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Gas-phase Generations and Rearrangement of Silathiones, R*2*Si=

by

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Gas-phase generations and rearrangement
of silathiones, $R_2Si=S$

by

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The generation of silathiones is shown to be possible by the retroene elimination of propene from allylthiodimethylsilane and 1-allylthio-1-hydrido-1,2,2,2-tetramethyldisilane. This retroene reaction of allylthiodimethylsilane has a very low activation energy ($E_a = 36.3$ kcal/mol, $\log A = 11.3$), when compared with carbon, oxygen or nitrogen homologs. The low activation energy is probably due to the strong Si-S π bond and the weak S-C bond. The low $\log A$ indicates that the formation of propene and silathione is via a 1,5-hydrogen shift from a six-centered transition state.

The trapping of (trimethylsilyl)methylsilathione by butadiene afforded a 5-membered ring (1-trimethylthio)-1-methyl-1-silacyclopent-3-ene) which is presumably due to the migration of a silyl group of silathione from silicon to

sulfur to generate a silylene which was trapped by butadiene. This is the first example of a silathione-silylene isomerization.

Another route demonstrated to generate silathione was the reaction of a silylene, $\text{Me}_2\text{Si:}$, with carbon disulfide. Dimethylsilylene is thought to form a transient 3-membered ring with CS_2 and the elimination of carbon sulfide produces dimethylsilathione.

The other method to produce silathione was the β -elimination of bis(trimethylsilythio)dimethylsilane. The β -elimination has an activation energy ($E_a = 33.8$ kcal/mol, $\log A = 10.5$).

The second example of a silathione-silylene isomerization was observed in the pyrolysis of 1,1-bis(trimethylsilythio)-1,2,2,2-tetramethyldisilane. The β -elimination of hexamethyldisilathiane initially produced trimethylsilylmethylsilathione whose trimethyl silyl group migrated from silicon to sulfur to give a corresponding silylene. This silylene was trapped by butadiene to yield a 5-membered ring. The possibility of formation of silylene via α -elimination was ruled out by the result that the α -elimination of methylthiopentamethyldisilane had a high activation energy ($E_a = 53.0$ kcal/mol, $\log A = 14.2$), while the β -elimination of bis(trimethylsilythio)dimethylsilane had a low activation energy ($E_a = 33.8$ kcal/mol, $\log A = 10.5$).

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Chong Bok Kim

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DEDICATION

To my mother, husband and daughter

INTRODUCTION

Since the first evidence of transient $R_2Si=S$ was reported by Sommer and Mclick,¹ there has been interest in the generation of silathiones ($R_2Si=S$) under mild condition and to examine their properties.

This dissertation will describe attempts to generate silathiones ($R_2Si=S$) and isomerize it to a silylene ($-\ddot{Si}-S-$).

Dimethylsilathione has been generated by the retro-ene reaction of allylthiodimethylsilane. Dimethylsilylene ($Me_2Si:$) was reacted with carbon disulfide to efficiently generate dimethylsilathione. It was discovered that decomposition of 1-allylthio-1-hydrido-1,2,2,2-tetramethyldisilane generated $(Me_3Si)Si(Me)=S$ (trimethylsilylmethylsilathione) which isomerized to a silylene which was trapped by butadiene. Bis(trimethylsilyl)dimethylsilane was found to extrude hexamethyldisilathiane via a favored β -elimination to generate a silathione rather than via α -elimination to generate a silylene.

LITERATURE SURVEY

The existence of an equilibrium between hexamethylcyclodisilthiane 1 and tetramethylcyclodisilthiane 2 has been established (eq. 1).^{2,3}

The equilibrium constants were determined by the study of proton nuclear magnetic resonance spectroscopy (NMR) at various temperatures and dilutions.³ The obtained equilibrium constants ($K = \frac{[(\text{CH}_3)_2\text{SiS}]_3^2}{[(\text{CH}_3)_2\text{SiS}]_2^3}$ 1/mol) were 13.2, 2.51, and 0.41 at 150°C, 200°C, and 250°C, respectively. The result indicated that the corresponding trimer $(\text{Me}_2\text{SiS})_3$ was converted to the dimer $(\text{Me}_2\text{SiS})_2$ at temperature above 200°C. High (low) temperatures and high (low) dilutions favored the formation of the tetramethylcyclodisilthiane (hexamethylcyclotrisilthiane).

Soysa and Weber⁴ suggested that the thermal equilibrium of 1 and 2 involved an intermediate possessing a silicon-sulfur double bond $[(\text{CH}_3)_2\text{Si}=\text{S}]$ (eq. 2,3). Trapping reactions of a silicon-sulfur double bond with hexamethylcyclotrisiloxane 4 or 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane 5 indicated the existence of silathione as an intermediate (eq. 4,5).⁴

Although there is a possibility in which a zwitter ion 8 would be an intermediate, the β -elimination of 1 probably extrudes dimethylsilathione which would insert into a Si-O bond of 4 or 5.

The first examples of transient $[\text{R}_2\text{Si}=\text{S}]$ ($\text{R}=\text{Me}, \text{Ph}$) were

inferred by Sommer and Mclick.¹ A benzene solution of 1,1-dimethylsilacyclobutane 9 and thiobenzophenone was pyrolyzed at 611°C. Diphenylethylene and tetramethylcyclo-disilthiane were identified as the two major products. Scheme 1 includes a possible mechanism which Sommer and Mclick suggested.

Scheme 1

Seyferth et al.⁵ thermolyzed 1,1,4,4,5,5-hexamethyl-2,3-

dithia-1-silacyclopentane 11 in a sealed NMR tube at 140°C. During the decomposition two signals at 1.62 (tetramethylethylene) and 0.79 ppm (tetramethylcyclodisilthiane) grew steadily. It was speculated that the dimethylsilathione intermediate was involved during the decomposition process (eq. 6).

Soysa and Weber⁴ copolyrized 1,1-diphenylsilacyclobutane 14 and thiobenzophenone in the presence of the trapping agent, cyclic $(\text{Me}_2\text{SiO})_3$ and obtained the products, $[\text{Me}_2\text{Si}=\text{S}]$ dimer (11% yield) and 1,1,3,3-tetramethyl-5,5-diphenylcyclotrisiloxane 17 (18% yield). The formation of these products was readily explained by extrusion of $[\text{Me}_2\text{Si}=\text{S}]$ from the ring expanded species (Scheme 2).

Another example apparently involving a transient dimethylsilathione $[(\text{CH}_3)_2\text{Si}=\text{S}]$ was reported by Soysa et al.⁶ The pyrolysis of 1,1,2,2-tetramethyl-1,2-disila-3,6-dithia-

The mechanism was explained in three steps. The first step involves a $[\pi 2s, \pi 2s, \pi 2s]$ cyclo-reversion of 12 to yield ethylene and two dimethylsilathione intermediates. The

second step is head to tail dimerization of the dimethylsilathione intermediate to yield tetramethylcyclodisilthiane 2. The third step involves a rapid redistribution between 18 and dimer of dimethylsilathione 2 to yield 19 and 20.

One alternative mechanism suggested involves an α -elimination of dimethylsilylene from 18 to produce 19. Rapid insertion of dimethylsilylene into a silicon-sulfur single bond of silathione dimer would give 20. This possibility can

not be ruled out because when dimethylsilylene was produced by photolysis (2537 Å) of dodecamethylsilylene in the presence of silathione dimer, a 26% yield of 20 was obtained. This is the first example of insertion of a silylene into a silicon-sulfur single bond.

Weidenbruch⁷ reported that dialkylsilathiones were formed in the copolyrolysis of 1,1,2,2-tetraalkyldisilanes 21 with elemental sulfur. The head-to-tail dimer of the desired silathione 23 was isolated 1,1,3,3-tetraalkyl-1,3-disila-2,4-dithiacyclobutane 24.

The sulfur insertion reaction into 1,1-di-*t*-butyl-1-silacyclobutane 25 yielded 2,4-di-*t*-butyl-2,4-dipropyl-1,3-disila-2,4-dithiacyclobutane 29 instead of the expected 1,1-di-*t*-butyl-1-sila-2-thiacyclopentane.⁷ The author proposed a mechanism involving biradicals (26, 27). There is

no evidence for the existence of intermediate 27.

Elimination of isopropene from 26 would directly yield 28.

The labile Ge-S bond of 5-anisyl-2,2,3,3-tetramethyl-5-thio-1,4,5,2,3-dithiaphosphadigermolane 30 was used to produce silathione $[\text{Me}_2\text{Si}=\text{S}]$, probably via transient the dithiaphosphasiletane 31.⁸ Dimethylsilathione was trapped by

D₃ to produce the 8-membered ring compound 6 in 25% yield. Intermediate 32 was polymerized.

Flash vacuum pyrolysis of (dimethylsilyl)(trimethylsilyl)thio ketene 33 at 700°C resulted in the formation of (trimethylsilyl)acetylene 37 and transient dimethylsilathione.⁹ Barton proposed a mechanism involving isomerization of 33 to α-thio ketocarbene 34 via a 1,2-shift of trimethylsilyl group. Rearrangement of 34 by 1,2-hydrogen migration from silicon affords silene 35 which would close and decompose to trimethylsilylacetylene 37 and dimethylsilathione. A combined yield of 71% was obtained for

dimer and trimer of dimethylsilathione.

The reaction of decamethylsilicocene 39 with phenyl isothiocyanate afforded dithiasiletane 42 via a silathione intermediate.

intermediate.¹⁰ The proposed mechanism involves an initial

[2+1]-cycloaddition, leading to the silirane 40. The three-membered ring system 40 reacts with phenyl isothiocyanate to give 42. Although attempts to trap the intermediate silathione were unsuccessful, the phenyl isocyanide was detected.

Pentacoordinated silicon hydride 43 reacted with carbon disulfide to give the first isolable silathione 46.¹¹

A possible route for decomposition of 44 involves the transient formation of a siladithietane 45, which is highly unstable and undergoes fragmentation to silathione 46 and thioformaldehyde. Addition of a small excess of S_8 to 43 also

gave 46. Although 46 was relatively long lived in solution ($t_{1/2}$: 3d in CDCl_3 at 25°C), extreme precautions had to be

taken to avoid exposure to minute amounts of air. X-ray analysis of compound 46 indicated that the $\text{Si}=\text{S}$ bond ($2.013\text{\AA}$) is shorter than a $\text{Si}-\text{S}$ single bond ($2.16\text{\AA}$).

Boudjouk and Samaraweera¹² pyrolyzed 1,1-di-*t*-butyl-1,2-

silthietane 49 in benzene at 200°C and obtained two compounds, 1,1,3,3-tetra-*t*-butyl-1,3-disilacyclobutane 48 and 1,1,3,3-tetra-*t*-butyl-1,3-disil-2,4-dithiacyclohexane 49 in 33% and 30% yields, respectively.

Compound 48 is the dimer of di-*t*-butylsilathione, $t\text{-Bu}_2\text{Si}=\text{S}$, and 49 is the result of insertion of the di-*t*-butylsilathione into di-*t*-butylsilathione 47. Copyrolysis of 47 with D_3 resulted in the insertion of a di-*t*-butylsilathione intermediate into one of the Si-O bonds of D_3 in 27% yield.

As the first example of a compound of tetravalent silicon containing a Si-S double bond, the OSiS molecule was prepared in an argon matrix and studied by IR spectroscopy.¹³ The stretching vibration ($\nu(\text{SiS})$) was seen at 643 cm^{-1} and the overtone $2\nu(\text{SiS})$ at 1290 cm^{-1} . The force constant was calculated as $4.86 (10^2\text{ Nm}^{-1})$. A bond order for the Si-S bond in OSiS was predicted to be 1.9.

Guimon et al.¹⁴ reported the first spectroscopic detection of dimethylsilathione by photoelectron spectroscopy. Dimethylsilathione was generated by pyrolysis (278°C , $5 \times 10^{-2}\text{ mbar}$) of the corresponding trimer. Although the bands observed suggested the presence of monomeric and dimeric species, the proper assignments were in agreement with theoretical ionization potentials calculated for dimethylsilathione (Table 1).

Table 1. Experimental and Calculated Vertical Ionization Potentials

Vertical ionization Potential	Assignment	Koopmans ^a
9.15	n(S)	9.46
10.10	$\pi(\text{Si}=\text{S})$	10.12
11.05	$\sigma(\text{Si}-\text{S})$	11.71
12.10	$\sigma(\text{Si}-\text{C})$	12.62

^aOptimized structural parameters by MNDO method;
Si-S 1.894 Å; Si-C 1.836 Å; C-Si-S 122.7°.

Gusel'nikov et al. made an attempt to isolate dimethylsilathione in Ar matrices by very low pressure pyrolysis (VLPP) of hexamethylcyclotrisilthiane, tetramethylcyclodisilthiane and 3,3-dimethyl-3-silathietane.¹⁵ However, silathione was not observed but the cyclic dimer of silathione was. The structure of dimethylsilathione and force constant $F(\text{Si}=\text{S})$ were determined theoretically by the CNDO/2 method. Si=S bond distance and $F(\text{Si}=\text{S})$ were 1.993 Å and 4.72 mdyn/Å, respectively. The values of vibrational frequencies (cm^{-1}) of dimethylsilathione were also calculated: 884 $\nu_{\text{S}}(\text{SiC}_2)$ (A_1), 735 $\nu_{\text{as}}(\text{SiC}_2)$ (B_2), 626 $\nu_{\text{S}}(\text{Si}=\text{S})$ (A_1), 200 $\nu_{\text{CSiC}}(A_1)$.

X-ray analysis of compound 46 which is the first isolable pentacoordinated silathione indicated that the Si=S bond (2.013 Å) is shorter than a Si-S single bond (2.16 Å).¹¹

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Silicon-sulfur double bonds are found by theoretical calculations to be thermodynamically and kinetically more stable than silicon-oxygen double bonds, but less stable and more reactive than carbon-oxygen double bonds.¹⁶ Compared to silanone, favorable overlapping between $p\pi(\text{Si})$ and $p\pi(\text{S})$ orbitals owing to a size similarity give a stronger π -bonding, while a small electronegativity difference between Si and S atoms cause less polarized Si^+-S^- bonding which results in the decreased reactivity. Kudo and Nagase¹⁶ compared energies released upon the addition of H_2 to $\text{H}_2\text{Si}=\text{S}$, $\text{H}_2\text{Si}=\text{O}$, and $\text{H}_2\text{C}=\text{O}$. The hydrogenation energy of $\text{H}_2\text{Si}=\text{S}$ was calculated to be 31.4 kcal/mol at the MP3/6-31G^{*} level. At the same level of theory, this value of $\text{H}_2\text{Si}=\text{O}$ was 51.6 kcal/mol, whereas the value of $\text{H}_2\text{C}=\text{O}$ was 29.6 kcal/mol. With these calculated hydrogenation energies, the π bond energies

$E_{\pi}(\text{Si}=\text{S})$, $E_{\pi}(\text{Si}=\text{O})$, and $E_{\pi}(\text{C}=\text{O})$ were estimated, respectively, as follows:

$$E_{\pi}(\text{Si}=\text{S}) = E(\text{Si}-\text{H}) + E(\text{S}-\text{H}) - E(\text{H}-\text{H}) - 31.4$$

$$E_{\pi}(\text{Si}=\text{O}) = E(\text{Si}-\text{H}) + E(\text{O}-\text{H}) - E(\text{H}-\text{H}) - 51.6$$

$$E_{\pi}(\text{C}=\text{O}) = E(\text{C}-\text{H}) + E(\text{O}-\text{H}) - E(\text{H}-\text{H}) - 29.6$$

Bond dissociation energies of 109 kcal/mol for $E(\text{H}-\text{H})$, 90^{17} for $E(\text{Si}-\text{H})$, 92^{18} for $E(\text{S}-\text{H})$, 104^{18} for $E(\text{O}-\text{H})$, and 98^{18} for $E(\text{C}-\text{H})$ were used. Therefore, the π bond energies $E_{\pi}(\text{Si}=\text{S})$, $E_{\pi}(\text{Si}=\text{O})$ and $E_{\pi}(\text{C}=\text{O})$ were calculated to be 42, 33 and 63 kcal/mol, respectively.

This suggested that the π bond in $\text{H}_2\text{Si}=\text{S}$ is significantly stronger than that in $\text{H}_2\text{Si}=\text{O}$, though it is much weaker than that in $\text{H}_2\text{C}=\text{O}$. Dimerization energies¹⁹ of $\text{H}_2\text{Si}=\text{O}$, $\text{H}_2\text{Si}=\text{S}$, and $\text{H}_2\text{C}=\text{O}$ were calculated by using the HF/6-31G* geometries, MP2/6-31G*//6-31G* relative energies, and HF/3-21G vibrational frequencies.

Dimerization of silathione should be about 36 kcal/mol less exothermic than that of silanone because the Si-S single bond is weaker than a Si-O single bond and the Si=S double bond is stronger than a Si=O double bond.

Schmidt et al.²⁰ estimated the π bonding energy by using the element's ability to form strong π bonds in a qualitative

manner. $E_{\pi}(A)$ represented the π bonding energy attributable to atom A.

$$E_{\pi}(A) = 1/2 D_{\pi}(H_m A = A H_m)$$

The values obtained were listed in Table 2.

Table 2. Atomic π Bond Energies (kcal/mol)

atom	E_{π}	atom	E_{π}
C	32.5	Si	12.5
N	30.0	P	17.0
O	37.5	S	23.0

They defined $E_{\pi}(A) = D_{\pi}(A=B_n) - E_{\pi}(B)$. As a gauge of the usefulness of this definition of E_{π} , D_{π} for the mixed $A=B$ bonds can be estimated from $D_{\pi}^{est}(H_m A = B H_n) = E_{\pi}(A) + E_{\pi}(B)$. These D_{π}^{est} values which are listed in Table 3 match well with the recommended values D_{π}^{rec} which are obtained by hydrogenation except for $Si=S$.

Schleyer and Kost²¹ evaluated π bond energies employing the MP4SDTQ/6-31G**/6-31G**+ZPE level of theory; 36.1 kcal/mol for $H_2Si=CH_2$, 55.8 kcal/mol for $H_2Si=O$, 43.6 kcal/mol for $H_2Si=S$, and 93.4 kcal/mol for $H_2C=O$. There are four values estimated for the π bond energy between silicon and sulfur: 42,¹⁹ 50,²⁰ 35.5,²⁰ and 43.6.²¹

Table 3. Comparison of Estimated π Bond Energies

bond	$D\pi^{rec}$	$D\pi^{est}$	error
Si=C	38	45	7.0
Si=N	36	42.5	6.5
Si=O	50	50	0.0
C=S	52	55.5	3.5
Si=S	50	35.5	-14.5

1,2-Hydrogen or silyl migration is of interest for silicon-sulfur or oxygen or carbon double bonds. Table 4 lists energy barrier for isomerization and relative stabilities of isomers.

1,2-Hydrogen or silyl migration from silicon to carbon has been achieved thermally²²⁻²⁴ and photochemically.²⁵ Silylene to silene rearrangement has also been performed thermally^{26,27} and photochemically.²⁵ Matrix isolation

studies of Drahnak et al.^{28a} and Arrington et al.,^{28b} on photogenerated²⁵ methylsilene 51 and dimethylsilylene 52 were interpreted as evidence for rapid thermal conversion of 51 to 52 at 100K. The apparent observation of conversion at 100K means that its barrier should be less than 5 kcal/mol.

Calculations of Yoshioka and Schaefer,^{29a} and Goddard et al.,^{29b} however, predict a sizable barrier of ~41 kcal/mol for the proposed isomerization in conflict with a low-temperature isomerization of 51 to 52.

An ion cyclon resonance study³⁰ provided evidence that 51 is 28 kcal/mol more stable than 52. In disagreement with the experimental work,³⁰ calculation,³¹ employing CI+Davidson method at the 6-31G*HF optimized geometries, indicated that the reaction is almost thermoneutral (or slightly exothermic): Dimethylsilylene 52 is more stable than methylsilaethylene 51 by 2.0 kcal/mol. Silylene 54 is more stable than silaethylene 53 by 3.4 kcal/mol. The energy barrier for conversion of 51 to 52 is 42.4 kcal/mol, whereas that for 53 to 54 is 39.3 kcal/mol.

Calculations³² using a new parametric SCF MO model (AM1) indicated that 53 is 23.5 kcal/mol more stable than 54. By the deprotonation energetics of the methylsilyl cation $\text{CH}_3\text{SiD}_2^+$,³³ it was found that silaethylene 53 is more stable than methylsilylene 54 by ~11 kcal/mol. However, Walsh³⁴ worked on decomposition reactions of various methylated

disilanes and provided evidence to support a value of $\Delta H_f^\circ(\ddot{\text{Si}}\text{HMe})=43.9$. Combined with Walsh's earlier estimate³⁵ for the heat of formation of 53, ΔH_f° was 39 kcal/mol, an energy difference between 53 and 54 is about 5 kcal/mol.

Grev et al.³⁶ determined the energy difference between 53 and 54 with ab initio quantum chemical techniques. The value was nearer 4 kcal/mol in contrast to the results of Shin, Irikura, Beauchamp, and Goddard,³³ which suggested 53 was 11 kcal/mol more stable than 54.

The barrier for the 1,2-H shift in 55 to 56 is 60.3 kcal/mol, while that of H_2CO is 86.5 kcal/mol³⁷ by the calculation employing CI(S+D+QC)/6-31G**//3-21G values. Silanone 55 is 2.2 kcal/mol less stable than silylene 56, while $\text{H}_2\text{C}=\text{O}$ is 54.2 kcal/mol more stable than $\text{H}\ddot{\text{C}}\text{OH}$.³⁷

Tachibana et al.³⁸ obtained the activation energy of the isomerization reaction from trans-hydroxysilylene to silanone as 68.06 kcal/mol, which is qualitatively in agreement with the previous theoretical estimate of 63.9 kcal/mol.³⁹ Dewar and Jie³² calculated the energy difference between 55 and 56 using AM1 calculation. Silanone 55 was 2.6 kcal/mol less stable than silylene 56.³² The barrier for the 1,2-H shift in 55 to 56 was calculated by Kudo and Nagase to be 57.5

kcal/mol.¹⁶ Silanone 55 was 2.4 kcal/mol less stable than silylene 56.¹⁶

The isomerization of silanimine 57 to aminosilylene 58 by 1,2-hydrogen shift was calculated to be 60 kcal/mol.⁴⁰ The planar silylene 58 was more stable than the planar 57 by 18 kcal/mol.

The barrier for the 1,2-H shift in 59 to 60 is 54.8 kcal/mol.¹⁶ Silathione 59 was calculated to be 8.9 kcal/mol more stable than silylene 60.

Table 4. Theoretical Predictions of the Energy Barrier (E_a) for Isomerization and the Relative Stabilities of Isomers ($\Delta E(A-B)$)

A	B	E_a (kcal/mol)	$\Delta E(A-B)$ (kcal/mol)	ref.
$H_2C=O \longrightarrow HC^{\ddot{}}-OH$		86.5	+54.2	37
$CH_3SiH=CH_2 \longrightarrow CH_3\ddot{Si}-CH_3$		41		29
			+28	30
		42.4	-2.0	31
$H_2Si=CH_2 \longrightarrow H\ddot{Si}-CH_3$		39.3	-3.4	30
			+23.5	31
			+11	37
			+4	34
			+5	33
$H_2Si=O \longrightarrow H\ddot{Si}-OH$		60.3	-2.2	35
		57.5	-2.4	16
			-2.6	31
$H\ddot{Si}-OH \longrightarrow H_2Si=O$		68.06		36
		63.9		37
$H_2Si=NH \longrightarrow H\ddot{Si}-NH_2$		60	+18	38
$H_2Si=S \longrightarrow H\ddot{Si}-SH$		54.8	+8.9	16

RESULTS AND DISCUSSION

Thermally induced retro-ene decomposition of allylsilanes has been found to be a very efficient technique for the generation of silenes.

Block and Revelle⁴¹ found that flash vacuum pyrolysis of diallyldimethylsilane 61 at 600°C resulted in the formation of dimethylsilacyclobutene and they proposed a retro-ene mechanism.

Barton and Burns,⁴² and Kreil et al.⁴³ generated silatoluene 65 by the pyrolysis of allylsilacyclohexadiene 64.

Solouki et al.⁴⁴ generated silabenzene 67 and Barton et

al. generated silafulvene 68⁴⁵ and silacyclopentadiene 69.⁴⁶

67 68 69

Maier et al.⁴⁷ generated silabenzene 67 via a retro-ene type decomposition of silylacetate 70.

7067

Barton and Bain⁴⁸ have generated silanones by the retro-ene elimination of propene from allyloxysilane 71.

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In addition Kinsley⁴⁹ has generated silanimine, $\text{Me}_2\text{Si}=\text{N}-\text{R}$

73 by retro-ene reaction of disilazane 72.

There has been no literature report on the retro-ene generation of π -bonds between silicon and sulfur. In an attempt to generate a silicon sulfur double bond, allylthiodimethylsilane 75 was prepared by the reaction of dimethylchlorosilane with allyl mercaptan 74 in the presence of base.

A trace amount of moisture hydrolyzed compound 81 to allyl mercaptan and siloxane. Most of compounds containing Si-S bond were extremely moisture sensitive. Therefore, glassware had to be flame-dried and special care taken to remove moisture.

A kinetic investigation was undertaken of the decomposition of compound 75. Kinetics were performed in a

pulsed stirred-flow reactor (SFR) designed after the system described by Baldwin et al.⁵⁰ Decomposition of allylthiodimethylsilane 75 was studied kinetically at 333°-425°C by measuring the first-order rate constants for formation of propene. The activation energy (E_a) was 36.3 kcal/mol and log A was 11.3. These kinetic parameters fit into the general context of retro-ene reactions involving a concerted [1,5]-hydrogen shift via a six-center transition state 76.

Martin et al.⁵¹ compared the rate of decomposition of the allyl sulfides, with allylamine⁵² and ether.⁵³⁻⁵⁶ Table 5 lists the literature values of activation parameters and the statistically corrected rate coefficients calculated at 375°C for several alkyl allyl ethers, amines, and sulfides.

Diallylamine,⁵⁴ triallylamine,⁵⁵ and diallyl sulfide decompose 2.5, 3.5 and 57 times faster, respectively, than

diallyl ether.^{50,51} They also decompose 32, 43 and 708 times faster, respectively, than methyl allyl amine. The allyl sulfides showed the highest rate of decomposition. Martin et al.⁵¹ interpreted the greater reactivity in the sulfides as due to the greater polarizability of the sulfur atom. The sulfur atom would allow a better stabilization of the negative charge developed on the α -carbon atom. Therefore, Martin suggested that the [1,5]-hydrogen shift occurs via a nonlinear configuration. The geometry of the transition state for the alkyl allyl sulfides would differ from that of the alkyl allyl ethers in being more like a regular hexagon with bond angles of about 120° .

Table 5. Kinetic Parameters for Decompositions of Allyl Compounds

	log A	E _a (kcal/mol)	kx10 ⁴ (sec ⁻¹) ^a	ref.
Amines				
methyl allyl	11.4	43.4	2.67	53
diallyl	11.0	37.1	84.5	54
triallyl	11.7	38.3	114.8	55
Ethers				
methyl allyl	11.1	41.6	3.87	52
ethyl allyl	11.8	43.6	6.90	53
benzylallyl	11.5	41.2	21.8	52
diallyl	11.9	40.9	33.0	52
Sulfides				
methyl allyl	11.2	38.2	75.0	50
benzyl allyl	10.9	33.7	1891	50
diallyl	11.0	33.0	1891	50

^aRate constants calculated at 375°C.

Similarly, we have found that thermolysis of allylthio-dimethylsilane occurs at a much faster rate than the C, N or O analogs.

Table 6. Kinetic Parameters of Allyl Silicon Compounds

No.	X	log A/s ⁻¹	E _a /kcal	temp/°C	k _{350°C}	ref.
<u>75</u>	S	11.3	36.3	333-427	3.62x10 ⁻²	
<u>71</u>	O	12.6	54.6	600-680	2.73x10 ⁻⁷	46
<u>77</u>	CH ₂ (radical)	15.5	68.4	532-593	3.10x10 ⁻⁹	57
	(total)	12.8	56.9	532-593	6.73x10 ⁻⁸	57
	(retroene)				6.42x10 ⁻⁸	57
<u>78</u>	NH	13.2	60.8	646-701	7.23x10 ⁻⁹	47

Allylthiodimethylsilane 75, allyloxydimethylsilane 71, and 4-dimethylsilyl-1-butene 77⁵⁷ decompose 5,000,000, 38, and 9 times faster, respectively, than N-allyldimethylsilazane 78.

The remarkably low energy of activation, 36.3 kcal/mol, is presumably due to a combination of the low C-S bond strength and the relatively strong Si-S π-bond (42 kcal/mol).⁵⁸

Evidence for the formation of dimethylsilathione was obtained by conducting a sealed-tube reaction of

allylthiodimethylsilane 81 with hexamethylcyclotrisiloxane (D_3) at 200°C for 11 hours. This led to the formation of

1,1,3,3,5,5,7,7-octamethyl-2,4,6-trioxa-1,3,5,7-tetrasilaoctane 6 which is presumed to result from insertion of dimethylsilathione into one of the Si-O bonds of D_3 in 77% yield. However, dimethylsilathione was not trapped by butadiene. When compound 75 was pyrolyzed through a

vertical quartz-tube packed with quartz chips at 400°C under

butadiene flow, no trapped product but dimethylsilathione dimer and trimer was observed.

Gas-phase, flow pyrolysis of 75 in a nitrogen flow (20 mL/min., at 450°C) afforded the dimer 2 and the trimer 1 of dimethylsilathione in 51 and 5% yield, respectively.

For comparison studies, allylthiotrimethylsilane 79 was synthesized. Synthesis of 79 was carried out by the reaction of allyl mercaptan with trimethylchlorosilane in the presence of quinoline as base and solvent.

Compound 79 did not decompose up to 480°C, while 75 was completely decomposed before 460°C. Decomposition of 79 happened in such a complicated manner that an attempt to obtain kinetic parameters failed. The stability of 79 at high temperature supports the theory that the rapid rate of decomposition of 75 is not due to homolysis of the C-S bond but due to a concerted retro-ene reaction.

The reaction of silylenes and carbon-carbon double bonds to generate silacyclopropanes has been investigated by Ishikawa and Kumada,⁵⁹ Childs and Weber,⁶⁰ Skell and Gokdstein,⁶¹ Lambert and Seyferth,⁶² Seyferth et al.,⁶³ and

Conlin and Gaspar.⁶⁴

It is well established that the silylene attacks the π bond of a carbonyl to produce the intermediate oxasilacyclopropane 83. The reaction of silylene with ketones has been investigated by Ando et al.^{65a,b} When 1,2-dimethoxy-1,1,2,2-tetramethyldisilane 80 was pyrolyzed with a five fold excess of acetophenone and a 40-fold excess of benzene in a nitrogen flow system at 800°C, the products included tetramethyldimethoxydisiloxane 81

(10%), styrene (31%), some polysilanes, and unreacted acetophenone.^{65a}

Styrene possibly arises from the 1,2-hydrogen shift of phenylmethylcarbene. A reasonable route can be either the cleavage of a silicon-carbon ring bond of intermediate oxasilacyclopropane 83 followed by the rupture of carbon-oxygen bond, or a [3-2+1] cycloelimination to give a primarily phenylmethylcarbene, which rearranges to styrene. The resulting dimethylsilanone could react with dimethyldimethoxysilane to give tetramethyldimethoxysiloxane 81. Recently, Ando et al.^{65b} observed a silacarbonyl ylide

and a silathiocarbonyl ylide in an isopentane/3-methylpentane matrix at 77K. Photolysis of trisilane in the presence of indanone or indanthione at 77K produced the corresponding ylides. Excitation of ylides with visible light gave silirane and thiasilirane, respectively, which were isolated. An ESR study of silacarbonyl ylide at 77K suggested that the

ground state of ylide is a zwitterionic structure rather than diradical. Upon excitation with visible light, presumably led to the diradical which readily underwent ring closure to yield silirane.

It was of interest to see if silylene would insert into a carbon-sulfur π -bond and produce silathione. Gas-phase flow pyrolysis of pentamethylmethoxydisilane **85** in a nitrogen flow system (20 mL/min., at 650°C) was employed to generate dimethylsilylene in the presence of a tenfold excess of carbon disulfide while the pyrolysate was collected at -78°C. The resulting products were the dimer **2** and trimer **1** of dimethylsilathione in 93 and 3% yield, respectively. Insertion of dimethylsilylene into a carbon sulfur π bond of carbon disulfide probably yields thiocarbonyl ylide which thermally or photochemically undergoes ring closure to give a 3-membered ring **86** and the subsequent elimination of carbon

sulfide produces dimethylsilathione as shown by the presence of dimer 2 and trimer 1.

D₃ was used to intercept Me₂Si=S in this reaction when conducted in a sealed tube at 297°C for 20 hours. The product 6, the result of the insertion of dimethylsilathione into one of the Si-O bonds of D₃, was obtained in 29% yield.

The eliminated carbon sulfide from 86 possibly forms a polymer and decomposes at high temperature. A brown-black residue which adhered to quartz debris was observed.

Yarbrough et al.⁶⁶ reported that CS polymerized to produce a black, amorphous polymer which was not soluble when extracted with organic solvents of varying polarity. Klabunde et al.⁶⁷ has reported that a brown-black CS polymer which adhered

tenaciously to metal and glass was very inert chemically and would slowly decompose at 150°C in an air or nitrogen atmosphere (rapid decomposition at 400°C).

A similar type of 3-membered (87, 88) ring has been known in the reaction of transition metals with carbon disulfide.

The cobalt complex was observed with $C_5H_5Co(PMe_3)CO$ 87 and CS_2 .⁶⁸ The rhodium complex was accessible from $C_5H_5Rh(PMe_3)-C_2H_4$ 88 and CS_2 by ethylene displacement.⁶⁹

87 (M-Co)

88 (M-Rh)

The reactive 3-membered ring 89 is probably involved in the reaction of decamethylsilicocene 42 with CS_2 .¹⁰

An initial [2+1]-cycloaddition led to the unstable thiasilirane 89, which immediately dimerized to give the cyclic thioester 90. They reported that there is a

possibility of generating $p\pi-p\pi$ double-bonded systems $R_2Si=S$ from reactive three-membered ring precursors of the type $R_2\overline{Si-X-C=Y}$.

Isomerization of silene 51 to silylene 52 via 1,2-H shift has been studied.^{70,71} Rearrangement of silene 93 to silylene 94 via 1,2-Si shift was reported by Barton et al.⁷²

Flash vacuum pyrolysis (840° , 10^{-4} torr) of 1-methyl-1-(trimethylsilyl)-1-silacyclobutane 92 gave rise to 1,1,3-trimethyl-1,3-disilacyclobutane 95. The mechanism

proposed involves an initial generation of silene 93 and rearrangement of 93, via 1,2 migration of $\text{Me}_3\text{Si}-$, to β -silylsilylene 94 followed by γ -CH insertion by 94 to form 95.

Barton and Hussmann,⁷³ and Linder et al.⁷⁴ observed that a silyl group of silanone migrated from silicon to oxygen (98 $\rightarrow$ 99).

The first example of isomerization of a silaimine to an

aminosilylene was observed by Zhang.⁷⁵ Silaimine 102 was produced via retro-ene elimination of propene from silazane 101 at 480°C. An aminosilylene was generated by 1,2-trimethylsilyl migration and trapped with butadiene to produce an adduct 104.

It was of interest to discover whether the trimethylsilyl-substituted silathione 105 would undergo an analogous rearrangement to silylene 106.

Initial efforts to generate the silathione utilized the retro-ene reaction of 1-allylthio-1-hydrido-1,2,2,2-tetramethyldisilane 111. Synthesis of 111 was difficult because both chloro substituents of 1,1-dichlorotetramethyldisilane were reduced by reducing agent or substituted by allylthio groups.

Conversion of compound 109 to 110 was achieved by electrophilic aromatic substitution⁷⁶ followed by desilylation.

A phenyl group attached to a silicon atom is readily removed by hydrogen chloride in the presence of a catalytic amount of aluminum chloride.⁷⁷

Copyrolysis of 1-allylthio-1-hydrido-1,2,2,2-tetramethyldisilane 111 and 1,3-butadiene at 348°C under N₂-flow afforded 1-methyl-1-(trimethylsilylthio)-1-silacyclopent-3-ene 114 and the silathione dimer, 113.

A total of 89% of 111 was consumed. Products 113 and 114 were obtained in 13 and 18%, respectively. The formation of 114 suggested that methyl(trimethylsilyl)silathione 105 had undergone trimethylsilyl migration from the silicon of the silathione to sulfur to produce the corresponding silylene 106. An alternative mechanism for the formation of 114 would

involve an initial [4+2] Diels-Alder cycloaddition to afford 128, followed by α -elimination to give a silylene, and insertion of silylene into C-S bond. However, Diels-Alder cycloaddition of dimethylsilathione to butadiene was not observed. An attempt was made to see if a silylene would insert into a C-S bond. Copyrolysis of 1,2-dimethoxy-

1,1,2,2-tetramethyldisilane 80 and 2,5-dihydrothiophene (2,5-DHT) was carried out at 485°C in a N₂-flow system. The pyrolysate was analyzed by GCMS. Among many GCMS, one had a molecular weight of 144 which corresponds to the silylene insertion product. However, the compound was inseparable from the product mixture.

Another attempt was made to see whether silylene 106 inserts into C-S bond. Copyrolysis of 111 and 2,5-DHT was performed at 340°C. The product corresponding to silylene insertion into 2,5-DHT was not observed by GCMS. Several products which we were not able to identify were obtained. At present, the mechanism involving the six-membered ring can

not be completely ruled out. Synthesis of six-membered ring and pyrolysis to give α -elimination would bring a good clue about mechanism.

Adduct 114 was independently prepared for structural identification. Hexamethyltrisilatrithiacyclohexane (1) was prepared in 58% yield by passing H_2S into the mixture of dimethyldichlorosilane and pyridine in hexanes.⁷⁸

Me₃SiSLi was prepared by treating the cyclotrisilthiane with MeLi, employing the route by Ruidisch and Schmidt.⁷⁹ The resulting anion was added to 1-chloro-1-methyl-1-sila-cyclopent-3-ene 116 to produce 114 in 25% yield after purification by preparative GC.

Bain et al.⁸⁰ investigated the thermolysis of (1-methoxymethyl)pentamethyldisilane 117 and (1-methoxyethenyl)pentamethyldisilane 120 and found that both prefer α -elimination to β -elimination.

It was of considerable interest to see if silicon-sulfur

compounds prefer α -elimination to β -elimination.

1,1-Bis(trimethylsilylthio)-1,2,2,2-tetramethyldisilane 124 was synthesized by the reaction of 1,1-dichloro-1,2,2,2-tetramethyldisilane with Me_3SiSLi and copolyolyzed it with butadiene. Copolyrolysis of 124 and butadiene at 340°C

afforded hexamethyldisilathiane 125, 1-methyl-1-(trimethylsilylthio)-1-silacyclopent-3-ene 114 and the dimer 113 of $(\text{Me}_3\text{Si})\text{Si}(\text{Me})=\text{S}$ in 72, 15 and 56% yield, respectively with 72% overall conversion.

Copolyrolysis of 124 and butadiene at 570°C produced 125 and 114 in 76% and 65%, respectively, based on the complete

consumption of starting material.

Pyrolysis at 340°C did not distinguish between α -elimination to give initial silylene and rapid isomerization to silathione, or β -elimination to produce silathione and isomerization to the silylene. To distinguish which elimination dominates, two compounds, 126 and 129, were studied. Disilane 126 was synthesized by the addition of a mixture of methane thiol, triethylamine, and THF into chloropentamethyldisilane.

Flash vacuum pyrolysis of 126 at 650°C (6×10^{-4} torr) afforded (methylthio)trimethylsilane 127 (58%) and 1-(methylthio)heptamethyltrisilane (6%) with 55% conversion. A stirred flow reactor (SFR) study of 126, over the temperature range 470.3 to 550.1°C gave $\log A = 14.2$ and activation energy, 53.0 kcal/mol as α -elimination kinetic

parameters for the formation of silylene. According to Davidson et al.,⁸¹ SFR study of methoxypentamethyldisilane 85, depending on the range of temperature, 400 to 460°C gave $\log A = 12.7$ and activation energy, 44.5 kcal/mol as α -elimination kinetic parameter for the formation of silylene. Thus methoxypentamethyldisilane 85 decomposes 29 times faster than 126 at 350°C. Decomposition of 126 by α -elimination required both a higher activation energy and larger A-factor than for methoxypentamethyldisilane. The low $\log A$ for methoxypentamethyldisilane is indicative of α -elimination involving a constrained three-centered transition state. An α -elimination involving a very loose three-centered transition state is indicated by the $\log A$, which is 14.2 for 126 and no observation of products which would come from a radical mechanism.

Compound 129 was synthesized by treating dichlorodimethylsilane with Me_3SiSLi . The Arrhenius parameters for decomposition were determined over a

temperature range of 327.4 to 413.2°C following the formation of hexamethyldisilathiane 125. An activation energy of 33.8

kcal/mol and log A of 10.5 was found. Thus the β -elimination of compound 129 was found to be another convenient route to generate silathione under extremely mild conditions. A low A-factor suggests that the β -elimination involves a four-centered transition state 130.

The combined studies of compound 126 and 129 indicated that β -elimination is much faster than α -elimination.

Therefore, compound 124 presumably produces silathione $(\text{Me}_3\text{Si})\text{Si}(\text{Me})=\text{S}$ by β -elimination and silathione isomerizes to silylene. When 129 was pyrolyzed under nitrogen-flow system, the products 125 (78%), silathione dimer 2 (55%) and silathione trimer 1 (12%) were obtained. An attempt was made

to trap dimethylsilathione with butadiene or 2,3-dimethyl-1,3-butadiene. However, silathione was not trapped by these two butadienes.

It was of interest to see which β -elimination takes place between siloxy group and silythio group. Compound 131 was

synthesized by treating chloropentamethyldisiloxane 130 with Me_3SiSLi . There are two likely pathways by which 131 may

decompose (eq. 7,8). The formation of a Si-O σ bond (128 kcal/mol) and a Si=S π bond (42 kcal/mol) (eq. 7) was favored over the formation of Si-S σ bond (99 kcal/mol) and Si=O π bond (33 kcal/mol) (eq. 8). Pyrolysis of 131 at 540°C yielded hexamethyldisiloxane 134 (58%) and the silathione dimer, tetramethylcyclodisilathiane (69%) with 62% overall conversion. No hexamethyldisilathiane 125 was observed. A SFR study of 131, over the temperature range 540.0 to 590.1°C, gave $\log A = 11.4$ and activation energy 44.1

kcal/mol as the kinetic parameters for the formation of hexamethyldisiloxane. A low log A indicates that the β -elimination involves a four-centered transition state. Bis(trimethylsiloxy)dimethylsilane 135 did not decompose even at 700°C under SFR system. However, (trimethylsiloxy)-

(trimethylsilythio)dimethylsilane 131 started to decompose at 540°C, while bis(trimethylsilythio)dimethylsilane 129 at 327°C. Replacement of a trimethylsilythio group of 129 by a trimethylsiloxy group increased the activation energy about 10 kcal/mol.

CONCLUSION

The elimination of propene via a retro-ene reaction of allylthiodimethylsilane 75 was found to be an excellent route to produce silathione cleanly under mild conditions. The activation energy, 36.3 kcal/mol, ($\log A=11.3$) of the retro-ene reaction was remarkably low, compared with carbon, oxygen or nitrogen analogs. Dimethylsilathione and (trimethylsilyl)methylsilathione 105 were generated by retro-ene reactions. Dimethylsilathione was not trapped by butadiene but was by insertion into D_3 .

Attempted trapping of (trimethylsilyl)methylsilathione by butadiene afforded a very interesting 5-membered ring compound, 1-(trimethylsilythio)-1-methyl-1-silacyclopent-3-ene 114. The formation of the 5-membered ring product is due to isomerization of the silathione by migration of a silyl group from silicon to sulfur to generate a silylene which was trapped by butadiene. This is the first example of a silathione-silylene isomerization.

Another route to generate silathione was explored. Silylene ($Me_2Si:$) reacted with carbon disulfide to ultimately produce a silathione. Dimethylsilylene presumably forms a transient 3-membered ring with CS_2 and the subsequent elimination of carbon sulfide produces dimethylsilathione.

Another method found to produce silathione was the

decomposition by β -elimination of bis(trimethylsilythio)-dimethylsilane 129. The SFR study of 129 revealed that the activation energy, 33.8 kcal/mol, ($\log A=10.5$) was as low as that of the retro-ene reaction of 75.

Pyrolysis of bis(trimethylsilyl)-1,2,2,2-tetramethyl-disilane 124 provided the second example of silathione-silylene isomerization. Silathione was formed via β -elimination of hexamethyldisilathiane 125 and migration of trimethylsilyl group from silicon to sulfur yielded silylene. This silylene was trapped by butadiene to yield a 5-membered ring 114. The possibility of silylene formation via α -elimination was ruled out by a comparison study of β -elimination and α -elimination. The α -elimination of methylthiopentamethyldisilane 126 required a high activation energy, 53.0 kcal/mol, ($\log A=14.2$). However, the β -elimination of bis(trimethylsilythio)dimethylsilane 129 required a low activation energy ($E_a=33.8$ kcal/mol, $\log A=10.5$). The β -elimination of (trimethylsiloxy)(trimethylsilythio)dimethylsilane 131 was found to be another route to generate dimethylsilathione. The SFR study of 131 gave $\log A$, 11.4 and activation energy, 44 kcal/mol.

EXPERIMENTAL

High resolution ^1H NMR (300 MHz) and ^{13}C NMR (75.5 Hz) spectra were recorded on a Nicolet NT-300 spectrometer. All chemical shifts are reported as parts per million (δ -scales), using CDCl_3 as a standard.

Infrared (IR) spectra were recorded on an IBM IR-90 series FT/IR spectrophotometer, which was coupled to a HP5880A capillary GC for GC/IR. All bands were reported in reciprocal centimeters (cm^{-1}).

Exact mass measurements were obtained on a Krotos MS50 operating at 70 eV. Mass spectra was recorded using a Hewlett Packard 5790 GCMS. Gas chromatographic (GC) analyses were performed on a Hewlett Packard 5790 fitted with a 30 meter capillary column. Preparative GC was performed on a GOW-MAC series 550. The column used will be described for the synthesis of each compound.

GC yields were determined using internal standards and appropriate response factors and adjusted for consumed starting material.

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 except in the case of the trapping experiments with butadiene. The products were collected in a

-78°C trap at the end of the quartz tube.

Flash vacuum pyrolyses (FVP) were carried out by slowly distilling compounds through a heated horizontal quartz pyrolysis tube packed with quartz chips, with product collection in a trap cooled with liquid N₂. Pressures were measured by an ion gauge placed behind a liquid N₂ trap.

A pulsed stirred-flow reactor (SFR) modeled after the design of Baldwin et al.⁵⁰ was used for kinetic experiments. Figure 1 contains a block diagram of the instrument. The SFR system used a 60 mL/min flow of helium to sweep the material through the reactor into a Varian 6000 GC which had the option of diverting the separated product, via a jet separator, into a quadrupole mass spectrometer (VG-SX300) for MS analysis. The reactor temperature was controlled to 0.1°C by a Digi-sense temperature controller. The pressure of the sample introduced was measured with a MKS Baraton transducer. The sample was introduced from a vacuum manifold to the reactor with the helium carrier gas. The choice of GC column of GC was dependent upon the nature of the products. The GC (FID) signals were recorded on a chart recorder as well as a Magnum XT/Mark 2 micro-computer for precise estimation of reactants and products.

Figure 1. Pulsed Stirred-Flow Reactor (SFR)

The kinetic equations that are used in this type reactor are well described in the literature.^{82a,b,c,d}

For a unimolecular decomposition $A \rightarrow B$ the mass balance for B can be written as follows.

$$kv[A] - u[B] = 0 \quad (1)$$

k = rate constant for the formation of B

v = volume of the reactor

u = volumetric flow rate

The value $kv[A]$ is representative of the formation of B from A while $u[B]$ is equal to the loss of B from the reactor. Rearranging equation (1) results in equation (2).

$$k = u[B] / v[A] \quad (2)$$

The ratio u/v is referred to as $1/\tau$ or the residence time. Therefore, it is very important to measure the volume of the reactor and precisely control the flow rate. The Arrhenius parameters were obtained by a plot of $\ln k$ vs $1/T$.

$$k = Ae^{-E_a/RT}$$

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

Synthesis of allylthiodimethylsilane 75

Allyl mercaptan and dimethylchlorosilane were purchased from Aldrich and Petrarch System, respectively. Allyl mercaptan was purified by preparative gas chromatography at 40°C. Allyl mercaptan (4.76 g, 0.064 mol) and quinoline (16.53 g, 0.128 mol) of quinoline were placed in a 50 mL three-neck flask equipped with mechanical stirrer, condenser, and addition funnel. Dimethylchlorosilane was added to the mixture dropwise and stirring was continued for 2 hours under nitrogen. After the reaction was complete, the mixture of products was distilled under reduced pressure at room temperature. Further purification was accomplished by preparative GC to afford 2.11 g of allylthiodimethylsilane 75 in 25% isolated yield. Product was characterized as follows: ^1H NMR (CDCl_3) δ 0.33 (d, 6H, $J=3.3$ Hz), 3.14 (d, 2H, $J=6.6$ Hz), 4.56 (septet, 1H, $J=3.3$ Hz), 4.98 (d, 1H, $J=9.9$ Hz), 5.11 (d, 1H, $J=16.8$ Hz), 5.83 (m, 1H, $J=9.9$ Hz, 16.8 Hz, 6.6 Hz); ^{13}C NMR (CDCl_3) δ -1.56, 30.34, 115.76, 136.43; IR 2129 cm^{-1} (Si-H); GCMS 132 (M^+ , 1), 131 (1), 117 (M^+-15 , 14), 91 (78), 90 (100); Exact MS: $\text{C}_5\text{H}_{12}\text{SSi}$ measured 132.04294, calculated 132.04290, error +0.3 ppm.

Trapping of dimethylsilathione by D₃ in a sealed tube

Compound 75 (0.28 g) and a 11.5-fold excess of D₃ were heated in a sealed tube at 200°C for 11 hours. The adduct 6 (1,1,3,3,5,5,7,7-octamethyl-2,4,6-trioxa-1,3,5,7-tetrasilol-8-thiacyclooctane) was obtained in 77% yield. Compound 6 was isolated by preparative gas chromatography on a 9'1/2" x 0.25" 10% SE-30-CW column at 100°C. Compound 6 was identified as follows: ¹H NMR (CDCl₃) δ 0.11 (s, 12H), 0.42 (s, 12H); ¹³C NMR (CDCl₃) δ 0.87, 5.38; GC-FTIR cm⁻¹ 1070, 1020; GCMS 312 (M⁺, 3), 297 (M⁺-15, 100); Exact MS C₈H₂₄O₃SSi₄ measured 312.05244, calculated 312.05233, error +0.4 ppm; M⁺-CH₃ measured 297.02884, calculated 297.02886, error <0.1 ppm.

Determination of Arrhenius parameters for decomposition of allylthiodimethylsilane 75

Approximately 0.08 torr 75 was introduced into the reactor. The data were collected by computer. The rate constants were determined by following the formation of propene. The temperature range studied was 333 to 425°C. The products were separated on a 5' 15% SE-30-CW column.

Table 7. Rate Constants for Decomposition of 75

<u>T°C</u>	<u>k x 10 (sec⁻¹)</u>	<u>T°C</u>	<u>k x 10 (sec⁻¹)</u>
333.4	0.1466	384.5	1.771
333.8	0.1625	385.8	1.792
347.2	0.3753	393.2	2.335
348.2	0.3800	393.6	2.427
355.6	0.5511	403.8	3.602
355.7	0.5013	404.7	3.821
355.7	0.5096	412.2	5.771
365.5	0.7640	413.4	5.643
365.8	0.8316	422.5	8.120
374.5	1.088	424.6	9.678
376.3	1.242		

E_a 36.33 $\pm$ 0.48 kcal/mol; log A 11.32 $\pm$ 0.17; $\Delta H^\ddagger$ 35.04
 $\pm$ 0.49 kcal/mol; $\Delta S^\ddagger$ -10.28 $\pm$ 0.76 eu; at T_{ave} = 378.6
 for reaction order 1.000.

Figure 2. Arrhenius Plot for Decomposition of 75

Pyrolysis of 75

Compound 75 (0.43 g) was pyrolyzed through a vertical quartz tube packed with quartz chips at 450°C under nitrogen flow. Pyrolysate was collected at -78°C. Compound 75 decomposed completely. Yields of dimer 2 and trimer 1 were 51 and 5%, respectively, using nonane as an internal standard. Products were isolated by preparative GC on 2' 15% SE-30-CW column at 100°C and product 2 was identified as follows: ^1H NMR (CDCl_3) δ 0.78 (s); ^{13}C NMR (CDCl_3) δ 10.0 (s); GC-FTIR cm^{-1} 2978, 2908, 1936, 1404, 1258, 833, 787, 679; GCMS 180 (M^+ , 19), 165 ($\text{M}^+ - \text{CH}_3$, 100); Exact MS: $\text{C}_4\text{H}_{12}\text{S}_2\text{Si}_2$ measured 179.99180, calculated 179.99191, error -0.6 ppm. Product 1 was identified as follows: ^1H NMR (CDCl_3) δ 0.655 (s); ^{13}C NMR (CDCl_3) δ 8.066; FTIR cm^{-1} 2959, 2899, 1400, 1252, 824, 785, 675; GCMS 272 ($\text{M}^+ + 2$, 2), 271 ($\text{M}^+ + 1$, 2), 270 (M^+ , 7), 257 (15), 256 (14), 255 (59), 167 (19), 166 (15), 147 (3), 135 (7), 131 (3), 91 (6), 90 (4), 75 (19), 74 (5), 73 (49), 59 (5), 45 (11), 43 (9); Exact MS: $\text{C}_6\text{H}_{18}\text{S}_3\text{Si}_3$ measured 269.98758, calculated 269.98786, error -1.02 ppm.

Synthesis of allylthiotrimethylsilane 79

Allyl mercaptan (2.06 g, 0.028 mol) and quinoline (13.6 g, 0.106 mol) were placed in a three-neck flask equipped with mechanical stirrer, condenser, and addition funnel.

Trimethylchlorosilane (3.72 g, 0.033 mol) was added slowly with stirring and stirring was continued for 2 hours under nitrogen. The rest of the procedures are the same as that for the synthesis of 75. A 15% yield of 79 was obtained.

Compound 79 was identified as follows: ^1H NMR (CDCl_3) δ 0.25 (s, 9H), 3.09 (d, 2H), 4.95 (d, 1H), 5.14 (d, 1H), 5.81 (m, 1H); GC-FTIR cm^{-1} 2957, 2920, 1637, 1433, 1406, 1250, 1229, 989, 916, 851, 752, 739, 692; GCMS 146 (M^+ , 20), 131 ($\text{M}^+ - \text{CH}_3$, 43), 73 (100); Exact MS $\text{C}_6\text{H}_{14}\text{SSi}$ measured 146.05867, calculated 146.05855, error +0.8 ppm.

Attempted determination of Arrhenius parameters for decomposition of 79

Approximately 0.15 torr 79 was introduced into the SFR reactor. The data were collected by computer. The rate constants were determined by following the formation of butene although there were CH_4 , C_2H_6 , and propene as by products. The temperature range studied was 480 to 530°C. The products were separated by a 5' 15% SE-30-CW column. Reliable results were not obtained since decomposition of 79 happened in such a complicated manner.

Copyrolysis of pentamethylmethoxydisilane 85 and carbon disulfide

A mixture of 0.23 g (1.4 mmol) pentamethylmethoxydisilane

85 and 10-fold excess of CS₂ was dropped to a vertical (0.75" x 1'9" quartz column which was packed with quartz chips. Based on the consumption of 85, 93 and 3% yield of dimer and trimer analogue, respectively, were obtained. Percent yields were corrected by using nonane as an internal standard. The dimer of dimethylsilathione was isolated by preparative GC and identified by ¹H NMR, ¹³C NMR, GC-FTIR, GCMS, and Exact MS. Spectroscopic data for the dimer was exactly matched with the data of the dimer from the decomposition of 75 (retro-ene reaction).

Trapping of dimethylsilathione by D₃ in a sealed tube

A mixture of pentamethylmethoxysilane 85 (0.16 g), a 10-fold excess of CS₂, and a 10-fold excess of D₃ was heated in a sealed tube at 297°C for 20 hours. A 29% yield of the insertion product 6 was obtained. Product 6 was isolated by preparative gas chromatography on a 9'1/2" x 0.25" 10% SE-30-CW column at 100°C. Spectroscopic data of 6 was matched with the trapped product from the copyrolysis of 75 and D₃.

Synthesis of 1-hydrido-1-phenyl-1,2,2,2-tetramethyldisilane

109

Phenylmagnesium bromide (3M in diethyl ether) was purchased from Aldrich. 1,1-Dichloro-1,2,2,2-tetramethyl-

disilane 108⁸³ was obtained by the reaction of tris(trimethylsilyl)silane 107,⁸⁴ from the reaction of trichloromethylsilane and chlorotrimethylsilane with lithium, with two equivalents of phosphorus pentachloride.

Seventy-seven mL of 3M phenylmagnesium bromide (0.231 mol) in diethyl ether was added via a syringe at room temperature to 1,1-dichloro-1,2,2,2-tetramethyldisilane (39.1 g, 0.201 mol) in 250 mL diethyl ether in a round bottom flask equipped with a condenser with nitrogen inlet and outlet. After addition was complete, the reaction mixture was refluxed overnight.

The reaction mixture was filtered through a celite-packed filter under nitrogen. To the filtrate was added 105 mL of 1M lithium aluminum hydride (0.105 mol) in diethyl ether.

The mixture was refluxed for 3 days. Solvent was removed by distillation. Distillation of the residue at 58°C (1.5 torr) yielded 16.5 g (41%) of 1-hydrido-1-phenyl-1,2,2,2-tetramethyldisilane 109:

¹H NMR (CDCl₃) δ 0.193 (s, 9H), 0.478 (d, 3H), 4.283 (q, 1H), 7.469 (m, 5H); ¹³C NMR (CDCl₃) δ -7.992, -1.772, 127.890, 128.821, 134.686, 136.045; FTIR cm⁻¹ 621, 677, 704, 798, 856, 879, 1107, 1246, 1312, 1427, 1485, 2095, 2895, 3053, 3069; GCMS 194 (M⁺, 7), 179 (M⁺-15, 6), 135 (41), 121 (14), 105 (22), 73 (100), 53 (13), 45 (33), 43 (49); Exact MS C₁₀H₁₈Si₂ calculated 194.09510, measured 194.09471, error +2.0 ppm.

Synthesis of 1-chloro-1-hydrido-1,2,2,2-tetramethyldisilane

110

Aluminum chloride (0.5 g) was placed in a 500 mL three-neck flask equipped with addition funnel and condenser in a nitrogen glove bag. The flask was taken out of the glove bag and cooled to -23°C under nitrogen. Chloroform (300 mL), freshly distilled from calcium chloride, was added via a syringe to the AlCl_3 .

1-Hydrido-1-phenyl-1,2,2,2-tetramethyl- disilane 109 (18.3 g, 0.098 mol) was slowly added to the above flask. Dry hydrogen chloride gas was passed through the chloroform and the disilane for 3 hours at -23°C . The mixture was allowed to warm to room temperature and then stirred for 21 hours. The aluminum complex was removed by distillation under reduced pressure. A second vacuum distillation removed the solvent and further purification was accomplished by preparative GC (7' 15% SE-30-CW column at 70°C). A 23% yield (3.4 g) of 1-chloro-1-hydrido-1,2,2,2-tetramethyldisilane 110 was obtained: ^1H NMR (CDCl_3) δ 0.206 (s, 9H), 0.568 (d, 3H), 4.791 (q, 1H); ^{13}C NMR (CDCl_3) δ -2.841, -1.364; GC-FTIR cm^{-1} 656, 705, 729, 802, 849, 1258, 1407, 2133, 2904, 2963; GCMS 152 (M^+ , 2), 137 (M^+-15 , 3), 117 (4), 79 (3), 75 (4), 74 (9), 73 (100), 63 (6), 59 (8), 45 (17), 43 (21); Exact MS $\text{C}_4\text{H}_{13}\text{ClSi}_2$ calculated 152.02456, measured 152.02443, error +0.9 ppm.

Synthesis of 111

Allyl mercaptan (1.46 g, 20 mmol) and triethylamine (2.02 g, 20 mmol) was added to a stirred solution of 1-chloro-1-hydrido-1,2,2,2-tetramethyldisilane 110 (3 g, 20 mmol) in 50 mL of tetrahydrofuran at -78°C in a 250 mL three-neck flask with mechanical stirrer, addition funnel, and condenser. The reaction mixture was warmed to room temperature. After the removal of salts by celite filtration, the filtrate was distilled to remove the solvent by vacuum distillation. A 20% yield (0.5 g, 4 mmol) of 111 was obtained by preparative GC (1.5' 15% SE-30-CW column at 80°C). Compound 111 was characterized as follows: ^1H NMR (CDCl_3) δ 0.181 (s, 9H), 0.407 (d, 3H, $J=4.2$ Hz), 3.205 (d, 2H, $J=7.2$ Hz), 4.403 (q, 1H, $J=4.2$ Hz), 5.040 (d, 1H, $J=9.9$ Hz), 5.155 (d, 1H, $J=16.8$ Hz), 5.877 (d of d of t, 1H, $J=16.8, 9.9, 7.2$ Hz); ^{13}C NMR (CDCl_3) δ -2.277, 0.997, 31.937, 115.910, 136.408; GC-FTIR cm^{-1} 710, 795, 845, 914, 988, 1254, 1408, 1639, 1832, 2099, 2905, 2959, 3090; GCMS 175 (M^+-15 , 0.3), 150 (5), 149 (32), 147 (4), 115 (3), 101 (3), 75 (8), 74 (9), 73 (100), 59 (14), 45 (25), 44 (4), 43 (16), 41 (11); Exact MS $\text{C}_7\text{H}_{18}\text{SSi}_2$ calculated 190.06619, measured 190.06678, error -3.1 ppm, $\text{C}_7\text{H}_{18}\text{SSi}_2\text{-CH}_3$ calculated 175.04330, measured 175.04303, error -1.5 ppm.

Copolyrolysis of 111 and butadiene

A flow pyrolysis using 1,3-butadiene as the carrier gas was conducted with 0.4138 g (2.17 mmol) of 111 through a quartz-chip packed tube at 348°C. In addition to vinylcyclohexene and high molecular weight products from butadiene, and unreacted 111 (11%), the products were 114 (18%) and 113 (12%). Products were isolated by preparative GC (1.5' 15% SE-30-CW column at 100°C). Product 114 was characterized as follows: ^1H NMR (CDCl_3) δ 0.361 (s, 3H), 0.491 (s, 2H), 1.498 (d of d, 2H, $J=18.0$, 1.2 Hz), 1.587 (d, 2H, $J=18.0$ Hz), 5.893 (s, 2H); ^{13}C NMR (CDCl_3) δ 2.349, 3.918, 21.220, 130.459; GC-FTIR cm^{-1} 3032, 2966, 2905, 1786, 1609, 1404, 1258, 1204, 1103, 945, 849, 825, 775, 721; GCMS 202 (M^+ , 58), 187 (M^+-15 , 100), 159 (20), 148 (22), 133 (83), 97 (27), 96 (21), 73 (51), 45 (22); Exact MS $\text{C}_8\text{H}_{18}\text{SSi}_2$ calculated 202.06678, measured 202.06690, error +0.6 ppm. Product 113 was characterized as follows: ^1H NMR (CDCl_3) δ 0.215 (s, 18H), 0.866 (s, 6H); ^{13}C NMR (CDCl_3) δ -3.593, 9.380; GC-FTIR cm^{-1} 2959, 2905, 1400, 1250, 858, 845, 799, 702, 621; GCMS 298 (M^++2 , 7), 297 (M^++1 , 8), 296 (M^+ , 24), 281 (M^+-CH_3 , 11), 223 (58), 163 (21), 131 (13), 73 (100); Exact MS $\text{C}_8\text{H}_{24}\text{S}_2\text{Si}_4$ measured 296.03993, calculated 296.03966, error +0.9 ppm.

Synthesis of 116

Dimethyltetrachlorodisilane was synthesized by the route of Watanabe et al.⁸⁵ Copyrolysis of dimethyltetrachlorodisilane and butadiene was carried out at 500°C to yield compound 116.⁸⁶

Synthesis of 114

To 1.08 g (4 mmol) of hexamethylcyclotrisilathiane in 30 mL diethyl ether was added 8.6 mL (12 mmol) of MeLi and refluxed for 2 hours under Ar. The resulting yellow anion solution was added slowly via a cannula to 1-chloro-1-methyl-1-silacyclopent-3-ene 116 and the resulting mixture was refluxed for 2 hours. Lithium chloride salt was removed after precipitation by centrifugation (6000 rpm x 30 min). The solvent was distilled off under reduced pressure. Further purification was carried out by preparative GC on a 1.5' 15% SE-30-CW column at 120°C. A 25% yield (0.2 g) of 114 was obtained. Compound 114 was characterized by ¹H NMR, ¹³C NMR, and GCMS.

Synthesis of 2,5-dihydrothiophene

2,5-Dihydrothiophene was synthesized by the route of Everhardus et al.⁸⁷

A solution of 11.08 mL (0.1 mol) of cis 1,4-dichloro-2-butene in 50 mL of MeOH and a solution of 24 g (0.1 mol) of

$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in 50 mL of MeOH were added simultaneously to a well stirred mixture of 50 mL of MeOH and 50 mL of DMSO over a period of 30 minutes, maintained at room temperature. After 5 minutes of additional stirring, 2 g of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was added to destroy 3,4-epithio-1-butene and stirring continued for 10 minutes. Addition of a small amount of pentane caused the polymers to cluster. The mixture was poured into ice-water and extracted with pentane. The pentane extracts were washed with water and dried over MgSO_4 . The pentane solvent was removed by simple distillation. The residue was distilled under reduced pressure and further purified by preparative GC on 5' 15% SE-30-CW column. A 46% yield (4.0 g, 0.046 mol) of 2,5-dihydrothiophene was obtained.

Copyrolysis of 2,5-dihydrothiophene (2,5-DHT) and 1,2-dimethoxy-1,2,2,2-tetramethyldisilane

A mixture of 2,5-DHT (0.234 g, 2.7 mmol) and 1,2-dimethoxy-1,2,2,2-tetramethyldisilane (0.039 g, 0.22 mmol) was pyrolyzed through a vertical quartz tube packed with quartz chips at 485°C under nitrogen flow (20 mL/min). Pyrolysate was collected at -78°C. Among many GCMS peaks, one had molecular weight of 144 which corresponds to be the silylene insertion product 135: 146 ($\text{M}^+ + 2$, 7), 145 ($\text{M}^+ + 1$, 13), 144 (M^+ , 80), 129 (98), 115 (10), 111 (11), 107 (25), 101 (9), 95 (15), 91 (7), 89 (68), 76 (16), 75 (28), 69 (8),

59 (100), 53 (11), 45 (24), 43 (21), 41 (8). However, the compound was inseparable from the mixture.

Copolyrolysis of 2,5-DHT and 111

A mixture of 2,5-dihydrothiophene (567 mg, 6.6 mmol) and 111 (49 mg, 0.26 mmol) was pyrolyzed through a vertical quartz tube packed with quartz chips at 340°C under flow of nitrogen (20 mL/min). Pyrolysate was collected -78°C. The product corresponding to silylene insertion into 2,5-DHT was not observed by GCMS. Several products which we were not able to identify were obtained.

Synthesis of 124

Methylolithium (63 mL, 90 mmol) was slowly added to 8.0 g (30 mmol) hexamethylcyclotrisilathiane in 50 mL dry diethyl ether. The mixture was refluxed for 2 hours. The resulting anion was added to a solution of 1,1-dichloro-1,2,2,2-tetramethyldisilane (8.01 g, 45 mmol) in 30 mL of ethyl ether via cannula. Lithium chloride salt was removed after precipitation by centrifugation (6000 rpm x 30 min). Diethyl ether was distilled off under reduced pressure. Further purification was accomplished by preparative GC on a 2' 15% SE-30-CW column at 130°C. A 48% yield (5.19 g, 21.6 mmol) of 124 was obtained. Product 124 was characterized as follows: ^1H NMR (CDCl_3) δ 0.199 (s, 9H), 0.409 (s, 18H), 0.727 (s,

3H); ^{13}C NMR δ -2.087, 4.400, 6.508; GC-FTIR cm^{-1} 779, 845, 1254, 1408, 2905, 2963; GCMS 328 ($\text{M}^+ + 2$, 1), 327 ($\text{M}^+ + 1$, 1), 326 (M^+ , 3), 311 ($\text{M}^+ - 15$, 1), 253 (4), 223 (5), 165 (44), 147 (6), 133 (6), 131 (4), 73 (100), 45 (26); Exact MS $\text{C}_{10}\text{H}_{30}\text{S}_2\text{Si}_4$ calculated 326.08616, measured 326.08661, error -1.38 ppm.

Copyrolysis of 124 and 1,3-butadiene

Pyrolysis of 124 (864 mg) was conducted in a vertical quartz-chip packed tube to 340°C by dropwise addition via syringe. The tube was continuously swept with 1,3-butadiene at a rate of 60 mL/min. The pyrolysate was collected at -78°C and an internal standard of undecane was added. Yields were determined by GC and are corrected for 28% recovery of starting material. The products 125 (72%), 114 (15%), and 113 (56%) were isolated by preparative GC and characterized by GCMS, ^1H NMR, ^{13}C NMR, Exact MS, and GC-FTIR. Product 125 was identified as follows: ^1H NMR (CDCl_3) δ 0.269 (s), ^{13}C NMR (CDCl_3) δ 4.044 (s), GCMS 178 (M^+ , 6), 165 (6), 164 (8), 163 (42), 147 (2), 90 (47), 77 (4), 76 (2), 61 (3), 59 (11), 58 (4), 57 (3), 55 (3), 53 (2), 46 (2), 45 (34), 44 (7), 43 (21), 42 (4). Product 113 was characterized as follows: ^1H NMR (CDCl_3) δ 0.215 (s, 18H), 0.866 (s, 6H); ^{13}C NMR (CDCl_3) δ -3.593, 9.380; GC-FTIR cm^{-1} 2959, 2905, 1400, 1250, 858, 845, 799, 702, 621; GCMS 298 ($\text{M}^+ + 2$, 3), 297 ($\text{M}^+ + 1$, 8), 296

(M^+ , 24), 281 ($M^+ - CH_3$, 11), 223 (58), 163 (21), 131 (13), 73 (100); Exact MS $C_8H_{24}S_2Si_4$ measured 296.03993, calculated 296.03966, error +0.9 ppm. Product 114 was identified as follows: 1H NMR ($CDCl_3$) δ 0.361 (s, 3H), 0.491 (s, 2H), 1.498 (d of d, 2H, $J=18.0$, 1.2 Hz), 1.587 (d, 2H, $J=18.0$ Hz), 5.893 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 2.349, 3.918, 21.220, 130.459; GC-FTIR cm^{-1} 3032, 2966, 2905, 1786, 1609, 1404, 1258, 1204, 1103, 945, 849, 825, 775, 721; GCMS 202 (M^+ , 58), 187 ($M^+ - CH_3$, 100), 159 (20), 148 (22), 133 (83), 97 (27), 96 (21), 73 (51), 45 (22); Exact MS $C_8H_{18}SSi_2$ calculated 202.06678, measured 202.06690, error +0.6 ppm.

Compound 124 (1.81 g, 5.6 mmol) was dripped in a vertical quartz-chip packed tube at 570°C with flow of excess butadiene (60 mL/min). The pyrolysate was collected at -78°C and an internal standard of undecane was added. Yields were determined by GC. Compound 124 was completely consumed. The products 125 (76%) and 114 (65%) were obtained.

Synthesis of 126

Methane thiol (17.3 g, 0.36 mol), triethylamine (30.3 g, 0.30 mol), and THF (100 mL) were placed in a 250 mL three-neck flask equipped with mechanical stirrer, condenser (dry ice) and addition funnel under nitrogen at -78°C. Dry ice/isopropanol bath was changed to dry ice/ethylene glycol bath (-15°C) and 1-chloropentamethyldisilane was dropped in

slowly. The reaction mixture was stirred continuously for 4 hours and allowed to warm to room temperature. The salt was removed by celite filtration under nitrogen. THF was distilled out under reduced pressure. Crude 126 was further purified by preparative GC on a 7' 15% SE-30-CW column at 130°C in 21% yield. Compound 126 was characterized by ^1H NMR, GCMS and Exact MS:⁸⁸ ^1H NMR (CDCl_3) δ 0.133 (s, 9H), 0.327 (s, 6H), 1.990 (s, 3H); IR cm^{-1} 694, 756, 795, 833, 868, 957, 1254, 1319, 1404, 2901, 2959; GCMS 178 (M^+ , 2), 163 (43), 105 (11), 131 (3), 73 (100); Exact MS $\text{C}_6\text{H}_{18}\text{SSi}_2$ calculated 178.06662, measured 178.06678, error -0.9 ppm.

Determination of Arrhenius parameters for α -elimination of 126

A mixture of 0.05 torr of 126 and 100 torr of acetylene was introduced into the SFR reactor at the desired temperature. The data were collected by computer. The rate constants were determined over a temperature range of 470.3 to 550.1°C by following the rate of Me_3SiSMe formation. The column used was 10' 20% SE-30-CW column.

Table 8. Rate Constants of α -Elimination of 126

<u>T°C</u>	<u>k x 10 sec⁻¹</u>	<u>T°C</u>	<u>k x 10 sec⁻¹</u>
470.3	0.394	520.1	3.610
473.6	0.695	520.1	3.750
480.6	0.673	530.7	6.030
490.5	1.040	540.3	9.320
500.2	1.580	550.1	12.950
510.3	2.330	550.1	13.210
<u>510.3</u>	<u>2.460</u>		

E_a 52.99 $\pm$ 0.54 kcal/mol; log A 14.18 $\pm$ 0.15; $\Delta H^\ddagger$ 51.43 $\pm$ 0.54 kcal/mol; $\Delta S^\ddagger$ 2.43 $\pm$ 0.69 eu. at T_{ave} = 511.9°C for reaction order 1.000.

Figure 3. Arrhenius Plot for Decomposition of 126

Flash vacuum pyrolysis of 126

Flash vacuum pyrolysis of 126 (1.81 g) was conducted at 650°C (6×10^{-4} torr) by slow distillation of 126 through a horizontal tube packed with quartz chips. The pyrolysate was collected at -196°C. After addition of a measured amount of nonane as an internal standard, the yields were measured by GC. The yields were corrected for 45% recovery of starting material. The products Me_3SiSMe (58%) and $\text{Me}_3\text{Si}-(\text{Me})_2\text{Si}-(\text{Me})_2\text{Si-SMe}$ (6%) were obtained.

Methylthiotrimethylsilane was isolated by preparative GC on a 7' 15% SE-30-CW at 30°C. Methylthiotrimethylsilane was characterized as follows: ^1H NMR (CDCl_3) δ 0.298 (s, 9H), 1.984 (s, 3H); GC-FTIR⁸⁹ cm^{-1} 756, 845, 949, 1256, 1323, 1447, 2125, 2862, 2966; GCMS 122 ($\text{M}^+ + 2$, 3), 121 ($\text{M}^+ + 1$, 3), 120 (M^+ , 30), 105 ($\text{M}^+ - 15$, 100), 73 (27); Exact MS $\text{C}_4\text{H}_{12}\text{SSi}$ measured 120.04294, calculated 120.04290, error +0.3 ppm. Product, 1-methylthioheptamethyltrisilane was isolated by preparative GC (2' 15% SE-30-CW column at 80°C) and

identified as follows: ^1H NMR (CDCl_3) δ 0.074 (s, 9H), 0.114 (s, 6H), 0.318 (s, 6H), 1.953 (s, 3H); ^{13}C NMR (CDCl_3) δ -6.600, -1.518, -0.865, 8.456; FTIR cm^{-1} 2951, 2926, 2893, 1400, 1315, 1246, 959, 864, 835, 806, 729, 690; GCMS 236 (M^+ , 2), 221 ($\text{M}^+ - 15$, 14), 189 (1), 163 (20), 133 (6), 131 (21), 116 (45), 105 (9), 101 (6), 73 (100), 59 (16); Exact MS $\text{C}_8\text{H}_{24}\text{SSi}_3$ measured 236.09120, calculated 236.09066, error

+2.27 ppm.

Synthesis of 129

To hexamethylcyclotrisilathiane (0.029 mol, 7.90 g) in ethyl ether (50 mL) was added methyllithium (0.088 mol, 63 mL) at room temperature under argon. The mixture was refluxed for 2 hours and added to 5.66 g (0.044 mol) dichlorodimethylsilane in 30 mL ethyl ether. The reaction mixture was refluxed for another 2 hours. After removal of salt by precipitation and centrifugation (6000 rpm x 30 min), the solvent was removed by distillation under reduced pressure. Further purification was performed by preparative GC on a 2' 15% SE-30-CW at 100°C. Three grams of 129 was obtained. Compound 129 was characterized as follows: ^1H NMR (CDCl_3) δ 0.393 (s, 18H), 0.646 (s, 6H); ^{13}C NMR (CDCl_3) δ 3.962, 8.822; GC-FTIR cm^{-1} 694, 802, 845, 1258, 1408, 2905, 2966; GCMS 270 ($\text{M}^+ + 2$, 1), 269 ($\text{M}^+ + 1$, 1), 268 (M^+ , 5), 253 ($\text{M}^+ - \text{CH}_3$, 13), 165 (37), 163 (4), 147 (3), 73 (100), 59 (5), 45 (25); Exact MS $\text{C}_7\text{H}_{21}\text{S}_2\text{Si}_3$ measured 268.06269, calculated 268.06273, error -0.18 ppm, $\text{C}_7\text{H}_{21}\text{S}_2\text{Si}_3 - \text{CH}_3$ measured 253.03924, calculated 253.03926, error +0.08 ppm.

An attempt to trap dimethylsilathione from 129 with
1,3-butadiene or 2,3-dimethyl-1,3-butadiene

Compound 129 (0.21 g, 7.8 mmol) was pyrolyzed in a vertical tube furnace with use of a quartz chip packed tube with 1,3-butadiene (60 mL/min) as the carrier gas at 348°C. Pyrolysate was collected at -78°C. Dimethylsilathione insertion product was not detected by GCMS analysis. The dimer and trimer of dimethylsilathione were observed.

The mixture of 0.183g (0.67 mmol) 129 and 1.83 g (22.3 mmol) 2,3-dimethyl-1,3-butadiene was dropped slowly into a vertical tube packed with quartz chips at 340°C. No trapped product was observed by GCMS. However, the dimer and trimer of dimethylsilathione were detected.

Determination of Arrhenius parameters for β -elimination of
129

Approximately 0.2 μ L of 129 was introduced into the SFR reactor at the desired temperature. The data were collected by computer. The rate constants were determined over a temperature range of 327.4 to 413.2°C by following the rate of $\text{Me}_3\text{SiSSiMe}_3$ formation. The column employed was 30 m x 0.541 mm DB-5 capillary tube.

Table 9. Rate Constant of β -Elimination of 129

<u>T°C</u>	<u>k x 10 sec⁻¹</u>	<u>T°C</u>	<u>k x 10 sec⁻¹</u>
327.4	0.179	378.2	1.501
327.4	0.186	378.6	1.570
334.5	0.242	388.6	2.353
335.2	0.253	390.5	2.416
343.1	0.353	394.0	2.930
345.7	0.379	396.1	3.008
356.5	0.563	404.7	4.131
358.8	0.672	406.0	3.863
369.2	0.988	412.4	6.382
370.1	1.053	413.2	7.201

E_a 33.77 $\pm$ 0.53 kcal/mol; log A 10.52 $\pm$ 0.18; $\Delta H^\ddagger$ 32.49
 $\pm$ 0.53 kcal/mol; $\Delta S^\ddagger$ -13.93 $\pm$ 0.83 eu; at T_{ave} = 371.510 for
 reaction order 1.000.

Figure 4. Arrhenius Plot for Decomposition of 129

Pyrolysis of 129

Compound 129 was pyrolyzed in a quartz-chip packed tube under nitrogen flow (20 mL/min) at 310°C. Pyrolysate was collected at -78°C and an internal standard of undecane was added. Yields were determined by GC and corrected for 45% recovery of starting material. The products 125 (78%), silathione dimer 2 (55%), and silathione trimer 1 (12%) were obtained. The products were isolated by preparative GC (1.5' 15% SE-30-CW column). Product 125 was identified as follows: ^1H NMR δ 0.269 (s); ^{13}C NMR δ 4.044; GCMS 178 (M^+ , 6), 165 (6), 164 (8), 163 (42), 147 (2), 90 (47), 77 (4), 76 (2), 75 (17), 74 (11), 73 (100), 71 (2), 61 (3), 59 (11), 58 (4), 57 (3), 55 (3), 53 (2), 46 (2), 45 (34), 44 (7), 43 (21), 42 (4); Exact MS $\text{C}_6\text{H}_{18}\text{SSi}_2$ measured 178.00634, calculated 178.06678, error -2.47 ppm. Product 2 was characterized as follows; ^1H NMR (CDCl_3) δ 0.78 (s); ^{13}C NMR (CDCl_3) δ 10.0 (s); FTIR cm^{-1} 2978, 2908, 1936, 1404, 1258, 833, 787, 679; GCMS 182 ($\text{M}^+ + 2$, 3), 181 ($\text{M}^+ + 1$, 3), 180 (M^+ , 19), 168 (2), 167 (17), 166 (16), 165 (100), 135 (6), 91 (3), 90 (5), 89 (3), 77 (3), 76 (3), 75 (24), 74 (5), 73 (36), 61 (5), 60 (2), 59 (4), 58 (2), 45 (9), 44 (2), 43 (14), 42 (3); Exact MS $\text{C}_4\text{H}_{12}\text{S}_2\text{Si}_2$ measured 179.99180, calculated 179.99191, error -0.6 ppm. Product 1 was identified as follows: ^1H NMR (CDCl_3) δ 0.655 (s); ^{13}C NMR (CDCl_3) δ 8.066; FTIR cm^{-1} 2959, 2899, 1400, 1252, 824, 785, 675; GCMS 272 ($\text{M}^+ + 2$, 2), 271

($M^+ + 1$, 2), 270 (M^+ , 7), 257 (15), 256 (14), 255 (59), 167 (19), 166 (15), 147 (3), 135 (7), 131 (3), 91 (6), 90 (4), 75 (19), 74 (5), 73 (49), 59 (5), 45 (11), 43 (9); Exact MS $C_6H_{18}S_3Si_3$ measured 269.98758, calculated 269.98786, error -1.02 ppm.

Synthesis of 131

Methylmagnesium bromide (24.6 mL, 73.8 mmol) was slowly added to a solution of 1,3-dichlorotetramethyldisiloxane (15 g, 73.8 mmol) in ethyl ether (30 mL). After addition was complete, the reaction mixture was refluxed overnight.

The salt was removed by decantation. To the resulting solution was added Me_3SiSLi (59.0 mmol) which was prepared by treating hexamethylcyclotrisilathiane (5.3 g, 19.6 mmol) with methyllithium (42.0 mL, 59.0 mmol). The reaction mixture was refluxed for 3 hours. After removal of salt by centrifugation (4000 rpm x 30 min), the residue was distilled under reduced pressure at room temperature to remove ethyl ether. Further purification was performed by preparative GC (1.5' 15% SE-30-CW column at 80°C). Product 131 was characterized as follows: 1H NMR ($CDCl_3$) δ 0.343 (s, 6H), 0.321 (s, 9H), 0.085 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 1.933, 3.908, 5.987; GCMS 252 (M^+ , 1), 239 (6), 238 (8), 237 (31), 149 (28), 147 (12), 131 (5), 75 (8), 74 (9), 73 (100), 59 (7), 45 (19), 43 (7); Exact MS $C_8H_{24}OSSi_3$ measured 252.08507,

calculated 252.08558, error -2.01 ppm.

Pyrolysis of 131

Compound 131 (0.211 g, 0.84 mmol) was dripped in a vertical quartz-chip packed tube at 540°C with flow of nitrogen (20 mL/min). The pyrolysate was collected at -78°C and added. Yields were determined by GC. The products hexamethyldisiloxane 134 (58%) and tetramethylcyclo-disilathiane 2 (69%) were obtained with 62% overall conversion. Further purification was performed by preparative GC (1.5' 15% SE-30-CW column at 80°C). Product 134 was identified as follows: ^1H NMR (CDCl_3) δ 0.034 (s); ^{13}C NMR (CDCl_3) δ 1.954; FTIR cm^{-1} 2959, 2901, 1578, 1439, 1412, 1302, 1254, 1182, 1059, 933, 847, 756, 689, 619; GCMS 149 (8), 148 (16), 147 (M^+-15 , 100), 131 (6), 87 (3), 75 (2), 74 (2), 73 (23), 72 (3), 66 (16), 59 (13), 52 (8), 51 (2), 45 (16), 44 (3), 43 (7); Exact MS $\text{C}_6\text{H}_{18}\text{OSi}_2$ measured 162.08928, calculated 162.08962, error -2.1 ppm, $\text{C}_6\text{H}_{18}\text{OSi}_2\text{-CH}_3$ measured 147.06611, calculated 147.06615, error -0.29 ppm. Product 2 was characterized as follows: ^1H NMR (CDCl_3) δ 0.766 (s); ^{13}C NMR (CDCl_3) δ 10.009; FTIR cm^{-1} 2978, 2908, 1936, 1404, 1258, 833, 787, 679; GCMS 182 (M^++2 , 3), 181 (M^++1 , 3), 180 (M^+ , 19), 168 (2), 167 (17), 166 (16), 165 (100), 135 (6), 91 (3), 90 (5), 89 (3), 77 (3), 76 (3), 75 (24), 74 (5), 73 (36), 61 (5), 60 (2), 59 (4), 58 (20), 45 (9), 44 (2), 43 (14), 42

(3); Exact MS $C_4H_{12}S_2Si_2$ measured 179.99180, calculated 179.99191, error -0.6 ppm.

Determination of Arrhenius parameters for decomposition of 131

Compound 131 (0.04 torr) was introduced into the SFR reactor at the desired temperature. The data were collected by computer. The rate constants were determined over a temperature range of 540.0 to 590.1°C by following the rate of hexamethyldisiloxane 134 formation. The column used was 30 m x 0.541 mm DB-5 capillary tube.

Table 10. Rate Constants of β -Elimination of 131

<u>T°C</u>	<u>k sec⁻¹</u>	<u>T°C</u>	<u>k sec⁻¹</u>
540.0	0.3416	569.6	0.7909
549.8	0.4600	579.6	1.149
549.8	0.4627	579.6	1.186
559.8	0.6053	580.2	1.237
559.9	0.5999	590.1	1.622
569.5	0.8043	590.1	1.627

E_a 44.08 $\pm$ 1.08 kcal/mol; log A 11.36 $\pm$ 0.28; $\Delta H^\ddagger$
 42.41 $\pm$ 1.08 kcal/mol; $\Delta S^\ddagger$ -10.60 $\pm$ 1.29 eu; at
 T_{ave} = 568.167°C for reaction order 1.0000.

Figure 5. Arrhenius Plot for Decomposition of 131

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