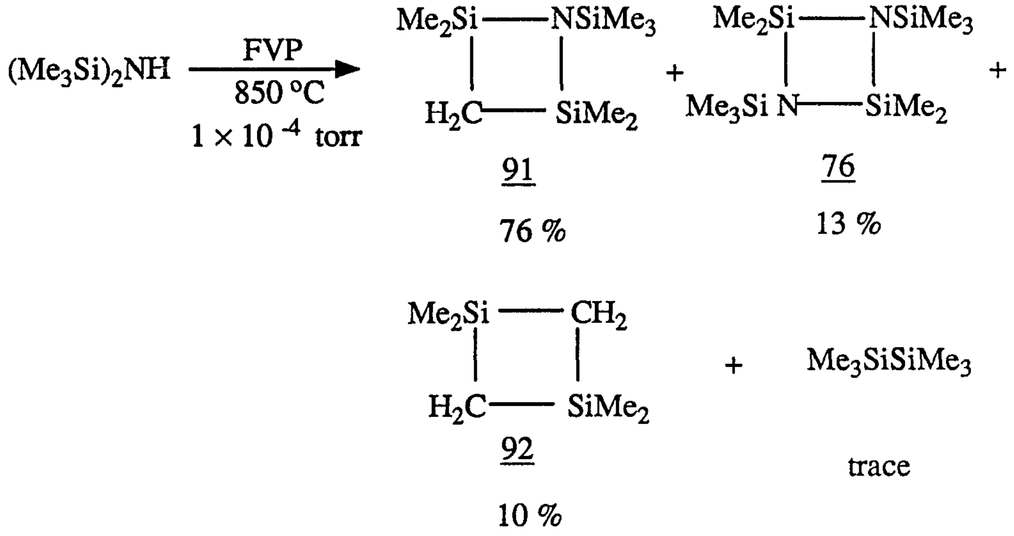
Organopolysilazanes do suffer one major disadvantage over the previously discussed techniques in the synthesis of

Si_3N_4. The primary problem with this technique is the formation of not only silicon nitride but also silicon carbide and carbon.[32a,b]

These impurities at times are the major product of the pyrolysis. They also tend to affect some of the physical properties of the silicon nitride, such as high temperature strength and rate of oxidation.

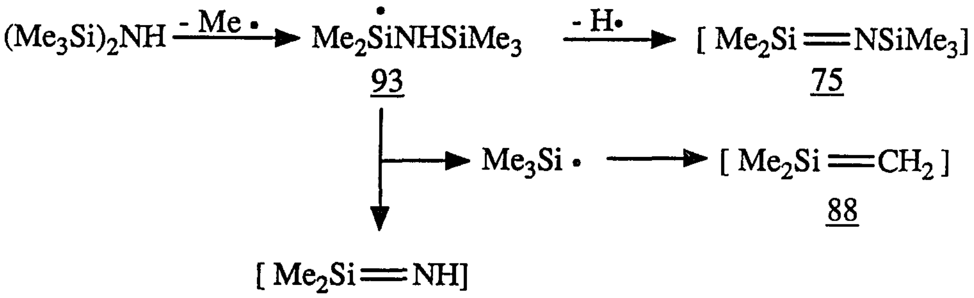
In order to learn more about how to limit the formation of silicon carbide and carbon it is important to understand what types of intermediates are involved in the decomposition of organopolysilazanes. There is an inherent difficulty in using polymers to determine chemical behavior. Examples of such difficulties are in product characterization and kinetic determinations. In order to develop the chemistry of polymers other researchers have used monomer models to help predict the chemical behavior of a polymeric system. Examples of such studies are cited in reference 33.

The model monomer first chosen for this study was hexamethyldisilazane. As expected this material is very stable under flash vacuum conditions and did not decompose below 800°C. At 850°C, 32% of the starting material decomposed to four products. The major product was 91.



This product most likely had arisen from the head-to-tail reaction of a silanimine and a silene. The identification of this product was somewhat difficult due to an overly simplistic proton NMR spectrum when chloroform was used as the solvent. The proton spectrum in chloroform showed only two types of hydrogens while the carbon spectrum showed the presence of three types of carbon atoms. Changing the NMR solvent to benzene revealed that three types of protons were present in a ratio consistent with the proposed structure of 91. 1,1,3,3-Tetramethyl-1,3-disilacyclobutane 92 was also difficult to identify because it coeluted with hexamethyldisilazane in the gas chromatograph. The presence of 92 was revealed by searching the spectrum for the parent ion of 92 as well as the M^+ -15 peak for this product. The presence of 92 supports the proposed origin of 91 since its presence would be demanded if 1,1-dimethylsilene was a reactive intermediate in this reaction. The characterization of the cyclodisilazane 75 was accomplished by comparison of NMR spectral data with those present in the literature.[34]

A mechanism to account for these results is outlined below. It involves homolytic cleavage of a silicon carbon



$2\,\underline{75} \longrightarrow \underline{76}$

$2\,\underline{88} \longrightarrow \underline{92}$

$\underline{75} + \underline{88} \longrightarrow \underline{91}$

bond in hexamethyldisilazane as the first step. This step produces a methyl radical and amino radical 93. The methyl radical undoubtedly produces methane by hydrogen abstraction or ethane by recombination with another methyl radical. Amino radical 93 can then lose a hydrogen to produce silanimine 75, dimerization of which produces 76. The mechanism to produce silene 88 is difficult to speculate upon. Silene 88 may arise by loss of trimethylsilyl radical from radical 93. Trimethylsilyl radical is known to produce silene 88.[35a,b,c] Trimethylsilyl radical may also arise by cleavage of the silicon nitrogen bond in hexamethyldisilazane. Other mechanisms can be considered such as loss of hydrogen followed by loss of methyl radical from hexamethyldisilazane to account for these products as

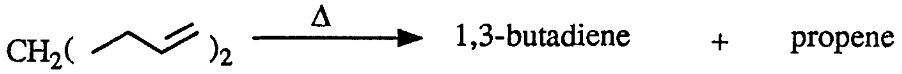
$$(\mathrm{Me_3Si})_2\mathrm{NH} \xrightarrow{-\mathrm{H}\bullet} (\mathrm{Me_3Si})_2\mathrm{N}\bullet \xrightarrow{-\mathrm{Me}\bullet} [\,\mathrm{Me_2Si{=}NSiMe_3}\,]$$

75

well. It is difficult to say which mechanism is most likely since bond energies for silazanes are far from certain.

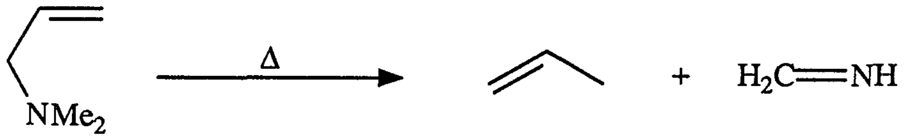
The isolation of cyclodisilazane 76 and heterocycle 91 suggests that silanimines are reactive intermediates in the decomposition of silazanes. The available methods of generating silanimines are severely limited if one must incorporate this functionality into a polymeric backbone. Since one of the goals of this work was to see if one could limit the formation of silicon carbide and carbon in silicon nitride prepared from organopolysilazanes, it was thought that a new method of generating silanimine would need to be developed which would contain an organic leaving group. Hopefully this would in turn limit the formation of silicon carbide and carbon in the ceramic products.

One method of generating multiple bonds that has not been used to synthesize silanimines is the retroene elimination of propene. This reaction has been used to generate alkenes[36a] and imines.[36b]



E_a = 46.9 Kcal/Mole

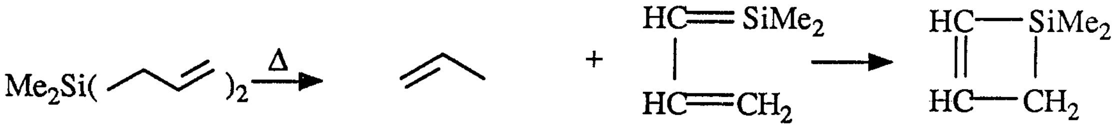
log A = 11.3



E_a = 43.4 Kcal/mole

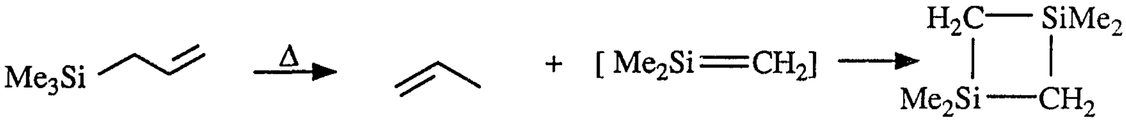
log A = 11.4

The retroene reaction has also been used in a number of systems which generate multiple bonds to silicon. Block and

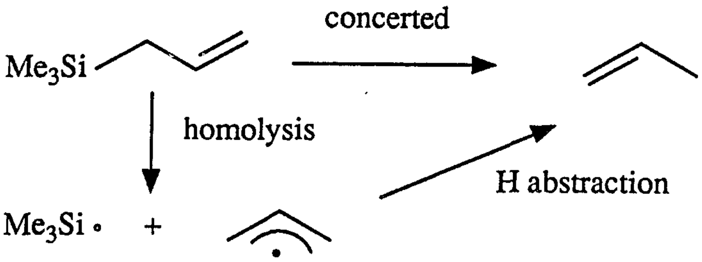


E_a = 47.4 Kcal/mole

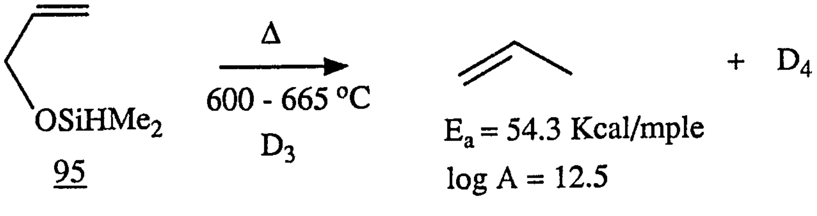
log A = 11.2



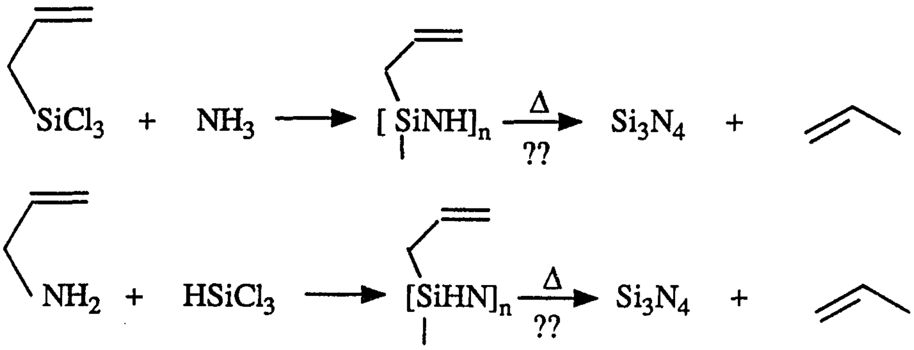
Revelle[37a] and Auner et al.[37b] have studied the pyrolysis of diallyldimethylsilane. While the pyrolysis of allyltrimethylsilane has been the subject of much controversy in the past,[37c,d,e] the issue was settled in the work of Barton et al.[37e] which determined that allyltrimethylsilane decomposed by two mechanisms. The E_A and the log A for the concerted



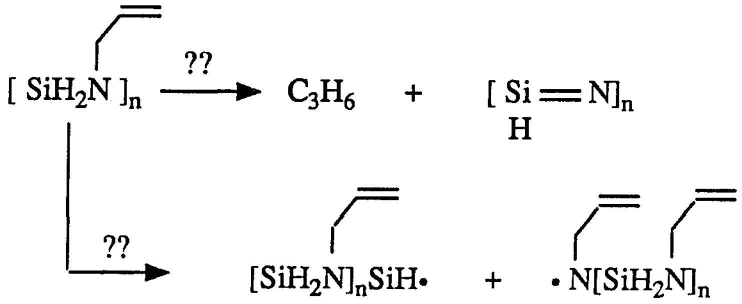
process was determined to be 55.0 kcal/mole and 11.6 respectively. Barton and Bain[37f] have generated silanones by the retroene elimination of propene from allyloxysilane 95. The E_A and log A were determined to be 54.3 kcal/mole and 12.5. No evidence of homolytic cleavage of the oxygen allyl bond was obtained.



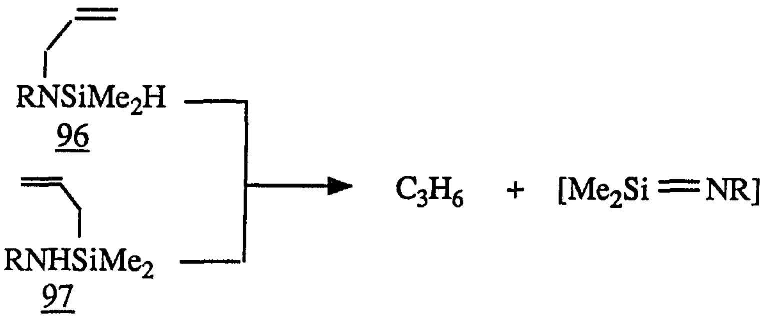
The incorporation of an allyl group into a polysilazane framework should be very easily accomplished. The following reactions show two possible routes to allylpolysilazanes that could be useful in synthesizing silicon nitride. In



both reactions the required substitution pattern (α hydrogens on silicon or nitrogen) would be assured in the polymer framework. The possibility of using linear polymers is also of interest if the retroene reaction would occur with a much lower energy of activation than the typical decomposition pathways that linear polysilazanes undergo.

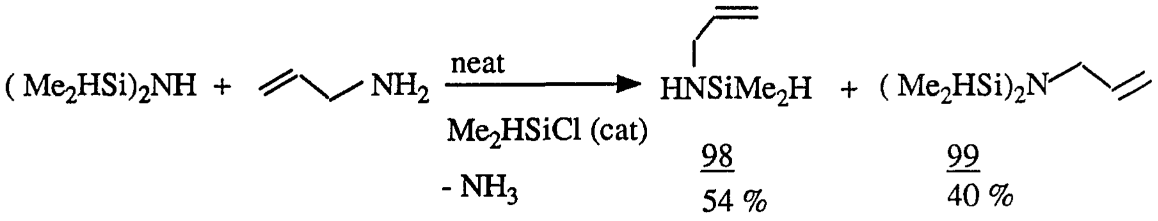


There are two different retroene reactions that could be incorporated into a polysilazane framework which could



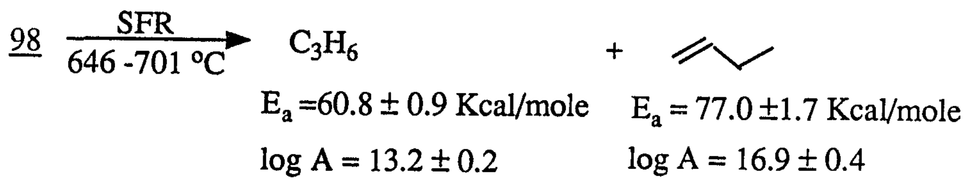
generate silanimines. In order to determine which substitution pattern, 96 or 97, would most easily produce propene, the kinetic parameters for such processes were determined using a stirred flow reactor (SFR).[38] A diagram of the system used as well as the relevant kinetic equations are outlined in the experimental section.

The first type of allylsilazane that was studied contained the allyl group upon nitrogen. The synthesis of 98 has been reported by Webb and Olsen.[39] The synthesis



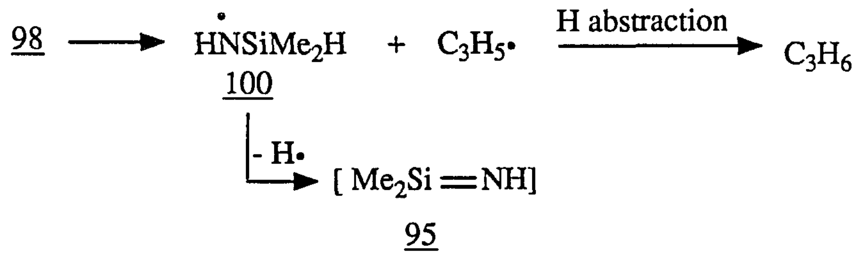
involves the transilation of a dimethylsilyl group from 1,1,3,3-tetramethyldisilazane to allyl amine. This reaction is accomplished without solvent in the presence of a catalytic amount of dimethylsilylchloride in 54% yield. The major byproduct is the bissilylated allylamine 99 which was formed in 40% yield. This product 99 also obtained by allowing the monosilated allyl amine to stand for prolonged periods.

N-allyl-1,1-dimethylsilazane 98 was studied under SFR conditions and was found to begin to decompose at 650°C to propene as well as butene. No silicon-containing products were characterized. Attempts to trap 1,1-dimethylsilanimine



were not successful. Two traps were employed, mainly methanol and hexamethylcyclotrisiloxane. The inability to trap the intermediate as will be discussed later is likely due to the reactivity of the adduct, which will be shown to decompose under these conditions.

The kinetic data suggest that some of the propene is arising from homolysis of the nitrogen allyl bond followed by hydrogen abstraction. The conclusion arises from the A



factors discussed previously for retroene reactions. The values of the log A factors typically associated with an entirely concerted 6-centered process producing propene are in the range of 11-12. This range will be used to help determine if some of the propene is arising by a radical process. Attempts to trap the allyl radical with D_8 toluene were successful, evidenced by deuterium incorporation into the propene formed. This trapping does not give a good indication to the amounts of allyl radicals present in the reaction because of the similar stabilities of allyl and benzyl radicals.[40a,b] Barton and Bain[37f] have shown that propene does not incorporate deuterium when pyrolyzed in the presence of D_8-toluene.

$$\underline{98} \; \underset{674\ ^\circ C}{\xrightarrow[C_7D_8]{SFR}} \; \underset{10\,\%}{C_3H_5D} \; + \; \underset{0\,\%}{C_4H_7D}$$

$$C_3H_6 \; + \; 20\,C_7D_8 \; \xrightarrow[640\ ^\circ C]{SFR} \; \underset{0\,\%}{C_3H_5D}$$

The origin of butene is less certain. The high log A of 17.0 suggests that this product arises from a rate determining step which involves the homolytic cleavage of a bond in the starting material. The mechanisms by which butene may be formed in this reaction will be discussed in detail later.

A more realistic model for a polysilazane is the N-allyl-1,1,3,3-tetramethyldisilazane 99 isolated as a byproduct in the synthesis of N-allyl-1,1,1-dimethylsilazane 98. Disilazane 99 decomposed at a lower temperature than 98 with an energy of activation of 54.5 ± 0.5 kcal/mole and log A of 12.9 ± 0.1. Butene did not appear until the higher

$$\underline{99} \xrightarrow[580-650\ ^{\circ}\mathrm{C}]{\mathrm{SFR}} \mathrm{C_3H_6} \quad + \quad \underset{\underline{101}}{[\mathrm{Me_2HSiN{=}SiMe_2}]}$$

$$E_a = 54.5 \pm 0.5\ \mathrm{Kcal/mole}$$

$$\log A = 12.9 \pm 0.1$$

temperatures of the kinetic run, so the Arrhenius parameters were not determined.

The silanimine was trapped in a separate experiment with methanol. This points out an advantage of the SFR apparatus

$$\underline{99} \xrightarrow[\substack{630\ ^{\circ}\mathrm{C} \\ \mathrm{MeOH(g)}}]{\mathrm{SFR}} \underset{\underline{102}}{\mathrm{Me_2HSiNHSiMe_2OMe}} \quad + \quad \mathrm{C_3H_6}$$

over other techniques since in the gas phase methanol does not react with silazanes as it would in the liquid phase. The trapped adduct was characterized by GCMS and an

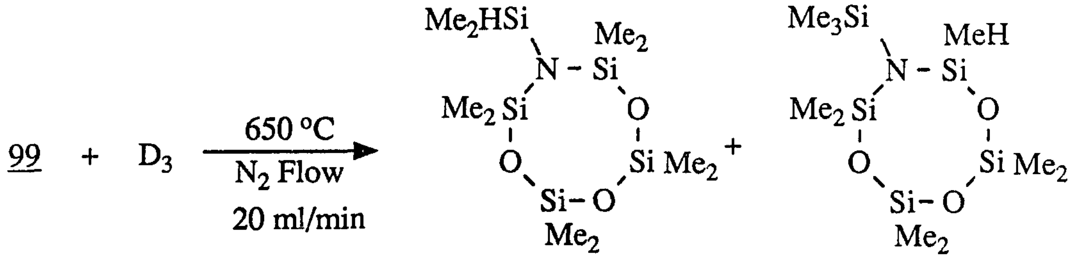
$$(\mathrm{Me_3Si})_2\mathrm{NH} \quad + \quad \mathrm{MeOH} \xrightarrow[\text{liq. phase}]{} 2\,\mathrm{Me_3SiOMe} \quad + \quad 2\mathrm{NH_3}$$

independent synthesis. The preparation of disilazane 102 is outlined here. The synthesis began with chlorine/methoxy redistribution between dimethoxydimethylsilane and dichlorodimethylsilane to produce methoxychlorodimethylsilane in 86% yield. Silane <u>103</u> was then mixed with chlorodimethylsilane in hexanes and ammonia was bubbled through the solution. The desired product <u>102</u> was produced in 11% yield. The other two possible disilazanes, 1,1,3,3-tetramethyldisilazane and 1,3-dimethoxy-1,1,3,3-tetramethyldisilazane were also observed.

$$Me_2Si(OMe)_2 \quad + \quad Me_2SiCl_2 \xrightarrow[25\ ^\circ C]{neat} \underset{\underset{86\ \%}{\underline{103}}}{Me_2SiOMeCl}$$

$$\underline{103} \quad + \quad Me_2SiHCl \xrightarrow[hexanes]{NH_3} \underset{11\ \%}{\underline{102}}$$

The silanimine was trapped in a very low yield (< 5%) when hexamethyltrisiloxane was used as the trap. The problem again is that β elimination (reverse of the trapping reaction) is very facile at these temperatures. Later in

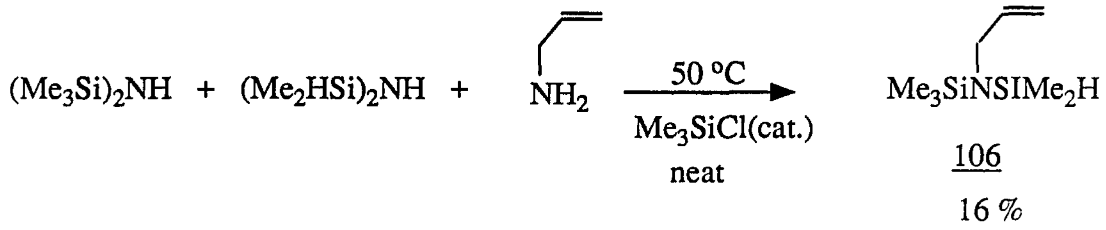


<u>104</u>
5 %

<u>105</u>
trace

this discussion the rationale for observing two trapped products will be discussed.

A similar set of experiments was performed with the pentamethyl derivative 106, the synthesis of which is outlined here. The Arrhenius parameters for the



decomposition of 106 to produce propene are somewhat higher than those for 99 and the rationale for this is not clearly understood. The imine was trapped with methanol as before

$$\underline{106} \xrightarrow[600 - 652\,^{\circ}C]{SFR} C_3H_6 + C_4H_8 + [Me_2Si{=}NSiMe_3]$$

C_3H_6: $E_a = 58.3 \pm 0.9$ Kcal/mole, $\log A = 13.7 \pm 0.2$

C_4H_8: $E_a = 71.1 \pm 0.8$ Kcal/mole, $\log A = 16.6 \pm 0.2$

and the methoxydisilazane 107 characterized by an independent synthesis.

$$\underline{106} \xrightarrow[\substack{630\,^{\circ}C \\ MeOH(g)}]{SFR} \underset{\underline{107}}{Me_3SiNHSiMe_2OMe}$$

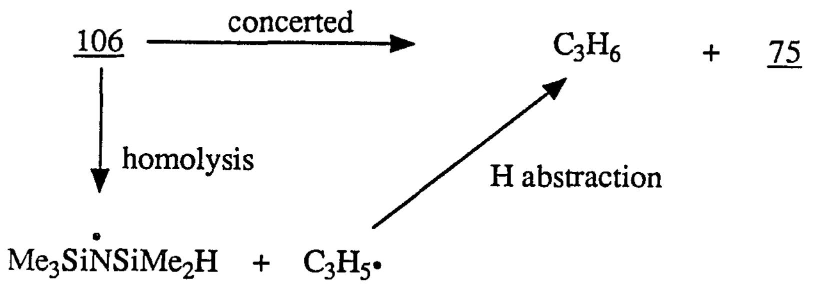
$$\underline{103} + Me_3SiCl \xrightarrow[hexanes]{NH_3} \underset{27\ \%}{\underline{107}}$$

The high log A of 13.7 for the formation of propene suggests that some of the propene is arising from the homolysis of the nitrogen allyl bond. This was confirmed by performing the experiment in the presence of D_8 toluene. The result shows that allyl radicals are formed by the

$$\underline{106} \xrightarrow[\substack{650\,^{\circ}C \\ C_7D_8}]{SFR} \underset{5\,\%}{C_3H_5D}$$

homolysis of the nitrogen allyl bond in <u>106</u>. This experiment demonstrates that homolysis of the nitrogen allyl bond is occurring to some degree in <u>106</u>.

In summary <u>106</u> is producing propene by two separate mechanisms. The first is a concerted retroene elimination that involves a 6 centered transition state leading to the



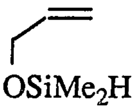
formation of propene and silanimine <u>75</u>. The second mechanism is a homolytic mechanism whereby the nitrogen allyl bond cleaves to produce an allyl radical and an amino radical. The allyl radical produced in this step then abstracts hydrogen to produce propene. It is difficult to estimate how much of each mechanism is contributing to the overall decomposition, since trapping of the allyl radical is not an efficient process.[40a,b]

Likewise 98 most likely decomposes by the two mechanisms outlined above. This conclusion is based on similar evidence. Silazane 99 decomposed largely by the concerted mechanism. The only evidence for this conclusion is that the Arrhenius parameters for its decomposition are similar to those reported by Barton and Bain.[37f]

$$\underline{99} \xrightarrow{\text{SFR}} C_3H_6 + \underline{101}$$

$$E_a = 54.5 \pm 0.5 \text{ Kcal/mol}$$

$$\log A = 12.9 \pm 0.1$$



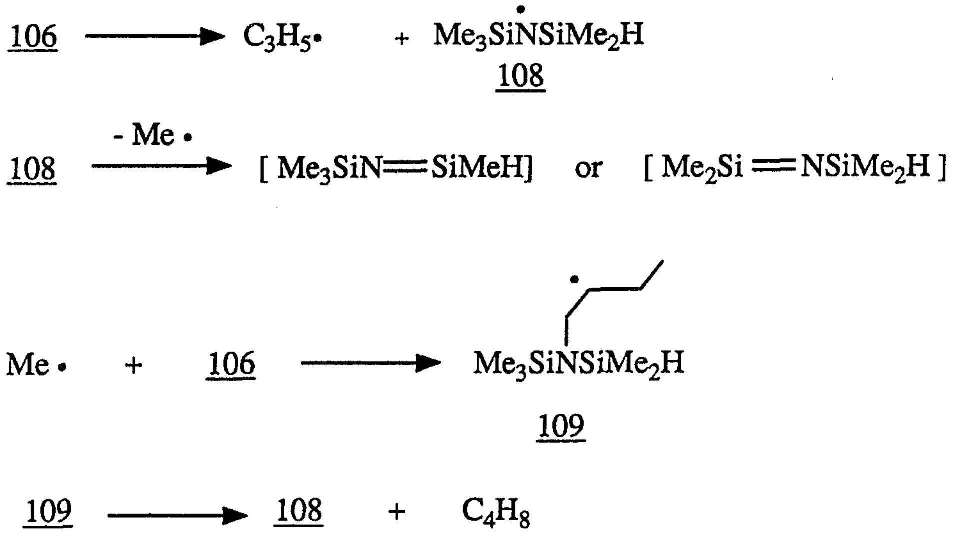
95

$$\xrightarrow[\substack{600-665\ ^\circ\text{C} \\ D_3}]{\text{SFR}} C_3H_6 + D_4$$

$$E_a = 54.3 \pm 0.4 \text{ Kcal/mol}$$

$$\log A = 12.5 \pm 0.1$$

One aspect of this work that has not been discussed is the origin of butene in the product mixture. The most straightforward mechanism to account for this product is outlined here. It involves homolytic cleavage of the



nitrogen allyl bond to produce an allyl radical and amino radical 108. The bond strength of this nitrogen allyl bond is estimated to be 10-15 Kcal/mole lower than the silicon hydrogen bond or the silicon methyl bond.[41] The methyl radical which is produced in the second step then adds to the olefinic portion of the starting material to produce the carbon based radical 109. β cleavage of 109 can then produce amino radical 108 and butene.

In order to test this mechanism the Arrhenius parameters for the formation of butene were determined in a large excess of toluene, since toluene is a good scavenger of methyl radicals.[42] Although the Arrhenius parameters remained within the original error limits, the rate constants were reduced by one half. Examples of rate constants are also given. The use of a 10 fold excess of

$$\begin{array}{llll}\underline{106} \xrightarrow[600 - 658\ ^\circ C]{SFR} & C_3H_6 & + & C_4H_8 \\ & E_a = 58.3 \pm 0.9 \text{ Kcal/mole} & & E_a = 71.1 \pm 0.8 \text{ Kcal/mole} \\ & \log A = 13.7 \pm 0.2 & & \log A = 16.6 \pm 0.2 \\ & & & k \text{ at } 650\ ^\circ C = 0.5752 \text{ sec}^{-1}\end{array}$$

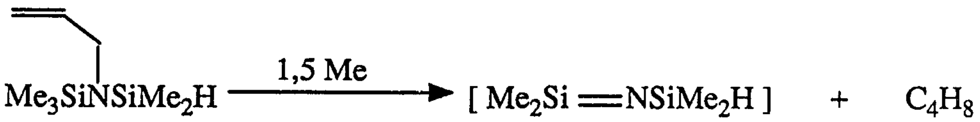
$$\begin{array}{llll}\underline{106} \xrightarrow[625 - 665\ ^\circ C,\ C_7H_8]{SFR} & C_3H_6 & + & C_4H_8 \\ & E_a = 62.0 \pm 2.5 \text{ Kcal/mole} & & E_a = 71.8 \pm 0.9 \text{ Kcal/mole} \\ & \log A = 14.5 \pm 0.6 & & \log A = 16.4 \pm 0.4 \\ & & & k \text{ at } 650\ ^\circ C = 0.3318 \text{ sec}^{-1}\end{array}$$

ethylene also only moderately retarded the formation of butene. The lowering of rates in these experiments supports

$$\begin{array}{ll}\underline{106} \xrightarrow[650\ ^\circ C,\ C_2H_4]{SFR} & C_4H_8 \\ & k = 0.2778 \text{ sec}^{-1}\end{array}$$

the mechanism that was outlined previously. These experiments also indicate that another mechanism is operative in the formation of butene since scavenging of methyl radicals by toluene did not eliminate the production of butene.

A second possible mechanism involves a 1,5 methyl shift from 106 to produce butene. The highly positive entropy of



$$\mathrm{Me_3SiN(CH_2CH{=}CH_2)SiMe_2H} \xrightarrow{1,5\ \mathrm{Me}} [\mathrm{Me_2Si{=}NSiMe_2H}] + \mathrm{C_4H_8}$$

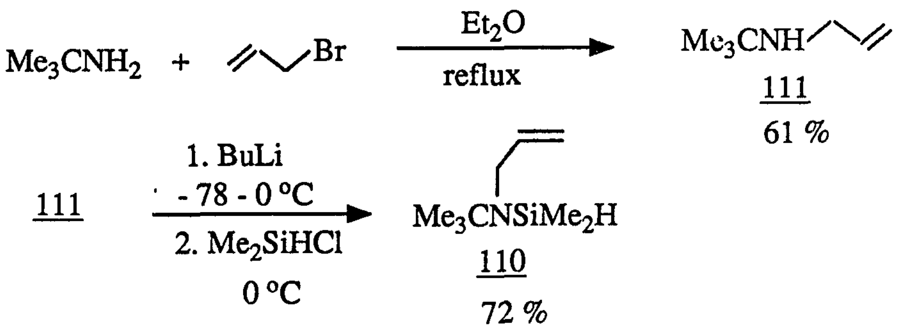
106

activation ($\Delta S^{\ddagger} = 12.4 \pm 1.6$ eu at 638.0°C) is difficult to rationalize if a concerted mechanism is involved.

Mechanisms can also be written which involve intermolecular ene reactions which could produce butene. The experiments such as crossover experiments and detailed pressure dependence studies could be performed to address this point.

In conclusion butene formation is occurring by at least two mechanisms. The first is outlined earlier, which involves methyl radical addition to the olefinic portion of the starting material. The other possible mechanisms are difficult to speculate upon since the Arrhenius parameters indicate a radical process is involved even when the radicals are scavenged. One possibility to explain the results above relates to the effectiveness of toluene trapping of methyl radicals under our conditions.

In order to learn how an alkyl group in the place of the non-active silyl group would affect the decomposition of these types of compounds, silazane 110 was prepared in two steps. The first step was alkylation of t-butyl amine with allylbromide in 61% yield. The allyl amine 111 was then



treated with butyllithium followed by quenching with chlorodimethylsilane.

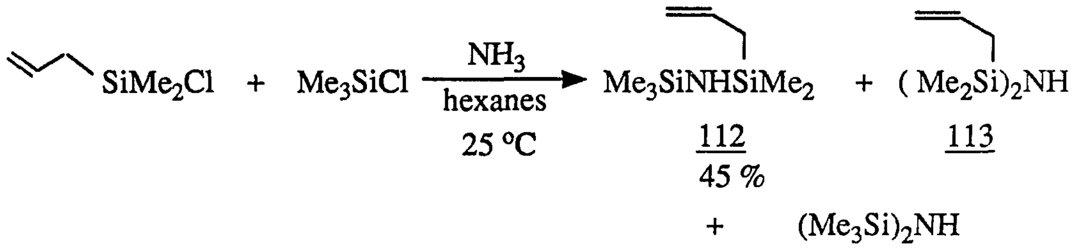
Decomposition of 110 yielded a number of hydrocarbon products. The high yield of isobutene indicates that decomposition is primarily occurring by homolysis of the nitrogen carbon bond in the t-butyl group. The large amounts of methane and ethane are also suggestive of a radical mechanism. Replacement of the t-butyl group with

$$\underline{110} \xrightarrow[640\ ^{\circ}\mathrm{C}]{\mathrm{SFR}} CH_4 + C_2H_6 + C_3H_6 + C_4H_8$$

42 %(Combined C_1+ C_2) 16 % 76 %

anything having hydrogens. to the nitrogen, i.e., methyl, results in the retroene elimination occurring at these hydrogens to produce an imine as opposed to a silanimine. This reaction will be discussed in some detail later in this thesis.

The second substitution pattern investigated was with the allyl group on silicon in a silazane. The synthesis of 112 was accomplished in one step by condensing a mixture of allyldimethylchlorosilane and trimethylchlorosilane with ammonia. Disilazane 112 was isolated in 45% yield along with hexamethyldisilazane and bis(allyldimethylsilyl)-disilazane 113.



Under SFR conditions 112 decomposes very cleanly to propene and silanimine 75, which dimerizes to cyclodisilazlane 76. There were no other hydrocarbons

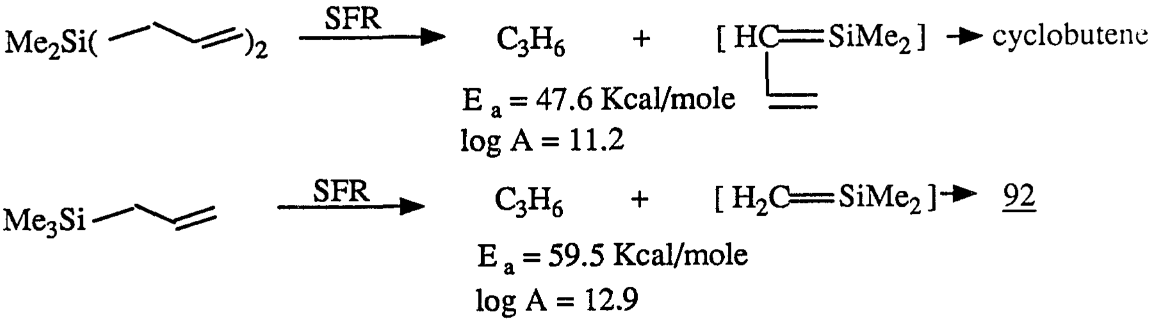
$$\underline{112} \xrightarrow[505 - 565\ ^\circ C]{SFR} C_3H_6 \quad + \quad \underline{75}$$

$$E_a = 46.4 \pm 0.3 \text{ Kcal/mole}$$

$$\log A = 12.1 \pm 0.1$$

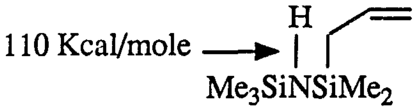
produced other than propene and no silicon-containing products other than cyclodisilazane 76.

The log A of 12.1 translates into an entropy of activation equal to -7.2 ± 0.3 eu. This highly negative value suggests that all of the propene is arising in a concerted six centered elimination of propene. This is in contrast to the first substitution pattern in which the allyl group is substituted on the nitrogen of the silazane framework. Others have understood such differences in reactivity based upon the bond strength of the bonds formed or broken in each type of reaction. As an example Auner et al.[37b] have shown that diallyldimethylsilane decomposes with an energy of activation of 47 kcal/mole, while Barton et al.[37e] have shown that allyltrimethylsilane decomposes to

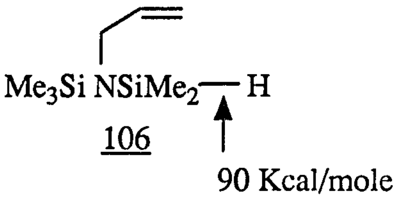


propene with an energy of activation of 59 kcal/mole. This difference in E_A is attributed partially to the difference in the bond strength of the C-H bond that is broken in the reaction.

This type of analysis does not work in the case under discussion since the estimated bond strength of the N-H and Si-H bonds are 110 kcal/mole[41b] and 90 kcal/mole[41a] respectively. The analysis is complicated by the lack of



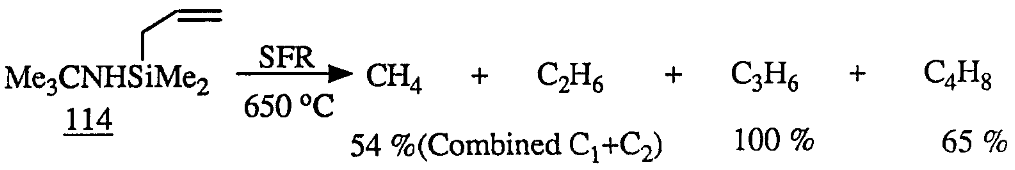
112



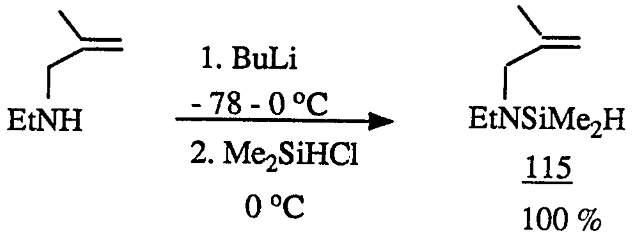
106

data available on the allyl bond strengths, but using estimates from Barton et al.[37e] and Egger and Cocks[41c] for these allyl bond strengths results in a weaker N-allyl bond strength. Since in the Si-allyl substituted case both bonds being broken are stronger than the corresponding bonds in the N-allyl pattern this type of analysis fails to explain why the Si-allyl case is so much more reactive. A comment is needed at this point about the accuracy of such estimates of bond strengths. Walsh[41b] is very uncertain about the bond strengths he has calculated for the N-H bond in hexamethyldisilazane or the N-C bond in heptamethyldisilazane which were used to estimate the N-H bond strength in 112 and the N-C bond strength in 106.

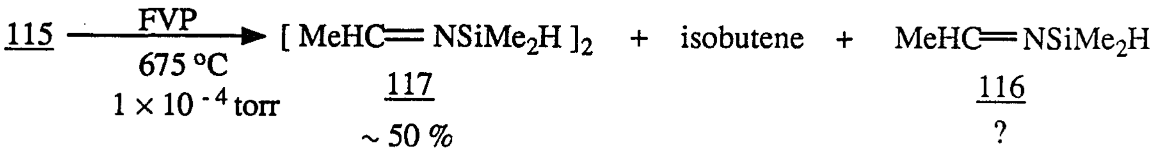
Substitution of the trimethylsilyl group with a t-butyl group resulted in large amounts of butene formation as illustrated below.



It was of interest, as mentioned earlier, to see if the retroene elimination of propene to produce silanimines would be competitive with the same reaction producing imines. With that in mind 115 was prepared in quantitative yield.



Thermolysis of silazane 115 under flash vacuum pyrolysis conditions yielded isobutene and 117. The isolated dimer contained both infrared frequencies (2112 cm^{-1}) and proton



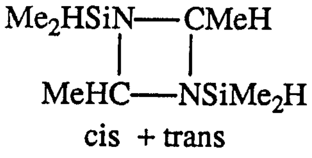
$$\underline{115} \xrightarrow[\substack{675\,^{\circ}C \\ 1 \times 10^{-4}\,torr}]{FVP} \underset{\substack{\underline{117} \\ \sim 50\ \%}}{[\,MeHC{=}NSiMe_2H\,]_2} + \text{isobutene} + \underset{\substack{\underline{116} \\ ?}}{MeHC{=}NSiMe_2H}$$

NMR peaks that show the presence of Si-H bonds. Clearly the retroene reaction had occurred on the C-H bond as opposed to the available Si-H bond. This is hardly unexpected based on the higher stability of the imine as compared to the silanimine that would have been produced.

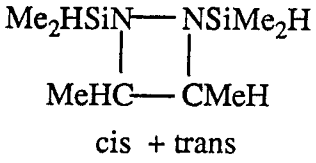
Isolation of the dimer was accomplished by preparative gas chromatography. Analysis of this material by proton NMR revealed that the dimer decomposed at least partially to the monomer 116. This is evident by doublet of quartets at

7.659 ppm. The coupling constants for these peaks were 5.0 Hz and 1.0 Hz. This peak was coupled to a doublet at 1.930 ppm. The 1.0 Hz coupling constant may be from coupling with the silyl-hydride functionality. The position of these peaks as well as the carbon NMR spectrum which had a resonance at 157.197 ppm, and the infrared spectrum which had a strong absorption at 1672 cm^{-1} strongly suggests that the dimer 117 decomposes to the monomer in solution.

The structure of the dimer 117 is less certain. Two possibilities exist, either the 1,3-diazetidine or 1,2-diazetidine rings 118 or 119. Both types of ring systems are known in the literature although the 1,3-isomer is much less common and much less stable, particularly if the ring is not heavily substituted with bulky organic groups.[43a,b,c,d] The 1,3-isomer is very stable if the carbons in the ring are carbonyl groups.[43d]



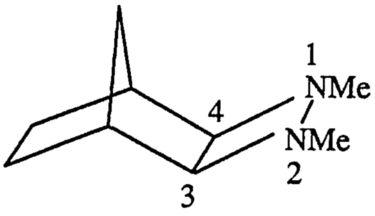
118



119

The dimer isolated in this reaction had a proton spectrum with a quartet at 4.383 ppm. This was coupled to a doublet (J = 6.2 Hz) at 1.332 ppm. These data do not differentiate between the 1,2- or 1,3-diazetidine structure.

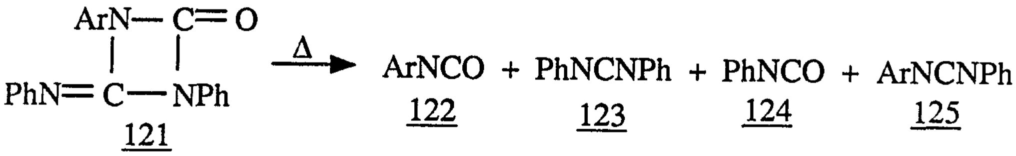
The carbon NMR spectrum contains peaks at 78.162 and 157.197 ppm, the peak at 157.197 ppm arises from the imine. Although no examples of 1,3-diazetidines exist which are substituted with simple alkyl groups many 1,2-isomers are known with simple alkyl groups at the 3,4 positions. An example from the work of Landis et al.[43b] shows the 3,4 carbons of <u>120</u> have resonances at 64.0 ppm. This is well up field from the observed peak at 78.162 ppm. On the basis of this data the structure of the dimer is assigned as a mixture of 1,3-diazetidines which decomposes to the imine in solution. The presence of cis and trans isomers is indicated by a very small doublet at 1.360 ppm. No corresponding quartet was found.



<u>120</u>

$$\underline{118} \xrightarrow{\Delta} \underline{116}$$

The decomposition of 1,3-diazetidines to monomeric imines is not without precedent. Neumann and Fischer[44] have studied the decomposition of <u>121</u> and found that the ring

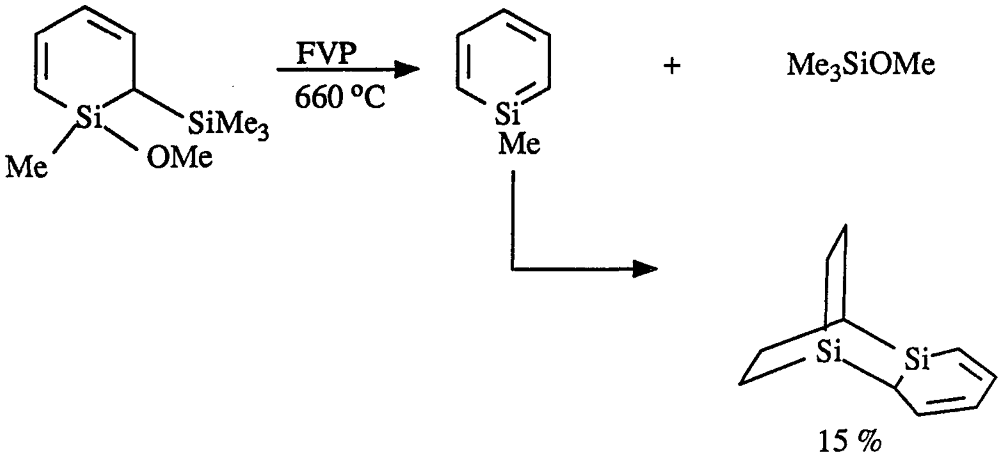


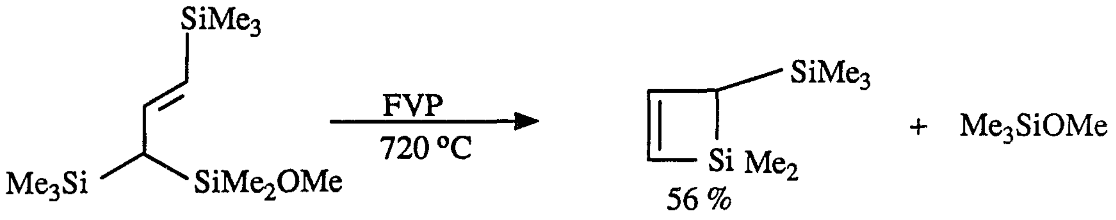
opens in both ways which produces two isocyanates, 122 and 124 as well as the corresponding carbodimides 123 and 125. Although this reaction does not occur at room temperature it could quite possibly occur at room temperature if less bulky substituents were present on the diazetidine ring.

A second method of generating silanimines investigated during this research was the β elimination of methoxysilanes from trisilazanes. The β elimination of methoxysilanes has been used by a number of researchers to generate multiple bonds to silicons, namely silenes.[45a,b]

A few examples of this reaction are given here. the yields are at times quite poor. Bain et al.[45c] have studied the kinetics of such processes and have found that fairly high temperatures are required to induce elimination of Me_3SiOMe. The energy of activation in such cases is correspondingly high.

Kazoura and Weber[22a,b] have studied the decomposition of methoxy substituted trisilazanes in the gas phase. Their results suggest that the reaction may be an extremely facile means of generating silanimines. The problems observed in





$$\underset{\underline{134}}{Me_3SiCH_2SiMe_2OMe} \xrightarrow[618 - 697\ ^{\circ}C]{SFR} Me_3SiOMe \quad + \quad \underline{92}$$

$E_a = 54.2$ Kcal/mole
$\log A = 12.4$

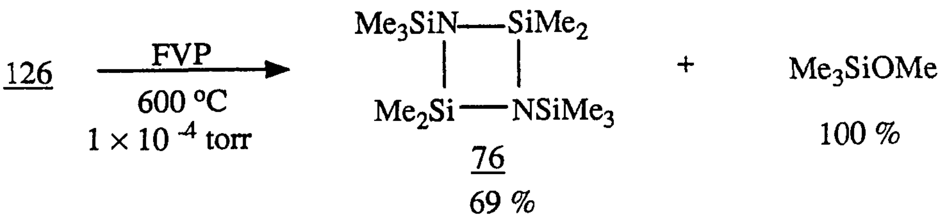
that work (12 products) probably arise from the reversible nature of this reaction when the silanimines can rearrange (see Literature Survey).

$$\underline{68} \underset{+\,Me_3SiOMe}{\overset{-\,Me_3SiOMe}{\rightleftarrows}} \underset{\underline{69}}{[\,Me_3Si\,N{=}SiMeOMe]} \xrightarrow{1,3\ Me} \underset{\underline{71}}{[\,Me_2Si{=}NSiMe_2OMe]}$$

In order to study the reaction kinetics of such reactions the number of products needed to be reduced. if the mechanism postulated by Kazoura and Weber[22a,b] is correct this reaction can be greatly simplified by replacing one of the methoxy groups in 68 with a methyl group. Trisilazane 126 was prepared by treating hexamethyldisilazane with butyl lithium, followed by quenching of the lithium amide with dimethylmethoxychlorosilane. Trisilazane 126 was isolated as a waxy solid in 59% yield.

$$(Me_3Si)_2NH \xrightarrow[\text{2. } Me_2SiOMeCl]{\text{1. BuLi} \atop -78\text{ - }0\ ^\circ C} \underset{\underset{59\ \%}{\underline{126}}}{(Me_3Si)_2NSiMe_2OMe}$$

Decomposition of trisilazane 126 under flash vacuum conditions yielded only two products, methoxytrimethylsilane (100%) and cyclodisilazane 76 in 69% yield. The isolation of only one cyclodisilazane 76 and one methoxysilane



indicated that 126 would be a good candidate with which to study the reaction kinetics of the β elimination reaction.

Study of 126 under SFR conditions was not as easy as expected. The primary problem with using this compound is its very low vapor pressure. The original design of our SFR instrument requires that the compounds have fairly large vapor pressures. Since 126 is a waxy solid it did not have a sufficient vapor pressure to study under our SFR conditions. The apparatus has been modified somewhat to accommodate nonvolatile material but the rate constants determined in this manner do not agree very well with those determined in the original design. A rough determination of rate constants was undertaken using the modified introduction method.

When 126 is decomposed in the absence of a silanimine trap the rate constants were significantly decreased compared to the decomposition of 126 in the presence of D_3. This result suggests that the reverse reaction is occurring

$$\underline{126} \xrightarrow[430\ ^{0}C]{SFR} Me_3SiOMe$$

without D_3 $k_f = 1.210\ sec^{-1}$

with 20 fold excess D_3 $k_f = 2.934\ sec^{-1}$

to a significant degree.[46] This is consistent with the results of Kazoura and Weber[22a,b] in which they propose that the reverse reaction of β elimination is occurring under flash vacuum conditions.

$$\underline{68} \underset{+\,Me_3SiOMe}{\overset{-\,Me_3SiOMe}{\rightleftarrows}} \underline{69}$$

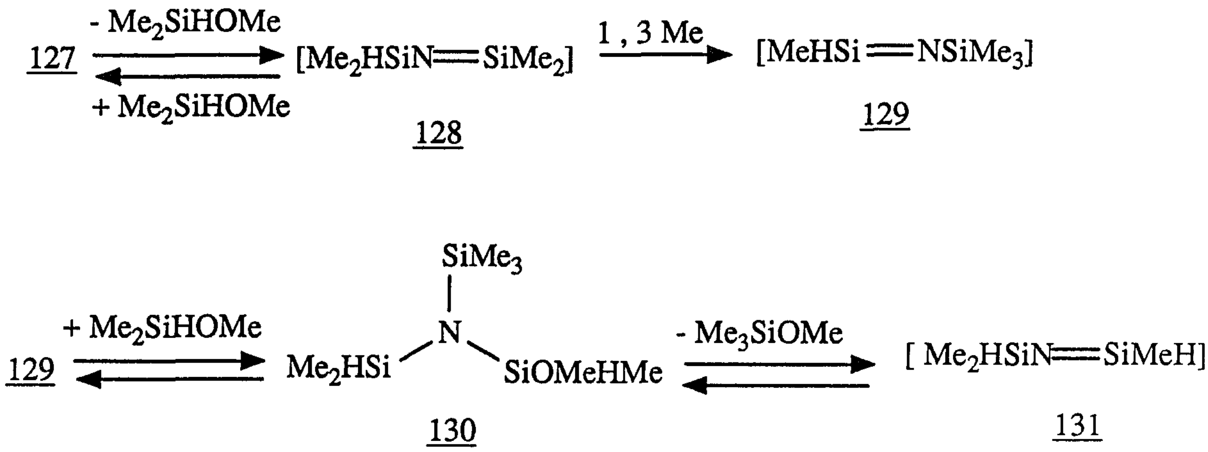
In order to study the kinetics of such reactions a compound with sufficient volatility had to be designed to accommodate the limitations of our SFR instrument. The synthesis of 127 was analogous to that described for 126.

$$(Me_2HSi)_2NH \xrightarrow[\substack{\text{2. } Me_2SiOMeCl \\ 0\,^\circ C}]{\substack{\text{1. BuLi} \\ -78\,^\circ - 0\,^\circ C}} \underset{\substack{\underline{127} \\ 92\,\%}}{(Me_2HSi)_2NSiMe_2OMe}$$

Decomposition of 127 under SFR conditions revealed a large number of products. This is not entirely unexpected

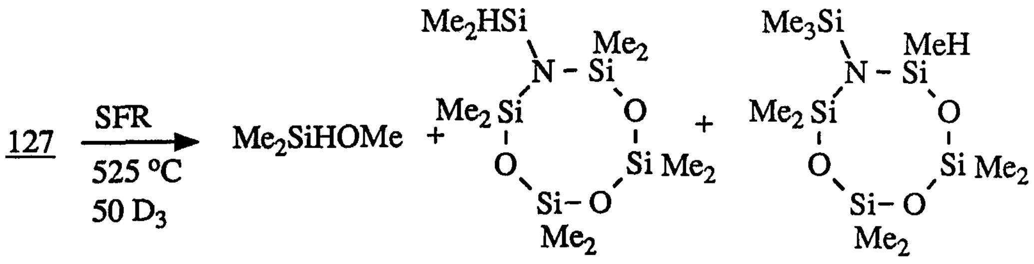
$$\underline{127} \xrightarrow[525\,^\circ C]{SFR} Me_2SiHOMe + Me_3SiOMe + \underset{\text{3 isomers}}{[Me_2HSiN{=}SiMe_2]_2}$$
$$+ \underset{\text{2 isomers}}{[Me_2HSiN{=}SiMeH]_2}$$

since the first formed silanimine could rearrange in a similar fashion to that seen previously.[22a,b] The reaction scheme is outlined here.



The initial β elimination product 128 rearranges by a 1,3-methyl shift to silanimine 129 which can be trapped by dimethylmethoxysilane to produce trisilazane 130. Trisilazane 130 can then eliminate trimethylmethoxysilane to produce a silanimine which is 14 atomic units less in mass than the initially produced silanimine. Each of the silanimines produced could react with any other silanimine present to generate a large number of silanimines.

When the decomposition of 126 was performed in a 50 fold excess of D_3 the product mixture consisted of dimethylmethoxysilane and heterocycles 132 and 133 in a three to one ratio. These two heterocycles result from the trapping of silanimines 128 and 129 with D_3. The characterization of 132 was obtained by performing the reaction under flow



132 3

133 1

pyrolysis conditions since the SFR technique does not allow the isolation of any material. Heterocycle 132 was formed

$$\underline{127} \xrightarrow[\substack{535\ ^\circ\mathrm{C} \\ D_3}]{N_2\ \mathrm{flow}} \underset{50\ \%}{Me_2SiHOMe} + \underset{34\ \%}{\underline{132}} + \underset{\mathrm{trace}}{\underline{133}}$$

in 34% yield, while dimethylmethoxysilane was formed in 50% yield under these conditions. The separation of heterocycles 132 and 133 was a tedious task and no pure 133 could be obtained.

The major product was assigned the structure 132 due to its spectral features. The proton NMR had resonances at 0.204 ppm (s, 12 H); 0.225 ppm (d, J = 3.5 Hz, 6 H); 0.348 ppm (s, 12 H); 4.680 (hep, J = 3.5 Hz, 1 H) while the broad band decoupled carbon NMR had peaks at 1.177, 1.593, 4.122 ppm. These data strongly suggest a symmetrical structure such as 132 over the 1,3-methyl shift isomer 133. The retention time of this product was identical to the product formed in highest yield in the SFR experiments.

The use of a silanimine trap in the kinetic runs was needed since the reverse reaction was occurring under these conditions. The use of a fifty fold excess of D_3 eliminated the formation of trimethylmethoxysilane so it was under these conditions that the kinetic parameters for this reaction were determined. The kinetic parameters were determined by following the formation of dimethylmethoxysilane.

$$\underline{127} \xrightarrow[\substack{476 - 526\ ^{\circ}C \\ D_3}]{SFR} Me_2SiHOMe + \underline{132} + \underline{133}$$

$$E_a = 51.7 \pm 0.5\ \text{Kcal/mole}$$

$$\log A = 14.4 \pm 0.1$$

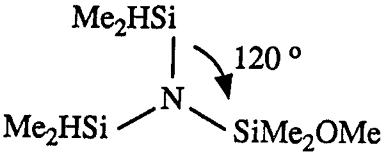
The energy of activation in this reaction is comparable to that reported by Bain et al.[45c] for the β elimination of trimethylmethoxysilane from 134 but the log A is increased significantly. The origin of the high log A value is

$$\underset{\underline{134}}{Me_3SiCH_2SiMe_2OMe} \xrightarrow[618 - 697\ ^{\circ}C]{SFR} Me_3SiOMe + \underline{92}$$

$$E_a = 54.2 \pm 0.3\ \text{Kcal/mole}$$

$$\log A\ 12.4 \pm 0.1$$

difficult to speculate upon. One factor that may be influencing the log A is the geometry of the molecule in question. Trisilazanes are known to be planer[47a,b] with Si-N-Si bond angles of 120°, while 134 probably has Si-C-Si bond angle of 109°. This would increase the strain present



127

in the transition state which may be a contributing factor to the large log A.

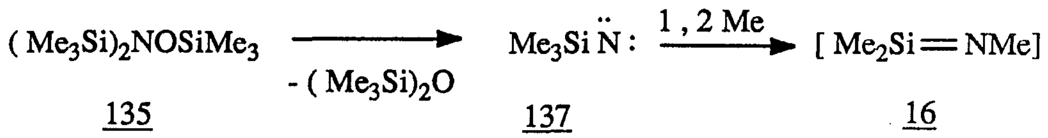
An additional factor that may be contributing to the high log A is the polar nature of the Si-N bond in trisilazanes.[48] This could increase the strain in the transition state as well as contribute to a more polar transition state, therefore, increasing the log A value.

Other reactions that are believed to involve four centered transition states with a large amount of ionic character also have high log A values. An example is given below which is thought to have a highly ionic transition state.[49] These explanations are certainly open to discussion.

$$\text{t-BuCl} \xrightarrow{\Delta} \text{isobutene} + \text{HCl}$$

$E_a = 44.7$ Kcal/mole
log A = 13.7

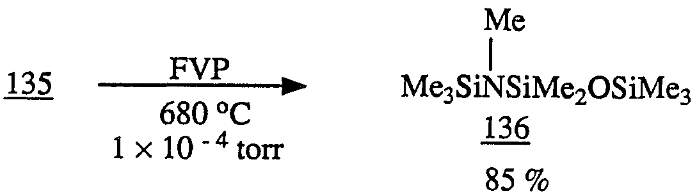
A third method of generating silanimines investigated in this research was the α elimination of disiloxanes from persilated hydroxyamines. The synthesis of N,N,O-tri-strimethylsilylhydroxyamine was accomplished in two



$$\underset{\underline{135}}{(Me_3Si)_2NOSiMe_3} \xrightarrow[-(Me_3Si)_2O]{} \underset{\underline{137}}{Me_3Si\ddot{N}:} \xrightarrow{1,2\,Me} \underset{\underline{16}}{[Me_2Si{=}NMe]}$$

steps from hydroxyamine hydrochloride. The procedure that was employed is outlined in reference 50a.

The thermolysis of 135 under flash vacuum conditions yields a single volatile product. The product had the following proton NMR spectrum, 0.290-0.440 ppm which consisted of three singlets and a singlet at 2.440 ppm. The carbon spectrum had peaks at 0.952 ppm, 1.546 ppm, 1.955 ppm and 30.050 ppm. These data suggest that the product had the structure 136.



$$\underline{135} \xrightarrow[\substack{680\,^{\circ}C \\ 1 \times 10^{-4}\,torr}]{FVP} Me_3Si\overset{\overset{\displaystyle Me}{|}}{N}SiMe_2OSiMe_3$$

136

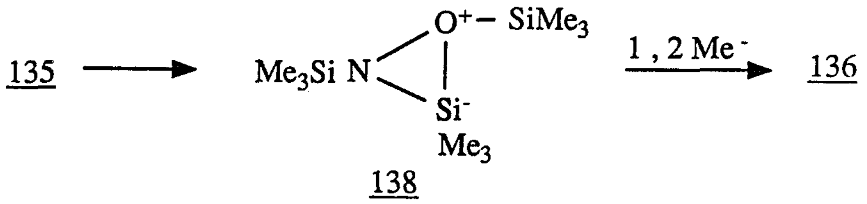
85 %

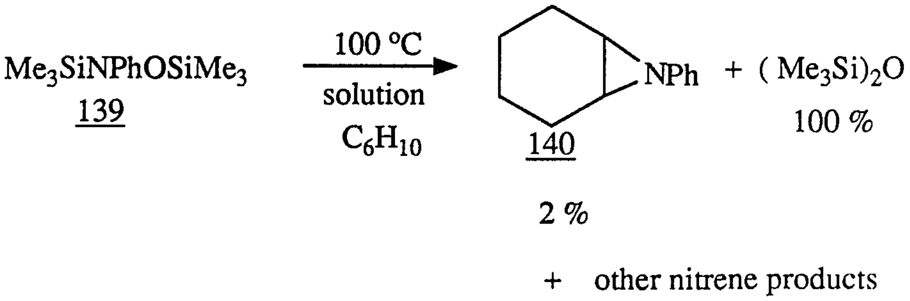
This product may have arisen by one of two mechanisms. The first involves loss of hexamethyldisiloxane by an α elimination process. This step produces nitrene 137 which would then undergo a 1,2-methyl migration to produce silanimine 16 which can be trapped by hexamethyldisiloxane.

$$\underset{\underline{135}}{(Me_3Si)_2NOSiMe_3} \xrightarrow[-(Me_3Si)_2O]{} \underset{\underline{137}}{Me_3Si\ddot{N}:} \xrightarrow{1,2\ Me} \underset{\underline{16}}{[Me_2Si{=}NMe]}$$

$$\underline{16} \xrightarrow{+(Me_3Si)_2O} \underline{136}$$

The second mechanism involves a zwitterionic intermediate 138 which undergoes a migration of a methyl anion to form the final product. This latter mechanism has been postulated to occur in the solution phase thermolysis of 135.[50b,c,d] Tsui et al.[50e,f] and Chang et al.[50a] have found that replacement of one of the silyl groups on nitrogen with a phenyl group leads to nitrene formation. No products suggestive of the zwitterionic mechanism were observed.



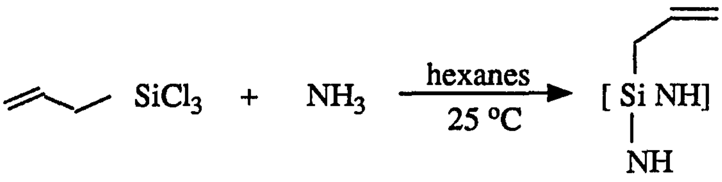


The pyrolysis of 135 was performed in the presence of D_3 in hopes of determining which mechanism was operative. Flow pyrolysis of 135 yielded no trapped product. Since no trapping product was observed the rearrangement must be a unimolecular process consistent with the zwitterionic mechanism.

$$\underline{135} \xrightarrow[\substack{460\ ^{\circ}\mathrm{C} \\ D_3}]{N_2\ \mathrm{flow}} \underset{100\ \%}{\underline{136}}$$

In conclusion three methods of generating multiple bonds between silicon and nitrogen were investigated. The retroene reaction and the β elimination of methoxysilanes were successful routes to silanimines. The α elimination of disiloxanes from hydroxyamines was not a successful means of generating silanimines since an alternative reaction pathway was available to these molecules. The next section describes the results of an investigation into polymers that may undergo the retroene reaction.

A preliminary study of polysilazanes was undertaken to see if the reactions discussed would lead to useful routes to silicon nitride. In the retroene reaction the position of the allyl group was very important. When the allyl group was on the silicon silanimines were generated at lower temperatures. The synthesis of a polymer with this structure was accomplished by condensing allyltrichlorosilane with ammonia. Polymer 141 was isolated from the



141

50 %

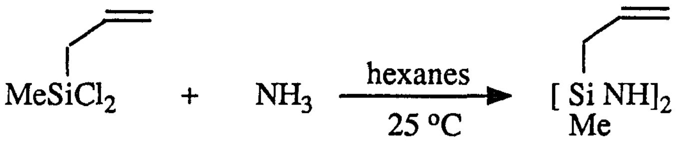
reaction mixture by filtration through celite to remove ammonium chloride followed by distillation of hexanes away from the polymer by vacuum distillation. Very soon after isolation of the material it solidified into an insoluble resin. Others have observed this same effect in similar polysilazanes prepared in this manner.[51]

Polymer 141 was initially studied using thermal gravimetric analysis. The study shows that the polymer begins to decompose at 300°C with the sharpest weight loss occurring between 500° to 700°C. After 700°C the polymer lost very little weight.

Polymer 141 was also heated to 1400°C in argon. Elemental analysis of the product revealed that carbon was still present in the ceramic. In hopes of limiting the formation of carbon based inpurities the rate of heating was reduced. Analysis of this material by XPS[52] (X-Ray Photoelectron Spectroscopy) still showed the presence of carbon.

The polymer 141 was also heated in a vacuum system in which the gases could be analyzed by mass spectrometry. Up until 300°C no volatile material was observed in this experiment. From 300°C up to 500°C the major volatile product observed was propene with lesser amounts of ethane and methane being observed. Gradually over the temperature range of 500°C to 700°C the amount of propene formed was reduced to nothing while methane became the major product. The amount of ethane produced was very small at 700°C. Above 850°C the only hydrocarbon observed was methane, hydrogen also became evident at this point in the pyrolysis. When the temperature had reached 950° the only product seen was hydrogen. A summary of these data are given in Table 1. The occurrence of methane and ethane is a bit puzzling. To speculate upon a mechanism for this process would be tenuous at best.

A second allyl silazane was prepared which has a linear structure. The polymer consisted primarily of low molecular



142

66 %

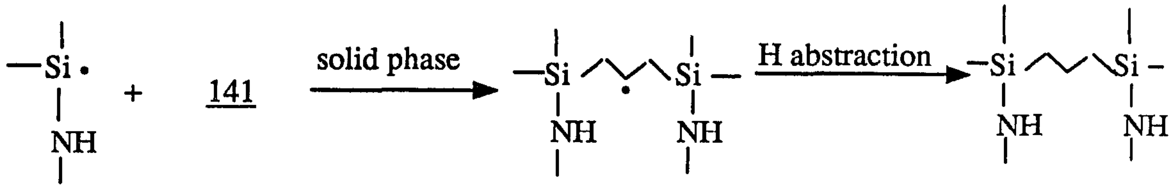
weight oligomers with a molecular weight of 600 daltons. Pyrolysis of 142 in a nitrogen flow resulted in a yield of

Table 1. Volatile products produced in the pyrolysis of <u>141</u>

Temp. Range (°C)	Major Product	Minor Products
300-500	propene	methane, ethane
500-700	methane	ethane
700-850	methane	
850-950	methane	hydrogen
950-1400	hydrogen	

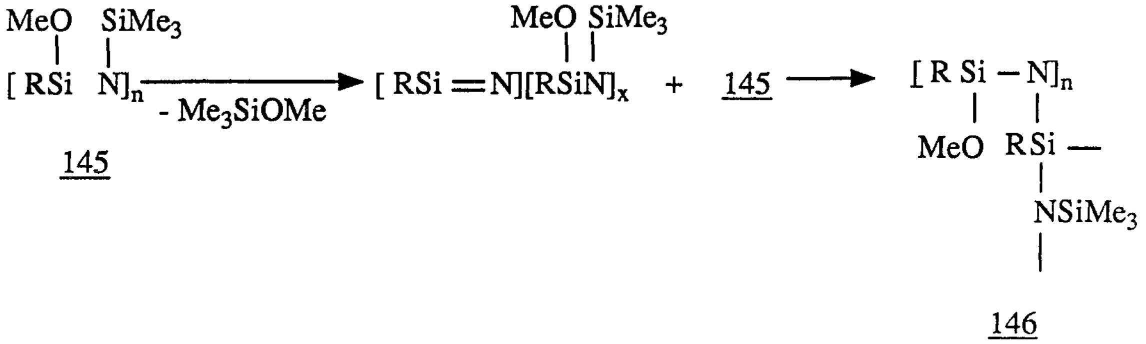
only 6% of a ceramic material. This ceramic char contained 30% carbon which was determined by elemental analysis. No further study of this polymer was undertaken.

In conclusion the behavior of polymeric silazanes under thermal conditions is very different from the decomposition modes which silazanes undergo in the gas phase. A number of things could be studied to see if this technique of generating multiple bonds between silicon and nitrogen in a polymer could be used to prepare high purity silicon nitride. One suggestion is to do the pyrolysis in the liquid phase. This may limit radical reactions between polymer chains which is probably the reason methane was

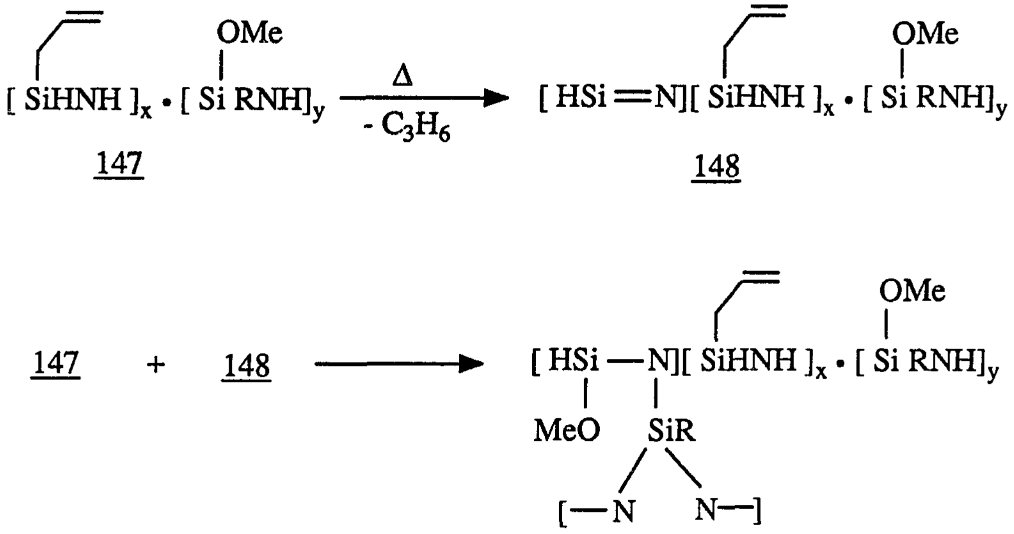


formed in the reaction. The rate at which such polymers should be heated is also worthy of more study.

The synthesis and decomposition of polymers which could produce silanimines by a β elimination of reaction warrants study. This may be a useful technique for crosslinking linear polysilazanes. One could also prepare copolymers



with methoxydichlorosilanes and allyl dichlorosilanes. This may also produce highly crosslinked polymers which are more useful in preparing silicon nitride. One important factor



in all of these studies is preparing a polysilazane which will generate a reactive intermediate which could be trapped by another polymer molecule. If this technique is useful the groups on silicon and/or nitrogen could be varied to maintain the solubility of the polymer but minimize the formation of carbon based impurities.

CONCLUSIONS

A new method of generating silanimines has been discussed. This involves the retroene elimination of propene from allylsilazanes. The position of the allyl group has been found to be extremely important. When the allyl group is on nitrogen the silazanes decompose by both radical and concerted mechanisms. This is found to be the case in both silazanes and disilazanes. If the allyl group is substituted on silicon, disilazane 112 decomposes only by a concerted mechanism.

The β elimination of methoxysilanes from trisilazanes was also studied under SFR conditions. The log A for such processes is very high suggesting that the transition state is very polar in nature. These two kinetic investigations are the first such investigations on the generation of silanimines.

The decomposition of polymeric silazanes with the possibility of retroene reactions was studied. The ceramic produced by pyrolysis of polymer 141 contained large amounts of carbon. The major volatile product in this pyrolysis was methane. The mechanism by which this polymer decomposed is not certain.

EXPERIMENTAL

All spectral data were obtained on the same instruments as that in Section 1 of this thesis. The gas chromatographic data were also recorded on the same instruments.

All yields for the pyrolysis experiments were determined by gas chromatography and are corrected for unconsumed starting material. Elemental analysis was performed by Desert Analytics, Tucson, Arizona, except the elemental analysis of the ceramic chars were performed by Multi Chem Laboratories, Lowell, Massachusetts.

Flash vacuum pyrolysis experiments were performed by distilling the compounds through a horizontal quartz tube packed with quartz chips. The tube was evacuated to 10^{-4} torr behind the liquid nitrogen trap in which the product mixture was collected. The flow pyrolysis experiments were performed by dripping the starting material through a vertical tube packed with quartz chips. The reactant was swept through the tube by a 20 ml/min flow of nitrogen. The products were collected in a -78°C bath at the end of the quartz tube.

The kinetics experiments were performed on a stirred flow reactor that was originally designed by Baldwin et al.[53] The kinetic equations that are used in this type reactor are well established. The reader is referred to the references indicated.[54a,b,c,d]

For a unimolar decomposition A → B the mass balance for B can be written as follows with k_1 equal to the rate constant for the formation of B. The value $k_1v[A]$ is

$$kv[A] - u[B] = 0$$

representative of the formation of B from A while u[B] accounts for the loss of B from the reactor. Rearranging the equation results in a very simple expression for the

$$k = \frac{u[B]}{v[A]}$$

rate constant for the formation of B. The constant u/v is

u = volumetric flow rate

v = volume of the reactor

often referred to as 1/T or the residence time. This residence time can be determined one of two ways. The most straightforward is to physically measure the volume of reactor and control the flow rate very precisely. Davidson et al.[55] have shown that varying the flow rate of a system which has a known reactor volume gives the same rate constants regardless of the flow rate. This serves to show that the technique is giving correct results. The second means of measuring the reactor volume is to take a reaction in which rate constants are known such as the isomerization of cyclopropane to propene and substitute the known rate constant into the kinetic equation for the stirred flow

$$k = \frac{u[B]}{v[A]}$$

reactor. In this case every variable can be measured or is known except v the reactor volume.

A number of conditions must be satisfied in order to obtain accurate kinetic data. Firstly the reactor must be designed to give perfect mixing and the reactant must be introduced in a perfect plug.[53]

After determination of rate constants at various temperatures the Arrhenius parameters were determined by a plot of ln k vs 1/T in the usual fashion from the Arrhenius equation.

$$\ln k = -E_a/RT \quad + \quad \ln A$$

The calculations were performed assuming a first order decomposition. Davidson et al.[55] and others[54] have extended the use of the stirred flow reactor to higher order reactions as well as reversible and parallel reaction. The reader is referred to those references cited above for more detailed discussions of these kinetic equations. The enthalpy and entropy of activation were determined by use of the following equations which are derived from transition state theory.[56]

$$E_a = \Delta H + RT$$
$$k = C\,(e^{-\Delta H/RT}) \cdot (e^{\Delta S/R})$$

C = rate of activated complex decomposition in T. S. theory.[56]

The technique involves a sample loop which is connected to the stirred flow reactor. The design must allow for pulsing the material into the reactor in a perfect plug. This is achieved primarly by using a large flow rate, typically 60 ml/min of helium is the carrier gas. Introduction of the sample is done by simple vacuum line techniques. The system as designed has a major limitation in that only "volatile" substances can be used.

The reactor temperature is precisely controlled by a Digi-Sense temperature controller. The reactor is connected directly to a Varian 6000 gas chromatograph. Two gas chromatography columns were used in these experiments, one which was packed with 25% SE 30 on Chromsorb W 25' in length and a 9' column with a similar loading of liquid phase.

The gas chromatograms were recorded on a chart recorded as well as a Magnum XT/Mark 2 microcomputer. The microcomputer also contained the appropriate programs to measure the area of the peaks of the product and reactant. The absolute quantities of product and reactant were measured by the use of response factors which were determined at low temperatures. Figure 1 contains a block diagram of the instrument.

All of the compounds studied using the SFR were purified by preparative gas chromatography using either a 9' or 15' column packed with 25% SE 30 on Chromosorb W. The separations were generally done with a temperature program that varied with the purity and the retention time of the desired products. Final purity was checked by analytical gas chromatography using a dimethylsilicone capillary column and ranged from 99.5 to 100% purity.

Flash vacuum pyrolysis of hexamethyldisilazane

Hexamethyldisilazane (0.635 g, 0.0039 moles) was distilled through a quartz tube packed with quartz chips which was heated to 850°C and evacuated to 1 x 10^{-4} torr. The mass recovery was 87% (0.554 g). Four products were isolated along with the starting material (68%). Hexamethyldisilane was observed in trace amounts and characterized by GC-MS and GC retention time. The second product observed was 1,1,3,3-tetramethyl-1,3-disilylcyclo-

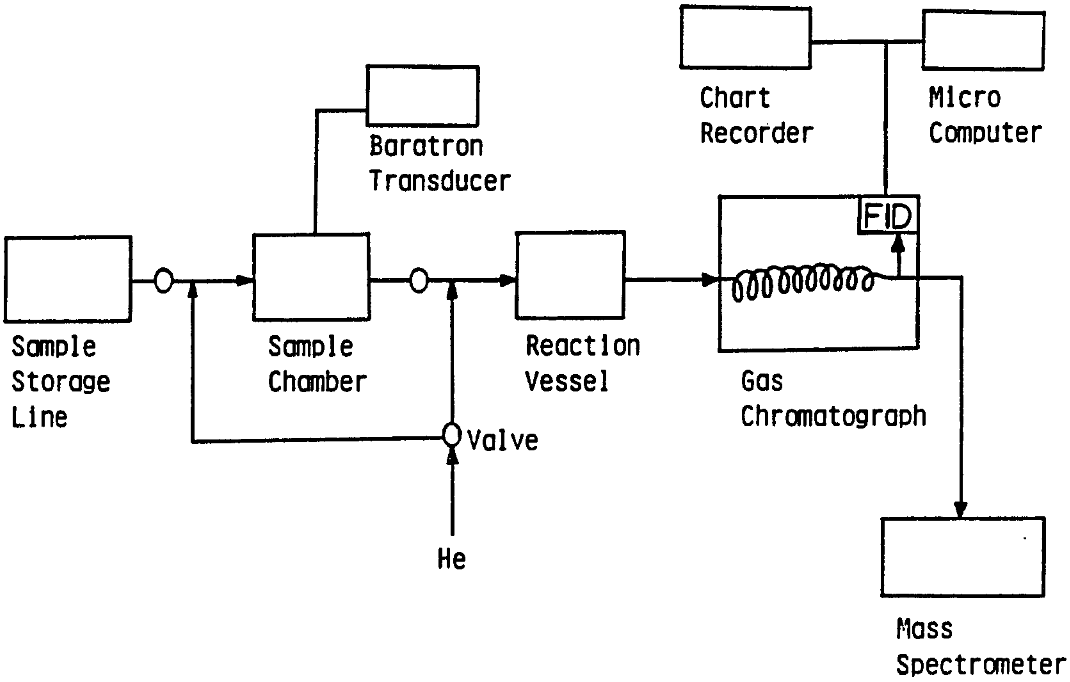


Figure 1. Pulse stirred-flow reactor (SFR)

butane. This product coeluted with hexamethyl-disilazane in the gas chromatograph. The product was observed by searching the gas chromatograph mass spectrum for the ions 144 and 129. It was determined independently that these ions did not arise from the hexamethyldisilazane. Mass spectrum of 1,1,3,3-tetramethyl-1,3-disilylcyclobutane 144 (22.5) M^+; 129 (100) M^+ -15; 101 (21.9); 59 (20.4). The yield is estimated to be 10%. The third product observed was 1,1,3,3-tetramethyl-2-trimethylsilyl-1,3-disilyl-2-azocyclobutane <u>91</u>. The product had the following spectral properties. ^1H NMR (C_6D_6, 300 MHz). δ 0.082 (s, 9 H); 0.269 (s, 12 H); 0.290 (s, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 2.453, 3.290, 4.584. Mass spectrum 217 (5.5) M^+; 202 (100) M^+ -15. Exact mass calculated for $C_8H_{23}NSi_3$ 217.11384, found 217.11343 error 1.8 ppm. The fourth product isolated was 1,1,3,3-tetramethyl-2,4-trimethylsilylcyclodisilazane (13%). It was identified by its mass spectrum 290 (5.3) M^+; 275 (100) M^+ -15 and ^1H NMR ($CDCl_3$, 300 MHz) δ -0.014 (s, 2 H); 0.227 (s, 3 H). This product assignment agrees very well with the NMR data published by Schmidbaur.[57]

Preparation of N-allyl-1,1-dimethylsilazane (98)

The procedure of Webb and Olson was followed.[39] To a round bottom flask flushed with dry nitrogen fitted with a reflux condenser and stir bar was added 1,1,3,3-tetramethyldisilazane (3.3 g, 0.025 moles) and allylamine (3.8 g, 0.067

moles). To this solution was added 0.1 ml of dimethylchlorosilane and the solution heated for four hours at 80°C. The N-allyl-1,1-dimethylsilazane was isolated by preparative gas chromatography in 54% yield (3.0 g, 0.026 moles). Also observed was disilated allylamine. The N-allyl-1,1-dimethylsilazane had the following spectral properties. ^1H NMR (300 MHz, $CDCl_3$) δ 0.129 (d, J = 3.0 Hz, 6 H); 0.550 (s, broad, 1 H); 3.670 (m, 2 H); 4.450 (h, J = 3.0 Hz, 1 H); 4.986 (d of d, J_A = 10.2 Hz, J_B = 1.7 Hz, 1 H); 5.124 (d of d, J_a = 15.3 Hz, J_B = 1.7 Hz, 1 H); 5.904 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) -1.592, 45.343, 113.166, 140.337. Mass spectrum 115 (24.6) M^+; 114 (23.8) M^+ -1; 110 (29.1) M^+ -15; 86 (43.3); 59 (100). Exact mass calculated for $C_5H_{13}NSi$ (M^+) 15.08194, measured 115.08173, calculated for $C_4H_{10}NSi$ (M^+ $-CH_3$) 100.05814, measured 100.05825. This product is somewhat unstable. The decomposition products are allylamine and N-allyl-1,1,3,3-tetramethyldisilazane.

Determination of Arrhenius parameters for propene formation from N-allyl-1,1-dimethylsilazane (98)

Approximately 0.1 torr of the silazane was introduced into the reactor in the standard way. Data analysis was as usual. The temperature range studied was from 646.4°C to 701.3°C.

Table 2. Rate constants for the formation of propene from N-allyl-1,1-dimethylsilazane (<u>98</u>) in SFR

T(°C)	k(sec^{-1})	T(°C)	k(sec^{-1})	T(°C)	k(sec^{-1})
646.4	0.0572	667.4	0.1147	687.5	0.2402
646.4	0.0591	667.4	0.1192	687.5	0.2219
653.3	0.0682	674.3	0.1496	693.5	0.2631
653.3	0.0684	674.3	0.1521	693.5	0.2851
660.3	0.0863	681.4	0.1874	701.3	0.3629
660.3	0.0855	681.4	0.1832	701.3	0.3662

log A=13.2 ± 0.2 $\Delta S^{\ddagger}$ = -2.4 ± 1.0 eu at Tavg = 674.0°C

E_a=60.8±0.9 kcal/mole $H^{\ddagger}$=58.9±kcal/mole at Tavg=674.0°C

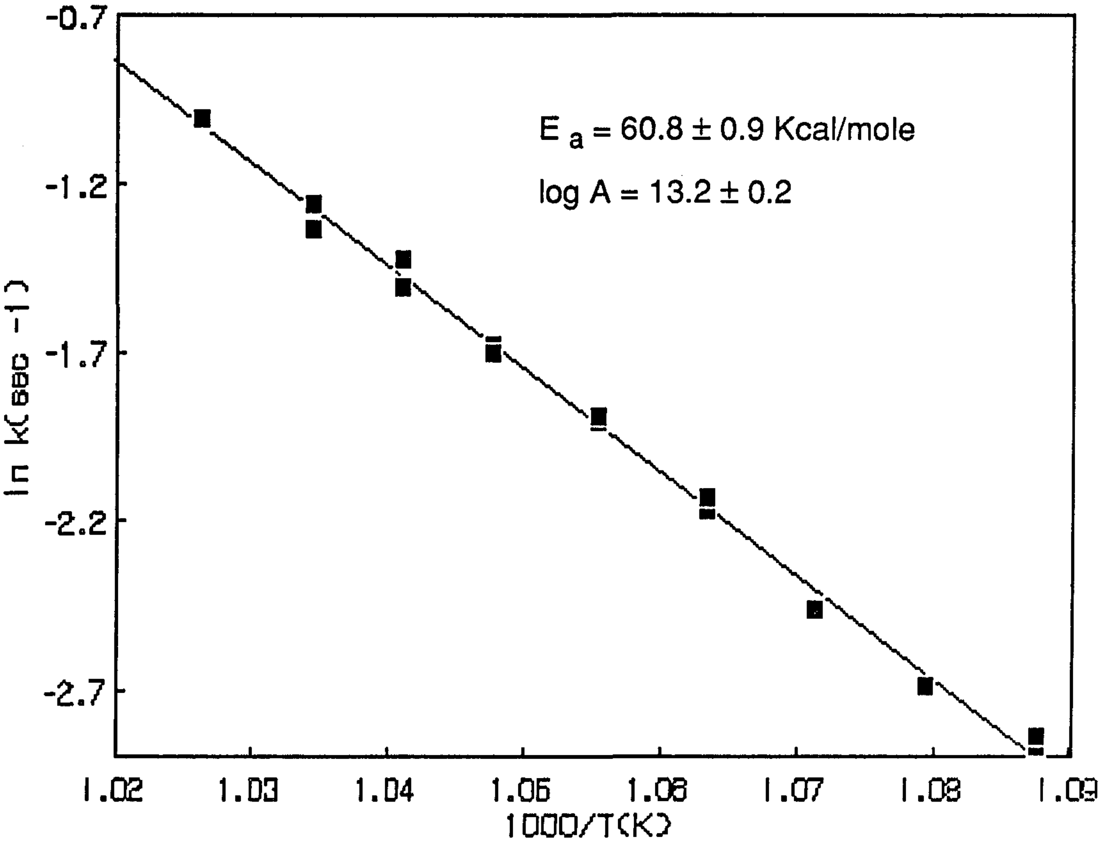


Figure 2. Arrhenius plot for the formation of propene from 98

Determination of Arrhenius parameters for butene formation from N-allyl-1,1-dimethylsilazane (98)

Approximately 0.1 torr of the silazane was introduced into the reactor in the usual way. Data analysis was as usual. The temperature range studied was from 646.4°C to 701.0°C.

Trapping of allyl radicals with D_8 toluene in the pyrolysis of N-allyl-1,1-dimethylsilazane (98)

A 100:1 mixture of toluene to 98 was prepared in the sample loop of the SFR. The mixture was allowed to stand for 10 minutes then injected into the SFR reactor in the usual manner. A portion of the product mixture was split to the mass spectrometer. The intensity of ion 43 was compared to that of nondeuterated propene.

Preparation of N-allyl-1,1,3,3-tetramethyldisilazane (99)

To a round bottom flask fitted with a magnetic stir bar and inlet septum was added 75 ml of dry ether, triethylamine (7.0 g, 0.069 moles) and dimethylchlorosilane (4.3 g, 0.046 moles). The solution was cooled to -78°C (isopropanol, dry ice) and allylamine (1.3 g, 0.023 moles) was added in one portion. The solution was warmed to room temperature and allowed to stir overnight. The solution was filtered through celite to remove triethylammonium chloride and the product isolated by distillation (1.62 g, 40%). The

Table 3. Rate constants for the formation of 1-butene from N-allyl-1,1-dimethylsilazane (98) in SFR

T(°C)	k(sec^{-1})	T(°C)	k(sec^{-1})	T(°C)	k(sec^{-1})
646.4	0.0401	667.4	0.1093	687.5	0.2256
646.4	0.0372	667.4	0.1091	687.5	0.2253
653.4	0.0536	674.3	0.1338	693.6	0.2991
653.4	0.0495	674.3	0.1347	701.3	0.3891
660.3	0.0665	681.4	0.1767		
660.3	0.0633	681.4	0.1783		

log A=16.9 ± 0.4 $\Delta S^{\ddagger}$=14.4 ± 1.8 ea at Tavg=671.0°C

Ea=77.0±1.7 kcal/mole $\Delta H^{\ddagger}$=75.1±1.7 kcal/mole at Tavg=671.0°C

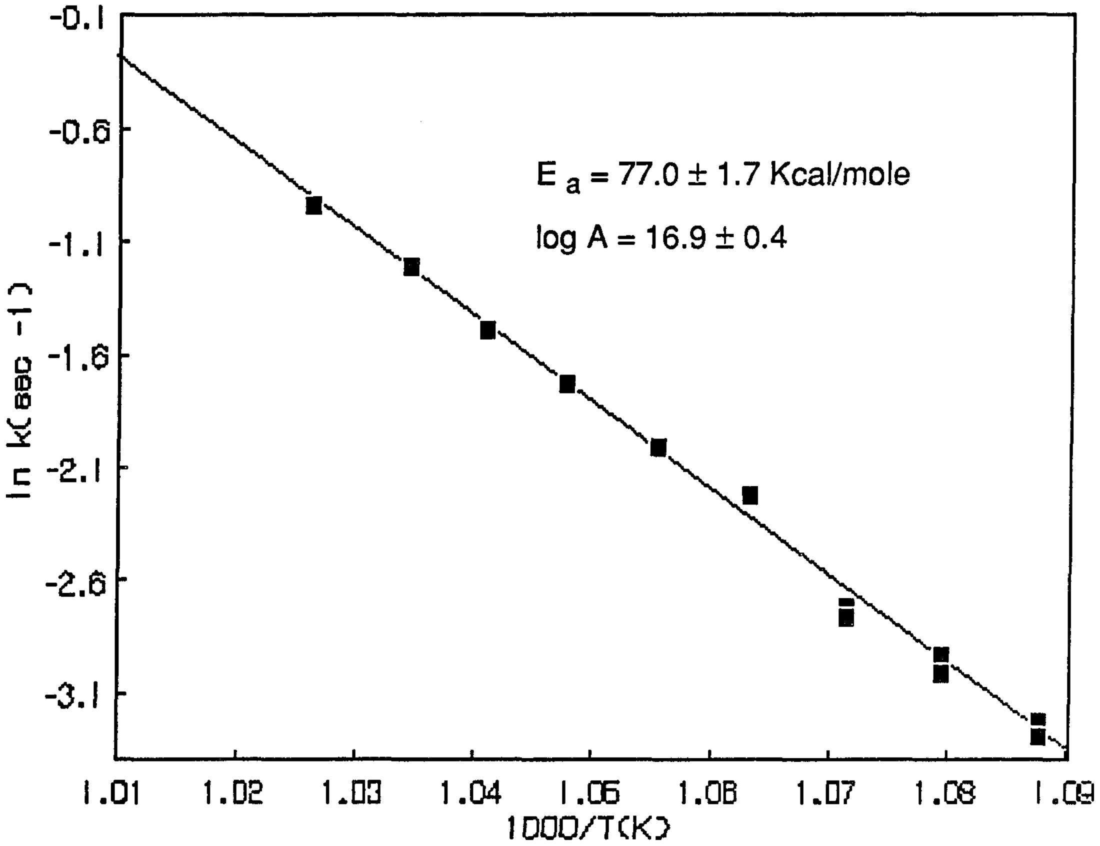


Figure 3. Arrhenius plot for the formation of butene from 98

N-allyl-1,1,3,3-tetramethyldisilazane had the following spectral properties. ^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.147 (d, J = 3.0 Hz, 12 H); 3.444 (d, J = 5.1 Hz, 2 H); 4.436 (p, J = 3.1 Hz, 2 H); 4.989 (d of d, J_A = 10.2, J_B = 1.0 Hz, 1 H); 4.989 (d of d, J_A = 10.2, J_B = 1.0 Hz, 1 H); 5.099 (d of d, J_A = 17.1 Hz, J_B = 1.0 Hz, 1 H); 5.769 (m, 1 H). ^{13}C NMR (75 MHz, CDCl$_3$) δ -0.545, 48.159, 113.910, 139.987. IR (neat) ν 3080; 3009; 2957; 2124; 1643; 1454; 1415; 1250; 878 cm^{-1}. Mass spectrum 173 (40.5) M$^+$; 172 (34.2) M -1; 158 (100) M -15; 59 (68.3). Exact mass calculated for $C_7H_{19}Si_2N$ 173.10561, measured 173.10529, calculated for $C_6H_{16}Si_2N$ (M-CH$_3$) 158.08213, measured 158.08220. Analysis calculated for $C_7H_{19}Si_2N$ 48.48 C; 11.04 H; 8.08 N; measured 48.08 C; 11.13 H; 8.17 N. This product can also be isolated as a byproduct in the preparation of N-allyl-1,1-dimethylsilazane 98.

Determination of Arrhenius parameters for propene formation from N-allyl-1,1,3,3-tetramethyldisilazane (99)

Approximately 0.1 torr of the starting material was introduced into the sample loop and the pressure allowed to equilibrate. The sample was sweep into the reaction vessel by a pulse of helium (60 ml/min). The temperature range was varied from 580.1°C and 650.4°C.

Table 4. Rate constants for the formation of propene from N-allyl-1,1,3,3-tetramethyldisilazane (99) in SFR

T(°C)	$k(\text{sec}^{-1})$	T(°C)	$k(\text{sec}^{-1})$	T(°C)	$k(\text{sec}^{-1})$
580.1	0.0957	622.2	0.3906	650.4	1.0755
580.1	0.0866	622.2	0.3753	650.4	1.0547
587.2	0.1141	629.2	0.4963	615.1	0.3084
587.2	0.1190	629.2	0.4954	615.1	0.3071
594.0	0.1465	636.2	0.6262	601.3	0.1933
594.0	0.1427	636.2	0.6310	601.3	0.1840
608.3	0.2421	643.2	0.8150		
608.3	0.2464	643.2	0.7940		

$\log A = 12.9 \pm 0.1\ \text{sec}^{-1}$ $\Delta S^{\ddagger} = -3.1 \pm 0.6$ eu at Tavg=615.2°C

$E_a = 54.4 \pm 0.5$ kcal/mole $\Delta H^{\ddagger} = 52.7 \pm 0.5$ kcal/mole at Tavg=615.2°C

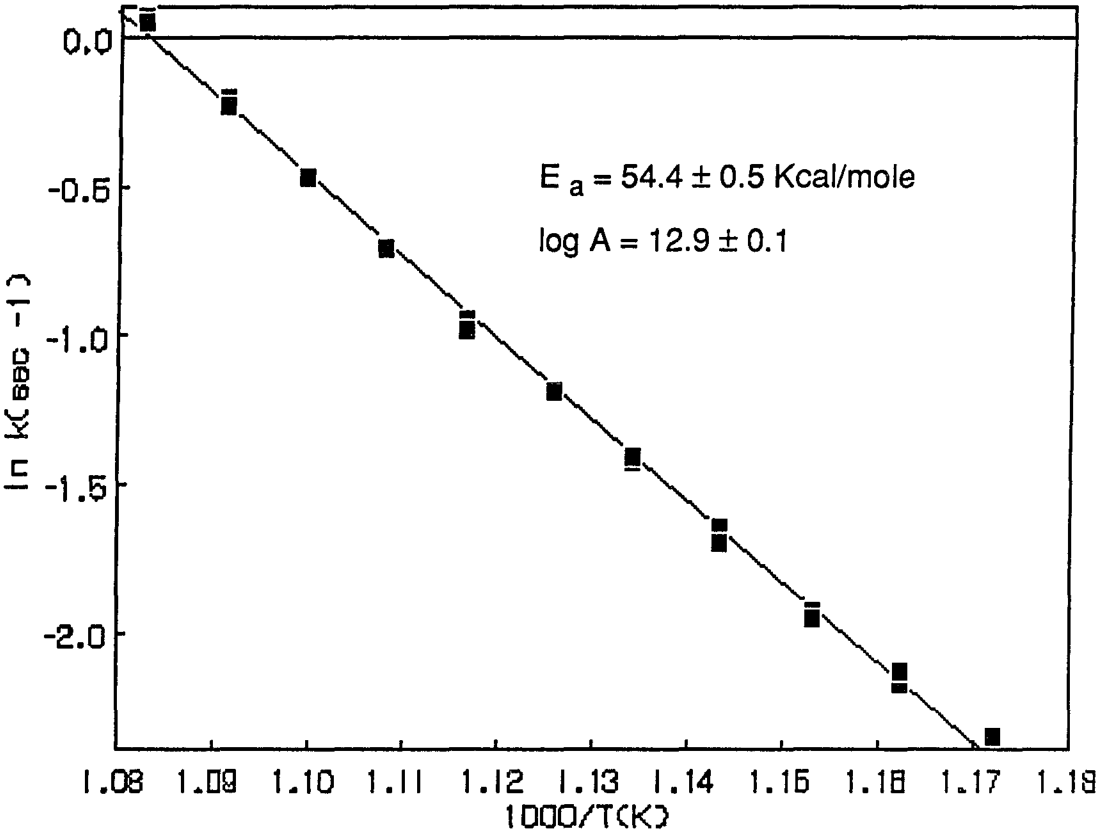


Figure 4. Arrhenius plot for the formation of propene from <u>99</u>

Trapping of N-dimethylsilyl-1,1-dimethylsilanamine (101) with methanol in the SFR

The reactant N-allyl-1,1,3,3-tetramethyldisilazane was introduced the sample loop at 0.5 torr. This was followed by 10 torr of methanol. The reactant and the methanol were allowed to mix in the gas phase and the mixture was introduced into the reactor in the usual manner. The reactor was previously heated to 642.9°C. The products were followed by mass spectrometry as they eluted from the gas chromatograph. The trapped product (20%) was observed by mass spectrometry and had the following mass spectrum. 163 (0.3) M^+; 162 (10.0) $M^+ -1$; 148 (35.2) $M^+ -15$; 118 (100); 101 (10.3). The retention time and mass spectrum were found to be identical with an independently synthesized sample of 1-methoxy-1,1,3,3-dimethydisilazane and the agreement was excellent.

Synthesis of methoxychlorodimethylsilane (105)

To a round bottom flask equipped with a stir bar and flushed with nitrogen was added dimethyldichlorosilane (10.6 g, 0.082 moles) and dimethyldimethoxysilane (11.2 g, 0.093 moles). The solution was allowed to stir overnight. The methoxychlorodimethylsilane was formed in 85% yield.

Synthesis of 1-methoxy-1,1,3,3-tetramethyldisilazane (102)

The procedure of Weibrecht and Rochow[58] was used except that methoxychlorodimethylsilane was synthesized by the chlorine/methoxy redistribution between dimethoxydimethysilane and dichlorodimethylsilane. To a round bottom flask which was fitted with an inlet septum, a gas inlet tube and a stir bar was added ~ 200 ml of dry Skelly B, methoxychlorodimethylsilane (10.2 g, 0.082 moles) and dimethylchlorosilane (7.9 g, 0.083 moles). Dry ammonia was bubbled through the solution for two hours. The ammonium chloride as removed by filtration. The solvent was removed by distillation at atmospheric pressure. The GC yield of 102 was 11.5%. The product had the following spectral properties. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.112 (s, 6 H); 0.160 (d, J = 3.2 Hz, 6 H); 3.434 (s, 3 H); 4.467 (h, J = 3.2 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ -1.071; 0.659; 49.562. IR (neat) ν 3302, 3141, 2959, 2829, 2116, 1256, 1178, 1090, 910, 841, 800, 764, 723, 644. Mass spectrum 163 (1.7) M^+; 162 (4.2) M^+ -1; 148 (100) M^+ -15; 118 (96.2); 59 (33.9). Exact mass calculated for $C_5H_{16}NOSi_2$ (M^+ -1) 162.07705, measured 162.07685, calculated for $C_4H_{14}NOSi_2$ (M^+ -15) 148.06140, measured 148.06133. Elemental analysis for $C_5H_{17}NOSi_2$ calculated 36.16% C, 10.49% H, 8.57% N, found 36.85% C, 10.77% H, 8.31% N.

Flow pyrolysis of 99 in the presence of D_3

The N-allyldisilazane 99 (0.133 g, 0.00077 moles) and D_3 (0.600 g, 0.0027 moles) was dissolved in 1 g of toluene. This mixture was dripped down a vertical pyrolysis tube with a 20 ml/min flow of nitrogen. The products were collected in a -78°C bath at the end of the tube. The GC yield of 132 was 5%. A trace of 133 was also observed. The spectral properties of this compound are recorded elsewhere in this thesis.

Preparation of N-allyl-1,1,3,3-pentamethyldisilazane (106)

To a round bottom flask which was flushed with nitrogen equipped with a stir bar and reflux condensor was added 1,1,3,3-tetramethyldisilazane (2.1 g, 0.016 moles), hexamethyldisilazane (3.2 g, 0.020 moles) allylamine (1.9 g, 0.033 moles) and 0.1 ml of trimethylchlorosilane. The solution was heated at reflux for 18 hours. The desired disilazane had the following spectral properties. ^1H NMR (300 MHz, $CDCl_3$) 0.082 (s, 9 H); 0.122 (d, J = 3.2 Hz, 6 H); 3.425 (d, J = 4.9 Hz, 2 H); 4.456 (p, J = 3.2 Hz, 1 H); 4.970 (d of d, J_A = 10.2 Hz, J_B = 1.6 Hz, 1 H); 5.090 (d of d, J_A = 17.1 Hz, J_B = 1.5 Hz, 1 H); 5.758 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ -0.237, 1.253, 47.359, 113.615, 140.756. IR (neat) ν 3080, 3010, 2955, 2928, 2131, 1506, 1456, 1417, 1250, 916, 873, 837 cm^{-1}. Mass spectrum 187 (17.4) M^+; 172 (100) M^+ -15; 130 (19.8); 119 (22.1); 73 (51.0); 59 (31.3).

Exact mass calculated for $C_8H_{21}NSi_2$ (M^+) 187.12126, measured 187.12159. Calculated for $C_7H_{18}NSi$ (M^+-CH_3) 172.09778 measured 172.09794. Elemental analysis for $C_8H_{21}NSi_2$ calculated 51.26% C, 11.29% H, 7.47% N, found 51.26% C, 11.67% H, 7.54% N. A number of other products were observed but were expected in this reaction.

Determination of Arrhenius parameters for propene formation from N-allyl-1,1,1,3,3-pentamethyldisilazane (106)

Approximately 0.1 torr of the silazane was introduced into the reactor in the usual way. Data analysis was as usual. The temperature ramge studied was from 600.5°C to 658.3°C.

Determination of Arrhenius parameters for 1-butene formation from N-allyl-1,1,1,3,3-pentamethyldisilazane (106)

Approximately 0.1 torr of the reactant was introduced into the reactor by the standard way. Data analysis was as usual. The temperature range studied was from 600.5°C to 658.3°C.

Trapping of N-trimethylsilyl-1,1-dimethylsilanimine (15) with methanol

The reactant 106 was introduced into the sample loop at 0.5 torr. This was followed by 10 torr of methanol. The reactant and trapping agent were allowed to mix in the gas phase and the mixture was swept into the reaction vessel in

Table 5. Rate constants for the formation of propene from N-allyl-1,1,1,3,3-pentamethyldisilazane (106)

T(°C)	k(sec^{-1})	T(°C)	k(sec^{-1})	T(°C)	k(sec^{-1})
600.5	0.1325	635.4	0.4697	652.2	0.8162
621.7	0.2803	635.4	0.4682	652.2	0.8165
621.7	0.2819	642.5	0.5736	612.0	0.1899
628.3	0.3473	642.5	0.5682	658.3	1.0878

log A=13.7±0.2 $\Delta S^{\ddagger}$=0.1±1.0 eu at Tavg=633.1°C

Ea=58.3±0.9 kcal/mole $\Delta H^{\ddagger}$=56.5±0.9 kcal/mole at Tavg=633.1°C

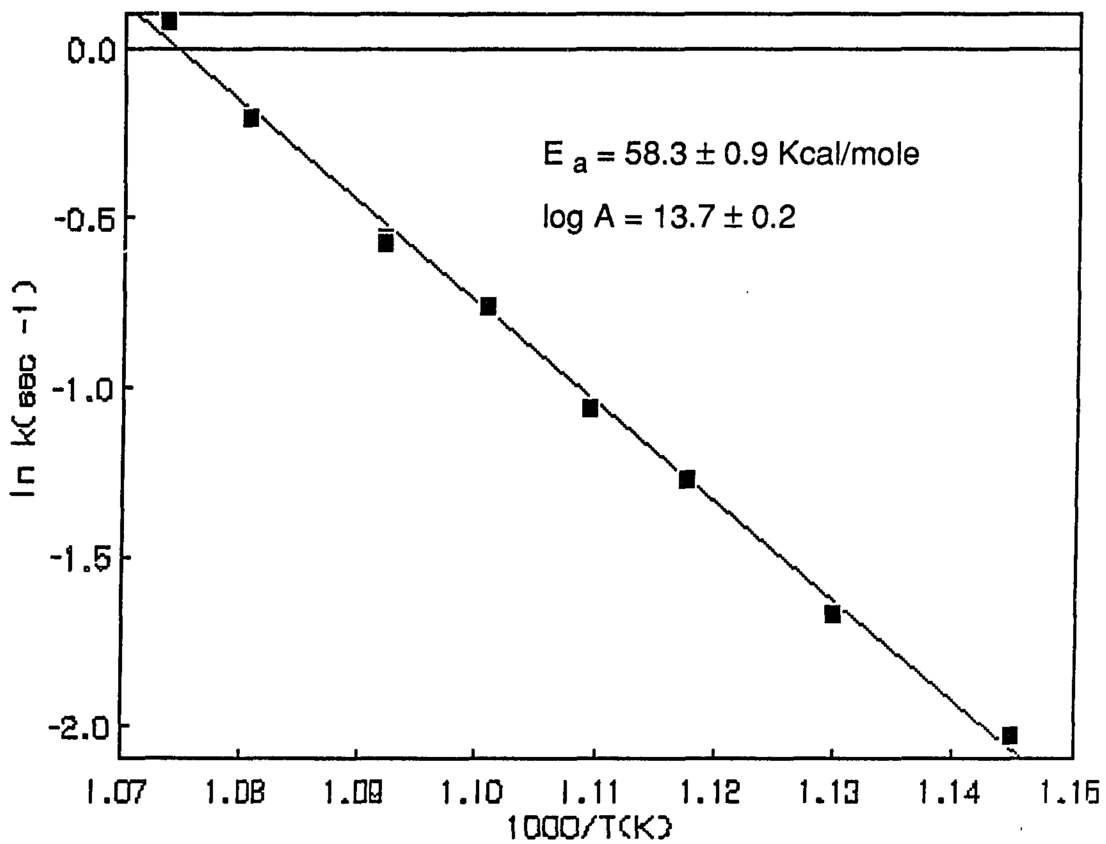


Figure 5. Arrhenius plot for the formation of propene from <u>106</u>

Table 6. Rate constants for the formation of 1-butene from N-allyl-1,1,1,3,3-pentamethyldisilazane (106) in SFR

T(°C)	k(sec^{-1})	T(°C)	k(sec^{-1})	T(°C)	k(sec^{-1})
621.7	0.1488	635.4	0.2752	652.2	0.5752
621.7	0.1491	642.5	0.3722	612.0	0.0985
628.3	0.2183	642.5	0.3659	658.0	0.7549
635.4	0.2712	652.2	0.5768	600.5	0.0590

log A=16.6±0.2 $\Delta S^{\ddagger}$=13.0±0.9 eu at Tavg=633.6°C

Ea=71.1±0.8 kcal/mole $H^{\ddagger}$=69.3±0.8 kcal/mole at Tavg=633.6°C

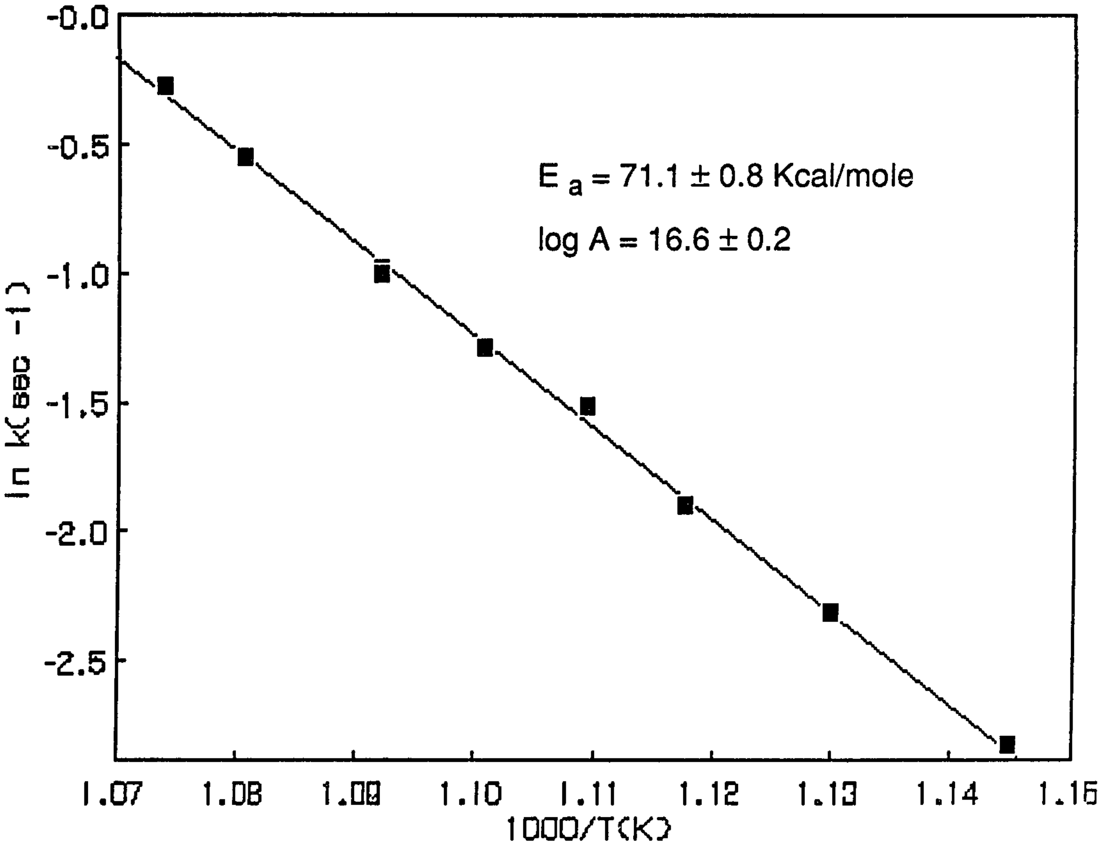


Figure 6. Arrhenius plot for the formation of butene from 106

the usual manner. The reactor was previously heated to 650°C. The products were observed by mass spectrometry as they eluted from the gas chromatograph. The trapped product, 1-methoxy-1,1,3,3,3-pentamethyldisilazane had the following mass spectrum. 162 (49.4) M^+ -15; 132 (100); 116 (19.3); 73 (35.7); 59 (49.8). The retention time and mass spectrum were found to be identical with an independently synthesized sample of 1-methoxy-1,1,3,3,3-pentamethyldisilazane.

Synthesis of 1-methoxy-1,1,3,3,3-pentamethyldisilazane (107)

The procedure was exactly that followed in the synthesis of 102. The following reagents were used: 200 ml hexanes, trimethylchlorosilane (12.8 g, 0.12 moles) and methoxychlorodimethylsilane (14.8 g, 0.12 moles). The yield of 107 was 27%. 1-Methoxy-1,1,3,3,3-pentamethyldisilazane had the following spectral properties. ^1H NMR (300 MHz, $CDCl_3$) δ 0.083-0.093 (2 singlets, 15 Hs); 0.600 (s, broad, 1 H); 3.414 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) -0.621, 2.257, 49.471. Mass spectrum 162 (100) M -15; 132 (92.7); 73 (15.5); 59 (19.3). Exact mass calculated for $C_6H_{19}NOSi_2$ 177.10053, measured 177.10090, calculated for $C_5H_{16}NOSi_2$ 162.07705, measured 162.07692. Elemental analysis calculated for $C_6H_{19}NOSi_2$ 40.62% C, 10.80% H, 7.90% N found 40.84% C, 11.07% H, 7.86% N. Two other products were observed, hexamethyldisilazane (15%) and 1,3-dimethoxy-1,1,3,3-tetramethyldisilazane (10%).

Trapping of allyl radicals with D_8-toluene in the pyrolysis of N-allyl-1,1,1,3,3-pentamethyldisilazane 106

The procedure was exactly as that for 98.

Determination of Arrhenius parameters for butene formation from N-allyl-1,1,1,3,3-pentamethyldisilazane (106) in the presence of toluene

Approximately 0.1 torr of the reactant was introduced into the sample chamber. This was followed by 10 torr of toluene. The reactant and toluene were allowed to mix in the gas phase for 7-10 minutes. At this time the mixture was pulsed into the reactor in the usual way. The reaction was not very clean due to the reactivity of the toluene at the "high" pressures used. Pyrolysis of 10 torr of toluene was also performed in the absence of the reactant and no C_4 hydrocarbons were formed. Data analysis was performed in the usual manner.

Determination of Arrhenius parameters for propene formation from N-allyl-1,1,1,3,3-pentamethyldisilazane (106) in the presence of toluene

Approximately 0.1 torr of the reactant was introduced into the sample chamber. This was followed by 10 torr of toluene. The reactant and toluene were allowed to mix in

Table 7. Rate constants for the formation of 1-butene from N-allyl-1,1,1,3,3-pentamethyldisilazane (106) in the presence of 100 fold excess of toluene in SFR

T(°C)	k(sec^{-1})	T(°C)	k(sec^{-1})	T(°C)	k(sec^{-1})
625.3	0.0957	645.5	0.2153	618.2	0.0650
625.3	0.0925	655.6	0.3318	618.2	0.0661
635.5	0.1344	655.1	0.3474		
635.4	0.1337	665.	0.5367		

log $A=16.4\pm0.4$ $\Delta S^{\ddagger}=12.4\pm1.6$ eu at Tavg=638.0°C

$Ea=71.8\pm1.5$ kcal/mole $H^{\ddagger}=70.0\pm1.5$ kcal/mole at Tavg=638.0°C

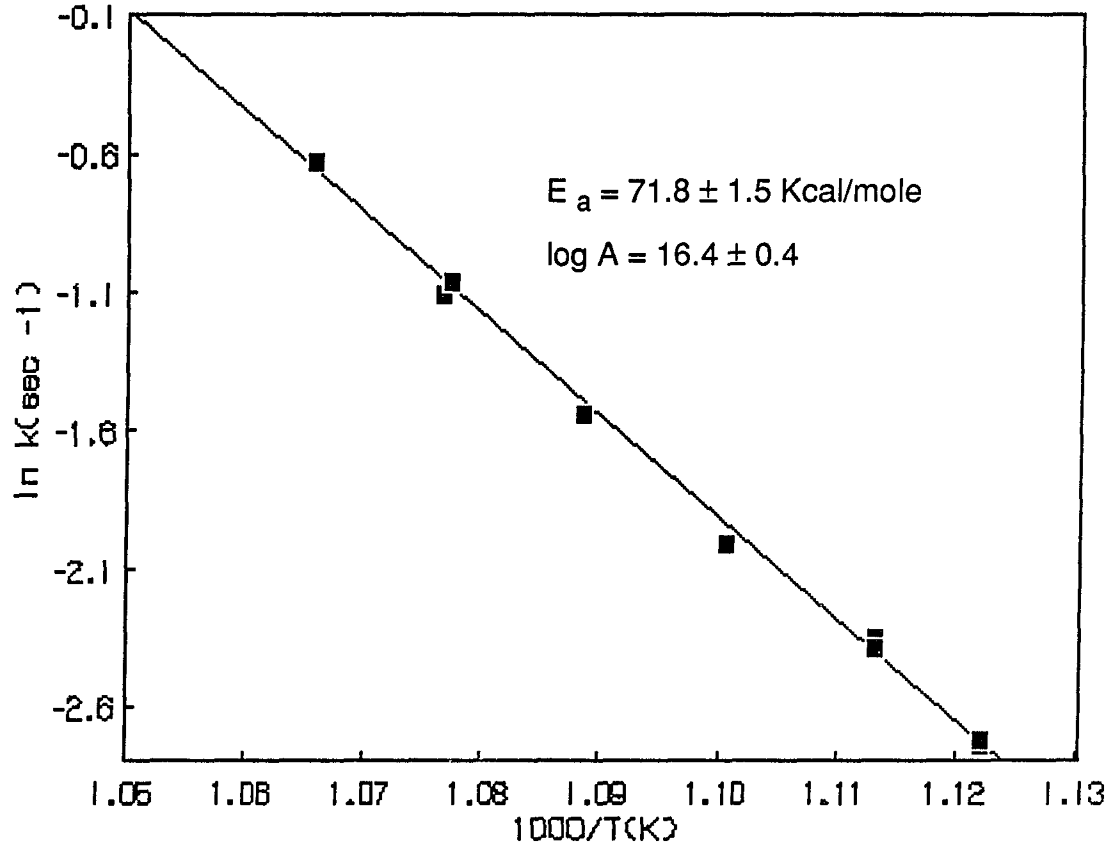


Figure 7. Arrhenius plot for the formation of butene from <u>106</u> in the presence of 100 fold excess of toluene

the gas phase for 7-10 minutes. At this time the mixture was pulsed into the reactor in the usual way. Data analysis was done in the usual manner.

Pyrolysis of 106 in the presence of ethylene

The reaction was carried out exactly as before for the trapping of allyl radicals with toluene in the pyrolysis of 106. The ethylene to 106 ratio was 10:1.

Synthesis of N-allyl-t-butylamine (111)

To a round bottom flask equipped with a stir bar, reflux condenser and inlet septum was added 100 ml of ether and t-butylamine (13.9 g, 0.19 moles). To this solution was added allylbromide (7.0 g, 0.058 moles). The solution was allowed to reflux overnight. The solution was washed with three portions of water (100 each) and dried over Na_2SO_4. The volatiles were removed by distillation and product isolated in 61% yield. Also observed was < 5% of the N-N-diallyl-t-butylamine. Spectral properties of N-allyl-t-butylamine. ^1H NMR (300 MHz, $CDCl_3$) δ 0.750 (s, broad 1 H); 1.109 (s, 9 H); 3.194 (d, J = 5.4 Hz, 2 H); 5.041 (d of q, J_A = 10.2, J_B = 1.5, 1 H); 5.157 (d of q, J_A = 17.1, J_B = 1.5, 1 H); 5.924 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.016, 45.679, 50.238, 115.110, 137.746. Mass spectrum 113 (0.7) M^+; 98 (79.2) M^+ -15; 58 (18.0); 57 (10.8); 56 (18.3); 41 (100) C_3H_5.

Table 8. Rate constants for the formation of propene from N-allyl-1,1,1,3,3-pentamethyldisilazane (106) in the presence of 100 fold excess of toluene in SFR

T(°C)	k(sec^{-1})	T(°C)	k(sec^{-1})	T(°C)	k(sec^{-1})
625.3	0.2799	635.5	0.3915	655.6	0.7974
625.3	0.2836	645.7	0.6001	665.4	1.3029
635.5	0.4096	645.5	0.5201		
635.4	0.3835	655.	0.8347		

log A=14.5±0.6 $\Delta S^{\ddagger}$=3.7±2.7 eu at Tavg=642.4°C

Ea=62.0±2.5 kcal/mole $\Delta H^{\ddagger}$=60.2±2.5 kcal/mole at Tavg=642.4°C

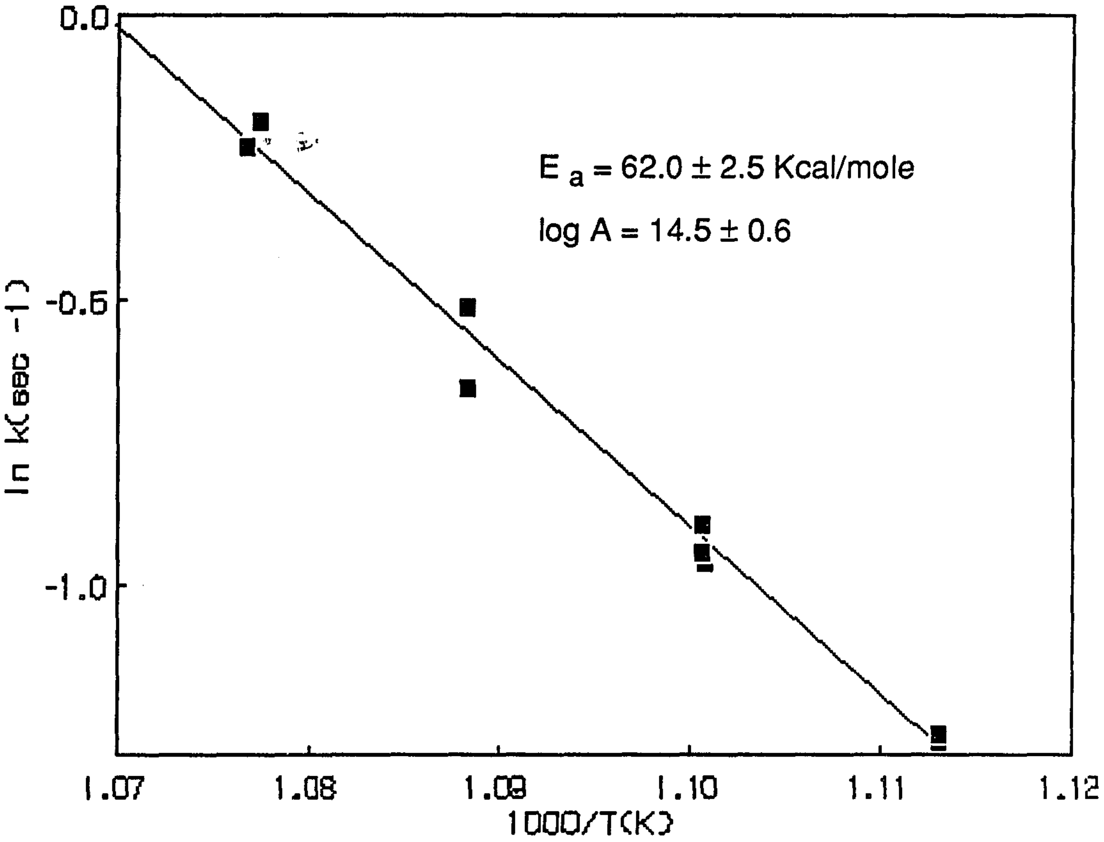


Figure 8. Arrhenius plot for the formation of propene from <u>106</u> in the presence of 100 fold excess of toluene

Synthesis of N-allyl-N-t-butyl-1,1-dimethylsilazane (110)

To a round bottom flask fitted with an inlet septum and a stir bar was added 20 ml of dry ether and 111 (0.50 g, 0.0044 moles). To this mixture was added butyllithium (1.8 ml, 0.0044 moles) while the solution was cooled to -78°C. The solution was allowed to warm to 0°C over two hours and dimethylchlorosilane (0.42 g, 0.0044 moles). The mixture was then allowed to stir for two hours at room temperature. The lithium chloride was removed by filtration through celite and the product concentrated by distillation. The GC yield of 110 was 72%. The product had the following spectral features. Mass spectrum 171 (4.4) M^+; 156 (100) M -15; 114 (52.9); 98 (19.5); 73 (38.7); 59 (84.0).

Pyrolysis of N-t-butyl-N-allyl-1,1,-dimethylsilazane (110) in SFR

The silazane (0.00026 moles) was introduced into the reactor in the usual way. The hydrocarbons were analyzed by gas chromatography. Yields were calculated by predetermined response factors. The response factor for the combined yield of methane and ethane were approximated. The yield of methane + ethane was 42%, propene 16%, isobutene 76%. No silicon containing products were characterized.

Synthesis of 1-allyl-1,1,3,3,3-pentamethyldisilazane (112)

To a 3 necked round bottom flask fitted with a mechanical stirrer, gas inlet tube and a reflux condenser was added 175 ml of dry hexanes. To this was added trimethylchlorosilane (3.6 g, 0.033 moles) and allyltrimethylchlorosilane (4.5 g, 0.033 moles). Dry ammonia was bubbled through this solution for one hour. The solution was stirred for three hours at room temperature and the ammonium chloride removed by filtration through celite. The hexanes were removed by distillation at atmospheric pressure. The yield of the desired product was 45%. 1-Allyl-1,1,3,3,3-pentamethyldisilazane had the following spectral properties. ^1H NMR (300 MHz, $CDCl_3$) δ 0.052 (s, 15 H); 1.518 (d, J = 7.6 Hz, 2 H); 4.838 (m, 2 H); 5.772 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl^3$) δ 0.368, 2.602. 27.195, 112.773, 135.300. IR (neat) ν 3375, 3078, 2956, 2898, 1631, 1394, 1252, 1184, 1035, 935, 838, 752. Mass spectrum 172 (7.2) M -15; 146 (100) M -41; 130 (59.7); 73 (23.4); 41 (21.3). Exact mass calculated for $C_8H_{21}NSi_2$ (M^+) 187.12126 measured 187.12173 calculated for $C_7H_{18}NSi_2$ (M^+ $-CH_3$) 172.09778 measured 172.09810, calculated for $C_5H_{16}NSi_2$ (M^+ $-C_3H_5$) 146.18213 measured 146.18200. Elemental analysis calculated for $C_8H_{21}NSi_2$ 51.26% C, 11.29% H, 7.47% H, measured 51.17% C, 11.60% H, 7.35% N. Two other products were also observed; 1,3-diallyl-1,1,3,3-tetramethyldisilazane and hexamethyldisilazane.

Determination of Arrhenius parameters for propene formation from 1-allyl-1,1,3,3,3-pentamethyldisilazane (112)

Approximately 0.1 torr of the silazane was introduced into the reactor in the usual way. The temperature range studied was from 505°C to 565°C. Data analysis was as usual.

Attempted trapping of silyl radicals in the pyrolysis of 1-sllyl-1,1,3,3,3-pentamethyldisilazane 112

A 100:1 mixture of methylchloride to 112 was prepared in the SFR sample loop. The material was injected into the SFR reactor. A portion of the product mixture was split off to the mass spectrometer. No peaks corresponding 1-chloro-1,1,3,3,3-pentamethyldisilazane or trimethylchlorosilane were observed.

Synthesis of N-t-butyl-1-allyl-1,1-dimethylsilazane (114)

To a N_2 flushed dry 100 ml flask was added t-butylamine (2.1 g, 0.628 moles) 50 ml of dry ether. The solution was cooled to -78°C and butyllithium (11.2 ml, 0.028 moles) added over 20 minutes. The solution was warmed to room temperature and the allyldimethylchlorosilane (3.8 g, 0.028 moles) added in one portion. The mixture was allowed to stir for one hour at room temperature and the lithium

Table 9. Rate constants for the formation of propene from 1-allyl-1,1,3,3,3-pentamethyldisilazane (<u>112</u>) in SFR

T(°C)	k(sec^{-1})	T(°C)	k(sec^{-1})	T(°C)	k(sec^{-1})
505.9	0.1150	525.0	0.2381	545.2	0.4851
515.6	0.1667	535.5	0.3408	555.4	0.6999
515.6	0.1699	535.5	0.3355	555.4	0.7097
525.0	0.2340	545.2	0.4833	565.2	0.9466

log A=12.1±0.1 $\Delta S^{\ddagger}$=-7.2±0.4 eu at Tavg-535.4

Ea-46.4±0.3 kcal/mole $\Delta H^{\ddagger}$=44.8±0.3 kcal/mole at Tavg=535.4

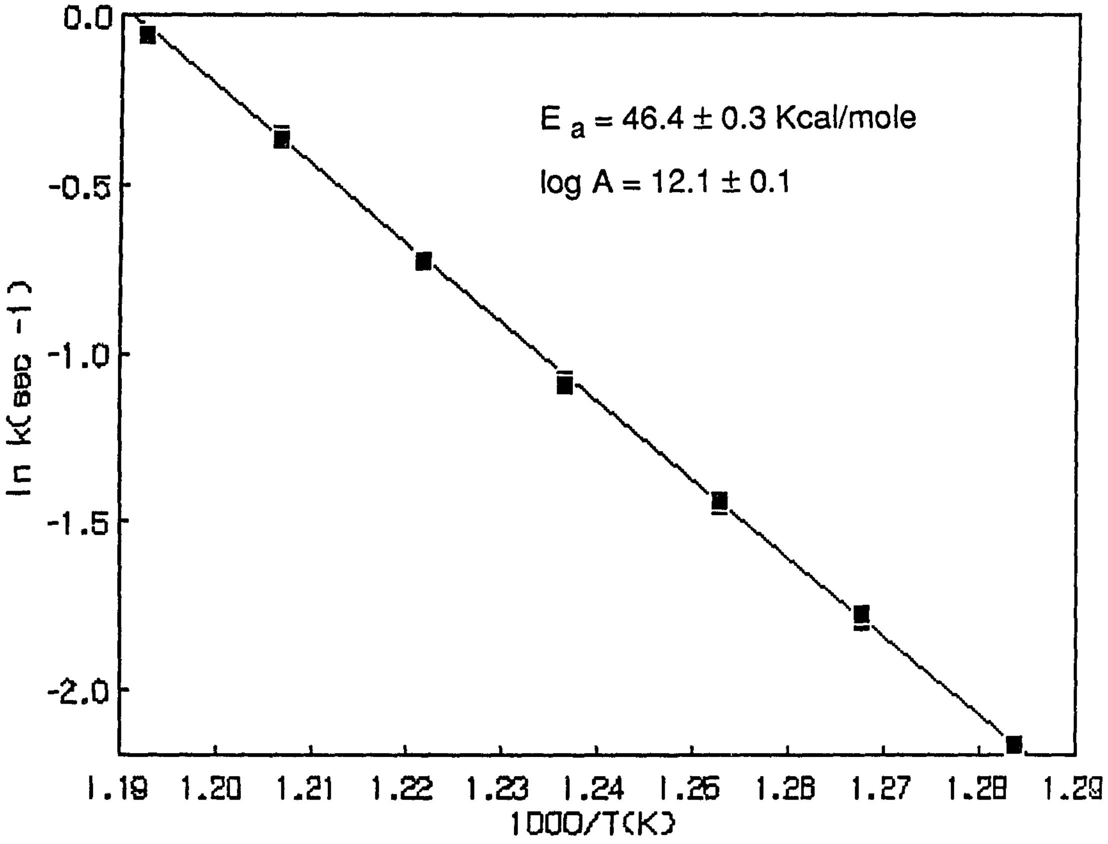


Figure 9. Arrhenius plot for the formation of propene from 112

chloride removed by filtration through celite. The ether was removed by distillation at atmospheric pressure. The yield of the product was 50%. The N-t-butyl-1-allyl-1,1-dimethylsilazane had the following spectral properties. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.062 (s, 6 H); 1.141 (s, 9 H); 1.551 (d, J = 8.0 Hz, 2 H); 4.829 (m, 2 H); 5.809 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.545, 26.990, 33.866, 49.432, 112.613, 135.647. IR (neat) ν 3389 (s), 3078, 2968, 2908, 1632, 1465, 1396, 1379, 1251, 1229, 1198, 1018, 892, 856, 831, 638. Mass spectrum 171 (0.4) M^+; 156 (4.8) M^+ -15; 130 (100) M^+ -15; 74 (98.9); 73 (97.8); 59 (34.0); 41 (51.2). Exact mass calculated for $C_9H_{21}NSi$ (M^+) 171.14433 measured 171.14398, calculated for $C_8H_{18}NSi$ (M^+ -15) 156.12086 measured 156.12104, calculated for $C_6H_{16}NSi$ (M^+ -41) 130.10520 measured 130.10526.

Pyrolysis of N-t-butyl-1-allyl-1,1-dimethylsilazane (114) in SFR

The silazane (1.16 torr) was introduced into the reactor heat to 651°C in the usual fashion. The hydrocarbons were analyzed by gas chromatography. Yields were calculated by predetermined response factors. The response ractor for the methane and ethane combined yields was approximated. The yield of methane + ethane was 54%, propene 95% and isobutene 65%. No silicon containing products were isolated.

Preparation of N-ethyl-N-2-methylallyl-1,1-dimethylsilazane (115)

To an oven-dried dried flask fitted with an inlet septum and a stir bar was added 20 ml of dry ether and N-ethyl-N-2-methylallylamine (1.5 g, 0.015 moles). The solution was cooled to -78°C and 2.5 M butyllithium (6.2 ml, 0.015 moles) added over ten minutes. The solution was warmed to 0°C and dimethylchlorosilane (1.5 g, 0.016 moles) added in one portion. The solution was allowed to stir for one hour after warming to room temperature. The solution was filtered through celite to remove lithium chloride. The yield of product was quantitative (2.6 g, 0.015 moles). The N-ethyl-N-2-methylallyl-1,1-dimethylsilazane had the following spectral properties. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.126 (d, J = 3.1 Hz, 6 H); 0.951 (t, J = 7.0 Hz, 3 H); 1.639 (s, 3 H); 2.712 (q, J = 7.0 Hz, 2 H); 3.269 (s, 2 H); 4.436 (h, J = 3.1 Hz, 1 H); 4.777 (s, 1 H); 4.815 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ -1.314, 14.964, 20.982, 41.168, 53.239, 110.635, 144.935. IR (neat) ν 3072, 2964, 2866, 2125, 1653, 1441, 1373, 1250, 1184, 1142, 1013, 903, 831 cm^{-1}. Mass spectrum 157 (7.8) M$^+$; 142 (35.3) M -15; 116 (60.5); 86 (18.7); 59 (100). Exact mass calculated for $C_8H_{19}SiN$ 157.12868 measured 157.12848. Elemental analysis for $C_8H_{19}SiN$ calculated 61.07% C, 12.17% H, 8.90% N found 61.33% C, 12.84% H, 9.08% N.

Flash vacuum pyrolysis of N-ethyl-N-2-methylallyl-1,1-silazane (115)

Compound 115 (0.182 g, 0.0012 moles) was distilled through a quartz tube in the usual fashion which was heated to 675°C. The GC yield of the dimer 117 was 53%. The yield of monomer 116 was 30%. This compound was not isolated. The spectral properties of the monomer dimer mixture. ^1H NMR (300 MHz, $CDCl_3$) δ 0.12-0.19 (3 doublets with coupling constants of 2.7 Hz, 3.3 Hz and 3.3 Hz, 90 H); 1.332 (d, J = 6.2 Hz, 40 H); 1.360 (d, J = 6.3 Hz, 5 H); 1.930 (d, J = 4.9 Hz, 19 H); 1.986 (d, J = 4.9 Hz, 5 H); 4.3-4.5 (m, includes Si-H hep J = 3.3 Hz and a quartet J = 6.2 Hz, total 124 H); 7.659 (d of q, J_A = 4.9 Hz, J_B 0.9 Hz, 6 H); 7.772 (d of q, J_A = 5.0 Hz, J_B = 0.9 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.592, 0.857, 21.929, 26.513, 78.162, 157.197 ppm. IR (neat) ν 2957, 2850, 2112, 1672 (strong), 1434, 1382, 1365, 1249, 1159, 1132, 1099, 1001, 897, 770 cm^{-1}. Mass spectrum of dimer 202 (0.6) M^+; 201 (3.3) M^+ -1; 187 (13.1) M^+ -15; 161 (375); 101 (34.3); 86 (100); 59 (92.9); 43 (73.3). Exact mass calculated for $C_8H_{21}N_2Si_2$ (M^+) 201.12434, measured 201.12395, calculated for $C_7H_{19}N_2Si_2$ (M^+ $-CH_3$) 187.10854, measured 187.10870. Elemental analysis calculated for $C_8H_{21}N_2Si_2$ 47.46% C, 10.96% H, 13.84% N measured 47.30% C; 11.28% H; 14.05% N.

Synthesis of bis(trimethylsilyl)-methoxydimethylsilyltrisilazane (126)

To a 100 ml round bottom flask equipped with a stir bar and an inlet septum was flushed with dry nitrogen. To this flask was added hexamethylsilane (3.9 g, 0.024 moles) and 75 ml of dry ether. The solution was cooled to -78°C and butyllithium (9.6 ml, 0.024 moles) was added over 20 minutes. The solution was warmed to 0°C and the methoxytrimethylchlorosilane (3.0 g, 0.024 moles) was added in one portion. The solution was allowed to warm to room temperature and stir for one hour. The lithium chloride was removed by filtration through celite. The product was isolated as a waxy solid with a melting point of 34-35°C (59% yield). The bis(trimethylsilyl)-methoxydimethylsilyltrisilazane had the following spectral properties. ^1H NMR (300 MHz, $CDCl_3$) δ 0.181-0.190 (two singlets, 24 Hs); 3.383 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 2.520, 5.024, 49.268. Mass spectrum 234 (100) M -15; 130 (92.4); 100 (26.2); 89 (22.3); 73 (61.5); 59 (49.7). Exact mass calculated for $C_9H_{27}NSi_3O$ 249.14004 measured 249.14022, calculated for $C_8H_{24}NSi_3O$ 234.11656 measured 234.11658.

Flash vacuum pyrolysis of bis(trimethylsilyl)-methoxydimethylsilyltrisilazane (126)

The trisilazane <u>126</u> (0.109 g, 0.00043 moles) was allowed to distill through a quartz tube packed with quartz chips which was heated to 600°C. The products were trapped in liquid nitrogen. The mass recovery was 85%. Two products were observed, trimethylmethoxysilane (100%) and 1,1,3,3-tetramethyl-2,4-di(trimethylsilyl)cyclodisilazane (69%). Both yields are corrected for unreacted starting material. Identification of both products was done by comparing retention times and mass spectrums of previously prepared samples.

Determination of rate constants for the decomposition of 126

The experiments were performed on the SFR as usual except that the sample loop was heated to 70°C with heating tape. The rate constants for three temperatures are compared with and withoug D_3 present as a trap.

Synthesis of bis(dimethylsilyl)methoxydimethylsilyltrisilazane (127)

To a round bottom flask equipped with a stir bar and flushed with nitrogen was added 1,1,3,3-tetramethyldisilazane (3.8 g, 0.029 moles) and 150 ml of dry ether. The solution was cooled to -78°C and butyllithium (11.5 ml, 0.029 ml) added over 20 minutes. The solution was warmed to 0°C and the dimethylmethoxychlorosilane (4.3 g, 0.029 moles) added in one portion. The solution was warmed to room temperature and allowed to stir for one hour. The lithium chloride was removed by filtration through celite. The

Table 10. Rate constants for the decomposition of 126 in the presence of D_3 and without the presence of D_3

Temp. (°C)	k(sec^{-1}) without D_3	k(sec^{-1}) with D_3
440°C	1.630	4.258
431°C	1.210	2.934
420°C	0.835	1.834

product was produced in 92% yield. The bis(dimethylsilyl)-methoxydimethylsilyltrisilazane had the following spectral properties. ^1H NMR (300 MHz, $CDCl_3$) δ 0.170 (s, 6 H); 0.208 (d, J = 3.5 Hz, 12 Hs); 3.418 (s, 3 H); 4.497 (h, J = 3.5 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.649, 1.038, 49.839. IR (neat) ν 2959, 2120, 1419, 1254, 1097, 991, 962, 910, 833, 813, 786. Mass spectrum 221 (5.6)M^+ -1; 206 (98.6) M^+ -15; 130 (100); 73 (34.5); 59 (74.8). Exact mass calculated for $C_7H_{23}NOSi_3$ (M^+) 221.10876 measured 221.10914, calculated for $C_7H_{22}NOSi_3$ (M^+ -H) 220.10093, calculated for $C_6H_{20}NOSi_3$ (M^+ -CH_3) 206.08528 measured 206.08562.

Flow pyrolysis of bis(dimethylsilyl)methoxydimethylsilyltrisilazane (127) in the presence of hexamethylcyclotrisiloxane

A mixture of the starting material (0.209 g, 0.0009 moles) and D_3 (0.733 g, 0.0033 moles) was dissolved in 0.9 g of toluene. The solution was dripped through a quartz tube heated to 535°C. A flow of 20 ml/nitrogen was used as the carrier gas. The pyrolysate was collected in a dry ice isopropanol bath with a mass recovery of 90%. Four products were observed: dimethylmethoxysilane (50%), trimethylmethoxysilane (trace), and two products with mass of 353. This molecular weight corresponds adducts between D_3 and a silanimine with a mass of 131. The ratio of these products was 16:1. The major product <u>132</u> was isolated and had the following spectral characteristics. ^1H NMR (300 MHz, C_6D_6) δ 0.204 (s, 12 H); 0.225 (d, J = 3.5 Hz, 6 H); 0.348 (s, 12 H); 4.680 (h, J = 3.5 Hz, 1 H). ^{13}C NMR (75 MHz, C_6D_6) δ 1.177, 1.593, 4.122. IR (neat) ν 2964, 2904, 2129, 1411, 1259, 1074, 981, 933, 856, 804, 688 cm^{-1}. Mass spectrum 353 (1.0) M^+; 352 (3.0) M^+ -1; 338 (100) M^+ -15; 264 (17.0); 73 (38.6). Exact mass calculated for $C_{10}H_{30}NO_3Si_5$ (M^+ -1) 352.10721 measured 352.10709, calculated for $C_9H_{27}NO_3Si_5$ 338.09157 measured 338.09142.

<u>Determination of Arrhenius parameters for dimethylmethoxysilane formation from bis(dimethylsilyl)methoxydimethylsilyltrisilazane (127) in the presence of D_3</u>

Approximately 0.1 torr of the silazane was introduced into the sample loop. This was followed by introducing ~ 2.0 torr of D_3. The mixture was allowed to equilibrate in the gas phase in the sample loop for 10 minutes. At this

Table 11. Rate constants for the formation of dimethylmethoxysilane from bis(dimethylsilyl)methoxydimethylsilyltrisilazane (127) in the presence of D_3

T(°C)	k(sec^{-1})	T(°C)	k(sec^{-1})	T(°C)	k(sec^{-1})
476.2	0.2469	497.4	0.5838	518.5	1.6667
476.2	0.2471	497.4	0.6656	518.5	1.6096
483.3	0.3372	504.3	0.8013	461.8	0.1225
483.3	0.3382	504.3	0.8650	461.8	0.1263
490.2	0.4566	511.0	1.1146	526.7	2.1846
490.2	0.4641	511.0	1.1275	526.7	2.1462

log A=14.4±0.1 $\Delta S^{\ddagger}$=3.7±0.6 eu at Tavg=496.6°C

Ea=51.7±0.5 kcal/mole $\Delta H^{\ddagger}$=50.1±0.5 kcal/mole at Tavg=496.6°C

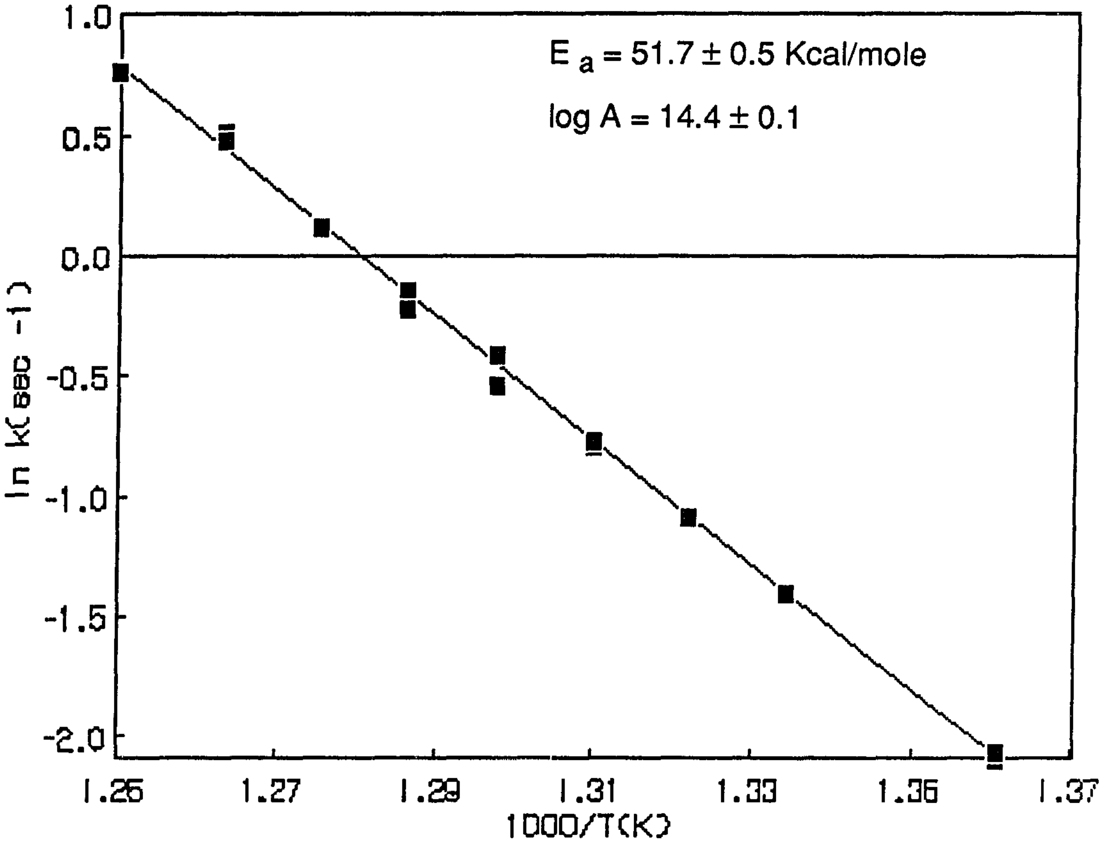


Figure 10. Arrhenius plot for the formation of $Me_2SiHOMe$ from <u>127</u>

time the mixture was introduced into the reactor in the usual fashion. Data analysis was performed as usual. The temperature range studied was 461.8°C to 526.7°C.

Synthesis of N,O-bistrimethylsilylhydroxylamine

The procedure of Chang et al.[50a] was used. In an oven dried flask which was flushed with nitrogen and fitted with a reflux condenser and a stir bar was added 10 ml of dry hexanes and hexamethyldisilazane (7.7 g, 0.048 moles). To this solution was added hydroxyaminehydrochloride (2.2 g, 0.032 moles). This solution was heated to 50°C for 20 hours. The ammonium chloride was removed by filtration and the hexanes removed by distillation of atmospheric pressure. The N,O-bistrimethylsilylhydroxyamine was isolated from the hexamethyldisilazane by preparative gas chromatography. The product had identical spectral characteristics as those reported by Chang et al.[50a]

Synthesis of N,N,O-tris(trimethylsilyl)hydroxylamine (135)

To a round bottom flask equipped with a stir bar and inlet septum was added N,O-bis(trimethylsilyl)hydroxylamine (0.507 g, 0.0029 moles) and 25 ml of dry ether. The solution was cooled to -78°C and butyllithium (1.1 ml, 0.0029 moles) was added over five minutes. The solution was warmed to 0°C and trimethylchlorosilane was added in one portion. The solution was warmed to room temperature and added to stir for one hour. The product was isolated by filtration through celite and removal of the solvent by distillation. The yield of the product was 91%. The N,N,O-tris(trimethylsilyl)hydroxylamine had the same spectral properties as those reported by Nowakowski and West.

Flash vacuum pyrolysis of N,N,O-tris(trimethylsilyl)-hydroxylamine (135)

The amine (0.148 g, 0.00059 moles) was distilled through a hot tube (680°C) packed with quartz chips (1 x 10^{-4} torr) and heated to 680°C. The product was isolated in a liquid nitrogen trap. The product mixture contained traces of hexamethylsiloxane and (t-trimethylsilyl-1-methylamino)-1,1,3,3,3-pentamethylsiloxane. The product 136 had the following spectral properties. ^1H (300 MHz, $CDCl_3$) δ 0.440 (3 singlets, 29 Hs); 2.440 (s, 3 H). ^{13}C (75 MHz, $CDCl_3$) δ 0.952, 1.546, 1.955, 30.050. IR (neat) ν 2958, 2898, 1411, 1259, 1190, 1047, 910, 838, 784, 752, 684 cm^{-1}. Mass spectrum 249 (4.4) M^+; 234 (67.5) M^+ -15; 145 (50.9); 73 (100); 58 (25.8); 45 (25.5). The mass spectrum of the product is much different from the starting material. Exact mass calculated for $C_9H_{27}NOSi_3$ 249.14006 measured 249.14049.

Flow pyrolysis of N,N,O-tris(trimethylsilyl)-hydroxylamine (135) hydroxylamine in the presence of D_3

The starting material (0.082 g, 0.00033 moles) and D_3 (0.232 g, 0.0010 moles) were dissolved in nonane (1.169 g). The solution was dripped through a vertical quartz tube packed with quartz chips which was heated to 460°C. The product mixture was collected in a dry ice isopropanol bath. The product had identical spectral characteristics as the N-methyl derivative obtained in the flash vacuum pyrolysis of N,N,O-tris(trimethylsilyl)hydroxylamine.

Synthesis of polysilazane 141

To a 250 ml round bottom flask fitted with a stir bar, a gas inlet tube connected to an anhydrous ammonia tank and a septum was added allyltrichlorosilane (6.0 g, 0.034 moles) and 200 ml of Skelly B. Ammonia was bubbled through the solution for one hour. The ammonium chloride that forms was removed by filtration through celite. The hexanes were removed by distillation at 0.1 torr. The yield of product 141 was 50%. This was based on a stoichometry of 1:15 silane:ammonia ratio. The polymer became insoluble upon standing overnight.

Thermal gravimetric analysis of 141

The polymer was weighed and the weight loss was recorded as a function of temperature. Figure shows the TGA curve.

Table 12. Temperature program for the pyrolysis of 141

T(°C)	Time (hr)
200	1
400	2
800	2
1400	3

Pyrolysis of 141 in argon

The polymer was weighed in a graphite boat (0.103 g) and heated in an alumina tube with the following program. The ramp between temperatures was approximately 10°C/min. After heating at 1400°C for three hours the ceramic was cooled to room temperature and weighed. The material had lost 32 mg in weight for a yield of ceramic material of 69%. Elemental analysis of this sample revealed 28.3% C and 20.0% N.

Pyrolysis of 141 in a vacuum system with a mass spectrometer inlet

The polymer was heated in a graphite boat which was placed in a quartz tube. The tube was connected to the vacuum line and the volatiles trapped by a liquid nitrogen bath. Upon warming the trap the gases were introduced to the mass spectrometer by a capillary inlet tube. Gases which were not trapped by liquid nitrogen (methane, hydrogen) were observed by in a similar manner except after each check the system was reevacuated to remove CH_4 and H_2 fro the gas handling system.

Synthesis of 142

The procedure was exactly as that for the synthesis of 141 except that allylmethyldichlorosilane (10.8 g, 0.069 moles) was used. The polymer was isolated in 66% yield. The polymer had a molecular weight of 600 daltons and the following infrared spectra. 3490, 3360, 3010, 2957, 2850, 1630, 1430, 1395, 1254, 1167, 1034, 993, 895, 795 cm^{-1}.

Pyrolysis of 142 in argon

The procedure was exactly that for the pyrolysis of 141. The remaining ceramic was 6.9% of the original weight of the polymer pyrolyzed. The remaining polymer distilled from the alumina tube and condensed outside the hot zone.

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