sleeve. The solvent was removed under reduced pressure, and the resultant oil was chromatographed on a thick layer plate by using hexane as the eluant. The major band contained 100 mg of a crystalline solid, mp 87-88 °C, whose structure was assigned as 3-ethynyl-3-methyl-1,2,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane (**60**): mp 87-88 °C; IR (KBr) 3.08, 3.40, 6.30, 6.77, 7.00, 7.30, 7.76, 8.40, 13.30, 14.80, 15.05 μm; NMR (benzene-d_6, 100 MHz) δ 1.60 (s, 3 H), 2.20 (s, 1 H), 2.50 (d, 1 H, J = 5.0 Hz), 2.98 (dd, 1 H, J = 9.0 and 5.0 Hz), 3.23 (d, 1 H, J = 9.0 Hz), 6.8-7.5 (m, 15 H); m/e 346 (M$^+$), 331, 315, 293, 254, 253, 252, 239.

Anal. Calcd for $C_{27}H_{22}$: C, 93.60; H, 6.40. Found: C, 93.46; H, 6.47.

Triplet-Sensitive Irradiation of 3-Ethynyl-3-methyl-1,2,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane (60). A mixture containing 176 mg of **60** and 36 mg of thioxanthone in 200 mL of benzene was irradiated under an argon atmosphere for 105 min by using a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Uranium glass filter sleeve. The solvent was removed under reduced pressure, and the resulting oil was chromatographed on a silica gel column by using hexane as the eluant. The major fraction contained 68 mg (39%) of a crystalline solid, mp 106-107 °C, whose structure was assigned as 6-*endo*-ethynyl-6-*exo*-methyl-1,2,3-triphenylbicyclo[3.1.0]hex-2-ene (**62**) on the basis of its spectral properties: IR (CHCl$_3$) 3.03, 3.32, 3.43, 4.79, 6.28, 6.72, 6.95, 7.28, 9.35, 9.80, 10.80, 11.05, 14.05 μm; NMR (CDCl$_3$, 100 MHz) δ 1.50 (s, 3 H), 1.95 (s, 1 H), 2.20 (d, 1 H, J = 10.0 Hz), 2.75 (d, 1 H, J = 18.0 Hz), 3.50 (dd, 1 H, J = 18.0 and 10.0 Hz), 6.8-7.40 (m, 15 H); UV (95% ethanol) 280 nm (ϵ 11 000); m/e 346 (M$^+$), 345, 332, 317, 293, 291.

Anal. Calcd for $C_{27}H_{22}$: C, 93.60, H, 6.41. Found: C, 93.83; H, 6.64.

The minor fraction contained 22 mg (13%) of a clear oil whose structure was assigned as 6-*exo*-ethynyl-6-*endo*-methyl-1,2,3-triphenylbicyclo[3.1.0]hex-2-ene (**63**) on the basis of its spectral characteristics: IR (CHCl$_3$) 3.01, 3.31, 3.40, 4.73, 6.24, 6.68, 6.90, 7.89, 8.27, 9.30, 14.30 μm; NMR (CDCl$_3$, 90 MHz) δ 1.18 (s, 3 H), 1.92 (d, 1 H, J = 6.0 Hz), 2.00 (s, 1 H), 3.04 (d, 1 H, J = 18.0 Hz), 3.49 (dd, 1 H, J = 18.0 and 6.0 Hz), 6.95-7.41 (m, 15 H); UV (95% ethanol) 275 nm (ϵ 9550); m/e 346 (M$^+$), 345, 332, 317, 313.

Anal. Calcd for $C_{27}H_{22}$: C, 93.60; H, 6.41. Found: C, 93.74; H, 6.38.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for financial support.

Nuclear Spin Polarization Effects in Radical Ion Pair Reactions. A Comparison between Triplet State and Radical Ion Reactivity†

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Received May 27, 1981. Revised Manuscript Received August 17, 1981

Abstract: A series of radical cations has been generated from appropriate hydrocarbons by photoinitiated electron transfer to chloranil and cyanosubstituted aromatic hydrocarbons. ^{1}H and ^{13}C CIDNP effects observed during these reactions allow an insight into the structure of the intermediates and into their rearrangements in solution. The observed reactions are quite different from those observed for triplet states. Thus the radical cations of *cis-* and *trans*-diphenylcyclopropane (**1**) were found to be conformationally stable whereas the triplet state allows ready interconversion. The radical cation, **10**, of quadricyclane was found to rearrange to **8**, the radical cation of norbornadiene, whereas the triplet state allows ready conversion in the opposite direction. The triplet state of benzonorbornadiene (**11**) rearranges to benzonortricyclene (**12**) but no interconversion is observed for the corresponding radical cations. Finally, the interconversion of three different radical cations, a monomer cation, an (open) adduct cation, and a (closed) dimer cation, is discussed in the electron transfer induced dimerization of olefins and in the cleavage of olefin cyclodimers. The observed reactivity differences between triplet states and radical ions eliminate radical ions as intermediates in typical triplet sensitized rearrangements.

The progress of solution photochemistry during the last 2 decades has been marked not only by new experimental techniques and by new mathematical approaches, but also by new ideas concerning the nature of short-lived reaction intermediates. Accordingly, the interpretation of experimental findings in terms of mechanistic details is influenced sometimes by prevailing ideas and, occasionally, published results are reinterpreted in terms of a more fashionable intermediate. Among the short-lived species, which have enjoyed "fashionable" status, are triplet states,[2] phantom triplets,[3] exciplexes,[4] and most recently, radical ions.[5]

It is not always trivial to positively identify the involvement of one of these intermediates. For example, it may be difficult to differentiate between reactions involving triplet states as key intermediates and reactions proceeding via radical ions. This potential difficulty is due to the nature of many typical triplet sensitizers. They are strong electron acceptors in the excited state and, therefore, may react with an appropriate substrate by triplet energy transfer or by electron transfer.

For several years, we have been interested in photoinitiated electron transfer reactions and have applied the CIDNP technique to gain an insight into the structure and reactivity of radical ions.[6] This technique is based on the interpretation of greatly enhanced

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† Dedicated to George S. Hammond, a pioneer in exploring triplet state reactivity, on the occasion of his 60th birthday.

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NMR signals in either absorption or emission, which may be observed during reactions proceeding via pairs of radicals or radical ions. According to the radical pair theory[7] the directions and intensities of these effects are determined by several parameters, including the spin multiplicity of the precursor, the magnetic properties (electron g factor and hyperfine coupling constants) of the radical intermediates, and the type of reaction by which the polarized product is formed. For the results discussed in this paper we have taken advantage of the fact that the polarization patterns reflect the hyperfine coupling patterns of the radical intermediates and thereby reveal their structures. Without going into details, we note that structural assignments can be made only if it can be established that the observed polarization is not due to an alternative polarization mechanism[8] and is not distorted as a result of spin–lattice relaxation[9] or cross relaxation.[10] These potential sources of error have been considered in all experiments discussed in this paper and their involvement has been eliminated in each case.

We have generated the radical cations of hydrocarbons by reaction with photoexcited acceptors and, among these, chloranil has proved to be especially useful.[6g,11,12] Because of the extremely low reduction potential of this quinone,[13] the reactions of its triplet state with many donors are strongly exothermic. Accordingly, a wide variety of radical cations can be generated and their reactions can be studied in polar solvents. A comparison of these reactions with those observed during triplet photosensitization is useful for assessing the involvement of radical ions in triplet sensitized reactions and for delineating reactivity differences between radical ions and triplet states.

In the paper presented here, we discuss several photosensitized rearrangements involving either the formation or the cleavage of cyclopropane and cyclobutane compounds. Among the reactions discussed are the geometric isomerization of the diphenylcyclopropanes,[11] the interconversion of norbornadiene and quadricyclane,[12] the possible interconversion of benzonorbornadiene and benzonortricyclene, and the electron transfer induced cyclodimerization of olefins and the cleavage of olefin dimers.[14] The first facets of many of these photoreactions were uncovered nearly 20 years ago; yet they have remained at the focal point of considerable attention.

The reactions discussed here involve primarily the unpaired spin but not the charge of the radical cations. Substantially different reactions are observed in the presence of substrates which are nucleophiles and/or bases. These react by nucleophilic attack or by deprotonation; reactions of this type are well documented.[15]

Experimental Section

Typical samples used in this study contained 2×10^{-2} M of an electron acceptor and the same concentration of an electron donor hydrocarbon in acetone-d_6 (Aldrich, Gold label) or acetonitrile-d_3 (Merck, Sharp & Dohme, 99%). These samples were deoxygenated by purging with argon for 3 min and irradiated in the probe of a Bruker WH 90 Fourier Transform NMR spectrometer with the collimated beam of a 1000-W Hanovia high-pressure mercury lamp. Because the absorption of chloranil (λ_{max} = 290 nm, $\epsilon = 2.5 \times 10^4$) is considerably greater than that of the donors (e.g., benzonortricyclene, λ_{max} 265, 272, 278 nm, $\epsilon \sim 9 \times 10^2$; benzonorbornadiene, λ_{max} 261, 268, 275 nm, $\epsilon \sim 5 \times 10^2$) greater than 95% of the incident light was absorbed by the acceptor.

A pulse angle of 90° was generally employed to minimize the total acquisition time for the CIDNP spectra. The total acquisition time for a ^{1}H CIDNP spectrum (25 sweeps) was typically 100 s. During this irradiation time the chemical conversion of the donor was ≤5% as judged by NMR examination. In view of this finding, the observed effects cannot be ascribed to secondary processes but have to be assigned to the primary photoreaction. This conclusion is demonstrated most clearly in the system chloranil–quadricyclane[12] where a chemical conversion actually occurs. In this reaction the polarization pattern of the rearranged product (norbornadiene) clearly originates in the radical cation of the reactant and not in the radical cation of the product.

Table I. Nuclear Spin Polarization Observed for 1,2-Diphenylcyclopropane and Hyperfine Couplings Patterns of Related Radicals and Radical Ions

protons	CIDNP	2	3	4	5
aromatic	A	−[a]	−	−[a]	−[a]
benzylic	A	+	+	−	−
secondary	E	+		+	+

[a] Weak positive hfc's for the aromatic meta protons are neglected in the presence of the strong, negative hfc's of the ortho and para species.

Radical Cations of Small-Ring Hydrocarbons

In the following section we will discuss reactions involving the radical cations of three pairs of isomeric hydrocarbons: a pair of geometric isomers (*cis*- and *trans*-diphenylcyclopropane), a pair of valence isomers (norbornadiene and quadricyclane), and a pair of isomers related by a more complex rearrangement (benzonorbornadiene and benzonortricyclene).

1,2-Diphenylcyclopropane

The photosensitized geometric isomerization of diphenylcyclopropane (**1**) was first reported by Hammond and co-workers.[16] Since then, numerous publications have been devoted to the elucidation of various facets of this reaction.[17] The interaction of **1** with triplet sensitizers caused ready isomerization ($\phi \approx 0.3$), a result which was ascribed to triplet energy transfer and rearrangement either in the triplet state or, alternatively, upon its deactivation. The reactions of **1** with aromatic hydrocarbons also resulted in geometric isomerization and, in this case, exciplexes were suggested as logical intermediates.[18] Finally, the involvement of radical ions was invoked to account for the nuclear spin polarization effects observed during the reactions of **1** with excited singlet acceptors[11,18] and with triplet chloranil.[11] The key to many of these results lies in the the nuclear spin polarization effects observed during the photoreaction of chloranil with **1**.

The observation of CIDNP effects requires a pair of paramagnetic intermediates and we have considered four such pairs. However, all but one pair can be eliminated. Hydrogen abstraction from **1** may generate tetrachlorosemiquinone and the cyclopropyl radical, **2**, whereas electron transfer might generate the chloranil radical anion paired with a radical cation, either with "localized" π spin density (**3**) or with fully delocalized spin density (**4** or **5**). Two of these intermediates, the radical, **2**, and the localized radical cation, **3**, can be eliminated, because the observed polarization pattern (Figure 1) is incompatible with their involvement (Table I). For the reaction discussed here the radical pair theory predicts emission for nuclei with positive hyperfine coupling constants

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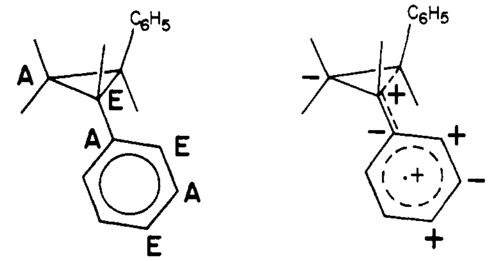
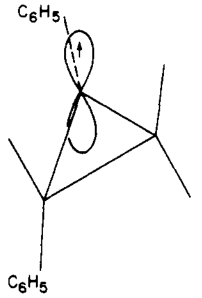
Chart I. ^{13}C CIDNP Pattern and ^{13}C Hyperfine Coupling Pattern of *trans*-1,2-Diphenylcyclopropane Radical Cation



whereas negative hyperfine coupling constants would lead to enhanced absorption.[11]



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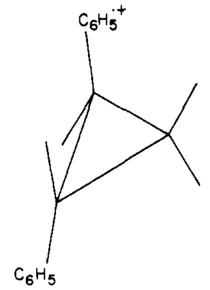

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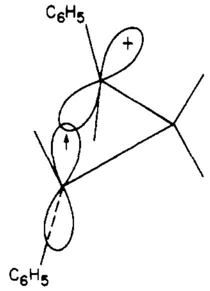

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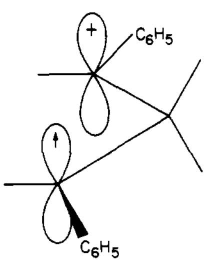

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The ^{13}C polarization observed during this reaction (Figure 2) leads to the same conclusion. The ^{13}C NMR spectrum of *trans*-**1** shows five lines since the carbon atoms in the ortho and para positions have identical chemical shifts. During the photoreaction with chloranil the signals representing the benzylic cyclopropane carbons and the carbon atoms in the ortho and para position of the aromatic ring appear in emission. The remaining signals show enhanced absorption; the signals of the quaternary and of the meta carbons are of comparable intensity and somewhat more strongly polarized than the secondary cyclopropane carbon. These results support a structure with positive spin densities not only in the ortho and para positions but also in the benzylic position. Accordingly, they are incompatible with the involvement of either the cyclopropyl radical, **2**, or the "localized" radical cation, **3**.

Both delocalized radical cations, on the other hand, are fully compatible with the pattern of ^1H and ^{13}C polarization. The principal difference between these structures lies in the arrangement of the substituents relative to the plane of the cyclopropane ring. In one of the open structures (**4**), each pair of substituents lies in a plane perpendicular to the ring and the benzylic π orbitals overlap in the plane of the ring. In the other delocalized structure (**5**) the entire π system lies in one plane. This intermediate should provide a ready pathway for isomerization upon reverse electron transfer. The fact that neither the CIDNP experiment nor a product analysis after prolonged irradiation gave any evidence for the formation of a rearranged product allowed us to rule out the fully coplanar structure, **5**, in favor of structure **4**. In summary, the results suggest that the energy surface of the diphenylcyclopropane radical cation has minima for two geometric isomers of structure type **4** corresponding to the cis and trans isomers of the parent hydrocarbon. An interconversion of these species could proceed via structure **5** or via a structure with one pair of substituents in the ring plane. However, neither potential transition state appears to be accessible at room temperature.

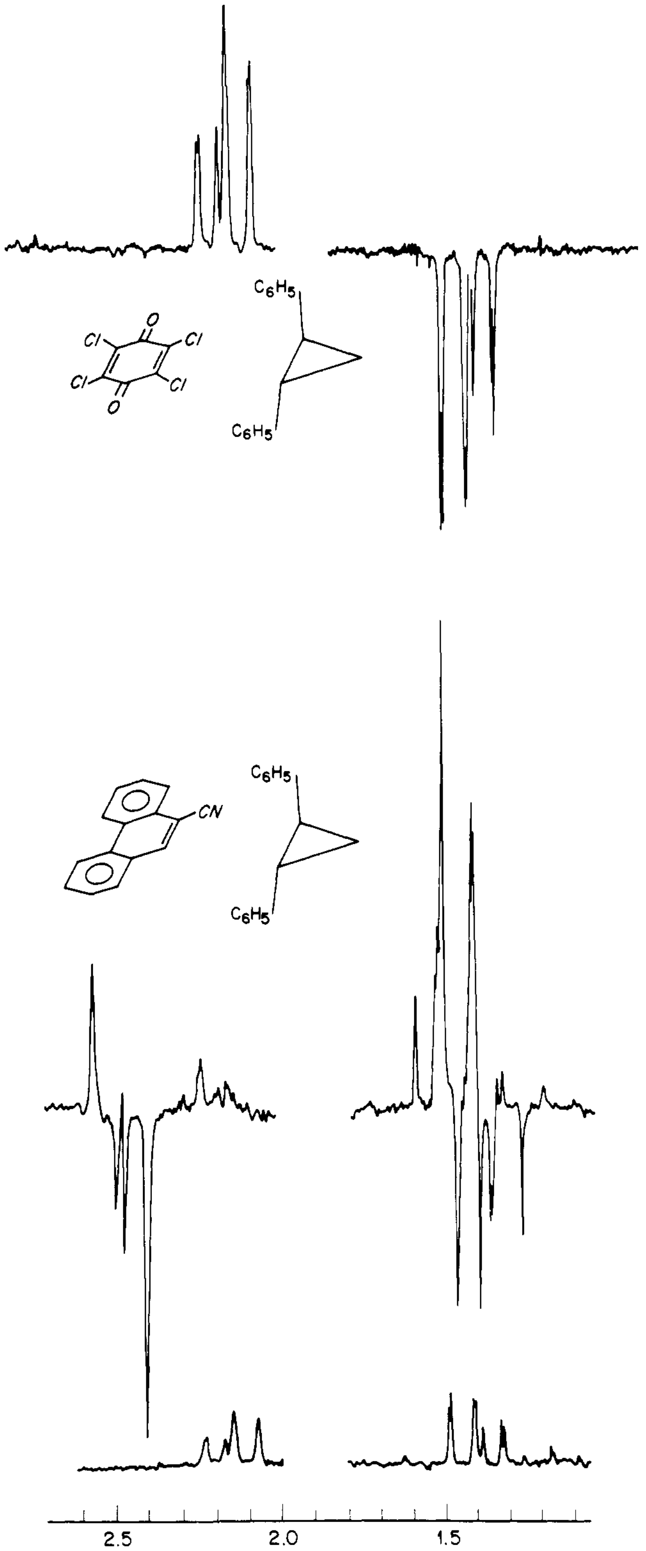


Figure 1. ^1H NMR spectra (90 MHz) observed during the irradiation of chloranil (0.02 M; top) or 9-cyanophenanthrene (0.02 M; center) in acetonitrile-d_3 solutions containing 0.02 M *trans*-1,2-diphenylcyclopropane. A dark spectrum of the hydrocarbon is shown as the botton trace.

The reactions of excited-singlet sensitizers with **1** in polar solvents also resulted in CIDNP effects[11,18] which are similar in some respect to those observed with chloranil, yet lead to a principally different interpretation. The observed effects (Figure

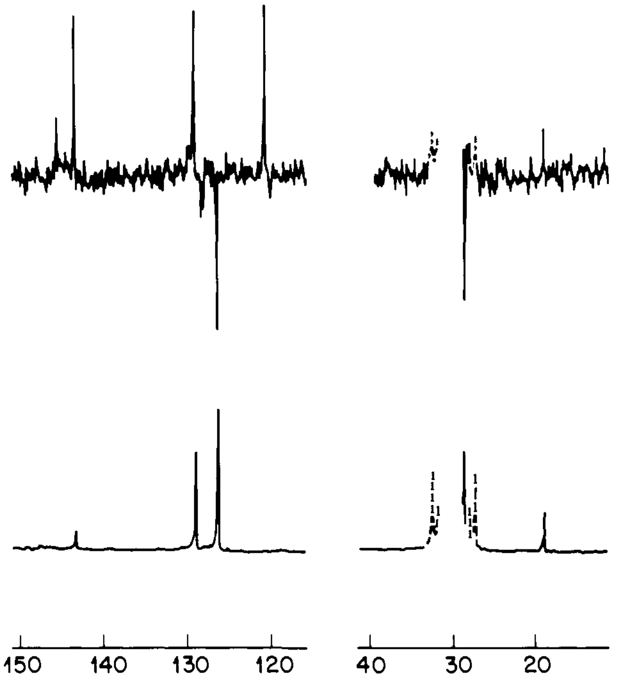
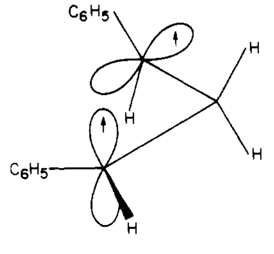


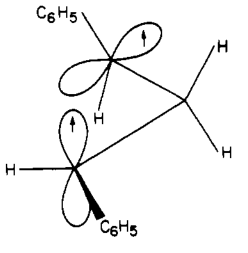
Figure 2. ^{13}C NMR spectra (22.5 MHz) observed during the photoreaction of chloranil (0.02 M) in acetonitrile-d_3 solutions containing 0.02 M *trans*-1,2-diphenylcyclopropane (top) and a 10% solution of the hydrocarbon in the dark (bottom). The dark spectrum is an accumulation of 2900 transients whereas the CIDNP spectrum is an accumulation of 250 transients.

1) suggest an intermediate with the same hyperfine coupling pattern as **4**; yet, the observation of a polarized, rearranged cyclopropane suggests an intermediate of different reactivity. One possible explanation for these results involves the intermediacy of a different radical cation, **5**. However, this explanation has to be rejected since this species was found to be inaccessible. A more likely explanation involves the consecutive formation of two different intermediates, the earlier one accounting for the polarization pattern, the second one accounting for the rearrangement.

The consecutive involvement of the radical cation, **4**, and of the triplet state, ^{3}**1**, is compatible with all experimental results. The cation is formed by electron transfer to the excited singlet state of the sensitizer. The resulting radical ion pair undergoes hyperfine induced intersystem crossing followed by singlet recombination to regenerate the reactants, or by triplet recombination to populate a diphenylcyclopropane triplet state. The energies of the intermediate radical ion pairs[19] do not permit an efficient population of the spectroscopic triplet state.[20] However, the intermediate in the triplet photosensitized isomerization of **1**, very likely a perpendicular triplet state, appears accessible energetically.[18] This triplet state may collapse to either the reactant or the rearranged cyclopropane.



^{3}1-Z



^{3}1-E

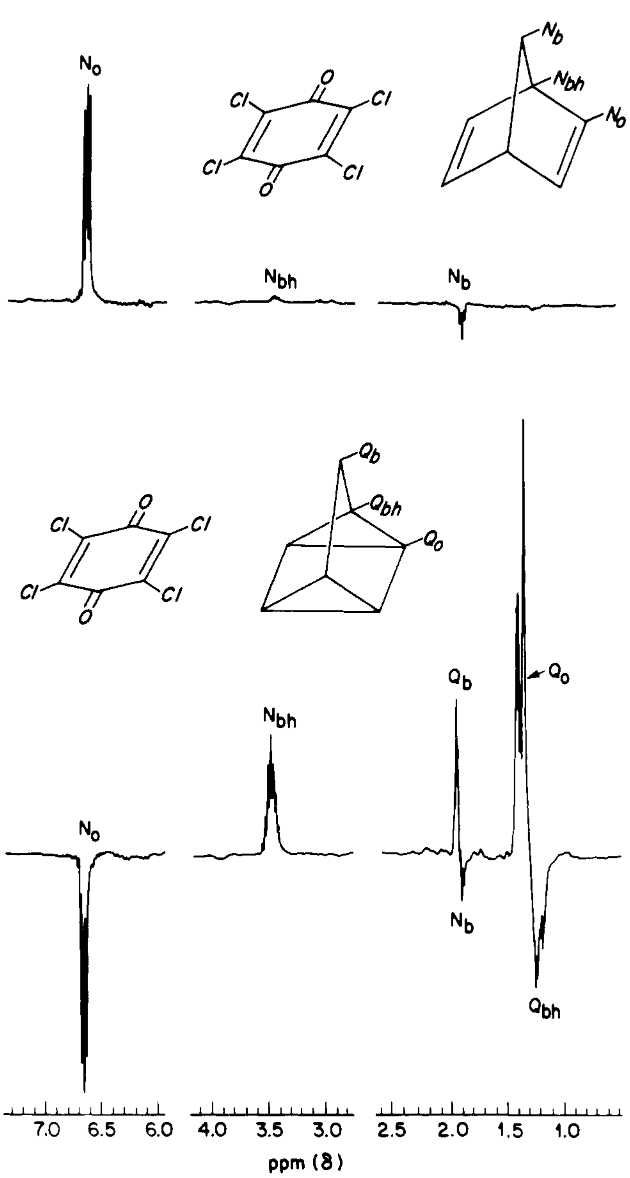


Figure 3. ^1H NMR spectra (90 MHz) observed during the photoreaction of chloranil (0.02 M) with norbornadiene (0.02 M; top) and quadricyclane (0.02 M; bottom). The resonances of norbornadiene and quadricyclane are denoted N and Q, respectively. Lower case indices identify the bridgehead (bh), bridge (b), and olefinic/cyclobutane positions (o).

A comparison of the two CIDNP experiments shows that two different intermediates with principally different reactivities are involved. The triplet state allows for geometric isomerization whereas the radical cation, **4**, is conformationally stable. This difference can be ascribed to principally different energy surfaces. The radical cation surface has two minima with geometries corresponding to the cis and trans substrates. These are separated by a barrier sufficient to prevent interconversion. In contrast, the triplet surface has minima which allow deactivation to either isomer with comparable ease.

Norbornadiene–Quadricyclane

The interconversion of norbornadiene (**6**) and quadricyclane (**7**) is well characterized in the excited singlet and triplet states.[21] In contrast, the energy surface of the radical cations derived from this pair of valence isomers poses some interesting problems. The photoelectron spectra of **6** and **7** reveal the existence of two discrete radical cation states,[22] a conclusion which is supported by MINDO/3

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[19] Calculated according to $\Delta G = E_{(D/D^+)} - E_{(A^-/A)} - e^2/\epsilon a$ from the reduction potential of the acceptor, the oxidation potential of the donor, and from a Coulomb term (~0.2 eV) accounting for ion pairing: Knibbe, H.; Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1968**, *72*, 257.

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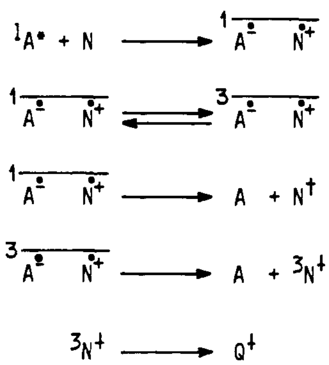
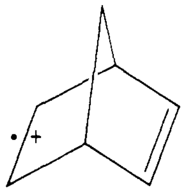
Scheme I



calculations.[22c] On the other hand, the observation that the mass spectra of the two valence isomers have nearly identical fragmentation patterns prompted the conclusion that their molecular ions are identical with regard to energy and structure.[23] A third experimental technique, γ irradiation of frozen solutions, resulted in the formation of a single species from both **6** and **7**. This species was identified as a norbornadiene radical cation.[22c] Finally, the application of the CIDNP technique resulted in the observation of significantly different polarization patterns (Figure 3) for the reactions of chloranil with **6** and with **7**.[12] These results are incompatible with the concept of a single intermediate, **9**, for both reactions. Rather, they provide evidence that two discrete radical cations, **8** and **10**, respectively, with lifetimes greater than several nanoseconds are derived from the two hydrocarbons.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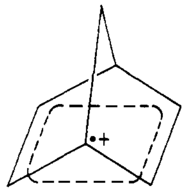
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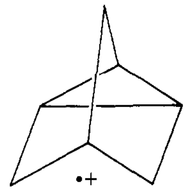
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Another significant conclusion derived from the CIDNP study concerns the interconversion of the two radical cations in the chloranil photosensitized reactions. The radical cation derived from quadricyclane apparently rearranges readily whereas no evidence was found that would support the isomerization of the radical cation derived from norbornadiene. We explain this difference by assuming an energy surface with two intermediates of different energies. Available thermochemical and electrochemical data support this assignment. The ground state of **7** lies at least 22 kcal/mol[24,25] and possibly as much as 27 kcal/mol[26] above that of **6**. The oxidation potential of **7** (0.91 vs. SCE)[27] is 0.63 V lower than that of **6** (1.54 V vs. SCE).[27] Accordingly, the energy of **10** lies between 9 and 14 kcal/mol above that of **8**. This energy difference is sufficient to account for substantially different interconversion rates of the two species.

As in the case of 1,2-diphenylcyclopropane, the reaction of singlet acceptors with **6** also gives rise to CIDNP effects. These show the polarization pattern compatible with the intermediacy of **8** but also show evidence for the formation of the valence isomer. Once again, these results can be explained by the consecutive involvement of the radical cation, **8**, and of the triplet state, ^{3}**6**. The energy of the radical ion pair generated by electron transfer from **6** (E_{ox} = 1.54 V)[27] to 1-cyanonaphthalene (E_{red} = −1.8 V vs. SCE)[28] lies well above the triplet states of both the donor (E_{T} = 68–70 kcal/mol)[29] and the acceptor ($E_{\mathrm{T}} \sim$ 57 kcal/mol)[28,30] so that triplet recombination is energetically feasible. This sequence of reactions is shown in Scheme I, where A and D denote, respectively, acceptor and donor, an asterisk denotes an excited state, and daggers denote polarized products.

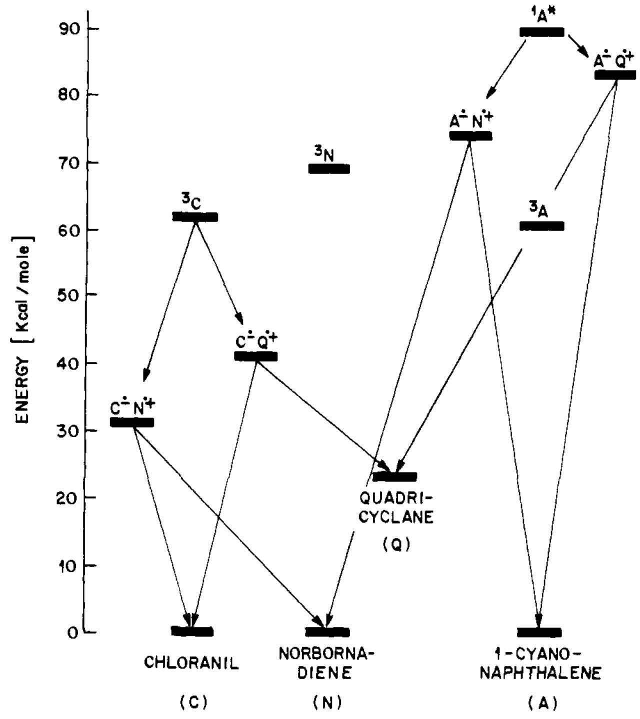
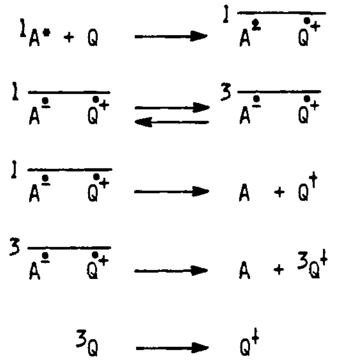


Figure 4. Energy levels of relevant intermediates in the photoreactions of chloranil and 1-cyanonaphthalene with norbornadiene and quadricyclane.

Scheme II



In contrast to the reaction of singlet sensitizers with **6** and of triplet sensitizers with **6** or **7**, the reaction of 1-cyanonaphthalene with **7** did not produce any polarization. While it is rarely prudent to draw conclusions from the failure to observe CIDNP effects, we note that this result is not incompatible with a special feature postulated for the triplet energy surface of the system norbornadiene–quadricyclane.[21c] Because of the efficient triplet sensitized conversion of **6** to **7** it was suggested that the geometry of the minimum lies closer to the quadricyclic than to the bicyclic valence isomer. If this premise is accepted, no net polarization is expected in the reaction of 1-cyanonaphthalene with **7**. Both singlet recombination of the resulting ion pair and triplet recombination would regenerate quadricyclane and the complementary polarization components associated with these reactions would

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Table II. Polarization Observed for Benzonortricyclene and Hyperfine Coupling Patterns of Related Radical Ions

position	CIDNP	**14**	**15**	**16**	**17**
H_1	E	+	+	+	−
H_4	A	+	−	−	+
H_5			−	+	
H_{6endo}	E		+		
H_{6exo}	E		+		
H_7	A		+	−	

cancel each other (Scheme II).

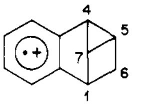
Regardless of the detailed features of the triplet energy surface, it is clear that its single minimum makes it principally different from the radical ion surface which has two minima. In the triplet manifold, norbornadiene is readily converted to quadricyclane whereas the radical cations show a conversion only in the opposite direction.

Benzonorbornadiene–Benzonortricyclene

In analogy to the photosensitized rearrangement of norbornadiene, the triplet photosensitized reaction of benzonorbornadiene (**11**) leads to a more complex ring system, benzonortricyclene (**12**).[31] This interconversion has been formulated as a di-π-methane rearrangement.[32] The radical cations of these valence isomers can be generated by photoreaction with chloranil and their potential interconversion can be evaluated.

The ^1H CIDNP effects observed during the reaction of chloranil with **11** indicate that the benzonorbornadiene radical cation, **13**, has a delocalized structure with negative hyperfine coupling in the aromatic moiety and in the olefinic bond, whereas strong ^{13}C emission for the quaternary carbon indicates high-spin density in that position. Additional CIDNP signals indicate the formation of at least one rearrangement product but there is no evidence for a conversion of **13** to the radical cation of benzonortricyclene. In view of the precedent provided by the norbornadiene radical cation, the failure of **13** to rearrange to a more highly strained species is not unexpected. The more important question remains whether the radical cation derived from benzonortricyclene will undergo a reorganization analogous to the di-π-methane rearrangement. This reorganization would result in radical cations related to either benzonorbornadiene or benzonorcaradiene.

The reaction of chloranil with benzonortricyclene gives rise to a complex CIDNP pattern which allows an insight into the structure of the radical cation only after a detailed examination of the NMR spectrum of **12** and a thorough evaluation of several potential intermediates. Three structure types were considered: the simplest intermediate would have charge and spin localized in the benzene ring (**14**); in two others, one benzylic cyclopropane bond is broken or weakened (**15** or **16**); the third structure type is one in which a benzylic cyclobutane bond is broken (**17**). This intermediate could be a strategic intermediate in the formation of benzonorcaradiene.



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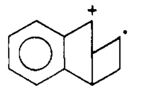

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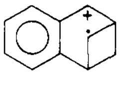

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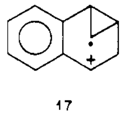

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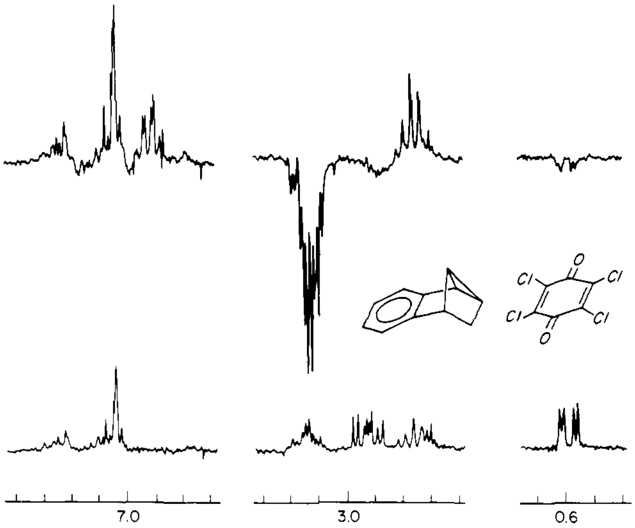
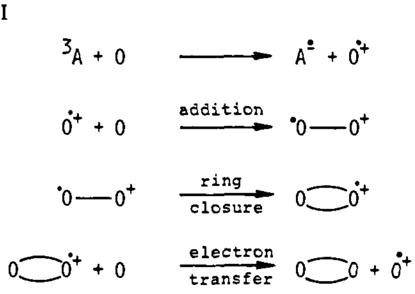


Figure 5. ^1H NMR spectra (90 MHz) of an acetonitrile-d_3 solution containing chloranil (0.02 M) and benzonortricyclene (0.02 M) in the dark (bottom) and during UV irradiation (top).

Scheme III



Two of these structures can be eliminated by considering the polarization of only the benzylic protons (Figure 5) in the light of the hyperfine coupling patterns expected for the four structures, **14**–**17** (Table II). For this reaction the radical pair theory[7] predicts emission for nuclei with positive hyperfine coupling and enhanced absorption for nuclei with negative hyperfine coupling. Proton H-1 appears as a partially obscured doublet of triplets at 3.3 ppm showing strong emission whereas proton H-4 appears as a triplet at δ 2.6 ppm showing weakly enhanced absorption. The observation of opposite polarization for the two protons is incompatible with the localized structure (**14**) as the sole contributing structure, whereas a consideration of the polarization determining parameters eliminates the structure with an opened cyclobutane ring (**17**). This structure would lead to signal directions opposite to those observed. The different annelation of the two remaining structures should manifest itself in different hyperfine coupling patterns (Table II). However, the weak effects observed for the protons H-4, H-5, H-6_{endo}, and H-7 do not allow a clear-cut differentiation between structures **15** and **16** and the actual intermediate may have contributions from both as well as from structure **14**, which is a resonance structure of both.

Regardless of the structural details of the benzonortricyclene radical cation, it is quite clear that this intermediate does not undergo rearrangement to the radical cations of either benzonorbornadiene or benzonorcaradiene. Once again, the reaction products of triplet states are quite different from those of radical ions.

Electron Transfer Induced Cyclodimerization of Olefins and Cleavage of Olefin Dimers

The reaction of photoexcited acceptors with olefins generates the radical cations of these substrates initiating a variety of reactions. We have found evidence that they undergo geometric isomerization and that they are involved in degenerate electron exchange with the parent olefin.[6g] Instead of the degenerate exchange, radical ions may react with olefins by addition to generate an extended radical cation. This reaction initiates the formation of olefin dimers, a process which is completed after two additional steps, ring closure to form a secondary adduct and electron transfer from a suitable reaction partner.

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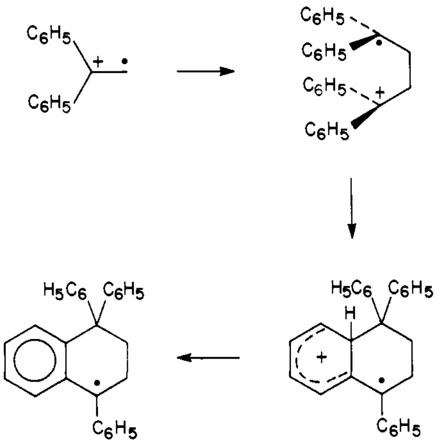
This mechanism explains several features of electron transfer sensitized dimerizations which set them apart from triplet sensitized dimerizations. For example, under typical reaction conditions the radical ions may have comparably short lifetimes so that the addition reaction may not compete efficiently with the annihilation of the ions by reverse electron transfer even at diffusion controlled rates. These considerations explain the lower efficiency of electron transfer induced dimerizations relative to triplet sensitized dimerizations. On the other hand, the bifunctional nature of the adduct radical cations causes their thermodynamic stability to depend on the delocalization of the unpaired spin and of the positive charge. It is well established that head-to-head adducts are usually preferred over head-to-tail adducts.[33] In the stability of the primary adducts lies the key to the high selectivity of electron transfer induced dimerization of olefins. The detailed mechanism of this type of dimerization is quite different from triplet photosensitized dimerizations of olefins which usually are less selective.

The photoreaction of chloranil with olefins such as dimethylindene, *N*-vinylcarbazole, or phenyl vinyl ether[6g] results in strong polarization for the olefins (e.g., Figure 6, top), but fails to give rise to dimer polarization. The absence of dimer polarization requires a reaction mechanism which allows the relaxation of the polarization inherent in the monomer radical cations. Accordingly, the combined lifetimes of the three consecutive radical ions, i.e., the time elapsed between the generation of the olefin radical cation and the electron transfer to the closed dimer radical cation, must be longer than the typical relaxation time of a radical ($^2T_1 \approx 10^{-6}$ s). At least one of the steps leading to the dimer must be inefficient. The ring closing reaction is likely to be the least efficient step of cyclodimerization since the most stable adduct radical cation may experience severe steric repulsion of the carbon centers in the 1- and 4-position. This may force the intermediate into an alternative pathway. For example, the electron transfer induced dimerization of 1,1-diphenylethylene features a 1,6- rather than a 1,4-ring closure.[34]



In contrast to other olefins, the reaction of chloranil with acenaphthylene gives rise to monomer as well as dimer polarization. The olefinic singlet appears in enhanced absorption whereas the cyclobutane singlets of cis and trans dimer show emission.[35] We do not consider this result as evidence for a different dimerization mechanism. The dimer polarization is significantly weaker than the olefin polarization. The principal reason for its observation may well lie in the simplicity of the dimer spectra.

Scheme IV

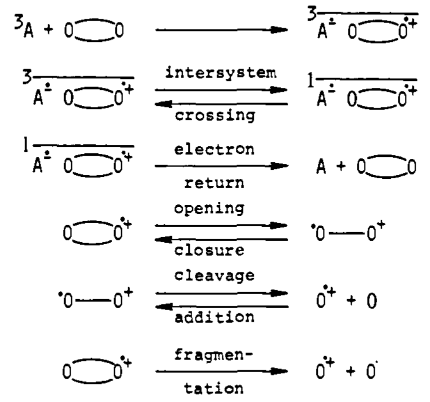


Table III. Polarization Observed for Dimethylidene Dimer and Hyperfine Coupling Patterns of Related Radical Ions

	CIDNP	20	21	22
H_α	E	+	−	−
H_β	E	(+)	+	−

In order to observe dimer formation, the overall rate of the "forward" reactions, addition and closure (Scheme III), must be faster than the overall rate of the "reverse" reactions, opening and cleavage (Scheme IV). If this condition is not met, olefin dimerization will not occur, and dimers will suffer cleavage via a reaction sequence which is essentially the reverse of that described above. For example, the dimer of dimethylthymine is cleaved efficiently upon electron transfer to photoexicted (triplet) anthraquinone.[6c] Apparently, the resulting dimer cation suffers ring opening and cleavage more rapidly than the radical ion pair can undergo intersystem crossing. As a result, essentially no electron return to the dimer cation is possible. Of course, these results do not allow one to differentiate between a two-step sequence, ring opening followed by cleavage, and a concerted one-step fragmentation. In other systems opening and cleavage (or their mechanistic eqivalent) are comparably slower so that intersystem crossing and electron return become competitive. In such systems dimer and monomer polarization are observed simultaneously. For example, the photoreaction of chloranil with the dimethylindene dimer resulted in emission for the cyclobutane signals of the dimer and enhanced absorption for the olefinic signal of the monomer. The opposite signal directions indicate that the polarized monomer and the polarized dimer are generated by different mechanistic pathways. The observation of monomer polarization places a limit on the lifetimes of the intermediate radical ions since, regardless of the mechanism of product formation, these lifetimes must be sufficiently short to prevent complete relaxation. The range of nuclear spin–lattice relaxation times for radicals dictates that the lifetimes cannot be longer than 10^{-6} s.

The polarization pattern observed during the reaction of the dimer for both monomer and dimer (Figure 6, bottom) during its reaction with photoexcited chloranil allows an even farther reaching conclusion. This polarization is unusual because the benzylic (H_α) and the homobenzylic (H_β) cyclobutane protons show emission of comparable intensities and because the two olefinic doublets show enhanced absorption of comparable intensities. This pattern is quite different from that observed during the reaction of the monomer (Figure 6, top). These results appear to suggest an intermediate in which H_α and H_β have hyperfine coupling constants of comparable magnitude and of identical sign. Neither the closed (**19**) nor the open (**20**) radical cation derived from the dimer meet this requirement. On the other hand, a cyclobutane radical cation (**21**), which is consistent with the observed polarization pattern (Table III), appears energetically unfavorable since this structure fails to utilize any element of stabilization.

The observed polarization can be explained as a cooperative effect[36] of two consecutive radical ion pairs, containing the

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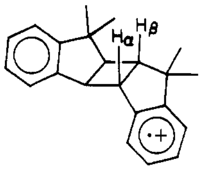
[33] (a) Ledwith, A. *Acc. Chem. Res.* **1973**, *5*, 133. (b) Farid, S.; Shealer, S. E. *Chem. Commun.* **1973**, 677. (c) Kuwata, S.; Shigemitsu, Y.; Odaira, Y. *J. Chem. Soc. D*, **1972**, 2. (d) Kuwata, S.; Shigemitsu, Y.; Odaira, Y. *J. Org. Chem.* **1973**, *38*, 3803.

[34] Neunteufel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 4080.

[35] Finn, B. M., unpublished results.

[36] (a) den Hollander, J. A. *Chem. Commun.* **1975**, 352. (b) den Hollander, J. A. *Chem. Phys.* **1975**, *10*, 167.



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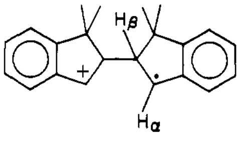

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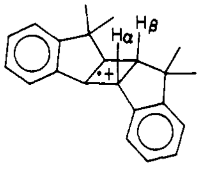

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chloranil radical anion and the open (**20**) or closed cation (**19**), respectively, derived from the dimer.[37] This assignment implies that the two species, **19** and **20**, have comparable lifetimes and that the ring-opening step is reversible, all in all a strong argument for the two-step mechanism of ring cleavage and against the concerted fragmentation mechanism.

In summary, the electron transfer induced cyclodimerization of olefins and the cleavage of olefin dimers show evidence for the interconversion of three types of radical cations. Although in some cases (dimethylthymine dimer radical cation) the reaction is decidedly unidirectional, other systems provide evidence for the reversibility of each individual step.

Conclusion

Radical cations have been found to undergo simple reactions such as radical additions to olefins, cleavage of cyclopropane or cyclobutane bonds, and fragmentations. However, they apparently do not undergo the more complex reorganizations which are characteristic for molecules in the triplet state. The differences in radical ion and triplet state reactions are explained as a consequence of substantially different energy surfaces.

The observed reactivity differences tend to argue against the involvement of radical ions in triplet photosensitized rearrangements such as the conversion of **6** to **7** or **11** to **12**, and a large number of additional structural reorganizations. Further support for this conclusion can be derived from the fact that the radical cations discussed in this paper were generated under optimal conditions, i.e., in highly polar solvents and with a sensitizer of negligible reduction potential. In contrast, typical triplet photosensitized conversions are carried out in solvents of lower polarity and with sensitizers of considerably higher reduction potentials. These considerations eliminate radical ions as intermediates in most typical triplet sensitized rearrangements.

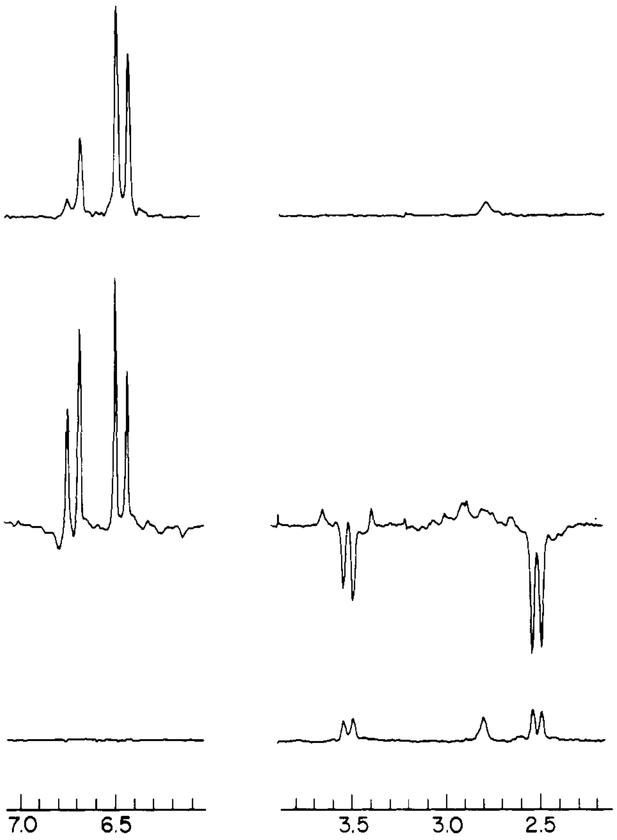

Figure 6. ^{1}H NMR spectra (90 MHz) observed during the irradiation of chloranil (0.02 M) in acetonitrile-d_3 solutions containing dimethylindene (0.02 M; top) and its cyclodimer (0.02 M; center). A dark spectrum of the dimer (0.02 M) is shown as the bottom trace.

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[37] Hutton, R. S., unpublished results.