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(10) Effects of micelles on electrophilic aromatic substitution products have been reported only once previously: D. A. Jaeger and R. E. Robertson, *J. Org. Chem.*, **42**, 3298 (1977).

(11) At present this explanation is highly speculative.

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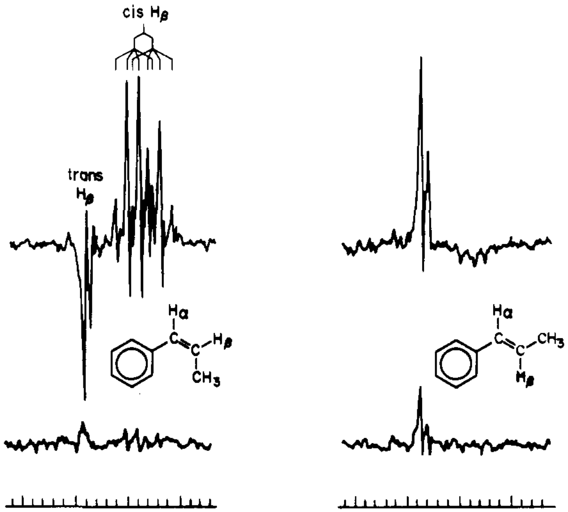
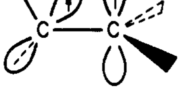


Figure 1. 60-MHz ^1H NMR spectra (olefinic region) observed during the irradiation of tetrachlorobenzoquinone (0.02 M) in acetonitrile-d_3 solutions containing 0.02 M *cis*- (left) or *trans*-1-phenylpropene (right). The reactant olefin and a dark spectrum are shown below each CIDNP spectrum. The aromatic and allylic regions are not shown.

Photosensitized Isomerization of Electron Donor and Acceptor Styrenes. Recombination of Radical-Ion Pairs in the Singlet and Triplet States

Sir:

The light-induced interactions between photosensitizers and olefins may involve a variety of mechanisms including (a) triplet energy transfer to populate the olefin triplet state (**1**), (b) electron transfer to generate olefin radical ions (e.g., **2**) paired with sensitizer derived ions, or (c) addition to form biradicals. (**3**). Magnetic resonance techniques are potentially useful for the study of these reactions: degenerate triplet energy transfer or degenerate electron exchange between a radical ion and its diamagnetic precursor may give rise to line broadening;[1-3] the interaction of radical-ion pairs may induce nuclear[2,3] or electron[4] polarization; finally, the magnetic interactions in biradicals may result in nuclear spin polarization effects.[5] In this communication we discuss CIDNP effects observed during the irradiation of suitable sensitizers in the presence of β-substituted electron donor or electron acceptor styrenes. The effects observed for donor and acceptor styrenes are different indicating two different mechanisms of isomerization.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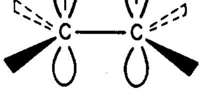
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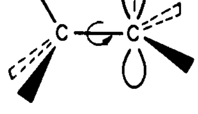
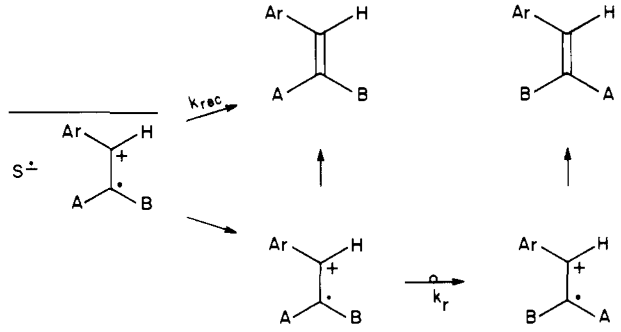


3

The mechanism of donor olefin isomerization is illustrated for the pair tetrachlorobenzoquinone (TCQ), *cis*-1-phenylpropene (*c*-PP). During UV irradiation of this system, the doublet of quartets representing the olefinic proton in the β position and the aromatic signal appear in strongly enhanced absorption (*A*), whereas the methyl doublet appears in emission (*E*); at the same time, the complex olefinic spectrum of the trans isomer (*t*-PP) shows *E* with approximately one third of the intensity of *c*-PP (Figure 1, left).

The effects observed for *c*-PP can be explained on the basis of the radical-pair theory of CIDNP[6] by a mechanism analogous to those of most previously reported cases of radical-ion-pair-induced polarization.[2,3] This mechanism involves electron transfer from *c*-PP to the triplet state of the sensitizer, ^{3}TCB, generating the radical ions, $TCB^{-}\cdot$ ($g = 2.0056$) and $c\text{-}PP^{+}$ ($g = 2.0027$), and reverse electron transfer in this pair to regenerate the reactants in their singlet ground states (μ, $\epsilon > 0$; $\Delta g < 0$). The opposite signal directions of the aromatic and olefinic protons on the one hand and the methyl group on the other hand suggest that the nuclei in the corresponding positions of $c\text{-}PP^{+}\cdot$ have hyperfine coupling constants of opposite sign, $a_{\text{ring}}, a_\beta < 0 < a_{CH_3}$, reflecting the spin density distribution of the radical cation.

The polarization of the isomerized olefin can be explained as originating in the same ion pair where that of *c*-PP is generated ($\mu > 0$; a_β, $\Delta g < 0$). However, the opposite signal direction of *t*-PP suggests an alternative mechanism of product formation ($\epsilon < 0$).[6] A plausible mechanism involves cis–trans isomerization of free-radical cations and electron exchange with the reactant olefin. In this reaction, the "escape" polarization is partitioned between reactant and rearranged olefin according to the extent of rearrangement. The unrearranged ions involved in this reaction will weaken the "in cage" polarization of the reactant styrene.



It follows that the rate of the radical-ion rearrangement (k_r) is crucial: it must be slower than the electron return (recombination) after intersystem crossing (k_{rec}) but competitive with the regeneration of reactant olefin from "escaped" radical ions. A decrease in k_r is expected to result in weaker enhancements of rearranged and reactant olefin: because of a smaller yield of rearranged olefin a larger fraction of the escape polarization would be transferred to the reactant olefin. This prediction is confirmed in the reaction of the trans isomer. Because the trans

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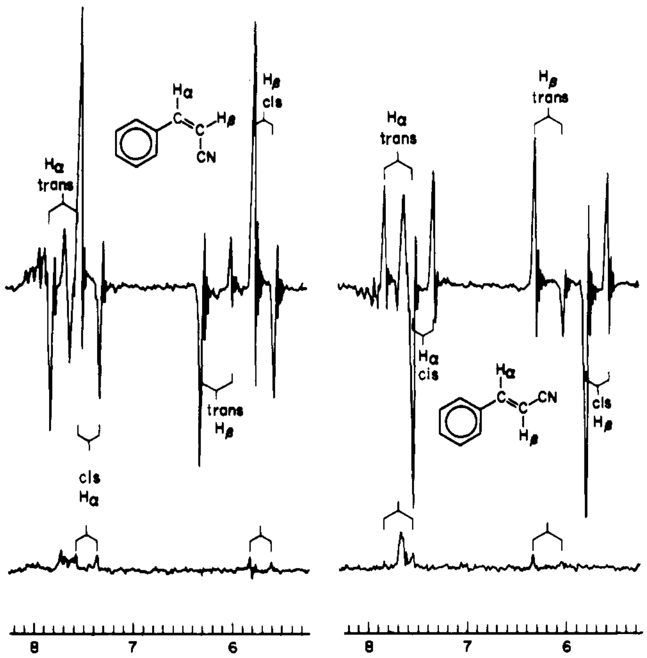


Figure 2. 60-MHz ^{1}H NMR spectra observed during the irradiation of triphenylene (0.01 M) in acetonitrile-d_3 solutions containing 0.02 M *cis*- (left) or *trans*-cinnamonitrile (right). The reactant olefin and a dark spectrum are shown with each CIDNP spectrum.

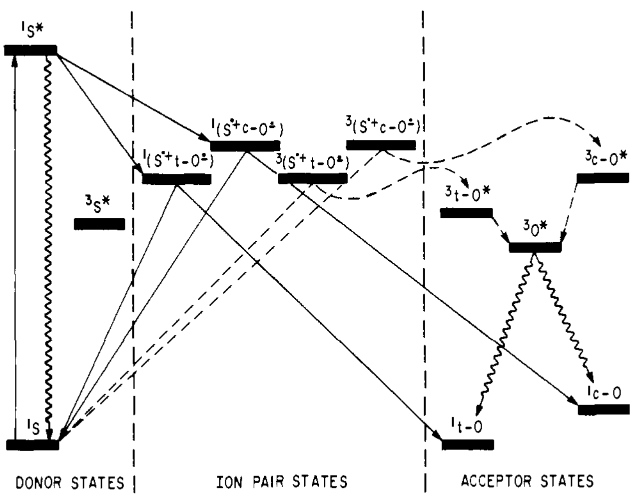
to cis isomerization is endothermic and, therefore, slower than the reverse reaction, the effects observed in this reaction are considerably weaker (Figure 1, right) than those observed in the reaction of *c*-PP.

In summary, the CIDNP effects observed in the electron-transfer-induced isomerization of donor olefins show greater enhancement for the reactant than for the rearranged olefin and higher overall intensities in the reaction of a cis than of the corresponding trans isomer. These effects are compatible with the interconversion of two different radical ions of different energies.

The reaction of acceptor styrenes (cinnamates, cinnamonitriles) with photoexcited electron donors (aromatic hydrocarbons) show principally different features. For example, the irradiation of triphenylene (Tr) in the presence of *cis*- or *trans*-cinnamonitrile (CN) results in strong polarization of the reactant olefin (*A* plus *A*/*E* multiplet effect) as well as the rearranged olefin (*E* plus *E*/*A*). It is evident (Figure 2) that the reactions of cis and trans isomers produce similar overall intensities and that in the reaction of either isomer the enhancement of reactant and rearranged olefin are comparable. These effects are incompatible with the interconversion of two isomeric radical anions; rather, they suggest a single intermediate in the isomerization.

The polarization of the reactant olefins is that expected for electron transfer from ^{1}Tr* to CN ($\mu < 0$) and reverse electron transfer to regenerate the reactants in their ground states ($\epsilon > 0$); in this assignment we assume that $CN^{-}\cdot$ has negative hyperfine coupling constants in the α and β positions ($a < 0$) and a g factor slightly larger ($\Delta g > 0$) than that of $Tr^{+}\cdot$ (2.0027).[7] The polarization of the rearranged olefins is formally that of free-radical products ($\epsilon < 0$), but the apparent efficiency of polarization transfer to the products suggests a different mechanism. We note that the free energy of the radical-ion pairs[8] is higher than the triplet energy of the acceptor styrenes[12] and we invoke recombination of triplet ion pairs to generate the triplet state, ^{3}CN, along with the ground state of Tr. The crossover to the rearranged olefin can occur via a perpendicular triplet state, which we suggest as the common intermediate in the interconversion of the isomers.

Scheme I



This state should decay to the two isomers at a ratio characteristic for each pair of isomers but independent of which isomer is the reactant. Accordingly, the polarization due to triplet pair recombination is partitioned between reactant and isomerized olefin, weakening the "in cage" polarization of the reactant olefin to the same extent to which the polarization of the rearranged olefin falls short of its potential maximum. The proposed mechanism is summarized in Scheme I where S and O, respectively, denote the sensitizer and the olefin.

The principles underlying this mechanism are well documented. The recombination of triplet ion pairs has been established for several donor-acceptor systems[14] as a mechanism for the formation of "fast triplets" and has been invoked recently to explain the CIDNP effects observed in the photoreaction of aromatic hydrocarbons with tertiary amines.[15] Perpendicular triplet states are generally accepted as intermediates in the photoinitiated rearrangement of stilbenes.[16] A mechanism similar to that postulated here was proposed by Taylor for the photosensitized interconversion of the dicyanoethylenes.[17]

It is noteworthy that the triplet energy of Tr (E_T = 2.1 eV)[10] also lies below the free energy of the ion pair. This may limit the extent of isomerization since reverse electron transfer may populate ^{3}Tr and ^{1}CN as well as ^{1}Tr and ^{3}CN. The relative energies of ion pair and reactant triplet states can be varied by the proper choice of the reactant. Attempts to delineate the energetic requirements for optimal yields of the electron-transfer-induced rearrangements are in progress.

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(8) Calculated according to $\Delta G = E_{(Tr/Tr^{+}\cdot)} - E_{(CN^{-}\cdot/CN)} - e^2/\epsilon a$.[9] The oxidation potential of triphenylene is 1.65 V vs. SCE,[10] the reduction potential of *trans*-cinnamonitrile is −1.81 V, and that of the cis isomer is −1.82 V vs. SCE;[11] ΔG = 1.65 + 1.8–0.2 = 3.25 eV.

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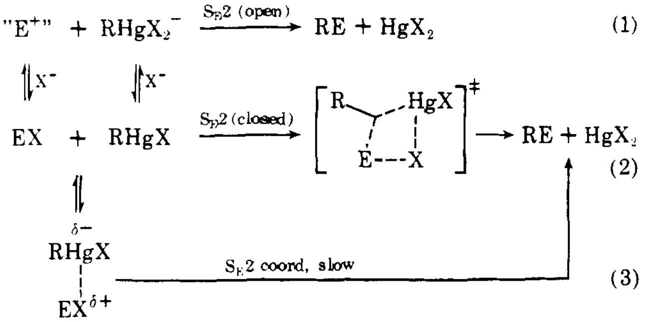
A Rate Sequence for S_E2 Retention with Large Steric and Large Electronic Effects

Sir:

Relative rate sequences are useful for explaining reactivity trends with respect to mechanism and for the assignment of mechanisms to new reactions. For S_N2 reactions the principal effect of structure on rate is one of steric retardation upon increased branching at the α- and β-carbon atoms, understood in terms of a "pentavalent" inversion transition state.[1] For S_N1 (carbonium ion) reactions electronic effects are paramount.[2] In contrast to nucleophilic substitution, there are no simple rules for electrophilic aliphatic substitution governing either stereochemistry or the interplay of steric and electronic substituent effects.[3] Presented herein for an S_E2 reaction which proceeds with retention of configuration is a rate sequence which indicates the superposition of a large steric effect on an opposing large electronic effect.

Electrophilic cleavages of alkylmercuric halides exhibit marked catalysis by added halide ion, which can be rationalized in terms of improved leaving group ability and enhanced C–Hg bond nucleophilicity, provided by either (i) a pre-kinetic equilibrium complexing of the substrate organomercurial, forming $RHgBr_2^-$ (eq 1), or (ii) a pre-kinetic equilibrium



complexing of the electrophile "E^+", which effects reaction via the concerted S_E2 (closed) (eq 2) or the two-step S_E2 (coordination) (eq 3) mechanism.[3,4]

Table I. Pseudo-Third-Order Rate Constants for the One-Bromide Ion-Catalyzed Bromine Cleavage of Alkylmercuric Bromides in Methanol at 25.0 °C at 0.30 M Ionic Strength

	RHgBr, R	$k_{3A}K_2$ or $k_{3B}K_1$, s^{-1} M^{-2}
α branching	methyl	1.68
	ethyl	18.1
	isopropyl	1310
	tert-butyl	5660
β branching) (primary R)	ethyl	18.1
	n-propyl	7.43
	isobutyl	2.09
	neopentyl	0.2903
β branching (secondary R)	isopropyl	1310
	sec-butyl	1016
	$Me_2CHCH(Me)$-	
	$Me_3CCH(Me)$-	53.3
γ branching) (primary R)	*n*-propyl	7.43
	n-butyl	8.32
	$Me_2CHCH_2CH_2$-	
	$Me_3CCH_2CH_2$-	12.5

The present study examined the reaction of a series of (saturated) alkylmercuric bromides with bromine in methanol

$$RHgBr + Br_2 \xrightarrow[\text{methanol}]{Br^-\text{ (large excess)}} RBr + HgBr_2 \qquad (4)$$

wherein the effects of branching in the α-, β-, and γ-carbon atoms could be independently assessed. The catalytic effect of added bromide ion was studied by measuring rates as a function of $[Br^-]$ at a constant ionic strength of 0.30 M (NaBr plus $NaClO_4$). The progress of reaction was followed spectrophotometrically (monitoring the disappearance of bromine color[5]) at 25.0 °C, and first-order dependence in each reactant was demonstrated. The rates of the uncatalyzed reactions are very slow and could not be measured with reproducible accuracy;[6] so only the rates of the one-anion-catalyzed reactions

$$Br_2 + RHgBr_2^- \xrightarrow{k_{3A}}$$

$$Br_3^- + RHgBr \xrightarrow{k_{3B}} \qquad (5)$$

are reported here. Pseudo-third-order rate constants (Table I), referring to either of two kinetically indistinguishable reactions (eq 5), were obtained from the experimentally observed second-order rate constants according to the following analysis:

$$\text{rate} = k_{obsd}[Br_2]_t[RHgBr]_t \qquad (6)$$

(subscript t refers to the summed concentration of all forms of the reactant)

$$Br_2 + Br^- \overset{K_1}{\rightleftharpoons} Br_3^- \quad RHgBr + Br^- \overset{K_2}{\rightleftharpoons} RHgBr_2^- \qquad (7)$$

$$\text{rate} = k_2[Br_2][RHgBr] + \left\{\begin{matrix} k_{3A}[Br_2][RHgBr_2^-] \\ \text{or} \\ k_{3B}[Br_3^-][RHgBr_2] \end{matrix}\right\} \qquad (8)$$

$$k_{obsd} = \frac{k_2 + \left\{\begin{matrix} k_{3A}K_2 \\ \text{or} \\ k_{3B}K_1 \end{matrix}\right\}[Br^-]}{\{1 + K_1[Br^-]\}\{1 + K_2[Br^-]\}} \qquad (9)$$

The value of K_1 (methanol, 25 °C, μ = 0.2 M) has been determined[8] to be 177 M^{-1}. Although no systematic measurement of the mercurial equilibrium constants K_2 has been performed, the handful of published data indicates that these

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