the HOMO polarization is accentuated, while that of the LUMO is decreased. Here the π_{CN} influence on both orbitals increases. Once again, the contributions of the cyano group to the HOMO and LUMO in various models prove the validity of this explanation.

The results not only indicate that the cyano group can act as a donor in cases of extreme electron demand (at least where HOMO polarization is concerned), but removes the uncertainty as to the "true" HOMO polarization in unsymmetrical electron-deficient alkenes.[20] As an electrophile approaches such a species, the less substituted terminus gains electron density and is, therefore, the predicted site of attack by electrophiles.[21]

Secondary orbital interactions[22] are also expected to influence regioselectivities of cycloadditions when primary interactions provide little preference for one regioisomer. For example, a nucleophile attacking the substituted carbon of propene will experience repulsive secondary orbital interactions with the hydrogen orbital part of the LUMO. This further reduces the "effective" LUMO coefficient at the substituted carbon. Similarly, an electrophile attacking the substituted carbon of acrylonitrile will experience a destabilizing secondary orbital interaction with the carbon of the cyano group. In the cases under consideration, these effects reinforce the "reversal" of polarization discussed earlier.

By contrast, alkenes substituted by donors such as alkoxy or amino groups, which lack π acceptor orbitals, cannot experience the reversal of polarization demonstrated here for methyl substituted alkenes. If polarization reversal is most important, then reactions such as 1–3 with RO or R_2N substituents instead of Me will give meta orientation, since the LUMO will have the larger coefficient at the substituted carbon. If secondary orbital interactions dominate, these substituents will direct attack of nucleophiles to the more remote carbon, and ortho or para orientation will still be observed. Such an experimental test is in progress.

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Simultaneous Observation of Nuclear Spin Polarization and Line Broadening. Evidence for an Alternative Polarization Mechanism

Sir:

We report the simultaneous observation of chemically induced nuclear spin polarization and of line broadening during the ultraviolet irradiation of m-fluoro-α,α,α-trifluoroacetophenone (K) in the presence of 1,4-dimethoxybenzene (Q). Both effects are ascribed to the intermediacy of radical ions, $K^-\cdot$ and $Q^+\cdot$, generated by electron transfer from Q to photoexcited K. The quencher concentration dependence of the
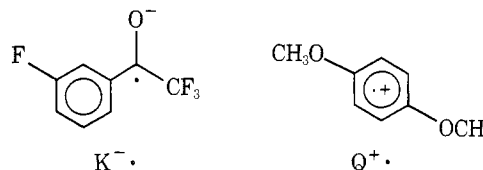
two effects is substantially different: the spin polarization shows a maximum near $[Q] = 10^{-1}$ M, whereas the broadening is optimized near $[Q] = 6 \times 10^{-3}$ M. We interpret these findings as evidence for two nonidentical precursors for the radical ions: the triplet state of the ketone, ^3K, and an electron spin polarized state, $^3K^{\ddagger}$, respectively. This assignment implies an alternative spin polarization mechanism, the photo-triplet-Overhauser mechanism.[1,2]

The observation of CIDNP effects in photoinitiated electron-transfer reactions is well established.[3,4] In several donor–acceptor systems, illumination results in line broadening.[3c-e,4] Occasionally, both effects are observed simulta-
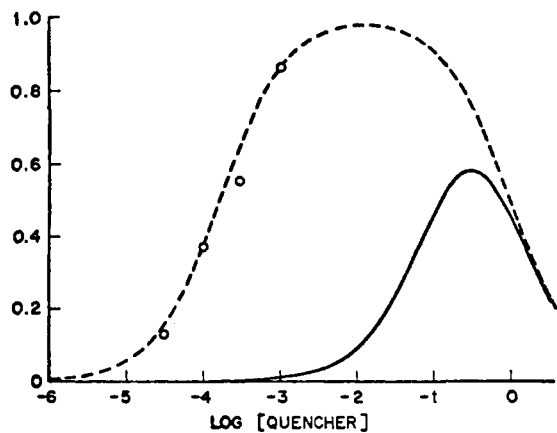
Figure 1. Probabilities of radical ion-pair formation in the quenching of the electron-spin polarized triplet state (solid curve) and of the equilibrated triplet state (dashed curve) of m-fluoro-α,α,α-trifluoroacetophenone by dimethoxybenzene. The points represent relative CIDNP *emission* intensities observed in acidic solutions.

Figure 2. ^{19}F NMR spectra (56 MHz) observed during the irradiation of m-fluoro-α,α,α-trifluoroacetophenone (0.06 M) in acetonitrile in the presence of varying concentrations of dimethoxybenzene.

neously. The significance of the results reported here follows from an analysis of the parameters determining the CIDNP signal intensity and the degree of line broadening, respectively.

Most CIDNP effects[5] originate in radical (ion) pairs;[6] their magnitude is proportional to the concentration of pairs, e.g., $[K^-\cdot\ Q^+\cdot]$. Line broadening effects can be ascribed to degenerate exchange reactions between radical ions and their diamagnetic precursors;[3c-e,7] the extent of line broadening, ΔT_2^{-1}, is proportional to the steady-state concentration, $[K^-\cdot]$, of the radical ions involved in the exchange.[7] The concentration of both, ion pairs and free ions, should be directly proportional to the fraction, T, of photoexcited molecules which are quenched by an electron-transfer mechanism. Consequently, one expects the degree of line broadening and the magnitude of radical-pair induced spin polarization to show parallel trends as T is varied.

The probability of triplet quenching, T, is given by[2b]

$$T \propto \frac{^3k_q[Q]}{^3k_q[Q] + ^3\tau^{-1}} \times \frac{^1\tau^{-1}}{^1k_q[Q] + ^1\tau^{-1}} \qquad (1)$$

where $^1\tau$, $^3\tau$, and ^1k_q, ^3k_q are the lifetimes and quenching rate constants for the excited-singlet and triplet states, respectively. The quencher concentration dependence of this probability is shown in Figure 1 (dashed curve) for the following parameters: $^1\tau$ was assumed to be 10^{-10} s and ^3k_q and $^3\tau$ were assumed to have similar values as those measured by Wagner and co-workers[8] ($^3k_q = 10^{10}$ L mol^{-1} s^{-1}; $^3\tau \approx 6 \times 10^{-6}$ s) for the analogous reaction of α,α,α-trifluoroacetophenone. This curve has a maximum close to the quencher concentration where maximum broadening is observed (Figure 2).

In contrast, the spin polarization follows a different quencher concentration dependence; it has a maximum at quencher concentrations more than an order of magnitude higher than those resulting in maximum broadening and vanishes at quencher concentrations below 10^{-2} M. To account for this failure of the CIDNP effects to follow the relative yield of radical-ion formation we consider accelerated spin-lattice relaxation due to the presence of the paramagnetic ions. However, the steady-state concentration, $[K^-\cdot]$, which can be derived from ΔT_2^{-1}, does not appear to be high enough to affect the relaxation time. In the system K–Q, the broadening showed a positive temperature coefficient; therefore, it should fall into the strong pulse limit where $\Delta T_2^{-1} = k_e [K^-\cdot]$. Given a rate constant of exchange, $k_e = 10^8$ L mol^{-1} s^{-1},[9] the maximum line broadening, $\Delta T_2^{-1} = 7$ Hz (observed at $[K] = 6 \times 10^{-2}$ M, $[Q] = 6 \times 10^{-3}$ M), indicates a radical-anion concentration, $[K^-\cdot] < 10^{-7}$ M, far short of the concentrations
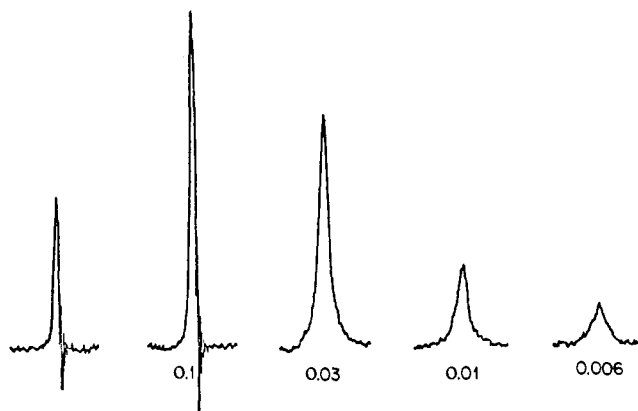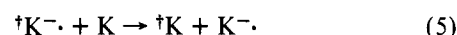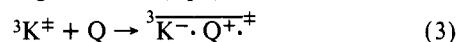
which could affect T_1.[10]

Consequently, we assign the concentration dependence of the CIDNP effects to the involvement of a precursor with a considerably shorter lifetime than the triplet state of K. We suggest that this intermediate is an electron spin polarized triplet state generated by selective intersystem crossing from the initially excited singlet state, $^1K^*$. Spin polarized triplet states have relaxation times in the nanosecond range;[2,11] the probability of quenching such a state is[2b]

$$T^{\ddagger} \propto \frac{^3k_q[Q]}{^3k_q[Q] + ^3T_1^{-1}} \times \frac{^1\tau^{-1}}{^1k_q[Q] + ^1\tau^{-1}} \qquad (2)$$

where $^3T_1$ is the electron spin-lattice relaxation time of the spin polarized triplet state. The probability curve, $T^{\ddagger}$, is shown in Figure 1 (solid curve) for a relaxation time, $^3T_1 = 10^{-9}$ s, and parameters, $^1\tau$ and ^1k_q, as discussed above. The rate constants of quenching the relaxed and the polarized triplets are assumed to be identical. The curve, $T^{\ddagger}$, describes the observed CIDNP intensities reasonably well.

Postulating an electron spin polarized triplet state as the source of the observed polarization implies an uncommon polarization mechanism known as the triplet-Overhauser mechanism. It involves transfer of the electron polarization to a radical ion (eq 3), generation of nuclear polarization via electron-nuclear cross relaxation (eq 4), and fast transfer of this nuclear polarization to a neutral diamagnetic product in a degenerate exchange reaction (eq 5):

$$^3K^{\ddagger} + Q \rightarrow {}^3\overline{K^-\cdot\ Q^+\cdot}^{\ddagger} \qquad (3)$$

$$^{\ddagger}K^-\cdot \rightarrow {}^{\dagger}K^-\cdot \qquad (4)$$

$$^{\dagger}K^-\cdot + K \rightarrow {}^{\dagger}K + K^-\cdot \qquad (5)$$

(Here, † and ‡ denote nuclear and electron polarization, respectively.) The observed signal direction is compatible with this mechanism provided that the cross relaxation is predominantly scalar.[1,2]

The subtle balance between line broadening and nuclear polarization is sensitive to the acidity of the solution.[2,13] The identification of Overhauser-induced polarization is aided by the absence of radical-pair induced polarization. In the system, K–Q, no net product formation occurs; therefore both the "escape" and the "recombination" polarization are transferred to the ketone and cancel each other as long as the lifetimes of the radical ions between exchanges ($\tau = k_e^{-1} \times [K]^{-1} \approx 2 \times 10^{-7}$ s) are shorter than their spin-lattice relaxation times, $^2T_1$ (typically $\geq 10^{-5}$ s).[2,12] In the presence of acid, the ketyl anions will be protonated resulting in decreased exchange rates and increased "lifetimes". Accordingly, the line broadening should be reduced, the fortuitous cancellation of radical-pair polarization should be eliminated, and the Overhauser-induced

polarization should be decreased since the polarization of the ketyl radicals can decay before it is transferred to K. These considerations are borne out by strong, unbroadened emission signals observed during irradiation of K in acidic solutions containing Q. This signal direction is compatible with the radical pair theory (μ, ϵ, $a_{CF_3} > 0$; $g_K > g_Q$), while the signal intensity follows the relative yield of triplet quenching (Figure 1) at quencher concentrations where no CIDNP effects are observed in the absence of acid.

We close with a comment on a recent report by Closs and Czeropski[3f] who eliminated the interference of line broadening by accumulating the NMR data while interrupting the UV irradiation. This technique promises to be exceedingly useful. However, in the unique system K–Q the two effects carry different information: the line broadening reflects the yield of triplet quenching; the spin polarization is evidence for an unusual polarization mechanism. In this special case, elimination of the broadening would destroy essential information.

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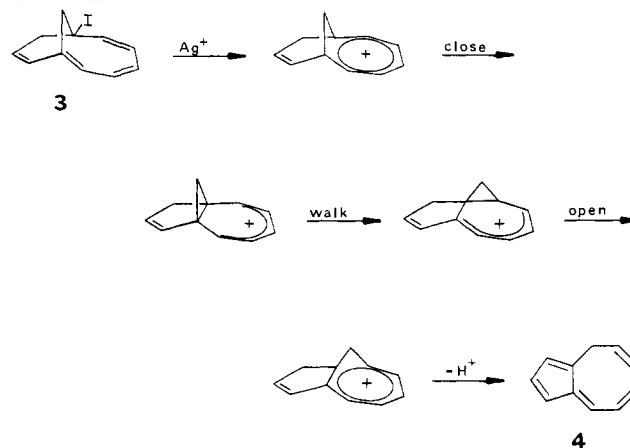## Circumambulatory Rearrangements of 1,7-Bridged Homotropylium Cations

Sir:

Experimental studies by Berson and Jenkins[1] have established that thermal circumambulatory rearrangement of homotropylium cation (Scheme I) must be impeded by an energy barrier ($\Delta F^{\ddagger}$) of *at least* 27 kcal/mol. On the basis of ab initio molecular orbital calculations, Hehre[2] estimates a value of fully 43 kcal/mol for this symmetry allowed process[3] in the parent ion. Temporary disruption of aromaticity has been cited as a possible explanation for this high barrier;[1,2] however, there still remains some disagreement[4] as to whether the "open" structure **1** or the "closed" structure **2** better represents the preferred geometry for homotropylium cation.
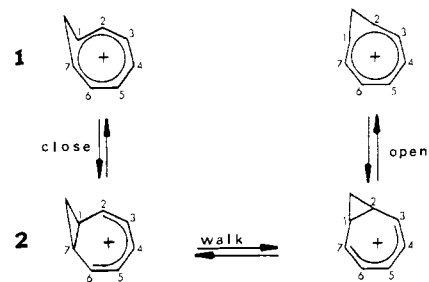
Scheme I

Scheme II

Until this year, the search for ground-state circumambulatory rearrangements in homotropylium cations has gone unrewarded.[1,5] Success was finally achieved by Childs and Rogerson[6] who prepared a homotropylium cation bearing substituents specifically designed to favor circumambulatory rearrangement by *electronic* effects. We have found that *steric* effects can also favor circumambulatory rearrangements in homotropylium cations and herein present evidence to support the following conclusions: (1) Homotropylium cations can be constrained in the closed form **2** by incorporation of an additional three-atom bridge across the homoconjugation gap, i.e., between positions 1 and 7 in **2** (cf. analogously constrained norcaradienes).[7] (2) Circumambulatory rearrangement or "cyclopropane walk" in such closed homotropylium cations is an inherently facile process. (3) The large energy barrier to thermal circumambulatory rearrangement in unconstrained homotropylium cations, therefore, must be associated with the ring-closure step (**1** → **2**, $\Delta F^{\ddagger} > 27$ kcal/mol). (4) It follows, then, that the open structure **1**, rather than the closed structure **2**, better represents the preferred ground-state geometry of unconstrained homotropylium cations.

Our concern with this problem arose inadvertently while exploring synthetic approaches to 1,5-methano[10]annulene.[8] Thus, iodotetraene **3** was prepared[9] and treated with various reagents in an effort to remove the elements of HI. With silver ion (AgOAc, acetone, 25 °C, 15 min) we found that iodide **3** gives pentaene **4**[10] (39% yield), the formation of which might best be explained by the mechanism depicted in Scheme II. Ionization and ring closure may occur either sequentially, as illustrated, or concertedly;[11] however, the subsequent cyclopropane walk[12] must proceed with little difficulty for neither lower temperature (0 °C) nor added base (i-Pr$_2$NEt) suppresses this unwelcomed rearrangement.

An analogous rearrangement was observed on treatment of iodotrienone **5**[13] with mild base (DBN, CHCl$_3$, 25 °C, 5 min). Scheme III outlines a mechanism which could account for the formation of tetraenone **8**[14] in this reaction (85% yield). Presumably, elimination of HI from **5** produces the desired tetraenone **7**, either directly or via **6**, but subsequent proton