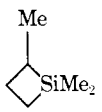
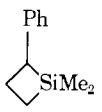
Table I. Yields of [$Me_2Si$=CHR] adducts vs. [$Me_2Si$=$CH_2$] adducts



1b



1c

| Silacyclobutane | Temp, °C | % yield[a] of 1:1 adduct 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 $Me_2SiCH_2Si(Me_2)CHMe$. [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, [$Me_2$-Si=$CH_2$], 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 [$Me_2$Si=CHMe] adducts (46–59%) and also of [$Me_2$-Si=$CH_2$] 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 [$Me_2$Si=CHMe] and [$Me_2$Si=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 [$Me_2$Si-=$SiMe_2$] 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 [$Me_2$Si=$CH_2$] which must arise via an initial Si–$C_2$ or $C_3$–$C_4$ bond breakage (this argument also applies to the [$Me_2$Si=$CH_2$] 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 [$Me_2$Si=$CH_2$] produced in the thermolysis of **1b** or **1c.**

**Acknowledgments.** We thank the National Science Foundation for generous support of this research and Mr. Kei Miyano for mass spectral studies.

## References and Notes

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(2) Trisubstituted silaethenes have never been reported. In the sole reference[1g] concerning a tetrasubstituted silaethene, [$Me_2$Si=C(Me)$CO_2$Et] 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 ($\sigma_p$) 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

reference measurements. In addition, our value for the chemical shift of $N_2$ could be influenced by liquid oxygen contamination which is claimed[5] to shift the $^{14}N_2$ resonance to lower field. The $^{15}N$ resonance is sharp (line width <0.5 ppm) and, because of rapid quadrupolar relaxation of the $^{14}N$ nucleus, it displays no evidence of $^{15}N$–$^{14}N$ scalar coupling.

Our value for the chemical shift in liquid nitrogen is consistent with the value found by Kent and Wagner[5] and casts further doubt on the earlier measurement by Holder and Klein.[4] Both the primary[9] and secondary isotope effects are likely to be small.

## References and Notes


(1) Supported by the Public Health Service, Research Grant No. GM-11072, from the Division of General Medical Sciences and by the National Science Foundation.
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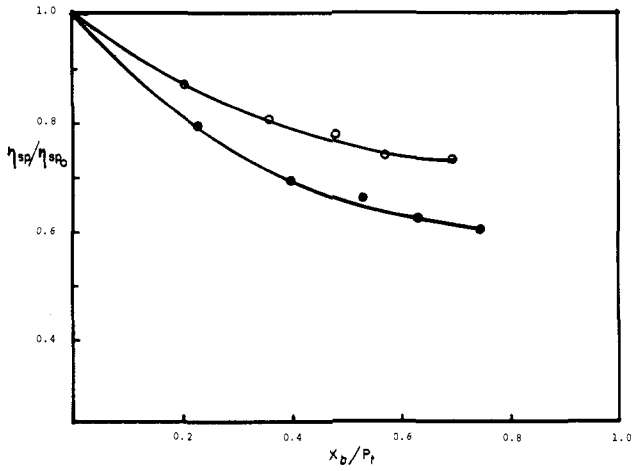


**Figure 1.** The effect of bound L-lys-L-pheA (●) and L-lys-D-pheA (○) on the relative specific viscosity of DNA ($X_b$ represents the concentration of bound peptide and $P_t$ the total DNA concentration in $P/1$). Viscosity measurements were carried out at near infinite dilution of salmon sperm DNA (0.26 m$M$ in $P/1$) in 10 m$M$ 2-($N$-morpholino)ethane sulfonate (Mes) buffer pH 6.2 (5 m$M$ in $Na^+$) using the low shear Zimm viscometer at 37.5°.

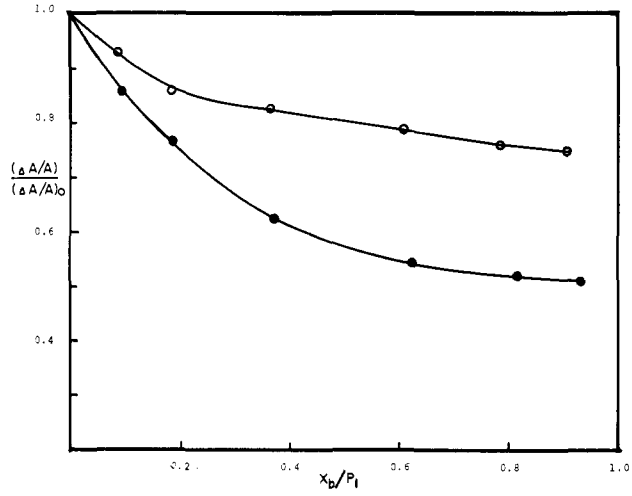


**Figure 2.** The effect of bound L-lys-L-pheA (●) and L-lys-D-pheA (○) on the relative reduced dichroism of DNA ($X_b$ represents the concentration of bound peptide and $P_t$ the total DNA concentration in $P/1$). Flow dichroism measurements were carried out at 25 ± 1° and at 260 nm using a Cary 15 spectrometer with a Glan-Taylor calcite polarizing prism. DNA (3 m$M$ $P/1$) solution was flowed through a quartz capillary (0.415 mm radius) by means of a Sage syringe pump. The shear rate in all experiments was maintained constant at 2600 $sec^{-1}$. At the highest concentration used in these studies, the peptide contribution to the absorbance at 260 nm is found to be less than 1%. It should be noted that identical results are also obtained at lower DNA concentrations (0.5 mM $P/1$) which indicate that the effects are caused by a molecular conformational change rather than aggregation.

## Stereospecific Interaction of Dipeptide Amides with DNA. Evidence for Partial Intercalation and Bending of the Helix

*Sir:*

Recent studies from these laboratories have shown that small molecules may exert a pronounced effect on the tertiary structure of DNA.[1] This communication reports the studies on the interaction of the diastereomeric dipeptide amides, L-Lys-L-PheA (**1**) and L-Lys-D-PheA (**2**) with DNA. Figures 1 and 2 show the effect of bound peptide on the relative specific viscosity and reduced dichroism of DNA solution, respectively. Figure 3 shows the $^1H$ NMR signal of the phenyl protons of **1** and **2** in the presence and absence of DNA. Table I summarizes the $^1H$ NMR data obtained with these systems, i.e., the chemical shift, $\delta$, and the spin–lattice relaxation time, $T_1$. (Experimental details are given in the legends of the table and figures.)

A number of interesting observations may be made. (1) The dipeptide amide, L-Lys-L-PheA (**1**), exhibits a larger decrease in the relative specific viscosity ($\eta_{sp}/\eta_{sp0}$, where $\eta_{sp}$ and $\eta_{sp0}$ are the specific viscosity in the presence and absence of peptide, respectively) of the DNA solution than the corresponding diastereomer, L-lys-D-pheA, **2** (Figure 1). (2) The value of the reduced dichroism ratio, $(\Delta A/A)/(\Delta A/A)_0$ (where $\Delta A = A_{\parallel} - A_{\perp}$ and $A$ is the absorbance of a stationary DNA solution at 260 nm; $(\Delta A/A)$ and $(\Delta A/A)_0$ refer to the reduced dichroism of DNA complex and free DNA, respectively), is significantly diminished in the presence of the bound peptides. The decrease is more pronounced in the presence of L-lys-L-pheA than with the diastereomer L-lys-D-pheA (Figure 2). (3) In the presence of DNA (i.e., base-pair to peptide ratio of 7.2, 3.6, 2.4, and 0.5) large differences in the chemical shifts and line broadening of the $^1H$ NMR signals of the aromatic protons of **1** and **2** are observed (Figure 3 and Table I). For example, the L-lys-D-pheA, **2**, exhibits slight broadening and upfield