Table II. Kinetic α-Deuterium Isotope Effects for the Addition of Semicarbazide and Phenylhydrazine to Substituted Benzaldehydes in Aqueous Solution at 25.00° [a]

Nucleophilic reagent	Catalyst	Substrate *p*-Methoxy	 *m*-Bromo	 *p*-Nitro
Semicarbazide	Hydrated proton[b]	1.216 ± 0.006	1.218 ± 0.004	1.154 ± 0.013
	Water[c]	1.310 ± 0.004	1.288 ± 0.005	1.293 ± 0.009
Phenylhydrazine	Hydrated proton	1.208 ± 0.010		1.126 ± 0.007
	Water	1.276 ± 0.011		1.163 ± 0.006

[a] Errors are given as the standard deviation of the mean of three determinations. [b] Isotope effects for the proton-catalyzed reaction were measured near pH 2. Under these conditions, neither the water reaction nor the rate of carbinolamine dehydration contributes significantly to the overall reaction rate. [c] It is impossible to choose values of pH for the measurement of isotope effects for the water reaction at which other reactions do not make significant contributions to the overall rate. Since the measured isotope effects for the proton-catalyzed attack reaction and the proton-catalyzed dehydration of the carbinolamine are both smaller than the effects measured for the water reaction, the recorded values are minima.

It proved impossible to choose values of pH at which the water-catalyzed attack reaction could be measured independently; generally both the acid-catalyzed attack of the nucleophile and the acid-catalyzed dehydration of the carbinolamine contributed significantly to the observed rate constants even at the optimal values of pH. Consequently, the indicated isotope effects for the water-catalyzed reactions are *minimum* values.

Employing the secondary deuterium isotope effects as indicators of the degree of progress toward tetrahedral geometry (*i.e.*, the extent of carbon–nitrogen bond formation), one may draw the following conclusions. First, the extent of progress along the reaction coordinate at the transition state decreases with (i) increasing substrate reactivity, (ii) increasing reactivity of the nucleophilic reagent, and (iii) increasing acid strength of the catalyst. These observations are all consistent with theoretical expectations[11,12] and with conclusions drawn earlier on the basis of less direct lines of evidence.[2,3,9,10] Second, in the case of the water-catalyzed reactions, it is possible that proton transfer may contribute significantly to the overall rate of carbinolamine formation. This is suggested by the fact that the kinetic isotope effects are nearly as large as the equilibrium ones, indicating that carbon–nitrogen bond formation is nearly complete in the transition state (Tables I and II). This conclusion is, of course, consistent with the observation of general acid catalysis for the attack of nitrogen nucleophiles on carbonyl carbon.[2,3] Third, the smaller kinetic isotope effects for the proton-catalyzed reaction indicate that this is not a diffusion-controlled reaction of the proton with an addition intermediate.

Finally, the kinetic α-deuterium isotope effect for semicarbazone formation in the region of rate-determining acid-catalyzed carbinolamine dehydration has been determined: for *m*-bromobenzaldehyde k_D/k_H is 1.271 ± 0.009 and for *p*-methoxybenzaldehyde the corresponding quantity is 1.287 ± 0.015. These values, too, are near the maximum expected indicating that the transition state for carbinolamine dehydration has a nearly tetrahedral geometry.[13] These results accord with earlier findings of large secondary deuterium isotope effects for attack of water and hydroxide ions on protonated Schiff bases.[14] Consequently, it appears possible that, for some cases at least, proton transfer reactions involving interconversion of the various forms of the carbinolamine intermediates partially determine the reaction rate under neutral and basic conditions.

Acknowledgment. Professor V. J. Shiner, Jr., has materially contributed to these studies through his generous advice and guidance concerning the measurement and interpretation of secondary deuterium isotope effects.

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Influence of Ion Pairing on Intramolecular Electron-Transfer Rates in the Anion Radical of 1,2-Di(9-carbazyl)ethane

Sir:

Over the past several years there have been a number of investigations into the modification of the magnetic properties of anion radicals by ionic association.[1,2] Both the structure and the dynamic behavior of ion pairs have been elucidated using magnetic resonance techniques, *e.g.*, splitting due to the cation,[3] line broadening,[4] selective line width effects,[5] and minor changes in proton hyperfine coupling constants and *g* values.[6] Observation of these various phenomena can be taken as proof of the existence of ion pairing but the converse is not necessarily true. In this communication we report the esr spectra of the anion radicals of *N*-ethylcarbazole (**1**) and 1,2-di(9-carbazyl)ethane (**2**) in tetrahydrofuran (THF) and 1,2-dimethoxyethane

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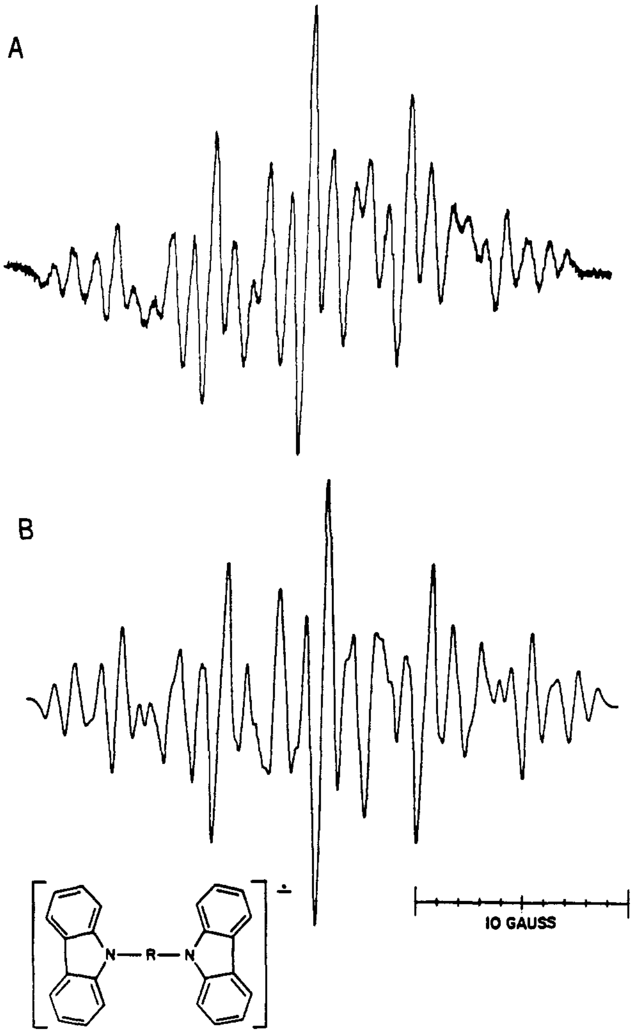

Figure 1. Esr spectrum of **2** in THF (A), −60°, and (B) a computer simulation with $\nu_e = 7.5 \times 10^5$ sec^{-1} and a line width of 0.159.

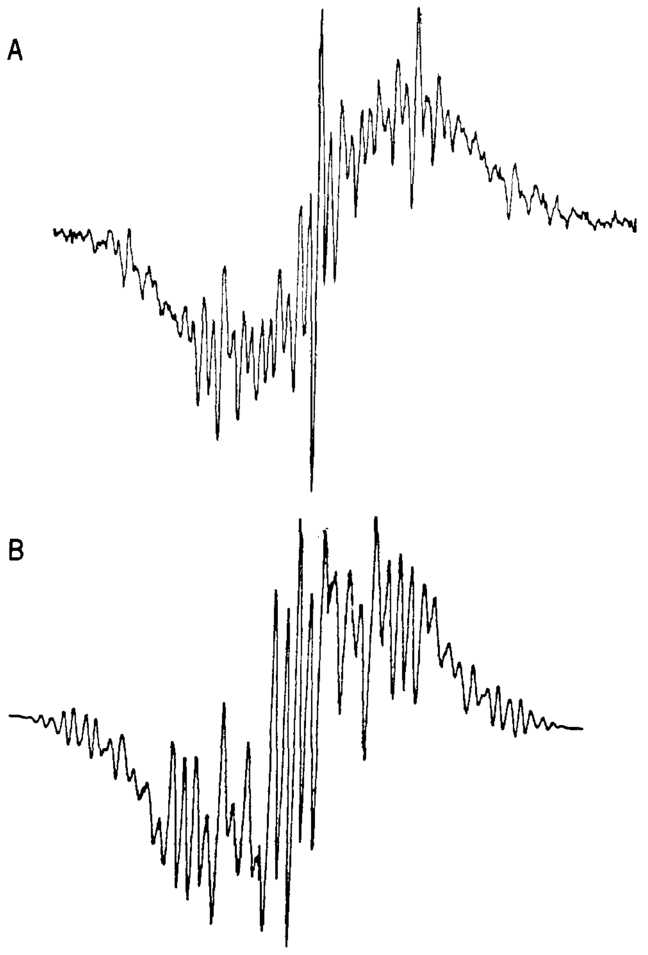

Figure 2. Esr spectrum of **2** in DME (A), −60°, and (B) a computer simulation with $\nu_e = 1 \times 10^7$ sec^{-1} and a line width of 0.159.

(DME). In the esr spectrum of the anion radical of **1** it is not possible to detect hyperfine coupling to the counterion, ^{39}K, which has a nuclear spin $^3/_2$, in either THF or DME. From the esr spectrum of the anion radical of **2** it is possible to determine the rate of transfer of magnetization between the two carbazole rings, and it is observed that the exchange is approximately an order of magnitude greater in DME than in THF.

The anion radicals of **1** and **2** were prepared using standard procedures by contacting the respective solutions with a freshly distilled potassium mirror. The esr spectrum of **1** in THF or DME can be simulated with four sets of two equivalent protons with hyperfine coupling constants 5.045, 4.675, 2.228, 0.915 G and one nitrogen with 0.117 G and a line width of 0.15 G.

The esr spectrum of **2** in THF is reproduced in Figure 1A and in DME in Figure 2A. The simulated spectra, Figures 1B and 2B, were calculated using a program of the format described by Harriman and Maki[7] taking into consideration the exchange of magnetization between the two ring systems. Within the exchange range $5 \times 10^5 < \nu_e < 10^8$ sec^{-1}, the esr spectra change appreciably and a matching with the experimental spectrum provides an estimate of ν_e. Although an exact matching is not always possible, it is relatively easy to establish a value for ν_e where the principal features of the spectra are closely simulated. Any minor discrepancies that occur result from the sensitivity of the calculated spectrum to small changes in line width and exchange frequency. The simulated spectra, Figures 1B and 2B, which most closely match the experimental spectra, were calculated using ν_e values which differ by an order of magnitude; *i.e.*, the exchange rate is faster in DME than in THF.

The factors which control ν_e in the anion radicals of a series of diarylalkanes have been discussed previously.[8] The value of ν_e is exponentially dependent on the "self trapping energy," E_0, between the electron and the ring and

$$E_0 = S_0 + S_0'$$

where S_0 is the solvation energy term and S_0' is the electron vibration interaction. The dielectric constants for THF and DME at −60° are 10.98 and 11.05, respectively,[9] and, therefore, E_0 and hence ν_e should be the same for the two solvents. The smaller value of ν_e observed in THF can be explained by an ion-pairing effect since E_0 would then contain an additional term proportional to the electrostatic interaction between the ^{39}K cation and the carbazole ring; a contri-

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bution to E_0 of approximately 2 kcal/mol would account for the order of magnitude difference in the exchange rates. Gerson[10] has shown that the unpaired electron can move between the two rings in the paracyclophane radical anion on a time scale which is fast compared to the motion of the counterion. In intermolecular electron-transfer processes, the electron-transfer and counterion-transfer processes are assumed to coincide with one another.[11,12] The observations reported in this communication lead to the conclusion that the electron-transfer rate in these more weakly interacting systems is very sensitive to the structure and energetics of the ion pair and is more strongly coupled to internal rearrangements than in the case of the paracyclophanes.

The inability to observe the metal splitting may be related to the preferential association of the ^{39}K cation with the nitrogen position in the carbazole ring. Examination of the Hückel coefficients for the carbazole molecule (calculated using the heteroatom parameters of Streitwieser[13]) reveals a large excess charge density but an extremely small unpaired spin density at the nitrogen. This is fully consistent with the interpretation of the esr spectrum of **1**.

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Reactivity of Geometrically Constrained Cyclopropylcarbinyl Systems

Sir:

As a result of the many detailed solvolytic studies designed to generate cyclopropylcarbinyl cations,[1–8] numerous structures invoking varying degrees of delocalization have been proposed to account for the specific interactions required or suggested by the various rate enhancements and rearrangements observed in the particular systems studied. Thus, bicyclobutonium,[5] tricyclobutonium,[8] bisected or symmetrical[2] and unsymmetrical[6] homoallylic, and delocalized cyclobutyl[4,7] (symmetrical bicyclobutonium) ions have been proposed.

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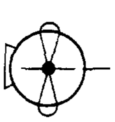
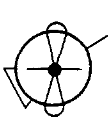
An alternative view arises from consideration of the energy or stabilization of the cyclopropylcarbinyl cation solely (or predominantly) as a function of the angle of rotation of the cyclopropyl group against the planar carbinyl cation; that is, as a function of overlap of a p orbital with the rich in p character exocyclic cyclopropane ring orbitals.

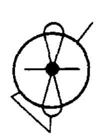
It is generally conceded that the bisected conformation **1** of the cation is the most stable,[9] molecular orbital calculations indicating extremes of stabilization of 9–26 kcal/mol between the bisected (**1**) and perpendicular (**4**) conformations.[2b] Cyclopropylcarbinyl cations in which the bisected conformation is precluded for steric reasons have been observed to have decreased stability.[10,11]



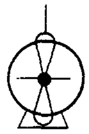
0°
(bisected)
1



30°
2



60°
3



90°
(perpendicular)
4

Recent studies have shown that the perpendicular conformation **4** results in strong *destabilization* of the cation.[2b,d,3a,b] However, there have been no studies of systems in which the ions must be geometrically constrained to conformations in between the bisected (**1**) and the perpendicular (**4**) such as **2** and **3** (30 and 60° off-bisected, respectively). To this end we have synthesized and report preliminary results of studies on the solvolyses of two bridgehead cyclopropylcarbinyl systems, 1-tricyclo[3.2.2.0^{2,4}]nonanyl tosylate (**7-OTs**) and *exo*-1-tricyclo[3.3.1.0^{2,4}]nonanyl 3,5-dinitrobenzoate (**6-ODNB**).

Bridgehead systems were chosen for this study because they are tertiary and hindered from the backside and undergo solvolysis by a limiting mechanism.[12] The bicyclic framework is sufficiently rigid that the carbonium ions formed should have very nearly the same geometry as the initial state. Rearrangements to homoallylic ions[13] or to cyclobutyl derivatives are precluded due to the resultant increase in strain. Rearrangement to another cation can thus have no effect on the reactivity of these cyclopropylcarbinyl compounds.

The tertiary bridgehead alcohol, **7-OH**, was prepared from 1-cyclohexa-1,3-dienyl acetate *via* a Diels–Alder reaction with cyclopropene.[14] Hydrolysis of the adduct followed by hydrogenation on Pd/C gave the alcohol **7-OH**.[15] The tosylate **7-OTs** was prepared according to the method of Coates and Chen.[16] The resulting white crystalline tosylate rapidly turned red at room temperature and became a red oil within a few minutes. Acetolyses were carried out using standard

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