

sidered unambiguous experimental evidence for such a transfer of spin density onto the ligands.²⁶ The absence of observable ¹⁴N superhyperfine coupling in the NH₃-bound form of the S₂ state EPR spectrum, however, argues against a large change in the covalency of the Mn site due to ligation of NH₃ molecules. In fact, ligand superhyperfine couplings are rarely resolved in Mn complexes having direct coordination of ¹⁴N atoms to Mn ions.^{25,27,28}

Alternatively, it is possible to account for a reduction in the observed hyperfine line spacing by invoking a change in the exchange couplings between the Mn ions in the Mn site, since the hyperfine coupling from each Mn ion in an exchange coupled Mn tetramer or Mn dimer complex is scaled by the projection of the individual ion's spin angular momentum onto the total spin angular momentum.²⁹ In Mn tetramer and also in Mn dimer complexes²⁸ the largest term of the effective spin Hamiltonian is that of the exchange coupling. A model for the Mn site consisting of a Mn tetramer complex containing two antiferromagnetically exchange-coupled Mn dimers that are coupled together through ferromagnetic exchange³⁰ is compatible with the known stoichiometry of Mn in the O₂-evolving complex¹ and with the magnetic properties of the S₂ state as previously described.¹² Altering the size of the exchange coupling between the Mn ions can cause large changes in the ⁵⁵Mn hyperfine coupling constants and in the magnetic properties observed. Work in our laboratory shows that altering the exchange coupling parameters for a 3Mn^{III}-Mn^{IV} tetramer complex can account for both the reduction of the hyperfine line spacing and the near-Curie law temperature dependence of the S₂ state EPR spectrum in NH₄Cl-treated samples.³⁰ Thus, we attribute the change in the observed spacing of the hyperfine lines in the EPR signal from the NH₃-bound form of the S₂ state to a significant change in the exchange interactions between the Mn ions caused by the binding of one or more NH₃ molecules.

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The finding that the Mn site binds ligands in an EPR-detectable manner raises several new questions and possibilities concerning the structure of the Mn site and its coordination properties. Further studies are in progress to determine the number of exchangeable coordination sites on the Mn site and to determine the steric environment of the ligand-binding site(s). The results of this paper indicate that the S₂ state multiline EPR spectrum will provide a spectroscopic probe sensitive to ligand exchange at the Mn site, which should greatly facilitate studies of the coordination chemistry involved in the mechanism of photosynthetic O₂ evolution.

Conclusions

The effects of NH₃ binding to the O₂-evolving complex are consistent with coordination of one or more NH₃ molecules directly to the Mn site detectable in the S₂ state by EPR spectroscopy. The novel S₂ state EPR spectrum produced in the presence of NH₄Cl with illumination at 0 °C shows a near-Curie law temperature dependence which is significantly different from the temperature dependence of S₂ state EPR signals observed in untreated samples, showing that the binding of NH₃ significantly alters the exchange couplings between the Mn ions. Such a change in exchange couplings between Mn ions also accounts for the more than 20% reduction in hyperfine line spacing in the EPR spectrum of the NH₃-bound form of the S₂ state relative to the hyperfine line spacing in the S₂ state EPR spectrum observed in untreated samples. Because of the likelihood that NH₃ binds in competition with H₂O to the substrate binding site of the O₂ evolving complex, causing inhibition of photosynthetic O₂ evolution activity, our results indicate that the EPR-detectable Mn site is the H₂O-binding site. Since previous work strongly implicates this same Mn site in the process of accumulation of oxidation equivalents, it is probable that a single Mn site exists on the electron donor side of PSII, functioning both in the oxidation of bound H₂O molecules and in the storage of oxidation equivalents. The finding that the Mn site binds ligands in a EPR-detectable manner suggests new possibilities for the study of the coordination chemistry of the Mn site.

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Pyrolytic, Kinetic, and Theoretical Studies on the Isomerization of Me₂HSiCH₂· to Me₃Si·

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Abstract: Evidence for the isomerization of ·CH₂SiHMe₂ to Me₃Si· via a 1,2-migration of hydrogen has been obtained through pyrolytic studies of 4-(dimethylsilyl)-1-butene which decomposes through loss of the allyl radical to produce ·CH₂SiHMe₂. Rearrangement to Me₃Si· was established by product analysis and trapping with methyl chloride. Kinetic analysis afforded a barrier of ca. 41 kcal/mol in excellent agreement with a calculated barrier of 42.6 kcal/mol achieved with fourth-order perturbation theory corrections (MP4) and addition of zero-point vibrational corrections.

Although silicon-centered radicals are significantly more stable than are nonresonance stabilized carbon-centered radicals,¹ only

two examples of rearrangement of R₃Si-·R' to R₂Si-CR'·R have been reported, and both of these have silicon as the migrating group, R. The key step in the extensively studied isomerization of hexamethyldisilane² involves a 1,2-silyl migration in **1** to produce

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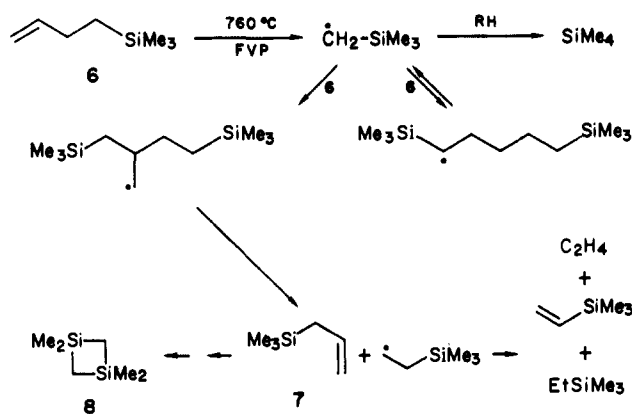
[†]Dow Corning Predoctoral Minority Fellow, 1981-1983.

[‡]The University.

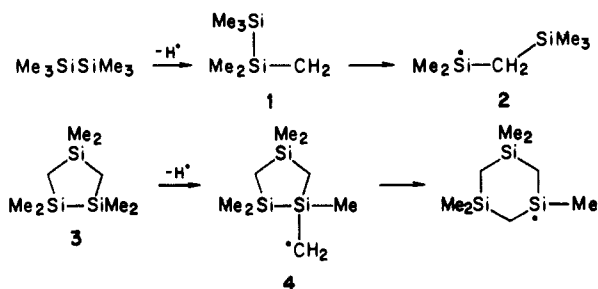
[⊥]North Dakota State University.

(1) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

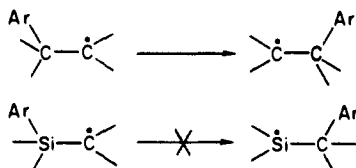
Scheme I



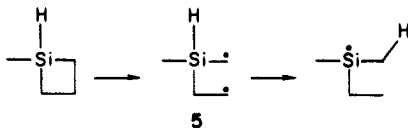
silyl radical **2**, and it has been shown that ring expansion of **3** proceeds through a 1,2-silyl shift from silicon to carbon in radical **4**.³



In view of the numerous documented cases of 1,2-migrations in all-carbon radicals, the absence of analogous isomerizations (except for the above two cases) for α -silyl radicals is surprising. For example, the 1,2-aryl shift from carbon to a carbon-centered radical is well-known,⁴ but the analogous aryl shift from silicon to carbon is not observed.⁵



Recently, the rearrangement of silyl-substituted, carbon-centered radicals has received attention due to the possibility⁶ that this rearrangement could be involved in the thermal decomposition of hydrosilacyclobutanes via the intermediacy of radical **5**. Since the hydrogen migration is an unprecedented reaction, we have



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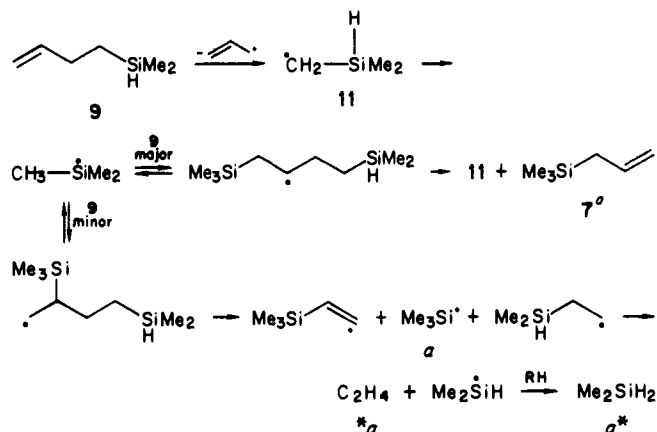
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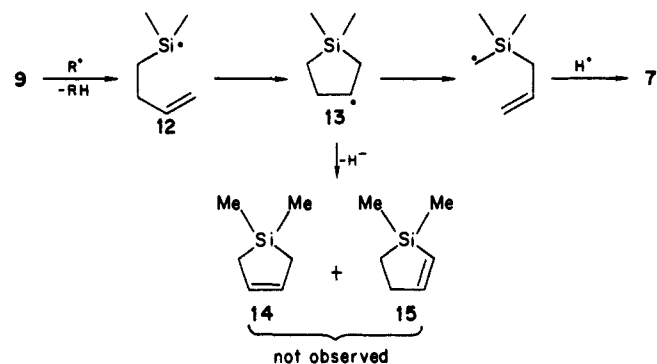
(6) Barton, T. J.; Burns, S. A.; Burns, G. T. *Organometallics* **1982**, *1*, 210. The results which we now report render this suggestion thermodynamically untenable.

Scheme II

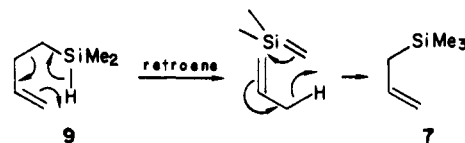
Route A



Route B



Route C



undertaken a collaborative effort to gain evidence about this isomerization through the synthesis and gas-phase pyrolysis of a suitable precursor of the model system, $\text{Me}_2\text{HSi-CH}_2$, kinetic analysis, and theoretical calculations.

Results and Discussion

Flash Vacuum Pyrolytic Generation of α -Silyl Radicals. No methods existed for the gas-phase thermal production of an α -silyl radical so the homolytic cleavage of the carbon-allyl bond of 3-butenylsilanes was investigated. Published bond dissociation energies¹ indicated that the carbon-allyl bond in a 3-butenylsilane should be ca. 15 kcal/mol weaker than the Si-C bond. Thus, 3-butenyltrimethylsilane (**6**) was synthesized and subjected to FVP at 760 °C. Under these conditions, only 10% decomposition of **6** occurred to produce five major products which were identifiable by GCMS comparison with authentic samples. The products were tetramethylsilane, trimethylvinylsilane, ethyltrimethylsilane, allyltrimethylsilane (**7**), and 1,3-disilacyclobutane (**8**) in ratios of ca. 2:1:2:2:1. All of these products are readily explicable by mechanisms (Scheme I) initiated by the expected C-C bond homolysis. The formation of **8** from **7** via the intermediacy of $\text{Me}_2\text{Si=CH}_2$ is a well-established transformation.⁷ However, under these conditions, the major route to this silene is probably dissociation of $\text{Me}_3\text{SiCH}_2^\cdot$ (-Me[•]).

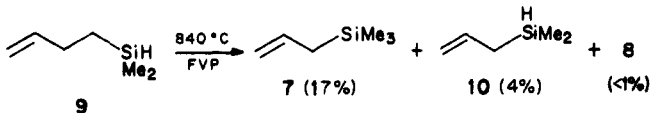
Since the behavior of **6** appeared to establish decomposition of butenylsilanes as the method for generation of α -silyl radicals, 3-butenyldimethylsilane (**9**) was synthesized and pyrolyzed (FVP) at 840 °C. Only a 56% mass recovery was realized, but the

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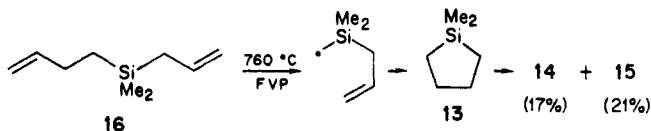
Table I. Pyrolysis of **9** and **6** with Excess MeCl

	Me ₃ SiCl formation		total decomposition	
	silane	log <i>A</i>	<i>E</i> (kcal)	<i>E</i> (kcal)
9		15.5 ± 0.4	68.4 ± 1.7	12.8 ± 0.2
6		14.6 ± 0.4	68.6 ± 1.7	12.1 ± 0.3
				56.9 ± 0.7
				54.7 ± 1.4

pyrolysate contained only two major products (in addition to 25% unreacted **9**) which were isolated by preparative GC and identified as allyltrimethylsilane (**7**, 17%) and allyldimethylsilane (**10**, 4%). A trace of disilacyclobutane **8** (<1%) was detected by GCMS.



Although the formation of **7** is in keeping with C–C bond homolysis in **9** to produce α -silyl radical **11**, rearrangement to Me₃Si[•], and trapping by **9** (Scheme II, route A), and thus would represent the first evidence for the 1,2-hydrogen migration in an α -silyl radical, other mechanistic possibilities exist. Formation of allyltrimethylsilane **7** can also be rationalized (Scheme II, Route B) by a chain process involving cyclization of butenylsilyl radical **12** to silacyclopentyl radical **13** followed by C–C bond homolysis. The presence of this path was not supported by the observation that silacyclopentenes **14** and **15** were not formed in any detectable amounts. These silacycles would have been expected from radical **13**, as when allyl(3-butenyl)dimethylsilane (**16**) was pyrolyzed (FVP) at 760 °C **14** and **15** were produced in 17% and 21% yields, respectively. It is assumed that the thermolysis of **16** proceeds through cyclization to radical **13**, and since not a trace of **7** could be detected in the product analysis by GCMS, we can eliminate Route B of Scheme II.



More difficult to distinguish from Route A is decomposition of **9** via retroene elimination of propene followed by a silene/propene ene reaction to form **7** (Scheme II, Route C). Although retroene elimination from a silylhydride is, to our knowledge, without literature precedent, retroene formation of the silicon-carbon double bond is well-established.⁷ Furthermore, the ene reaction of 1,1-dimethylsilene and propene can be inferred from various literature results.⁸ The relative importance of Routes A and C could be established either by isotopic labeling or by kinetic analysis, and we turned to the latter method as the potentially less ambiguous of the two.

Kinetics of the Thermolyses of Butenylsilanes **6 and **9**.** Kinetic analysis of the thermal decomposition of butenyltrimethylsilane **9** was performed in a previously described⁹ low-pressure pyrolysis (LPP) system with continuous monitoring by a quadrupole mass spectrometer. In these experiments, and others at higher pressure in a stirred flow reactor (SFR), the same products were found as in the FVP experiments, together with several minor products. The number of the latter increased with increasing pressure, confirming the importance of bimolecular reactions in the pyrolysis of alkenylsilanes.⁷ In our earlier study of the decomposition of allyltrimethylsilane,⁷ we found that copyrolysis with methyl chloride was effective in distinguishing between radical and molecular processes, such as retroene elimination, by acting as an efficient trap for Me₃Si[•] via chloride transfer. Indeed, copyrolysis of **9** and MeCl was found to produce Me₃SiCl, and the

Table II. Arrhenius Parameters for Reactions in Scheme III

reaction	log <i>A</i>	<i>E</i> , kcal/mol	source
1	15.5	68.4	this work
2	13.5	varied	this work
3	13.5	<i>E</i> ₂ + 8.9	from thermochemistry
5	9.5	14.3	adapted from <i>b</i>
6	8.1	7.2	<i>c</i>
7	8.5	9.6	<i>d</i>
8	8.0	9.1	adapted from <i>e</i>
9	9.5	17.9	<i>b</i>
10	7.6	4.1	same as reaction 4
11	10.1	47.9	this work (calculated by difference)
12	15.0	81.0	<i>d</i>
13	7.6	4.1	same as reaction 4
14	12.5	49.5	see text
15	8.1	7.2	<i>c</i>
16		fast	see text
17	8.5	9.6	<i>d</i>

^aCadman, P.; Tilsley, G. M.; Trotman-Dickenson, A. F. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 914. Davidson, I. M. T.; Matthews, J. I. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 2277. ^bReference 2e. ^cArthur, N.; Bell, T. N. *Rev. Chem. Intermed.* **1978**, *2*, 37. ^dReference 10. ^eCurrie, J.; Sidebottom, H. W.; Tedder, J. M. *Int. J. Chem. Kinet.* **1974**, *6*, 481.

kinetics of the formation of this product were determined over a temperature range of 805 to 866 K. The Arrhenius parameters for the formation of Me₃SiCl are given in Table I. For comparison, also included is the copyrolysis of MeCl and butenyltrimethylsilane **6**, a system which a priori would have been expected to be a much more likely generator of Me₃Si[•]. It was gratifying to find that at 850 K **9** produces Me₃SiCl more than nine times more rapidly than does **6**, where formation of Me₃SiCl constituted <10% of the total decomposition.

If it is assumed that the initially formed radical Me₂HSiCH₂[•] (**11**) isomerizes to Me₃Si[•] at a rate which is fast relative to the initial homolysis, then formation of Me₃SiCl is a measure of the latter. Indeed, the *A* factor of 15.5 is quite reasonable for the homolysis to form the allyl radical.^{7,10} There is some uncertainty over bond dissociation energies in analogous hydrocarbons¹¹ with current estimates of *D*(C₂H₅–C₂H₅) ranging from 81.7 to 86.2 kcal/mol. Furthermore, an α -silyl group appears to have some stabilizing effect.¹² Accordingly, *E*_{act} for formation of Me₃SiCl from **9** is entirely consistent with C–C homolysis; thus, Route A of Scheme II is the only path to survive kinetic analysis. Since the allylic stabilization energy¹⁰ is ca. 14 kcal/mol, *E*_{act} for **9** relates to a "normal" alkyl–alkyl bond dissociation energy of (68.4 + 14) 82.4 kcal/mol.

For the isomerization reaction, Me₂HSiCH₂[•] → Me₃Si[•], ΔH is simply *D*(Si–H) – *D*(C–H)¹³ = 90.3 – 99.2 = –8.9 kcal/mol. Harding¹⁴ has calculated that the analogous 1,2-H shift in CH₃CH₂[•] has an *E*_{act} of 46 kcal/mol ($\Delta H = 0$). To the extent that Harding's results are an appropriate analogy for the isomerization of Me₂HSiCH₂[•], we would expect the *E*_{act} of our isomerization to be less than 46 kcal/mol by up to ca. 9 kcal. We have tried to test this question experimentally and to obtain some estimate of the magnitude of the isomerization barrier. We hoped to monitor the isomerization by measuring the relative rates of formation of Me₃SiH and Me₃SiCl in pyrolysis with varying amounts of added MeCl, since Me₂HSiCH₂[•] should mainly abstract H while Me₃Si[•] mainly abstracts Cl. However, this approach failed since we find that neither Cl abstraction by the carbon radical nor H abstraction by Me₃Si[•] can be ignored.

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(11) Tsang, W. *J. Am. Chem. Soc.* **1985**, *107*, 2872.

(12) Jackson, R. A.; Ingold, K. U.; Griller, D.; Nazran, A. S. *J. Am. Chem. Soc.* **1985**, *107*, 208. We are aware of the potential of this method to provide quantitative data on the ability of silicon to stabilize both α - and β -carbon-centered radicals and will report in detail our results on these questions in a subsequent paper.

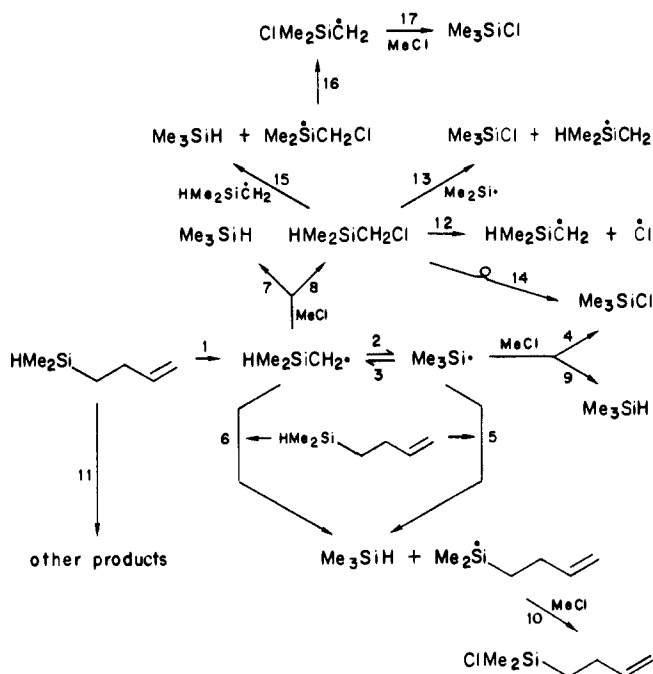
(13) Doncaster, A. M.; Walsh, R. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 2908.

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Scheme III

Radical Reactions in the Pyrolysis of $\text{HMe}_2\text{Si}-\text{CH}_2\text{CH}=\text{CH}_2$ with MeCl

Competitive experiments with varying proportions of added MeCl and Et_2SiH_2 suffered from the same disadvantage, compounded by some decomposition to $\text{Et}_2\text{Si}^\cdot$.

The most useful results were obtained simply by measuring the ratio (R) of Me_3SiCl formed to $\mathbf{9}$ decomposed in pyrolyses of $\mathbf{9}$ with added MeCl. The effect of added MeCl was to inhibit the bimolecular reactions of $\mathbf{9}$ in Scheme II, thus reducing the rate constants for decomposition of $\mathbf{9}$ by about one-third. The results in Table I for formation of Me_3SiCl and for total decomposition of $\mathbf{9}$ in the presence of a 10-fold excess of MeCl gave values of the ratio (R) of Me_3SiCl formed to $\mathbf{9}$ decomposed ranging from $R = 0.354$ at 805 K to $R = 0.556$ at 866 K. The dependence of R on the size of the isomerization barrier was calculated by numerical integration of Scheme III (Table II). In principle, Me_3SiCl is not a unique measure of reaction 4, and hence of the concentration of $\text{Me}_3\text{Si}^\cdot$ radicals, because Me_3SiCl is also known¹⁵ to be formed by radical-induced rearrangement of $\text{HMe}_2\text{SiCH}_2\text{Cl}$, observed as a minor product in our experiments (unimolecular dissociation by reaction 12 was negligibly slow, even at 866 K). To ensure that this rearrangement did not invalidate our conclusions, we included the following in Scheme III: (i) reaction 13; (ii) the reaction sequence 15–17, with reaction 16 assumed to be so fast as to be quantitative; and (iii) the overall reaction 14 with no assumptions as to mechanism, the Arrhenius parameters for which were directly measured by pyrolyzing $\text{HMe}_2\text{SiCH}_2\text{Cl}$ [synthesized by LiAlH_4 reduction of $\text{ClMe}_2\text{SiCH}_2\text{Cl}$ (Cambrian Chemicals)] in our LPP and SFR apparatus. The calculated results at 866 K, where the experimental value of R was greatest, are illustrated in Figure 1. The experimental results at 805 K could be simulated equally well. From the sensitivity of R to values of E_2 greater than 40 kcal/mol, we found that the best overall agreement with experiment was obtained with $E_2 \approx 41$ kcal/mol. Under these conditions, 99.9% of the Me_3SiCl came from reaction 4, even though the alternative routes to Me_3SiCl must be overestimated; reaction 16 may not be fast,¹⁵ while reaction 14 almost certainly subsumes contributions from reactions 13 and 15–17. Because these reactions are so minor, it does not matter that other reactions of comparable rate,

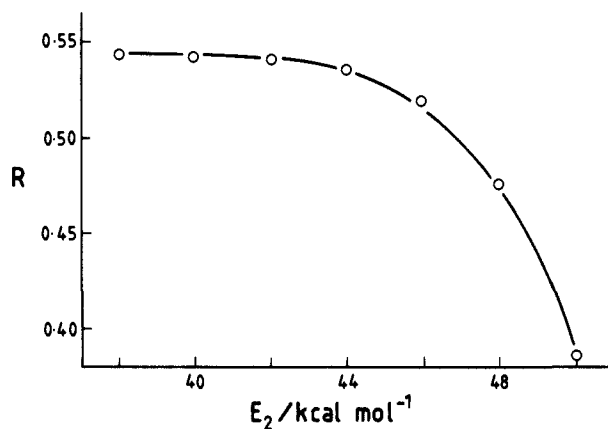
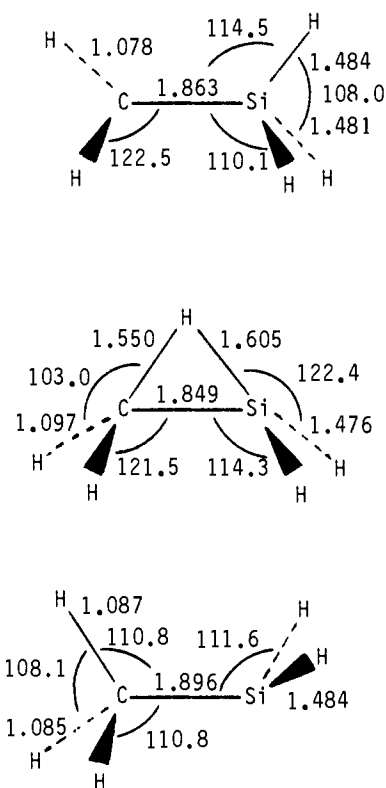
Figure 1. Dependence of R on E_2 at 866 K.

Figure 2. 6.31G** structures. Bond lengths in angstroms, angles in degrees.

such as radical additions, have been omitted from Scheme III. We conclude that E_2 is greater than 40 and less than 44 kcal/mol, probably ca. 41 kcal/mol.

Theoretical Calculations

Preliminary predictions of the structures of the radicals $\text{CH}_3\text{SiH}_2^\cdot$ and $\text{SiH}_3\text{CH}_2^\cdot$ and the transition state connecting them (within C_s symmetry) were carried out at the SCF level with the 3-21G basis set.¹⁶ For each structure, the second derivative matrix has the appropriate number of negative eigenvalues (zero for the two isomers and one for the transition state). At this level of computation, the methyl radical is found to be planar at the carbon end, while the silyl radical is predicted to be pyramidal with an

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internal rotation barrier of just 1 kcal/mol. The effect on this barrier of improving the basis set to 6-31G*¹⁷ and adding correlation corrections in the form of third-order perturbation theory (MP3)¹⁸ is negligible.

The structures of SiH₃CH₂^{*}, staggered CH₃SiH₂, and the transition state, refined with the 6-31G** basis set,¹⁷ are summarized in Figure 2. Once again, these C_s structures have been verified to be minima and transition state, respectively. While the transition state appears to connect SiH₃CH₂^{*} with eclipsed, rather than staggered, CH₃SiH₂^{*}, the internal rotation barrier of the latter is rather small, as noted above. Furthermore, it is quite possible that the structure rotates through C₁ symmetry to the staggered product along the minimum energy path. The transition state structure is closer to that of SiH₃CH₂^{*}, with the SiH bond length only 0.12 Å longer than the originating bond in the parent. Further support for this is provided by the larger atomic spin density on carbon than on silicon at the transition state.

To obtain realistic energetics for the isomerization SiH₃CH₂^{*} → CH₃SiH₂^{*}, single point calculations were carried out with fourth-order perturbation theory corrections (MP4),¹⁹ including triple excitations. At this computational level, the reaction is predicted to be exothermic by 13.8 kcal/mol, with an activation energy of 44.2 kcal/mol. Addition of zero-point vibrational corrections reduces these values to 10.8 and 42.6 kcal/mol. These are in excellent agreement with the experimental estimates of 8.9 and 41 kcal/mol noted above.

All calculations were performed with use of an IBM version of Gaussian82.²⁰

Experimental Section

¹H and ¹³C NMR spectra were obtained on a Nicolet Model 1280 300-MHz spectrometer. All chemical shifts were reported as parts per million (δ scale) with TMS, benzene, chloroform, or acetone as internal standards. IR spectra were recorded on an IBM IR/90 series FTIR spectrometer. GCMS data were collected at 70 eV on a Finnegan Model 4023 quadrupole mass spectrometer, and exact mass measurements were obtained on an AEI MS-902 mass spectrometer. Gas chromatographic separations were performed on a Varian-Aerograph series 1700 instrument.

Combustion analyses were performed on previously unreported compounds by MicAnal, Tucson, AZ.

Unless otherwise specified, the yields reported herein were determined by GC with use of internal standards and predetermined response factors. The peak areas and response factors were obtained on either a Varian-Aerograph series 1700 or a Hewlett-Packard series 5790A gas chromatograph.

Synthesis of 3-Butenyldimethylsilane (9).²¹ To a stirred mixture of excess Mg turnings in 125 mL of dry THF under N₂ was added dropwise a solution containing 14.1 g (0.15 mol) of 4-bromo-1-butene and 20.0 g (0.15 mol) of chlorodimethylsilane dissolved in 100 mL of dry THF. After 8 h, the reaction mixture was hydrolyzed with excess H₂O and transferred to a separatory funnel containing 100 mL of pentane. The pentane layer was extracted with H₂O, separated, dried over Na₂SO₄, and filtered. Distillation (65–75 °C) provided 13.6 g (80%) of 9. The spectral properties of 9 matched those in the literature:²¹ ¹H NMR (DCCl₃) δ 0.13 (d, *J* = 3.69 Hz, 6 H), 0.71–0.78 (m, 2 H), 2.11–2.19 (m, 2 H), 3.89–3.94 (m, 1 H), 4.95 (d of d, *J*_{gem} = 1.61 Hz, *J*_{cis} = 10.06 Hz, 1 H), 5.04 (d of d, *J*_{gem} = 1.61 Hz, *J*_{trans} = 17.06 Hz, 1 H), 5.86–6.06 (m, 1 H); ¹³C NMR (DCCl₃) δ -4.36, 13.46, 28.52, 113.09, 141.2; IR (neat) 2116 cm⁻¹ (SiH); mass spectrum *m/e* (% rel intensity) 113 (M - 1, 1%), 99 (16), 86 (14), 72 (22), 71 (26), 59 (100), 58 (23) calculated

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for SiC₆H₁₃ (M - 1) *m/e* 113.07866, measured *m/e* 113.07872. Anal. Calcd for C₆H₁₃Si: C, 63.06; H, 12.38. Found: C, 63.41; H, 12.54.

Synthesis of 3-Butenytrimethylsilane (6). The synthesis of 3-butenytrimethylsilane was accomplished by the method of Rowley and Jarvie.²² To a stirred mixture of excess Mg turnings in 10 mL of dry THF under N₂ was added a small portion of 1-bromo-3-butene for initiation. The remainder of the 1-bromo-3-butene (2.0 g, 14.8 mmol total) and 1.6 g (14.8 mmol) of trimethylchlorosilane were dissolved in 20 mL of dry THF and added dropwise to the solution. After 10 h, the reaction mixture was hydrolyzed with excess H₂O and then transferred to a separatory funnel containing 50 mL of pentane. The pentane layer was extracted with H₂O, separated, dried over Na₂SO₄, and filtered. After removal of the solvent, 1.0 g (53%) of 3-butenytrimethylsilane (6) was isolated by preparative gas chromatography on a 9 ft, 20% OV-101/Chromosorb W column at 130 °C. The ¹H NMR of 6 exactly matched that reported by Rowley and Jarvie:²² ¹H NMR (DCCl₃) δ 0.00 (s, 9 H), 0.57–0.62 (m, 2 H), 2.01–2.09 (m, 2 H), 4.86–5.02 (m, 2 H), 5.81–5.95 (m, 1 H); ¹³C NMR (DCCl₃) δ -1.60, 15.90, 28.09, 112.65, 141.80; mass spectrum *m/e* (% rel intensity) 113 (M - 15, 28), 85 (20), 74 (8), 74 (100), 59 (56), 58 (8), 55 (5).

FVP of 3-Butenytrimethylsilane (6). A slow distillation of 0.1054 g (0.823 mmol) of 6 was carried out at 25 °C (1 × 10⁻⁴ mmHg) through a quartz tube packed with quartz chips and heated to 760 °C. The pyrolysate was collected in a trap cooled with liquid nitrogen. At 760 °C, only ca. 10% decomposition of 6 was observed by GC. Four compounds could be identified by GCMS to be the major components of the pyrolysate. The compounds were tetramethylsilane (TMS) [*m/e* (% rel intensity) 88 (3), 74 (18), 73 (100), 59 (4), 57 (4), 55 (5)], vinyltrimethylsilane²³ [*m/e* (% rel intensity) 100 (9), 86 (8), 85 (100), 73 (12), 72 (9), 60 (5), 59 (70)], ethyltrimethylsilane [*m/e* (% rel intensity) 102 (2), 87 (11), 81 (8), 73 (57), 67 (100), 59 (35), 55 (6), 54 (52), 53 (10)], and 1,1,3,3-tetramethyl-1,3-disilacyclobutane (8)²⁴ [*m/e* (% rel intensity) 144 (29), 130 (15), 129 (100), 113 (5), 101 (16), 73 (9), 59 (14), 57 (5)].

FVP of (3-Butenyl)dimethylsilane (9). A slow distillation of 0.1407 g (1.23 mmol) of 9 was done at 25 °C (1 × 10⁻⁴ mmHg) through a quartz tube packed with quartz chips and heated to 840 °C. The pyrolysate was collected in a trap cooled with liquid nitrogen and represented a 56% mass recovery. Analysis of the pyrolysate by GC showed two major products along with unreacted 9 (25%). A trace amount (<1%) of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (8) was also identified by GCMS to be present in the pyrolysate. The two major products were isolated by preparative GC on a 15 ft, 20% OV-101/Chromosorb W column at 130 °C. One of the products was identified as allyltrimethylsilane 7 (17%).^{25,26} The NMR of 7 matched that published by Fleming:²⁶ ¹H NMR (DCCl₃) δ 0.03 (s, 9 H), 1.52 (d, *J* = 8.0 Hz, 2 H), 4.60–5.01 (m, 2 H), 5.43–6.05 (m, 1 H); mass spectrum *m/e* (% rel intensity) 114 (10), 99 (20), 77 (18), 73 (100), 71 (9), 59 (25). The other compound was identified as allyldimethylsilane 10 (4%). The NMR, mass spectrum, and GC retention time of 10 exactly matched that of an authentic sample.

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Registry No. 6, 763-13-3; 7, 762-72-1; 9, 18163-02-5; 11, 34377-79-2; SiH₃CH₂^{*}, 51220-22-5; CH₃SiH₂^{*}, 24669-75-8; 4-bromo-1-butene, 5162-44-7; chlorodimethylsilane, 1066-35-9; 1-bromo-3-butene, 5162-44-7; trimethylchlorosilane, 75-77-4.

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