it still exhibited more than a one-third of the initial activity.

Other organic solvents, including isopropyl ether, butyl acetate, and chloroform (all presaturated with the aqueous Tris buffer, pH 7), were also suitable as the reaction medium for the ADH catalysis. It should be stressed that both the enzyme and NADH were insoluble in all of these solvents and therefore were trapped in the hydration layer on the surface of the glass beads. In the systems described, which represented a suspension of ADH and NADH (codeposited onto glass beads) in a monophasic organic solvent,[10] the water content was crucial—if no aqueous buffer was added to the water-saturated solvent or if the latter was not presaturated with water, then no enzymatic activity was expressed.

We then employed ADH/NADH in organic solvents for preparative, stereospecific reduction of carbonyl compounds (Scheme IA). The aforedescribed experimental design was scaled up (using isopropyl ether as a solvent) and used for asymmetric enzymatic reduction of 2-phenylpropionaldehyde and 2-chlorocyclohexanone. As the first two entries in Table I indicate, millimolar quantities of the corresponding alcohols of high optical purity were obtained.

The direction of the ADH-catalyzed production of optically active compounds in organic solvents can be reversed if the system is appropriately modified. Using the approach depicted in Scheme IB (isobutyraldehyde is employed for the enzymatic regeneration of NAD$^+$), racemic *trans*-3-methylcyclohexanol and *cis*-2-methylcyclopentanol were preparatively converted to the corresponding *S* ketones of 100% and 96% ee, respectively (Table I).

The experimental strategy developed herein should be applicable to the use of other NAD$^+$/NADH-dependent dehydrogenases in organic solvents—either alone or coupled with horse liver ADH for cofactor regeneration. Some of the advantages of conducting enzymatic oxidoreductions in organic solvents vs. water are a much greater solubility (and, e.g., in the case of 2-chlorocyclohexanone, stability) of substrates, significantly higher cofactor turnover numbers,[12] the ease of enzyme immobilization and reuse (a major bottleneck in preparative transformations catalyzed by ADH[4e]), and product recovery.

Experimental Section

Horse liver alcohol dehydrogenase (EC 1.1.1.1) was purchased from Sigma Chemical Co. as a crystalline powder with a specific activity of 1.5 units/mg of protein. Glass beads (nonporous), 75–150 μm in diameter, were also purchased from Sigma. All chemicals used in this work were obtained commercially and were of the highest purity available.

Enzymatic oxidoreductions in organic solvents were carried out as described in the text and footnotes to Table I (no reactions were detected when ADH was omitted from the system). The time courses of all reactions studied were followed by gas chromatography: periodically, 1-μL aliquots of the liquid phase were withdrawn and analyzed with use of a 5 m capillary column with 530 μm fused silica gel (Hewlett-Packard) (N_2 carrier gas, 30 mL/min, detector and injector port temperature 250 °C). In the case of the last two entries in Table I, precolumn derivatization with acetic anhydride[13] was employed to improve the GC separation between the alcohol and the ketone. All yields quoted in footnotes to Table I are calculated on the transformed material only.

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(11) After each run, the biocatalyst-bearing glass beads were separated from solution by decantation and added to the next fresh substrate solution (an addition of 0.5% aqueous buffer was unnecessary in all but the first runs, presumably because the glass beads were already "saturated" with water).

(12) Compared to the same compounds converted in water by the enzyme, e.g., see: Lemiere, G. L.; Lepoivre, J. A.; Alderweirdeldt, F. C. *Tetrahedron Lett.* **1985**, *26*, 4527–4528. This may be due to a high effective concentration of the cofactor in the microenvironment of the enzyme in organic solvents.

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Electron-Transfer Reactions of Bicyclo[4.2.1]nonatrienes: Formation of a Bishomoheptafulvene Radical Cation

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Abstract: The radical cation ($3^{\bullet+}$) of 9-methylenebicyclo[4.2.1]nona-2,4,7-triene undergoes rapid intramolecular cyclization to generate an isomeric radical cation ($15^{\bullet+}$) derived from a tetracyclic structure. In contrast, the hydrocarbon **15** suffers

$3^{\bullet+}$ $15^{\bullet+}$

retrocyclization to regenerate **3**. The comparative stability of $15^{\bullet+}$ is ascribed to its bishomoaromatic character. Four radical cations of less unsaturated model compounds support the assigned structure.

The concepts of both bicycloaromaticity[1,2] and homoaromaticity[3] have been proposed in order to account for the enhanced stability of molecules possessing interacting, nonplanar π-systems. Homoaromaticity encompasses systems where a cyclic array of $(4n + 2)\pi$ electrons is interrupted by an aliphatic fragment, whereas bicycloaromaticity deals with π-systems of diverse topologies (e.g., spirocyclic, longicyclic, etc.). Homoaromaticity has been documented particularly well in carbonium ion chemistry, whereas bicycloaromaticity has been demonstrated less frequently. Yet, neither effect has been documented in radical cation chemistry. Indeed, it has been shown only very recently that the radical cations derived from barbaralane and several derivatives adopt a 5π-electron bishomoaromatic structure.[4] The only other ex-

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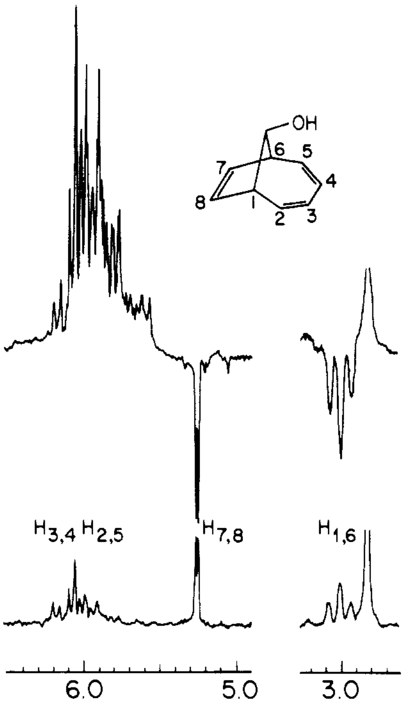
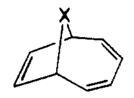
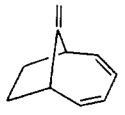


Figure 1. ^{1}H NMR spectra (90 MHz) of a 0.02 M solution each of 9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (**2**) and chloranil in acetone-d_6 in the dark (bottom) and during UV irradiation (top).

ample of an open-shell homoaromatic system is the homocyclooctatetraene radical anion reported by Katz and Winstein and their co-workers.[5–7] As part of a research effort exploring unusual radical cation structures, we have investigated a series of radical cations derived from bicyclo[4.2.1]nonatrienes, **1–3**. In particular, we were interested in the potential impact of bicycloaromaticity as a factor in determining radical cation structures. For comparison with the radical cation of 9-methylenebicyclononatriene (**3**) two partially hydrogenated derivatives, 9-methylenebicyclonona-2,4-diene (**4**) and 9-methylenebicyclonon-2-ene (**5**), were also studied.



1) X = >C=O
2) X = >CHOH
3) X = >C=CH$_2$



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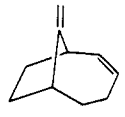

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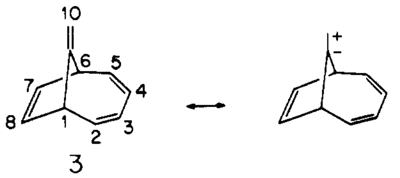
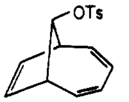
Since this study concentrates on the radical cation derived from 9-methylenebicyclo[4.2.1]nona-2,4,7-triene (**3**), evidence for bicycloaromatic character in **3** is of particular interest. Perturbations of the π-electronic structure of **3** might be reflected in the shielding/deshielding effects in the ^{13}C NMR spectrum.[8,9] Relative to the hydrogenated model compound **6**, the exocyclic double bond is slightly polarized: the resonances of C9 and C10 appear at 148 and 105 ppm, respectively, compared to 159 and 104 ppm for **6**. These findings can be explained by a zwitterionic resonance structure with the positive charge at C10. The stability of this structure may derive from the bicycloaromaticity of the bicyclononatrienyl anion fragment. On the other hand, a bishomocyclopentadienide anion may account for the zwitterionic stability. In any case, it appears that the above zwitterion is more stable than the zwitterion in which the charges are reversed. The latter is also predicted to be bicycloaromatic.[2]



3

Evidence for enhanced stability in the bicyclononatrienyl cation is found in solvolysis studies. Diaz, Winstein, and co-workers found that the acetolysis of **7** proceeds several orders of magnitude more rapidly than do those of either **8** or **9**.[10,11] The bicycloaromaticity of the intermediate cation coupled with π-assisted ionization was invoked to explain the observed rate enhancement. Interestingly, the acetolysis of **7** results in a substantial rearrangement to dihydroindenyl acetate (**12**). Evidently, the stability of the nonatrienyl cation (**10**) is not sufficient to prevent rearrangement to the very stable bishomotropylium cation (**11**). The latter has been generated in superacid solutions from a number of precursors and characterized spectroscopically.[12]



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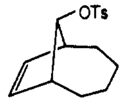

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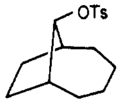

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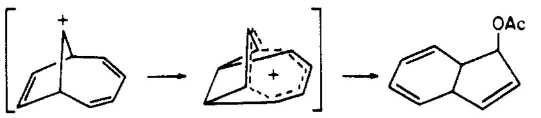

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We use the technique of photoinduced electron transfer (PET) to generate hydrocarbon radical cations. Typically, quinones such as chloranil and fluoranil are used as photoexcited electron acceptors because they are strong oxidants and because they 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,[13–21] which previously had eluded detection or identification by any other technique.

Experimental Section

The bicyclononatrienyl derivatives were synthesized according to published procedures. Bicyclo[4.2.1]nona-2,4,7-trien-9-one (**1**) was

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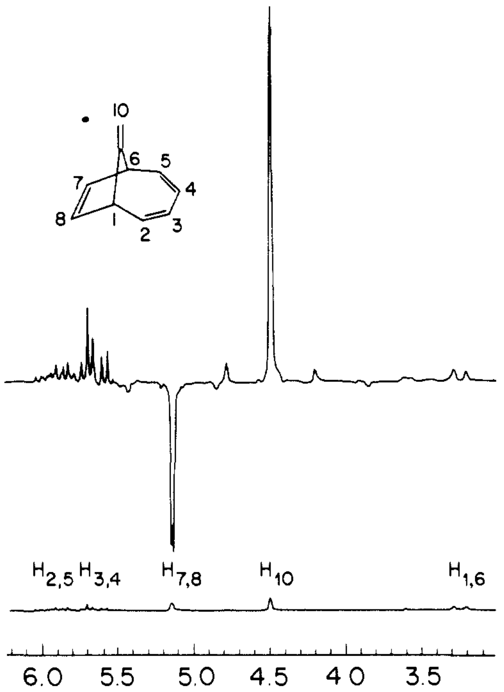

Figure 2. ^1H NMR spectra (90 MHz) of a 0.02 M solution each of 9-methylenebicyclo[4.2.1]nona-2,4,7-triene (3) and chloranil in acetone-d_6 in the dark (bottom) and during UV irradiation (top).

prepared by condensation of cyclooctatetraene dianion with dimethylcarbamoyl chloride and purified by distillation.[22] Reduction of trienone **1** with $NaBH_4$ and sublimation afforded bicyclo[4.2.1]nona-2,4,7-triene-9-ol (**2**).[22] 9-Methylenebicyclo[4.2.1]nona-2,4,7-triene (**3**) was prepared from **1** via Wittig reaction and purified by distillation.[23] Diimide reduction of **3** afforded 9-methylenebicyclo[4.2.1]nona-2,4-diene (**4**) as the major product, whereas diimide reduction of **2** followed by Jones oxidation and Wittig reaction gave mainly 9-methylenebicyclo[4.2.1]-non-2-ene (**5**) in poor yield.[24,25] Both compounds were isolated by gas chromatography on 10% Bentone 34 and 10% Apiezon L (20 ft, 100 °C, 60 cm^3/min). The electron acceptor, chloranil (Eastman Organic Chemicals), was used without purification, as were the deuterated solvents, acetone-d_6 (99.9%, Aldrich) and acetonitrile (99.7%, MSD Isotopes).

Samples containing 0.02 M each of the bicyclic hydrocarbon and chloranil were deaerated by purging with Ar for 2 min. They were irradiated in Pyrex tubes in the probe of a Bruker WH90 FT NMR spectrometer with the collimated beam of an Osram 200W high-pressure mercury lamp. A copper–constantan thermocouple was used to measure the sample temperature for the experiments conducted below ambient temperature.

Results

The bicyclic hydrocarbons show strong nuclear polarization effects during irradiation with chloranil. For all substrates studied, the protons attached to the isolated double bond (H7,8) appear in emission (Figures 1 and 2), whereas the protons of the butadiene system show absorption (Figures 1–3). The exo-methylene protons (H10) show varying behavior: they appear in absorption in **3** and **5** (Figure 4), but they show emission in **4**. Bridgehead protons also display diversity: they show emission in **2**, weak emission in **4**, and almost no effect in **1**. However, they appear in absorption in **3** and show both emission and absorption in **5**. To this overview we add the following subtle details. The protons of the ethylene moiety (H7,8) show a much stronger effect in **3** than in **1** or **2**. The butadiene polarization in **3** is unique, since the terminal protons (H2,5) are less strongly polarized than the internal protons (H3,4), whereas the reverse is observed for **2** and **4**.

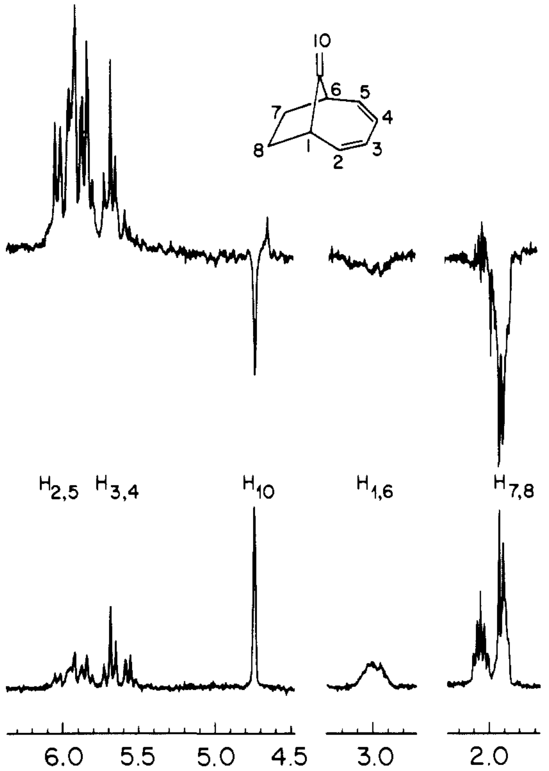

Figure 3. ^1H NMR spectra (90 MHz) of a 0.04 M solution each of 9-methylenebicyclo[4.2.1]nona-2,4-diene (**4**) and chloranil in acetone-d_6 at −50 °C in the dark (bottom) and during UV irradiation (top). The dark spectrum has been subtracted from the light spectrum in the top trace.

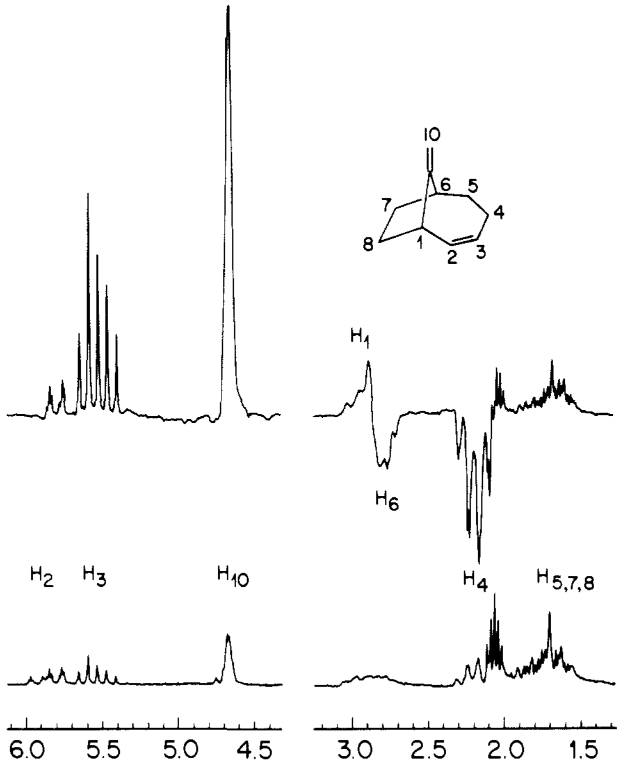

Figure 4. ^1H NMR spectra (90 MHz) of a 0.02 M solution each of 9-methylenebicyclo[4.2.1]non-2-ene (**5**) and chloranil in acetone-d_6 in the dark (bottom) and during UV irradiation (top).

A study of the temperature dependence of the polarization observed for **3** proved to be most enlightening. Irradiation at temperatures below 0 °C gave rise to a new polarized product

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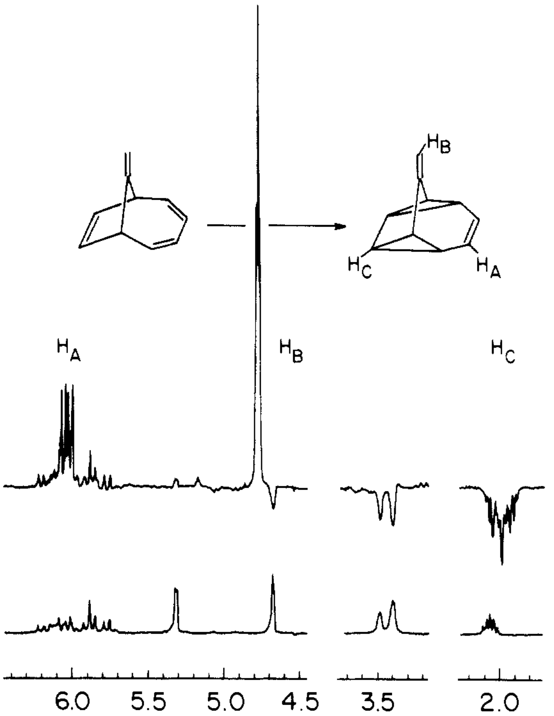


Figure 5. ^{1}H NMR spectra (90 MHz) of a 0.02 M solution each of **3** and chloranil in acetone-d_6 at −47 °C in the dark (bottom) and during UV irradiation (top). The dark spectrum was subtracted from the light spectrum to produce the top trace.

as indicated by a doublet of doublets at 6.03 ppm in absorption, a triplet at 4.78 ppm in absorption, and a multiplet at 1.98 ppm in emission. Below −40 °C, the polarization of the starting material was dramatically altered (Figure 5). The exo-methylene, ethylene, and bridgehead protons changed signal directions, whereas the butadiene protons remained in absorption. However, at these temperatures the terminal protons showed stronger absorption than the internal ones. The diamagnetic product generated in this reaction did not persist, even when the irradiation was carried out at −70 °C.

Discussion

With the exception of compound **3**, the nuclear polarization effects indicate radical cation structures with unpaired spin density distributions closely reflecting the atomic coefficients of the highest occupied molecular orbitals (HOMOs). In compounds **1**, **2**, and **4** the HOMOs essentially are butadiene HOMOs. The carbonyl, exo-methylene, and ethylene fragments of these molecules are not expected to contribute to the HOMO, because of a mismatch in symmetries and energies. Indeed, photoelectron spectroscopy has shown that even the first ionization band of **3** is a butadiene transition resembling those of bicyclo[4.2.1]nonatriene and cycloheptadiene.[26] Accordingly, only the butadiene carbons should have positive spin densities and their protons negative hyperfine coupling constants (hfc's) with the unpaired electron. This would explain the enhanced absorption observed for the butadiene protons. Further, the terminal protons (H2,5) should be more strongly coupled than the internal protons (H3,4), since the atomic coefficients of the butadiene HOMO are larger at the terminal than at the internal carbons. This ordering is readily apparent in compound **4** (Figure 3), but somewhat less apparent in **2** because of spectral overlap. However, decoupling the bridgehead protons (H1,6) during irradiation collapsed the butadiene multiplet to an AA′BB′ spectrum, thus revealing the difference in polarization intensity.

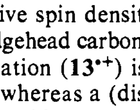
The remaining protons in **1**, **2**, and **4** show either no polarization or the signal direction compatible with positive hfc's, indicating that no spin density is present at the corresponding carbon centers. The polarization of the bridgehead protons (H1,H6) in **1** and **4** is very weak in contrast to the polarization in **2**. This difference could be attributed to differences in orientation of these protons relative to the partially occupied orbitals. In **1** and **4** these protons may lie more nearly in the nodal plane of the π-system than in **2**. Finally, the protons at C7 and C8 are strongly polarized even though they are farther removed from the spin density than the bridgehead protons. Evidently, the through-bond interaction with the unpaired spin is considerable.

Table I. Hyperfine Coupling Patterns Predicted for Various Radical Cations and CIDNP Effects Observed for Methylenebicyclo[4.2.1]nonatriene and Its Tetracyclic Valence Isomer

	hyperfine coupling patterns[a]				CIDNP effects	
	3$^{\bullet+}$	**13**$^{\bullet+}$	**14**$^{\bullet+}$	**15**$^{\bullet+}$	**3**	**15**
$H_{1,6}$	+	+	+	−	A[b]	*c*
$H_{2,5}$	−[d]	−[d]	−	−	A[b]	*c*
$H_{3,4}$	−	−	−	−[d]	A	A
$H_{7,8}$	+	+	−	+	E	E
H_{10}	+	*e*	−	−[d]	A	A

[a] Negative hfc's are predicted for H's attached to C's with positive electron spin densities. [b] Weak effects. [c] Negligible effects. [d] Major negative hfc. [e] Negligible or weak coupling based on analogy to fulvene radical cations: Abelt, C. J.; Roth, H. D. *J. Am. Chem. Soc.* **1985**, *107*, 6814–6818.

Compound **5** is the only substrate discussed in this paper which does not contain a butadiene moiety. Therefore, the intermediate radical cation must adopt a different structure. The CIDNP effects show this intermediate to have a distorted spin density distribution. Clearly, the principal spin density lies at C3 and C10 with only a small fraction at C2 (and C9). The radical cation can be described as a homobutadiene structure in which a partial bond has developed between C2 and C9. An analogous structure was proposed for the 9-methoxybicyclo[4.2.1]nona-2,4-dien-9-yl cation in superacid solutions.[27] Of special interest is the polarization observed for H1: the enhanced absorption signal suggests a negative hfc, typically observed for protons directly attached to carbon atoms bearing positive spin density. However, it is quite difficult to imagine a radical cation structure in which the bridgehead carbon, C1, has positive spin density. Accordingly, we explain the H1 polarization as a result of cross relaxation, which has been demonstrated for products undergoing rapid degenerate electron exchange.[28-30]



5$^{\bullet+}$

The radical cations discussed above provide models for the possible structure of the radical cation derived from **3**. None of these structures is entirely consistent with the polarization observed for **3** at room temperature (Table I). For example, a simple butadiene radical cation (**3**$^{\bullet+}$) similar to those of **1**, **2**, and **4** can be ruled out by the positive spin density indicated for the exo-methylene and for the bridgehead carbon atoms. A (symmetrical) bishomofulvene radical cation (**13**$^{\bullet+}$) is not consistent with the bridgehead polarization, whereas a (distorted) homohexatriene structure similar to **5**$^{\bullet+}$ could account for the CIDNP effects. However, since a homohexatriene structure is not indicated for the radical cation of **4**, it is equally unlikely for **3**$^{\bullet+}$. Of course, none of these structures can account for the rearrangement product observed at low temperatures. Finally, a bishomoaromatic radical

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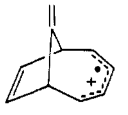
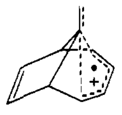
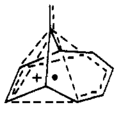
cation ($14^{\bullet+}$) can be eliminated, because the enhanced absorption of the ethylene protons precludes positive spin density on the corresponding carbon atoms.



$3^{\bullet+}$



$13^{\bullet+}$



$14^{\bullet+}$

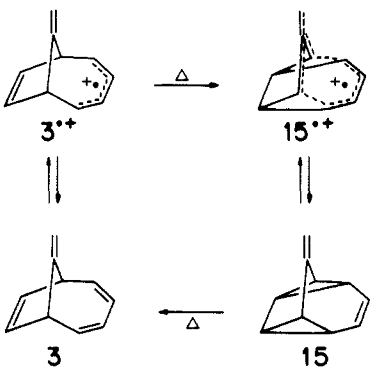
The CIDNP results for **3** are best interpreted in terms of a bishomoheptafulvene radical cation structure ($15^{\bullet+}$) which implies a rearrangement of the carbon skeleton. The spin polarization effects are consistent with the proposed intermediate: large negative hfc's for the outer butadiene and bridgehead protons, and positive hfc's for the ethylene protons. This structure is also consistent with the low-temperature results where a new polarized product is observed. The evidence points to **15** as the source of these signals. The chemical shifts of 6.0, 4.8, and 2.0 ppm are certainly consistent with the ethylene, exocyclic methylene, and cyclopropane moieties. Coupled with this is the fact that the new product must be closely related to **3** since it regenerates the bicyclic tetraene even at low temperatures. This relationship is revealed most clearly by the temperature-dependent polarization of the exocyclic methylene protons. Below −47 °C the protons of **15** display strongly enhanced absorption, which decreases with increasing temperature and vanishes near 0 °C. Over the same temperature range the corresponding protons of **3** show the complementary development, i.e., increasingly intense absorption. These results are consistent with the notion that above −47 °C the thermal rearrangement of **15** is fast enough so that the effects induced in $15^{\bullet+}$ appear increasingly in **3** until the rearrangement is so fast that **15** is not even observed (~0 °C).

The CIDNP effects at low temperatures allow an insight into the mechanism for the formation of **15**. First, the initially formed radical cation, $3^{\bullet+}$, must have a structure similar to $1^{\bullet+}$, $2^{\bullet+}$, and $4^{\bullet+}$ with spin and charge confined to the butadiene moiety. Evidence for this conclusion comes from the enhanced absorption observed for the butadiene protons of **3** at very low temperatures (−70 °C). Significantly, the terminal protons show a larger enhancement than the internal ones, whereas the involvement of $15^{\bullet+}$ should result in the reverse intensity distribution. A polarization pattern of the latter type is, of course, observed for the major polarized product, **15**. Both products show the polarization indicative of geminate electron return, suggesting a rapid (though not complete) rearrangement of $3^{\bullet+}$ to $15^{\bullet+}$ during the ion pair lifetime ($\tau \leq 10^{-7}$ s). Since the polarization patterns observed for the two products are different, a rapid equilibration $3^{\bullet+} \rightleftarrows 15^{\bullet+}$ must be excluded.

In contrast to the radical cation energy surface, that of the neutral precursor features the reverse rearrangement, $\mathbf{15} \rightarrow \mathbf{3}$. This is evident from the polarization observed above −47 °C, which clearly originates in $15^{\bullet+}$ but is transferred to **3** (Figure 2). These effects are rationalized by a mechanism involving geminate recombination of the ion pair ($\rightarrow$**15**) followed by rearrangement (**15** $\rightarrow$ **3**). Our results provide crude kinetic data concerning the intramolecular retro-Diels–Alder reaction. Under our reaction conditions the lifetime of **15** is about 1 s at −10 °C; assuming a preexponential factor of $10^{12.8}$ typical for unimolecular reactions, this corresponds to a barrier of 15 kcal/mol. Although we have no evidence for the reverse rearrangement, **3** $\rightarrow$ **15**, an intramolecular Diels–Alder reaction, we note that this type of cyclization has been invoked to explain the thermal isomerization of bicyclo[4.2.1]nona-2,4,7-triene to dihydroindene.[31] This reorganization also has precedent in the cation rearrangement observed during the acetolysis of **7**.[10,11]

Our results provide the first detection and (NMR) characterization of the elusive tetracyclo[4.3.0.0.^{2,9}0^{5,7}]non-3-ene system, and they suggest the interconversions shown in Scheme I. This mechanism is intriguing for two reasons: because it invokes a rapid [3 + 2] cation radical Diels–Alder reaction; and because it requires dissimilar energy surfaces for the radical cation and its parent molecule.

Scheme I



The finding of dissimilar energy surfaces for radical cation and parent is contrary to the widely held notion that these energy surfaces should be similar, although the energy differences and the barriers for interconversion should be reduced on the radical cation energy surface. For the system discussed here, both surfaces appear to have minima at comparable geometries. However, their relative energies are inverted. On the radical cation surface the (formally) tetracyclic isomer is preferred, whereas the bicyclic isomer is more stable on the parent energy surface. The difference can be explained as the result of two cooperative effects: release of strain and increased delocalization of spin and charge, effects which we have invoked repeatedly to explain unusual radical cation structures.[14,17-19] In the system discussed here, the radical cation $15^{\bullet+}$, should derive an incremental degree of stabilization from its bishomoaromatic (bishomoheptafulvene) structure.[4] On the other hand, the increase in strain energy should be only a fraction of that expected for formation of two cyclopropane moieties, since the two pivotal bonds are only partially formed. The neutral molecule, of course, experiences the full impact of cyclopropane strain and does not have the benefit of homoaromaticity, hence, the rapid retro-Diels–Alder reaction of **15** to **3**.

As for the unusual [3 + 2] cycloaddition, we note that the cation radical Diels–Alder reaction is considered to be a concerted reaction in which the radical cation serves as dienophile, i.e., a reaction of the [4 + 1] type.[32-34] However, in the system discussed here a [4 + 1] cycloaddition is unlikely because this reaction would require in essence an intramolecular electron transfer from an ethylene moiety to a butadiene radical ion; such a transfer is endothermic by nearly 20 kcal/mol.[8] Thus it is understandable that the cyclization proceeds via an alternative pathway. What is surprising is the apparent ease of the [3 + 2] cycloaddition, which is considered a symmetry-forbidden reaction.[32-34] The barrier for this intramolecular cyclization can be estimated as <5 kcal/mol, based on a preexponential factor of $10^{12.8}$ typical for unimolecular reactions and a rate constant of $>10^{7}$ s^{-1} for the rearrangement (vide supra) at −70 °C.

The existence of such a rapid [3 + 2] cycloaddition, regardless of whether it is concerted or stepwise, may suggest a somewhat greater mechanistic variety for radical cation cycloadditions than previously considered. The notion of mechanistic variety is, of course, also supported by the existence of singly linked dimer radical cations as intermediates in the electron transfer induced dimer cleavage[18] or dimerization[35] in solution and in the gas phase.[36]

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Conclusion

This study fails to support bicycloaromaticity as a significant factor in determining radical cation structures. In contrast, homoaromaticity is seen to provide stabilization to the extent that the intramolecular [3 + 2] cycloaddition of $3^{\bullet+}$ to homoaromatic $15^{\bullet+}$ is extremely rapid. This system is the second example of a homoaromatic radical cation structure type. As with several other recent examples from our laboratory, we note that the potential energy surfaces of radical cation and the corresponding neutral parent may be substantially different. In this paper we have shown that the equilibrium between two structures (**3** and **15**) is shifted dramatically on the radical cation surface. The chemistry of organic radical cations continues to be an exciting area of study.

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Carbene and Silicon Routes as Methods for the Generation and Dipolar Cycloaddition Reactions of Methyl Nitrile Ylide

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Abstract: Methyl nitrile ylide was generated by both a photochemical and desilylation route and has been characterized by UV spectroscopy and by its kinetic and cycloaddition behavior. The dipole is formed by the addition of singlet methylene to acetonitrile and shows a strong transient absorption at 280 nm which is quenched by the addition of standard dipolarophiles. The relative rates of formation of 1,3-dipolar adducts and the relative rates of quenching of the transient absorption are in excellent agreement. Generation of the dipole from a silylthioimidate followed by dipolar cycloaddition also gave rise to related cycloadducts. The ratio of cycloadducts obtained from an unsymmetrically substituted dipolarophile was found to be strikingly dependent on the purity of the silylthioimidate. The different product ratios result from the operation of an alternate mechanism which involves the thiophenol that is released in the decomposition of silylthioimidate to the nitrile ylide. The initially generated dipole is believed to react with excess thiophenol to give a "half-capped" dipole which undergoes a subsequent conjugate addition to the unsymmetrical dipolarophile.

The widespread use of the 1,3-dipolar cycloaddition reaction stems in part from the frequent need to synthesize five-membered heterocyclic rings and the customarily high efficiency of such cycloadditions.[1-4] One of the more interesting members of the 1,3-dipole family is the nitrile ylides.[5] This class of dipoles has traditionally been prepared by (a) treatment of imidoyl halides with base,[6] (b) thermal or photochemical elimination of phosphoric acid esters from 4,5-dihydro-1,3,5-oxazaphospholes,[7] and (c) photolysis of aryl-substituted azirines.[8-10] More recently, nitrile ylides have been observed to be formed upon photolysis of carbene precursors in nitrile solvents. The nitrile ylides formed in this manner have been trapped by olefinic dipolarophiles.[11-14] A long-standing restriction to the further use of nitrile ylides in organic synthesis stems from the fact that simple alkyl-substituted systems are not easily prepared. In searching for alternate ways to form these dipoles, we have discovered two new and general methods for nitrile ylide formation. Generation of an intermediate having nitrile ylide reactivity was achieved from the photolysis of diazomethane or diazirine in acetonitrile. The 1,3-dipole formed in this manner can be readily trapped with a variety of dipolarophiles to give cycloadducts in high yields. An alternate route to the same dipole involves desilylation of an appropriately substituted nitrilium cation. Thus, silylthioimidate **1** serves as a convenient nitrile ylide precursor and undergoes smooth dipolar cycloaddition with a variety of dipolarophiles in the presence of silver fluoride according to Scheme I.

Scheme I

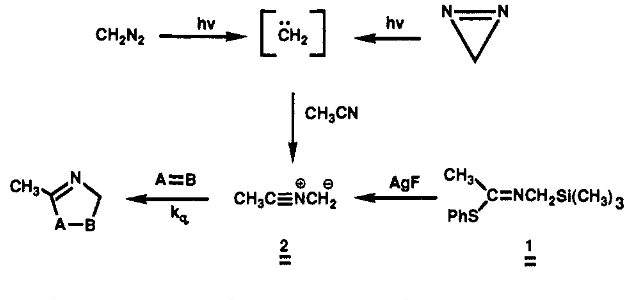

Table 1. Rate Constants for the Reactions of Methyl Nitrile Ylide with Various Quenchers at 298 K in Air-Saturated Acetonitrile

quencher	k_q, $M^{-1}\ s^{-1}$[a]
maleic anhydride	$(4.5 \pm 0.3) \times 10^9$
fumaronitrile	$(2.18 \pm 0.08) \times 10^9$
diethyl fumarate	$(7.9 \pm 0.3) \times 10^8$
dimethyl acetylenedicarboxylate	$(1.5 \pm 0.1) \times 10^8$
diethyl maleate	$(5.7 \pm 0.3) \times 10^7$
benzaldehyde	$(3.2 \pm 0.2) \times 10^7$
acrylonitrile	$(5.6 \pm 0.2) \times 10^6$
methyl acrylate	$(3.28 \pm 0.07) \times 10^6$
methyl propiolate	$(4.4 \pm 0.3) \times 10^5$

[a] Pulsed laser photolysis (Lambda Physik EMG 101 Excimer Laser, 308 nm, 20 ns) of diazirine (ca. 0.003 M) in air-saturated acetonitrile.

Results and Discussion

Pulsed excimer laser photolysis of diazirine (ca. 0.003 M) or diazomethane (ca. 0.05 M) in air-saturated acetonitrile at room temperature produced a transient absorption ($\tau > 100\ \mu s$) with λ_{max} at 280 nm (Figure 1). This transient is not observed in the absence of acetonitrile or the methylene precursor. On the basis

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* Dedicated to Cheves Walling on the occasion of his 70th birthday.

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