Table I. Isotope Effect Data in the Photorearrangement

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

NMR[a] measurement symbol	k_H/k_D sample A[b]	k_H/k_D 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, $k_H/k_D = 0.911 \pm 0.003$		

[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.[1,2] 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

Acknowledgment. We are grateful for very valuable exchanges with Dr. David F. Eaton which were of great aid in the preparation of this manuscript. This work is dedicated to Professor Egbert Havinga of the Gorlaeus Laboratoria of Leiden on the occasion celebrating his attainment of emeritus status.

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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

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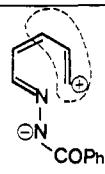
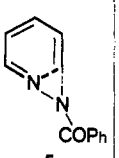
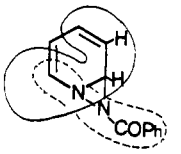
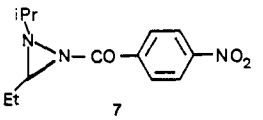
Table I. Calculated Isotope Effects

Transition State Model	 4 Dissociative	 5 Concerted	 6 Associative[b,c]
Effective Mass Model	(26 + C)---14		(40 + 2C)···(C + 133)
Estimated[a] k_{12}/k_{13}	1.0637[13] Value assuming full dissociation in TS.	1.0253	0.9869 Value assuming full bonding in TS.
Experimental			0.9876 ± .0018

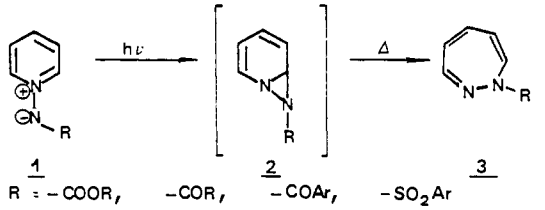
[a] Not corrected[17,18] for the naturally abundant ^{15}N. [b] The curved lines, both dotted and continuous, are intended to delineate the atoms encompassed on both sides of the critical bond of the model used in computing the effective mass ratio according to the cut-off procedure.[10] [c] The ^{12}C-N stretch frequency required for the cut-off calculations and for calculation of the ^{13}C-N frequency was (estimated 853 cm^{-1}) based on Raman spectral measurements of the model compound **7d**. [d] We are greatly obliged to Professor Harold Hein for providing a generous sample of **7** on which the Raman measurements



7

were carried out. The frequency assignment is consistent with typical values for C-C and C-N stretching frequencies in cyclopropanes and aziridines.[19]

trapping and/or observation of **2** as a transient species in flash photolysis has not succeeded.[8] It has also been shown[9] that the photoexcited state which is the precursor of **3** is a singlet and that triplet states lead to decomposition products.



1 **2** **3**

R = -COOR, -COR, -COAr, $-SO_2Ar$

The Bigeleisen-Mayer equation[10] derived from transition-state theory allows us to calculate the magnitudes of the relative rates of reaction for the light (k_L) and heavy (k_H) isotopes of an element at the seat of a thermal reaction in each of three possible structures of the activated complex, i.e., the values of k_{12}/k_{13}, respectively, in an associative, a concerted, and a dissociative transition state when ^{13}C replaces ^{12}C at the carbon center undergoing bond making and breaking in the photoisomerization of **1** to **3** (where R = benzoyl).

For purposes of the "cut-off" method[11] (see Table I) employed for calculating the k_{12}/k_{13} in the dissociative mechanism, it was assumed that this transition state resembled a zwitterionic species (**4**) or an analogous diradical (triplet or singlet) without effect on the calculated result. The model for the concerted process depicted as **5** was the basis for computing k_{12}/k_{13} when the carbon seat of reaction was half-bonded to each of the two nitrogen centers. The transition state for the associative mechanism was assumed to resemble the possible

Table II. Experimental Isotope Effects[a]

R_H/R_L[b]	$-\ln(R_H/R_L)$	f[c]	$-\ln(1-f)$	exptl K_{12}/k_{13}
0.5244	0.6455	0.443	0.585	0.9874 ± 0.0018
0.5219	0.6503	0.663	1.088	0.9889 ± 0.0018
0.5188	0.6562	0.773	1.483	0.9879 ± 0.0024
0.5131	0.6672	0.860	1.966	0.9853 ± 0.0015
0.5127	0.6681	0.923	2.564	0.9884 ± 0.0015
			av	0.9876 ± 0.0018

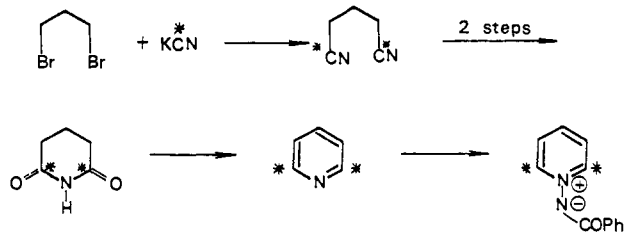
[a] Calculated from the data in accordance with the derived relationships

$$k_H/k_L = \frac{\ln(R_{A_f}/R_{A_0})}{\ln[(1-f)(1+R_{A_0})/(1+R_{A_f})]} + 1$$

$$\ln(R_H/R_L)_f = (k_H/k_L - 1)\ln(1-f) + \ln(R_H/R_L)_0$$

where $R_{A_f} = R_H/R_L$ at f, and $R_{A_0} = R_H/R_L$ at $f = 0$. A least-squares calculation based on a plot of $\ln(R_H/R_L)_f$ vs. $\ln(1-f)$ affords a values of the straight-line intercept, $-\ln(R_H/R_L)_0$, from which it was computed that $(R_H/R_L)_0 = 0.5283$. This treatment eliminates all contributions to the isotope effect due to any possible isotopic fractionation in sample handling and eliminates the need to correct for ^{13}C and ^{2}H of natural abundance in the rest of the substrate. A measured value of R_0 was not considered since such a result could bias the computed results. The isotope effect may also be obtained from the slope of the plot to give identical results. [b] The ratio of the intensities of the parent peaks two mass units apart in the mass spectrometer, each value representing the average of 20 000 determinations. [c] The fraction of reactant converted to photoproduct.

Scheme I



intermediate **2** in which the carbon center was fully bonded to each of the nitrogens. It could be expected, however, that the experimental value would be slightly higher than the calculated since full bonding is not to be realized in a TS resembling **2.**

The isotopically (^{13}C) labeled substrate **1** was synthesized by the procedures outlined in Scheme I. When samples of a mixture of labeled and unlabeled substrate **1** were subjected to wide-band photoexcitation to bring about various degrees of conversion to the photoproduct **3,** the unreacted material could be recovered nearly quantitatively. The extent of change in isotopic content in the starting and recovered substrate for each degree of conversion was estimated by means of the high-precision, mass-spectrometric technique previously developed for measurement of heavy-atom isotope effect.[12]

Table II presents a compilation of the data obtained in these experiments. Clearly, the inverse isotope effect, which corresponds to the experimental results obtained ($k_{12}/k_{13} = 0.9876 \pm 0.0018$), is indicative of the greater bonding preference for the heavier isotope; it is to be reconciled only with the associative mechanism. For cases in which bond rupture of any degree is proceeding in the transition state, k_L/k_H will always be greater than unity.[13] The calculated quantities listed in Table I provide the basis for an understanding as to how far removed the interpretation of the results can be from the possibility of experimental error. In point of fact, moreover, an inverse heavy-atom isotope effect is extremely rare[13] and its finding in the present instance must be regarded as strong evidence of the occurrence of the diazanorcaradiene intermediate which has previously eluded identification by more direct methods.[8]

One apparent reservation which may be held with respect to the interpretation of the results (Tables I and II) arises from

the possibility that the isotopic molecules of **1** (^{12}C and ^{13}C) can be expected to exhibit slightly different extinction coefficients at some wavelengths of the irradiating beam, i.e., the selective excitation of a specific absorption band associated with one isotopic species to the exclusion of the others. An example of this is Hochstrasser's tetrazine photolysis[14] in which laser excitation of a band width of 0.6 cm^{-1} was used to selectively populate the 0-0 band of the n-π^* state of $^{12}C\ ^{14}N_4H_2$ in an argon matrix at 4 K, with no coabsorption by undesired species occurring. However, the overall effect on total energy in this case is really exceedingly small; only 0.05-kcal/mol energy difference is noted for [^{13}C]tetrazine compared with the ^{12}C species, with an energy of the lowest excited state near 50 kcal/mol, so that the total perturbation of the vibronic energy was only 0.1%. Moreover, such an effect would be operating in the opposite direction to the inverse isotope effect observed since the lighter isotope is usually associated with the higher extinction coefficient. For all these reasons, therefore, it can be assumed with confidence that, with the use of wide-band excitation in the photorearrangement under consideration, an isotope absorption effect on the magnitude of the kinetic isotope effect would not be discernible.[15,16]

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(15) A referee has kindly pointed out that we may have observed a magnetic isotope effect resulting from a singlet to triplet crossing.[16] This is unlikely in view of the fact that the triplet state leads to photolytic N-N bond cleavage rather than diazepine.[9] Under the reaction conditions employed in this work only the latter is formed. Moreover, this conclusion is confirmed by the results reported in the previous article.[5] Therein, an inverse secondary deuterium isotope effect ($k_H/k_D \ll 1.0$) was found, contrary to the normal isotope effect ($k_H/k_D \gg 1.0$) to be expected for a mechanism involving crossing to the triplet state; see N. J. Turro, "Molecular Photochemistry", W. A. Benjamin, New York, 1965, p 70.
(16) The origins of a magnetic isotope effect, which could conceivably give rise to an inverse value of k_{12}/k_{13}, have been discussed in several recent articles: (a) A. L. Buchachenko, *Russ. Chem. Rev. (Engl. Transl.)*, **45**, 375 (1976); (b) R. Z. Sagdeev, K. M. Salikhov, and Yu. M. Molin, *Ibid.*, **46**, 297 (1977); (c) R. Z. Sagdeev, T. V. Leshina, M. A. Kamkha, O. I. Belchenko, Yu. N. Molin, and A. I. Rezvukhin, *Chem. Phys. Lett.*, **48**, 89 (1977); (d) N. Hata, *Chem. Lett.*, 547 (1976). However, these reports clearly demonstrate experimentally that a mechanism involving singlet crossing to triplet shows a normal rather than the inverse isotope effect found here.
(17) A nitrogen isotope effect correction was not made because this is a *maximum* calculated value of the isotope effect. A correction for the isotope effect of naturally abundant ^{15}N (0.37%) would have resulted in a very slightly lower magnitude.
(18) A correction for a naturally abundant ^{15}N isotope effect was not made because this is a minimum value for the dissociative transition state. Such a correction would have led to a slightly greater value of k_L/k_H.
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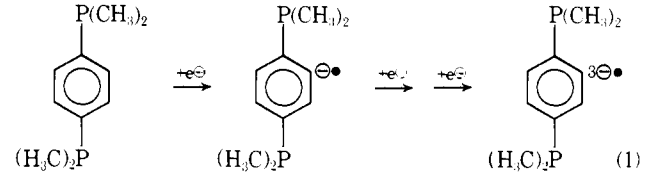
Radical Anion and Radical Trianion of 1,4-Bis(dimethylphosphino)benzene[1,2]

Sir:

Surveying nonmetal compounds with low first ionization potentials as promising radical cation precursors,[3] we observed, much to our surprise, that the title compound rather accepts electrons to form not only the radical anion[4-6] but also the ESR spectroscopically detectable radical trianion[7-11] (eq 1).



(1)

The compound—synthesized via a more convenient odorless route[12]—exhibits in the low energy region of its photoelectron spectrum four ionizations (Table I). Comparison with those of the π isoelectronic tetramethyl-*p*-phenylenediamine reveals that (i) the first ionization energy of the phosphorus derivative is too high ($IE_1 > 8$ eV) to obtain the corresponding radical cation[1-3] in solution and (ii) dimethylamino substituents exercise a much larger perturbation of the benzene π system ($IE_1 = 9.24$) than $(H_3C)_2P$ groups, inductively ($\Delta IE = 9.24 - IE_3$) as well as by conjugation ($\Delta IE = IE_2 - IE_1$ or $\Delta IE = IE_4 - IE_3$).

The relatively poor donor effect of dimethylphosphino substituents in benzene π radical cation states (Table I) led to the expectation that, on the other hand, they might stabilize the π radical anion states—analogously to the phosphorus substituted π systems[4-6] or to numerous other known species with third row elements groups, e.g., like R_3Si[13] and contrary to R_2N substituents.[14] Electrochemical reduction in a solution of $R_4N^+BF_4^-$ in RCN mixtures or reaction with Na or K in ethers under addition of dicyclohexyl-18-crown-6 yielded the ESR spectrum of the radical anion (Figure 1, A with simulation B). Prolonged contact with the alkali metal without addition of any complexing reagent generated finally the radical trianion (Figure 1, C with simulation D). Both ESR spectra exhibit 195 signals due to sets of each 2-, 4-, and 12-equiv nuclei with nuclear spin $I = 1/2$, but different (temperature dependent[2]) coupling constants (Table II).

The different spin populations in the radical anion and the radical trianion can be discussed using the squared HMO coefficients of an 8-center π system modified for the phos-

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