(12) (a) Singlet H_2SiCH_2: C_{2v} symmetry, planar, $r(SiC) = 1.637$ Å, $r(SiH) = 1.418$ Å, $r(CH) = 1.073$ Å, $\angle HSiC = 122.7°$, $\angle HCSi = 123.1°$, total energy $E = -325.22640$ au. (b) Triplet H_2SiCH_2: C_s (see ref 11b), $r(SiC) = 1.849$ Å, $r(SiH) = 1.430$ Å, $r(CH_1) = 1.081$ Å, $\angle H_1CSi = 123.0°$, $\angle H_2CSi = 123.1°$, $\angle HSiC = 109.2°$, $\angle H_1CSiH$ (dihedral) $= \pm121.8°$, $E = -325.22895$ au. (c) Singlet H_2SiCH: C_s, staggered, $r(SiC) = 1.912$ Å, $r(SiH_1) = 1.421$ Å, $r(SiH_{23}) = 1.425$ Å, $r(CH) = 1.120$ Å, $\angle H_1SiC = 110.9°$, $\angle H_{23}SiC = 109.4°$, $\angle H_1SiH_{23} = 109.0°$, $\angle HCSi = 103.9°$, $E = -325.15630$ au. (d) Triplet H_3SiCH: C_2, staggered, $r(SiC) = 1.834$ Å, $r(SiH_1) = 1.423$ Å, $r(SiH_{23}) = 1.424$ Å, $r(CH) = 1.085$ Å, $\angle H_1SiC = 110.5°$, $\angle H_{23}SiC = 110.0°$, $\angle H_1SiH_{23} = 109.1°$, $\angle HCSi = 132.1°$, $E = -325.23330$ au.
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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

$$X \underset{-h\nu}{\overset{h\nu}{\rightleftharpoons}} X^* \overset{\Delta}{\longrightarrow} Y \overset{b}{\underset{}{\rightleftharpoons}} Z \qquad (1)$$
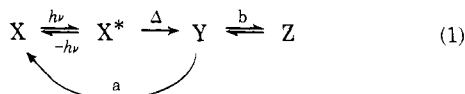
the intermediate Y, the temperature dependence of the fluorescence yield is independent of the rate ratio a/b, but a direct, concerted, transition of X^* to Z, which did not involve the intermediate Y and its thermal conversion to Z, requires that quantum yield be inversely related to the fluorescence 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 Ullman[3] 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 known[4] and could conceivably influence the outcome of purely photoreactions 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 argument[6] 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 protiobenzene.[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_H/k_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
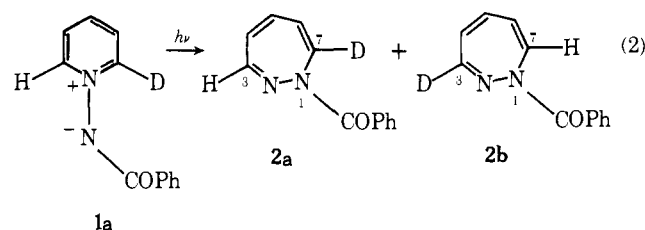
isotope effects in this reaction arising from differences in extinction coefficients of competing isotopic substrates since the competing isotopic reaction sites are in the same molecule. The relative rates at the isotopically substituted centers depend on the localization of the absorbed energy in the 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 manner[9-11] from 2-deuteriopyridine. This precursor, in turn, was made by a precedented 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-

Table I. Isotope Effect Data in the Photorearrangement

$$1a \xrightarrow{h\nu} 2a + 2b$$

NMR[a] measurement symbol	k_H/k_D sample A[b]	sample B[b]
α[c]	0.913	0.908
β[c]	0.906	0.914
γ[c]	0.914	0.912
δ	0.912	
ϵ	0.910	
	av 0.911	av 0.911

overall average, k_H/k_D = 0.911 ± 0.003

[a] A Bruker HFX-90 NMR instrument equipped with a deuterium probe and Fourier transform was used for D analysis. The kinetic isotope effects were calculated from NMR integrations of the deuterium content at carbons 3 and 7 of the diazepine products using a Fourier transform procedure. Deuterium signals at 0.070 and −0.918 ppm relative to $CDCl_3$ were integrated over a 500-Hz sweep by signal averaging over 512 pulses using a 4.2-s delay between pulses and a 4K FID. The upfield signal at −0.918 ppm was assigned to the C-7 deuterium and that at 0.070 ppm to the C-3 based on a comparison with analogous diazepines (T. Sasaki, K. Kanematsu, A. Kakehi, I. Ichikawa, and K. Hayakawa, *J. Org. Chem.*, **35**, 426 (1970)). [b] The ratios of deuterium content (at C-3 to C-7) for each of the samples of product (eq 2) follow: sample A, ~30% reaction; sample B, ~60% reaction. [c] The Fourier waves from measurements α, β, and γ were reprocessed 15 times each. The values given are an average of all these data processing trials.

pyridinium ylides cannot be due to an isotope absorption effect,[4,5] or to be a consequence of the invalidity of transition-state theory applied to primary photoprocesses.[6] Rather, these results provide the basis for a general criterion and a method of detecting the occurrence of thermally activated steps in a photoreaction process, while characterizing the nature of the thermal transition state and possible reaction intermedaites through kinetic isotope effect measurements.[12] In the present instance the large, inverse, secondary deuterium isotope effect observed is indicative of a thermal transition state in which the carbon seat of rearrangement is increasing its covalency. An intermediate Y (as depicted in eq 1) closely resembling this transition state and having the structure of **3** is fully supported by the kinetic isotope effect data.

3
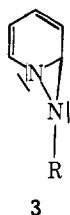
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Identification by Means of Heavy-Atom Isotope Effects of a Photoactivated Reaction as a Ground-State Process

Sir:

Ullman[1] has cogently advocated the argument that the vibrational energy in a structure arising from an electronically excited state via an isoenergetic crossing could be localized in those bonds most affected by the electronic configuration change. Such photochemical reactions behave as though they were regulated by the activation energies of parallel thermal reactions.[2,3] Consequently, if a photoinduced reaction process were of this nature, it should be possible to treat it in the context of transition state theory as a thermal reaction.[4] In a previous article[5] the finding of a secondary deuterium isotope effect has been invoked for testing a photorearrangement presumed to take place via a crossing from a low-lying electronic to a vibrationally excited ground state of the reactant. A heavy-atom isotope effect study has now been carried out in the interests of establishing the kinetic isotope effect as a general criterion for identifying photoactivated, thermal processes of this nature, while obtaining direct characterization of the transition-state structure.

In the usual photochemical process, activation to the excited state through which reaction passes involves a significant alteration in the electronic configuration of the substrate. In such cases the electronic partition functions of isotopically related bonds, involved in the bond making and breaking in the transition state, are taken to be nearly identical. Moreover, any differences in their vibrational partition functions arising in the course of photoactivation *cannot* ordinarily be anticipated on the basis of transition-state (TS) theory,[4] as is the case in purely thermal activation processes. It is therefore considered unlikely that such photochemical reactions would exhibit a measurable heavy-atom isotope effect. The latest compendium on the subject of isotope effects in organic chemistry[6a] bears out this expectation, in that it offers no example of photochemical change in which the occurrence of such an isotope effect is found to be of mechanistic interest.[6b]

The photoinduced rearrangement of 1-iminopyridinium ylides (**1**) has been presumed to proceed via the 1,7-diazanorcaradiene (**2**) by electrocyclization of the aromatic 1,3 dipole of **1**, followed by a thermally allowed disrotatory rearrangement to the (1*H*)-1,2-diazepine (**3**).[7] In general, chemical