shifted from that of the native pigment, probably due to the interaction of the electronegative N>O group with the negative counterion which is proposed to be in the region of the chromophore ring.[9] The ESR spectra indicate that the environment of the chromophore ring has a high degree of orientation and is rigid within the membrane although a slight increase in mobility occurs on dark adaptation.

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Theoretical Studies of the 1,2-Hydrogen Shift. 11. The Controversial Barrier Height between Silaethylene and Methylsilylene

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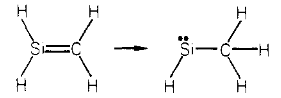
Earlier papers in this series[1-10] have emphasized that for one of the simplest reaction types, the 1,2-hydrogen shift, theory is now able to make constructive additions and amendments to what is known from experiment. For example, our research and that of Pople and co-workers[11-13] have demonstrated that the singlet rearrangements of hydrocarbon diradicals such as methylcarbene ($CH_3\ddot{C}H$) and vinylidene ($CH_2{=}C{:}$) occur with little or no barrier. In distinct contrast, the analogous triplet rearrangements face substantive barriers, e.g., ~40 kcal for the methylnitrene ($CH_3\ddot{N}\cdot$) rearrangement to methylenimine.[6] Thus a number of general trends are beginning to appear in this area.

A particularly controversial problem lying within the scope of the 1,2-hydrogen shift is the magnitude of the barrier between silaethylene and methylsilylene



(1)

In an earlier theoretical study, Goddard, Yoshioka, and Schaefer (GYS)[7] predicted this barrier to be 41 kcal at the unlinked cluster corrected configuration interaction (CI) level of theory employing a standard double-ζ (DZ) basis set.[14] The examination of analogous studies performed at a higher level of theory would appear to suggest[8-13] that extension of the basis set, treatment of higher order correlation effects, and correction for zero-point vibrational energies would all reduce the predicted barrier, but not to less than 25 kcal.

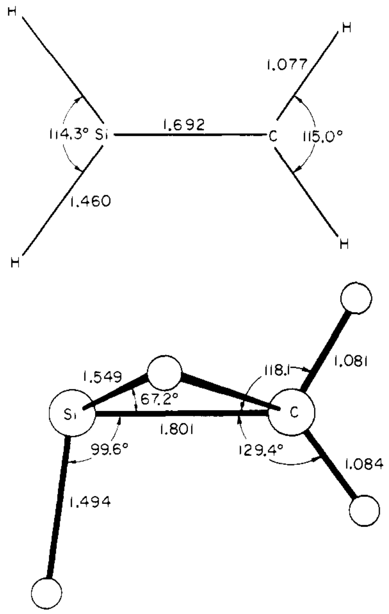
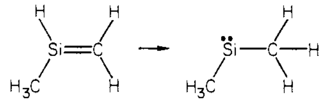


Figure 1. Theoretical DZ + P SCF stationary-point geometries for silaethylene and the transition state connecting it with methylsilylene. Bond distances are in angstroms.

In light of this theoretical background, the publication of dissenting back-to-back experimental communications[15,16] on this topic came as something of a surprise to us. Conlin and Wood[15] reported evidence that the reaction of 1-methylsilaethylene to dimethylsilylene



(2)

is rapid. Specifically they point to pyrolysis of methylsilacyclobutane leading to the isolation of products characteristic of dimethylsilylene reactions. Moreover, Conlin and Wood suggested that the isomerization (1) of the parent silaethylene might be even more rapid than (2).

In the second communication, Drahnak, Michl, and West (DMW)[16] present matrix isolation results which suggest that reaction 2 proceeds rapidly at 100 K, and the product dimethylsilylene is then trapped. DMW cite the previously discussed GYS theoretical study[7] but conclude that "unless the additional methyl [i.e., the difference between reactions 1 and 2] has a dramatic effect, this (theoretical) result is not compatible with our interpretation. No simple alternatives have occurred to us." Thus there would appear to be a conflict between the theoretical prediction[7] that the barrier is not less than ~25 kcal and the experimental deduction that this same barrier is perhaps 5 kcal or less.

In light of this apparent discrepancy between theory and experiment, it was deemed imperative to reexamine the barrier for reaction 1 at a higher level of theory. Specifically, it was thought that the addition of polarization basis functions might significantly alter the earlier predictions.[7] Therefore a set of p functions (orbitals exponent $\alpha = 1.0$) was added to each of the four hydrogen

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[1] C. E. Dykstra and H. F. Schaefer, *J. Am. Chem. Soc.*, **100**, 1378 (1978).

[2] M. P. Conrad and H. F. Schaefer, *J. Am. Chem. Soc.*, **100**, 7820 (1978).

[3] J. D. Goddard and H. F. Schaefer, *J. Chem. Phys.*, **70**, 5117 (1979).

[4] H. F. Schaefer, *Acc. Chem. Res.*, **12**, 288 (1979).

[5] T. L. Allen, J. D. Goddard, and H. F. Schaefer, *J. Chem. Phys.*, **73**, 3255 (1980).

[6] J. Demuynck, D. J. Fox, Y. Yamaguchi, and H. F. Schaefer, *J. Am. Chem. Soc.*, **102**, 6204 (1980).

[7] J. D. Goddard, Y. Yoshioka, and H. F. Schaefer, *J. Am. Chem. Soc.*, **102**, 7644 (1980).

[8] Y. Osamura, J. D. Goddard, H. F. Schaefer, and K. S. Kim, *J. Chem. Phys.*, **74**, 617 (1981).

[9] Y. Osamura, H. F. Schaefer, S. K. Gray, and W. H. Miller, *J. Am. Chem. Soc.*, **103**, 1904 (1981).

[10] J. D. Goddard, Y. Yamaguchi, and H. F. Schaefer, *J. Chem. Phys.*, **75**, 3459 (1981).

[11] J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, *Int. J. Quantum Chem.*, **14**, 545 (1978).

[12] R. Krishnan, M. J. Frisch, J. A. Pople, and P. v. R. Schleyer, *Chem. Phys. Lett.*, **79**, 408 (1981).

[13] J. A. Pople, presented at the Texas Conference on Theoretical Approaches to Chemical Dynamics, Mar 2-4, 1981, Austin, Texas.

[14] T. H. Dunning and P. J. Hay, *Mod. Theor. Chem.* **3**, 1-27 (1977).

[15] R. T. Conlin and D. L. Wood, *J. Am. Chem. Soc.*, **103**, 1843 (1981).

[16] T. J. Drahnak, J. Michl, and R. West, *J. Am. Chem. Soc.*, **103**, 1845 (1981).

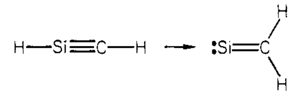
0002-7863/81/1503-7366$01.25/0

atoms, as were d functions on carbon ($\alpha = 0.75$) and silicon ($\alpha = 0.6$). The technical specification of this double-ζ plus polarization (DZ + P) basis is then Si(11s7p1d/6s4p1d), C(9s5p1d/4s2p1d), H(4s1p/2s1p). Although heavy-atom d functions are known[14] to be important for such systems, it was also thought that the p functions on hydrogen (particularly those on the migrating hydrogen) might lower the predicted barrier.

The transition-state geometry for the silaethylene rearrangement was determined here at the DZ + P self-consistent-field (SCF) level of theory and is seen in Figure 1 along with the analogous DZ + P SCF structure for the reactant molecule. Comparison with the earlier DZ SCF transition state[7] shows the two structures to be qualitatively similar. The appropriate total energies are −329.05439 (silaethylene) and −328.98320 (transition state) hartrees, yielding a predicted barrier of 44.7 kcal, only 0.3 kcal below the DZ SCF barrier height.[7] Thus it is seen that at the SCF level the addition of polarization functions has little effect on either the reaction mechanism or energetics.

With the full DZ + P basis set, CI including all single and double excitations was carried out, with the restriction that the core molecular orbitals (Si 1s, 2s, $2p_x$, $2p_y$, $2p_z$ and C 1s) were deleted. For silaethylene in point group C_{2v} there are 9003 configurations while the transition state, with no elements of symmetry (point group C_1), the CI involved 32 131 configurations. The variational energies obtained for silaethylene and the rearrangement transition state are −329.29703 and −329.22858 hartrees, respectively, yielding a barrier of 43.0 kcal. Appendage of the Davidson correction[17] for unlinked clusters yields a final prediction of 40.6 kcal for the classical barrier.

One surprising result of this research is that the most reliable predicted barrier height for reaction 1 is qualitatively the same as the 45.0 kcal predicted[7] at the relatively simple DZ SCF level. As noted earlier, polarization basis functions and correlation effects typically provide a considerable reduction in such predicted barriers.[9–12] That is to say, relative minima on a potential surface are typically treated more correctly at a simple level of theory than are transition states. The invalidation of this trend in the present case is almost certainly due to the relative inability of the simple methods to describe the silaethylene ground state. That is, silaethylene is just as difficult to describe electronically as is its transition state to methylsilylene. Interestingly, the same qualitative result has been found for the related silacetylene rearrangement



(3)

There Gordon and Pople[18] find that polarization functions and correlation effects actually *increase* the rearrangement barrier.

Unless there exists a different, lower energy pathway for reaction 2, it would appear that alternate interpretations of the experiments of Conlin and Wood[15] and of Drahnak, Michl, and West[16] should be sought.[19,20]

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Cucurbituril

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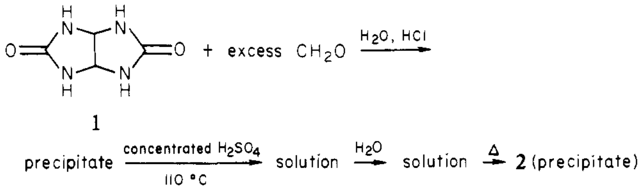
Some 75 years ago Behrend et al. reported materials from acidic condensation of glycoluril (**1**) with an excess of formaldehyde.[1] The initial product so obtained should probably be regarded as a cross-linked, aminal-type polymer by virtue of its physical properties (amorphous character, insolubility in all common solvents). In seeking a more tractable material from this precipitate, the previous workers resorted to treatment with hot, concentrated sulfuric acid, which eventually dissolves the substance (as we have confirmed). When such solution is diluted with cold water, filtered, and subsequently boiled, a crystalline precipitate (**2**) is obtained, which Behrend characterized as $C_{10}H_{11}N_7O_4 \cdot 2H_2O$. Although no structure for **2** was offered, the substance proved exceedingly stable toward a number of potent reagents. Also, a series of crystalline complexes incorporating a surprising variety of metal salts and dye stuffs was recorded.[1]



Intrigued by this report, we repeated the preparation and obtained **2** without difficulty in somewhat less than the specified yield (40–70%). Spectral characterization enhanced our curiosity. In the infrared region, the carbonyl absorption (1720 cm^{-1}, KBr) suggested retention of the glycoluril nucleus. The proton NMR spectrum, containing only three signals of equal intensity, indicated a nonaromatic structure of high symmetry: δ^{Me_4Si} (90% HCOOH) 5.75 (s, glycoluril methines), and 4.43, 5.97 (d, $|J|_{gem} = 15.6$ Hz, nonequivalent methylene hydrogens, N–CH_aH_b–N). This evidence implies the stoichiometry $nC_4H_6N_4O_2 + 2nCH_2O \rightarrow (C_6H_6N_4O_2)_n + 2nH_2O$, which is in reasonable agreement with elemental analysis of **2** (as a hydrate).[1,2] However, the material proved insufficiently volatile for mass spectral molecular weight determination, even by the technique of field desorption ionization. Consequently, an X-ray crystallographic structure determination was undertaken.

Although the parent substance proved unsuitable for this purpose, satisfactory crystals of a calcium bisulfate complex of **2** were obtained from sulfuric acid solution. This material was of composition $(C_6H_6N_4O_2)_3 \cdot CaSO_4 \cdot H_2SO_4 \cdot (H_2O)_{6.5}$ and crystallized in the triclinic system with $a = 11.948$ (3) Å, $b = 10.391$ (3) Å, $c = 15.667$ (5) Å, $\alpha = 92.15$ (8)°, $\beta = 115.18$ (5)°, $\gamma = 109.66$ (6)°. The observed density was consistent with two of the above formulas per unit cell. The structure was solved in space group $P\bar{1}$ by direct methods (MULTAN). The solution, based on 3686 observed, absorption-corrected, unique data, has been refined to a conventional R of 0.0673.

The organic moiety (**2**) is a cyclic hexamer of dimethanoglycoluril as shown in Figure 1.[3] Fuller details of the crystal structure will be provided elsewhere. Briefly, however, the organic macrocycle encircles a crystallographic center of symmetry, with calcium ions coordinated to urea carbonyl oxygen atoms of adjacent molecules of **2**. Octacoordination of the metal is completed with water and sulfate ligands. The center of each hexamer is

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(17) S. R. Langhoff and E. R. Davidson, *Int. J. Quantum Chem.*, **8**, 61 (1974).

(18) M. S. Gordon and J. A. Pople, *J. Am. Chem. Soc.*, **103**, 2945 (1981).

(19) The seemingly remote possibility remains (suggested by DMW[16]), of course, that the additional methyl group in reaction 2 could provide a qualitative difference between reactions 1 and 2.

(20) The transition state seen in Figure 1 was determined via analytic gradient techniques, beginning from the earlier determined[7] DZ SCF transition state structure. Since both structures contain no elements of symmetry (point group C_1), there are no constraints on the geometrical optimization.

(1) Behrend, R.; Meyer, E.; Rusche, F. *Liebigs Ann. Chem.* **1905**, *339*, 1.

(2) Found: C 40.92, H 4.17, N 30.17 (Galbraith); C 36.66, H 4.53, N 30.08 (Behrend et al.,[1] average values).

(3) The spectral evidence previously cited is quite in accord with this structure. Magnetic nonequivalence of the methylene protons arises from endo- and exocyclic orientations.