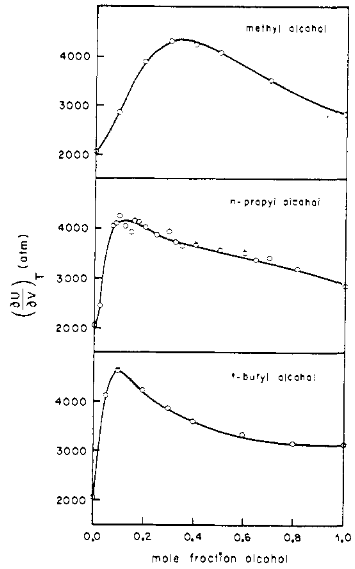

Figure 1. Energy–volume coefficients for alcohol–water mixtures at 30.0°.

aqueous alcohol mixtures it is possible systematically to study the effect of varying the "hydrophobic" character of the organic component in admixture with water. Accordingly, we report in this communication energy–volume coefficients for various mixtures of water with methyl alcohol, *n*-propyl alcohol, and *tert*-butyl alcohol.

The energy–volume coefficient is related to the thermal pressure coefficient, $(\partial P/\partial T)_V$, by the "thermodynamic equation of state"

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad (1)$$

We have measured the experimentally accessible thermal pressure coefficients at a number of temperatures in the range 20–55° for the various alcohol–water mixtures using a constant-volume thermometer of the general type described by Lau, Malcolm, and Fenby.[4] Full details of the experimental procedure will be published at a later date. Energy–volume coefficients for various mixtures at atmospheric pressure and at 30° were calculated using eq 1 and are considered accurate to ±1%.

Plots of the energy–volume coefficient *vs.* solvent composition for the three alcohol–water systems examined are shown in Figure 1. The most important feature of these plots is the maximum in $(\partial U/\partial V)_T$ which occurs in the highly aqueous region of solvent composition for all systems. Such a maximum in $(\partial U/\partial V)_T$ indicates that the internal energy of the system is most sensitive to isothermal volume change at that composition. It is not unreasonable to assume that the energy of a highly structured liquid will be a sensitive function of volume. Hence the observed maximum in the so-called internal pressure is in keeping with the concept of optimization of structure by small additions of alcohol to the system.[3]

It is seen from Figure 1 that the maxima for mixtures of the two larger, or more hydrophobic, alcohols with water occur at lower alcohol mole fractions than in the case of the methyl alcohol–water system. The relative positions of the maxima are maintained if the data are plotted against volume fraction instead of mole fraction as shown in Figure 1. This relationship appears to be quite general for other properties of alcohol–water mixtures.[3] An additional feature of these data is the relative constancy in size of the maxima in all three systems. This observation is surprising, since other structure-sensitive properties of these mixtures tend to pass through much larger extrema in the case of the aqueous *tert*-butyl alcohol system than in the case of the aqueous methyl alcohol system.[3] Accordingly, it seems that the factors responsible for the size of the maxima in $(\partial U/\partial V)_T$ for the systems discussed here are not particularly sensitive to the hydrophobic nature of the alcohol.

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Received July 24, 1970

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[4] C. F. Lau, G. N. Malcolm, and D .V. Fenby, *Aust. J. Chem.*, 22, 855 (1969).

The Formation of Alkene Radical Cations in Solution and the Structure of the Cyclooctatetraene Radical Cation

Sir:

Alkene radical cations have been proposed as transient intermediates in various oxidation reactions of olefins,[1] and their absorption spectra reported in the solid state.[2] However, except for a few highly conjugated olefins,[3,4] no simple olefinic radical cations have been observed in solution.[5]

By a modification of our method for the generation of aromatic radical cations,[6] we have now been able to observe the esr spectra of simple olefinic radical cations in solution. The modification involved the addition of 10% $BF_3 \cdot CH_3COOH$ to the cobaltic acetate–trifluoroacetic acid solution so as to increase the oxidizing power of the cobaltic ion.[7] Using the previously described flow system, we were able to obtain esr spectra for the radical cations derived from a variety of tetrasubstituted olefins.

The esr spectrum of the tetramethylethylene radical cation, the central portion of which is shown in Figure 1, consisted of at least nine equally spaced lines separated by 16.6 G; the splitting was due to four identical methyl groups.

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(1) C. E. H. Bawn and J. A. Sharp, *J. Chem. Soc.*, 1854 (1957); L. Eberson, K. Nyberg, M. Finkelstein, R. C. Peterson, S. D. Ross, and J. J. Uebel, *J. Org. Chem.*, 32, 16 (1967); S. D. Ross, M. Finkelstein, and J. J. Uebel, *ibid.*, 34, 1018 (1969); B. Belleau and Y. K. Au-Young, *Can. J. Chem.*, 47, 2117 (1969); H. Weingarten and J. S. Wager, *J. Org. Chem.*, 35, 1750 (1970).

(2) T. Shida and W. H. Hamill, *J. Amer. Chem. Soc.*, **88**, 5386 (1966).

(3) Only the radical cations of tetraphenylethylene,[4a] bifluorene,[4b] and tetrathio-[4c] and polyamino-[4d]substituted ethylenes have been observed.

(4) (a) I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, **43**, 2712 (1965); (b) I. C. Lewis and L. S. Singer, *ibid.*, **44**, 2082 (1966); (c) D. H. Geske and M. V. Merritt, *J. Amer. Chem. Soc.*, **91**, 6921 (1969); (d) K. Kuwata and D. H. Geske, *ibid.*, **86**, 2101 (1964); B. C. Gilbert, R. H. Schlossel, and W. M. Gulick, Jr., *ibid.*, 92, 2974 (1970).

(5) Olefinic radical cations have recently been observed on synthetic zeolites by Dr. P. L. Corio and Dr. S. Shih in our laboratory.

(6) R. M. Dessau, S. Shih, and E. I. Heiba, *J. Amer. Chem. Soc.*, **92**, 412 (1970).

(7) S. S. Lande and J. K. Kochi, *ibid.*, 90, 5196 (1968).

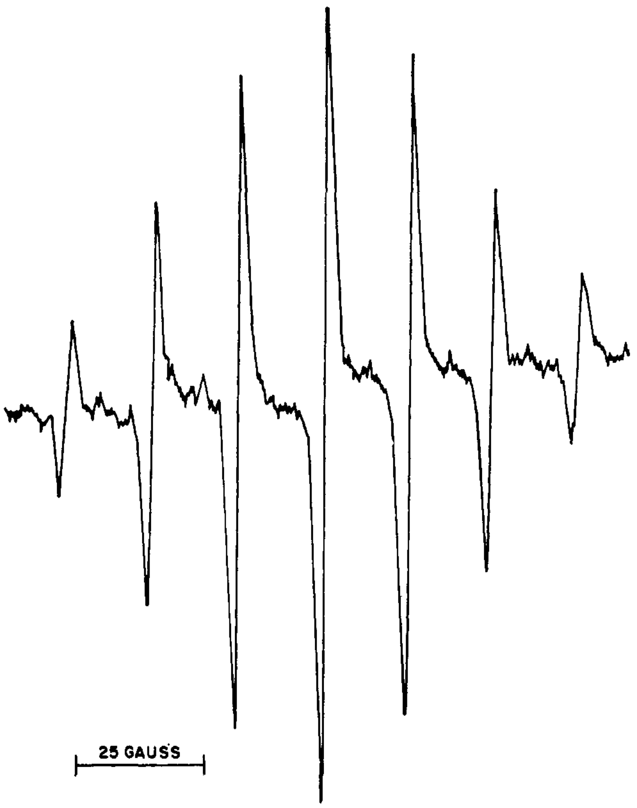


Figure 1. Central portion of the esr spectrum of the radical cation derived from 2,3-dimethylbutene-2.

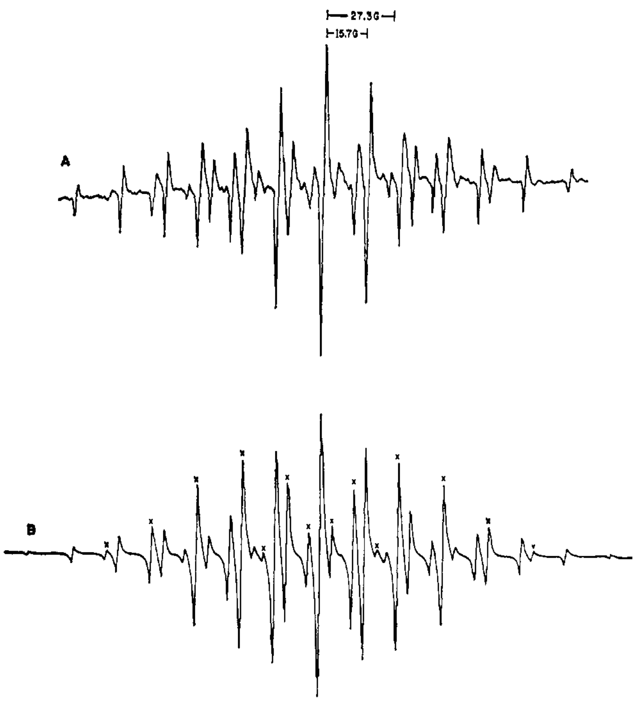
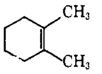


Figure 2. The 1,2-dimethylcyclohexene radical cation: A, observed esr spectrum; B, computer-simulated spectrum. Note the line-broadening effect on the peaks marked.

In the dimethylcyclohexene radical cation esr spectrum (Figure 2), two different splittings were observed, one of 15.7 G and one of 27.3 G. The smaller splitting was assigned to the two methyl groups while the larger splitting of 27.3 G was assigned to the four β-methylene hydrogens. The large value of the latter splitting constant can be understood in terms of conformational effects due to the cyclic structure of the radical cation.[8] At room temperature, the four β-methylene protons appeared almost identical, although a small alternating line-width effect[9] was observed in the esr spectrum due to axial–equatorial interconversions of these protons.

The radical cations derived from 2,3-dimethylpentene-2 and 2,3,4-trimethylpentene-2 were also observed, and the hyperfine splitting constants obtained from their esr spectra are included in Table I. All three allylic methyl groups in these radical cations appeared identical due to the broad line widths (2–2.5 G) observed in these two cases. The R values[8] for the ethyl (1.0) and the isopropyl (0.3) groups indicate that the ethyl group rotates freely in the radical cation at room temperature whereas the isopropyl does not.

Table I. Hyperfine Splitting Constants of Olefinic Radical Cations

Olefin	$A_{\mathrm{CH_3}}$	$A_{\mathrm{CH_2,CH}}$	R
$(CH_3)_2C{=}C(CH_3)_2$	16.6		
	15.7	27.3	1.7
$(CH_3)_2C{=}C(CH_3)CH_2CH_3$	16.4	16.4	1.0
$(CH_3)_2C{=}C(CH_3)CH(CH_3)_2$	16.4	5.5	0.3

In view of the symmetrical nature of these olefinic radical cations, the π-spin density at each of the two olefinic carbon atoms would be expected to be equal to 0.5. Applying the usual McConnell relation[10] $a_{\mathrm{CCH_3}}{}^{\mathrm{H}} = Q_{\mathrm{CCH_3}}{}^{\mathrm{H}}\rho_{\mathrm{C}}$, one obtains $Q_{\mathrm{CCH_3}}{}^{\mathrm{H}} = 32.6$ for these olefinic radical cations. This value falls between that found for the hexamethylbenzene radical cation[6] ($Q = 38.7$) and that reported for the neutral *tert*-pentyl radical[11] $(CH_3)_2CCH_2CH_3$ ($Q = 22.8$). These differences support the contention that in addition to a strong dependence of Q on charge density, other factors are also involved.[12]

The Cyclooctatetraene Radical Cation. In contrast to the cyclooctatetraene (C_8H_8) radical anion[13] which has been extensively studied, very little is known about the corresponding cation. Cyclooctatetraene and its ions are of considerable theoretical interest in view of the numerous possible geometries.[14] Cyclooctatetraene itself is known to have a tub-shaped conformation[15] (I), whereas both the mono- and dianions

[8] D. H. Geske, *Progr. Phys. Org. Chem.*, 4, 125 (1967).

[9] A. Hudson and G. R. Luckhurst, *Chem. Rev.*, 69, 191 (1969); P. D. Sullivan and J. R. Bolton, *Advan. Magn. Resonance*, 4, 39 (1970).

[10] H. M. McConnell, *J. Chem. Phys.*, 24, 632, 764 (1956).

[11] R. W. Fessenden and R. H. Schuler, *ibid.*, 39, 2147 (1963); P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 90, 7155 (1968).

[12] G. R. Underwood and V. L. Vogel, *J. Chem. Phys.*, 51, 4323 (1969).

[13] (a) T. J. Katz and H. L. Strauss, *ibid.*, 32, 1873 (1960); (b) T. J. Katz, *J. Amer. Chem. Soc.*, 82, 3784, 3785 (1960); (c) T. J. Katz, W. H. Reinmuth, and D. E. Smith, *ibid.*, 84, 802 (1962); (d) H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *ibid.*, 85, 2360 (1963); (e) G. Schröder, "Cyclooctatetraene," Verlag Chemie, Weinheim/Bergstr., Germany, 1965.

[14] M. J. S. Dewar, A. Harget, and E. Haselbach, *J. Amer. Chem. Soc.*, 91, 7521 (1969).

[15] I. L. Karle, *J. Chem. Phys.*, 20, 65 (1952); W. B. Person, G. C. Pimentel, and K. S. Pitzer, *J. Amer. Chem. Soc.*, 74, 3437 (1952); F. A. L. Anet, *ibid.*, 84, 671 (1962).

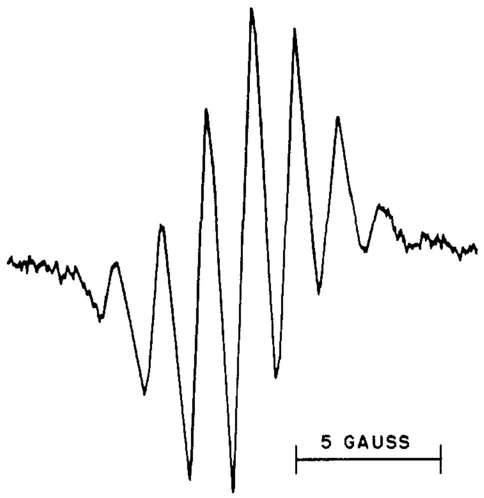
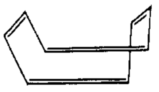


Figure 3. The esr spectrum of the cyclooctatetraene radical cation.

appear to be planar[13] (II). Recent theoretical calculations by Dewar, *et al.*,[14] predicted a nonplanar structure for the radical cation, and it was the purpose of this work to experimentally test this hypothesis.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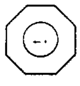
II

The previously unreported cyclooctatetraene radical cation was prepared in pure trifluoroacetic acid (no BF_3 added) by cobaltic ion oxidation of cyclooctatetraene (10^{-3}–10^{-2} *M*) in a rapid mixing flow system. The esr spectrum (Figure 3) obtained under these conditions consisted of seven equally spaced lines separated by 1.5 G (with a peak-to-peak line width of 0.6 G). The observed line intensities were consistent with splittings caused by eight equivalent hydrogen atoms, the two outer lines being too small to be observed.

The reported[13d] proton splitting for the planar radical anion was 3.2 G. By analogy to aromatic ions,[16] the corresponding splitting for the radical cation would be expected to be somewhat greater than 3.2 G, if the geometry of the two ions were identical. The small splitting of 1.5 G found in the radical cation supports a nonplanar configuration for the cation. Spin polarization of the C–H bond by the spin on the α carbon will generate a *negative* spin density at the hydrogen atom. In a tub-shaped ion radical, the hydrogen can also interact in a hyperconjugative manner with a spin on a β carbon. This will generate a *positive* spin density at the hydrogen atom. The partial cancellation of these spin densities results in the lower splitting constant observed.

Further studies on other olefinic radical cations are currently in progress.

Acknowledgment. Helpful discussions with Drs. E. I. Heiba, P. L. Corio, and S. Shih as well as the skillful technical assistance of Mr. R. J. Cier are gratefully acknowledged.

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[16] G. Vincow, in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N. Y., 1968, p 151.

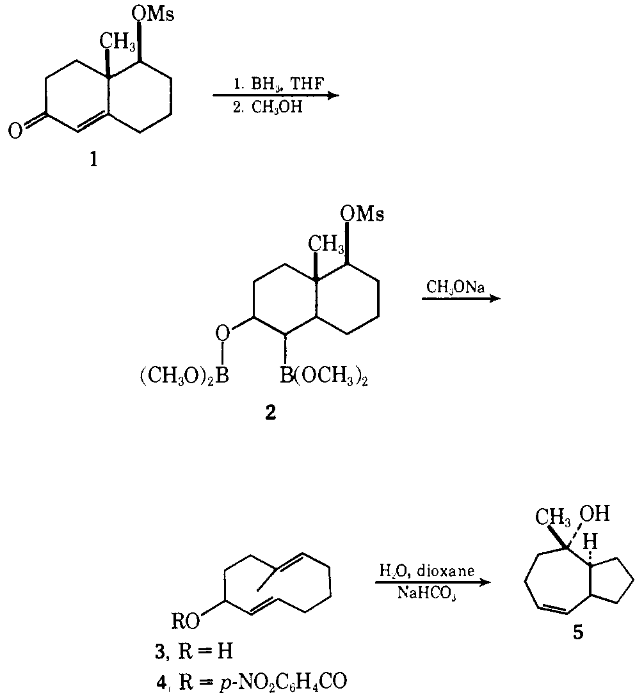
A New Synthetic Approach to Hydroazulenes

Sir:

A sizable group of natural products possess substituted hydroazulenic carbon skeletons, yet there are but a few general routes to such compounds.[1] During the past several years we have been seeking efficient stereoselective synthetic approaches to hydroazulenes which might solve the problems posed by this class of compounds. This report discloses preliminary findings on a novel approach based upon the positionally and stereochemically selective cyclization of cyclodecadienyl derivatives.[2]

Scheme I depicts the essential features of the synthetic pathway. The unsaturated keto mesylate **1**,[3] upon treatment with excess diborane in THF followed by methanolic sodium methoxide, afforded the cyclodecadienol **3**[4] [$\delta_{TMS}^{CCl_4}$ 1.70 (vinyl CH_3), 3.89 (carbinyl H, multiplet), 4.74, and 5.20 ppm (vinylic H's, multiplets)]

Scheme I



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(1) *Cf.* J. A. Marshall and J. J. Partridge, *J. Amer. Chem. Soc.*, **90**, 1090 (1968); *Tetrahedron*, **25**, 2159 (1969), and references cited therein; J. A. Marshall, N. H. Andersen, and P. C. Johnson, *J. Org. Chem.*, **35**, 186 (1970); C. H. Heathcock and R. Ratcliffe, *Chem. Commun.*, 994 (1968); M. Kato, H. Kosugi, and A. Yoshikoshi, *ibid.*, 185 (1960).

(2) An electrophile initiated *trans,trans*-1,5-cyclodecadiene cyclization process has been postulated in the biogenesis of hydroazulenes by J. B. Hendrickson [*Tetrahedron*, **7**, 82 (1959)]. Recently both acid-catalyzed and thermal cyclizations of *trans,trans*-1,5-cyclodecadiene monoepoxides have been effected: E. D. Brown and J. K. Sutherland, *Chem. Commun.*, 1060 (1968); E. D. Brown, T. W. San, and J. K. Sutherland, *Tetrahedron Lett.*, 5025 (1969).

(3) *Cf.* C. B. C. Boyce and J. S. Whithurst, *J. Chem. Soc.*, 2680 (1960).

(4) Satisfactory combustion analysis data were secured for this substance.