of J_{12} in the range of very weak interactions ($|J_{12}| <$ $10^2 A_i$) where J can be considered unchanged. The diagram corresponds to the case of Berson, et al.,[2] where the monomers have triplet ground states ($J >$ 0) and where the S state correlates with the ground state of the dimer ($J_{12} < 0$).

To include the hyperfine interactions, $\mathcal{3C}_{hyp}$, the electron spin functions are multiplied with the nuclear spin functions, $N_i, N_j \ldots N_k N_l \ldots$, where N_i denotes the spin of the ith nucleus. The product functions thus generated from T_m', T_m'', and S' are eigenfunctions of the total Hamiltonian. This result shows conclusively that no CIDNP can be expected to originate from a weakly interacting singlet–triplet pair or a singlet–singlet pair. In contrast, the functions derived from Q_m, T_m, and S are mixed by $\mathcal{3C}_{hyp}$. For the CIDNP effect, the only off-diagonal elements of interest are those connecting with S, the only state leading directly to dimeric products. It is found that no off-diagonal elements exist between S and any of the Q_m states, but that $\mathcal{3C}_{hyp}$ mixes S with T_m.[7] These elements are conveniently ordered into two groups, 4 and 5, distinguishing between S, T_0 mixing, in which the z component of the nuclear spin functions remain unchanged, and S, $T_{\pm 1}$ mixing accompanied by a change in the z component of both electron and nuclear spins.[8]

$$\langle T_0, N_i, N_k | \mathcal{3C} | S, N_i, N_k \rangle =$$
$$2(\sum A_i N_i - \sum A_k N_k)/\sqrt{6} \quad (4)$$

$$\langle T_{\pm 1}, N_i, N_k | \mathcal{3C} | S, N_i \pm 1, N_k \rangle = \pm A_i/\sqrt{3}$$
$$\langle T_{\pm 1}, N_i, N_k | \mathcal{3C} | S, N_i, N_k \pm 1 \rangle = \mp A_k/\sqrt{3} \quad (5)$$

Because of the small magnitude of the off-diagonal elements, mixing will be important only in regions of near degeneracy which, as shown in Figure 1, exist for very small values of $|J_{12}|$ and for $|J_{12}| \sim \frac{1}{2} g \beta H_0$, where S becomes degenerate with T_0 and T_{-1}, respectively. In large magnetic fields, mixing of S with T_{+1} can be neglected over the whole region of J_{12}.

If the time dependence of the Hamiltonian for a reacting system is treated by a step function of J_{12} as previously elaborated,[4] transitions among states will occur with probabilities which are proportional to the squares of the off-diagonal matrix elements connecting the states. In the experiment of Berson, et al.,[2] in which the triplet pairs are generated by diffusive encounters of triplet monomers, all states of Q_m, T_m, and S are populated with equal probability. The steady-state population, however, decreases from Q_m to T_m to S because of the difference in exit channels available to the systems in the different states. Diffusive separation is possible for all states; T_m has an additional channel leading to a triplet with intermediate bonding character, while S leads directly to dimer ground state. This population difference can induce a net flow of molecules from either T_0 or T_{-1} to S via transitions occurring with probabilities depending on the magnitude of (4) and (5) and, thus, on the nuclear spin states. If T_0, S transitions predominate, the resulting polarization in the dimer will show the

"multiplet effect," where each nuclear spin multiplet will have an equal number of enhanced absorption and emission lines.[9] In contrast, if T_{-1}, S transitions are preponderant, all lines in the spectrum should occur in emission. The experimental spectrum is of the latter type, requiring for this mechanism an average value of J_{12} in the triplet pair, closer to $\frac{1}{2} g \beta H_0$ than to 0. This is in sharp contrast to most, if not all, radical-pair reactions reported so far where, at large fields, T_0, S mixing accounts for the observations.

A second, and perhaps more likely, possibility for CIDNP to develop reveals itself if one follows the molecules in T_m states to the region of *strong* interactions. In the case at hand, the energy minimum of these states corresponds to structure 1, where one

1
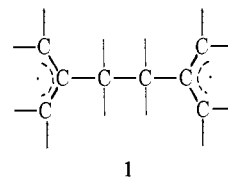
bond is completed with the remaining two unpaired electrons at maximum separation.[10] If the exchange coupling, J_{12}', in the biradical is small, hyperfine-induced singlet–triplet mixing occurs as previously elaborated for radical pairs.[4] However, with the reasonable assumption that formation of 1 is irreversible, T_0, S mixing cannot yield CIDNP because of the lack of a competitive process, leaving only transition from T_{-1} to S to induce polarization. The corresponding off-diagonal elements of the appropriate two-electron Hamiltonian[4c] take the form of (5) (except that the normalization factor is $1/\sqrt{8}$), predicting emission for all nmr transitions.

In conclusion it may be stated that triplet dimerizations can give rise to CIDNP signals with the polarizations originating either in the region of weak interactions between the triplet molecules or in transitions of the resulting triplet biradicals if the exchange coupling is small enough. While the former mechanism can give either multiplet or emission spectra, the latter can give rise only to pure emission.

(9) For nonidentical triplets, the Δg term can result in pure emission or absorption, even when T_0, S mixing is the only process.[4c,8]

(10) The same state is formed when T_m' and T_m'' are reaching strong interactions.

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Stabilities of Trivalent Carbon Species. II. Homoaromatic and Antihomoaromatic Species Derived from Protonated Cyclooctatetraene[1]

Sir:

We recently reported results of cyclic voltammetric measurements in concentrated sulfuric acid by means of

(7) There exist off-diagonal elements between Q_m and T_m which, however, do not contribute to the solution of the problem.

(8) If two nonidentical triplets form a pair, (4) contains a term $\frac{1}{2} \Delta g \beta H_0$, where Δg is the difference in isotropic g factor of the two components.[4c]

(1) Part I: M. Feldman and W. C. Flythe, *J. Amer. Chem. Soc.*, **91**, 4577 (1969).

Table I. Reduction of Carbonium Ions in Sulfuric Acid

Cation	Concn, mM	—10.2 M H₂SO₄—		—13.8 M H₂SO₄—		—17.0 M H₂SO₄—		λmax, nm
		$-\epsilon^a$	i_p^b	$-\epsilon$	i_p	$-\epsilon$	i_p	
Tropylium	0.445	1.05	13	1.23	20		c	275
Dibenzotropylium	0.445	0.44	7	0.62	5	0.87	6	530
		1.18^d	3	c		c		
Homotropylium	0.95^e	f		0.92	24	1.11	82	313

^{a} Reduction peak potential, ±0.015 V, vs. Hg–Hg₂SO₄, 17 M H₂SO₄; scan rate = 20 V/sec; T = 25°. ^{b} Peak current, microamperes. ^{c} Obscured by solvent reduction. ^{d} Potential for reaction 2. ^{e} Concentration of homotropylium ion in 13.8 M H₂SO₄ is 0.27 mM, determined from absorbance at 313 nm. ^{f} Cation not formed.

which the stabilities of aromatic and antiaromatic species related to triphenylmethyl could be determined.[1] In this paper we describe the electrochemical behavior of cyclooctatetraene in H₂SO₄, which involves species of considerable current interest.

Protonation of cyclooctatetraene generates a carbonium ion I-R⁺ which has been shown to have considerable 1,7 overlap in its π-electron system, as revealed by its nmr[2] and uv[3] spectra, and has been called monohomotropylium cation.[4] The cyclic π system which confers unusual stability to the cation (homoaromatic) should destabilize the corresponding anion (antihomoaromatic) as discussed by Winstein.[4] One would expect that the preferred configuration for the anion would be the cyclooctatrienyl II-R⁻. Only indirect evidence for the nature of the C₈H₉ anion is available, for example from the reduction of cyclooctatetraene which yields only the monocyclic trienes,[5] and suggests that the anion is II-R⁻. Protonation of the monohomocyclooctatetraene dianion yields only the bicyclic product shown.[6]

	6π electrons	
I-R⁺	6π electrons	II-R⁺
I-R·	7π electrons	II-R·
I-R⁻	8π electrons	II-R⁻
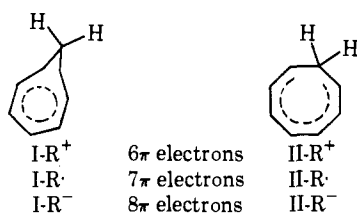
In the reduction of species related to triphenylmethyl[1] two reduction peaks are observed which correspond to a solvent-dependent reversible reduction of the carbonium ion to the radical (eq 1) and a solvent-insensitive reduction of the radical to the hydrocarbon

$$R^+ + e \rightleftarrows R\cdot \tag{1}$$

$$R\cdot + e + H^+ \longrightarrow RH \tag{2}$$

(2) J. L. Rosenberg, J. E. Mahler, and R. Pettit, *J. Amer. Chem. Soc.*, 84, 2842 (1962).

(3) S. Winstein, C. G. Kreiter, and J. I. Brauman, *ibid.*, 88, 2047 (1966).

(4) For a review of homoaromaticity, see S. Winstein, *Quart. Rev., Chem. Soc.*, 23, 141 (1969).

(5) A. C. Cope and F. A. Hochstein, *J. Amer. Chem. Soc.*, 72, 2515 (1950); L. E. Craig, R. M. Elofson, and I. J. Ressa, *ibid.*, 75, 480 (1953); W. O. Jones, *J. Chem. Soc.*, 1808 (1954).

(6) M. Ogliaruso and S. Winstein, *J. Amer. Chem. Soc.*, 89, 5290 (1967). An alternative structure for the anion, III-R —, may be formed by a geometrically unfavorable conrotatory reaction of II-R⁻, and is therefore not considered further.

III-R⁻
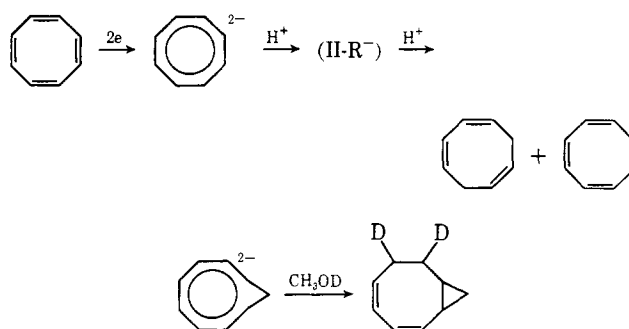
(eq 2). The voltammogram of tropylium ion in sulfuric acid is characterized by one peak which corresponds to reduction of the cation to the radical, subsequent rapid dimerization of the radical, and adsorption of the dimer on the mercury electrode. The reduction to hydrocarbon (cycloheptatriene) is not observed, although a cyclic voltammetric investigation of tropylium in aprotic solvents disclosed that the radical may be reduced to cycloheptatrienyl anion at a very negative potential.[7] Dibenzo[a,d]tropylium behaves like triphenylmethyl systems, with two one-electron reductions as in eq 1 and 2.

In order to compare the behavior of homotropylium with tropylium it is necessary to use an acid concentration sufficient to protonate cyclooctatetraene yet dilute enough so that the very negative tropylium peak is not obscured by the hydrogen wave from the solvent. In 14 M H₂SO₄ the concentration of homotropylium cation, as determined from reduction peak currents as well as from uv absorbance, is about 30% the concentration in 17 M H₂SO₄. Assuming identical diffusion coefficients for homotropylium and tropylium cations, the ratio of peak currents for the reduction of equal concentrations of the ions in 14 M H₂SO₄ using identical scan rates (20 V/sec) is 1.98:1. This indicates that the homotropylium cation, unlike the other cations we have studied, undergoes a *two*-electron reduction to the hydrocarbon (eq 3).

$$R^+ + 2e + H^+ \longrightarrow RH \tag{3}$$

The reduction potentials of dibenzotropylium, homotropylium, and tropylium cations in 14 M H₂SO₄ are −0.62, −0.92, and −1.23 V, respectively. These potentials follow the low-energy electronic transitions of the cations. The experimental data are summarized in Table I.

To account for the unique two-electron reduction of homotropylium cation, we first make the reasonable assumption that the cationic species undergoing reduction is in fact I-R⁺. Winstein and coworkers[3] have

(7) R. Breslow and W. Chu, *ibid.*, 92, 2165 (1970).

found that the free energy required for conversion of I-R⁺ to II-R⁺ is 22.3 kcal/mol, a barrier high enough to strongly implicate I-R⁺ as the electroactive species.[8] The radical formed first by electron transfer to I-R⁺ must be I-R·, in accord with the Franck–Condon principle. However, if the radical I-R· were further reduced directly to I-R⁻ (or the hydrocarbon RH), by analogy with tropylium and dibenzotropylium, the potential for this reduction should be more negative than the reduction of I-R⁺ to I-R·.[9] Alternatively, I-R· could convert to II-R· before electron transfer, and, from the HMO descriptions of an electron-accepting nonbonding MO in II-R· and an antibonding MO in I-R·, the reduction of II-R· is expected to occur at a more positive potential than I-R·. The overall scheme is summarized in eq 4. The scheme as pre-

$$I\text{-}R^+ \xrightarrow{e} I\text{-}R\cdot \longrightarrow II\text{-}R\cdot \xrightarrow{e} II\text{-}R^- \xrightarrow{H^+} RH \qquad (4)$$
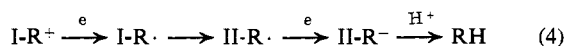
sented implies that I-R· is antihomoaromatic, i.e., that it is less stable than the isomeric radical II-R· in which the conjugated system is not cyclic. Extension of the available orbital argument to the anions suggests that II-R⁻ is preferred to I-R⁻, but experimental confirmation is lacking.

Breslow[10] has demonstrated the utility of electrochemical methods in obtaining otherwise unavailable information on very unstable antiaromatic species, such as triphenylcyclopropenyl anion. We suggest that this method is even more valuable in the study of antihomoaromatic species because these may be generated by electron-transfer reactions of the corresponding homoaromatic species, before they revert to the more stable linearly conjugated isomer. Attempts to prepare antihomoaromatic species by chemical reactions such as protonation[11] should yield preferentially the linearly conjugated species and not the desired intermediate.

Acknowledgment. We record our debt to the late Professor S. Winstein who encouraged us in this work.

(8) If the isomerization of I-R⁺ to II-R⁺ precedes electron transfer to II-R⁺, then the reduction potential reflects the free-energy changes for the isomerization and the electron transfer, as in the reduction of cyclooctatetraene to its planar radical anion: T. J. Katz, W. H. Reinmuth, and D. E. Smith, *J. Amer. Chem. Soc.*, **84**, 802 (1962). If the free energy for isomerization is accounted for, the potential for II-R⁺ + e ⇌ II-R· is approximately 0 V, which appears to be more positive than is reasonable. The antiaromatic 9-phenylfluorenyl cation[1] is reduced at −0.19 V in 14 M H₂SO₄.
(9) An apparent two-electron reduction is also observed for other ions in very concentrated acid because the first peak shifts to more negative potentials as acid concentration is increased and is eventually superimposed on the second.[1] It may be inferred that the solvent-insensitive potential for reaction 2 of homotropylium ion cannot be more negative than −0.92 V, the observed potential in 14 M H₂SO₄, and thus the potential for reaction 2 is more positive than reaction 1 in 17 M H₂SO₄. This behavior is unique among the ions studied to date.
(10) R. Breslow and K. Balasubramanian, *J. Amer. Chem. Soc.*, **91**, 5182 (1969).
(11) P. Warner and S. Winstein, *ibid.*, **91**, 7785 (1969).
(12) NASA Predoctoral Trainee, 1965–1968; American Chemical Society Division of Analytical Chemistry Summer Fellow, 1968.

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Solvolytic Behavior of Bicyclo[3.1.0]hex-3-en-2-yl Derivatives. Some Observations on the Mechanism of Photolysis of Benzene in Hydroxylic Media[1]

Sir:

As an extension of earlier studies[2] of degenerate sigmatropic rearrangements in which a cyclopropane ring circumambulates the periphery of a cyclic conjugated system, we have investigated the behavior of bicyclo[3.1.0]hex-3-en-2-yl cation (**1**). A companion paper[3] reports the rearrangement, which occurs only in strongly acidic medium. The present work describes the solvolytic chemistry of the bicyclo[3.1.0]hex-3-en-2-yl system and its relevance to a study of the mechanism of the photochemical hydration of benzene.
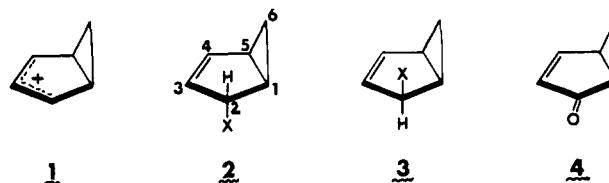
Reaction of exo alcohol 2–OH[4] with thionyl chloride or better with hydrogen chloride in CH₂Cl₂ gives chloride 2–Cl containing minor amounts of epimeric chloride 3–Cl. Hydrolysis or methanolysis of the chloride mixture in the presence of buffer gives exo alcohol 2–OH or exo methyl ether 2–OMe. The absence of endo alcohol 3–OH is established by comparison of the nmr spectrum of the crude hydrolysis product with that of authentic 3–OH, obtained as the major alcohol (∼70%) from LiAlH₄ reduction of the corresponding ketone **4**. A mixture of 2–OH-2-d and 3–OH-2-d results from **4** and LiAlD₄.

Methanolysis (in 50 vol % MeOH–CH₃CN) of the deuterated trifluoroacetates 2–O₂CCF₃-2-d and 3–O₂CCF₃-2-d gives exo methyl ether 2–OMe with 0.5 deuterium at positions 2 and 4 but none at position 1, 3, or 5 (analysis by nmr). Similarly, treatment of an acetonitrile solution of 2–OH-2-d and 3–OH-2-d with 3 mol % of p-toluenesulfonic acid results in complete mixing of the deuterium label between positions 2 and 4 within 1 min but no detectable deuteration elsewhere even after 26 hr.[5] The latter experiment involves repeated formation of the cationic intermediates and shows that the solvent capture rate (k_s) is at least 1.6 × 10³ times the rate of sigmatropic rearrangement (k_r).

(2) (a) J. A. Berson and M. R. Willcott, III, *J. Amer. Chem. Soc.*, **87**, 2751, 2752 (1965); **88**, 2494 (1966); *Rec. Chem. Progr.*, **27**, 139 (1966); (b) J. A. Berson, P. W. Grubb, R. A. Clark, D. R. Hartter, and M. R. Willcott, III, *J. Amer. Chem. Soc.*, **89**, 4076 (1967); (c) J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).
(3) P. Vogel, M. Saunders, N. M. Hasty, Jr., and J. A. Berson, *J. Amer. Chem. Soc.*, **93**, 1551 (1971).
(4) (a) E. Farenhorst and A. F. Bickel, *Tetrahedron Lett.*, 5911 (1966); (b) the stereochemical assignment[4a] is confirmed by the nmr spectra of **2** and **3**: N. M. Hasty, Jr., Ph.D. Thesis, University of Wisconsin, 1970, p 22 ff.
(5) More vigorous conditions, e.g., treatment of the chloride with AlCl₃ or pyrolysis of the trifluoroacetate, give polymeric materials and small yields of benzene.