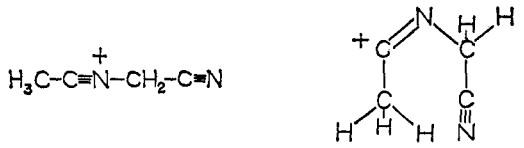
was eliminated in the HCN. These results suggest that the intermediate in this reaction may result from attack by the primary carbonium ion on the basic nitrogen atom of the neutral molecule. The nitrogen atom in the intermediate can be sp hybridized (I) or sp^2 hybridized (II).



I II

Both of these structures are consistent with retention of the neutral's nitrogen in the product ion, but I gives no explanation for the exclusive loss of the neutral's hydrogen in HCN. Structure II immediately allows close proximity of the incipient hydrogen and cyano parts of the product HCN. There is no way of establishing whether the HCN eliminated is HCN or HNC. Reasonable transition states lead to either product. HCN elimination may be more likely since isocyanides in general are less stable than the corresponding cyanides. In either case the loss of hydrogen exclusively from the neutral in HCN favors the cyclic complex. The selectivity of the hydrogen atom elimination in HCN is interesting in view of the early conclusions concerning significant hydrogen atom mobility in ions.[11] These experiments illustrate the considerable potential of icr in elucidating reaction mechanisms.

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(11) F. H. Field and J. L. Franklin, *Pure Appl. Phys.*, Academic Press Inc., New York, N. Y., 1957, pp 185–194.

(12) National Institutes of Health Postdoctoral Fellow, 1967–1968.

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A Classical Anion Radical from *trans*-Fused Bicyclo[6.1.0]nona-2,4,6-triene[1]

Sir:

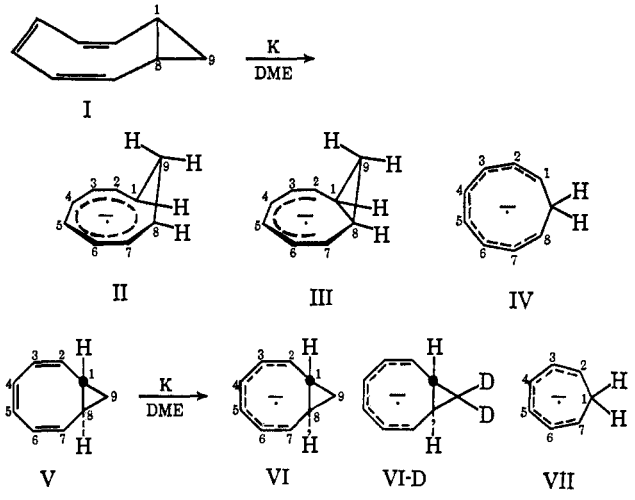
It was recently reported[2] that addition of an electron to the monomethylene adduct of cyclooctatetraene (monohomocyclooctatetraene, I) at low temperatures produces a nine-electron nonclassical homoaromatic monohomocyclooctatetraene anion radical, II. The homoaromatic structure II is definitely preferred over the classical one (III) with a complete cyclopropane ring or the classical planar one (IV) with negligible 1,8 interaction.[2a] The cyclooctatetraene methylene adduct I employed for the generation of anion radical II possesses a *cis* fusion of the cyclopropane and eight-membered rings. We could anticipate that it would be very instructive to generate an anion radical from a *trans*-fused monomethylene adduct of cyclooctatetraene (V) and to compare this anion radical with II. The *trans*-fused V has recently become available,[3] and we can now report the generation of the corresponding anion radical from it.

Brief treatment of V in glyme (DME) with a potassium mirror at −90° produces an anion radical whose esr spectrum can be recorded at −90°. As summarized in Table I, this spectrum is very different from that of II[2] generated from *cis*-I. It consists of more than 60 well-resolved lines spread over 37.7 G, and it can be simulated excellently with hyperfine splitting constants (a_H) of 8.11, 5.61, 4.22, and 0.46 G, each for two protons (Figure 1). Evidently, the a_H value for the two remaining protons must be essentially zero (< |0.10 |G). The assignment of the a_H value of 0.46 G to the C_9

Table I. Hyperfine Splitting Constants (a_H) and Q Values for Anion Radicals II and VI

		Values for hydrogen at position 1	2	3	4	9	9
II[c]	a_H	5.72	0.87	5.12	1.99	4.54	12.18
	Q[d]	27.40					
VI	a_H[a]	5.61	8.11	<|0.10|	4.22	0.46	0.46
	Q[e]	24.66					
	a_H[a]	4.22	8.11	<|0.10|	5.61	0.46	0.46
	Q[e]	27.44					
VII	a_H		7.64	0.59	4.90	2.16[b]	2.16[b]
	Q[e]	26.26					

[a] a_H values are ±0.08 G. [b] C_1 in VII. [c] These a_H values are more accurate than those originally reported.[2a] They have been obtained from better resolved spectra than those formerly employed.[2a] The present values are quite similar to those of Katz and Talcott[2b] for II in liquid ammonia and those of F. J. Smentowski, R. M. Owens, and B. D. Faubion, *J. Am. Chem. Soc.*, **90**, 1537 (1968), for II in DME or THF with K, Na, or Li as counterion. The alteration of a_H values in no way affects the previous discussion of the structure[2a] of II. [d] Q value for H_{1-8}. [e] Q values for H_{2-7}.



I II III IV V VI VI-D VII

(1) (a) Research supported in part by the National Science Foundation; (b) research supported in part by the U. S. Army Research Office (Durham); (c) acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(2) (a) R. Rieke, M. Ogliaruso, R. McClung, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 4729 (1966); (b) T. J. Katz and C. Talcott, *ibid.*, **88**, 4732 (1966).

(3) (a) E. Vogel, W. Grimme, and W. E. Bleck, private communication of unpublished work at Köln; (b) see footnote 9 of E. Vogel, W. Grimme, and E. Dinne, *Tetrahedron Letters*, 391 (1965); (c) G. Petrowski, unpublished work at University of California at Los Angeles; (d) 9,9-dideuterio-V was derived from 9,9-dideuterio-I.[2a]

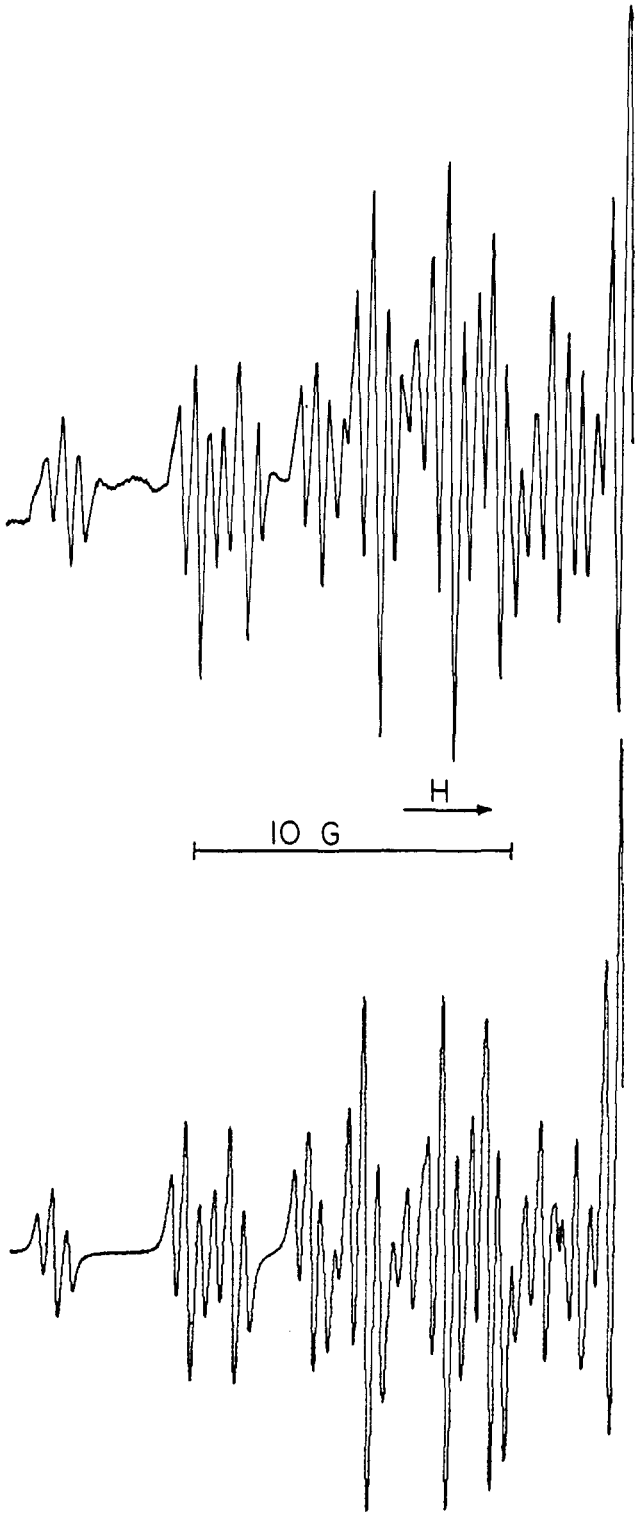


Figure 1. Esr spectra of VI: upper, observed; lower, calculated using 0.160-G line width and Lorentzian line shape; only half-spectra shown.

protons is clear from the spectrum of the anion radical prepared from the 9,9-dideuterio-V[3d] (Figure 2). In this spectrum the 0.46-G splitting is no longer observed. The anion radical from V showed no tendency to rearrange to II on long observation (6 hr) at −90°. Raising the temperature to −60° caused the spectrum of the anion radical from V to disappear, with no evidence at any point of an isomerization to II.

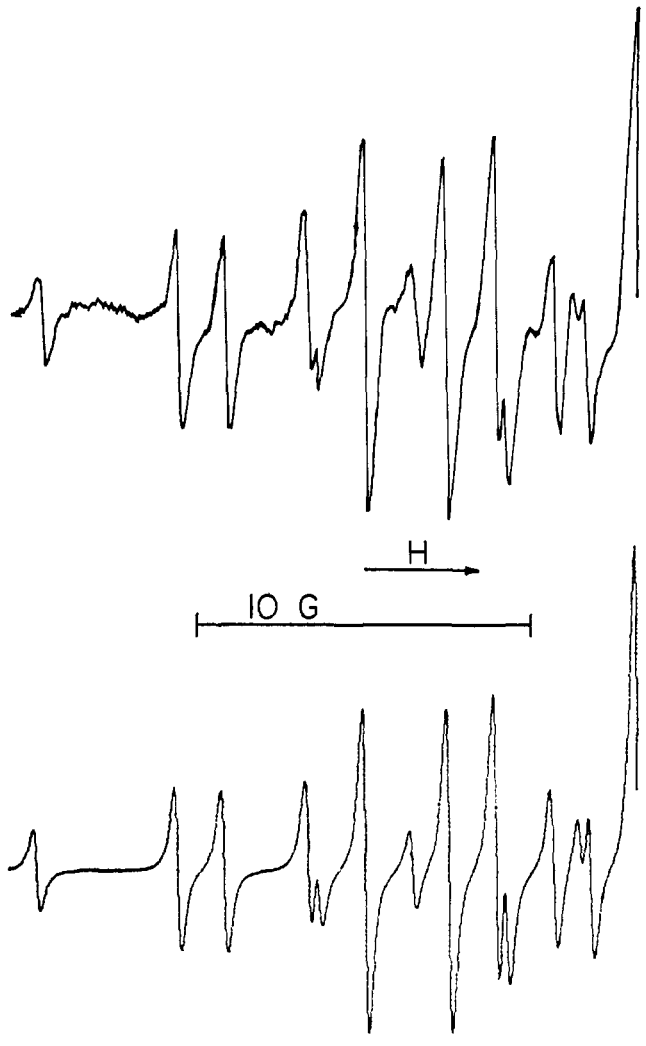


Figure 2. Esr spectra of VI-D: upper, observed; lower, calculated using 0.200-G line width and Lorentzian line shape; only half-spectra shown.

All the features of the spectrum of the anion radical from V are in line with a classical structure VI, the *trans*-fused analog of III, containing an essentially fully closed cyclopropane ring and a hexatriene anion radical system. Such a structure is supported by the small and equal a_H values for the two C_9 protons (0.46 G) and the fact that the pattern of the remaining a_H values is appropriate for a hexatriene anion radical system. The assignment of the a_H values to the different protons, summarized in Table II, was based on calculated spin densities at C_2 to C_7 of a hexatriene π system. With either Hückel or more sophisticated McLachlan[4a] calculated spin densities (ρ) one predicts the same sequence of a_H values for C_2 to C_7 and simulates the values quite well with the McConnell relation,[4b] $a_H = Q\rho$ (Table II). A remaining ambiguity in the a_H assignments is whether the 5.61 and 4.22 values belong to $C_{1,8}$ and $C_{4,5}$, respectively, or *vice versa*. While we are inclined to favor somewhat the former assignment, attempts are underway to prepare suitably labeled materials with which to resolve this question.

Not only can the pattern of a_H values for C_2 to C_7 in VI be simulated by calculations for a hexatriene π

(4) (a) A. D. McLachlan, *Mol. Phys.*, 3, 233 (1960); $\lambda = 1.00$; (b) H. M. McConnell *J. Chem. Phys.*, 23, 632, 764 (1956).

Table II. Calculated a_H Values for Anion Radicals II and VI ($a_H = Q\rho$)

Species	Calculation	a_H values for hydrogens at positions 1	2	3	4
VI, Q = 27.44	Hückel[a] ρ		0.2716	0.0538	0.1746
	Hückel[a]		7.45	1.48	4.79
	McLachlan[a]		9.97	−0.76	4.51
	McLachlan[b]		9.32	−0.48	4.88
	McLachlan[c]		8.64	−0.15	5.22
	Assigned		8.11	<|0.10|	5.61
VI, Q = 24.66	Hückel[a]		6.70	1.33	4.31
	McLachlan[a]		8.96	−0.69	4.05
	McLachlan[b]		8.38	−0.43	4.39
	McLachlan[c]		7.77	−0.13	4.70
	Assigned		8.11	<|0.10|	4.22
II, Q = 27.40	Hückel[d] ρ	0.1677	0.0769	0.1549	0.1008
	Hückel[d]	4.59	2.11	4.24	2.76
	McLachlan[d]	6.10	0.99	4.75	1.88
	Assigned	5.72	0.87	5.12	1.99

[a] $\beta_{23} = \beta_{34} = \beta_{45} = 1.00\beta_0$. [b] $\beta_{23} = \beta_{45} = 1.00\beta_0$; $\beta_{34} = 0.90\beta_0$. [c] $\beta_{23} = \beta_{45} = 1.00\beta_0$; $\beta_{34} = 0.80\beta_0$. [d] $\beta_{18} = 0.600\beta_0$; $\beta_{12} = 0.890\beta_0$; $\beta_{23} = 0.925\beta_0$; $\beta_{34} = 0.808\beta_0$; $\beta_{45} = 1.00\beta_0$.

system, but it is experimentally quite similar to that for a known hexatriene anion radical, namely VII, generated from cycloheptatriene by Levy and Myers[5] (Table I). A strong argument in favor of structure VI may be based on the observed Q value. Thus, the sum of a_H values, 24.66 or 27.44, for C_2 to C_7 is a reasonable value for Q. On the other hand, the sum of a_H values, 35.88, for C_1 to C_8 is well out of the range of known Q values. This strongly supports structure VI with the C_1–C_8 cyclopropane electrons excluded from the delocalized π-electron system. The observed a_H value of 5.61 or 4.22 G for $C_{1,8}$ is also appropriate for protons β to the hexatriene anion radical system in VI.

The inclusion of the C_1–C_8 cyclopropane electrons in the delocalized electronic system in anion radical II and their exclusion in VI is very significant. The difference between the two cases may be understood with the aid of an orbital symmetry argument of the type employed by Woodward and Hoffmann[6,7] for electrocyclic reactions. Examining the highest occupied molecular orbital in an octatetraene anion radical, the conversion of a cyclononatetraene anion radical (*e.g.*, IV) to a bicyclic hexatriene anion radical (*e.g.*, III) and the reverse reaction are predicted to be disrotatory. The opening of the anion radical from *cis*-I leads to the anion radical of the all-*cis* cyclononatetraene, and geometry is favorable for a compromised delocalized electronic system intermediate in character between the bicyclic hexatriene and monocyclic cyclononatraene anion radical extremes. *trans*-V has the C_2–C_7 hexatriene system in a nearly planar arrangement. Thus, the situation is more favorable for conjugation in the triene portion of the hydrocarbon[8] or in a triene anion radical system than it is in the tub-like *cis*-I. The disrotatory opening of anion radical VI is toward a very uncomfortable *trans,cis,cis,cis*-cyclononatetraene anion radical. Models of the *trans,cis,cis,cis*-tetraene show the relative orientation of olefinic groups to be very unfavorable for conjugation in the hydrocarbon and in the corresponding anion radical. It is also very unfavorable for a C_1–C_8 interaction in the latter. It is thus clearly more advantageous for VI to remain a relatively favorable hexatriene type anion radical than to open partially or fully.

The occurrence of nonclassical electron delocalization in any particular system depends on stereoelectronic and quantum mechanical factors. This is illustrated by the pair of anion radicals discussed above, namely, classical VI and nonclassical II. Another illustration is provided by the $C_8H_9^+$ species from protonation of cyclooctatetraene. Thus, the free $C_8H_9^+$ and its six-π-electron metal carbonyl complexes, $C_8H_9^+Mo(CO)_3$ and $C_8H_9^+W(CO)_3$, are nonclassical homotropylium species,[9] while the four-π-electron iron complex, $C_8H_9^+Fe(CO)_3$, is a classical one.[9]

Acknowledgment. We are grateful to Drs. D. Kivelson and R. Holtzer for the use of their esr and programmed plotting facilities.

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(6) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 87, 395 (1965).
(7) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1, 17 (1968).
(8) For example, the λ_{max} for ultraviolet absorption is at 311 mμ for V[3] and at 247 mμ for I.

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Synthesis of a Branched-Chain Sugar

Sir:

In this communication we wish to report a facile synthesis of a branched-chain sugar by application of the oxo reaction[1] to 1,2,4,6-tetra-*O*-acetyl-3-deoxy-α-D-*erythro*-hex-2-enopyranose. In earlier work[2,3] it was shown that glycals react with carbon monoxide and hydrogen to give epimeric anhydrodeoxyalditols and anhydrodeoxyaldoses having one more carbon than the starting compound. When 1,2,4,6-tetra-*O*-acetyl-3-deoxy-α-*erythro*-hex-2-enopyranose (I)[4] was allowed to react with synthesis gas in the presence of preformed dicobalt octacarbonyl at 150–160° for 2 hr, a mixture of oxo products was obtained. After the product was freed from catalyst, it was fully acetylated using acetic anhydride and pyridine. Preparative vpc of the latter acetate on an Aerograph Model 1525 using a 12-ft column of Chromosorb W carrying 10% (by weight) silicone gum rubber SE-52 operated at 280° gave compound II (having the longest retention time), isolated in about 30% yield. Alternatively, the mixture was partially separated by column chromatography using alumina as adsorbent and ether as developer. Substance II was recrystallized from ether–petroleum ether (bp 30–60°), mp 100°, $[\alpha]^{22}$ +58° (*c* 4, benzene). *Anal.* Calcd for $C_{17}H_{24}O_{11}$: C, 50.47; H, 5.98; mol wt, 404. Found: C, 50.41; H, 5.98; mol wt, 404 (added 43 to parent peak) (*m/e* 361, loss of CH_3CO).[5]

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(2) A. Rosenthal and D. Abson, *Can. J. Chem.*, 42, 1811 (1964).
(3) A. Rosenthal and D. Abson, *J. Am. Chem. Soc.*, 86, 5356 (1964).
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(5) Molecular weight by mass spectroscopy using an A.E.I.-M.S.9 spectrometer.