

shows it to be tetragonally compressed with four short Fe-S bonds [2.233 (7)-2.236 (7) Å, which approximately parallel to the idealized S_4 axis] and eight long Fe-S bonds [2.269 (7)-2.280 (8) Å, which are perpendicular to the S_4 axis]. The factors that cause the distortions in the $[\text{Fe}_4\text{S}_4]$ units of iron-sulfur proteins and their model compounds as well as the biological significance of these distortions are not well understood.^{4,20-22}

Chemical and electrochemical oxidation of orange-brown solutions **1** and **2** produce intense red-brown solutions of **3** and of $[\text{Fe}_4\text{S}_4(\text{S}-2,3,5,6\text{-Me}_4\text{C}_6\text{H}_4)]^{1-}$ (**4**). Upon oxidation of HP_{red} to HP_{ox} , the major band in the visible spectrum shifts to longer wavelengths,²³ which is the same trend observed on conversion of **1** into **3** and **2** into **4**.²⁴ Interestingly, the stability of **3** and **4** are very sensitive to solvent conditions; neither compound is stable in DMF or CH_3OH . Chemical, electrochemical, and electronic spectral studies indicate that **3** is more stable than **4** and that both **3** and **4** are most stable in solvents of low polarity (with the stability in DMF \ll $\text{CH}_3\text{CN} < \text{CH}_2\text{Cl}_2$). These observations are relevant to the situation in biological systems, where the unique stability of the $[\text{Fe}_4\text{S}_4]^{3+}$ core of the HP proteins has been attributed to the hydrophobic environment of the iron-sulfur center.^{4,25} Chemical and spectroscopic studies of **3** and related $[\text{Fe}_4\text{S}_4]^{3+}$ clusters are continuing.

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Registry No. **1**, 96455-57-1; **1**⁻, 96455-63-9; **2**, 96455-59-3; **2**⁻, 96455-64-0; **3**, 96455-61-7; **4**, 96455-62-8; $[(\text{C}_6\text{H}_5)_2\text{Fe}]\text{BF}_4$, 1282-37-7.

Supplementary Material Available: Tables of fractional atomic coordinates and thermal parameters (2 pages). Ordering information is given on any current masthead page.

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(24) The electronic spectra of **1-4** in CH_2Cl_2 solution are as follows: for **1** $\lambda = 410$ (ϵ 24 500), 335 (19 400), 245 nm sh (52 800); for **2**, 414 (22 200), 342 (18 200), 245 nm (sh) (42 300); for **3**, 475 (28 100), 328 (13 400), 276 (sh) (23 700), 236 nm (sh) (48 000); for **4** (electrolysis solution), 458 (23 600), 331 (13 800), 274 (13 800), 240 nm (sh) (41 900).

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Dimethylsilylene: A Trisilane and a Geminal Diazide as New Photochemical Precursors. Evidence for an Absorption Maximum near 450 nm

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The yellow species ($\lambda_{\text{max}} \cong 450$ nm) produced by the irradiation of **1**³⁻⁵ or **2**⁴ in a hydrocarbon glass at 77 K (characterized by UV-vis absorption and emission) and of **1**³⁻⁵ or **3**⁶ in Ar or N_2 matrices at 10 K (characterized by UV-vis and IR) and by the flash pyrolysis⁶ of **4** or **5** with trapping in Ar or N_2 matrices (characterized by UV-vis and IR) has been identified³⁻⁶ as dimethylsilylene **6**.

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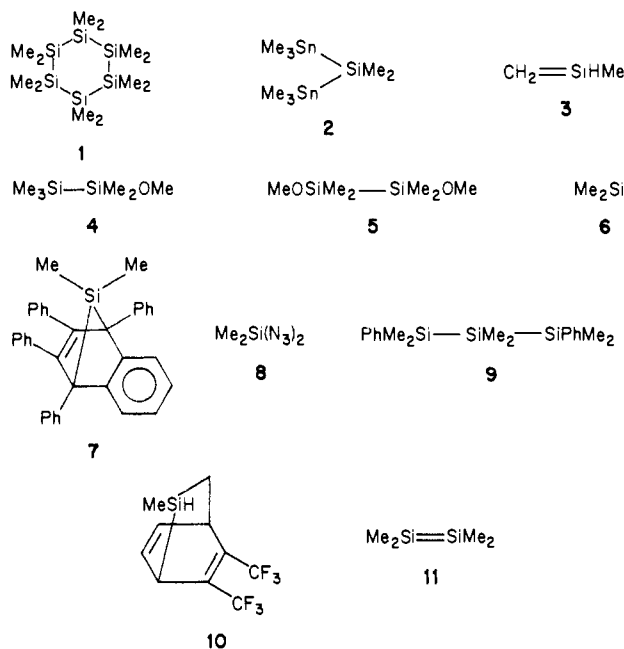
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This assignment has been recently questioned^{7,8} since room-temperature flash photolysis of **1** and **7**, two known photochemical precursors of **6**, did not yield detectable absorption at 450 nm. Instead, flash photolysis of **1**⁸ produced a species absorbing at 350 nm in hydrocarbon solution and at 300 nm in tetrahydrofuran, whose reactivity toward Et_3SiH and MeOH was similar to that of a silylene. The authors proposed that (i) either the absorption maximum of **6** in a hydrocarbon undergoes a 100-nm hypsochromic shift from a rigid solution at 77 K to a fluid solution at 298 K (ii) or the original structure assignment³ is wrong.

We now wish to report additional evidence which favors the original assignment,³ using **8** and **9** as new precursors for **6**. We propose that (i) either the above hypsochromic shift alternative applies, although this seems unlikely for reasons discussed below, or (ii) the proposed reassignment⁸ of the 350-nm maximum to ground state **6** is wrong.

The irradiation^{9a} of matrix-isolated **8** at 10 K induced an intense yellow color. Comparison of matrix IR and UV-vis spectra with those previously obtained by irradiation of **1**³⁻⁶ or **3**⁶ showed that the yellow species originally assigned as **6** is a major product. Irradiation with visible light bleached the color as reported earlier³⁻⁶ and converted the yellow species to 2-silapropene **3** (characterized by IR and UV⁴⁻⁶). As expected,⁶ UV irradiation^{9b} of **3** caused reversion to the yellow species. Difference spectroscopy yielded the IR spectra of **3** and **6**. Photoselection with linearly polarized light confirmed the earlier polarization results.⁵ As a function of the matrix, the λ_{max} values of **6** were N_2 430, Ar 450, Kr 455, and Xe 470 nm. Although significant, these solvent shifts were not nearly as large as the 150-nm hypsochromic shift reported⁶ for CH_3SiH upon going from Ar to N_2 matrix.

UV irradiation^{9a} of **9**¹⁰ in rigid 3-methylpentane at 77 K produced a yellow glass with broad absorption bands at 326 and 450 nm. The latter had the characteristic location and broad shape obtained using other precursors for **6**. The bands disappeared upon

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(9) (a) At 254 nm (low-pressure Hg lamp). (b) At 248 nm (KrF excimer laser).

(10) Synthesized by adding a THF solution of PhMe_2SiLi (from 1.49 g of Li, 0.2 mol, and 8.27 mL of PhMe_2SiCl , 0.05 mol) dropwise to 3 mL of Me_2SiCl_2 (0.025 mol) in 20 mL of THF at 0 °C. When the red color of PhMe_2SiLi persisted, the addition was stopped and 10 mL of H_2O added. Extraction with hexane, drying over MgSO_4 , and distillation yielded 2.4 g (30%) of **9**: bp 147-150 °C (0.7 mm); ¹H NMR (CDCl_3) δ 0.36 (s, 6 H), 0.54 (s, 12 H), 7.36 (m, 10 H); MS (70 eV), m/z 328 (M^+ , 2.4%), 193 ($\text{M}^+ - \text{PhMe}_2\text{Si}$, 13%), 135 (PhMe_2Si , 43%), 133 (100%); exact mass for $\text{C}_{18}\text{H}_{20}\text{Si}_3$ m/e calcd 328.1491, found 328.1500.

warmup. In a glass doped with Et_3SiH , warmup yielded the expected trapping product.¹¹

We conclude that both **8** and **9** are photochemical precursors for the yellow species originally assigned as **6**.

The evidence for the assignment is as follows: (i) The formation of this molecule (as characterized by its broad visible band with $\lambda_{\text{max}} = 450 \text{ nm}$ and its rich IR spectrum) has now been directly observed using seven widely different precursors (**1-5**, **8**, and **9**) which only possess the SiC_2H_6 moiety in common (for **2** and **9**, only the visible spectra were measured). In each case, the formation of **6** was preceded or at least plausible.¹² Since **2**, **3**, and **8** only contain one Si atom, so does the yellow species. The reversible photochemical interconversion³⁻⁶ of the yellow species with **3** in matrix isolation proves that the two molecules are isomeric; note that the independent access to **3** by pyrolysis of **10** is secured beyond reasonable doubt.⁶

(ii) Chemical trapping experiments with Et_3SiH ,³ $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$,³ $n\text{-C}_4\text{H}_9\text{CH}=\text{CH}_2$,¹³ N_2O ,¹³ and oxirane¹³ yield the expected trapping products; their formation in N_2O and oxirane-doped matrices was directly followed by spectroscopy.

(iii) The 450-nm transition has the expected energy,¹⁴ polarization,⁵ band shape, and fluorescence Stokes shift.³ The pattern of IR frequencies is very similar to those of SnMe_2 ¹⁶ and GeMe_2 ,¹⁷ fits qualitative expectations, and agrees with MNDO calculations.⁵ Both IR bands for which a comparison is presently possible have the correct polarizations.

(iv) The species yields no ESR signal and is stable indefinitely in matrix isolation, as expected for the ground state of a simple silylene.

Before the proposed reassignment^{7,8} could be seriously considered, an alternative interpretation of (i)-(iv) would have to be found. None has been suggested,^{7,8} nor have we been able to think of any. The conclusion that the yellow species is ground-state dimethylsilylene **6** seems inescapable.

It is conceivable that the 350-nm species observed in the flash photolysis experiments⁸ also is ground-state **6** as suggested⁸ and that the 100-nm shift is due to the difference in the temperature and/or viscosity of the hydrocarbon environment. This explanation seems unlikely since spectra of the yellow species taken at 10 and 77 K do not differ much and a wide variation in the nature of the matrix has a clearly detectable but much smaller effect. Why, then, was **6** most likely not observed in the flash photolysis experiments, and what is the 350-nm species?

(11) Irradiation for 6 h led to 74% conversion. GLC analysis after warmup revealed the presence of $\text{Me}_2\text{PhSi-SiPhMe}_2$ (29%) and $\text{Et}_3\text{SiSiMe}_2\text{H}$ (43%).

(12) Matrix photolysis of geminal diazides in the carbon series leads to carbenes: Barash, L.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1967**, *89*, 3931. The behavior in solution is different: Moriarty, R. M.; Kleigman, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 5959. Solution irradiation of geminal diazidosilanes did not produce evidence for silylenes: Ando, W.; Tsumaki, H.; Ikeno, M. *J. Chem. Soc., Chem. Commun.* **1981**, 597.

(13) Arrington, C. A.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 6176.

(14) The absorption spectrum of SiH_2 is established beyond doubt and extends from 480 to 650 nm; Bueger, H.; Eujen, R. *Top. Curr. Chem.* **1974**, *50*, 19. Numerous polysilane precursors of substituted organic silylenes other than **6** have been irradiated in rigid glasses, yielding products with broad visible absorption bands similar to that of **6**, with λ_{max} (77 K, 3MP) ranging from 400 to 580 nm (the values for a series of alkylsilylenes correlate with excitation energies calculated by the INDO/S method). They have been identified as substituted silylenes by trapping reactions (unpublished results: cf. ref 15). Methylsilylene [λ_{max} (77 K, 3MP) = 480 nm], when prepared by rearrangement of silaethylene,⁶ has λ_{max} (10 K, Ar) = 480 nm. In the case of phenylmethylsilylene [λ_{max} (77 K, 3MP) = 490 nm] a room-temperature flash photolysis of a 10^{-3} M trisilane precursor yielded a transient with λ_{max} (room temperature, C_6H_{12}) = 440 nm which decayed within tens of μs with second-order kinetics and showed high reactivity toward O_2 , and unexpectedly low reactivity toward several other trapping agents. The transient was tentatively assigned as PhSiMe . The shift in λ_{max} might be due to conformational effects, since rotation about the Ph-Si bond may well be nearly free, but it is also possible that the transient is not ground-state PhSiMe : Gaspar, P. P.; Boo, B. H.; Chari, S.; Ghosh, A. K.; Holten, D.; Kirmaier, C.; Konieczny, S. *Chem. Phys. Lett.* **1984**, *105*, 153.

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It is perhaps appropriate to indicate a few possibilities that have not been considered in print.^{7,8} Most likely, ground-state **6** has escaped detection because its 450-nm absorption band is relatively weak and very broad (10^{-4} M solutions were used⁸). It is also conceivable that it is formed on a time-scale slower than 8 μs , either from the 350-nm species or from an unobserved species, and that dimerization then interferes with a buildup of its concentration. The 350-nm species could be, for instance, a minor ground-state or triplet-state byproduct with a high extinction coefficient which happens to be quenched with Et_3SiH and MeOH , or it could be a ground-state or excited-state intermediate in the production of ground-state **6**, such as the lowest triplet state of **6**.¹⁸ The notion that the 350-nm absorption is due to an electronically excited species is in line with its solvent-independent unimolecular decay with a 8- μs lifetime, a property for which no interpretation has been proposed⁸ and which is not expected of ground-state **6** in inert solvents. In the absence of adventitious scavenger impurities, **6** should decay in a second-order process and, at the low precursor concentrations used, more slowly, even if its dimerization is diffusion controlled. In summary, we believe that alternative interpretations of the presently available flash photolytic data exist.

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Registry No. **6**, 6376-86-9; **8**, 4774-73-6; **9**, 4098-97-9; PhMe_2SiLi , 3839-31-4; Me_2SiCl_2 , 75-78-5; Et_3SiH , 617-86-7; $\text{Me}_2\text{PhSiSiPhMe}_2$, 1145-98-8; $\text{Et}_3\text{SiSiMe}_2\text{H}$, 31732-54-4.

(18) The agreement of the λ_{max} with that observed for the fleeting warmup product of matrix-isolated **6** and tentatively assigned to **11**¹⁵ may well be coincidental.

Selective Alkali Metal and Hydrogen Reduction of Benzene to Cyclohexene

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In connection with our interest of developing catalytic systems for the selective hydrogenation of arenes to cyclic olefins,² we have explored the reactivity of benzene and other aromatic radical anion systems with molecular hydrogen. Deep blue solutions containing the benzene radical anion are typically prepared at subambient temperatures by contacting benzene with alkali metals in the presence of ether solvents³ or of cation-complexing crown ethers and cryptands.⁴ In our experience, benzene solutions of the cryptand C222 ether⁵ in the presence of Na/K alloy rapidly

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