Electron-Transfer-Induced Reorganization of Bicyclo[6.1.0]nonatriene and Derivatives[†]

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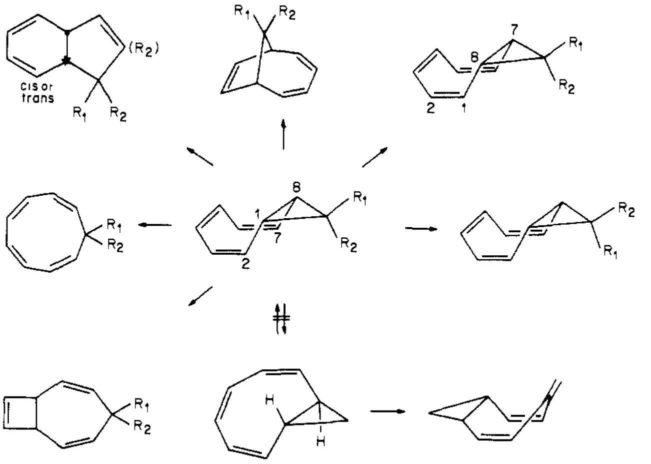
Abstract: The radical cations of bicyclo[6.1.0]nonatriene (**1a**) and several derivatives (**1b–f**) have been generated by photoinduced electron transfer in solution. The radical cation **3a**, derived from the parent, has a weakened cyclopropane bond with spin (and charge) density at C_1 and C_8. Electron return in singlet pairs regenerates **1a**, whereas triplet recombination gives rise to cyclononatetraene (**6**). Electron-withdrawing substituents at C_9 (Cl, **1c**) cause spin and charge to be restricted to the triene moiety. The 9,9-diphenyl derivative **1d** undergoes electron-transfer-induced rearrangement to 7-(β,β-diphenylethenyl)-cycloheptatriene, whereas the spirofluorene derivative **1f** is converted to a barbaralane derivative **9f**. The homoaromatic radical cation **10f** is suggested as an intermediate in this remarkable rearrangement.

Among the many systems that have aroused the curiosity of mechanistic organic chemists, the bicyclo[6.1.0]nonatriene system commands special interest because of a multiplicity of intriguing rearrangements. The originally reported thermal conversion of the parent system and the dichloro derivative to bicyclo[4.3.0]-nonatriene (dihydroindene) derivatives[1] revealed but one facet of the wealth of possible rearrangements. Both cis- and trans-fused dihydroindenes can be formed,[2] and the rearrangement can occur with or without migration of a C_9 substituent.[3] Several ring systems were postulated as intermediates in these rearrangements, among them tricyclo[4.3.0.0^{7,9}]nonadiene,[1] bicyclo[5.2.0]nonatriene,[4–6] and *all-cis-*[7–11] as well as several *mono-trans*-cyclononatetraenes.[5,9,12–14] Several of these were later identified by NMR spectroscopy in solution.[10] Electron-withdrawing substituents (CN)[15,16] or a spirocyclopentadiene[17] or spirofluorene group[18] in the 9-position divert the course of the rearrangement to the bicyclo[4.2.1]nonatriene system. Under milder conditions the [6.1.0] system undergoes more subtle changes, either epimerization at C_9[19–21] (R_1 = COOMe) or circumambulatory migration of C_9 without epimerization.[22] Finally, a trans-fused derivative, which does not interconvert with its cis-fused isomer, gave rise to homoheptafulvene.[23] In view of the wealth of possible structures derived from the parent system, we were interested in the corresponding radical cations, particularly in their structural features and in their rearrangements.



Recent advances in the continually expanding radical-cation field[24–33] have revealed numerous unusual structures and various

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[†] This paper is dedicated to Professor Emanuel Vogel, in whose laboratory H.D.R. and T.M. gained insight and inspiration, on the occasion of his 60th birthday.

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interesting rearrangements of radical cations derived from strained ring systems. Several studies have also brought to light pronounced substituent effects affecting both structures and rearrangements. Of particular interest have been the intermediates derived from compounds containing cyclopropane[34-43] or bicyclobutane groups[44-49] or from structures containing two[50,51] or more adjacent cyclobutane moieties.[52-54] Some of the structural features have been discussed as manifestations of electronic effects such as homoaromaticity,[55] homoconjugation,[38] or spiroconjugation.[42] As for the rearrangements, most examples appear to be governed by the release of ring strain.[26] However, the conservation of orbital symmetry has been discussed in several instances[56-63] and postulated as the guiding principle in at least one specific case.[64]

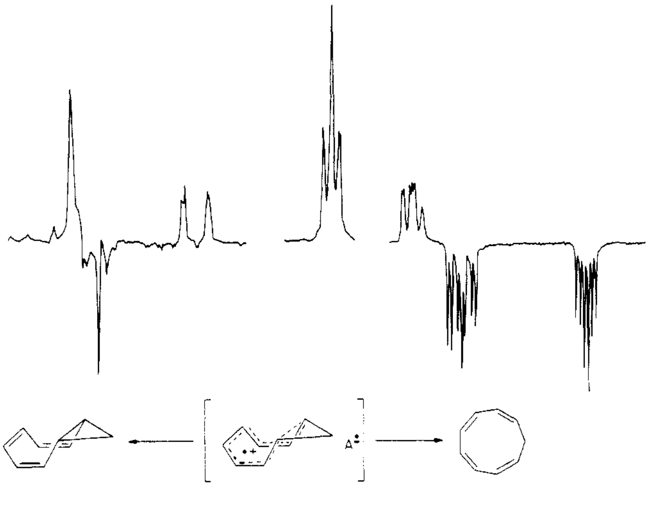
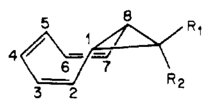


Figure 1. ^{1}H NMR spectra (90 MHz) of an acetone-d_6 solution containing 0.02 M each of chloranil and bicyclo[6.1.0]bicyclononatriene (**1a**) in the dark (bottom) and during UV irradiation (top). In addition to the starting material, a rearrangement product **6** and a chloranil adduct show polarization.

In this paper we discuss radical cations of bicyclo[6.1.0]nonatriene and derivatives, in which substituents in the 9-position have a pronounced effect on both the structures and rearrangements of the carbon skeleton. We have investigated seven systems, **1a–f** and **2b**.



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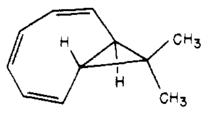

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a: R_1, R_2 = H
b: R_1, R_2 = CH_3
c: R_1, R_2 = Cl
d: R_1, R_2 = C_6H_5
e: R_1–R_2 = CH=CHCH=CH
f: R_1–R_2 = *o*-C_6H_4-*o*-C_6H_4

We use the technique of photoinduced electron transfer (PET) to generate hydrocarbon radical cations. Typically, quinones such as chloranil and fluoranil are used as photoexcited electron acceptors because they are strong oxidants and because they react via their triplet excited states. The resulting triplet radical ion pairs undergo spin sorting, leading to nuclear polarization in the regenerated hydrocarbon. These CIDNP effects can be related to the unpaired spin densities in the transient radical cation. The spin density distribution, in turn, provides an integral portion of the structural information. In this manner, numerous radical cations have been characterized, which previously had eluded detection or identification by any other technique.

Materials and Methods

Bicyclononatriene and its derivatives are accessible by carbene or carbenoid addition to cyclooctatetraene (Aldrich) or by reaction of appropriate *gem*-dihalide reagents with cyclooctatetraene dianion. The parent hydrocarbon was prepared by the Simmons–Smith route, whereas the dichlorocarbene adduct was prepared by employing the basic hydrolysis of chloroform, both time-honored preparations going back to

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Vogel and Kiefer.[1] The diphenyl derivative and the spirocyclopentadiene and spirofluorene derivatives were prepared by photolysis of the corresponding diazo compound. The cis-fused 9,9-dimethylbicyclononatriene is accessible via reaction of 2,2-dichloropropane with cyclooctatetraene dianion,[2] whereas the trans-fused isomer was recently prepared by pyrolysis of the cycloadduct obtained from 2-diazopropane and cyclooctatetraene.[65] We are indebted to Professor F. G. Klärner for samples of the two dimethyl derivatives.

Samples containing 2×10^{-2} M of an electron acceptor (chloranil, fluoranil) and typically the same concentration of an electron donor (bicyclo[6.1.0]nonatriene and derivatives) in acetone-d_6 were deoxygenated by purging with argon for 2 min. They were irradiated through Pyrex with the collimated beam of a 200-W Osram high-pressure mercury lamp in the probe of a Bruker WH90 Fourier transform NMR spectrometer. A pulse angle of 90° was employed to minimize the required acquisition time, since it could be shown that the polarization patterns and relative intensities were the same as those obtained with pulse angles as low as 30°.

Results and Discussion

Bicyclononatriene and Simple Derivatives. The radical cation derived from bicyclononatriene poses an interesting structure problem. The salient feature of this intermediate is the degree of bonding between carbon atoms C_1 and C_8. The possible structures include a "triene" radical cation **3** in which the key bond is unaffected and a cyclononatetraene radical cation **5** in which little or no bonding remains. An intermediate structure **4**, in which the key bond is weakened but not broken, is intriguing because it is potentially homoaromatic. An argument for the preferred structure of the parent radical cation can be based on the symmetry of the frontier molecular orbitals (FMOs) of the two fragment components hexatriene and cyclopropane. As the HOMO of hexatriene is symmetrical, it will interact preferentially with the symmetrical HOMO of cyclopropane. However, the ionization energies of the two fragments (8.3 eV for the triene vs 10.5 eV for cyclopropane)[66] are less than perfectly matched. Nevertheless, ionization of **1a** might give rise to a radical cation in which the tertiary, tertiary cyclopropane bond is substantially weakened and C_1 and C_8 are positions of major spin density.

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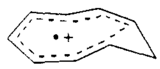

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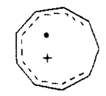

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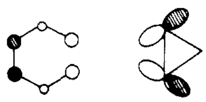
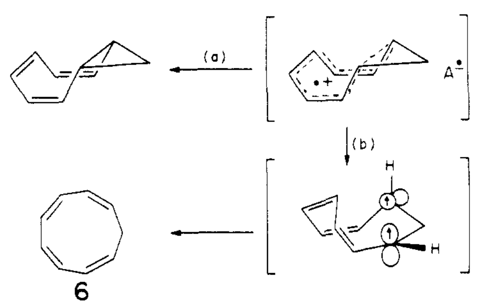


This prediction is borne out by CIDNP effects observed during the photoreaction of chloranil with **1a** (Figure 1). The substantially enhanced absorption signals of the allylic protons ($H_{1,8}$; 1.35 ppm) and the strong emission signals observed for the secondary cyclopropane protons ($H_{9,9}$; −0.1, 0.15 ppm) indicate positive spin density for C_1 and C_8 and, thus, eliminate structure **3a**. The choice between structures **4a** and **5a** is based on the fact that **1a** is regenerated upon electron return in singlet pairs, suggested by the observed signal directions. Since singlet recombination usually occurs with a minimum of structural changes, and since no rearranged or ring-opened products are formed by that mechanism, a relatively close relationship is suggested between the radical cation in question and the parent hydrocarbon **1a**. Hence, appreciable bonding between C_1 and C_8 is suggested, a finding best accommodated by structure **4a**.

The CIDNP spectrum (Figure 1) further indicates the formation of a second product, *all-cis*-cyclononatetraene (**6**). Its involvement is clearly documented by the characteristic triplet at 3.0 ppm, which is strongly enhanced, and by the olefinic signal at 5.7 ppm, which appears in emission. The formation of **6** suggests that the residual bonding can be released under relatively mild conditions. The polarization pattern once again is compatible with the intermediacy of **4a**, but the reversed signal directions indicate a different mechanism of formation. Two such mechanisms are conceivable, either ring opening (**4a** → **5a**) of a free-radical cation or triplet recombination of **4a** and its semiquinone counterion. Electron back-transfer in a triplet pair could populate the triplet state of **1a**, which subsequently could decay to **6a**. We favor the involvement of triplet recombination, because the formation of **6** appears to be temperature independent in the range +26 to −53 °C. This finding suggests a very low barrier to ring opening, significantly lower than would be compatible with the conversion **4a** → **5a**. In fact, the rearrangement may occur without activation because the geometries of the radical cations **4a** and **5a** very likely do not correspond to minima on the potential energy surface of the triplet state. The unfavorable interaction between two unpaired spins in close proximity may well destabilize the closed form of the triplet to the extent that a twisted open form becomes lower in energy. Neither the proposed triplet recombination nor the involvement of the bicyclononatriene triplet state is without precedent. The triplet recombination of radical ion pairs has been postulated in a variety of systems based on time-resolved optical spectroscopy[67-69] or CIDNP evidence.[27,34,70] The formation of **6** from **1a** via a triplet state has precedent in the triplet-photosensitized conversion of 9-chlorobicyclononatriene to the corresponding cyclononatetraene.[71]



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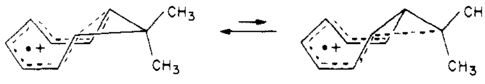
Simple electron-donating or -withdrawing groups at C_9 of the parent system change the spin density distribution in the resulting radical cations significantly. For the 9,9-dimethyl derivative **1b**, the CIDNP results indicate a radical cation with spin density in the olefinic segment and on the cyclopropane carbons C_1 and C_8. This assignment is based on the strongly enhanced absorption observed for the olefinic multiplet at 5.8 ppm and the allylic signal at 1.2 ppm. In addition, the methyl signals at 1.1 and 0.9 ppm appear in emission (Figure 2). These effects may indicate some spin density at C_9 and suggest a structure, **7b**, in which the C_1–C_9 (or the C_8–C_9) bond is weakened. However, the methyl polarization is weak compared to that of the allylic protons. Therefore, it could also be explained as a "long-range" coupling through two C–C bonds; such couplings are not without precedent,[72] and they are indicated particularly for rigid structures of appropriate geometries. Whatever the cause of the methyl polarization, the symmetrical structure **4b** must be the major contributor to the overall structure.



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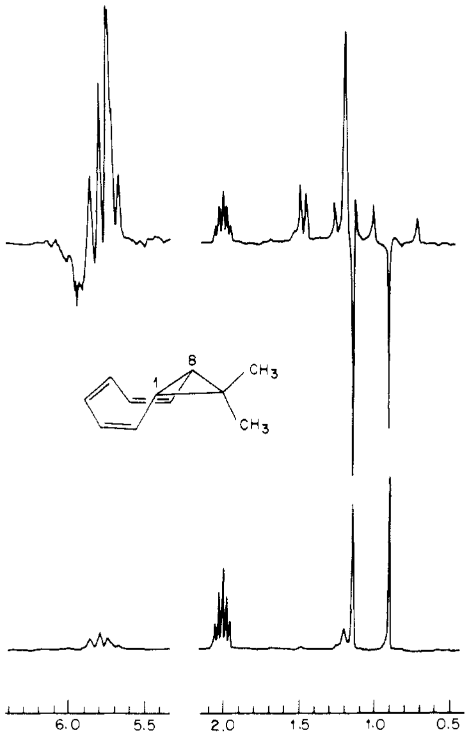
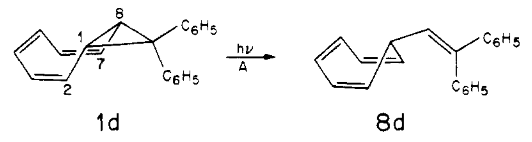


Figure 2. ^{1}H NMR spectra (90 MHz) of an acetone-d_6 solution containing 0.02 M each of chloranil and 9,9-dimethylbicyclo[6.1.0]nonatriene (**1b**) in the dark (bottom) and during UV irradiation (top).

While electron-donating substituents at C_9 cause a somewhat extended delocalization of spin and charge, electron-withdrawing substituents appear to have the opposite effect. For example, the 9,9-dichloro derivative **1c** shows no polarization at all for the allylic protons ($H_{1,8}$), whereas the olefinic multiplet is strongly enhanced. The lack of polarization for $H_{1,8}$ rules out significant spin density on $C_{2,7}$ and suggests that the corresponding radical cation has spin and charge density restricted to the unsaturated segment C_3–C_6, furthest away from the dichloromethylene moiety. This radical cation is an example of structure type **3**. The failure of the dichlorocyclopropane moiety to interact with the triene radical cation to delocalize spin and charge is tentatively ascribed to an inductive effect of the geminal dichloro moiety. Such an effect might increase the mismatch of orbital energies between the triene and the cyclopropane fragments. However, this assignment awaits confirmation by different techniques, particularly photoelectron spectroscopy.

Since neither spin nor charge is delocalized onto the cyclopropane ring, no rearrangement of this moiety can be expected, and none is observed. A radical cation with similarly restricted spin density was obtained by oxidation of pentamethylbenzyl chloride; in this species spin and charge appear to be limited to the carbon atoms in the meta and para positions.[51]

Diphenylbicyclononatriene. More pronounced changes in spin density distribution are observed for the radical cations of bicyclononatrienes **1d–f**. The unsaturated moieties in these derivatives cause substantial changes in the spin density distributions and manifest themselves in two significant reorganizations. To our knowledge, these are without precedent in radical ion chemistry. The 9,9-diphenyl derivative **1d** undergoes an electron-transfer-induced rearrangement to 7-(β,β-diphenylethenyl)cycloheptatriene (**8d**).



The formation of **8d** is a special example of a cyclopropane-to-propene conversion. This reaction type requires that one C–C bond be broken and one substituent undergo a 1,2 sigmatropic shift; it is one of the principal thermal reactions of cyclopropane derivatives. In the radical cation reaction discussed here, the migration encompasses a ring contraction, the shift of C_7 from C_8 to C_1 (or of C_2 from C_1 to C_8). Once again, the CIDNP effects elucidate important facets of this reaction. Only the reaction product **8d** shows polarization: The signals representing H_A, H_B, and H_C are enhanced, whereas the triply allylic multiplet appears in emission (Figure 3). These results indicate positive spin density for both the vinyl group and the cycloheptatriene moiety and might be interpreted in terms of a single radical cation with extensively delocalized spin density. On the other hand, the frontier molecular orbitals of the two fragments are incompatible in the preferred conformation.

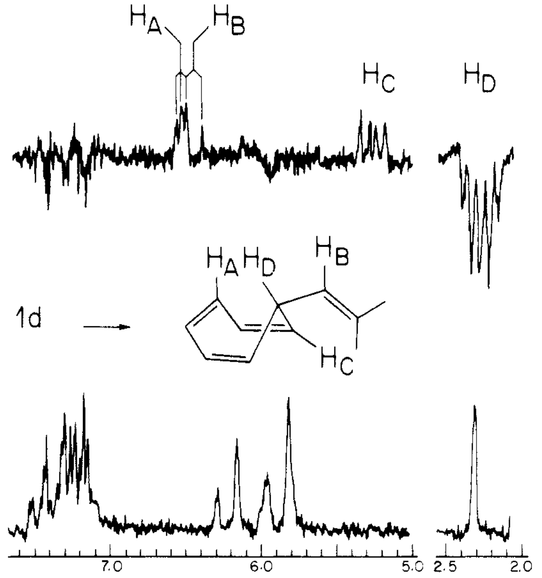
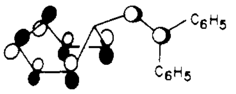
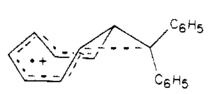


Figure 3. ^{1}H NMR spectra (90 MHz) of an acetone-d_6 solution containing 0.02 M each of chloranil and 9,9-diphenylbicyclo[6.1.0]nonatriene (**1d**) in the dark (bottom) and during UV irradiation (top). Only selected protons of a rearranged product, 7-(β,β-diphenylethenyl)cycloheptatriene (**8d**), are polarized.



Accordingly, we assume the existence of two independent radical cations, localized in the cycloheptatriene and diphenylethene moieties. The ionization potentials of the two fragments are similar, suggesting comparable probabilities of being oxidized. CIDNP effects generated in two model radical cations support this assignment.

Irradiation of acceptor molecules in the presence of cycloheptatriene gives rise mainly to strong emission for the doubly allylic methylene group; the analogous reaction of 1,1-diphenylethylene results in enhanced absorption for the methylene protons. Here, as in related systems, the lack of phenyl polarization is interpreted as evidence that the spin is located mainly on the terminal carbon, whereas the charge is delocalized throughout the diphenylmethyl moiety.



7d

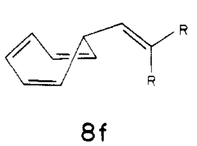
The failure to observe polarization for the starting material suggests that the rearrangement of the primary bicyclononatriene radical cation is rapid and efficient. Furthermore, the observed polarization pattern indicates the rearranged radical cation as the paramagnetic species in which the polarization is induced. Accordingly, the primary radical cation has a limited lifetime, possibly shorter than a nanosecond. The substantially lowered barrier reflected in this lifetime is in keeping with the apparently prevailing notion that radical-cation rearrangements generally have low barriers. In this specific case, the lowering can be attributed to two factors: spin and charge are extensively delocalized, and the key cyclopropane bond is weakened substantially compared to the neutral parent system.

Bicyclononatrienes with Spiroannelation at C$_9$. The last structure type investigated, derivatives **1e** and **1f**, contains spiroannelated unsaturated substituents in the 9-position. Although the orbital symmetry of the individual fragments does not lend itself to spiroconjugative stabilization, it nevertheless appeared interesting to identify the primary electron-donor fragments and to probe the potential rearrangements of the corresponding radical cations.

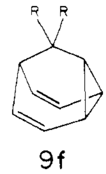
For the butadienylidene derivative **1e**, the CIDNP results indicate that the radical cation has spin and charge largely localized in the cyclopentadiene ring, although the "triene protons" also show some polarization. The fact that a diene moiety is the primary electron donor in the presence of a triene should not be considered surprising in view of available precedent. Although the ionization of a triene typically should be more facile than that of a diene, the spiroheptadiene moiety has a much lower ionization potential (7.9 eV)[73] than can be expected for a nonplanar triene ($\mathrm{IP}_{c\text{-}C_7H_8}$ 8.4 eV).[74] The observed polarization pattern has precedent in the spin density distributions of both the fulvene[75] and the spiro[2.4]heptadiene radical cations.[76]

In view of the ready thermal and photochemical rearrangement of **1e** to the corresponding bicyclo[4.2.1]nonatriene one might have expected a similar rearrangement on the radical-cation energy surface. However, no such reaction is observed. The failure of the spiroannelated radical cation to undergo cyclopropane ring opening resembles a similar lack of reactivity found for the spiro[2.4]heptadiene radical cation.[76] It reflects the incompatible symmetries of the butadiene and cyclopropane FMOs in the geometrical rearrangement dictated by the rigid structure. On the other hand, the absence of a sigmatropic shift analogous to the **1d** → **8d** rearrangement reflects the paucity of spin and charge density in the eight-membered ring.

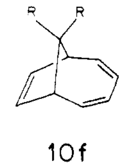
The final derivative to be discussed, fluorenespirobicyclo[6.1.0]nonatriene (**1f**), differs from **1d** by a seemingly minor feature: The two aryl groups of **1f** are linked and, thus, are held coplanar, whereas in **1d** they are not connected. Yet, this system reacts in dramatically different fashion. Irradiation of electron acceptors in the presence of **1f** gives rise to three divergent products. In addition to fluorenespiroethenylcycloheptatriene (**8f**), this reaction yields fluorenespirobarbaralane (**9f**) as the major product and fluorenespirobicyclo[4.2.1]nonatriene (**10f**). These rearrangements are remarkable in several ways. We will comment on some of the interesting aspects in the following sections.



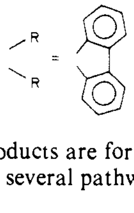
8f



9f



10f



The fact that three products are formed in comparable yields indicates the existence of several pathways with similar barriers.

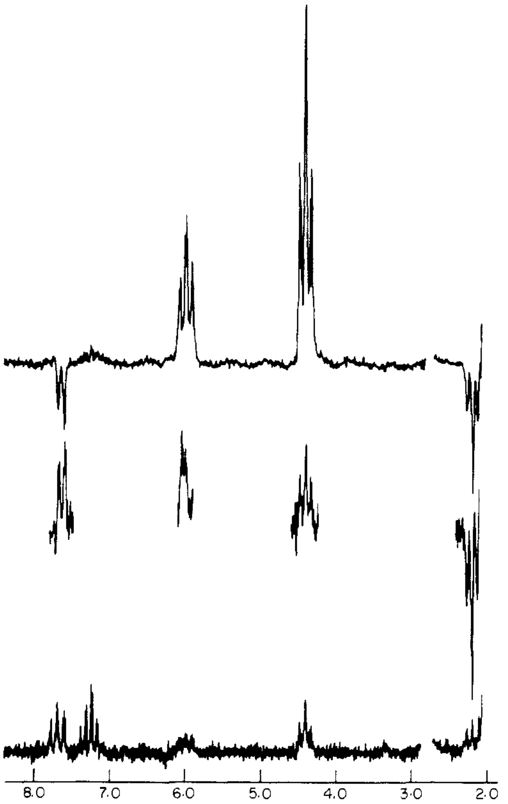


Figure 4. ^{1}H NMR spectra (90 MHz) of an acetone-d_6 solution containing 0.02 M each of chloranil and fluorenespirobarbaralane (**9f**) in the dark (bottom) and during UV irradiation (top). Irradiation of chloranil in the presence of fluorenespirobicyclo[6.1.0]nonatriene (**1f**) generates the same barbaralane derivative with a different polarization pattern (center), indicating the involvement of a different radical-cation intermediate as a precursor of 9f.

This poses the interesting question of whether the three products are derived from one common intermediate, such as the radical cation of **1f**, or whether they are formed via several different intermediates, possibly of unrelated types. Several observations have a bearing on the mechanism, foremost among them the effect of solvent polarity upon quantum efficiency. The formation of **9f** decreased by a factor of 100 when the solvent was changed from acetonitrile (ϵ 37) to benzene (ϵ 2.3). This observation strongly implicates a radical (cat)ion as the key intermediate. In contrast, the quantum yields of **8f** and **10f** were reduced only modestly, by factors of 4 and 2, respectively, suggesting an alterative mechanism. Considering the nature of the reagents, the possible intermediacy of an exciplex needs to be considered. This possibility is supported by the observation of a broad, featureless emission (505 nm) upon irradiating 9,10-dicyanoanthracene in the presence of **1f** in benzene solution.

The involvement of a radical ion pair mechanism in the formation of **9f** is also supported by the fact that the barbaralane derivative is the only polarized product in the CIDNP spectrum (Figure 4, center). The bridgehead protons show emission, whereas the olefinic protons (6.0 ppm) and those alternating between cyclopropane and olefinic character (4.4 ppm) show enhanced absorption. This polarization differs in important details from that generated in an authentic sample of barbaralane **9f** (Figure 4, top trace). For example, the signal at 4.4 ppm representing four barbaralane protons shows much weaker enhancement. Most significantly, the doublet at 7.65 ppm representing the ortho protons (H$_{1,8}$) of the fluorene system appear in enhanced absorption. These differences can be explained by the involvement of (an) additional radical cation(s), as (a) short-lived precursor(s) to the barbaralane radical cation **12f**.

The nature of this (these) intermediate(s) and the details of its (their) conversion deserve comment. Model considerations suggest that this reaction and the formation of **10f** have to ov-

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[73] Gleiter, R.; Heilbronner, E.; de Meijere, A. *Helv. Chim. Acta* **1971**, *54*, 1029–1037.

[74] Bodor, N.; Dewar, M. J. S.; Worley, S. D. *J. Am. Chem. Soc.* **1970**, *92*, 19–24.

[75] Abelt, C. J.; Roth, H. D. *J. Am. Chem. Soc.* **1985**, *107*, 6814–6818.

[76] Roth, H. D.; Schilling, M. L. M.; Abelt, C. J. *J. Am. Chem. Soc.* **1986**, *108*, 6098–6099.

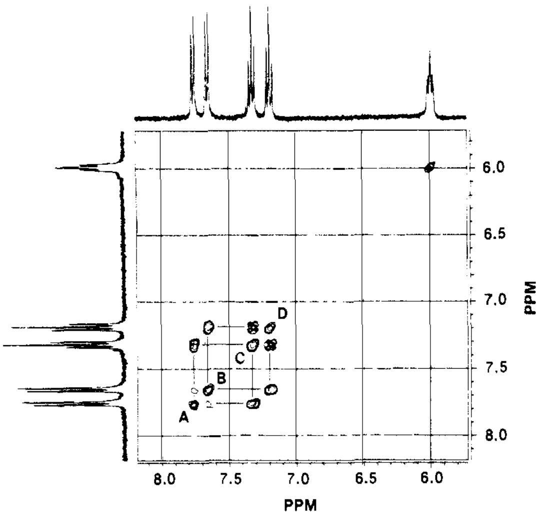
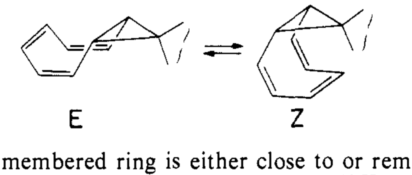


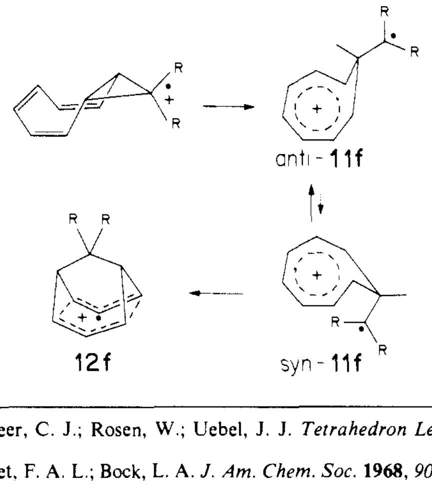
Figure 5. ^{1}H 2D COSY spectrum (360 MHz; 5.5–8.0 ppm) of fluorenespirobarbaralane (**9f**) in acetone-d_6 at 20 °C. The spectrum documents three strong ${}^3J$ (ortho) couplings and a weak ${}^5J$ (para) coupling. Since none of the fluorene protons shows any interaction with any proton of the barbaralane moiety, only a relative assignment of the fluorene protons is possible.

ercome serious steric obstacles. The bicyclononatriene system has two conformers, an extended (E) and a coiled one (Z) in which



the three-membered ring is either close to or remote from the central double bond of the olefinic system.[19,77] The extended conformer is clearly favored, yet the rearrangements leading to **9f** (and **10f**) can occur only in the coiled conformer. The conversion of E to Z requires an inversion of the triene system. Although this process has not been documented for the bicyclononatriene system, its intrinsic barriers should be similar to those established for cyclooctatetraene derivatives (near 15 kcal/mol).[78] However, the coiled conformer of **1f** must be destabilized by the presence of the bulky fluorene moiety. It would appear that the steric repulsion could be somewhat alleviated if the rearrangement proceeds via a ring-opened radical cation with a single link between the eight-membered ring and the fluorene moiety. In such a species the fluorene group could rotate by ~90° into an orientation allowing overlap with and bonding to the π orbitals of carbon atoms C_4 and/or C_3/C_5.

In view of these considerations, a singly linked species **11f** and a "localized" fluorene radical cation are the most plausible candidates for the additional intermediate(s). Its (their) identification requires an unambiguous assignment of the aromatic resonances of **9f**, and particularly of the enhanced signal at 7.65 ppm. The assignment of this resonance as due to the ortho protons may be intuitively obvious but is in fact difficult to establish. The *J*-correlated 2D spectrum (Figure 5) shows three strong (ortho) couplings and one weak (para) interaction, allowing the *relative* assignment of the four signals without identifying the ortho protons. The 2D NOE spectrum (Figure 6) allows the *absolute* assignment, but only because of a weak cross peak between H_B and the four-proton signal (4.4 ppm) of the barbaralane moiety. Models show an average distance near 3.5 Å between each ortho proton and the two related barbaralane protons, placing the NOE interaction near the current threshold of detectability.



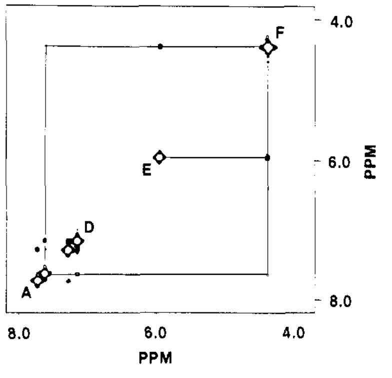


Figure 6. ^{1}H 2D NOESY spectrum (500 MHz) of fluorenespirobarbaralane (**9f**) in acetone-d_6 at 25 °C. The weak cross peak with the averaged four-proton barbaralane signal identifies H_B as the proton closest to the quaternary carbon.

Given the identity of H_B as the signal representing the ortho protons, the aromatic absorption observed during the rearrangement (Figure 4, center) supports an intermediate with spin density on the fluorenyl moiety. However, this evidence is insufficient to differentiate between localized and singly linked intermediates. We assume that both species are involved, the localized radical cation as primary product formed by electron transfer from the principal donor function and the singly linked species as the entity that facilitates the rearrangement. Considering the nature of the two fragments of the singly linked intermediate, we note that a fluorenyl cation ($4n\pi$ electrons) would be antiaromatic, whereas the cyclooctatrienyl cation [$(4n + 2)\pi$ electrons, homotropenylium] is the paradigm of homoaromacity.[79] Accordingly, a singly linked species with the charge in the eight-membered ring and the unpaired spin in the fluorenyl moiety (**11f**) should be preferred over the species with the reverse distribution of spin and charge, even though the extent of homoaromatic stabilization is limited. In fact, the CIDNP results indicate that the singly linked intermediate can be but a fleeting intermediate in the efficient rearrangement to the barbaralane radical cation. This is all the more remarkable as an inversion barrier near 18 kcal/mol has been established for the homotropenylium ion.[79]

The selectivity of the observed rearrangement is another feature inviting comment. In principle, the transannular reaction could involve either a 1,4 sigmatropic shift yielding the barbaralane radical cation **12f** or a 1,3- or 1,5-shift yielding the radical cation of the bicyclo[4.2.1]nonatriene derivative **10f**. Since both **9f** and **10f** are known compounds, their radical cations can be generated independently as short-lived intermediates.[80] Under these conditions neither radical cation shows any tendency to convert to the other. The observed selectivity, therefore, indicates that the pathway to one radical cation has a significantly lower barrier, running counter to any notion of indiscriminate radical cation rearrangements. It is not clear which feature causes this remarkable difference. A manifestation of orbital symmetry effects is no longer without precedent;[81] alternatively, the selectivity may

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(77) Cheer, C. J.; Rosen, W.; Uebel, J. J. *Tetrahedron Lett.* **1974**, *15*, 4045–4048.

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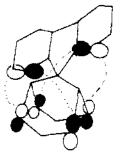
reflect the stabilization of the bishomoaromatic radical cation **12f**.

Barbaralane radical cations are significant, because they are the first group of homoaromatic radical cations. We have shown that substituents in the 9-position affect the nature of the bishomoaromatic systems and that the CIDNP effects may be strongly temperature dependent.[55] For the system discussed here, the barbaralane polarization indicates positive electron spin density for six carbon atoms. This polarization pattern is similar to that observed for 9-methylenebarbaralane above 50 °C, which was interpreted in terms of contributions from bishomoaromatic SOMOs of A_2 as well as B_2 symmetry.

However, in the radical cation derived from the fluorenylidene adduct **1f**, an alternative possibility needs to be considered, viz. spiroconjugation[82,83] of the fluorene moiety with two independent allyl groups (the antisymmetric combination of two allyl MOs corresponds to a bishomobenzene LUMO). The HOMO of fluorene is antisymmetric with respect to both symmetry planes of the barbaralane radical cation. Accordingly, it can interact only with two independent allyl moieties but not with a bishomobenzene system. The resulting radical-cation structure type is an alternative for the bishomoaromatic one with B_2 symmetry. Our results show that, despite favorable orbital interactions, the doubly allylic structure cannot be the exclusive one for the radical cation of **1f**. Accordingly, spiroconjugation is not a dominant effect for **11f**, and doubly allylic structures must be less significant in systems without spiroconjugation. This fact supports the assignment of bishomoaromatic structures to other barbaralane radical cations.



Finally, we comment on perhaps the most puzzling feature of the electron-transfer chemistry of the bicyclo[6.1.0]nonatriene system, namely the striking difference between the rearrangements of **1d** and **1f**. We consider two possible reasons for this divergence: The two derivatives may have different primary electron-donating groups, and the intermediate radical cations may have different spin and charge density distributions. First, it appears that the triene moiety (IP 8.3 eV)[66] is the primary electron donor of **1d**, whereas the fluorene moiety (IP 7.9 eV)[84] should be the primary donor of **1f**. Evidence for the fluorene moiety as the primary donor of **1f** is provided by the charge-transfer spectra of the two model systems bicyclo[6.1.0]nonatriene and fluorene, respectively, with tetracyanoethylene. The fluorene complex shows a much stronger charge-transfer absorption, and the appearance of the spectrum (λ_{max} 565, 420 nm) is very similar to the charge-transfer spectrum of **1f** with TCNE (λ_{max} 568, 402 nm). Accordingly, the divergent rearrangements could be ascribed to the involvement of two different primary radical cations, a triene radical cation in the case of **1d** and a fluorene radical cation in the case of **1f**.

3d

13f

R–R = o-C_6H_4-o-C_6H_4

Another important difference between the two systems lies in the ability of a pair of geminal phenyl groups to stabilize a positive charge at C_9, whereas the corresponding fluorene cation is destabilized due to its antiaromatic character (vide supra). Accordingly, the singly linked intermediates potentially formed by ring opening of the primary radical cations might have quite different spin density distributions and, for that reason, undergo divergent reactions. Whatever the decisive factor, the pronounced difference between the rearrangements of two seemingly similar systems remains a remarkable consequence of possibly quite subtle effects.

Conclusion

The photoinduced one-electron oxidation of bicyclo[6.1.0]nonatriene systems in solution gives rise to a variety of interesting radical-cation structures and several unusual rearrangements. Some of the products formed under these conditions are without precedent in either the thermal or the triplet-photosensitized reactions, raising the prospect of preparative usefulness. Finally, the preferential formation of the barbaralane radical cation **12f** over that of the bicyclo[4.2.1]nonatriene **10f** documents a degree of selectivity rarely, if ever, documented in radical-cation reactions.

Acknowledgment. We are indebted to Professor Frank G. Klärner (Bochum University) for samples of the 9,9-dimethylbicyclononatrienes, to Dr. Peter A. Mirau for the 2D NOE spectrum of fluorenespirobarbaralane, and to Dr. Robert C. Haddon for stimulating discussions.

Registry No. 1a, 26132-66-1; **1b**, 22647-29-6; **1c**, 49586-76-7; **1d**, 71837-38-2; **1e**, 114552-65-7; **1f**, 114672-75-2; **2b**, 88358-07-0; **3a**, 114611-97-1; **3b**, 114611-98-2; **6**, 23979-33-1; **8d**, 100064-25-3; **9f**, 114552-66-8; chloranil, 118-75-2.

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