Isomer II is readily converted, thermally, to its more thermodynamically stable isomer, I. For example, a benzene solution of II was refluxed under nitrogen for 5 hr to give I in quantitative yield. At room temperature there appears to be no interconversion of the two isomers, in the solid state, over a period of months.

Acknowledgments. We would like to thank Dr. A. D. English for obtaining the ^{11}B NMR spectra.

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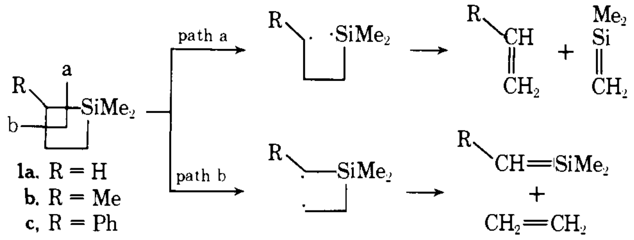
Silicon–Carbon (p_π–p_π) Multiply Bonded Intermediates. The First Thermal Generation and Reactions of 2-Substituted 1,1-Dimethyl-1-silaethenes [Me$_2$Si=CHR]

Sir:

Although silicon-carbon (p_π–p_π) multiply bonded intermediates have been the subject of considerable attention in recent years,[1] thermally generated tri- or tetrasubstituted silaethenes have never been reported.[2] Generation of 2-substituted 1-silaethenes from thermolysis of the appropriately substituted silacyclobutanes (eq 1) and an investigation of their chemistry would answer two important questions.

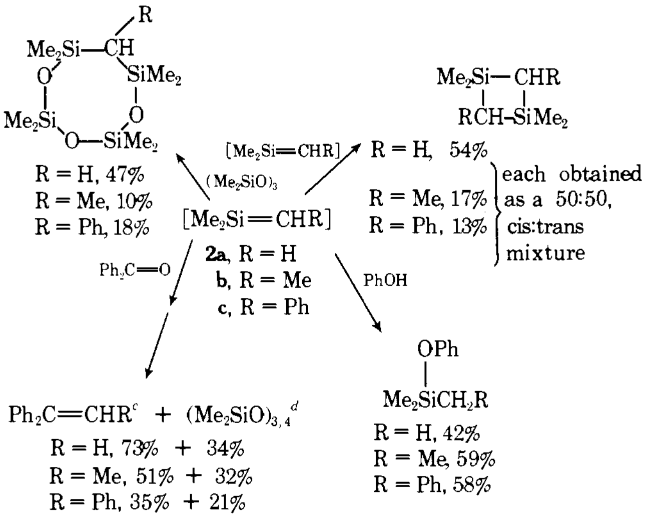


(1)

First, what is the initial step in the thermal decomposition of silacyclobutanes? Although gas phase kinetic data from the thermolysis of **1a** exclude a simultaneous rupture of Si–C and C–C bonds,[1a] the strength of the Si–C bond relative to that of the C–C bond is not known to a sufficient accuracy to predict which bond would break first.

Second, is the general chemical behavior of [R$_2$Si=CHR] intermediates similar to that already recorded[1] for [R$_2$Si=CH$_2$]? Information of this type is needed to answer the following question. Would isolation and study of a silaethene stabilized by substitution at both silicon and carbon provide a generally accurate picture of the properties of silaethenes in general or would such substitution drastically alter their properties?

Scheme I. Isolated Yields of the 1:1 Adducts from the Reaction of [Me$_2$Si=CHR][a] with Organic Substrates[b]



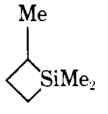
[a] Generated by thermolysis of the corresponding 2-substituted silacyclobutane. [b] [Me$_2$Si=CHR] generated in the presence of at least a two-fold molar excess of substrate. [c] Via a pseudo-Wittig reaction, see ref 1d. [d] From tri- and tetramerization of the [Me$_2$Si=O] produced in the pseudo-Wittig reaction, see ref 1d.

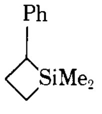
We wish to report the first thermal generation and also the reactions of two carbon-substituted silaethenes, 1,1,2-trimethyl-1-silaethene [Me$_2$Si=CHMe] (**2b**) and 1,1-dimethyl-2-phenyl-1-silaethene [Me$_2$Si=CHPh] (**2c**). Intermediates **2b** and **2c** were generated by gas phase thermolysis at 530–611° of the corresponding 2-substituted silacyclobutanes **1b** and **1c**[3] using a nitrogen flow system in a manner completely analogous to that reported for 1,1-dimethylsilacyclobutane (**1a**).[1d] Using otherwise identical reaction conditions it was observed that while **1a** and **1b** required approximately the same thermolysis temperature of 611° for complete decomposition, **1c** decomposed completely at 530°. The isolated products indicated that the predominant decomposition products of **1b** and **1c** were intermediates **2b** and **2c**, respectively, (minor amounts of **2a** were produced in all of these reactions and are discussed below). These observations provide evidence in support of C$_2$–C$_3$ bond scission as the initial step of thermal silacyclobutane decomposition (path b, eq 1). Although an initial Si–C$_4$ bond scission could account for the observed products, the reduction in E_a for **1c**, relative to **1a**, by ca. 6–8 kcal/mol by a substituent one atom removed from the bond undergoing scission appears unlikely.

The greatly diminished effect of a 2-methyl relative to a 2-phenyl substituent on the silacyclobutane activation barrier is in accord with an expected greater stabilization of the diradical intermediate by a phenyl group.

Scheme I summarizes the reactions of intermediates **2b** and **2c** with a variety of substrates together with the analogous reactions previously reported for intermediate **2a**.[1d,1h] Also included in Scheme I are the previously unknown reactions of silaethenes **2a–c** with (Me$_2$SiO)$_3$ in which the six-membered cyclotrisiloxane ring is expanded by one Si–C unit. This insertion reaction, similar to that of silanones [R$_2$Si=O] with (Me$_2$SiO)$_3$,[6] appears to be general for silaethenes and should be of considerable mechanistic interest and synthetic utility.

Table I. Yields of [$Me_2Si{=}CHR$] adducts vs. [$Me_2Si{=}CH_2$] adducts


1b


1c

		% yield[a] of 1 : 1 adduct			
Silacyclobutane	Temp, °C	From [$Me_2Si{=}CHR$]	From [$Me_2Si{=}CH_2$]	Adduct ratio, subst/unsubst	Trapping reagent[b]
1b	611	17 (20)[c]	~3[c]	~7	None
	611	51	13	~4	$Ph_2C{=}O$
	611	59	5	~12	PhOH
	611	46	4	~12	MeOH
	611	10 (25)[d]	6	1.6 (4)[d]	$(Me_2SiO)_3$
1c	530	13	Trace[e]	>30	None
	530	35	<2[e]	>17	$Ph_2C{=}O$
	611	35	6	6	$Ph_2C{=}O$
	530	58	Trace[e]	>30	PhOH
	530	18	<1[e]	>18	$(Me_2SiO)_3$

[a] Unless otherwise noted yields are based on the amounts of material actually isolated by preparative GLPC. [b] Molar excess of trapping reagent used was 2.4–3.2-fold for the benzophenone reactions and 4.8–11.1-fold for all other reactions. [c] Calculated from 6% isolated yield of $Me_2\overline{SiCH_2Si(Me_2)C}HMe$. [d] Includes a 15% isolated yield of $(Me_2SiCHMe)_2$. [e] Estimated from GLPC chromatogram, material not isolated.

Not included in Scheme I is the fact that thermolysis of **1b** or **1c** produces 1,1-dimethyl-1-silaethene, [$Me_2Si{=}CH_2$], as a minor product. The isolated absolute yields of 1,1,2-trisubstituted and 1,1-disubstituted silaethene adducts produced in the thermolyses of **1b** and **1c** are summarized in Table I.

All thermolyses of **1b** in the presence of reactive substrates (i.e., alcohols and ketones) gave similar yields of [$Me_2Si{=}CHMe$] adducts (46–59%) and also of [$Me_2Si{=}CH_2$] adducts (4–13%). These data indicate that the thermal decomposition of **1b**, like that of **1a**,[1a] is indeed unimolecular and is in no way influenced by the substrate used. Lower yields of [$Me_2Si{=}CHMe$] and [$Me_2Si{=}CHPh$] adducts, including dimers, together with a number of minor products are obtained either in the absence of a trapping reagent or with a less reactive trapping agent such as $(Me_2SiO)_3$. These results indicate that **1b** and **1c**, unless quickly trapped, will rearrange, presumably via an intramolecular pathway. This behavior is similar to that of [$Me_2Si{=}SiMe_2$] which, in the absence of a reactive trapping agent, rearranges to a number of isomeric products.[7]

The data from the thermolyses of **1c** at 530° indicate that under these conditions initial C_2–C_3 bond scission predominates by a factor of at least 20. Thermolysis of **1c** at 611° produces increased quantities of [$Me_2Si{=}CH_2$] which must arise via an initial Si–C_2 or C_3–C_4 bond breakage (this argument also applies to the [$Me_2Si{=}CH_2$] produced as a minor product in the thermolysis of **1b**). Work is currently in progress to determine whether an initial Si–C_2 as opposed to a C_3–C_4 bond rupture is responsible for the [$Me_2Si{=}CH_2$] produced in the thermolysis of **1b** or **1c**.

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(2) Trisubstituted silaethenes have never been reported. In the sole reference[1g] concerning a tetrasubstituted silaethene, [$Me_2Si{=}C(Me)CO_2Et$] was generated photochemically, and its reactions with alcohols were reported. Dimerization or reactions with other substrates were not mentioned.

(3) 1,1,2-Trimethylsilacyclobutane was prepared using a published procedure.[4] 1,1-Dimethyl-2-phenylsilacyclobutane (**1c**) was prepared from dimethyl(3-phenylpropyl)silane following the procedure reported[5] for the preparation of 1,1,2-triphenylsilacyclobutane. All new compounds reported were fully characterized by elemental analysis or an exact mass determination and their ir, NMR, and mass spectra. This information will be reported in detail in the full paper.

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Natural Abundance Nitrogen-15 Nuclear Magnetic Resonance—Liquid Nitrogen[1]

Sir:

Following the estimation by Ramsey[2] of the absolute value for the paramagnetic contribution (σ_p) to the absolute shielding of $^{15}N_2$ relative to the bare nucleus ^{15}N, considerable interest has been expressed[3] in establishing an absolute shielding scale for ^{14}N (and ^{15}N) nuclear magnetic resonance. This requires ^{15}N chemical shifts referenced to the $^{15}N_2$ resonance via some secondary standard, usually $^{15}NH_4{}^+$ or $^{15}NO_3{}^-$ in aqueous solution. To date, two measurements[4,5] of the resonance position of $^{14}N_2$ have been published as 14 and 70 ppm upfield from $^{14}NO_3{}^-$, but doubts have been expressed[6] about the accuracy of these values. One source of uncertainty in the reported chemical shifts arises from the line widths of the ^{14}N resonances. From the relaxation time data for liquid $^{14}N_2$ at 77°K of Armstrong and Speight,[7] we estimate the width at half height of the ^{14}N resonance to be ca. 30 Hz (9.5 and 7 ppm at 10 and 13 kG, respectively[4,5]).

We have measured the ^{15}N NMR spectrum of liquid nitrogen at its boiling point (77°K). Because the isotopes were at the natural abundance level (0.37% for ^{15}N), the species detected was $^{14}N{\equiv}^{15}N$. The spectrum was obtained by Fourier transformation of the sample response to a single (ca. 90°) pulse at 18.25 MHz, using the Bruker WH 180 instrument in an unlocked mode. Liquid nitrogen was contained in an unsealed nonspinning sample tube (20-mm o.d.) concentric with a second tube (25-mm o.d.). Optimum spectra were obtained within 1–2 min of the introduction of the sample into the field so that the spin–lattice relaxation time of ^{15}N in our samples was probably less than 1 min. The signal was referenced[8] to a 5 *M* solution of $^{15}NH_4{}^+{}^{15}NO_3{}^-$ in 2 *M* nitric acid at ca. 300°K, using a substitution method. The chemical shift was 65.6 ppm upfield from the $^{15}NO_3{}^-$ resonance or 288.8 ppm downfield from the $^{15}NH_4{}^+$ resonance. Additional experiments using an HFX-90 instrument (9.12 MHz; 13-mm tube inside a 15-mm tube) gave a value for the chemical shift 67.6 ± 1.5 ppm upfield from $^{15}NO_3{}^-$. We are unable to estimate any error due to the differing temperatures of the sample and