

Alkali Metal Reduction Studies of *cis*- and *trans*-Bicyclo[6.1.0]nona-2,4,6-trienes in Liquid Ammonia. Evidence for the High Basicity of Monohomocyclooctatetraene Dianions

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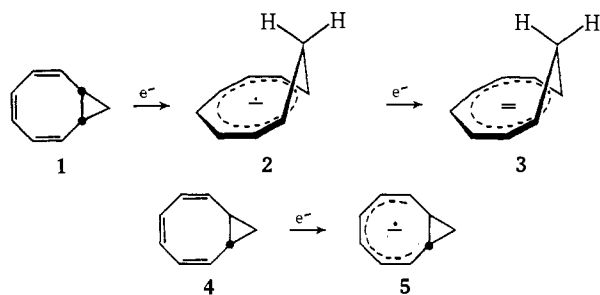
Abstract: The behavior of a series of *cis*-bicyclo[6.1.0]nona-2,4,6-trienes and of the related *trans* bicyclic system upon alkali metal (chiefly potassium) reduction in liquid ND₃ and NH₃ has been studied. Upon two-electron reduction in ND₃ at -60 to -78° , the *cis*-fused hydrocarbons underwent conversion to their homoaromatic dianions, which were spectroscopically visible (pmr) in certain instances. In the case of the parent molecule, deuteration by solvent was too rapid and only the monodeuterated cyclononatienyl monoanion was seen. This behavior was paralleled by all the congeners but at somewhat variable rates depending upon the degree and position of methyl substitution. The stereoselectivity of reduction of the *syn*- and *anti*-9-methyl derivatives attested either to the kinetic preference for reduction of the more strained folded conformation of these molecules or to preliminary reduction to classical radical anions. Also, alkyl substitution of the triene moiety led to positional regioselectivity in the deuteration of the respective dianions. In contrast, the *trans* bicyclic does not undergo reduction with central bond cleavage. As noted previously by Winstein in THF-*d*₆, electrocyclic ring opening of the intermediate radical anion cannot operate for steric reasons. In NH₃ (ND₃), this reactive species presumably experiences protonation (deuteration) and additional electron transfer to give a monoanion, subsequent protonation (CH₃OH) of which leads to 2,7-dihydro product. The various mechanistic ramifications are discussed.

The ground-state stabilization accruing to monocyclic systems endowed with a continuous periphery of $p\pi$ atomic orbitals is now recognized to be extendable, at least in part, to molecules whose topological construction is such that the cyclic array of p orbitals is interrupted by the insertion of a saturated carbon atom at one or more points.¹ The effects of homoaromatic delocalization have now been evidenced in a variety of examples, most of which partake of ionic character and possess, as a result, the added driving force of charge dispersal.² An interesting case in point is the finding by Winstein,³ Katz,⁴ and Smentowski⁵ that chemical reduction of *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**1**) proceeds through the nine-electron homoaromatic radical anion **2** to the delocalized monohomocyclooctatetraene dianion **3**. In contrast, bicyclic radical anion **5**

is produced exclusively upon similar reduction of *trans*-bicyclo[6.1.0]nona-2,4,6-triene (**4**) with a potassium mirror in tetrahydrofuran (THF) or dimethoxyethane (DME) solution at -90° .⁶ These observations agree fully with orbital symmetry considerations if the highest occupied MO's of **1** and **4** are the levels which control reactivity. Given this situation, reversal of the stereochemistry of central bond cleavage available to the neutral hydrocarbons should operate for radical anions **2** and **5**. This would require disrotatory cyclopropane ring fission in the latter species.³ Electrocyclic ring opening of **2** along this reaction channel to give *cis*-cyclononatetraene anion radical is accordingly allowed, but like behavior of **5** is prohibited by the high-strain energy and poor $p\pi$ overlap in the *trans,cis*³-cyclononatetraene anion radical.

The structures of **2** and **5** were inferred on the basis of their esr spectra, whereas structural assignment to dianion **3** was founded chiefly upon a detailed analysis of 1,8-orbital overlap and ring-current effects by pmr spectroscopy. Because of the limited solubility of dipotassio **3** in THF or DME at -60° , Winstein and coworkers were forced to record the pmr spectrum with a time-averaging computer (CAT).³ No variable-temperature studies were reported and, consequently, important information regarding the stability of **3** as a function of *T* is lacking.

Two reactions of dipotassio **3**, generated by the above method, have been documented. Protonation of **3** with methanol at -80° was observed to give bicyclic diene **6** as the major product in greater than 85% yield;⁷ reaction with carbon tetrachloride at -10° has afforded the related products **7** (60%) and **8** (30%).⁸



(1) For a review of the earliest work in the field of homoaromaticity, see S. Winstein, *Chem. Soc. Spec. Publ.*, No. 21, 1 (1967).

(2) A neutral hydrocarbon with ten-electron homoaromaticity potential has been described: L. A. Paquette, R. E. Wingard, Jr., and R. K. Russell, *J. Amer. Chem. Soc.*, **94**, 4739 (1972); see also E. Vogel, U. H. Brinker, K. Nachtkamp, J. Wassen, and K. Mullen, *Angew. Chem.*, **85**, 760 (1973).

(3) (a) R. Rieke, M. Ogliaruso, R. McClung, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 4729 (1966); (b) S. Winstein, G. Moshuk, R. Rieke, and M. Ogliaruso, *ibid.*, **95**, 2624 (1973).

(4) T. J. Katz and C. Talcott, *J. Amer. Chem. Soc.*, **88**, 4732 (1966).

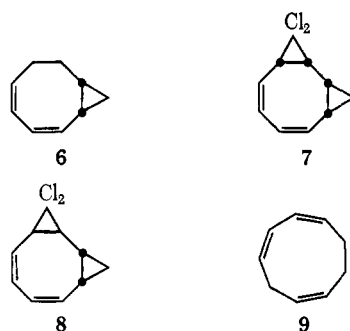
(5) F. J. Smentowski, R. M. Owens, and B. D. Faubion, *J. Amer. Chem. Soc.*, **90**, 1537 (1968).

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

(7) M. Ogliaruso and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 5290 (1967).

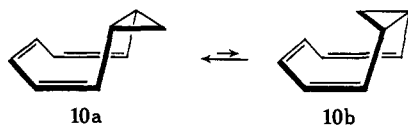
(8) M. Ogliaruso, *J. Amer. Chem. Soc.*, **92**, 7490 (1970).

Significantly different results have been realized upon reduction of **1** in more polar media, such as liquid ammonia (-78°) and hexamethylphosphoramide (HMPA)-THF (-30°).⁹ Under these conditions, only the monocyclic cyclononatriene **9** has been isolated



upon protonation. These data can be taken to reflect either differing modes of stepwise protonation of the *same* species (**3**) or the presence in NH_3 and HMPA solutions of a reactive intermediate *entirely different* than **3**. It remained to resolve this dichotomy.

Our interest in this question arose when it became clear from earlier electrochemical reduction studies that the behavior of **1**, **4**, and closely related molecules in THF and acetonitrile¹⁰ deviated widely from that of $4n$ cyclic polyolefins, such as cyclooctatetraene,¹¹ the 2-methoxyazocines,¹² and [16]annulene,¹³ which are recognized to give rise to resonance-stabilized "classical" ($4n + 2$) dianions. Both **1** and **4** experience one-electron transfer with considerably greater difficulty than cyclooctatetraene, the respective waves appearing in the region characteristic of medium-ring trienes. In substantial agreement with the earlier chemical data, **4** was seen to undergo a lone one-electron reduction, whereas **1** experienced a stepwise two-electron reduction. Unexpectedly, however, none of the electron-transfer processes were nernstian and cyclic voltammetry revealed no oxidizable product for any of the waves. These data were taken to mean that **1** preferred adoption in such media of its extended conformation **10a**, rather than its more sterically congested folded arrangement **10b**, and that reduction, like electrophilic at-



(9) (a) W. H. Okamura, T. I. Ito, and P. M. Kellett, *Chem. Commun.*, 1317 (1971); (b) T. I. Ito, F. C. Baldwin, and W. H. Okamura, *ibid.*, 1440 (1971).

(10) L. B. Anderson, M. J. Broadhurst, and L. A. Paquette, *J. Amer. Chem. Soc.*, **95**, 2198 (1973).

(11) (a) T. J. Katz, W. H. Reinmuth, and D. W. Smith, *J. Amer. Chem. Soc.*, **84**, 802 (1962); (b) R. D. Allendorfer and P. H. Rieger, *ibid.*, **87**, 2236 (1965); (c) T. J. Katz, M. Yoshida, and L. C. Siew, *ibid.*, **87**, 4516 (1965); (d) D. R. Thielen and L. B. Anderson, *ibid.*, **94**, 2521 (1972); (e) L. B. Anderson and L. A. Paquette, *ibid.*, **94**, 4915 (1972).

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

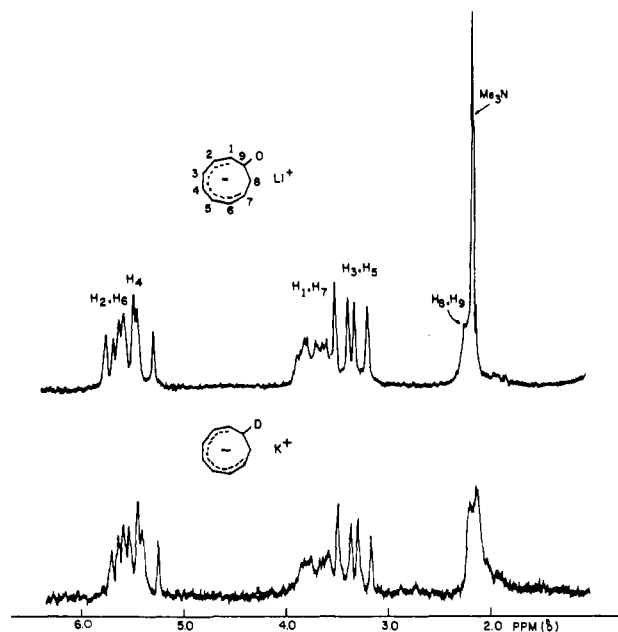


Figure 1. The 60-MHz pmr spectra of the Li-ND_3 (upper, -71°) and K-ND_3 (lower, -65°) reduction products of **1** (ND_3 solvent, Me_3N as internal standard; $\delta_{\text{NH}_3}^{\text{TMS}}$ for $\text{Me}_3\text{N} = 2.135$).¹⁷

tack,^{14,15} occurs with greater facility from the less stable conformation. The reasons for the inherent instability of the resulting dianion (assuming operation of an eec mechanism), whatever its structure, were not known.

In an attempt to resolve this issue, we have carried out a detailed pmr study of the fate of **1**, **4**, and related bicyclo[6.1.0]nonatrienes when reduced with potassium metal in ND_3 . Quenching and methylation findings of direct interest are also included.¹⁶ Data have been obtained which now reveal the exceptionally high basicity of homocyclooctatetraene dianions. Evidence substantiating the highly stereoselective nature of the reduction of *cis*-bicyclo[6.1.0]nonatrienes is also presented.

Results

cis-Bicyclo[6.1.0]nonatriene. When **1** was added to a deep blue solution of potassium metal in ND_3 at -78° , a dark red color developed rapidly. Pmr studies at -65° revealed such solutions to contain exclusively the monodeuterated anion **11**. Similar reaction with lithium gave the identical stable monoanion as judged from the pmr spectrum at -71° (Figure 1). These ND_3 solutions were prepared directly in pmr tubes on a vacuum line, and spectra were normally recorded approximately 35 min after mixing of the reagents. However, in one instance the spectrum

(14) (a) P. Warner and S. Winstein, *J. Amer. Chem. Soc.*, **93**, 1284 (1971); (b) L. A. Paquette, M. J. Broadhurst, P. Warner, G. A. Olah, and G. Liang, *ibid.*, **95**, 3386 (1973); (c) P. Warner, D. L. Harris, C. H. Bradley, and S. Winstein, *Tetrahedron Lett.*, 4013 (1970).

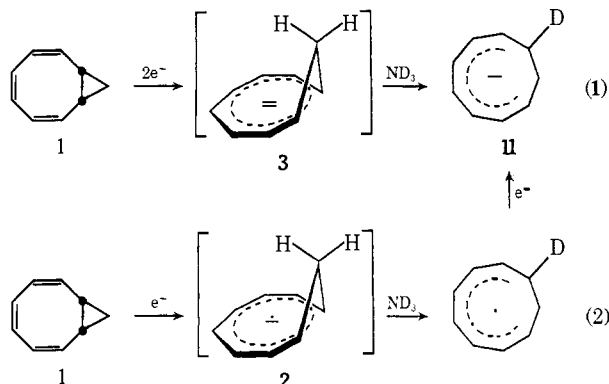
(15) (a) L. A. Paquette, M. J. Broadhurst, C. Lee, and J. Clardy, *J. Amer. Chem. Soc.*, **94**, 630 (1972); **95**, 4647 (1973); (b) L. A. Paquette and M. J. Broadhurst, *ibid.*, **94**, 632 (1972); (c) L. A. Paquette, M. J. Broadhurst, L. K. Read, and J. Clardy, *ibid.*, **94**, 2904 (1972); **95**, 4639 (1973); (d) T. Sasaki, K. Kanematsu, and Y. Yukimoto, *Chem. Lett.*, 1005 (1972).

(16) Details of the stereo- and regioselectivities of the methylation reaction are not yet complete and will be reported elsewhere at a later date.

(17) S. W. Staley and N. J. Pearl, *J. Amer. Chem. Soc.*, **95**, 3437 (1973). We are grateful to Professor Staley for supplying a copy of their spectrum.

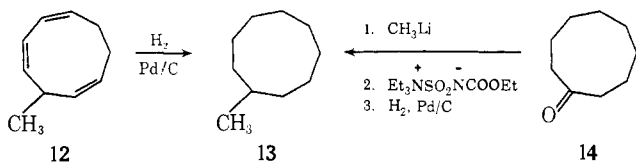
was recorded at -70° after only 4 min had elapsed; only the presence of the lithium monoanion was again evident. The gross structure of **11** is consistent with the spectral data; in particular, except for deuterium incorporation at C₉, the spectra in Figure 1 are essentially the same as that obtained by deprotonation of cyclonona-1,3,6-triene with amide ion.¹⁷

The formation of **11** may be rationalized either in terms of direct two-electron reduction to dianion **3** and ultimate protonation (deuteration) of the latter (eq 1), or a stepwise reduction sequence mediated by protonation (deuteration) of radical anion **2** (eq 2). A phenom-



nological distinction between these mechanisms was difficult to achieve in the present instance because of the high reactivity of the intermediates in the parent hydrocarbon system. For example, while it might prove possible to establish the presence of **3** by protonation of a reaction mixture prepared by reduction of **1** with 1 g-atom of potassium, it becomes necessary to assume knowledge about relative rates of electron transfer and protonation. This is not desirable. Consequently, the experimentally realized ratio of **1** (2 parts):**9** (1 part) cannot be taken as a true reflection of one or the other pathway. However, C₉-substituted derivatives of **1** are somewhat less reactive, and, in these examples, the operation of mechanism 1 appears to be favored (*vide infra*).

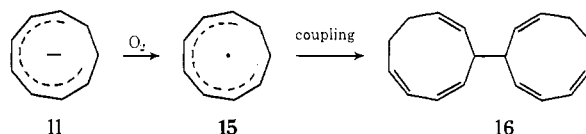
In an attempt to trap dianion **3**, excess methyl iodide was introduced 90 sec from mixing of **1** and potassium metal (2 equiv) in liquid ammonia at -78° . Upon workup, there was obtained chiefly a mixture of unreacted **1** and 5-methylcyclonona-1,3,6-triene (**12**). An identical reaction, but with an elapsed time of 35 min, gave **12** exclusively. No evidence was gained for the formation of dimethylated products. Translated into the terms of mechanism 1, these results imply simply that proton transfer from solvent is more facile than alkylation.¹⁸ Structural assignment to **12** follows from



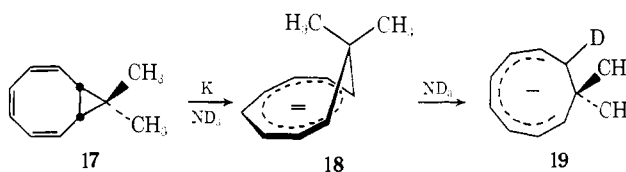
(18) Quenching studies involving crossover proton or deuterium transfer have proven impractical because of the inherent difficulty of removing all ND₃ or NH₃ of solvation prior to addition of the proton or deuterium source. The tenacity of the solvation forces are such that introduction of methanol (or CH₃OD) will not alter significantly the H/D uptake, when NH₃ (or ND₃) is present; deuterium incorporation proceeds at a high level (NH₃ cases), notwithstanding the large excess of unlabeled alcohol added.

its pmr spectrum and catalytic hydrogenation^{9b} to methylcyclononane (**13**), available by independent synthesis as shown.

When oxygen was introduced into a *concentrated* reaction mixture of **1** and lithium in liquid ammonia, and methanol subsequently added, there was isolated mainly triene **9** and the dimer **16**. The original observation of this oxidation by Okamura^{9b} was interpreted on the basis of one-electron oxidation of dianion **3**, selective coupling of the resulting radical anion (**2**), and ultimate protonation. Because we now recognize dianion **3** to be absent from these solutions, we prefer to view the process as an oxidation of **11** to give radical **15** which then couples.¹⁹



9,9-Dimethyl-*cis*-bicyclo[6.1.0]nonatriene. Allowing a solution of **17** in ND₃ to react with potassium at -78° for 30 min gave rise to a green solution, the pmr spectrum of which was appropriate for the homoaromatic dianion species **18**. As shown in Figure 2a, there is seen a four-proton multiplet at δ 5.0–5.8, a second olefinic region of area 2 centered at δ 4.05, absorptions due to H₁ and H₈ occurring at *ca.* δ 3.2, and widely separated methyl signals at δ 0.93 (partial overlap with solvent) and -1.62 . As regards peak assignments, the absorptions in the δ 5.0–5.8 region (area 4) are attributed to H₂, H₄, H₅, and H₇ based upon the expected deshielding at these sites, whereas the higher field two-proton olefinic multiplet is ascribed to H₃ and H₆, the positions assumedly of higher electron density. The apparent coupling constants, $J_{1,2} = J_{7,8} = 10$ Hz, $J_{2,3} = J_{6,7} = 10$ Hz, $J_{3,4} = J_{5,6} = 7.0$ Hz, and $J_{3,4} = J_{4,6} = 3.0$ Hz, suggest that the H₁-C-C-H₂ and H₃-C-C-H₄ dihedral angles approach 0° in support of the conclusion that the C₁-C₈ segment in **18** is



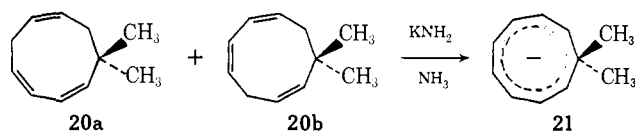
essentially planar. The appearance of an "inside" methyl absorption at δ -1.62 (CH_{3(a)}) and an outside methyl singlet at δ 0.93 (CH_{3(b)}) agrees fully with a diatropic²⁰ dianion formulation for **18**, where there exists significant 1,8 overlap and an appreciable ring current. These spectral data should be contrasted with those recorded by Winstein^{3a} for the parent system (**3**) in THF-*d*₈ or DME-*d*₈, where the entire set of six ring protons is observed as a multiplet at *ca.* δ 5.2–5.5.²¹

(19) Both Okamura^{9b} and we have observed that introduction of oxygen into a *dilute* solution of **11** in liquid ammonia leads to return of *cis*-bicyclo[6.1.0]nonatriene (**1**) in good yield. This remarkable effect of concentration was unexpected and is difficult to rationalize until more detailed studies are carried out.

(20) F. Sondheimer, *Accounts Chem. Res.*, **5**, 81 (1972).

(21) The reason for this discrepancy is not immediately apparent, except perhaps for the fact that the solvents used by Winstein share the common feature of possessing intense signals at δ 3.4–3.6 in their unlabeled (contaminating) counterparts, which introduced considerable difficulty in the form of solvent masking of neighboring proton signals.

When the above solution was kept at -65° for 45 min and the pmr spectrum rerecorded, partial conversion to monodeuterated monoanion **19** was noted (Figure 2b). This protonation (deuteration) reaction could be accelerated by removing the tube from the cold probe, allowing it to stand at room temperature for *ca.* 4 min, and recooling to -65° . Under these conditions, a color change from green to red was clearly apparent, and the spectrum realized was exclusively that of **19** (Figure 2c). The similarities between this spectrum and that obtained by deprotonation of **20** to **21** according to Staley and Pearl¹⁷ (Figure 2d) are



striking. The most significant differences are found in the expected diminution of the H_9 absorption in **19** to a one-proton signal and the appearance of added H-D spin-spin interaction between the deuterium atom and the adjoining H_1 and H_9 protons. Interestingly, the methyl groups in **19** and **21** appear as a six-proton singlet, signifying that the monoanion now no longer enjoys the conformational rigidity of the related dianion at -65° , and that the species is either rapidly flipping from one folded conformation to another or preferably a shallow twisted tub form.¹⁷

Quenching studies have also been performed. When **17** was reduced with potassium in dry NH_3 at -78° , a deep red solution was produced. After 35 min, addition of methanol furnished a colorless reaction mixture from which were isolated two isomeric products A and B in a ratio of 1:7, respectively.²² On the basis of spectral data (see Experimental Section), both compounds clearly correspond to the pair of structures represented by **20a** and **20b**; however, it has not been proven possible by such means to distinguish between them.

syn- and *anti*-9-Methyl-*cis*-bicyclo[6.1.0]nonatrienes. For several reasons, the focus of our interest was next directed to the stereoisomeric 9-methyl derivatives. Perhaps the most important single consideration concerned the stereochemistry of dianion formation, analysis of which was predicated upon the expectation that the distinctive widely separated "inner" and "outer" methyl absorptions of **18** would also carry over to the monoalkylated series. We would expect that a significant difference exists in the facility of electron transfer to the folded and extended conformations of a *cis*-bicyclo[6.1.0]nonatriene. Much in the manner required for effective Cope rearrangement, the most suitable electronic alignment and opportunity for maximum charge delocalization are attained when the cyclopropane ring is canted to the interior of the molecule (*cf.* **22b** and **24b**). Introduction of one or two electrons can now be accompanied directly by homoaromatic delocalization. Synchronous central-bond rupture

(22) Both Okamura^{9a} and Staley¹⁷ have isolated the nonatriene derivatives **20a** and **20b** by similar reactions. The ratio of **20a** to **20b** obtained by Okamura was 2.6:1.0, whereas the ratio realized by Staley was 1:2.6, this value comparing more closely with our figure of 1:9. The latter data perhaps reflect the utilization of more kinetically controlled quench conditions.

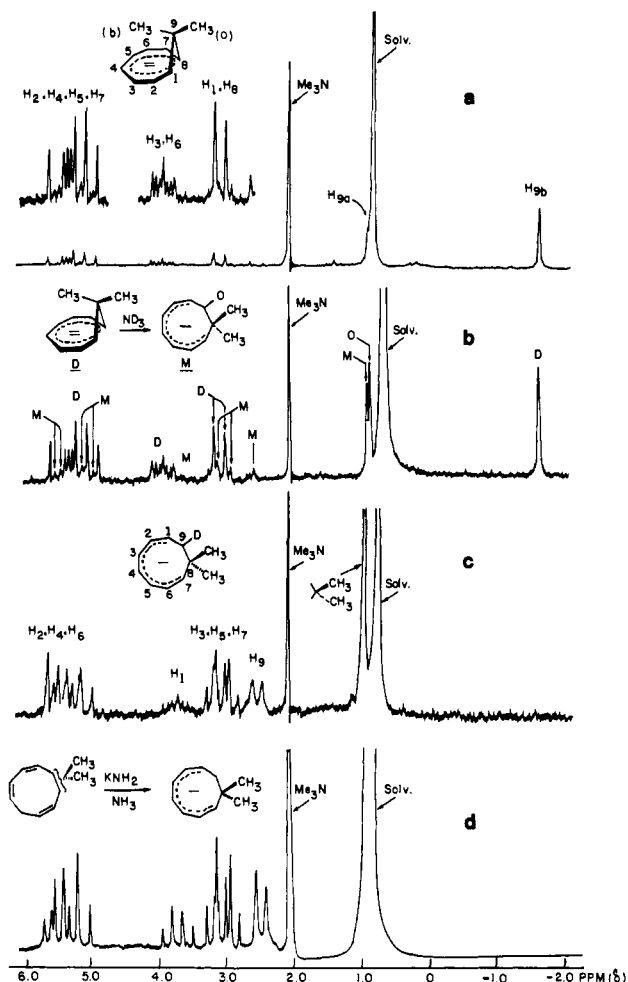
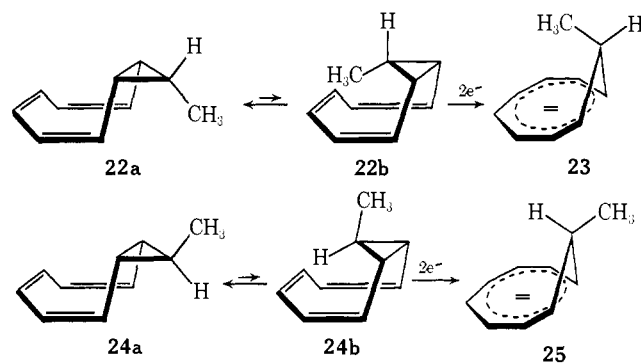


Figure 2. The 60-MHz pmr spectra of (a) homoaromatic dianion **18** in ND_3 at -65° ; (b) partial conversion of **18** to **19**, resulting upon storage at -65° for 45 min of the first solution; (c) monoanion **19** in ND_3 obtained by warming first solution to room temperature for 4 min and recooling to -65° ; (d) anion **21** in ND_3 at -65° . Trimethylamine is present as the internal standard; the low-field peak in curves a-c is an impurity.

is not likely during reduction of extended forms such as **22a** and **24a** because of poor orbital alignment; how-



ever, classical radical anions could intervene. Either pathway should lead to high levels of stereochemical control (at least initially); at issue was whether such stereoselectivity would be observed in dianion generation.

Although the neutral hydrocarbons **22** and **24** are probably capable of conformational ring flipping, would their dianions also invert? Or would pro-

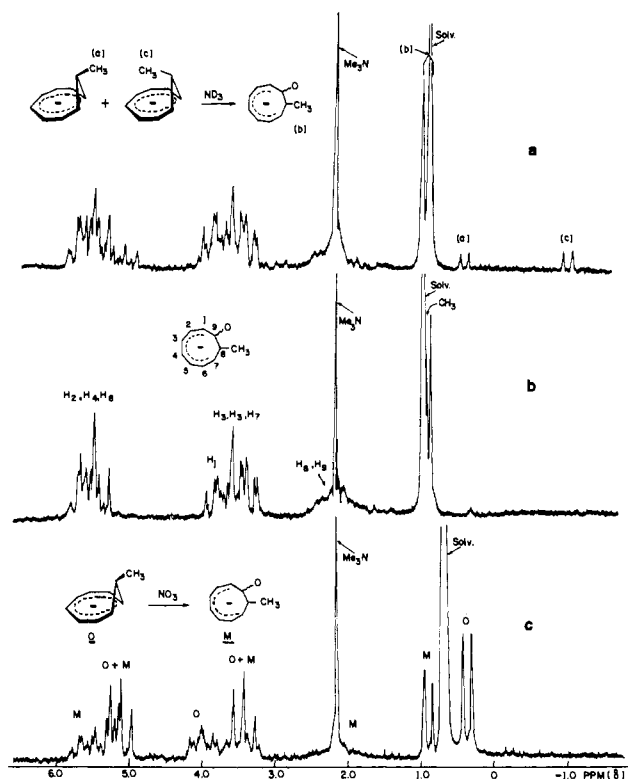
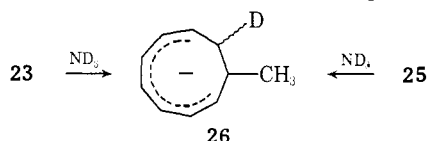


Figure 3. The 60-MHz pmr spectra of (a) mixture of **23**, **25**, and **26** obtained by reduction of **22** with potassium in ND_3 at -78° (35 min); (b) spectrum of **26** (ND_3 , -65°); (c) mixture of **25** and **26** obtained by reduction of **24** with potassium in ND_3 at -78° (35 min). Trimethylamine is present as the internal standard.

tonation (deuteration) to give monoanions occur with greater facility under the conditions employed? Interconversion at the ionic stage would necessitate translocation of an "inside" methyl substituent to the "outside" region, and *vice versa*. Provided that the monomethyl dianions resemble in their stability the dimethyl congener **18**, rather than parent system **3** (to permit recording of their spectra), and that the barrier to their interconversion is sufficiently slow on the nmr time scale in the vicinity of -65° (to permit observation of initially generated species), the distribution of stereoisomeric dianions would furnish a direct measure of the stereoselectivity of the process.

With these considerations in mind, **22** was allowed to react with potassium in ND_3 at -78° for 35 min, and the pmr spectrum of the resulting green solution was recorded. There was visible three sets of methyl doublets in the upfield region indicative of the generation of three discrete species (Figure 3a). All of the features of the spectrum point to the presence of dianions **23** and **25** admixed with a predominant amount of the deuterated monoanion **26**. Specifically, the



signal at $\delta -1.1$ is anticipated for the shielded methyl group in **23**, the doublet at $\delta 0.30$ to the "outside" methyl in **25**, and the absorption at $\delta 0.90$ to the methyl substituent in **26**, this being the least affected by shielding and deshielding regions. As in the dimethyl

example, removal of this sample from the probe for 5 min and recoiling to -65° led to a spectrum of pure **26** (Figure 3b).

In other experiments where **22** was allowed to react with potassium in ND_3 at -78° for only 5 min and the pmr spectra were immediately recorded at -65° , the doublet at $\delta 0.30$ due to **25** was now totally absent. Rather, the high-field doublet at $\delta -1.1$ and the monoanion methyl absorption at 0.90 were present at approximately equal intensities. A time study conducted on such a solution at -65° revealed the gradual disappearance of **23** with a concomitant buildup in the concentration level of **26**. At no time was the methyl signal of **25** in evidence.

These findings denote that **22** is converted upon reduction exclusively to dianion **23**. The situation at -65° is presumably such that deuterium transfer from ND_3 to **23** occurs sufficiently rapidly that its kinetic role precludes operation of the bridge-flipping process. On the other hand, at -78° deuteration is seemingly retarded to a level where bridge flipping can compete. Dianion **23** would be expected to possess an inherent driving force for conversion to **25**, in view of the relief of steric strain which must surely accompany the movement of "inside" methyl to the exterior surface of the homoaromatic framework.

For *anti*-9-methyl isomer **24**, reduction as above at -78° for 35 min led to a pmr spectrum consisting of upfield signals for dianion **25** (major) and monoanion **26** (Figure 3c). By qualitatively following the rate of deuteration of **25** by ND_3 at -50° (Figure 4), we found this species to be less rapidly consumed than its endo counterpart (**23**) but yet more reactive than the 9,9-dimethyl anion **18**. When the solution was allowed to warm, the spectrum of **26** (Figure 2b) was again obtained. Expectedly, in none of our experiments was conversion of **25** to **23** noted. We suggest on the basis of the apparent coupling constants that **25** is essentially a planar species: $J_{1,2} = 9$, $J_{1,9} = 9.0$, $J_{2,3} = 9$; $J_{3,4} = 6.5$, $J_{3,5} = 3.0$, and $J_{4,6} = 3$ Hz.

Treatment of **22** with potassium in liquid ammonia, followed by a methanol quench of the monoanion solution, furnished a mixture of two isomeric dihydro products in a ratio of 3:1. Both trienes conform satisfactorily to formulations **27** and **28**, but we have

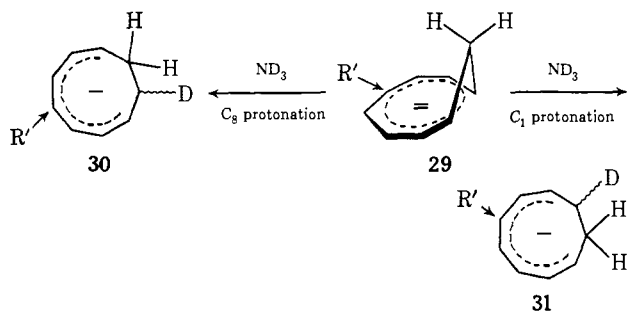


not established which is which. Protonation data on the monoanion derived from *anti* isomer **24** were essentially identical in terms of yield and product ratio, thereby implicating involvement of the same intermediate.

Ring Methylated *cis*-Bicyclo[6.1.0]nonatrienes. In the prescribed monohomocyclooctatetraene dianion examples, monoproteination (monodeuteration) by NH_3 (ND_3) is seen to operate exclusively at one of the *equivalent* basal carbons (C_1 or C_3) linked directly to the bridging sp^3 -hybridized center (C_9). This reactivity is perhaps best rationalized in terms of a kinetically favored process, the transition state of which properly reflects the stabilization accruing to the fully conjugated

cyclononatrienyl monoanion. It may be asked whether there should be any selectivity in this initial proton (deuterium) transfer if some element of dissymmetry were introduced onto the C₁-C₈ periphery and to what extent such selectivity would be manifested. Consideration of the electron-density distribution prevailing in cyclononatrienyl anions based upon pmr spectral data (Figures 1-3) reveals that C₁, C₃, C₅, and C₇ are rather more electron rich than C₂, C₄, and C₆. Direct correlation between chemical shift and charge density permits the additional inference that C₅ and C₇ may enjoy the greatest anionic charge localization of all.

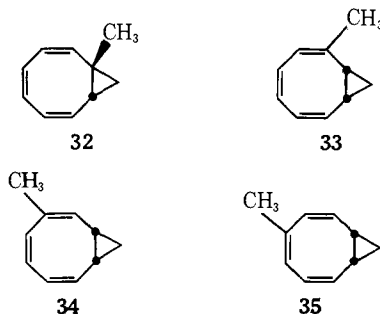
Let us now consider the situation where dianion **29** bearing an electron-donating substituent at C₄ is about to become deuterated by ND₃ solvent. Of the two pathways available to **29**, C₃ deuteration leads to **30** where the R' group is positioned specifically at C₄, while transfer of D⁺ to C₁ gives monoanion **31** with R'



situated at C₃. As can be seen, the thermodynamic stabilities of **30** and **31** are expected to differ appreciably. Were the transition states for these competing reactions to reflect all or nearly all of the magnitude of this stability differential, the possibility exists that **30** will be produced with a high level of regioselectivity.

Little is known about absolute or relative rate constants for capture of reactive dianions by weak acids such as ammonia. Paquette, Hansen, and Kakihana²³ have earlier examined the effect of methyl substitution upon the preferred protonation sites of the 2-methoxyazocinyl dianion (various quenching agents). These researchers noted that the presence of a methyl group at a customarily favored site was sufficient to discourage protonation at that position. It did not prove possible to determine whether this was a reflection of purely steric or purely electronic factors, or some combination of these two contributions. Additionally, ultimate protonation of the intermediate monoanions appeared not to be necessarily thermodynamically controlled.

For these reasons, we have included a study of the two-electron reduction of the four possible ring methylated *cis*-bicyclo[6.1.0]nonatrienes **32-35**. Synthetic en-



(23) L. A. Paquette, J. F. Hansen, and T. Kakihana, *J. Amer. Chem. Soc.*, **93**, 168 (1971).

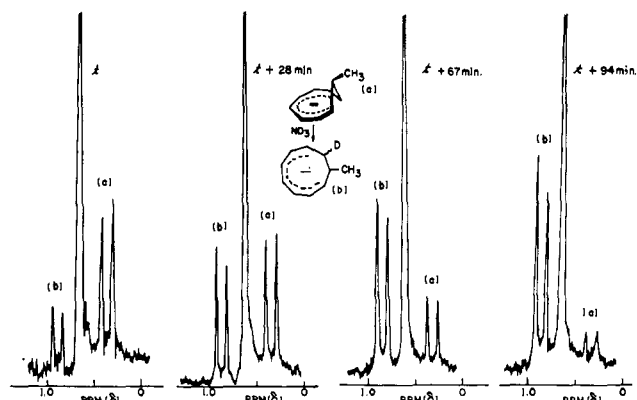
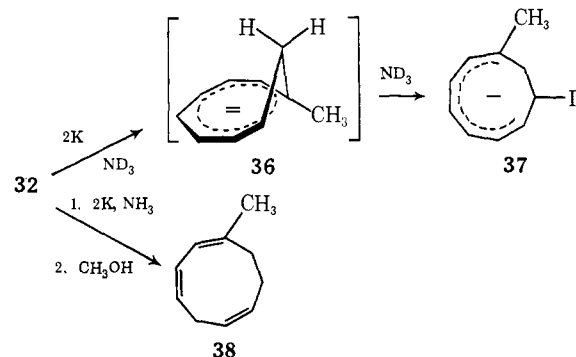


Figure 4. Time study of the deuteration of **25** by ND₃ at -50° ; t reflects *ca.* 30-min elapsed time at -75° ; before insertion into the pmr probe. The intense singlet is due to residual proton in the solvent.

try to this array of isomeric hydrocarbons had been developed earlier.^{15a} Selection of methylated derivatives was predicated not only upon their accessibility, but also in the expectation that subsequent correlation with the chemical reactivity of homoazocinyl dianions substituted with methyl groups could also be made.²⁴

The addition of **32** to a solution of 2 g-atoms of potassium in ND₃ at -78° produced a deep red solution, the pmr spectrum of which was recorded (at -65°) after a total elapsed time of 25 min at the lower temperature. Under these conditions, a well-defined series of signals clearly due to a single species was observed. From the presence of a methyl singlet at δ 1.65 and three closely grouped allylic hydrogens in the δ 2.2-2.55 region together with the absence of the H₁ proton, the monoanion structure **37** was deduced. The otherwise almost identical pmr features of **37** and **11** (see Table I) provide supportive evidence for the assignment. As indicated earlier, all of this material is probably formed by rapid deuteration of dianion **36**. A mechanistically important fact is that **36** undergoes highly selective deuterium transfer only to the nonmethyl bearing basal carbon (C₈). The correctness of the substitution pattern in **37** was substantiated chemically when the



reduction of **32** was effected in ammonia and the reaction mixture subsequently quenched with methanol. A single dihydro derivative was isolated, the spectral features of which (see Experimental Section) conform to structure **38**.

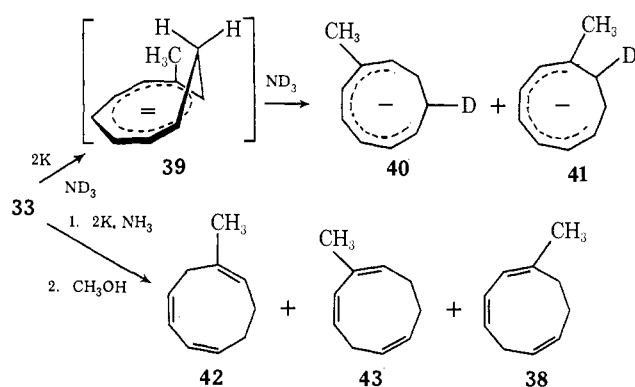
When **33** was treated with 2 equiv of potassium in ND₃ at -78° and the reaction monitored by pmr

(24) S. V. Ley, unpublished observations.

Table I. Summary of Pmr Chemical Shift Data for Various Cyclononatrienyl Anions^a

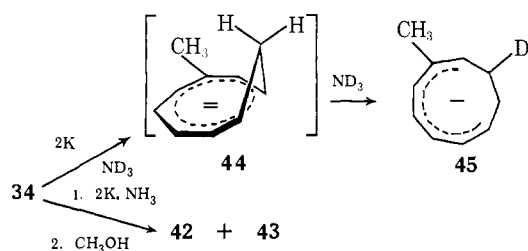
<i>cis</i> -Bicyclononatriene reduced	Anion	Chemical shift, δ							
		H ₁	H ₂	H ₃	H ₄	H ₅	H ₆	H ₇	H _{8,9}
1	11	3.73 (1-CH ₃)	5.57	3.35	5.47	3.35	5.57	3.73	2.05-2.3
32	37	1.45	5.6-5.8 (2-CH ₃)	3.15-3.5	5.38	3.02	5.3-5.7	3.35-3.8	2.2-2.55
33	40	4.04-4.3 ^b (1-CH ₃)	1.63	3.3	5.43	3.15	5.58	3.1-3.4 ^b	2.15-2.45
	41	1.45	5.6-5.8 (2-CH ₃)	3.15-3.5	5.38	3.02	5.3-5.7	3.35-3.8	2.2-2.55
34	45	4.04-4.3 ^b	1.63	3.3	5.43 (4-CH ₃)	3.15	5.58	3.1-3.42 ^a	2.15-2.45
35	47	3.85-3.45	5.65	3.27	1.65	3.27	5.65	3.85-3.45	2.4-2.2

^a 60 MHz, -65°, K⁺ salt, ND₃ solution, Me₃N as internal standard. ^b It is possible that these assignments may be reversed.



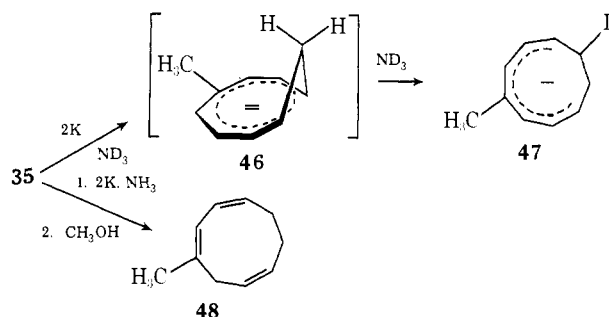
spectroscopy (at -65°), the rapid formation of monoanions **40** and **41** in the ratio of 3.3:1 (methyl signal integration) was seen. In this instance, the assignments were greatly facilitated by the strong similarity of the pmr spectra of **40** and **41** with those of **45** and **37**, respectively, which anions are produced in pure form in related reactions (see Table I). The formation of **40** and **41** can be accounted for on the basis of a somewhat greater kinetic preference for deuteration of dianion **39** at C₈ relative to C₁, the basal carbon adjacent to the methyl substituent. Three products were observed upon direct reduction-protonation; these were isolated by preparative vpc and identified as **42** (10%), **43** (67%), and **38** (23%) by a combination of spectral evidence, chemical reasoning based upon the 40:41 ratio, and direct comparison with the same compounds produced in certain of the isomeric examples. The further protonation of **40** (H instead of D) is unquestionably also effected to a significant degree by the methyl substituent, as reflected in the approximately sevenfold greater quantity of **43** produced relative to **42**.

Comparable reduction of **34** in ND₃ afforded only monoanion **45** in high yield, the structure of which has been assigned on the basis of spectral (Table I) and chemical data [quenching of protio counterpart gives



expectedly **42** (13%) and **43** (87%)]. The overwhelming directional effect of the methyl group in **44** upon the regioselectivity of proton (deuterium) capture, particularly when compared to the behavior of dianion **39**, was not entirely expected. A gradual fall off in the exclusivity of attack by H⁺ (D⁺) at C₈, as the methyl substituent is moved from C₁ to C₂ to C₃, etc., is obviously not operative. Such a reactivity order would convey chiefly a steric implication. However, if electronic and inductive effects also contribute significantly to the course of these reactions, digression from this regular pattern should be encountered. In view of the above findings, therefore, we conclude that such protonation reactions do not operate chiefly under the control of steric influences (see Discussion).

A further case in point is encountered in the behavior of **35** which undergoes reductive conversion exclusively, within the limits of pmr detectability, to monoanion **47**. Again, there exists a marked propensity for deuteration (protonation) of dianion **46** at C₈. In agreement with these findings, sequential treatment of **35** with K/NH₃ and methanol gave **48**. The symmetry of **47** (H

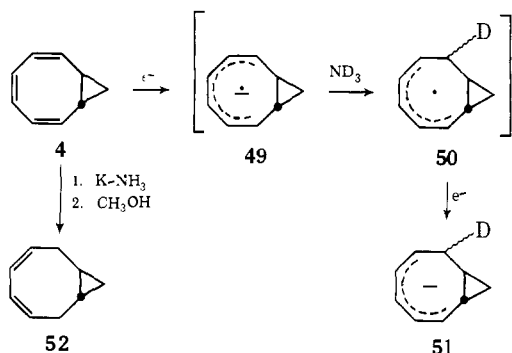


instead of D) does not allow but for the production of a single 1,3,6-cyclononatriene.

trans-Bicyclo[6.1.0]nonatriene. For comparison purposes, *trans* isomer **4** was treated with 2 g-atom equiv of potassium in ND₃ at -78° for 30 min, and the filtered reaction mixture was transferred to a pmr probe operating at -63°. Observation of a two-proton multiplet centered at δ 5.7 for H₃ and H₆, signals for H₂, H₄, H₆, and H₇ in the δ 2.7-4.0 region, and upfield absorptions above δ 1.0 assigned to H₁, H₈, and H₉ proved entirely compatible with monoanion formulation **51** (Figure 5). However, when the areas of these various regions were machine integrated, an incongruity with this proton distribution became apparent; furthermore, the dis-

parity became larger with time. We suspected that one or more positions were experiencing unusually facile H/D exchange, and this supposition was confirmed by warming the solution to room temperature for 60 min. Redetermination of the spectrum revealed an almost total disappearance of the absorptions due to H₂, H₄, and H₆ and a significant sharpening of the downfield signal at δ 5.7. In the original spectrum (Figure 5), it proved possible to extract apparent coupling constants of the following magnitude: $J_{2,3} = 9$, $J_{3,4} = J_{4,5} = 10$, $J_{5,6} = 11.5$, and $J_{6,7} = 5$ Hz.

Additional evidence that the cyclopropane ring of **4** remains intact under these conditions was provided by methanol quench studies on **4** subsequent to reduction with K-NH₃. Structural assignment to the oily hydrocarbon which was isolated by vpc was founded upon several pieces of spectroscopic data. Its mass spectral molecular weight of 120.0941 was in excellent agreement with that expected of a dihydro derivative (calcd for C₉H₁₂: m/e 120.0939). The bicyclic system displays a strong maximum at 234 nm (ϵ 9300) in the ultraviolet region as expected for a conjugated 1,3-cyclo-



octadiene chromophore.²⁵ Its pmr spectrum (CDCl₃) reveals a multiplet of area 4 in the olefinic region at δ 5.2–5.8 (H₃–H₆), broad doublets ($J = 17.5$ Hz) at δ 2.75 and 1.35 attributable to the pairs of deshielded and shielded protons attached to C₂ and C₇, and a multiplet (4 H) at δ 0.4–0.75 in the cyclopropyl region. Of direct relevance is the molecular symmetry demanded by these spectral features. In particular, only when the ring system is transfused as in **52** is the opportunity available to spatially orient the allylic protons at both C₂ and C₇, in such a manner that one is imbedded in the π framework of the diene moiety, while the other falls in the deshielding area of the cyclopropane ring.

A mechanistic rationalization of the formation of **51** and **52** is based on the premise that the initially generated radical anion **49** suffers irreversible deuterium (proton) transfer from solvent to one or the other terminus of the π system. This step is followed by further reduction of free radical **50** to give the spectroscopically observable monoanion **51**. Interestingly, ultimate protonation of **51** operates exclusively at C₇ to furnish only the diene of C₂ symmetry.

Discussion

The above data now provide definitive evidence concerning the exceptionally high basicity of homocyclooctatetraene dianions. For comparison, a variety of cyclooctatetraene dianions have similarly been gener-

(25) L. A. Paquette and R. W. Begland, *J. Amer. Chem. Soc.*, **88**, 4685 (1966).

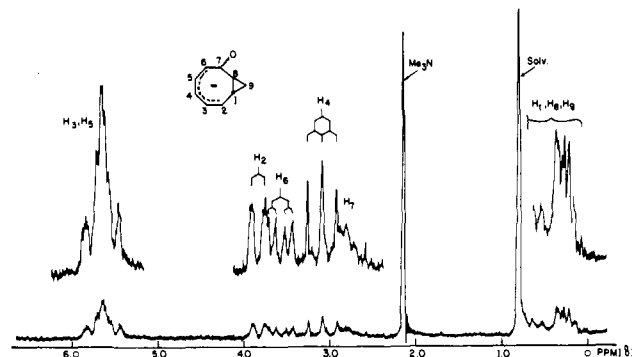


Figure 5. The 60-MHz pmr spectrum of the K/ND₃ reduction product of **4** (–63°, ND₃ solvent, Me₃N as internal standard).

ated by reduction with potassium in ND₃ at –65 to –78° and found to be entirely stable at these conditions.²⁴ Not unexpectedly, therefore, the homoaromatic species are not capable of delocalizing charge as efficiently as their planar $p\pi$ analogs and consequently reflect in their chemical properties the untoward effect of electron–electron repulsion.²⁶ The observed relative stability order **18** > **23** ~ **25** > **3** deserves comment. This relationship between the level of alkyl substitution at C₉ and rate of proton (deuterium) abstraction from ammonia can be understood if one makes direct analogy with small-ring chemistry. Thus, it is well recognized that incremental placement of alkyl groups on three-membered rings not only is generally conducive to their inherent stabilization (thermodynamic argument),²⁷ but also is reflected in the lowered transition-state energies of three-ring cyclizations (kinetic considerations).²⁸ Extrapolation of this effect to homocyclooctatetraenyl dianions would suggest that 9,9-dimethyl derivative **18** profits from a greater proximity of C₁ to C₈ and attendant-enhanced 1,8 orbital overlap as compared to its lesser substituted congeners.

The favorable interaction of orbitals, which operates in **3** and its derivatives, is particularly evident in the pmr spectra of these diatropic dianions. All of the olefinic protons absorb substantially downfield from the positions expected on the basis of charge-induced shifts alone, and the “inside” and “outside” methyl protons at C₉ are widely separated. However, the realization of thermodynamic stability is complicated by electronic factors (doubly negative charge) and the resulting kinetic instability of the dianions in liquid ammonia. As a consequence of the unique topological and hybridization (lowest bond order) features at C₁ and C₈ and the maximum delocalization to be gained from fully conjugated cyclonatrienyl anions, initial protonation of the dianions operates exclusively at one of these basal carbons. When a methyl group is present at C₁, protonation takes place exclusively at the unsubstituted basal center. In fact, the interesting observation has

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

(27) P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.*, **92**, 2377 (1970). For a particularly relevant example from the 1,6-methano[10]annulene area, see E. Vogel, *Pure Appl. Chem.*, **20**, 237 (1969); R. Bianchi, A. Mugnoli, and M. Simonetta, *J. Chem. Soc., Chem. Commun.*, 1073 (1972); H. Günther, H. Schmickler, W. Bremser, F. A. Straube, and E. Vogel, *Angew. Chem.*, **85**, 585 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 570 (1973).

(28) Consult, for example, the rate sequence for reaction of chlorohydrins with alkali: L. A. Paquette, “Principles of Modern Heterocyclic Chemistry,” W. A. Benjamin, New York, N. Y., 1968, p 13.

been made that methyl-bearing carbons in those dianions resulting from ring-substituted *cis*-bicyclo[6.1.0]nonatrienes do not experience protonation either in their transformation to monoanions or during ultimate conversion of the monoanions to 1,3,6-cyclo-nonatrienes. As already noted, this behavior cannot be attributed to steric effects but must find its origin chiefly in electrostatic causes.

Given the above findings, the polarographic behavior of *cis*-bicyclo[6.1.0]nonatrienes continues to defy satisfactory rationalization. That **1**, for example, undergoes reduction in two discrete one-electron steps could be taken to implicate transient passage through a radical anion to a dianion product. Additionally, that these electron transfers occur at more negative potentials than cyclooctatetraene need not be construed as reflecting the requirement for attainment of the thermodynamically less stable folded conformation and diminished $p\pi$ conjugation relative to the tetraene. However, the first and second reduction waves are both irreversible, suggesting that one or more chemical processes likely remove the primary product of electron transfer. Electrochemical formation of dianion **3** is consequently a very unlikely event; were this so, **3** would be rapidly destroyed by involvement in Hofmann elimination reactions^{11d,29} since this highly reactive basic species would be generated under aprotic conditions in the midst of a sizable concentration gradient of tetraalkylammonium ions. In brief, the prevailing situation is seemingly one in which **1** and its derivatives undergo polarographic reduction by means of an ece pathway of still undefined nature. It remains for future work to provide definitive answers to these questions and to the more general possibility of perhaps realizing a polarographic criterion of homoaromaticity.

Experimental Section

Proton magnetic resonance spectra were recorded with a Varian A-60A spectrometer; apparent splittings are given in all cases. Infrared spectra were obtained with a Perkin-Elmer Model 137 spectrophotometer, ultraviolet spectra with a Cary 14 instrument, and mass spectra with a A.E.I.-MS9 spectrometer operating at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Preparative vpc work was done on a Varian Aerograph A90-P3 instrument equipped with a thermal conductivity detector.

Method for Obtaining Pmr Spectra of Anions in ND₃. Approximately 0.5 ml of ND₃³⁰ was vacuum transferred to a small reaction vessel equipped with a miniaturized glass-encased magnetic stirring bar. Freshly cut potassium metal was introduced into the reaction vessel after removal of the serum cap under a positive nitrogen pressure. In practice, nitrogen was simply allowed to flow over the surface of the solid ND₃ during this operation. The cap was replaced, and the ND₃ was slowly allowed to thaw by gradual removal of the liquid-nitrogen cooling bath and replacement with a Dry Ice-isopropyl alcohol bath. Substrate was injected by syringe into the resulting dark-blue solution with simultaneous frequent agitation of the reaction mixture by means of an external magnet. When the reduction was complete, the mixture was frozen in the liquid-nitrogen bath and the serum cap removed under nitrogen and replaced with a pmr tube side arm containing a plug of glass wool in the upper portion. After regaining partial vacuum (40 cm), the reaction vessel was inverted by rotation about the F 10/30 joint and the tube rapidly cooled to -78° . The contents of the reaction

vessel upon thawing collected above the glass-wool plug. Filtration through the plug was achieved by rapidly removing the Dry Ice-isopropyl alcohol bath and replacing it with the liquid-nitrogen bath. The tube was sealed *in vacuo* in the customary fashion, and the solid in the pmr tube was *carefully* thawed by swabbing with cold Dry Ice-isopropyl alcohol solution. The pmr spectra were then recorded in precalibrated cold probes.

Reduction of *cis*-Bicyclo[6.1.0]nonatriene (1**) with Potassium in Liquid Ammonia. Methanol Quench.** Under a dry nitrogen atmosphere, 500 mg (4.24 mmol) of **1** was added dropwise to a stirred solution of potassium (340 mg, 8.7 mg-atoms) and liquid ammonia (10 ml) cooled to -78° . After stirring for 20 min at this temperature, the dark-red solution was treated dropwise with methanol (2 ml) to form a colorless mixture. Ammonia was allowed to evaporate and the residue was extracted with pentane (8×20 ml). The combined organic layers were washed with water (2×10 ml), dried, and carefully distilled through a 6-in. Vigreux column at atmospheric pressure. There was obtained in this manner 492 mg (98%) of pale yellow oil, vpc analysis of which, on three different columns, showed it to be a single component. The pure cyclonona-1,3,6-triene (**9**) was collected by vpc: $\nu_{\text{max}}^{\text{nat}}$ 3015, 2950, 2930, 2865, 1460, 780, 730, 720, and 670 cm^{-1} (all strong); $\delta_{\text{MS}}^{\text{CDCl}_3}$ 5.3–6.0 (m, 6, olefinic), 2.72 (t, $J = 7$ Hz, 2, bisallylic), 1.8–2.25 (m, 4, allylic).⁹

Reduction of **1. Methyl Iodide Work-up.** A 200-mg (1.7 mmol) sample of **1** was reduced as above with 134 mg (3.43 mg-atoms) of potassium in anhydrous liquid ammonia (10 ml). After the solution was stirred for 35 min at -78° , methyl iodide (1 ml) was added. Work-up identical with the above gave a pale yellow oil shown to be one component by vpc. Isolation by this technique (6 ft \times 0.25 in. 5% SE-30, 100 $^\circ$) gave 162 mg (73%) of 5-methylcyclonona-1,3,6-triene (**12**): $\nu_{\text{max}}^{\text{nat}}$ 3050, 2960, 2930, 2870, 1455, 776, 756, 728, and 677 cm^{-1} (all strong); $\delta_{\text{MS}}^{\text{CDCl}_3}$ 5.0–6.0 (m, 6, olefinic), 3.05 (br q, $J = 6.5$ Hz, 1, bisallylic), 1.4–2.5 (m, 4, allylic), and 1.02 (d, $J = 6.5$ Hz, 3, methyl).⁹

Methylcyclononane (13**). A. Hydrogenation of **12**.** Triene **12** (30 mg) was added to a suspension of prerduced 10% Pd/C (10 mg) in methanol (3 ml) under a hydrogen atmosphere. After cessation of hydrogen uptake, the catalyst was removed by filtration through a pad of Celite and the filtrate diluted with water (7 ml). The product was extracted with pentane (2×10 ml), and the combined organic layers were dried and carefully evaporated. Vpc isolation (3 ft \times 0.25 in. 5% SE-30, 90 $^\circ$) gave 19.5 mg of **13**, identical with the authentic sample in part B.

B. From Cyclononane (14**).** Methylolithium (1.4 ml of 1.9 M solution) was added dropwise to a stirred solution of **14** (254 mg) in dry ether (5 ml) cooled to -70° . Water (2 ml) was introduced after 30 min and the reaction mixture allowed to warm to room temperature. A further 10-ml portion of ether was added, and the organic phase was dried and evaporated to give 256 mg (90%) of crude 1-hydroxy-1-methylcyclononane.

A mixture of the carbinol (248 mg, 1.58 mmol), ethyl(carboxylsulfamoyl)triethylammonium hydroxide inner salt³¹ (440 mg, 2.0 mmol) and dry tetrahydrofuran (10 ml) was stirred under nitrogen at 50–55 $^\circ$ for 30 min. Water (25 ml) was added to the cooled mixture, and the product was extracted with pentane (3×25 ml). The pentane extracts were dried and carefully evaporated, and the residue was purified by preparative vpc (3 ft \times 0.25 in. 5% SE-30, 90 $^\circ$) to give 125 mg (57%) of 1-methylcyclononene: $\nu_{\text{max}}^{\text{nat}}$ 2980, 2930, 2860, 1480, and 1450 cm^{-1} (all strong).

By the usual method, 125 mg of the cycloalkene was hydrogenated over 10% Pd/C (15 mg) to give 101 mg (81%) of authentic **13**: $\nu_{\text{max}}^{\text{nat}}$ 2980, 2930, 2875, and 2855 cm^{-1} (all strong); $\delta_{\text{MS}}^{\text{CDCl}_3}$ 1.48 (br m, 17) and 0.88 (d, $J = 6$ Hz, 3).

Reduction of **1. Oxidative Monoanion Coupling.** A mixture of 236 mg (2 mmol) of **1**, 28 mg (4 mg-atoms) of lithium metal, and 30 ml of dry ammonia was stirred rapidly at -78° under nitrogen for 30 min. Oxygen (15 ml) was introduced *via* syringe over the surface of the mixture during 90 min, and a color change from deep red to pale orange was noted. Ammonia was allowed to evaporate slowly as the mixture warmed to room temperature, the color gradually changing to green and finally to yellow. The residue was cooled; methanol (1 ml) and water (15 ml) were added and the products extracted with pentane (3×15 ml). The combined pentane layers were washed with water, dried, and carefully evaporated to give 215 mg of an oil. Dissolution of this oil in a little methanol and cooling to 0 $^\circ$ caused crystallization of a white solid (52 mg, mp 82–84 $^\circ$), shown by pmr to be dimer **16**:⁹ $\delta_{\text{MS}}^{\text{CDCl}_3}$ 4.95–

(29) A. J. Fry and M. A. Mitnick, *J. Amer. Chem. Soc.*, **91**, 6207 (1969); A. J. Fry and R. G. Reed, *ibid.*, **91**, 6448 (1969).

(30) Prepared by reaction of magnesium nitride and deuterium oxide according to the directions of V. I. Melczynski, *Angew. Chem.*, **74**, 32 (1962). Several vacuum transfers of the NH₃ were made to guarantee maximum dryness of the solvent; the last transfer was effectively a distillation over elemental sodium.

(31) E. M. Burgess, H. R. Penton, Jr., and E. A. Taylor, *J. Amer. Chem. Soc.*, **92**, 5224 (1970); *J. Org. Chem.*, **38**, 26 (1973).

6.05 (m, 12, olefinic), 2.7–3.3 (m, 2, bisallylic), and 1.1–2.6 (m, 8, methylene).

The mother liquors were diluted with water (10 ml) and extracted with pentane (2 × 30 ml). Processing as above furnished 112 mg of an oil containing triene **9** and dimer **16** in a ratio of 9:1 (pmr analysis).

Reduction of 9,9-Dimethyl-*cis*-bicyclo[6.1.0]nonatriene (17) with Potassium in Liquid Ammonia. Methanol Quench. Reaction of 1.0 g (6.85 mmol) of **17**, as predescribed, with 0.54 g (13.8 mg-atoms) of potassium in 35 ml of dry liquid ammonia, followed by the addition of methanol, afforded 0.995 g of an oil. The presence of two isomers A and B was indicated by pmr (ratio 1:9) and vpc methods (ratio 12:88). Separation of the isomers by preparative vpc (18 ft × 0.25 in. 15% XF-1150, 100°) furnished the pure trienes **20a** and **20b**.

For isomer A (t_{ret} 13.75 min): $\nu_{\text{max}}^{\text{neat}}$ 2965, 2930, and 775 cm^{-1} (all strong); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.2–6.0 (m, 6, olefinic), 2.7 (t, $J = 6$ Hz, 2, bisallylic), 2.28 (d, $J = 7$ Hz, 2, allylic), and 1.0 (s, 6, methyl).

Anal. Calcd for $\text{C}_{11}\text{H}_{16}$: C, 89.12; H, 10.88. Found: C, 88.79; H, 11.11.

For isomer B (t_{ret} 19.5 min): $\nu_{\text{max}}^{\text{neat}}$ 3010, 2965, 1470, 1365, 810, 770, 732, and 655 cm^{-1} (all strong); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.15–5.9 (m, 6, olefinic), (dd, $J = 5$ and 7 Hz, 2, bisallylic), 2.27 (d, $J = 8$ Hz, 2, allylic), and 1.18 (s, 6, methyl).

Anal. Calcd for $\text{C}_{11}\text{H}_{16}$: C, 89.12; H, 10.88. Found: C, 89.02; H, 11.13.

Reduction of *syn*-9-Methyl-*cis*-bicyclo[6.1.0]nonatriene (22). Treatment of 500 mg (3.79 mmol) of **22** with potassium 298 mg, 7.65 mg-atoms in liquid ammonia (15 ml) as above, followed by quenching with methanol, afforded 487 mg of a pale yellow oil consisting of two isomeric components. These were separated by preparative vpc (18 ft × 0.25 in. 15% XF-1150, 100°) and identified as **27** and **28** (not individually distinguishable).

For isomer C (t_{ret} 10.25 min): $\nu_{\text{max}}^{\text{neat}}$ 3020, 2960, 2925, 2870, 1455, 780, 760, 712, 680, and 637 cm^{-1} (all strong); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.0–5.85 (m, 6, olefinic), 2.5–2.9 (m, 2, bisallylic), 1.7–2.5 (m, 3, allylic), and 1.06 (d, $J = 6.5$ Hz, 3, methyl).

Anal. Calcd for $\text{C}_{10}\text{H}_{14}$: C, 89.49; H, 10.51. Found: C, 89.47; H, 10.63.

For isomer D (t_{ret} 11.1 min): $\nu_{\text{max}}^{\text{neat}}$ 3010, 2960, 2915, 2875, 1447, 775, 726, and 670 cm^{-1} (all strong); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.1–5.9 (m, 6, olefinic), 2.5–2.9 (m, 2, bisallylic), 1.8–2.5 (m, 3, allylic), and 1.15 (d, $J = 7$ Hz, 3, methyl).

Anal. Calcd for $\text{C}_{10}\text{H}_{14}$: C, 89.49; H, 10.51. Found: C, 89.39; H, 10.70.

Reduction of *anti*-9-Methyl-*cis*-bicyclo[6.1.0]nonatriene (24). A 100-mg (0.757 mmol) sample of **24** was allowed to react with potassium (60 mg, 1.54 mg-atoms) in liquid ammonia (10 ml) according to the usual procedure. After the mixture was quenched with methanol (0.5 ml), work-up gave 84 mg of a pale yellow oil, vpc analysis of which revealed it to consist exclusively of **27** and **28**. The ratio of isomers C and D was 3:1, and the spectral properties of these substances were identical with those reported above.

Reduction of 1-Methyl-*cis*-bicyclo[6.1.0]nonatriene (32). By the usual method, 29 mg (0.22 mmol) of **32** was allowed to react with potassium (19 mg, 0.48 mg-atom) in dry ammonia (5 ml) at -78° . The red solution was treated after 25 min with 150 μl of methanol. Work-up gave 23 mg of oil, vpc analysis of which (6 ft × 0.25 in. 5% PPGA, 65° and 18 ft × 0.25 in. 15% XF-1150, 85°) indicated it to be homogeneous. Preparative vpc isolation gave pure **38**: $\nu_{\text{max}}^{\text{neat}}$ 3020, 3005, 2965, 2920, 2860, 720, 710, and 675 cm^{-1} (all strong); $\lambda_{\text{max}}^{\text{isooctane}}$ 226 nm (ϵ 3660); calcd for $\text{C}_{10}\text{H}_{14}$ *m/e* 134.1095, found

134.1097; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.25–5.9 (m, 5, olefinic), 2.65 (t, $J = 7$ Hz, 2, bisallylic), 1.98–2.2 (m, 4, allylic), and 1.74 (t, $J = 1$ Hz, 3, methyl).

Anal. Calcd for $\text{C}_{10}\text{H}_{14}$: C, 89.49; H, 10.51. Found: C, 89.73; H, 10.53.

Reduction of 2-Methyl-*cis*-bicyclo[6.1.0]nonatriene (33). Reduction of 90 mg (0.68 mmol) of **33** with 53.5 mg (1.37 mg-atoms) of potassium in 10 ml of dry ammonia at -78° as described above gave a red solution to which was added 250 μl of methanol after 30 min. After work-up, there was isolated 62 mg of oil, vpc analysis (18 ft × 0.25 in. 15% XF-1150, 85°) of which showed it to consist of three components in a ratio of 67:10:23. Isolation by this method afforded the pure trienes which were characterized as **43**, **42**, and **38**, respectively.

For **43** (t_{ret} 13.5 min): $\nu_{\text{max}}^{\text{neat}}$ 3025, 3010, 2970, 2945, 2920, 2860, 760, and 714 cm^{-1} (all strong); $\lambda_{\text{max}}^{\text{isooctane}}$ 220 sh nm (ϵ 2470); calcd for $\text{C}_{10}\text{H}_{14}$ *m/e* 134.1095, found 134.1097; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.25–5.8 (m, 5, olefinic), 2.66 (t, $J = 7$ Hz, 2, bisallylic), 1.9–2.15 (m, 4, allylic), and 1.75 (br s, 3, methyl).

Anal. Calcd for $\text{C}_{10}\text{H}_{14}$: C, 89.49; H, 10.51. Found: C, 89.50; H, 10.66.

For **42** (t_{ret} 15.5 min): $\nu_{\text{max}}^{\text{neat}}$ 3010, 2965, 2930, 755, and 677 cm^{-1} (all strong); $\lambda_{\text{max}}^{\text{isooctane}}$ 219 sh nm (ϵ 2900); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.2–5.9 (m, 5, olefinic), 2.7 (d, $J = 7$ Hz, 2, bisallylic), 1.8–2.1 (m, 4, allylic), and 1.75 (br s, 3, methyl); calcd for $\text{C}_{10}\text{H}_{14}$ *m/e* 134.1095, found 134.1097.

Anal. Calcd for $\text{C}_{10}\text{H}_{14}$: C, 89.49; H, 10.51. Found: C, 89.58; H, 10.48.

For **38** (t_{ret} 18 min), spectra were superimposable upon those of sample isolated above.

Reduction of 3-Methyl-*cis*-bicyclo[6.1.0]nonatriene (34). When 97.7 mg (0.75 mmol) of **34** was treated as above with potassium (59 mg, 1.51 mg-atoms) in liquid ammonia (10 ml), there was isolated 75 mg of an oil, analysis of which by vpc indicated a two-component mixture. Interpretation of the t_{ret} of these compounds suggested that they were **42** (13%) and **43** (87%), and the assumption was confirmed by isolation and direct comparison of the relevant spectra with those given earlier.

Reduction of 4-Methyl-*cis*-bicyclo[6.1.0]nonatriene (35). From 77 mg (0.58 mmol) of **35** and 45.4 mg (1.16 mg-atoms) of potassium, there was obtained, after reaction as predescribed, 55 mg of a vpc homogeneous oil identified as **48**: $\nu_{\text{max}}^{\text{neat}}$ 3020, 3000, 2960, 2940, 2910, 2855, and 750 cm^{-1} (all strong); $\lambda_{\text{max}}^{\text{isooctane}}$ 226 nm (ϵ 5350); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.3–6.0 (m, 5, olefinic), 2.72 (d, $J = 7.0$ Hz, 2, bisallylic), 1.9–2.15 (m, 4, allylic), and 1.82 (t, $J = 1$ Hz, 3, methyl).

Anal. Calcd for $\text{C}_{10}\text{H}_{14}$: C, 89.49; H, 10.51. Found: C, 89.52; H, 10.29.

Reduction of *trans*-Bicyclo[6.1.0]nonatriene (4). Reaction of 70 mg (0.593 mmol) of **4** with potassium (50 mg, 1.28 mg-atoms) in dry liquid ammonia (5 ml) at -78° for 15 min, followed by quenching of the red-colored reaction mixture with methanol (0.15 ml), afforded 62 mg of an oil. Purification by vpc techniques (6 ft × 0.25 in. 5% PPGA, 65°) led with poor recovery to **52**: $\nu_{\text{max}}^{\text{neat}}$ 3005, 2890, 1430, 1075, 1030, and 630 cm^{-1} (all strong); $\lambda_{\text{max}}^{\text{isooctane}}$ 234 nm (ϵ 9300); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.2–5.8 (m, 4, olefinic), 2.75 (br d, $J = 17.5$ Hz, 2), 1.35 (br d, $J = 17.5$ Hz, 2), and 0.4–0.75 (m, 4); calcd for C_9H_{12} *m/e* 120.0939, found 120.0941.

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