from the nature of the lone spin-containing d orbital.

The fact that the pyrrole substituent shifts exhibit primarily π contact shifts is evidenced by the similar magnitude of the downfield methyl and upfield pyrrole H shifts in deuterohemin reconstituted HRPCN[10] as well as by the downfield 4-H_α and upfield 4-H_β shifts in HRPCN.[10] The large asymmetry in the hyperfine shifts among the four pyrroles, however, is considerably greater than could conceivably arise from only rhombic dipolar shifts and arises from the fact that the spin-containing d orbital in HRPCN is primarily d_{yz} in character.[10] This predominantly d_{yz} can interact with the π orbitals of only pyrroles II and IV. Thus the increase in π contact shifts for two pyrroles and the decrease in the shifts for the other two pyrroles, as compared to a model complex, is observed in every low-spin cyanide derivative of a ferric hemoprotein and has been proposed to arise from π bonding with the axial histidyl imidazole, as discussed previously.[52,53] In HRPCN, this indicates that the axial imidazole plane is in the *xz* plane, as depicted schematically in Figure 1. In order that the spin-containing d orbital be primarily d_{yz}, this orbital must be higher in energy than d_{xz} and hence dictates that $\chi_y > \chi_x$.[54,55]

Thus our analysis dictates that amino acid residues located anywhere above or below pyrroles I and III should experience downfield axial and upfield rhombic shifts. Both the axial and rhombic terms yield downfield dipolar shifts for the amino acid residues over the pyrroles II and IV. Since noncoordinated amino acid can experience solely dipolar shifts, strongly upfield-shifted non-heme rsonances must arise from amino acid residues over pyrroles I and III.

This information on the expected direction of dipolar shifts for amino acids in the heme cavity, together with comprehensive NOE and variable-temperature studies of the remaining resolved resonance of HRPCN, should provide additional insight into the stereochemistry of the heme pocket of HRPCN. Such studies are in progress.

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(52) Shulman, R. G.; Glarum, S. H.; Karplus, M. *J. Mol. Biol.* **1971**, *57*, 93–115.

(53) Traylor, T. G.; Berzinis, A. P. *J. Am. Chem. Soc.* **1980**, *102*, 2844–2846.

(54) Palmer, G. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1979; Vol. 4, pp 313–353.

(55) Byrn, M. P.; Katz, B. A.; Keder, N. L.; Leven, K. R.; Magurany, C. J.; Miller, K. M.; Pritt, J. W.; Strouse, C. E. *J. Am. Chem. Soc.* **1983**, *105*, 4916–4922.

Communications to the Editor

First Demonstration of Solvolytic Generation of a Simple Silicenium Ion (R_3Si^+).[†] Access via 1,2-Methyl Migration[1]

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Carbenium ions are well-established reactive intermediates and their properties have been extensively studied.[2] In contrast, numerous attempts to generate in solution the isoelectronic silicenium ions (R_3Si^+) were unsuccessful.[3] Effective methods for the generation of carbenium ions[2] have repeatedly failed when applied to the analogous organosilicon precursors.[3] Progress was achieved only recently; Lambert et al.[4a] reported the preparation of two persistent silicenium ions (i.e., $(i\text{-PrS})_3Si^+$ and Ph_3Si^+) and Eaborn et al.[4b] provided evidence for the intermediacy of bridged delocalized silicon-containing cations in the solvolysis of a special group of highly sterically congested precursors. However, to the best of our knowledge, clear evidence for the solvolytic generation of a simple tricoordinated silicenium ion has not yet been presented.[3,4] We now present strong evidence that this elusive reactive intermediate (**2**) can be generated via a 1,2-methyl migration of a solvolytically produced α-silyl carbenium ion **1** (eq 1). We note

$$R_3SiCR'_2X \xrightarrow[-X^-]{\text{solvolysis}} \underset{\mathbf{1}}{R_3Si\overset{+}{C}R'_2} \xrightarrow{\sim R} \underset{\mathbf{2}}{R_2\overset{+}{Si}CR'_2R} \rightarrow \text{products} \qquad (1)$$

that similar processes, e.g., the $AlCl_3$-induced methyl migration from silicon to carbon, have been known since 1947.[5a] However, the general consensus[3,5b,c] has been that silicenium ions are not involved in these and other similar[5c] processes, believed to proceed via a four-centered transition state (or intermediate),[5b,c] but Barton et al.[5d] have recently challenged this conclusion.

Our starting point was theoretical. Ab initio calculations[6a] predict that α-silyl carbenium ions **1** are generally less stable than the isomeric silicenium ions **2**. For example, at 3-21G[6b] $(CH_3)_3SiC^+(CH_3)_2$ is 9.7 kcal·mol^{-1} less stable than $(CH_3)_2Si^+C(CH_3)_3$ and $CH_3C^+HSiH(CH_3)_2$ is less stable than $(CH_3)_2CHSi^+(CH_3)_2$ by 23.2 kcal·mol^{-1}. Furthermore, starting from **1** the calculated barriers for a 1,2-methyl shift are small, only a few kilocalories per mole.[7] Recent gas-phase experiments support these predictions. Thus, a MS/MS experiment shows that $(CH_3)_3SiCH(CH_3)Cl$ and $(CH_3)_2CHSi(CH_3)_2Cl$ produce

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[†] These species have also been named silylenium or silacenium ions.

(1) Reported in part at the Fourth European Symposium on Organic Chemistry (ESOC), Aix-en-Provence, France, Sept 2–6, 1985, and the VIII IUPAC Conference on Physical Organic Chemistry, Tokyo, Japan, Aug 24–29, 1986.

(2) *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience New York, 1976.

(3) (a) Review: Corriu, R. J. P.; Henner, M. *J. Organomet. Chem.* **1974**, *74*, 1. (b) Bickart, P.; Llort, F. M.; Mislow, K. *Ibid.* **1976**, *116*, C1. (c) Cowley, A. H.; Cushner, M. C.; Riley, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 624 and references therein.

(4) (a) Lambert, J. B.; Schulz, W. J., Jr., *J. Am. Chem. Soc.* **1983** *105*, 1671. Lambert, J. B.; McConnell, J. A.; Schulz, W. J., Jr. *Ibid.* **1986**, *108*, 2482. (b) Eaborn, C.; Lickiss, P. D.; Najim, S. T.; Romanelli, M. N. *J. Chem. Soc., Chem. Commun.* **1985**, 1754 and earlier work referenced therein.

(5) (a) Whitmore, F. C.; Sommer, L. H.; Gold, J. *J. Am. Chem. Soc.* **1947**, *69*, 1976. (b) Bott, R. W.; Eaborn, C.; Rushton, B. M. *J. Organomet. Chem.* **1965**, *3*, 455. (c) Brook, A. G.; Bassindale, A. R. In *Rearrangements in Ground and Excited States*; De-Mayo, P., Ed.; Academic: New York, 1980; Vol. II. (d) Robinson, L. R; Burns, G. T.; Barton, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 3935.

(6) (a) A slightly modified version of Gaussian 80 was used: Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1980**, *13*, 4046. (b) First row: Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. Second row: Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *Ibid.* **1982**, *104*, 2797.

(7) For example, in the rearrangement of $CH_3C^+HSiH(CH_3)_2$ to $(CH_3)_2CHSi^+H(CH_3)$ we estimate that the barrier for a methyl shift is only 2–3 kcal·mol^{-1}. This estimation is based on 6-31G* calculations corrected for the effect of correlation energy using the "additivity approximation" (see: Bouma, W. J.; Nobes, R. H.; Radom, L. *J. Am. Chem. Soc.* **1983**, *105*, 1743) and an MP3/6-31G* calculations for analogous smaller systems.

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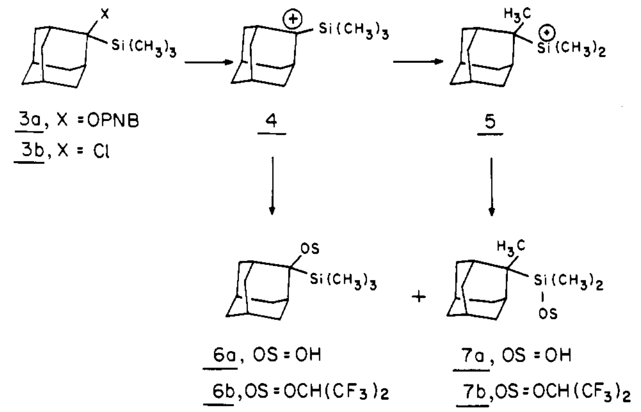
Scheme I

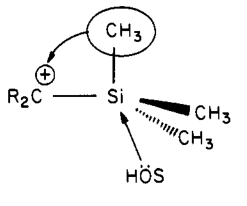


the *same* $C_5H_{13}Si^+$ ion, most likely $(CH_3)_2CHSi^+(CH_3)_2$.[8] Therefore, we decided to investigate similar rearrangements in the condensed phase.

We have recently shown[9] that solvolysis of **3** generates as the first intermediate an α-silyl carbenium ion **4** that is trapped by the solvent to give **6**. Rearrangement of **4** to the silicenium ion **5** and its capture by the solvent would give **7** as the reaction product (Scheme I). Solvolysis of **3a** in 80% acetone indeed yields a mixture of **6** and **7** (OS = OH) but the **7**:**6** product ratio is small, i.e., 9:91.[10] However, the yield of the rearranged products and thus the reaction fraction that proceeds via **5** (Scheme I) increases dramatically as the solvent nucleophilicity (*N*) is lowered.[11] The rearranged, **7**, to unrearranged, **6**, product ratios are 36:64, 68:32, and >99:1 in 93% trifluoroethanol (TFE), 98% TFE, and hexafluoroisopropyl alcohol (HFIP), respectively.[12] Similar results are observed with the chloride **3b**. Addition of water to the fluorinated solvents which increases its nucleophilicity,[11] as expected, reduces the **7**:**6** ratio. For example, in 95%, 87.5%, and 80% HFIP, **3b** yields **7**:**6** ratios of 85:15, 59:41, and 35:65, respectively (**7**:**6** is 64:36 in the solvolysis of **3a** in 95% HFIP). Similarly, with **3b** the addition of 40 equiv of 2,6-lutidine, which increases the nucleophilicity of the solvolysis medium, strongly reduces the **7**:**6** product ratio to 4:96 in 95% HFIP, compared to the unbuffered ratio of 85:15.

All the above data are *fully consistent* with the mechanism presented in Scheme I and *strongly support the formation of a silicenium ion* (either as a "free" ion or as an "ion pair"[2,13]) *in the solvolysis process*. The product–solvent dependency argues strongly against an alternative mechanism which involves a solvent-assisted methyl migration, depicted schematically in **8**,[5c] and which bypasses the silicenium ion **5** as a precursor to **7**. If rearrangement occurs via **8** the expectation is that increase in the solvent nucleophilicity would enhance the Si to C methyl migration and would increase the **7**:**6** product ratio,[14] but the opposite is observed (vide supra).

Some information on the selectivity of cationoid intermediates can be acquired by studying the product ratios (e.g., alcohol:ether) in binary solvent mixtures[2,15] (e.g., aqueous HFIP). Using the usual assumption[2,15] that the solvent selectivity $S = k_{H_2O}/k_{HFIP} = [ALCOHOL][HFIP)/[ETHER][H_2O]$, we obtain (in the range of 80–95% aqueous HFIP mixtures) a selectivity of $S(\mathbf{4}) = \mathit{7.8} \pm 2.6$ for carbenium ion **4**, in contrast to the "inverse selectivity" for silicenium ion **5** of $S(\mathbf{5}) = \mathit{0.42} \pm 0.01$.[16]



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The value of $S(\mathbf{4})$ is consistent with the selectivities in aqueous TFE[15a,b] of other carbenium ions (e.g., for the 1-adamantyl cation $k_{H_2O}/k_{TFE} = 0.83–2.60$[15a]), taking into consideration the lower nucleophilicity of HFIP.[11] In contrast the silicenium ion **5** exhibits an "inverse selectivity", $S(\mathbf{5}) < 1$; i.e., **5** is captured by HFIP ca. 2.4 times faster than by water. Further experiments are needed to clarify the reasons for this somewhat unusual behavior of **5**, and at this point we refrain from further speculation.

In conclusion, we have presented evidence which is fully consistent with the generation in solution of a silicenium ion via a 1,2-methyl shift in an α-silyl carbenium ion. Our study, coupled with the recent contributions by Lambert[4a] and Barton,[5d] calls for a reconsideration of silicenium ions as viable reaction intermediates in solution. We continue to explore the properties of **5** and extend our attempts to generate silicenium ions to other potential precursors and methods.

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(8) Apeloig, Y.; Drewello, T.; Karni, M.; Stanger, A.; Schwarz, H. *J. Chem. Soc., Chem. Commun.*, to be submitted.

(9) Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1985**, *107*, 2806.

(10) Determined by gas chromatography. Reactions were conducted in a sealed tube at 90 °C and were quenched after 12–14 h (solvolysis rates are given in ref 9). The solvent was buffered with 2 equiv of 2,6-lutidine. There was no significant change in the product composition with reaction time. The amount of unidentified products did not exceed 3%.

(11) Bentley, T. W.; Schleyer, P. v. R. *Adv. Phys. Org. Chem.* **1977**, *14*, 1. $N = 0.51$, -2.78, and -3.93 for 80% acetone, TFE, and 97% HFIP, respectively.

(12) The products consisted of mixtures of alcohols (OS = OH) and ethers (OS = OCH_2CF_3 or $OCH(CF_3)_2$); see below.

(13) A methyl-bridged **5** as the product-forming intermediate cannot be ruled out. Additional experiments are needed to clarify this subtle mechanistic point.

(14) The possibility (suggested by a referee) that in analogy to the 3-coordinated Si atom in **5** (vide infra), the 4-coordinated Si atom in **8** is also more selective for the fluorinated alcohols as compared to H_2O is unlikely. Thus, *t*-Bu_3SiCl reacts much faster with water or methanol than with TFE; see: Eaborn, C.; Saxena, A. K. *J. Organomet. Chem.* **1984**, *271*, 33.

(15) (a) Kaspi, J.; Rappoport, Z. *J. Am. Chem. Soc.* **1980**, *102*, 3829. (b) Richard, J. P.; Rothenberg, M. E.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1361. Richard, J. P.; Jencks, W. P. *Ibid.* **1984**, *106*, 1373.

(16) As calculated from the observed product distributions; e.g., in 80% HFIP **3b** yields **6a** (59.1%), **6b** (5.8%), **7a** (13.4%), and **7b** (21.7%).[10]

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^1H NMR Spectra of Rubredoxins: New Resonances Assignable to α-CH and β-CH_2 Hydrogens of Cysteinate Ligands to Iron(II)

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As the simplest member of the iron–sulfur class of metalloproteins, rubredoxin (Rd), serves as a prototype for the study of protein-bound high-spin iron in tetrahedral coordination by sulfur atoms.[1-3] Rds have been examined by a variety of physical

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(1) Eaton, E. A.; Lovenberg, W. In *Iron Sulfur Proteins*; Lovenberg, W., Ed.; Academic: New York, 1973; Vol. II, pp 131–162.

(2) Watenpaugh, K. D.; Sieker, L. C.; Jensen, L. H. *J. Mol. Biol.* **1979**, *131*, 509–522.

(3) Adman, E. T.; Sieker, L. C.; Jensen, L. H.; Bruschi, M.; LeGall, J. *J. Mol. Biol.* **1977**, *112*, 113–120.

0002-7863/87/1509-0273$01.50/0