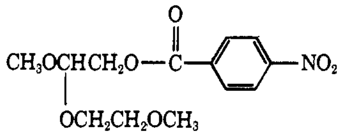
The foregoing results indicate that the major focus of anodic attack on 2-methoxyethanol is on the ether function rather than the hydroxyl group, and this observation accords with a prior expectation, since ethers have lower ionization potentials than alcohols.[1,2] It should also be noted that in the reactions with the fluoroborate supporting electrolyte, the proton transfer occurs solely from the methyl group, and there is no formation of acetals of glycolaldehyde, which would result, ultimately, if the proton were transferred from the methylene group.

In these reactions the initiating electrode mechanism is some form of direct electron transfer from 2-methoxyethanol. With an anion oxidizable at a potential lower than that required for the oxidation of 2-methoxyethanol, an alternative mechanism becomes possible. Nitrate ion is just such an anion[9] and makes possible a reaction sequence in which the initiating step is electron transfer from nitrate ion to give a nitrate radical, as shown in (5). The final products in this mechanism will depend not on a proton transfer, but on the position or positions from which a hydrogen atom is abstracted by the nitrate radical. Abstraction from the methylene group will result in acetals of glycolaldehyde, and abstraction from the methyl group will give rise to formals. Also reactions with nitrate ion might be somewhat less efficient than reactions with fluoroborate supporting electrolyte, since there is some disproportionation of the nitrate radical to give oxygen and oxides of nitrogen.

$$NO_3^- \longrightarrow e + NO_3\cdot \qquad (5)$$

These hoped for differences between oxidations in the presence of nitrate ion and oxidations in the presence of fluoroborate ion did materialize. The reactions with nitrate ion were, in fact, less efficient, and an additional product, IV, was obtained. The nmr spectrum of IV gave chemical shifts too closely spaced to permit analysis. The infrared spectrum of IV showed a strong hydroxyl band, and it was, therefore, converted to the *p*-nitrobenzoate, X. The nmr spectrum of X proved tractable and showed a singlet at τ 1.78 for the aromatic hydrogens, an AB_2 pattern ranging from τ 5.07 to 5.67 for the $-CH-CH_2$ grouping and a somewhat merged but distinguishable conglomerate consisting of an A_2B_2 pattern centered at τ 6.36 for the $-CH_2-CH_2-$ moiety, and singlets at τ 6.57 and 6.68 for the two methyl groups. Hydrolysis of IV gave glycolaldehyde, isolated as the 2,4-dinitrophenylosazone.



X

The formation of IV in these reactions is strong evidence to support the availability of two mechanisms for the oxidation of 2-methoxyethanol. IV results only from the hydrogen abstraction mechanism, but I and II could arise either from this mechanism or the mechanism observed with the fluoroborate supporting electrolyte. Since III is also obtained in the nitrate reactions, albeit in lower coulombic yield, it is probable that anode potentials high enough to effect direct electron transfer from 2-methoxyethanol are attained in the nitrate reactions, and I and II could be products of either or both mechanisms.

Electrochemical Reduction Studies of Several Bicyclo[6.1.0]nona-2,4,6-trienes and of *cis*-Bicyclo[6.2.0]deca-2,4,6-triene. Search for a Polarographic Criterion of Homoaromaticity

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Abstract: The reduction of *cis*- (**6**) and *trans*-bicyclo[6.1.0]nona-2,4,6-trienes (**9**), the 2,3-benzo derivative of **6** (**11**), and *cis*-bicyclo[6.2.0]deca-2,4,6-triene (**12**) has been studied by the techniques of polarography and cyclic voltammetry in tetrahydrofuran and acetonitrile solutions. In all cases, the first electron transfer occurs with considerably greater difficulty than cyclooctatetraene and is observed in the region characteristic of medium-ring trienes. Also, **9**, **11**, and **12** exhibit only one-electron reductions. The probable causative factors underlying these differences are elaborated.

The observation of effective electronic delocalization in a number of charged two- and six-electron systems in which conjugation is interrupted by one or more methylene groups (*e.g.*, **1–3**) has stimulated considerable interest in homoaromatic phenomena.[2–4] Other investigations have shown that related nonclassical structures can also arise in nine-[5] and ten-electron sys-

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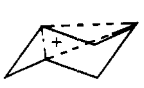
(1) Holder of a NATO postdoctoral fellowship (1970–1972), administered by the Science Research Council.

(2) For an extensive review of homoaromaticity, see S. Winstein, *Chem. Soc., Spec. Publ.*, No. 21, 1 (1967).

(3) M. J. Goldstein and R. Hoffmann, *J. Amer. Chem. Soc.*, **93**, 6193 (1971).

(4) L. A. Paquette, M. R. Short, and J. F. Kelly, *ibid.*, **93**, 7179 (1971).



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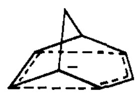

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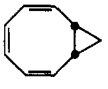
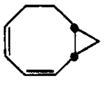
5

tems (*e.g.*, **4** and **5**).[6,7] For example, the esr spectrum observed for the radical anion obtained by treatment of *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**6**) with a small amount of potassium in glyme at −80° is incompatible with a classical structure possessing a fully formed cyclopropane ring.[5a] Rather, the spectrum is appropriate for a species with the symmetry level of **4** having substantial 1,8 interaction and a C_9 methylene group which is projected out of the plane defined by the remaining eight carbon atoms. Electrolysis of **6** in liquid ammonia saturated with tetramethylammonium iodide likewise produces this radical anion.[5b]

The importance of solvent and ion pairing in the generation, and perhaps stabilization, of such species has recently been unveiled during efforts designed to probe the nucleophilic character of **5**.[8] Protonation (CH_3OH) of monohomocyclooctatetraene dianion generated from reaction of **6** with 2 equiv of potassium (mirror) in 1,2-dimethoxyethane at −80° afforded a single main product identified as **7**.[8a] On the other hand, quenching (NH_4Cl) of the dilithium salt of **5** produced by reduction of **6** with 2 equiv of lithium in liquid ammonia gave chiefly **8**.[8b]



6



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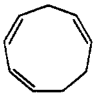
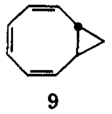
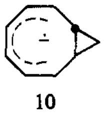


8

As shown by Winstein,[9] stereoelectronic as well as quantum mechanical factors also vitally affect the attainment of nonclassical electron delocalization by a particular system. Thus, the radical anion from **9** exhibits features in line with classical structure **10** which contains a closed cyclopropane ring and a hexatriene anion radical system. The exclusion of the internal cyclopropane electrons from the delocalized electronic system in this instance has been attributed to orbital symmetry restraints on the opening (disrotatory) of the three-membered ring which would result in formation of the highly strained *cis,trans*-cyclononatetraene radical anion.[3,9]

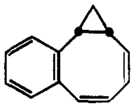


9

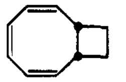


10

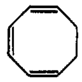
A useful and convenient, yet powerful, way to assess ease of anion radical formation is to examine the behavior of a given polyolefin under conditions of electrochemical reduction in a strictly anhydrous environment.[10–12] Because these requirements can easily be met,[13] our interest focused on the application of electrochemical methodology to possible quantitative experimental evaluation of homoaromaticity. This paper describes a study of the polarographic reduction of **6**, **9**, 2,3-benzobicyclo[6.1.0]nona-2,4,6-triene (**11**), and *cis*-bicyclo[6.2.0]deca-2,4,6-triene (**12**).



11



12



13

The compounds chosen for investigation represent two (**6** and **11**) for which nonclassical delocalization in their anion radicals might be anticipated, although modified somewhat in the case of **11** by the presence of benzo fusion. Trienes **9** and **12** were studied because they were expected to provide the requisite contrasting examples of hexatriene type anion radicals.

Results

***cis*-Bicyclo[6.1.0]nona-2,4,6-triene (6).** Electrolytic generation of the radical anion of **6** in liquid ammonia has been reported[5b] and apparently results in the production at low current densities of a free radical that is stable in the presence of solvated electrons. On the basis of this early report, it is not clear how higher current densities effect formation of the second product, purported to be methylcyclooctatetraene radical anion. Potential dependence of the reduction processes can give additional information of significant value in interpretation of the chemistry involved.

The polarography of **6** is shown in Figure 1 in two different solvent–background electrolyte systems. Quantitative data on these waves are summarized in Table I. In tetrahydrofuran (THF) containing 0.2 *M* tetrabutylammonium perchlorate (TBAP), two waves of equal height, separated by approximately 0.18 V, are observed. Two features of this electrochemical behavior are remarkable and differ significantly from that observed with cyclooctatetraene[10] and [16]annulene.[14] First, the half-wave potentials of the waves are very negative and, in fact, appear in the region characteristic of a medium-ring conjugated triene. The presence of the cis-fused cyclopropane ring does, however, appear to promote somewhat more facile reduction compared to **12** and **13** (see Table I). The slopes of the two waves indicate

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[5] (a) R. Rieke, M. Ogliaruso, R. McClung, and S. Winstein, *ibid.*, **88**, 4729 (1966); (b) T. J. Katz and C. Talcott, *ibid.*, **88**, 4732 (1966).

[6] (a) M. Ogliaruso, R. Rieke, and S. Winstein, *ibid.*, **88**, 4731 (1966); (b) M. Ogliaruso, *ibid.*, **92**, 7490 (1970).

[7] The synthesis of a neutral ten-electron hydrocarbon endowed with homoaromatic character has recently been reported: L. A. Paquette, R. E. Wingard, Jr., and R. K. Russell, *ibid.*, **94**, 4739 (1972).

[8] M. Ogliaruso and S. Winstein, *ibid.*, **89**, 5290 (1967); (b) W. H. Okamura, T. I. Ito, and P. M. Kellett, *Chem. Commun.*, 1317 (1971).

[9] G. Moshuk, G. Petrowski, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 2179 (1968).

[10] As regards the reduction of cyclooctatetraene, *cf.* (a) D. R. Thielen and L. B. Anderson, *J. Amer. Chem. Soc.*, **94**, 2521 (1972); (b) T. J. Katz, W. H. Reinmuth, and D. W. Smith, *ibid.*, **84**, 802 (1962); (c) R. D. Allendoerfer and P. H. Rieger, *ibid.*, **87**, 2236 (1965).

[11] The reduction of benzo-fused cyclooctatetraenes has been studied by (a) L. B. Anderson and L. A. Paquette, *ibid.*, **94**, 4915 (1972); (b) T. J. Katz, M. Yoshida, and L. C. Siew, *ibid.*, **87**, 4516 (1965).

[12] For the contrasting behavior of azocines (azacyclooctatetraenes), consult (a) L. A. Paquette, J. F. Hansen, T. Kakihana, and L. B. Anderson, *Tetrahedron Lett.*, 533 (1970); (b) L. B. Anderson, J. F. Hansen, T. Kakihana, and L. A. Paquette, *J. Amer. Chem. Soc.*, **93**, 161 (1971); (c) L. A. Paquette, L. B. Anderson, J. F. Hansen, S. A. Lang, Jr., and H. Berk, *ibid.*, **94**, 4907 (1972).

[13] The vacuum line apparatus required for such measurements has been previously described: J. L. Mills, R. Nelson, S. G. Shore, and L. B. Anderson, *Anal. Chem.*, **43**, 157 (1971).

[14] J. F. M. Oth, H. Baumann, J.-M. Gilles, and G. Schröder, *J. Amer. Chem. Soc.*, **94**, 3498 (1972).

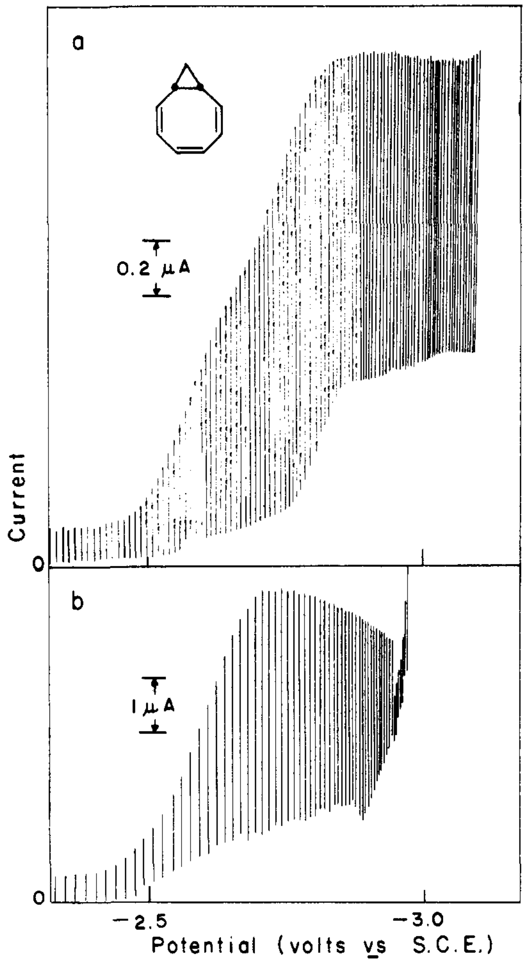


Figure 1. Polarography of 6 in (a) THF containing 0.2 M tetrabutylammonium perchlorate; (b) AN containing 0.1 M tetramethylammonium hexafluorophosphate.

Table I. Polarographic Half-Wave Potentials and Diffusion Current Constants

Polyene	Solvent	$E_{1/2}$ V vs. sce	Slope,[a] mV	$(I_\eta{}^{1/2})$[b]	n_{app}
6	THF[c]	−2.55	80	3.0	1
		−2.79	80	3.0	1
	AN[d]	−2.60	100	4.8	2
9	THF[c]	−2.50	110	4.4	1-2
11	AN[d]	−2.33	60	3.0	1
12	AN[d]	−2.59	50	3.8	1
	THF[c]	−2.83	60	3.6	1
13	THF[c]	−2.77	67	2.9	1

[a] Reciprocal slope of plot of E vs. log $[i/(i_d - i)]$. [b] Diffusion current constant times square root of viscosity, μA M^{-1} mg$^{-2/3}$ sec$^{1/2}$ cP$^{1/2}$. [c] 0.2 M in tetra-p-butylammonium perchlorate. [d] 0.1 M in tetramethylammonium hexafluorophosphate.

that the electron transfer processes are non-nernstian and cyclic voltammetry shows no reoxidizable product of either the first or second wave. In the case of cyclooctatetraene, the first wave is known to be non-nernstian, but the second electron transfer is quite rapid on the polarographic time scale. This behavior appears to have its origin in the rapid chemical reaction of the resulting radical anion with either the solvent or background electrolyte, or in some alternative self-immolative process.

Secondly, the addition of *ca.* 1 M water to the solvent does not substantially affect the observed electrochemistry. The combined waves increased only 10% in height and did not coalesce as has been observed with cyclooctatetraene.[10a] The half-wave potentials remained the same within ±10 mV. These observations suggest that the lifetime of the products of electron transfer are short and that moderate amounts of a strong proton donor do not significantly affect the rate.

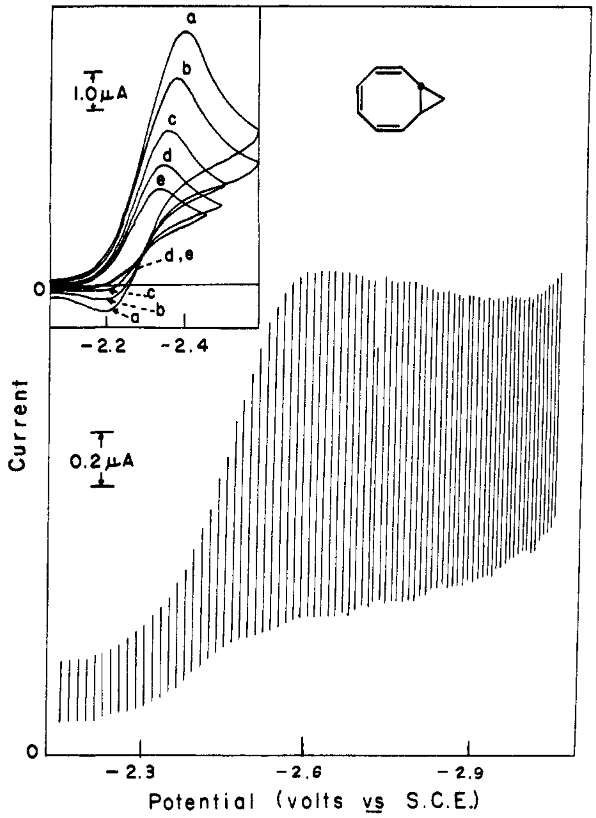


Figure 2. Polarography of 9 in THF containing 0.2 M TBAP Inset shows stationary electrode (Pt bead) cyclic voltammetry at scan rates of (a) 600, (b) 300, (c) 100, (d) 80, and (e) 40 mV/sec.

In acetonitrile (AN) solvent containing 0.1 M tetramethylammonium hexafluorophosphate (TMAHFP), two separate waves are not resolved but the diffusion current constant ($I_\eta{}^{1/2}$, corrected for solvent viscosity) is comparable to the sum of the two waves observed in THF. The overall two-electron addition was observed with an $E_{1/2}$ near the potential of the first wave in the ether solvent. Again in AN, no effect is observed on either $I_\eta{}^{1/2}$ or $E_{1/2}$ upon addition of water to the cell. The heights of the waves in both media were directly proportional to the concentration of polyene.

***trans*-Bicyclo[6.1.0]nona-2,4,6-triene (9).** The polarographic reduction of **9** differs significantly from that of cis isomer (**6**). Figure 2 typifies the observed electrochemical behavior. In THF, a single non-nernstian wave appears at −2.4 V *vs.* sce, positive of both the first wave for **6** and the wave for 1,3,5-cyclooctatriene (**13**). The diffusion current constant for this wave is intermediate between that expected for a one- and a two-electron transfer, and it appears to decrease slightly with enhanced concentration of depolarizer. Thus, as the concentration of **9** was increased from 0.3 to 1.5 mM, the value of $I\eta^{1/2}$ decreased from 4.4 to 4.1. Such behavior again provides strong basis for believing that a chemical reaction effectively removes the product of primary electron transfer from the medium as it is produced.

In this particular instance, cyclic voltammetry yielded direct evidence for the marginal stability of the radical anion in these media. The inset of Figure 2 presents the effect of enhanced voltage–scan rate on the appearance of an anodic peak. At 40 mV/sec, no evidence of a stable anion radical is apparent. However, when the scan rate is increased to 500 mV/sec, there appears a prominent anodic peak representing reoxidation of approximately one-half of the hydrocarbon reduced. Over the same region of change in scan rate, the value of $i_p/V^{1/2}$, a constant for diffusion-controlled systems, decreased by nearly 20%. Apparently, the radical anion reacts (relatively slowly in this case) with the solvent–electrolyte system to generate a product that is reduced at the same or more positive potential. In any case, no electroreducible material is in evidence as a reduction wave beyond the first wave. The limiting current continues at a steady plateau until the discharge of solvent at *ca.* −3.1 V.

2,3-Benzobicyclo[6.1.0]nona-2,4,6-triene (11). Fusion of a benzene ring to the cyclooctatetraene framework has been shown to cause a shift in the half-wave potential to a value more negative than that of the parent hydrocarbon.[11] On a comparable basis, it could be predicted that **11** should exhibit a half-wave potential more negative than the wave(s) for **6** if like reduction mechanisms are operative. The polarogram for **11** exhibits a single wave with a diffusion current constant appropriate for a one-electron transfer and a half-wave potential of −2.34 V. Thus, the barrier to addition of the first electron is seen to decrease with benzoannelation to the homocyclooctatetraene nucleus.

From the energetic viewpoint, it appears that electron addition to **11** does, however, more closely resemble the reduction of benzocyclooctatetraene than **6**. The increased difficulty associated with electron transfer to **6** relative to **11** is considered to be anomalous. It may well be a reflection of the triene character of **6**, the interposition of the cyclopropane ring effectively removing C_1 and C_8 from the conjugative system present in the cyclooctatetraene radical anion. Interpretation of this phenomenon must be advanced cautiously, however, because the polarographic waves for both compounds are nonnernstian and do not necessarily reflect the relative thermodynamic stabilities of the radical anions formed.

Cyclic voltammetry provides no indication of a reoxidizable product from the reduction of **11** in acetonitrile. A single peak is observed with an $E_{1/2}$ ($E_{p/2}$ − 28 mV) of −2.39 V, and there is no evidence for an anodic peak at the reduction potential or at more positive potentials.

cis-**Bicyclo[6.2.0]deca-2,4,6-triene (12).** This derivative of the cyclooctatriene system behaves in a fashion similar to the other bicyclic polyenes examined herein. A single one-electron wave is observed in both THF and AN. However, the half-wave potentials in the two solvents are quite negative. Figure 3 illustrates the electrochemical behavior. The quantitative values that were deduced from the data are summarized in Table I.

Apparently, the nonplanar conformation imparted to the eight-membered ring by the fused cyclobutane is sufficient to decrease the overlap between adjacent double bonds and increase the energy (potential) necessary to insert the first electron. Solvent has minimal effect on the process and cyclic voltammetry does not indicate a stable radical anion product in either THF or AN. As with **6**, the effect of added water was nil; neither the wave height nor the half-wave potential was altered significantly upon addition of 0.1 *M* water to the polarographic cell.

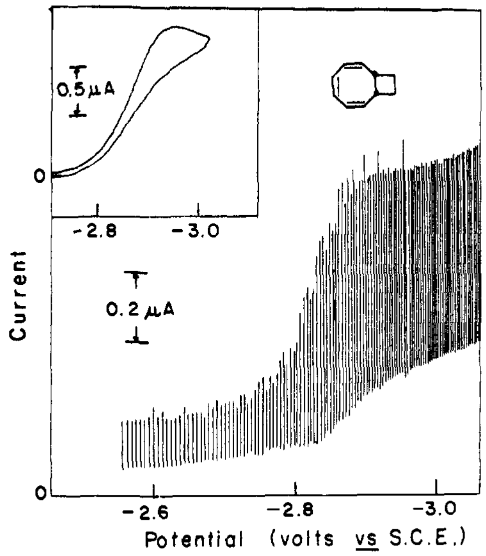
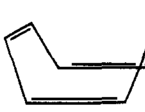


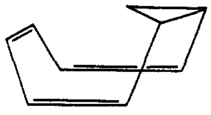
Figure 3. Polarography of **12** in THF medium containing 0.2 *M* TBAP. Inset shows cyclic voltammetry at a Pt bead at 500-mV/sec scan rate.

Discussion

Although the electrochemical reduction of *cis*-bicyclo[6.1.0]nonatriene (**6**) does bear certain similarities to the behavior of cyclooctatetraene (COT), there are many important differences. Close scrutiny in fact discloses that the major *apparent* similarity is the observation of two one-electron waves in tetrahydrofuran solvent. The first question which arises relates to the causative factors underlying the wide differences in the half-wave potentials for COT (−1.96 and −2.16 V) and **6** (−2.55 and −2.79 V). Neither polyene is planar in its ground state, but COT is thought to attain planarity readily upon conversion to its radical anion, presumably because only minor conformational readjustments are necessary to allow for pπ overlap. Disagreement exists regarding the chemical and electrochemical reactions which result in observation of the addition of a second electron to COT (accounted for by the wave at −2.16 V).[10,11] It would appear that the reduction products of **6**, **9**, **11**, and **12** are even more reactive than those of COT itself, and thus the mechanism of second electron addition more uncertain. Nevertheless, alternative interpretations of the chemical and electrochemical results reported here may be made upon assumption of the existence or nonexistence of the dianion as an electrochemical product of a second electron transfer.[10]

As already noted, the half-wave potential of the first-wave for **6** suggests that direct conversion to **4** may not operate; rather the highly negative $E_{1/2}$ value is better explained by hypothesizing that **6** behaves as a more or less typical conjugated medium-ring triene, at least to the extent that 1,3,5-cyclooctatriene (**13**) serves as a specific model. We consider these observations to reflect the preferred adoption by **6** in such media of the extended conformation (**6a**) rather than the more sterically congested folded conformation (**6b**). The somewhat (~0.2 V) more facile reduction of **6** relative to **13** could arise from the added strain inherent in **6**, a conclusion which receives some support from the behavior of **12**. More generally, however, other factors which remain presently unrecognized could be of significance here.

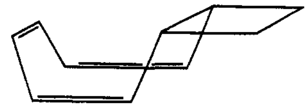

6a


6b

Recently, it has been established experimentally that only when **6** adopts folded conformation **6b** is orbital overlap of the internal cyclopropane bond with the adjacent π orbitals suitable for ring opening of the three-membered ring.[15] This same conformation has also been implicated in the thermal rearrangements of the *cis*-bicyclo[6.1.0]nonatrienes,[16] but this remains a topic of controversy.[17] The *apparent* noninvolvement of the C_1–C_8 cyclopropane electrons during the electrochemical reduction of **6** may be understood if conformer **6a**, the energetically preferred three-dimensional structure of this triene, is involved in the electrode reaction.

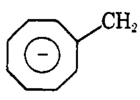
If single electron addition to the radical anion of **6** to form R^{2-} is energetically unfavorable in the available potential region, then some chemical process(es) must be coupled with the electron transfer, thus accounting for the second polarographic step. In this event the structure of the radical anion, whether or not it is homoaromatic or planar, will not bear a direct relationship to the appearance nor half-wave potential of such a kinetic second wave. If, on the other hand, the second wave can be assigned to dianion formation, then the absence of reoxidizable products indicates simply that the dianion lifetime is short compared with the time constant of the cyclic voltammetric experiment (~1 sec). The difference between half-wave potentials for formation of radical anion and dianion would then be quite comparable to those of COT, and similar interpretation of the thermodynamic stabilities of the two ions could be advanced.[10,11] That is, the balance between charge repulsion, Hückel aromaticity, ion pairing with TBA^+ or TMA^+, and strain induced by forming a planar species would account for the difference of approximately 0.25 V (5.7 kcal/mol) in the two reduction potentials.

With benzo homolog **11**, the energy of the highest occupied molecular orbital is seen to be appropriately perturbed by the adjacent aromatic ring. In this instance, addition of the first electron again results in formation of an unstable product, as revealed by cyclic voltammetry. Nevertheless, a second wave is not in evidence prior to discharge of solvent. The comparable behavior of *cis*-bicyclo[6.2.0]decatriene (**12**) is important and suggests that the overlap situation is equally poor in the ground state presumably because of dominance by its more stable extended conformation (**12a**) and the inability of the derived radical anion to undergo rapid conformational alteration prior to decomposition or degradative rearrangement. Thus, the situation becomes less favorable for conjugation in the triene portion as the fused ring is altered from three- to four-membered.

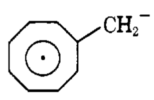

12a

A study of molecular models reveals that the consequence of the trans ring fusion in **9** is chiefly to flatten notably the triene moiety.[18] Such geometric enforcement of a very nearly planar polyenic structural component can be expected to facilitate the reduction process. However, this more favorable relative orientation of olefinic centers must be tempered by strain factors and by the fact that disrotatory opening of central cyclopropane bond is sterically inhibited.[9] Consequently, electrochemical reduction of **9** should give **10**. At issue was whether this species, recognized to be stable at −90° in dimethoxyethane with potassium as gegenion,[8] would exhibit a measurably finite existence under the present polarographic conditions at room temperature. In actuality, **9** did exhibit a single non-nernstian wave slightly positive of the $E_{1/2}$ values for **6**, **12**, and **13**. Furthermore, although no evidence was gained for a stable reoxidizable anion radical product at low (40 mV/sec) scan rates, a prominent anodic peak was observed upon increasing the sweep rate to 500 mV/sec (Figure 2). Evidently, **10** represents a species with an electronic system more stable under conditions of minimal ion pairing and solvation than those resulting from **6**, **11**, and **12**. This is probably due to the relative difficulty encountered by **10** in further chemical reaction involving the cyclopropane ring.

It is possible that the radical anion resulting from electron addition to the extended conformation (**6a**) of *cis*-bicyclo[6.1.0]nonatriene reacts ultimately by cleavage of an edge cyclopropane bond to afford initially new radical anions such as **14** and **15**. Such pathways remain, of course, to be established but are suggested by the work of Katz and Talcott,[5b] who identified methylcyclooctatetraene anion radical as a product of the electrolysis of **6** in liquid ammonia saturated with tetramethylammonium iodide.



14



15

Clearly, the present work did not provide a desired polarographic criterion of homoaromaticity. This is chiefly because nonclassical electron delocalization is particularly sensitive to stereoelectronic factors and the trienes examined herein adopt ground state conformations in which homoaromaticity is not incipiently favored. The study does serve, however, to provide an indication that electrochemical studies may serve as a viable technique for the evaluation of ground state conformations of polyolefins.

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[15] (a) L. A. Paquette, M. J. Broadhurst, C. Lee, and J. Clardy, *ibid.*, **94**, 630 (1972); (b) L. A. Paquette and M. J. Broadhurst, *ibid.*, **94**, 632 (1972); (c) J. Clardy, L. K. Read, M. J. Broadhurst, and L. A. Paquette, *ibid.*, **94**, 2904 (1972); (d) L. A. Paquette, M. J. Broadhurst, L. K. Read, and J. Clardy, submitted for publication.

[16] S. W. Staley and T. J. Henry, *ibid.*, **91**, 7787 (1969); J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, *ibid.*, **94**, 5845 (1972).

[17] S. W. Staley, *Intra-Sci. Chem. Rep.*, **5**, 149 (1971).

[18] Compare, for example, the widely differing electronic spectra of **6** (λ_{max} 247 mn) and **9** (λ_{max} 311 nm).

Experimental Section

Hydrocarbons **6**,[19] **9**,[9,20] and **12**[21] were prepared according to the literature methods.

2,3-Benzobicyclo[6.1.0]nona-2,4,6-triene (11).[22] Benzocyclooctatetraene (1.53 g, 0.01 mol)[23] was dissolved in liquid ammonia (*ca.* 250 ml) at −33° under a nitrogen atmosphere. Clean potassium metal (1.4 g, 0.036 g-atom) was added in small pieces and the mixture was stirred for 2 hr at this temperature. To the dark brown solution of the dianion was added dichloromethane (30 ml) dissolved in anhydrous ether (50 ml). The solution became light orange and no further change was observed during stirring at −33° for 6 hr. Solid ammonium chloride was introduced, after which most of the ammonia was allowed to evaporate from the resulting colorless solution under a stream of nitrogen. The residue was dissolved in water (100 ml) and the hydrocarbon product was extracted into pentane (2 × 30 ml). The pentane layer was washed several times with water, dried, and concentrated to a volume of 10 ml. This solution was passed through a small column of Florisil and the eluate was evaporated to yield a pale yellow oil (1.47 g, 87.5%). Nmr and vpc analysis of this material indicated it to be >95% pure. An analytical sample was obtained by preparative vpc purification on a 6 ft × 0.25 in. column packed with 5% SE-30 on Chromosorb W; $\lambda_{max}^{cyclohexane}$ two shoulders on long tailing absorption at 240 nm (ϵ 6250) and 215 (19,400); nmr $\delta_{TMS}^{CDCl_3}$ 7.0–7.6 (m, 4, aryl), 5.6–6.75 (m, 4, olefinic), and 0.4–2.85 (series of four overlapping m, 4, cyclopropyl).

Anal. Calcd for $C_{13}H_{12}$: C, 92.80; H, 7.20. Found: C, 92.58; H, 7.33.

Polarographic Measurements. The electrochemical apparatus employed in these experiments has been described previously.[12,13] Techniques for purifying solvents and background electrolytes and experimental procedures were identical with those utilized in the earlier work.[12,13]

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[19] (a) E. Vogel, *et al.*, *Justus Liebigs Ann. Chem.*, **653**, 55 (1962): *Tetrahedron Lett.*, 11, 673 (1963); (b) T. H. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, **86**, 5194 (1964).

[20] E. Vogel, W. Grimme, and W. E. Bleck, private communication of unpublished work at Köln.

[21] S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, **91**, 1239 (1969).

[22] Subsequent to the completion of this work, **11** was reported as a thermolysis product of 8,9-benzobicyclo[5.2.0]nona-2,4,8-triene: M. Kato, T. Sawa, and T. Miwa, *Chem. Commun.*, 1635 (1971). No spectral or analytical data were given.

[23] L. Friedman and D. F. Lindow, *J. Amer. Chem. Soc.*, **90**, 2329 (1968).

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exo-Tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-yl Carbonium Ion. A New $[CH]_9^+$ Species from Rearrangement of *anti*-Tricyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-yl Derivatives[1]

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Abstract: Acetolysis of *anti*-tricyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-yl tosylate (**1**-OTs) proceeds with stereospecific rearrangement to *exo,syn*-tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-yl acetate (**2**-OAc) and 6.8 × 10^4-fold rate enhancement compared with that of *endo*-bicyclo[3.2.0]hept-6-en-2-yl tosylate (**14**-OTs). The intermediate *exo*-tricyclo-[4.2.1.0^{2,5}]nona-3,7-dien-9-yl carbonium ion (**8**), a new $[CH]_9^+$ species, as well as its 1-deuterio (**8**-*1-d*), 1-methyl (**9**), and 1-phenyl (**10**) derivatives, were generated in fluorosulfonic acid at −78° from *anti*-tricyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-ol (**1**-OH) and the respective 6-deuterio (**1**-*6-d*-OH), 6-methyl (**6**), and 6-phenyl (**7**) alcohols, and observed by nmr spectroscopy. The simplified, time-averaged nmr spectrum exhibited by the phenyl-substituted carbonium ion (**10**) at +10° in fluorosulfonic acid is attributed to a twofold degenerate rearrangement of **10** by way of the stabilized 6-phenyltricyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-yl cation (**12**).

Recent investigations with polycyclic compounds of the type $[CH]_n$–X (n = odd integer) have revealed unusual solvolytic reactivities, numerous skeletal rearrangements, and novel degenerate isomerizations.[3] Although a substantial proportion of the lower members (n = 5, 7) in these ethynylogous families of structures have been prepared and studied,[3] relatively few of the more numerous, higher polycycles are known.[3,4] In view of the interesting properties uncovered thus far in the $[CH]_9$–X group,[3,5] we decided to examine the behavior of *anti*-tricyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-yl derivatives (**1**-OR), a new representative recently made available through the synthetic work of Cargill, King, Sears, and Willcott.[6] At the outset it seemed likely that this highly strained ring system would undergo a ring-expansion rearrangement to its bridged ring isomer, the *exo*-tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-yl carbonium ion, as is observed with other 2-bicyclo[3.2.0]heptyl deriva-

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[1] Taken in part from Ph.D. Thesis of K. Yano, University of Illinois, 1972.

[2] A. P. Sloan Foundation Fellow, 1971–1973.

[3] Recent review: R. E. Leone and P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, **9**, 860 (1970).

[4] Disregarding stereochemistry, the number of isomeric structures are as follows: 1 $[CH]_3$–X, 3 $[CH]_5$–X, 15 $[CH]_7$–X, and 90 $[CH]_9$–X: A. T. Balaban. *Rev. Roum. Chim.*, 11, 1097 (1966).

[5] Some examples are (a) homocubyl [P. v. R. Schleyer, J. J. Harper, G. L. Dunn, V. J. DiPasquo, and J. R. E. Hoover, *J. Amer. Chem. Soc.*, **89**, 698 (1967); J. C. Barborak and R. Petit, *ibid.*, **89**, 3080 (1967)], (b) 9-pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonyl [R. M. Coates and J. L. Kirkpatrick, *ibid.*, **92**, 4883 (1970)], (c) bicyclo[3.2.2]nona-3,6,8-trien-2-yl and barbaralyl [M. J. Goldstein and B. G. Odell, *ibid.*, **89**, 6356 (1967); W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967); J. C. Barborak, J. Daub, D. M. Follweiler, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 7760 (1969); P. Ahlberg, D. L. Harris, and S. Winstein, *ibid.*, **92**, 4454 (1970); J. B. Grutzner and S. Winstein, *ibid.*, **94**, 2200 (1972)].

[6] R. L. Cargill, T. Y. King, A. B. Sears, and M. R. Willcott, *J. Org. Chem.*, **36**, 1423 (1971). We are grateful to Professor Cargill for providing a sample of ketone **5** and experimental details concerning its synthesis.