Nuclear Spin Polarization Effects in Radical Ion Pair Reactions. Recombination in the Singlet and Triplet State

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Abstract: The nuclear spin polarization effects observed during photoinitiated electron transfer reactions of olefins with suitable reaction partners provide insights into electron spin effects on radical ion pair reactivity and serve to illustrate two spin-sorting principles. The mechanisms differ in the electron spin multiplicity dependence of the ion-pair reactions. In reactions involving the radical cation of phenyl vinyl ether or phenylpropene and the radical anion of chloranil, electron return is efficient for singlet pairs but energy forbidden for triplet pairs. In contrast, the pair phenylpropene radical anion–tetramethylphenylenediamine radical cation undergo recombination with similar efficiency in the singlet and triplet state because the pair energy lies above the triplet energy of phenylpropene. Finally, pairs such as stilbene cation–phenanthrene anion undergo triplet recombination more efficiently than singlet recombination suggesting that, in this system, the small gap between the pair energy and the triplet energy of stilbene allows faster electron return than does the larger gap between pair and ground state in qualitative agreement with the Marcus theory.

I. Introduction

In recent years photophysical studies have established that "fast" triplet states may arise from the interaction between a photoexcited electron donor (acceptor) and a quencher with electron acceptor (donor) character.[1] A reasonable mechanism for the formation of these triplets involves the following steps: (a) electron transfer to form a pair of radical ions; (b) hyperfine induced singlet–triplet mixing in these pairs; (c) "recombination" of an ion pair of triplet spin multiplicity, i.e., reverse electron transfer in a triplet pair. Hyperfine induced singlet–triplet mixing, the second step of this mechanism, is a key element in the radical-pair mechanism of chemically induced nuclear spin polarization (CIDNP).[2] Therefore, it is not unreasonable to search for CIDNP effects in products derived from fast triplets. Indeed, several cases of nuclear spin polarization have been associated with the "recombination" of triplet pairs by either electron return[3a,b,d-k] or coupling.[3c] In the paper presented here we examine several cases of nuclear spin polarization associated with the recombination of triplet pairs in the light of the underlying mechanistic principles and we delineate conditions that have to be met in order for these effects to be observed.

II. Spin Sorting Principles in Radical (Ion) Pair Reactions

Nuclear spin polarization effects can be explained by two fundamentally different mechanisms. One possible explanation involves electron–nuclear cross relaxation in electron polarized radicals or radical ions.[4] However, this mechanism has been carefully evaluated and confirmed in exceedingly few cases.[5] The overwhelming majority of all reported observations of nuclear spin polarization[3a,6] are compatible with the radical-pair theory[2] developed by Closs and co-workers[2a] and by Kaptein[2b] and Oosterhoff and refined by Adrian[2c] and by Pedersen and Freed.[2d]

The radical pair theory is based on two fundamental principles: (a) The rate of intersystem crossing in a newly generated radical (ion) pair is influenced by the spin states of the nuclei which are coupled to the electron spins; i.e., the rate of intersystem crossing is hyperfine dependent (b) the rates of radical (ion) pair reactions are electron spin dependent. Combined these principles provide a spin-sorting mechanism. For example, the competition of an electron spin dependent reaction or process with a reaction or process that is electron spin independent or has a different spin dependence will cause certain nuclear spin levels to be overpopulated in the radicals generating one type of product and to be depleted in the radicals leading to other types of products.

The nuclear spin states, which are sorted into a given type of product, are determined by four parameters which characterize the magnetic properties of the radical intermediates and the course of the reaction from precursor to product. These parameters are (a) the initial spin multiplicity (μ) of the pair, which is dictated by the precursor spin multiplicity; (b) the mechanism of product formation (ϵ) from the radicals, a reaction parameter which reflects the electron spin dependence of this step; (c) the sign of the hyperfine coupling constants (a) of the nucleus under investigation; (d) the difference (Δg) of the electron g factors of the two radicals.

Kaptein has expressed the relation between these parameters and the observed effects in terms of a simple sign rule:[7] each parameter is given a sign and the signal direction can be predicted by the product of these signs. In order to account for the observed effects, the signs must be assigned as follows: (a) the signal direction, Γ, is considered to be positive (negative) if absorption (emission) is observed; (b) $a > 0$ (<0) for positive (negative) hyperfine coupling constants; (c) $\Delta g > 0$ (<0) for the radical with larger (smaller) g factor; (d) $\mu > 0$ (<0) for radical pairs generated by a triplet (singlet) precursor; (e) $\epsilon > 0$ for products formed by geminate recombination whereas $\epsilon < 0$ for products formed after escape of the radicals from the cage. It is important to understand that in Kaptein's formalism a geminate recombination reaction is one restricted to pairs of singlet spin multiplicity, whereas an "escape" reaction usually is not subject to spin restrictions. The key to a spin sorting mechanism, then, lies in the electron spin dependence of the product-forming reactions. To date, at least three different spin-sorting mechanisms have been documented and in each mechanism the nature of the competition between the product-forming reactions is somewhat different and, accordingly, so is the meaning of ϵ. The three spin-sorting mechanisms can be summarized as follows.

1. Competition between In-Cage Reaction and Escape. Most commonly, spin sorting occurs as a result of the competition between an electron spin dependent radical pair reaction and the separation of the pairs by diffusion, a process which is electron spin independent. The reaction of the free radicals thus generated with diamagnetic substrates may lead to polarized "escape" products. This spin-sorting mechanism is operative in essentially all reactions involving pairs of neutral radicals

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and in a large number of cases involving pairs of radical ions as well. We note that for pairs of neutral radicals geminate pair reactions typically are singlet reactions such as recombination or disproportionation, whereas electron return is the most prominent geminate reaction for radical ion pairs. Accordingly, the spin sorting occurs because *only singlet pairs can undergo geminate recombination whereas triplet pairs can only diffuse apart* (aside from undergoing intersystem crossing).

2. Competition between Recombination and a Secondary Pair Reaction. A second spin sorting principle was invoked to explain the CIDNP effects observed during the photolysis of dibenzyl ketone in a micellar environment where genuine free-radical reactions do not occur and where the competition between geminate pair and escape reaction does not exist.[8] In this system two types of polarized products are observed: regenerated starting material, which has the polarization normally associated with a geminate recombination reaction, and a decarbonylation product, which shows the polarization normally associated with an escape reaction. In this case, the recombination of the primary pair competes with the decarbonylation to form a secondary pair. The nuclear spin states allowing fast intersystem crossing will predominate in the primary coupling product, whereas those causing slower intersystem crossing will accumulate in the secondary coupling product. Both reactions involve the geminate recombination of singlet pairs but there is a time lag between them. In this case we assign the reaction parameter, $\epsilon > 0$, to the recombination of the primary pair and the parameter $\epsilon < 0$ to the recombination of the secondary pair.

We note that the generation of a secondary radical pair from a primary one with retention of electron spin correlation ("pair substituion") is, in principle, unexceptional. Such processes have been invoked repeatedly to account for "memory"[9] and "cooperative"[10] effects. The only difference between these reactions and the one considered here lies in the timing of the key processes: recombination, pair substitution, and diffusion. In most cases spin sorting is caused by the competition between geminate reactions (primary and secondary recombination) and diffusion, whereas in the dibenzyl ketone reaction in a micellar environment the spin sorting is achieved by the competition between geminate recombination of the primary pair and the pair substitution reaction (decarbonylation). To our knowledge, this sorting mechanism has not been invoked for any other reaction but we see no reason why additional systems should not be uncovered which are governed by this or a similar principle.

3. Competition between Recombination in the Singlet and in the Triplet State. A third spin-sorting principle is operative in cases where the reactant triplet energies lie below (or closely above) the energy of the intermediate radical (ion) pair, so that electron return (recombination) in triplet pairs is energetically feasible.[3] In such a case the recombination of singlet pairs competes with that of triplet pairs. The photoreactions of hydrocarbon donors with electron-acceptor olefins capable of geometric isomerization are paradigmata of reactions governed by this spin sorting mechanism.[3a,b,d,i] These reactions make it possible to observe the effects due to singlet recombination and triplet recombination in separate products. We have suggested[3a] that the reaction parameter, $\epsilon > 0$, should be assigned to the product(s) derived from singlet recombination and the reaction parameter, $\epsilon < 0$, to the product(s) derived from triplet recombination. We prefer this usage of ϵ to a formalism in which ϵ differentiates geminate from escape reactions and where an additional parameter is needed to describe the "exit channel".[3e] Our recent identification of a third spin-sorting mechanism[8] and the spectre of additional parameters only serve to confirm this preference.

In the absence of a rearrangement only the predominant type of polarization can be observed; in this case, the parameter, $\epsilon < 0$, implies that the electron return in triplet pairs is more efficient than that in singlet pairs. Recombination in the triplet state is not completely restricted to pairs of radical ions; it has been invoked, for example, to explain the polarization observed for a meta coupling product in the photo-Claisen rearrangement of an aryl allyl ether.[3c]

In the following sections we will examine in detail nuclear spin polarization effects observed during the photoreactions of electron-acceptor or electron-donor olefins with suitable substrates. In several of these systems, the spin-sorting mechanism based on the competition of singlet and triplet recombination appears to be involved.

III. Experimental Section

The nuclear spin polarization experiments were carried out on a JEOL JNM-C-60-HL continuous wave spectrometer or on a Bruker WH 90 Fourier transform spectrometer. Both instruments were modified to permit UV irradiation of the samples in the area of the receiver coil. In the case of the JEOL instrument the collimated beam of an Osram 200-W high-pressure mercury lamp enters the probe in a direction parallel to the sample tube and is reflected onto the receiver coil by a front surface aluminum mirror mounted in front of it at an angle of 45°. The rear wall of the all-quartz insert is covered with aluminum. The probe of the Bruker instrument has a hole at the level of the receiver coil which permits irradiation from the rear without the use of mirrors. A high-pressure mercury lamp (200 or 1000 W) was used with this instrument. The duration of the irradiation was controlled by a pressure-activated shutter.

IV. Energetic Considerations

In a discussion of nuclear spin polarization effects accompanying photoinduced electron transfer reactions energetic considerations are of crucial importance. The efficiency of an electron-transfer reaction, either to generate a radical ion pair or to annihilate it by reverse electron transfer, is dictated by the change in free energy associated with it. In particular, the energy of the radical ion pairs relative to the reactant triplet states may be a crucial factor in determining the mechanism by which the diamagnetic reactants are regenerated from the pair. The free energy of a radical ion pair is given by[11]

$$\Delta G = E_{(D/D^+)} - E_{(A^-/A)} - e^2/\epsilon a$$

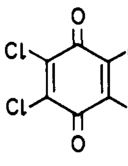
where $E_{(D/D^+)}$ is the one-electron oxidation potential of the donor, $E_{(A^-/A)}$ is the one-electron reduction potential of the acceptor, and $e^2/\epsilon a$ is a term accounting for ion pairing at a distance a in a solvent of dielectric constant ϵ.

We will discuss several systems in which the energy of the radical ion pair lies below the triplet energy of the reactant olefin as well as two systems where the pair energy lies above the reactant triplet energy. These systems illustrate different kinetic limits of two spin-sorting mechanisms. For this purpose we have chosen reactions involving olefins which undergo either geometric isomerization or dimerization so that we have the opportunity to probe the polarization of a reaction product as well as that of the regenerated reagents.

V. Reactions without Apparent Triplet Recombination

The irradiation of electron acceptors (benzoquinones or cyano-substituted aromatic hydrocarbons) in solutions containing donor olefins (dimethylindene, *N*-vinylcarbazole, phenyl vinyl ether) results in strong nuclear spin polarization of the olefins. The polarization mechanism operating in these systems is illustrated by the effects observed during the irradiation of chloranil (**1**) or dicyanoanthracene (**3**) in the presence of phenyl vinyl ether (**2**).

1. Electron Transfer from Phenyl Vinyl Ether to Photoexcited Acceptors. During the irradiation of dicyanoanthracene in an acetonitrile solution containing **2**, strong emission is observed for the complex aromatic spectrum of the olefin as well as for its terminal olefinic protons which appear as two dou-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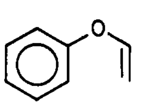
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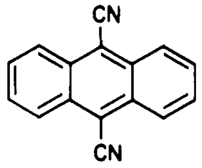
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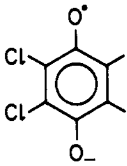
blets, ${}^3J_{cis} = 6.1$, ${}^3J_{trans} = 13.8$ Hz, each further split by a small geminal interaction, ${}^2J_{gem} = 1.5$ Hz. The doublet of doublets representing the internal proton shows weakly enhanced absorption (Figure 1). In contrast, when chloranil is used as acceptor/sensitizer, a near mirror image of Figure 1 is observed: now aromatic and terminal protons show enhanced absorption, whereas the internal proton shows weak emission.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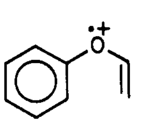
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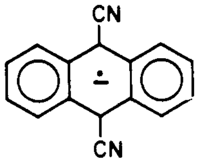
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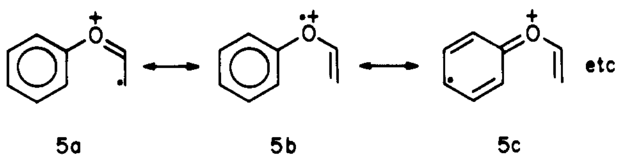
These effects are ascribed to the intermediacy of the radical ion pairs **4**-**5** and **5**-**6** formed by electron transfer from the olefin to the photoexcited acceptors, **1** and **3**, respectively. Both reactions are exothermic. In the case of chloranil as reaction partner, the redox potentials, $E_{(4/1)} = -0.02$ V vs. SCE[12] and $E_{(2/5)} = 1.75$ V vs. SCE,[13] suggest a pair energy, $\Delta G_{(4\text{-}5)}$, near 37 kcal/mol, well below the triplet energy (E_T = 62 kcal/mol)[14] and certainly below the excitation energy of the sensitizer. With dicyanoanthracene as reaction partner, the higher reduction potential of the sensitizer ($E_{(6/3)} = -0.82$ V vs. SCE)[15] causes the pair energy to be substantially higher ($\Delta G_{(5\text{-}6)} \approx 55$ kcal/mol) but again it lies well below the excitation energy of the sensitizer (E_S = 68 kcal/mol).[15] Accordingly, the formation of both pairs is exothermic. On the other hand, the triplet energy of the olefin, ~80 kcal/mol,[13] lies substantially above the energies of either pair; therefore, reverse electron transfer in triplet pairs to populate this state cannot be expected to compete efficiently with the electron-return process in the singlet state.

The polarization-determining parameters in this system are assigned as follows. The intensity pattern of Figure 1 indicates an intermediate with the spin density distribution of a π radical where the protons in the ortho, para, and β positions have strong negative hyperfine coupling constants ($a < 0$) whereas the α and meta protons have weak positive hyperfine coupling constants ($a > 0$).



The g factor of this radical cation, an estimated 2.0030, is clearly lower than that of the semiquinone anion (g_6 = 2.0062)[16] and is also assumed to be lower than that of dicyanoanthracene radical anion ($\Delta g < 0$). Because of its short singlet lifetime, photoexcited chloranil can only be quenched after it undergoes intersystem crossing to the triplet state ($\mu > 0$); in contrast, **3** has a substantially longer singlet lifetime and can thus be quenched as a singlet ($\mu < 0$). Accordingly, the difference in signal direction is caused by a difference in precursor spin multiplicity. Given these parameters, the signal directions observed in both reactions suggest a mechanism involving regeneration of the reactants by reverse electron transfer in geminate singlet radical ion pairs ($\epsilon > 0$), i.e., the mechanism invoked most commonly in electron transfer induced nuclear spin polarization effects.

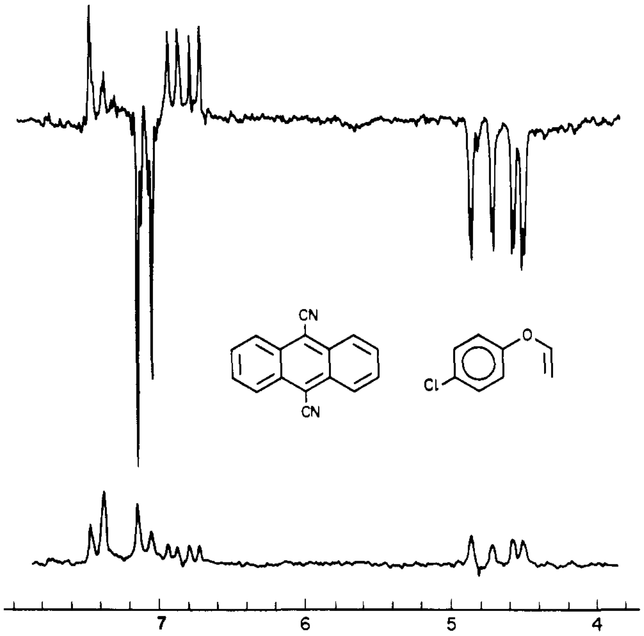
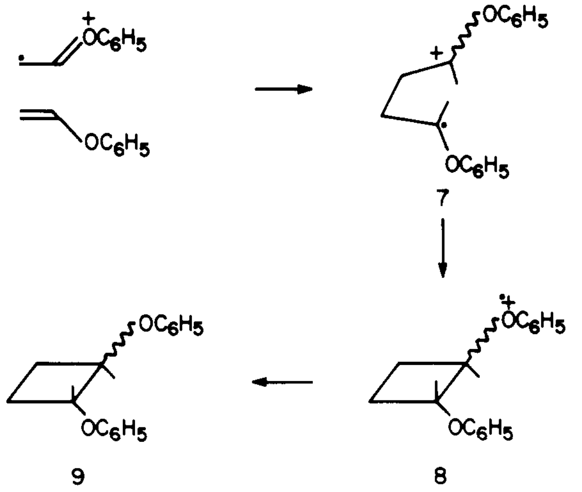


Figure 1. 90-MHz ^{1}H NMR spectra observed during the irradiation of 9,10-dicyanoanthracene (0.02 M) in an acetonitrile-d_3 solution containing p-chlorophenyl vinyl ether (0.02 M) and of the same solution in the dark (bottom).

This mechanism implies that a complementary polarization of equal intensity but opposite sign is carried by olefin radical cations which have a fate other than geminate pair recombination in the singlet state. In the reaction discussed here, the radical cations initiate the formation of head-to-head dimers with cyclobutane structure (**9**).[17] However, no evidence for a polarized reaction product is obtained, at least not in the early stages of the reaction. This lack of polarization can be explained if the reaction mechanism allows the complete relaxation of the complementary ("escape") polarization before the dimer formation is completed.



The formation of head-to-head dimers is explained by the addition of the cation, **5**, to unreacted olefin, ring closure of the resulting adduct radical cation, **7**, to form a secondary adduct (**8**), and electron transfer from a suitable reaction partner such as the olefin. The lack of polarization in the dimer requires that the delay between the spin-sorting step and the formation of **9** allows the "escape" polarization to relax. Since typical spin-lattice relaxation times of doublets are greater than 10^{-6}

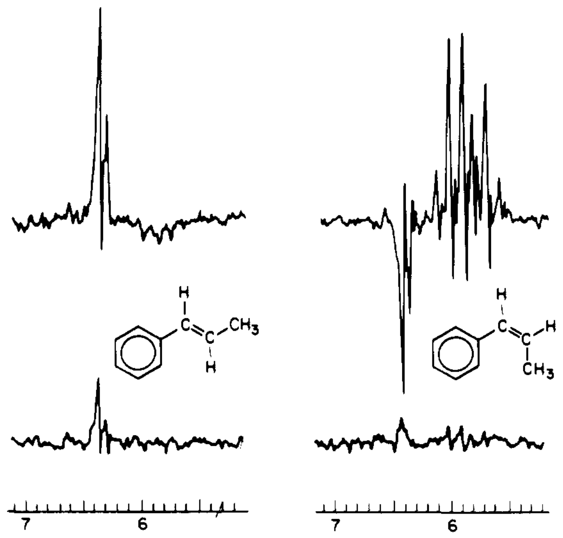


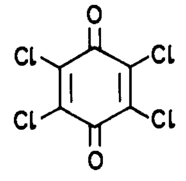
Figure 2. 60-MHz ^{1}H NMR spectra (olefinic region) observed during the irradiation of tetrachlorobenzoquinone (0.02 M) in nitromethane-d_3 solutions containing 0.02 M *cis*-(right) or *trans*-1-phenylpropene (left). The structure of the reactant olefin and a dark spectrum are shown below each CIDNP spectrum.

s,[6c] at least one of the three steps leading to **9** has to be inefficient to allow this relaxation.

In summary, the nuclear spin polarization observed during the interaction of electron acceptors with phenyl vinyl ethers represents an example of polarization due to the competition between in-cage reaction and escape. The escaping radical cations initiate the formation of a diamagnetic product other than the reactant but the escape polarization relaxes before the final step of this reaction is completed.

2. Electron Transfer from *cis*- and *trans*-Phenylpropene to Photoexcited Electron Acceptors. The reaction of photoexcited chloranil with the isomeric phenylpropenes (**10**) gives rise to effects which are principally similar to those discussed in the previous section but which show an important additional feature: not only the reactant olefin is polarized but also a reaction product, in this case the isomeric olefin (Figure 2).[3i] The signals representing the β hydrogen of the reactant olefin show enhanced absorption, whereas the corresponding nucleus of the rearranged olefin appears in emission. The key to the understanding of these effects lies in two observations: (a) in each case, the polarization of the regenerated reactant olefin is stronger than that of the rearranged olefin; (b) the reaction of the cis isomer results in stronger overall effects than does that of the trans isomer.[3i]

The energetics of this system and the spin-sorting principle governing the polarization are similar to those discussed above. The energy of the radical-ion pairs lies below the triplet energies of reactants and products so that only singlet pairs can recombine regenerating the reactants in their ground states. Radical-ion pairs which cannot recombine suffer separation by diffusion followed by isomerization of free-radical cations and/or electron exchange with unreacted olefin. In the exchange reaction, the "escape" polarization is partitioned between reactant and rearranged olefin according to the degree of rearrangement.



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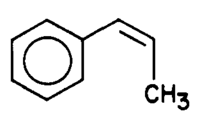

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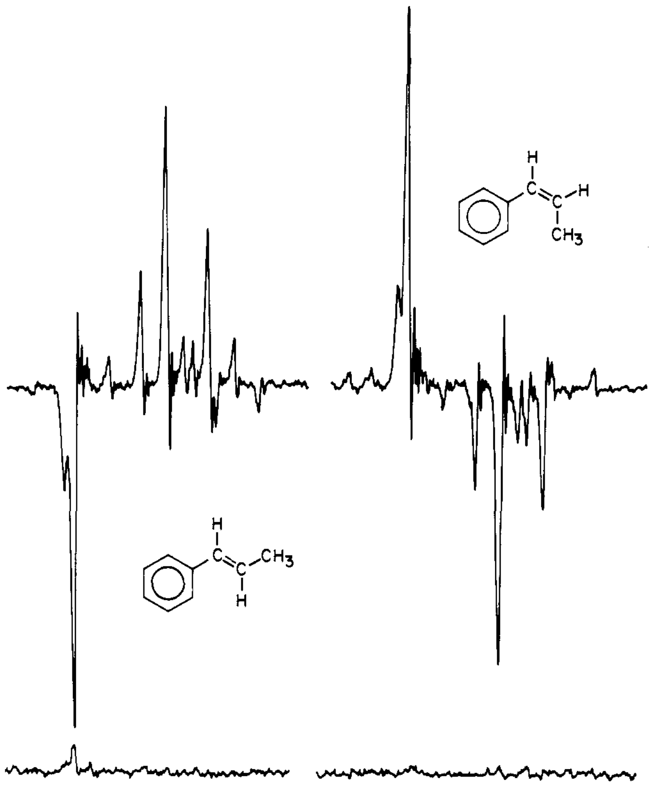


Figure 3. 60-MHz ^{1}H NMR spectra (olefinic region) observed during the irradiation of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (0.02 M) in acetonitrile-d_3 solutions containing 0.02 M *cis*-(right) or *trans*-1-phenylpropene (left). The reactant olefin and a dark spectrum are shown with each CIDNP spectrum.

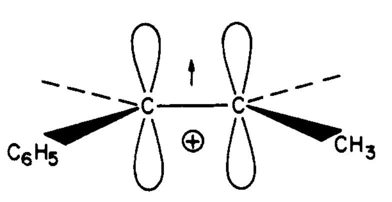
The fact that the "escape" polarization is observed, though weaker than the geminate pair polarization, indicates that the lifetime of the free-radical ions (**11**) before the exchange reaction is of the same order of magnitude as the spin-lattice relaxation times of the ions, thus allowing partial, but not complete, relaxation. The overall CIDNP intensity is determined by the efficiency of the rearrangement: the more efficient the isomerization, the more efficient the sorting of opposite spins into different products.

The efficiency of rearrangement is dictated by the energy surface of the radical cations. Similar to the olefin ground state, the radical ions have energy minima for arrangements allowing maximum conjugation, i.e., for the two planar structures **11**-*t* and **11**-*c* and a maximum at a close to perpendicular arrangement, such as **11**-*p*. Because of the steric interference of the substituents, the energy of the cis cation, **11**-*c*, lies closer to that of the maximum, **11**-*p*, than does the energy of the trans cation. Accordingly, the reaction of the cis isomer (whose radical cation requires a lower energy of activation for rearrangement) results in greater enhancements than does the reaction of the trans isomer (whose radical cation requires a higher energy of activation).

In summary, the photoreaction of chloranil with the isomeric phenylpropenes represents an example of nuclear spin polarization due to the competition between a geminate electron return ($\epsilon > 0$) and cage escape ($\epsilon < 0$). The escaping radical cations undergo cis-trans isomerization which allows the separate observation of the escape polarization. The differences between the reaction of the cis and that of the trans isomer can be ascribed to the interconversion of two different radical cations of different energies.

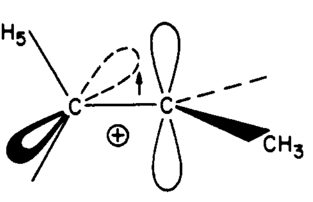
VI. Reactions with Apparent Triplet Recombination

Having illustrated the selection principle first and most



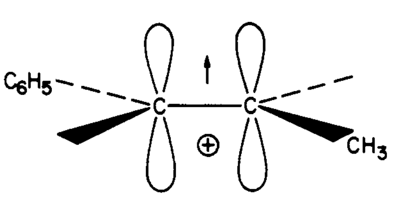
11-*c*

cis
RADICAL CATION



11-*p*

TRANSITION STATE



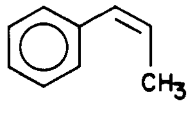
11-*t*

trans
RADICAL CATION

commonly invoked in radical ion pair induced nuclear polarization we turn to several systems which show effects with typical features suggesting an alternative spin selection principle. These systems have in common (a) that a radical ion pair is generated by quenching an excited singlet species or by excitation of a charge-transfer complex and (b) that the triplet state of one or both of the reactants lies below the energy of the intermediate radical ion pair. The spin polarization effects observed in theses systems are characterized by substantial contributions that can be ascribed to the recombination of triplet radical ion pairs. These effects and the sorting principle underlying them are best illustrated in systems involving the geometric isomerization of olefins because these systems allow the separate observation of effects due to singlet and triplet recombination. The relative intensities of these effects are dictated by the relative magnitude of several rates including those of singlet recombination, intersystem crossing, triplet recombination, and diffusional separation of the radical ions and can vary substantially.

In the following, we will discuss two systems, one in which reactant and rearranged olefin show comparable enhancements and one in which the rearranged olefin shows stronger polarization than the reactant.

1. Electron Transfer from Tetramethylphenylenediamine to *cis*- and *trans*-Phenylpropene. The two isomeric 1-phenylpropenes (**10**) are interconverted upon irradiation not only in the presence of electron acceptors but also when paired with electron donors. For example, the photoreaction of either isomer with *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (**12**) results in strong nuclear spin polarization effects for both reactant and rearranged olefin (Figure 3). Interestingly, these effects are different from those observed in the reaction with chloranil, both in direction and in relative intensity, indicating that there are important differences between the two reaction types.



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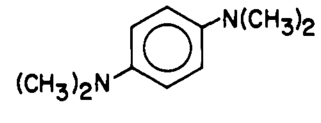

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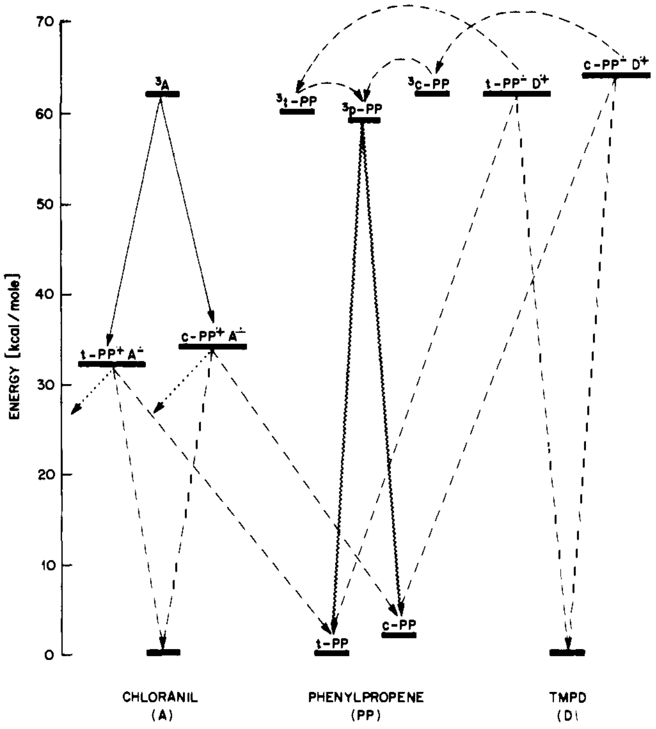
The most obvious difference lies in the "role change" of phenylpropene: it serves as a donor in the reaction with chloranil, whereas it is an acceptor in the reaction with tetramethylphenylenediamine. Accordingly, the phenylpropene radical anion (**13**) is generated along with the tetramethylphenylenediamine radical cation (**14**). However, this change should have little effect on either the direction or the relative intensity of the observed effects. The radical anions of aromatic hydrocarbons (e.g., **13**) have spin density distributions similar to those of the corresponding radical cations (e.g., **11**) and g factors very close to that of the free electron. Accordingly, the parameters a and Δg should be unchanged (a, $\Delta g < 0$; $g_{14} = 2.0030$;[18] $g_{13} = 2.0026$). The change in signal direction can be explained by different initial spin multiplicities: the pair **4**–**11** is generated by a triplet precursor ($\mu > 0$), whereas the pair **13**–**14** is formed in the singlet state ($\mu < 0$).

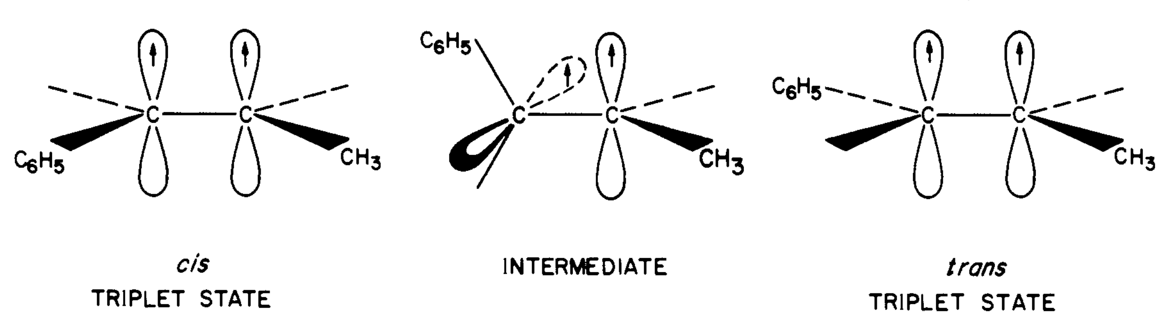
Scheme I. Energy Levels of Relevant Intermediates in the Photoreactions of Chloranil and Tetramethylphenylenediamine, Respectively, with the Phenylpropene Isomers[a]



[a] Electron-transfer reactions generating radical ion pairs are represented by solid lines, whereas recombination reactions are shown as dashed lines; the decay of a perpendicular triplet state to the ground state of the isomers is depicted by wavy lines and the diffusion of radical ions away from their counterions is denoted by dotted lines.

However, the most significant difference between the two systems lies in the energy of the radical ion pairs relative to the olefin triplet state (Scheme I). Because of the high reduction potential of **10** ($E_{A^-/A} \simeq -2.7$ V vs. SCE)[19] and despite a very low oxidation potential of the donor ($E_{D/D^+} = 0.16$ V vs. SCE)[20] the free energy of the pair **13**–**14** lies above the triplet state of phenylpropene ($E_T = 2.6$ eV),[21] allowing a special spin sorting mechanism to operate in this system. Both singlet and triplet pairs can undergo reverse electron transfer; singlet pairs regenerate the reactants in their ground states, whereas triplet pairs recombine to populate one reactant triplet state and one reactant ground state.

The triplet state, in contrast to the ground state and to the radical ions, has an energy minimum at or near a perpendicular structure because in this arrangement the overlap of the unpaired spins is minimized. Therefore, the triplet state can decay to the cis or to the trans configuration of the ground state regardless of the geometry of the radical ion from which it is generated. Accordingly, the polarization associated with triplet recombination ($\epsilon < 0$) is partitioned between reactant and

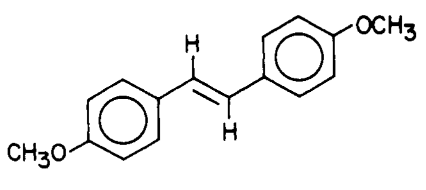


rearranged olefin as dictated by the degree of rearrangement.

In the framework of this mechanism the CIDNP intensities of reactant and rearranged olefin can vary widely. An efficient spin-sorting process requires a well-balanced competition between the key reactions at each stage of the overall mechanistic scheme. In the system discussed here, it is equally important that intersystem crossing (k_{isc}) competes adequately with singlet recombination ($^1k_{rec}$), that singlet and triplet recombination compete adequately with the diffusion process ($^1k_{diff}$, $^3k_{diff}$), and that the decay (^3k_d) of the triplet state results in a nontrivial degree of isomerization, γ. The qualitative features of the observed polarization, comparable enhancement of reactant and rearranged olefin and similar overall intensities in both reactions (Figure 3), allow the conclusion that γ is close to 0.5, that nuclear relaxation during the lifetime of the olefin triplet state is negligible, and that singlet and triplet pairs recombine with similar efficiencies.

Similarly balanced rate parameters govern the photoreactions of aromatic hydrocarbons with the isomeric 1,2-dicyanoethylenes,[3b] with the cinnamonitriles and several of their derivatives.[3i] and with maleates, fumarates, and several cinnamates.[22] That such balance is not a necessary condition for the spin-sorting mechanism discussed here is illustrated in the next section.

2. Electron Transfer from Stilbenes to Phenanthrenes. The photoinitiated isomerization of stilbene and numerous derivatives has been studied in detail. In the presence of electron acceptors such as phenanthrene or 9-cyanophenanthrene, the photoisomerization is accompanied by strong nuclear spin polarization effects as exemplified by a spectrum obtained in the system *trans*-dimethoxystilbene–9-cyanophenanthrene (**15**–**16**). During the irradiation of this system strong emission was observed for the olefinic and ortho protons of the rearranged (*cis*-) stilbene, whereas enhanced absorption was observed for the corresponding protons of the reactant (*trans*-) stilbene. At the same time the methoxy group of the rearranged olefin appeared in enhanced absorption, whereas that of the reactant showed emission. Interestingly, the rearranged olefin showed stronger effects than the reactant (Figure 4).



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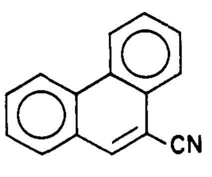

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These effects are ascribed to the intermediacy of a radical ion pair generated by electron transfer from the stilbene to the phenanthrene derivative and initiated by a singlet precursor ($\mu < 0$). The g factor of the dimethoxystilbene radical cation (**17**), because of spin delocalization to the oxygen function, should be larger than the g factor of the phenanthrene radical anion (**18**, $\Delta g > 0$). The hyperfine coupling constants of the olefinic and ortho protons of the radical cation are negative ($a < 0$), whereas those of the methoxy protons are positive ($a > 0$). Finally, the one-electron redox potentials of **15** ($E_{D/D^+} = +0.92$ V vs. SCE)[23] and **16** ($E_{A^-/A} = -1.92$ V vs. SCE)[24] place the pair energy (~2.7 eV) above the triplet energy of the stilbene (estimated to lie close to 2.1 eV)[25] so that electron return is feasible for singlet pairs ($\epsilon > 0$) as well as for triplet pairs ($\epsilon < 0$).

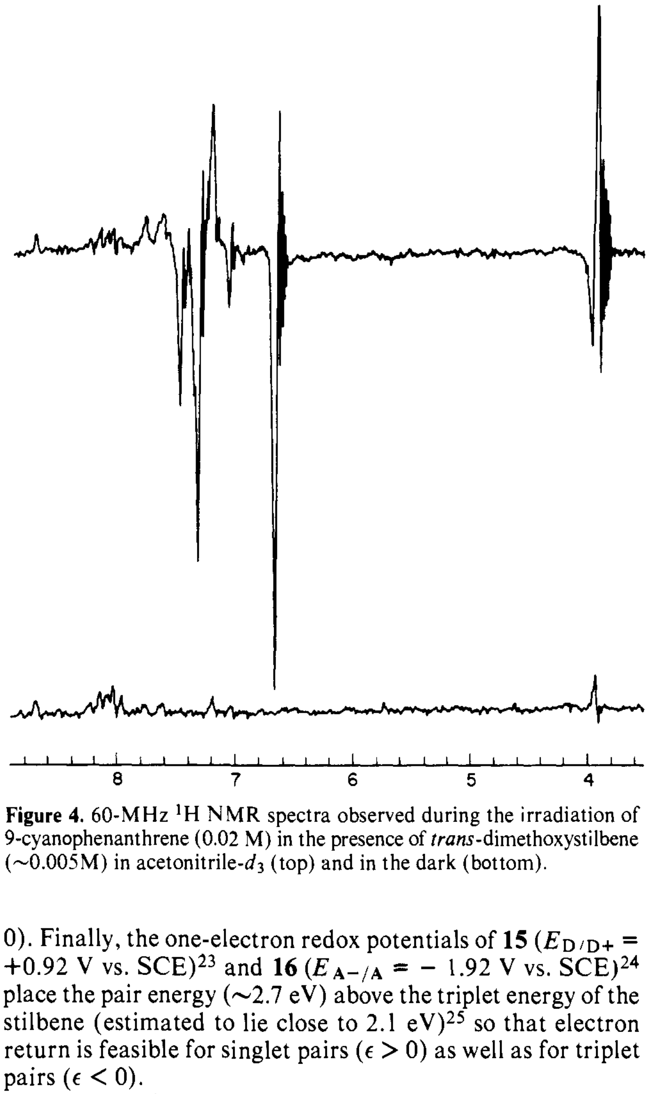


Figure 4. 60-MHz ^{1}H NMR spectra observed during the irradiation of 9-cyanophenanthrene (0.02 M) in the presence of *trans*-dimethoxystilbene (~0.005M) in acetonitrile-d_3 (top) and in the dark (bottom).

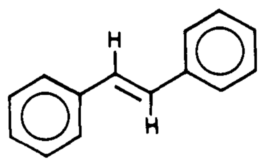
These considerations explain the signal directions of reactant and rearranged olefin but they fail to account for the different intensities observed for these products. The observed stronger polarization of a product directly derived from a triplet pair requires that triplet recombination is more efficient than singlet recombination. Such behavior is in agreement with the Marcus theory of electron transfer which predicts high rates of electron transfer between states lying close together and low electron-transfer rates between states separated by a large energy gap.

Time-resolved optical spectroscopy has shown this principle to be applicable in several systems, for example, in the radical ion pairs generated by the photoreaction of pyrene with several tertiary anilines.[1e] The energies of these radical ion pairs (~2.8 eV) lie far above the reactant grounds states but only slightly above the triplet state of pyrene (2.1 eV).[1e] As a result, triplet recombination competes more efficiently with diffusive separation than does singlet recombination. One of these systems was also studied by the CIDNP technique and the observed effects were again assigned to triplet recombination.[3e] These effects are weak because the same diamagnetic products result from singlet and from triplet recombination with similar efficiencies permitting only poor spin sorting.

In contrast, the stilbene–phenanthrene systems discussed here have the advantage that two different "products" are formed: the rearranged olefin results exclusively from triplet recombination, whereas the regenerated olefin results predominantly from singlet recombination, thus allowing a substantially more efficient spin selection. Without the isomerization, however, the observable net effects obviously would be much smaller than the individual contributions observed separately (cf. Figure 4).

3. Electron Transfer from Donor to Acceptor Olefin. The System Stilbene–Dicyanoethylene. So far we have limited the discussion to the polarization of only one reactant, the olefin. This was appropriate since the reaction partner either had no nuclei of spin $1/2$ (chloranil) or could not be expected to show appreciable polarization because of a reasonably close balance of singlet and triplet recombination efficiencies and because of the inability to undergo cis–trans isomerization.

The reaction of two olefins with each other presents an interesting complication, especially when the triplet energies of both olefins lie below the energy of the intermediate radical ion pairs, as in the reaction of *trans*-stilbene (**19**) with *trans*-1,2-dicyanoethylene (**20**),[3h] which generate stilbene cations, **21**, paired with dicyanoethylene anions, **22**. The reduction potential of the acceptor ($E_{\mathrm{A^-/A}} = -1.36$ V vs. SCE)[26] and the oxidation potential of the donor ($E_{\mathrm{D/D^+}} = 1.51$ V vs. SCE)[27] result in a pair energy, $\Delta G \approx 2.7$ eV, well above the triplet energies of donor and acceptor (2.1[25] and $\sim$2.4 eV,[3b] respectively). Accordingly, the triplet state of either reactant could be populated by recombination of triplet radical ion pairs. Indeed, the triplet states of both reactants have been postulated as intermediates.[3h]



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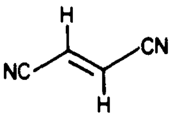

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During this reaction nuclear spin polarization effects are observed for both reactant olefins and for the rearranged stilbene (Figure 5); the complex aromatic multiplet and the olefinic singlet of *trans*-**19** appear in diminished absorption (i.e., *net emission*) as does the olefinic signal of *trans*-**20**, whereas both singlets of *cis*-**19** show *enhanced absorption.* These effects are governed by the following parameters. The light is absorbed by the stilbene or by a weak charge-transfer complex between the reactants;[3h] either excitation should lead to radical ion pairs initially of singlet spin multiplicity ($\mu < 0$). The olefinic protons of both radical ions and the ortho and para protons of the stilbene cation are assumed to have negative hyperfine coupling constants ($a < 0$). Finally, because of a contribution from the spin density on the cyano groups the g factor of **22** should be slightly larger that that of **21** ($g = 2.0026$). Given these parameters the observed effects indicate that the reactant (*trans*-) stilbene is regenerated by singlet recombination ($\epsilon > 0$), whereas the rearranged (*cis*-) stilbene and regenerated dicyanoethylene are formed by triplet recombination ($\epsilon < 0$).

In interpreting these results it is important to recognize that spin polarization effects which are consistent with triplet recombination ($\epsilon < 0$) reflect the spin multiplicity of the radical ion pair at the moment of reverse electron transfer but do not identify the reactant whose triplet state is populated. The polarization observed for donor and acceptor would be the same regardless of whether the triplet state of the donor or that of the acceptor is populated. Therefore, the assignment of which triplet state is involved has to be based on other criteria. For the reaction of stilbene with dicyanoethylene this assignment can be based on the precedent provided by the CIDNP effects observed during the reactions of these olefins with other reactants (vide supra). In these cases, the involvement of the triplet state was derived from a *characteristic polarization of the rearranged olefin.* Based on this precedent one would expect emission for the rearranged (*cis*-) dicyanoethylene if its triplet state were involved, whereas enhanced absorption for the rearranged (*cis*-) stilbene would indicate the involvement of the stilbene triplet. The results (Figure 5) are compatible only with the intermediacy of the stilbene triplet, whereas the observation of emission for the reactant (*trans*-)dicyanoethylene as well as the failure to observe any polarization for its rearrangement product argues strongly against the involvement of the acceptor olefin triplet state (Scheme II).

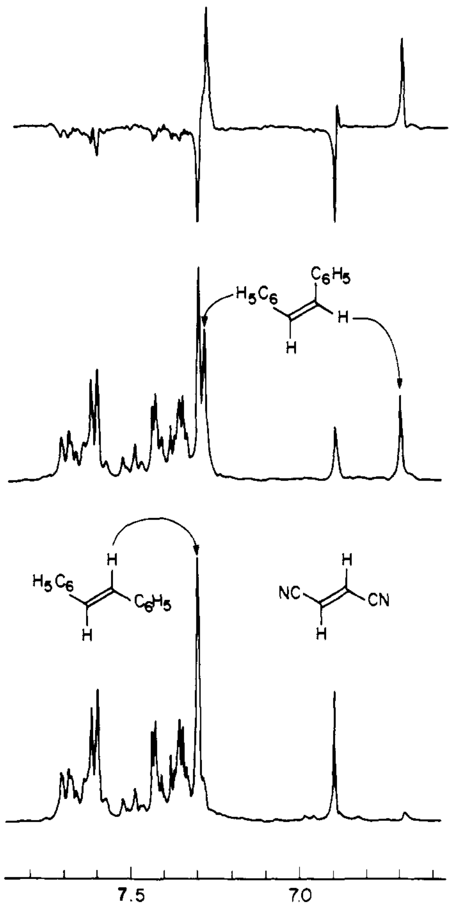
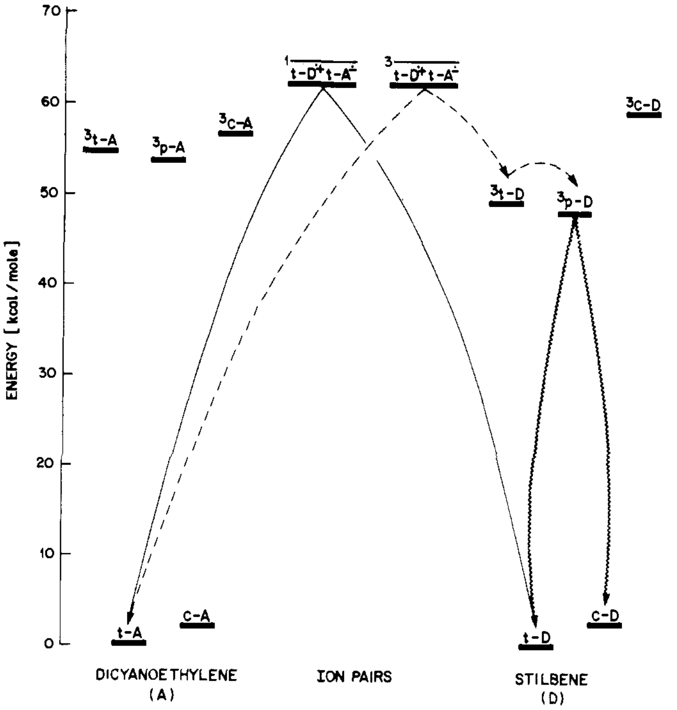


Figure 5. 90-MHz ^{1}H NMR spectra of an acetone-d_6 solution containing *trans*-stilbene (0.02 M) and *trans*-1,2-dicyanoethylene (0.02 M) in the dark (bottom) and during ultraviolet irradiation (center). The top trace represents the difference between the dark spectrum and that observed during irradiation.

As in the reaction with phenanthrene, the polarization of the rearranged stilbene is stronger than that of the reactant stilbene; once again this result is interpreted as evidence that triplet recombination is somewhat more efficient than singlet recombination and this assignment is confirmed by the finding that the reactant (*trans*-)dicyanoethylene shows the polarization typical for triplet recombination. We realize that the polarization observed during this reaction is weaker than any other effect discussed in this paper. Accordingly, the mechanistic assignments based on these results may be less convincing than the conclusions advanced in the other systems. Never-

Scheme II. Energy Levels of Relevant Intermediates in the Photoreaction of *trans*-Stilbene with *trans*-Dicyanoethylene[a]



[a] The recombination of singlet pairs to regenerate the reactants is indicated by solid lines, whereas triplet recombination is denoted by dashed lines; the decay of the perpendicular triplet state to the ground-state isomers is depicted by wavy lines.

theless, the effects shown by the two stilbene isomers as well as by *trans*-dicyanoethylene clearly indicate that the stilbene triplet state is populated by reverse electron transfer in the pair **21–22**, whereas absolutely no evidence is found for the involvement of the dicyanoethylene triplet. We note that our conclusions are consistent with the results of Lewis and coworkers,[28] who established that, of the two reactants, *trans*-stilbene is isomerized considerably more efficiently than is *trans*-dicyanoethylene. The conclusion of these workers, that a substantial fraction of the stilbene triplets is formed via an exciplex and not via separated radical ion pairs, is consistent with the relatively weak CIDNP effects observed in this system.

VII. Conclusion

Three spin-sorting mechanisms are potentially important in radical ion pair reactions. The most general mechanism involves the competition between geminate electron return, exclusively in singlet pairs, and separation by diffusion. Another, less common mechanism involves the competition between electron return in singlet pairs, to regenerate both reactants in the ground state, and electron return in triplet pairs, to populate one reactant triplet state. While these mechanisms have been shown to be involved in olefin photoreactions, a third potential mechanism involving the competition between two singlet reactions in the absence of cage escape or triplet recombination has yet to be demonstrated in radical ion reactions.

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