CONSECUTIVE RADICAL ION PAIRS IN THE CYCLOREVERSION OF A DIMETHYLINDENE DIMER: A CASE OF COOPERATIVE SPIN POLARIZATION EFFECTS

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Nuclear spin polarization effects observed during the electron transfer-induced cleavage of the *trans* head-to-head dimer of 3,3-dimethylindene are incompatible with the intermediacy of a single dimer radical cation. Instead, they are compatible with the 'cooperative' involvement of a localized, doubly linked and a delocalized, singly linked dimer radical cation. The mechanistic consequences for the cycloaddition and cycloreversion of radical cations are discussed.

INTRODUCTION

The chemistry of organic radical cations continues to attract considerable attention and a variety of techniques continue to be applied to elucidate their structures and to probe their rearrangements, cycloadditions and cycloreversions.[1–5] It is generally recognized that radical cation reactions have considerably lower activation barriers than do the corresponding reactions of their closed-shell precursors. This observation can be ascribed to the fact that the highest occupied molecular orbital (HOMO) of a radical cation is occupied by a single electron. Accordingly, the bond strength(s) of one or more key bonds must be reduced and hence, the bonds are more easily decoupled.

However, the barriers to some radical cation rearrangements appear to be even lower than might be expected from this simple model. We hve identified several systems in which the energy surfaces of radical cations and their diamagnetic precursors show a remarkable reversal of relative stabilities.[6–8] In particular, some radical cation cycloaddition/cycloreversions of diolefins or their dimers proceed via distinct intermediates, whereas the corresponding reactions of the diamagnetic precursors are concerted.[9,10] We report here results pertinent to a different cycloaddition/cycloreversion, viz. the electron transfer-induced dimerization of monoolefins leading to cyclobutanes. This reaction type is well established for a variety of substrates.[11–13] The selective formation of head-to-head dimers is compatible with a stepwise mechanism proceeding via a singly linked, bifunctional

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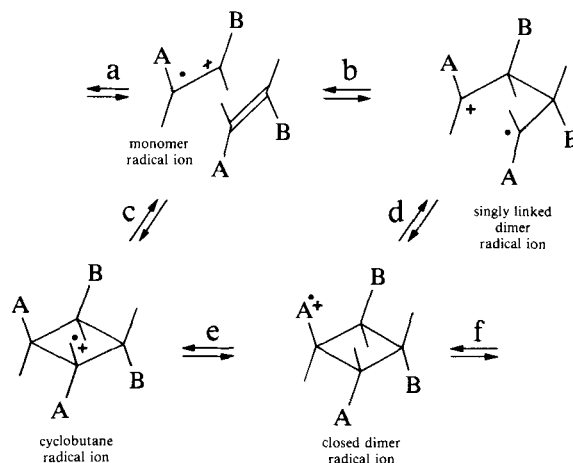
Scheme 1

intermediate, stabilized by delocalization of spin and charge (Scheme 1). Our results, observed during the photoinduced electron transfer reaction of a dimethylindene dimer, fully support the intermediacy of such species, but also require the involvement of a ring-closed dimer radical cation.

EXPERIMENTAL AND RESULTS

Method

The radical cations of electron-donor hydrocarbons can be generated as short-lived intermediates by electron

transfer to photoexcited acceptors.[4,14] In a magnetic field the resulting radical ion pairs undergo hyperfine induced singlet–triplet mixing. Diamagnetic products formed from these pairs in subsequent electron spin-dependent reactions show characteristic non-equilibrium populations in their nuclear spin levels. According to the radical pair theory, the directions and intensities of nuclear spin polarization (CIDNP) effects are determined by several parameters, including the spin multiplicity of the precursor, the magnetic properties (electron g factor and hyperfine coupling constants, hfc) of the radical intermediates and the type of reaction by which the diamagnetic, polarized product is generated from the paramagnetic (doublet) precursor.[15–18]

In many cases CIDNP effects induced in this fashion can be related directly to the signs and relative magnitudes of hyperfine coupling constants of the paramagnetic intermediates. The hfcs, in turn, can be interpreted in terms of carbon spin densities, revealing significant structural features of the intermediates. However, the interpretation of CIDNP results according to the radical pair theory is not without pitfalls.

A number of processes have been identified which may distort 'first-order' effects or generate misleading effects. For example, the existence of an alternative polarization mechanism has been established. The triplet Overhauser mechanism is based on different physical principles and has been found to dominate the spin polarization effects in a few systems.[19–22] Second, the observed polarization may be distorted as a result of different spin–lattice relaxation rates[23,24] or, less trivially, as a result of cross-relaxation.[25–28] Third, reactions proceeding via consecutive radical pairs with different magnetic properties may lead to polarization effects which are seemingly incompatible with the properties of either the primary or the secondary pair.[29,30]
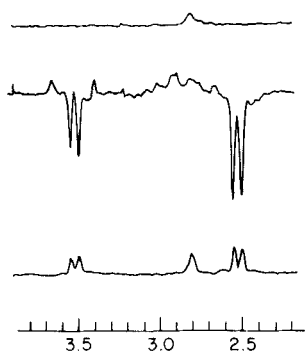

Figure 1. ¹H NMR spectra (2·1–3·9 ppm region) observed during the irradiation of chloranil (0·02 M) in acetonitrile-d_3 solutions containing dimethylindene (0·02 M) (top) and its trans head-to-head cyclodimer (0·02 M) (center). A dark spectrum of the dimer (0·02 M) is shown as the bottom trace
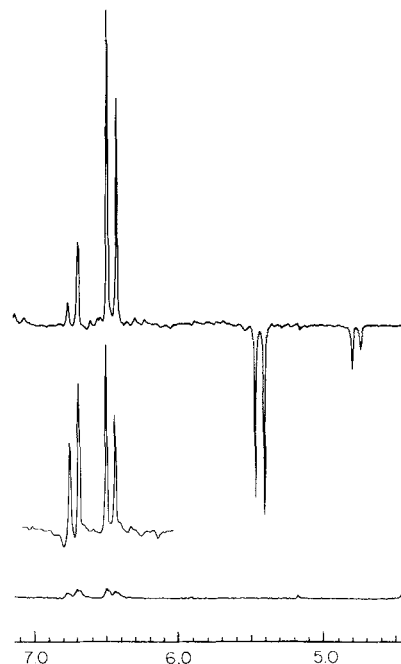

Figure 2. ¹H NMR spectra (5·5–7·1 ppm region) observed during the irradiation of acetone-d_6 solutions containing 0·02 M chloranil and dimethylindene (0·02 M) (top) and its dimer (0·02 M) (center). A dark spectrum of the monomer (0·02 M) is shown as the bottom trace. The emission doublets near 5·4 and 4·8 ppm are due to an adduct oxetane between the dimethylindene C=C and the quinone C=O bonds[48]

In this paper we report an analysis of CIDNP effects observed during the photosensitized cleavage of the trans head-to-head dimer of dimethylindene (1). During the UV irradiation of chloranil in the presence of 1 the benzylic (α) and the non-benzylic (β) cyclobutane protons of the dimer showed emission of comparable intensities (Figure 1). At the same time, the olefinic protons of the monomer showed enhanced absorption, also of comparable intensities for the α and β protons (Figure 2).

This polarization pattern, as the polarization observed by den Hollander,[29,30] is seemingly incompatible with the expected intermediates. It appears to suggest that the benzylic and non-benzylic protons of the intermediate have hyperfine coupling constants of identical (positive) sign and comparable magnitude.

Potential intermediates

The structure of the cyclobutane radical cation has been calculated by several groups. Bauld et al.[31] modeled the cycloaddition of ethene radical cation to ethene by the MNDO method. At this level of theory an

A (D_{2h})

B (D_{2h})

C (C_{2v})

D (C_{2v})
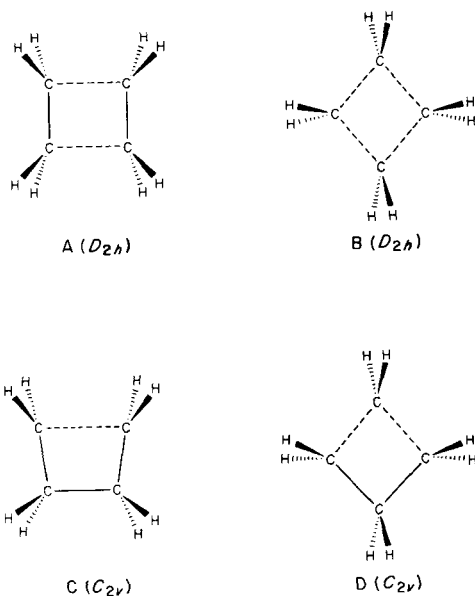
Scheme 2

unsymmetrical structure with one long one-electron C—C σ-bond is of lowest energy (Scheme 2, type C). Bouma et al.[32] carried out ab initio molecular orbital calculations. They found that loss of an electron from one of the e_u orbitals of cyclobutane leads to a Jahn–Teller unstable radical cation, which gives rise to distorted structures of D_{2h} and C_{2v} symmetry, respectively. Of four structures calculated, a rectangular structure with two weakened C—C bonds (type A) and a rhomboidal structure with four weakened C—C bonds (type B) were found to be of equal energy, 16 kJ lower than a C_{2v} structure with one weakened C—C bond.

Ushida et al.[33] observed EPR spectra for x- irradiated cyclobutane in frozen CFCl₃ solution. At 4 K these spectra showed four strongly coupled protons (two pairs with splittings of 49 and 14 G) and four weakly coupled protons (5 G). These findings were interpreted in terms of a radical cation that had undergone static Jahn–Teller distortion to a rhomboidal structure of C_{2v} symmetry (type D). Above 77 K the Jahn–Teller distortion is averaged out and a nearly isotropic nine-line spectrum is observed. Additional structure types compatible with the low-temperature ESR pattern can be envisaged and cannot be rigorously eliminated. A different structure was suggested on the basis of fluorescence detected magnetic resonance observed by Desrosiers and Trifunac[34] during the pulse radiolysis of tetramethylethene and anthracene-d_{10} in methylcyclohexane. The spectra are compatible with a dimer cation with eight equivalent methyl groups, and were interpreted as evidence for a radical cation with two weakened C—C bonds (type A).

We note, however, that a simulation of the FDMR spectra cannot distinguish between a species with four and eight methyl groups, especially not at the modest signal-to-noise ratios typical for these experiments. Hence, the intermediate of type C cannot be ruled out unambiguously.

Compared with the parent system and the symmetrically substituted one, the structure of the derivative considered here should be affected by the substitution pattern and by the nature of the substituents. The substitution pattern allows delocalization of spin and charge only for two (adjacent) ring positions. Therefore, the structure type C, in which the doubly benzylic C—C bond is weakened (and lengthened), should be strongly favored. The substituents have a lower ionization potential (IP_{benzene} 9·25 eV)[35] than the cyclobutane moiety (IP 10·7 eV);[36] hence, the primary ionization is expected to occur from one of the phenyl groups.

Accordingly, we consider three types of species to be potential key intermediates in the generation of the observed polarization (Scheme 3). First, we contemplate

2

3

4

a_α = 6.5G

a_α = -16G

a_α = -1.4G

a_β = 1.5G

a_β = 22G

a_β = -9.3G

Scheme 3
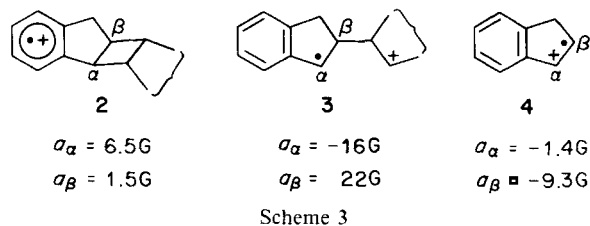
a radical cation, 2, in which charge and spin are localized in an aromatic moiety and the cyclobutane ring is unaffected. The singly occupied molecular orbital (SOMO) of this 'closed dimer' radical cation should resemble that of the indane radical cation. Second, we consider the radical cation 3, in which the doubly benzylic cyclobutane bond is broken (or weakened) and charge and spin are delocalized over the benzylic positions and into the aromatic moieties. Finally, in view of precedent for the fast fragmentation of dimer radical cations, we consider the dimethylindene (monomer) radical cation 4 as the possible origin of the observed polarization.

The 'closed' (doubly linked) radical cation has not been characterized by EPR, but the pertinent hyperfine coupling constants can be assigned on the basis of the following considerations. An EPR spectrum has been observed and hyperfine coupling constants have been determined for the indane radical anion,[37] which should have a geometry not too different from that of the radical cation 2. Based on the coupling constants measured for the radical anion and, taking into account the fact that the proportionality factor, Q, which determines the hyperfine coupling constants for a given carbon spin density is 30–40% greater for cations than

for anions,[38] we assign coupling constants of $+6 \cdot 5$ and $+1 \cdot 5$ G, respectively, for the α- and β-protons of **2**.

The 'open' radical cation **3**, again has not been observed. Its hyperfine coupling constants depend on its conformation; spin and charge may be delocalized throughout both benzyl groups or, alternatively, over one benzyl moiety each; the following assignments are based on the latter case. The benzylic proton, H_α, is assumed to have a typical benzylic hyperfine coupling, $a_\alpha = -16 \cdot 4$ G.[39] The non-benzylic proton coupling is assigned according to the empirical relationship[40]

$$a_\beta = A_0 + A_1 \cos^2 \Theta$$

where the constants $A_0 = 2$ G and $A_1 = 32$ G are derived from the 1-phenylethyl radical and Θ is assigned the value $38°$ on the basis of model considerations; hence, $a_\beta = +22$ G. Should spin and charge be delocalized over both benzylic groups, two α- and two β-couplings would result, each with half the magnitude indicated above. Finally, the hyperfine coupling constants of the dimethylindene radical cation **4** were assigned on the basis of calculated spin densities,[41] $\rho_\alpha = 0 \cdot 059$ and $\rho_\beta = 0 \cdot 403$, and with the relationship, $a = -23 \rho$. Hence, $a_\alpha = -1 \cdot 4$ G and $a_\beta = -9 \cdot 3$ G.

Given these hyperfine patterns (Scheme 3), the nuclear spin polarization effects expected for the three intermediates can be simulated on the basis of the radical pair theory. Other parameters used in the simulation include g factors of $2 \cdot 0048$ for the chloranil radical anion and $2 \cdot 0028$ for the radical cations; $\Delta g = 0 \cdot 0020$. In view of the short lifetime of the quinone excited-singlet state and the moderate concentration of the hydrocarbon/quencher employed in the experiment, the initial spin multiplicity of the ion pairs was assumed to be triplet. Finally, reaction products were assumed to be formed by reverse electron transfer in pairs of singlet multiplicity. The simulations of the pair reactions involving the chloranil radical anion and the closed dimer cation **2** and the open dimer cation **3** are shown in Figure 3b and c, respectively. Comparison of these simulations with the experimental results (Figure 3a) shows clearly that neither of the dimer cations can, by itself, account for the observed dimer polarization. Similarly, the intermediacy of the monomer radical cation cannot account for the monomer polarization observed during the cleavage of the dimer, although it explains satisfactorily the polarization observed during the photoinduced electron transfer reaction of the monomer (Figure 4).

Since conventional structures fail to explain the observed effects, we consider two additional structures: a hybrid of structure **2** and **3** and the radical cation **5**, in which charge and spin are nearly evenly distributed over the four carbon atoms of the alicyclic ring. As a result, the four cyclobutane protons have nearly equivalent hyperfine coupling constants (cf. structure types A and B, Scheme 2). However, this structure must
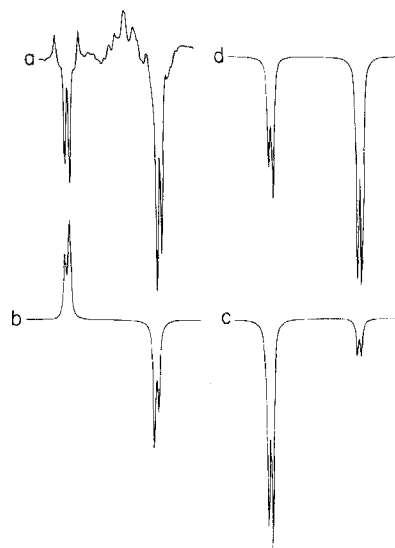

Figure 3. CIDNP effects observed for the cyclobutane signals of the dimethylindene dimer during the photoinduced electron transfer reaction with chloranil (a), and simulated spectra based on the radical pair theory and assuming a ring-opened (extended) dimer radical cation (b), a ring-closed (localized) dimer radical cation (c) and the consecutive ('cooperative') involvement of open and closed radical cations (d)
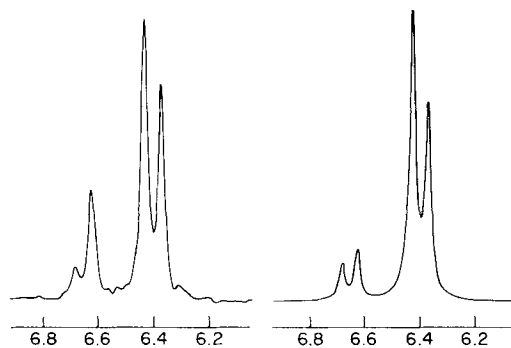

Figure 4. CIDNP effects observed for the olefinic signals of dimethylindene during the photoinduced electron transfer reaction with chloranil (left) and simulated spectrum based on the radical pair theory assuming the intermediacy of the monomer radical cation (right)

be eliminated for two reaons. First, it is incompatible with the direction of the observed spin polarization. The ring protons of the cyclobutane radical cation should have negative hyperfine coupling constants, which would lead to enhanced absorption instead of the observed emission. Second, this radical cation fails to utilize any element of benzylic stabilization, in direct conflict with the selective formation of head-to-head dimers and in direct contrast to several substituted

cyclopropane radical cations. For these species, structures utilizing benzylic (e.g. 6) or hyperconjugative stabilization (e.g. 7) are favored over alternative structures (e.g. 8), in which spin and charge are equally
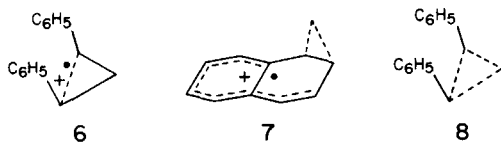
distributed over all three cyclopropane carbons. This assignment was based on CIDNP effects[42-44] and has been confirmed in one case by EPR results which, in addition, support the existence of a ring-opened, trimethylene species.[45]

The hybrid of structures 2 and 3 has to fulfill stringent requirements: the doubly benzylic bond must be weakened to allow some spin density to reach the α-carbons; this spin density must be large enough to induce a sufficiently large hfc in the β-protons, yet small enough to reduce (but not invert!) the positive hfc of the α-protons. We know of no precedent for this structure. Its closest analog is the radical cation of 1,2-diphenylcyclopropane, 6, which has the weakened doubly benzylic bond required, but strong, negative hfcs for the α-photons.

The hypothetical hybrid structure also has serious problems in explaining the polarization observed for the monomer (Figure 2, center). This polarization must originate in the same radical ion pair(s) as the dimer polarization, but by a different chemical pathway. The most plausible mechanism involves fragmentation of dimer radical cations after escape from their counter ions. However, this pathway presents a serious problem: since the hypothetical hybrid implies a relatively high bond order between the benzylic carbons (in addition to the β-carbon), it cannot undergo fragmentation readily!

Consecutive radical ion pairs

Since neither conventional intermediates nor the unconventional structures discussed in the preceding section can explain the observed effects, we have evaluated the potential involvement of two consecutive ion pairs, which might manifest itself in cooperative effects.

The nuclear spin polarization effects observed in products formed via two consecutive radical (ion) pairs can fall into three categories. In some cases the polarization is determined solely by the magnetic parameters of the original pair. This situation has been encountered in the thermal decomposition of acetyl peroxide; the net effects observed for ethane was ascribed to an acetoxy–methyl pair and a 'memory'

effect.[46,47] Alternatively, the observed polarization could be determined by the secondary pair. This is observed especially in cases where the primary pair is relatively short-lived on the time scale necessary for the development of CIDNP. Examples for this situation are found in the electron transfer-induced cleavage of dimethylthymine dimer[48] or in the electron transfer-sensitized cleavage of adducts between indene derivatives and quinones.[49] The effects in these systems can be explained by $S-T_0$ mixing in the secondary pair exclusively.

The most interesting case is that where the polarization is caused by singlet–triplet evolution in both the primary and the secondary pair. This possibility was first recognized by den Hollander[29,30] when he observed toluene polarization resulting from the decomposition of acetyl benzoyl peroxide. This product is formed via a primary pair (acetoxy–phenyl), which has a g factor difference but negligible hyperfine coupling in the methyl group. Subsequent decarboxylation leads to a secondary pair (methyl–phenyl) with identical g factors and sizeable hyperfine couplings. The resulting net effects were explained on the basis of the radical pair theory as a result of a 'cooperative effect' of the singlet–triplet evolution in both the primary and the secondary pairs.

The qualitative features of these effects can be approximated based on the combined magnetic parameters of the consecutive pairs. Cooperative effects can be expected to dominate when either the Δg or the hyperfine couplings of the second pair are significantly smaller than the corresponding parameters of the first pair. The relative contributions of the two pairs depend on their relative lifetimes, and a formal rate of interconversion can be derived from a simulation of the experimentally observed polarization pattern.

The conventional simulation program treats the re-encounter probability of a radical (ion) pair as a function of random diffusion and of hyperfine induced, nuclear spin-dependent singlet–triplet mixing. The modified program treats in addition the effects of changing hfcs and g factors as a result of chemical changes in the radical (ion) pair. Den Hollander's formalism allows for several consecutive changes in both radicals.

In our system, the dimer radical cation might undergo ring opening or closing $(2 \rightleftharpoons 3)$, fragmentation $(2, 3 \rightarrow 4)$ or deprotonation, whereas the radical anion may undergo protonation. In Den Hollander's formalism this is expressed as follows:
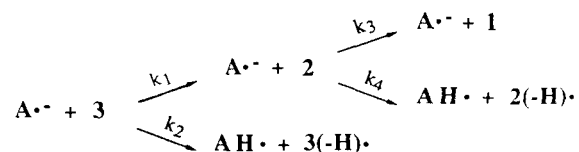
Since the polarized products and their polarization patterns allow us to eliminate proton transfer between the radical ions and also the involvement of the monomer radical cation, our simulation is based on the involvement of the ring-opened, extended radical cation 3 and the closed, localized species 2, each paired with the tetrachlorosemiquinone radical anion ($A^{\cdot-}$). The best match is achieved when the open ion is assumed to precede the closed species. Under these conditions, the effects predicted for the benzylic doublet are very sensitive to the chosen rate of interconversion as long as $k_1 \gg k_2 \gg k_3, k_4$. Over the range $1 \times 10^8 < k_1 < 5 \times 10^8 \, s^{-1}$ (with $k_2 = 3 \times 10^7, k_3, k_4 = 1 \times 10^5 \, s^{-1}$), the benzylic polarization changes from weakly enhanced absorption to strong emission nearly matching the polarization of the non-benzylic protons. The best fit to the experimentally observed polarization is achieved with a formal rate constant, $k_1 = 4 \times 10^8 \, s^{-1}$ (Figure 3d). In contrast, no agreement could be achieved with the closed species preceding the open species.

The successful simulation of the experimental effects with consecutive radical ion pairs and the failure of any simulation assuming a single radical ion pair suggest that both dimer radical cations are involved (cf. Scheme 1). Further, since regenerated dimer and newly generated monomer show complementary polarization, both must have the same chemical history, except for the electron spin-dependent, product-forming step. The dimer is regenerated by electron return, whereas fragmentation gives rise to the monomer radical cation.

The interconversion of two dimer radical cations invoked for the dimer cleavage must be involved also in the complementary electron transfer-induced dimerization of dimethylindene, as required by the principle of microscopic reversibility. This conclusion is not in conflict with the different CIDNP effects (cf. Figure 1 and 2) observed during the photoinduced electron transfer reaction of the olefin; the differences are readily explained by the different conditions prevailing in the two experiments. During the dimerization reaction limited olefin concentrations are employed ($2 \times 10^{-2} \, mol \, l^{-1}$) in order to observe the true olefin polarization. Under these conditions, dimer radical cations are formed only after a substantial delay (ca $2 \times 10^{-9} \, s$) and, the polarization is determined essentially by the monomer radical ion. In the dimer cleavage reaction, on the other hand, the radical ion pairs have largely diffused apart by the time the cleavage reaction occurs. Hence, the displayed polarization does not reflect the involvement of the monomer radical cation.

CONCLUSION

In view of the detailed mechanism suggested for the specific electron transfer-induced cycloaddition/cyclo-

reversion discussed above, it is interesting to consider the generality of this mechanism. Indeed, it is tempting to postulate a unifying scheme valid for all electron transfer-induced cyclobutadimerizations. However, subtle changes in the electron-donor character of the substitutents may profoundly affect the relative energies of the minima (intermediates) and/or maxima (transition structures) on the potential energy surfaces. Accordingly, the lifetime(s) of the intermediate(s) or the location (structure) of the minima may vary greatly, diverting the optimal pathway between reactant and product radical ions. Several mechanistic variants, including an essentially concerted pathway, remain viable alternatives in the general framework of radical cation cycloadditions/cycloreversions.

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