

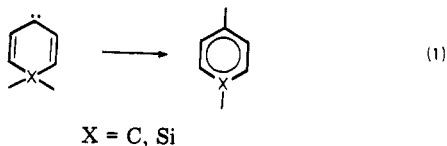
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- (46) This derivative was subsequently almost completely avoided. Its mass spectra below *m/e* 402 are largely identical with those of **3**.

Communications to the Editor

An ab Initio Molecular Orbital Calculation of the Structure of Silabenzene

Sir:

Silabenzene has proven to be an elusive molecule¹⁻³ despite the relative stability of similar heteroatomic analogues of benzene such as pyridine, phosphabenzene, arsabenzene, and stibabenzene.⁴ Attempts have been made to generate a substituted silabenzene with the following rearrangement of a singlet carbene:³



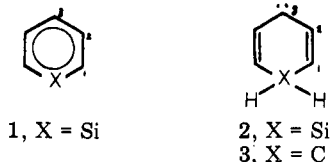
Although this reaction occurs readily for carbon,⁵ the silicon analogue does not appear to yield a silabenzene. In this communication we wish to report an ab initio investigation of the structure of silabenzene.⁶

The calculations were performed with the GAUSSIAN 70⁷ and the FORCE⁸ programs using the standard STO-3G basis set⁹ on the IBM 360/91 computer at Princeton. The force method¹⁰ was used to optimize fully all geometrical parameters in the structures reported. Because of difficulties associated with choosing a suitable, nonredundant internal coordinate system for cyclic molecules, the optimization was based on cartesian energy derivatives. An initial force constant matrix was obtained by transforming a simple, empirical valence force field using redundant internal coordinates to the cartesian coordinates system. (The accuracy of the initial force constant

matrix affects only the rate of convergence, but not the final outcome of the geometry optimization.) The force method, especially when combined with an empirically estimated force constant matrix, can be an order of magnitude more efficient than optimization methods based only on the energy. In addition, magnitudes of the residual forces at the optimized geometry provide an important check on the quality of the optimization (convergence level of $\sim 5 \times 10^{-3}$ mdyn for the root-mean-square energy gradient in cartesian coordinates). The results are summarized in Table I. To serve as a reference point, the structures for silaethylene^{11a-c} and the associated carbenes^{11d} were also optimized fully with the STO-3G basis.¹²

Inspection of the geometrical parameters for singlet silabenzene reveals that only small changes in the bond angles (relative to benzene) are necessary to accommodate the larger silicon. The C-C bond lengths are essentially the same as in benzene,¹³ and the Si-C bond length lies between the values for a single bond¹⁴ and a double bond,¹² displaying almost the same relative shortening found in benzene. Thus, the calculated structures would suggest that silabenzene possesses some degree of aromaticity. In the triplet state, these bond lengths increase somewhat; but, unlike silaethylene,^{11b} where the triplet undergoes a large conformational change, triplet silabenzene remains planar.

Further support for the aromatic character can be found in the molecular orbital (MO) energies and MO coefficients. The usual benzenoid pattern of orbital energies (-0.461, $2 \times (-0.283)$, $2 \times (0.271)$, 0.507 au calcd for C₆H₆ at STO-3G) is not strongly perturbed (-0.416, -0.278, -0.200, 0.256, 0.284, and 0.494 au), although the energy of the highest occupied MO is above that of benzene, suggesting less resonance

Table I. Theoretically Optimized Geometry of Silabenzene (1), 4-Silacyclohexadienylydene (2), and Cyclohexadienylydene (3)^a


parameter ^b	1 (singlet) ^c	1 (triplet) ^d	2 (singlet) ^e	3 (singlet) ^f
Bond lengths				
XC ₁	1.722	1.759	1.844	1.513
C ₁ C ₂	1.381	1.433	1.323	1.325
C ₂ C ₃	1.395	1.406	1.511	1.502
XH	1.419	1.428	1.425	1.093
C ₁ H	1.079	1.077	1.086	1.087
C ₂ H	1.086	1.076	1.086	1.084
C ₃ H	1.080	1.090		
Bond angles				
C ₁ XC ₅	110.3	113.6	102.6	111.9
XC ₁ C ₂	117.4	115.3	121.7	123.0
C ₁ C ₂ C ₃	125.1	122.9	129.4	126.0
C ₂ C ₃ C ₄	124.6	130.1	115.3	110.0
C ₂ C ₁ H	118.2	120.4	118.4	121.5
C ₁ C ₂ H	118.4	119.4	117.5	118.1
HXH			109.3	106.3

^a In each case, the initial structure had C_{2v} symmetry (nonplanar skeleton) and optimization without constraints leads to C_{2v} symmetry (planar skeleton). ^b Bond lengths in angstroms, angles in degrees. ^c Total energy: -476.04320 au. Energy of triplet at this geometry: -475.86167 au. ^d Total energy: -475.87230 au. ^e Total energy: -475.93878 au. Energy of triplet at this geometry: -476.02126 au. ^f Total energy: -227.73747 au. Energy of triplet at this geometry: -227.80701 au.

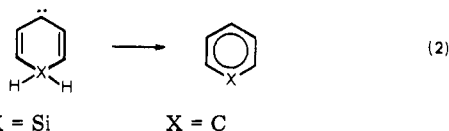
Table II. Charge Distribution in Silabenzene

	gross charge on fragment ^a			
	SiH	C ₁ H	C ₂ H	C ₃ H
σ	13.59	6.17	6.04	5.97
π	0.82	1.09	0.96	1.09

^a Number of electrons.

stabilization. The MO coefficients indicate that the π electron distribution is also benzene-like and delocalized over the entire heavy-atom framework. The Mulliken population analysis in Table II shows that the π-electron distribution is reasonably uniform, with the silicon having a somewhat smaller electron density than the carbons. Correspondingly, there is a charge buildup on the ortho and para carbons typical of a benzenoid π system. The σ framework shows a more distinct polarization of the C-Si bond than does the π-electron system. This suggests that silabenzene may have considerable ylide character, although this effect may be exaggerated by deficiencies inherent in the Mulliken population analysis. The elusive character of silabenzene may thus be due to its high reactivity as opposed to a lack of aromaticity.

Structures for the carbene **2** and **3** were also optimized. As shown in Table I, neither **2** nor **3** displays any unusual bonding or strong geometrical distortion.

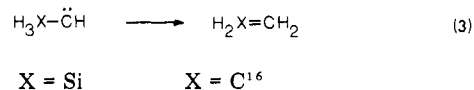


singlet -66 kcal/mol -97 kcal/mol (2a)
triplet¹⁵ 100 kcal/mol 28 kcal/mol (2b)

Although the use of a small basis set, neglect of electron correlation, and changes in zero point vibrational energy can result

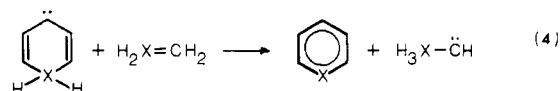
in considerable error in estimated heats of isomerization, the calculated energy differences for eq 2 are sufficiently large so that trends should be predicted correctly. The formation of silabenzene in rearrangement 2a of the singlet carbene is calculated to be 31 kcal/mol less exothermic than the formation of benzene. For triplet reaction 2b, the isomerization is thermodynamically favored to proceed in the opposite direction.

The difference in isomerization energies in reaction 2a might suggest a lack of resonance stabilization in silabenzene. However, this would contradict the interpretation of the calculated structure. The problem can be resolved by comparison with a simpler carbene rearrangement:



singlet -44 kcal/mol -65 kcal/mol (3a)
triplet¹⁷ 3 kcal/mol 6 kcal/mol (3b)

The triplet isomerizations are nearly thermoneutral. However, the formation of singlet silaethylene is calculated to be 21 kcal/mol less exothermic than the formation of ethylene, partially as a result of the lower strength of the Si-C π bond compared with the C-C π bond. The same effect is present in eq 2a and accounts for a large portion of the isomerization energy difference, with the remainder (10 kcal/mol) attributable to resonance energy differences. In fact eq 2a and 3a can be combined for an estimate of the resonance energy of silabenzene:¹⁸



X = Si (-22 kcal/mol)
X = C (-32 kcal/mol)

The value for benzene is in fair agreement with experiment and the *calculated resonance energy of silabenzene is 2/3 that of benzene*. Even though other isomers of C₅SiH₆ such as Dewar silabenzene¹⁹ or 1-silacyclohexadienylydene (cf. silaethylene vs. methylsilene^{11d}) may be competitive in stability, silabenzene appears to have all the attributes expected of an analogue of benzene.

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- (20) Address correspondence to the Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pa. 15213.

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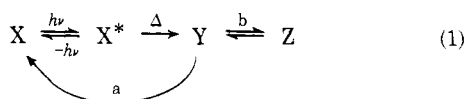
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The Significance of a Secondary Deuterium Isotope Effect in the Photorearrangement of 1-Iminopyridinium Ylides

Sir:

In photoreactions which appear to involve a thermally activated step, a comparison of the temperature dependence of the luminescence with the quantum yield is the current method of choice in characterizing the mechanistic pathway.¹ For instance, in the singlet process of eq 1, which converts X to Z via



the intermediate Y, the temperature dependence of the fluorescence yield is independent of the rate ratio a/b , but a direct, concerted, transition of X^* to Z, which did not involve the intermediate Y and its thermal conversion to Z, requires that quantum yield be inversely related to the fluorescence rate. An alternative approach to the problem of proving the occurrence of a thermal reaction step in the course of a photoreaction, through measurement of a kinetic isotope effect for the proposed vibrationally activated process, promises to be somewhat simpler to apply, and is the subject of this report.

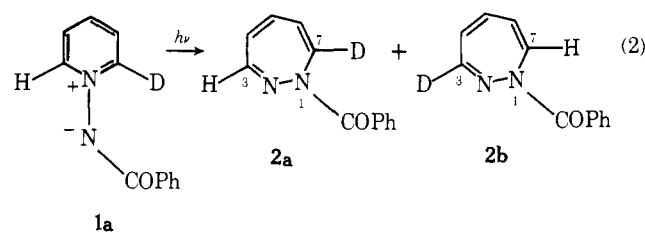
Streith and Cassal^{2a} have discussed the reversible conversion of **1** to **2** taking place readily upon exposure of a solution to UV radiation. The reverse reaction has now been effected by purely thermal means.^{2b} This permits an operational assumption similar to one made by Ullman³ that the same reaction transition state can be attained from either direction, and that the forward reaction brought about by photochemical means is comprised of an initial absorption and electronic transition to an excited singlet state. The latter crosses to a high vibrational level of the ground state, subsequently achieving the vibrational energy required to surmount a thermal reaction barrier. The kinetic isotope effect experiments of moment have been devised and carried out in the interests of providing a broad test of the validity of this assumption. In point of fact, however, these

experiments and their underlying premises must withstand the challenge of two important concerns (as follows).

A. Isotope effects on absorption processes are known⁴ and could conceivably influence the outcome of purely photochemical reactions having no thermal activation steps. A number of examples have been reported,^{4,5} but with the use of wide-band excitation there appears to be substantial likelihood that these effects would not be observed. Nonetheless, the kinetic isotope experiment was designed to circumvent this possible complication.

B. Isotope effects on primary photochemical processes have been anticipated by Hammond's argument⁶ that the rates of photochemical reactions cannot be described by traditional transition-state (TS) theory (Calvert and Pitts)⁷ because many of the assumptions made in the derivation of TS equations are considered invalid under photoexcitation conditions. Hammond prefers a treatment based on radiationless-decay theory. In effect, this treatment permits a separation of rate constants into electronic and vibrational components. For the case of an isotope effect, changes in the electronic part attributable to isotope substitution should be minor because nuclear changes make little difference to the valence part of the MO's. For cases of isotopic substitution not directly involved in bond homolysis, or rearrangement, a heavier isotope, for which the vibrational quanta are smaller than for a light, will react slower. This, at least, is one of the explanations provided for the observation that deuteriobenzene triplets decay slower than protio benzene.⁸ Hammond's argument appears relevant to the present case and our assumptions in applying it are that (i) the electronic part of the rate constant can be ignored, and (ii) the vibrational component predicts a normal $k_{\text{H}}/k_{\text{D}}$ in a secondary deuterium isotope experiment.

The experimental design, which was devised to come to grips with these theoretical concerns applied to the photorearrangement of 1-iminopyridinium ylides previously studied,² is embodied in the reactions of eq. 2. Thus, there can be no



isotope effects in this reaction arising from differences in extinction coefficients of competing isotopic substrates since the competing isotopic reaction sites are in the same molecule. The relative rates at the isotopically substituted centers depend on the localization of the absorbed energy in the critical bonds, a process which is affected only by the vibrational frequencies of H and D nuclei bonded to identical carbon atoms. Moreover, since these H and D nuclei are not directly involved in the course of rearrangement, the Hammond theory would predict that the deuterated carbon should be less reactive, if at all different from its protiated competitor in this respect.

The 2-deuterio-1-iminopyridinium ylide substrate **1a** was synthesized in the usual manner⁹⁻¹¹ from 2-deuteriopyridine. This precursor, in turn, was made by a preceded procedure involving exchange of 2-pyridinecarboxylic acid with D_2O followed by thermolytic decarboxylation to give a product with the required degree of 2-deuteration. The photorearrangement of **1a** was carried out in all other respects exactly as in the previous studies.² Samples taken at various extents of reaction completion showed, to all purposes, identical compositions of products **2a** and **2b** (See Table I).

Clearly the finding of a very large, inverse, secondary deuterium isotope effect in the photorearrangement of 1-imino-