Formation of Monohomocyclooctatetraene Dianions in Liquid Ammonia. Analysis of the Nucleophilic Reactivity of the Cyclononatrienyl Anions Generated Upon Solvent Protonation

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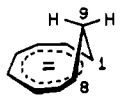
Abstract: Reactions of the cyclononatrienyl anion (**3**) and its 8-methyl (**20**) and 8,8-dimethyl (**4**) homologues, which are generated via in situ protonation by solvent ammonia of homocyclooctatetraene dianions, are shown to proceed at C(3) and C(5) which are the sites of highest electron density (^{1}H NMR analysis). For the parent system, these sites are equivalent by symmetry, but this is not so for its congeners, and the question of regioselectivity is addressed. Methanol quenching studies at −70 °C have now shown that **20** is attacked by a proton preferably at C(3) (ratio 3:1), whereas **4** undergoes preferential attack at C(5) (by factor of 7). However, methylation of the 8,8-dimehylcyclononatrienyl anion predominates at C(3) (1.97:1). The alkylation of **20** introduces the added feature of stereoselectivity. From the experimentally determined composition of **25** (40–42%), **26** (22–25%), **27** (27–33%), and **28** (5%), the following points emerge: (a) the 3:1 preference for protonation at C(3) is reduced during methylation to approximately 1:1; (b) the alkylation at C(3) proceeds with rather high stereoselectivity (8:1) for the trans isomer; (c) bonding of the methyl group to C(5) is almost statistical from the cis and trans directions; and (d) crossover in regioselectivity operates in the two reaction types opposite to the 8,8-dimethyl example. Structural assignments in all instances were made on the basis of catalytic hydrogenation, independent unequivocal synthesis of the resulting cyclononane derivative, and suitable application of ^{13}C NMR spectroscopy. The results are interpreted in terms of the exothermicity of the specific reaction and the degree of bonding accessibility available in the various low-energy conformations of the carbanions as they experience $sp^2 \rightarrow sp^3$ rehybridization. By variable temperature ^{1}H and ^{13}C NMR studies of certain *cis*-1,3,6-cyclononatriene products, it has proven possible to assess those conformational factors and differing steric strains which gain importance in these cyclic polyolefins.

In monohomoaromatic anions, an sp^3-hybridized carbon is inserted into a cyclic framework of $p\pi$ orbitals containing $(4n + 2)$ electrons with the result that the topology of the system no longer approaches planarity.[2] This conformational feature arises because the two ring members immediately flanking the saturated carbon must, for the purpose of maintaining electronic delocalization, suitably cant their p orbitals to achieve overlap. In certain cases, this distortion can be expected to introduce substantial conformational strain into the molecule. An example is the monohomocyclooctatetraene dianion (**1**)[3-5] which does not adopt the relatively strainless conformation **2** due to poor conjugative overlap in the resulting



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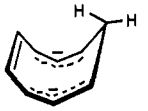

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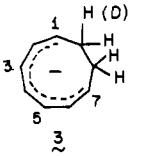
π network, but more closely approximates **1** where there is some twist present about each of the double bonds.[6] Clearly, a delicate interplay between minimization of angle and torsional strain on the one hand and maintenance of maximum $p\pi$ overlap is constantly in force.

Recently, the generation of **1** by alkali metal reduction of *cis*-bicyclo[6.1.0]nona-2,4,6-triene in liquid ammonia at −65 to −78 °C was shown to lead by rapid protonation (NH_3) or deuteration (ND_3) to the parent cyclononatrienyl anion (**3**).[4,5] In actuality, the ^{1}H NMR spectrum of **1** could not be recorded under these conditions due to its exceptionally facile conversion to **3.** However, mono- and dimethyl substitution of **1** and C(9) did suffice to retard the rate of proton (deuterium) transfer from solvent ammonia enough to permit direct spectral examination of the derived dianions.[5]

The observation of a lone signal for the four saturated protons (H(8),H(9)) in **3** and the relatively low value of its H(2),H(3) coupling constant (7.6 Hz) has led Staley and Pearl to conclude that **3** adopts a nonplanar conformation which experiences rapid flipping on the NMR time scale.[7] The ^{1}H spectral data for **4** are, in contrast, best accommodated by the



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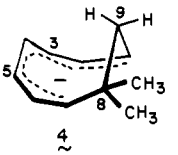

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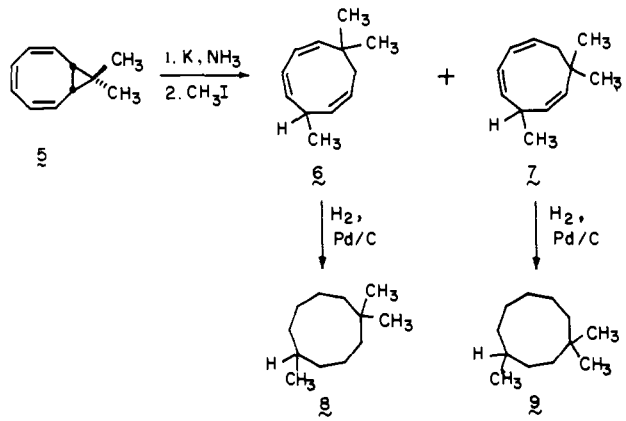
illustrated shallow twisted tub conformation having C(9) bent significantly out of plane and the gem-dimethyl groups bonded to C(8) (less sterically crowded) in a way which staggers them with respect to both H(7) and the H(9) pair.[7] Presumably, the monomethyl derivative would exhibit intermediate behavior.

Remarkably little is known about the chemistry of cyclic delocalized anions such as **3** and **4** other than the fact that protonation occurs at C(3) and C(5). In unlabeled **3,** these two sites are chemically equivalent, but in **4** this is not the case, and the question of site selectivity can be raised. Furthermore, in the monomethyl series regioselectivity *and* stereoselectivity both gain importance. Our limited knowledge of such systems made it appear that a study of the nucleophilic behavior of cyclononatrienyl anions could be quite informative. In this paper we report a detailed analysis of the products derived from protonation and methylation of various cyclononatrienyl anions, synthetic access to which was gained by the route previously described.[5]

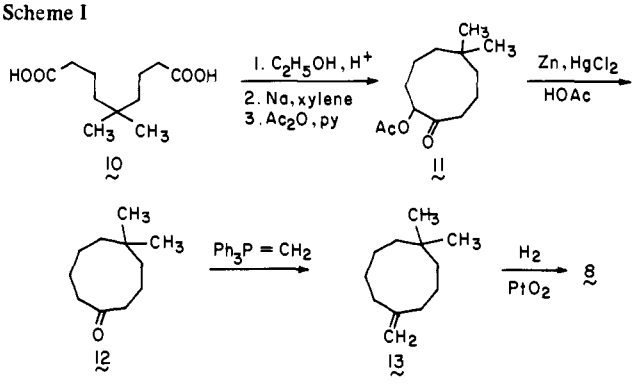
Results

Behavior of the 8,8-Dimethylcyclononatrienyl Anion. Addition of 2 g-atom equiv of potassium to 9,9-dimethylbicyclo[6.1.0]nona-2,4,6-triene (**5**) in liquid ammonia solution at −78 °C gradually led to development of the dark red coloration characteristic of **4** during 35 min. Treatment of this solution with excess methyl iodide gave rise to two isomeric $C_{12}H_{18}$



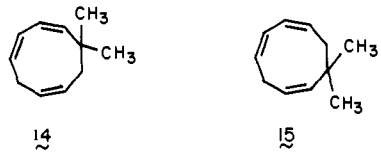
products in the ratio of 1.97:1. The major component (**6**) was a colorless liquid which exhibited (in $CDCl_3$) three well defined methyl signals [δ 1.15 (s), 1.05 (d, J = 6.5 Hz), and 0.85 (s)] under ordinary conditions. Rather comparable features were displayed by minor product **7** [δ 1.22 (s), 1.10 (s), and 1.05 (d, J = 6.5 Hz)]. Particularly interesting is the fact that **6** possesses a 9-methyl group which is substantially more shielded than either of the geminate methyl substituents in **7.** Individual catalytic hydrogenation of these trienes gave a single product in each instance which were considered to be the 1,1,4- and 1,1,5-trimethylcyclononanes. A distinction between these isomers was achieved by unequivocal synthesis of the latter as outlined in Scheme I beginning with δ,δ-dimethylazelaic acid (**10**).[8] Conversion to acetoxy ketone **11** served not only to facilitate purification of the acyloin but also to render the subsequent reduction[9] to ketone **12** more efficient. The major product is accordingly derived from alkylation of **4** at C(3).

Scheme I



When the deep red solution of monoanion **4** was quenched by the addition of methanol, a colorless reaction mixture resulted from which two isomeric $C_{11}H_{16}$ products were obtained in a ratio of 1:7. On the basis of their ^1H NMR spectra (see Experimental Section), the two compounds clearly correspond to the pair of triene structures represented by **14** and **15,** although it was not possible by such means alone to distinguish between them. Significantly, both isomers display a set of equivalent methyl groups at 40 °C, an observation which suggests an appreciable degree of conformational flexibility. The individual isomers have proven recalcitrant to isomerization when treated with catalytic quantities of base or acid under various conditions, and accordingly it has not been possible to establish unequivocally whether the observed ratio is the result of kinetic or thermodynamic control. However, on the basis of the data which follow and the seemingly large barrier which separates **14** from **15,** it appears likely that kinetic control is operative.

In Table I, the ^{13}C NMR spectra of **14** and **15** are compared directly with those of the lesser substituted 1,3,6-cyclononatrienes **16, 17,** and to the more substituted trimethyl species **6** and **7.** Analysis of the shift data provided by their saturated



carbon atoms has been found to serve convincingly for structural assignment. Thus, the 5-methyl derivative (**17**) is characterized by four high field signals. By means of its gated decoupled spectrum, the methyl group was shown to be responsible for the 21.47 ppm peak (quartet) and C(5) to be the source of the 33.45 ppm absorption (doublet). The remaining two signals at 24.82 and 29.51 ppm (triplets) were provisionally assigned to C(8) and C(9), respectively. That C(8) should appear upfield of C(9) was considered consistent with bonding of the latter to a 1,3-diene unit. Further ^{13}C NMR spectra of other structurally known cyclononatrienes indicates this initial assumption to be true (see later).

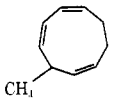
The emergent pattern for less prevalent dimethylcyclononatriene **14** consists of four absorptions at 37.88, 37.79, 30.30, and 29.30 ppm at 35 °C. The 29.30 signal is readily assigned to C(5) on the basis of its characteristic position downfield from Me_4Si and its triplet nature in the gated decoupled spectrum (i.e., full ^1H-^{13}C coupling). The pair of methyl groups is responsible for the 30.30 ppm peak which is broadened at 35 °C due to proximity to coalescence (vide infra). The quaternary carbon appears at 37.88 ppm (reduced intensity due to low NOE) and the second methylene carbon at 37.79 ppm. By similar techniques, the pattern of absorptions displayed by the major component (**15**) could be analyzed as follows: 29.46 (C_5), 31.40 (methyls), 37.71 (quaternary), and 42.52 ppm (CH_2). Placement of the geminal methyl groups on the cyclononatriene frame could now be inferred by examining their effect upon the β carbon atoms. Using 1,1-dimethylcyclohexane as a model,[10] for example, β shieldings should approximate +12.7 ppm. Given this parameter, **14** is seen to best accommodate the 9,9-disubstitution plan (β = +13.30) while **15** can be judged to be the 8,8-dimethyl derivative (β = +13.06) with a reasonable degree of confidence. Reversal of these assignments would generate a β value for **15** (+8.25 ppm) which falls well outside the normal range exhibited by such alicyclics.[11]

Unequivocal confirmation of these assignments was derived from comparison of the above shifts and additive parameters with those recorded for known structures **6** and **7.** In these cases, the C(5) signals appear at 33.32 and 33.26 ppm, in complete accord with the value previously recorded for **17.** More significant is the near identity of the C(8) shifts in these trimethyl derivatives (37.85 and 37.20) and the greater downfield shifting of C(9) in **7** (42.62) than in **6** (37.85). The remarkably close parallelism between the dimethyl and trimethyl series (Table I) substantiates our earlier assumption that a greater shielding effect is exerted at C(9) than at C(8).

With the establishment of **15** as the major protonation product, it was clear that matters had taken a somewhat unexpected turn. Protonation of **4** occurs preferably at C(5), in contradistinction to the higher reactivity of C(3) in methylation.

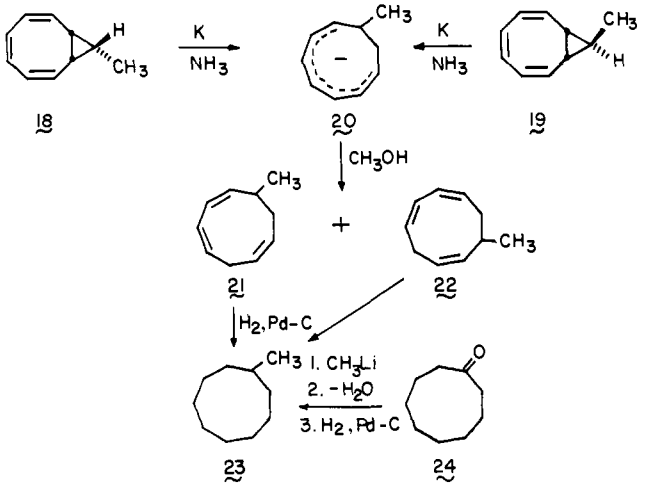
Nucleophilic Character of the 8-Methylcyclononatrienyl Anion. Synthesized by reduction of *syn-* (**18**) or *anti*-9-methylbicyclo[6.1.0]nonatriene (**19**) with potassium in liquid ammonia,[5] the 8-methylcyclononatrienyl anion (**20**) was found to experience low-temperature protonation (methanol) with formation of two products in a 3:1 ratio. It is immediately noted that there is one resonance signal in both of these trienes which lies within 0.9 ppm of the position predicted by an α substituent parameter of +6.0.[11] As there is no ambiguity attached to assignment of the carbon atom bearing one proton (doublet

Table I. Carbon-13 Shieldings of Several 1,3,6-Cyclononatrienes (22.63 MHz, $CDCl_3$ Solution)

Compd	Temp, °C	Olefinic carbons	C (5)	C (8)	C (9)	Methyl carbons
 16	35	132.73, 131.59, 126.85, 126.31, 125.82, 125.66	29.62[a]	24.49	29.46[a]	
 17	35	134.45, 133.64, 132.78, 128.73, 126.09, 123.23	33.45	24.82	29.51	21.47
14	50	143.19, 128.41, 127.68, 126.55, 126.14, 123.80	29.30	37.85[b]	37.85[b]	30.38,[b] 30.38[b]
	35	143.22, 128.38, 127.65, 126.52, 126.41, 123.77	29.30	37.79	37.88	30.30,[b] 30.30[b]
	0	143.12, 128.06, 127.41, 126.31, 126.20, 123.63	29.05	37.44	37.69	*c*
	−24	143.19, 127.92, 127.28, 126.20, 126.09, 123.61	28.97	37.31	37.61	34.37, 25.76
	−60	143.22, 127.71, 127.11, 125.98,[b] 125.98,[b] 123.58	28.84	37.12	37.50	34.50, 25.33
15	35	140.12, 130.14, 127.55, 126.14, 124.52, 122.96	29.46	37.71	42.52	31.40,[b] 31.40[b]
	−2	139.74, 130.14, 127.47, 125.87, 124.26, 122.77	29.30	37.71	42.30	31.32,[b] 31.32[b]
	−24	139.55, 130.22, 127.44, 125.71, 124.17, 122.66	29.23	37.77	42.19	31.99, 30.56
	−70	139.36, 130.51, 127.33, 125.39, 124.20, 122.53	29.08	37.93	41.98	31.83, 30.59
6	45	143.76, 133.94, 133.43, 126.06, 125.15, 124.07	33.61	38.06	38.17	33.78, 26.92, 21.28
	35	143.79, 133.59, 133.13, 125.66, 124.82, 123.90	33.32	37.85[b]	37.85[b]	*c*, 21.28
	20	143.79, 132.91,[b] 132.91,[b] 124.50,[b] 124.50,[b] 123.82	33.15	37.58	37.69	*c*, 21.04
	10	143.95, 132.89,[b] 132.89,[b] 124.55,[b] 124.55,[b] 123.85	33.05	37.63	38.09	35.93, 23.39, 20.88
	−15	144.08, 132.62,[b] 132.62,[b] 124.42, 124.01, 123.88	32.86	37.47	37.93	36.01, 23.25, 20.77
	−60	144.06, 132.38,[b] 132.38,[b] 124.28, 123.88, 123.69	32.70	37.34	37.58	36.01, 23.01, 20.72
7	45	138.58, 133.37, 131.03, 130.41, 126.74, 125.69	33.51	37.23	42.92	3307, 30.03, 22.74
	35	138.12, 133.00, 130.65, 130.38, 126.36, 125.66	33.26	37.20	42.62	32.64, 30.24, 22.79
	−24	136.58, 131.92, 130.60, 129.79, 126.36, 125.25	33.02	37.82	42.41	31.70, 30.94, 23.15
	−60	136.50, 131.97, 130.81, 129.62, 126.14, 124.98	32.94	37.90	42.22	31.69, 30.83, 23.15

[a] These values may be interchanged. [b] Superimposed signals. [c] No signals visible because of coalescence.

in the off-resonance mode), the close agreement is taken as basis for assigning **21** as the major product of protonation. Further substantiation is gained by assessing the β shielding



data in **21** and **22** which amount to +9.91 and +9.52 ppm, respectively. These methyl interactions with the ring structure agree closely in magnitude with existing precedent[11] and make it possible to rule out the alternative structural representations which would generate such widely disparate β values as +4.94 and +14.49 ppm. Accordingly, **20** favors protonation at C(3).

Methylation of this monoanion with methyl iodide proceeded smoothly to give four dimethylcyclononatrienes which were separated by gas chromatography on silver nitrate-glycerol columns at 65 °C. As judged from various runs beginning either with **18** or **19**, the compositions of these mixtures fall within the following limits (products cited in order of elution): 40–42% of **25**, 22–25% of **26**, 27–33% of **27**, and 5% of **28**. Using the approximate substituent parameters determined from the above discussion, **25** and **28** were tentatively classified as 1,5-dimethyl derivatives. The shifts of the saturated carbons in **26** and **27** were likewise in full agreement with their designation as 1,4-disubstituted stereoisomers (Table II).

Full structural assignment to this set of compounds was founded upon catalytic hydrogenation of each pure isomer over

Table II. Carbon-13 Shieldings of 8- and 9-Methyl Substituted 1,3,6-Cyclononatrienes (22.63 MHz, $CDCl_3$ Solution, 35 °C)

Compd	Olefinic carbons	C(5)	C(8)	C(9)	Methyl carbons
21	139.17, 130.54, 126.60, 126.17, 125.87, 123.26	29.59	34.40	35.93	23.01
22	138.78, 131.38, 126.33, 125.90, 125.73, 123.85	29.75	31.40	38.98	23.39
25	140.09, 134.78, 133.64, 127.92, 123.34,[a] 123.34[a]	33.45	34.85	36.50	23.93, 21.26
26	136.37, 134.16, 131.62, 131.13, 126.01, 123.28	33.88	31.56	39.44	23.79, 21.53
27	133.37, 133.21, 131.78, 131.55, 126.04, 125.42	33.59	33.10	36.80	22.69, 21.53
28	137.72, 132.40, 132.05, 126.90,[a] 126.90,[a] 123.61	34.18	34.37	34.94	22.88, 21.29

[a] Superimposed signals.

platinum at atmospheric pressure, and independent unequivocal synthesis of three of the four possible dimethylcyclononanes. These reductions were uneventful except in the case of **26** which in reactions of short duration gave a homogeneous symmetrical tetrahydro product (**30**). On the basis of its ^1H NMR spectrum which displayed absorptions at δ 5.07 (dd, J = 6.5 and 2 Hz, olefinic, 2), 2.3–2.7 (m, allylic, 2), 1.2–1.7 (m, methylenes, 10), and 1.95 (d, J = 6 Hz, methyls, 6), the monoolefin was unmistakably identified as a member of the 1,4-dimethyl subgroup. A convincing distinction between the cis and trans disposition of the alkyl substituents was not possible at this stage because of the symmetry (cis, C_s; trans, C_2) inherent in the two structures.

The independent synthesis of **31** and **32** was effected from the known bicyclo[5.2.1]decan-10-one[12] (**34**, Scheme II). Initial attempts to ring expand this ketone with diazomethane,[13] in the presence of such catalysts as boron trifluoride etherate[14] and lithium chloride[15] which are reputed to exert an activating influence, proved totally ineffective. Likewise, attempted conversion to the cyanohydrin according to the procedure of Lumb and Whitham[16] returned only starting material. In contrast, **34** did react with dimethylsulfonium methylide[17] to provide a mixture of expoxides **35** which underwent ring opening with sodium amide in liquid ammonia.[17,18] Nitrous acid deamination of **36** did give desired ketone **37**, but returned **34** as well by a relatively uncommon retrogression (ratio 2.6:1). Attempts to convert **37** to **38** either by methyllithium induced decomposition of the derived tosylhydrazone[19] or by dehydration of the alcohol with Burgess' reagent[20] produced only trace amounts of this olefin. Rather, an isomeric structure believed to be the bridgehead olefin was isolated, although no definitive proof of structure was made. The proper replacement of the carbonyl group by a double bond was achieved by pyrolysis[21] of the thiocarbonate O-esters of the epimeric alcohol mixture. The subsequent reductive ozonolysis sequence is well precedented.[22]

Scheme II

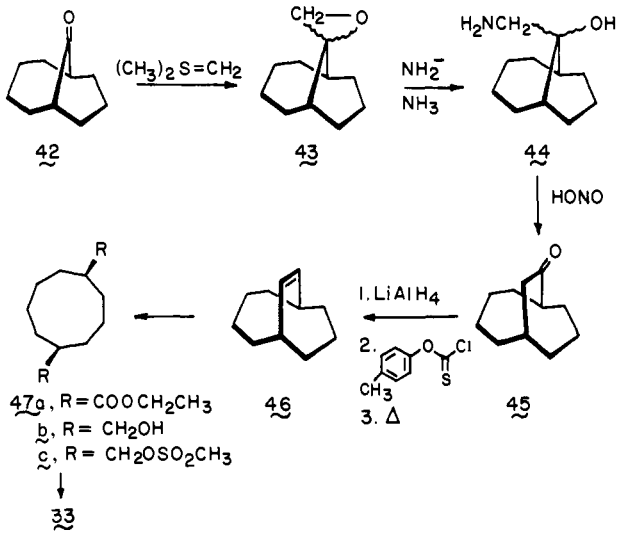
Access to authentic **33** was gained in an entirely comparable manner from bicyclo[4.3.1]decan-10-one[23] (**42**, Scheme III). Because of anticipated close similarities in the ^1H NMR spectra of **29** and **31–33**, recourse was made to Fourier transform techniques. Under these conditions of resolution, the two peaks which characterize the methyl doublet in all four saturated hydrocarbons can be easily distinguished on the basis of their chemical shifts alone (Table III). By this method, it was possible to demonstrate the correctness of the positional and stereochemical assignments for **26–28.** The structure of **25** follows by the process of elimination.

The several significant points which now emerge are: (a) the 3:1 preference for protonation of **20** at C(3) is greatly reduced during methylation (only 45–47% of **25** and **28**); (b) alkylation at C(3) proceeds with rather high stereoselectivity (8:1) for the trans isomer; (c) a comparable level of stereocontrol does not operate during alkylation at C(5), although the isomer ratio is slightly enriched in the trans form; (d) crossover in regioselectivity operates in the opposite direction to the 8,8-dimethylcyclononatrienyl anion example.

Table III. ^{1}H NMR Shift Data for the Dimethylcyclononanes (MHz, $CDCl_3$)

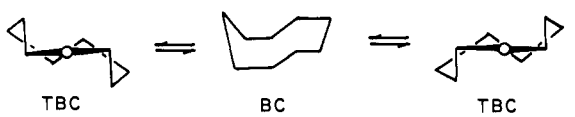
Compd	Methyl signal, ppm
29	0.909, 0.840
31	0.892, 0.823
32	0.867, 0.796
33	0.906, 0.835

Scheme III



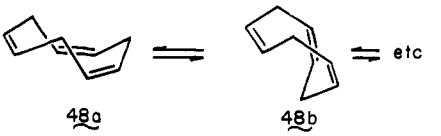
Dynamic Behavior of Certain *cis*^{3}-1,3,6-Cyclononatrienes. To the present time, information concerning conformational constraints in nine-membered rings has been derived chiefly from theoretical calculations,[24,25] x-ray diffraction studies,[26] and variable-temperature NMR investigations[27] of fully saturated derivatives. The combined weight of evidence indicates that the three C_2 conformations of cyclononane are of lower energy than the three C_s forms. From among the first triad, the twist-boat-chair (TBC) conformation is adopted by cyclononane and its 1,1-dimethyl and 1,1,4,4-tetramethyl derivatives in solution.[27] In contrast, the twist-chair-boat (TCB) is adopted by cyclononylamine hydrobromide[26a] and the cyclononanone mercuric chloride complex[26b] in the crystalline state, a likely reflection of lattice force constraints rather than inherent conformational stability of this form.

Although incremental methyl substitution of the cyclononane ring does not disturb the relative ordering of conformational stabilities, it does serve to increase the energy barrier of that conformational exchange process which interconverts one low-energy TBC form into its enantiomer (via the boat-chair



conformation). For 1,1-dimethylcyclononane ($\Delta G^{\ddagger}$ = 9 kcal/mol), the gem-dialkyl effect introduces a barrier significantly greater than that encountered in the parent hydrocarbon ($\Delta G^{\ddagger}$ = 6 kcal/mol), but much less than the one found in the 1,1,4,4-tetramethyl derivative (20 kcal/mol).[27]

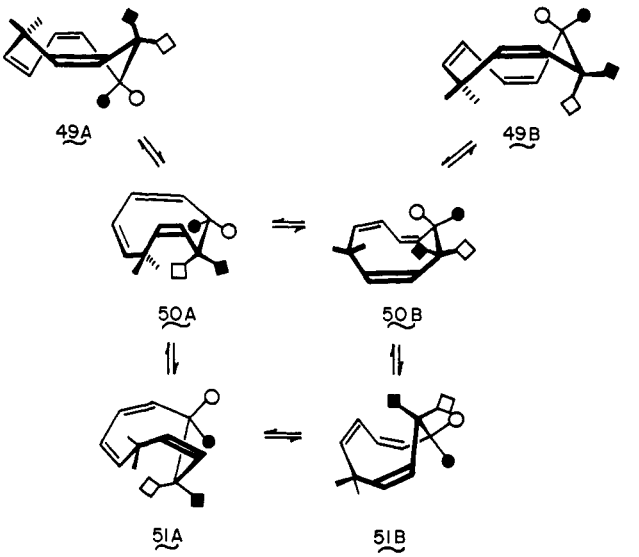
The gradual introduction of double bonds into the C_9 frame does not result in comparable stepped increases in strain. Thus, both *cis*- and *trans*-cyclononene, and the 1,5-dienes as well, are less strained than cyclononane, while *cis*^{3}-1,4,7-cyclononatriene (**48**) is 3.2 kcal/mol more strained.[28] X-ray analysis has determined **48** to have crown structure **48a** in the crystalline state;[29] in solution, interconversion between **48a** and several half-crown conformations such as **48b** occurs with $\Delta G^{\ddagger}$ = 14.5 kcal/mol.[30]



These DNMR studies of **48** represent to this time the only reference point for the conformational behavior of C_9 cyclic polyolefins. Since no systematic investigation of a series of cyclononatrienes had yet been undertaken, the dynamic NMR behavior of the several *cis*^{3}-1,3,6-cyclononatrienes available from the current study was investigated. With the instrumentation at our disposal, temperature dependence in the range +130 to −70 °C was best observed in the case of the four derivatives possessing a geminal dimethyl grouping (**6, 7, 14,** and **15**).

Representative ^{13}C NMR data for these four trienes at various temperatures have already been compiled in Table I. The corresponding ^{1}H NMR spectra (methyl proton regions only) are illustrated in Figures 1-4. The two types of spectra for **14** and **15** reveal that the geminal dimethyl groups become equivalent near 0 °C. The conformational process which probably accounts for this facile site exchange involves interconversion of structure **49A** into the different but isoenergetic form **49B** by transient passage through the more highly folded forms **50A** → **51A** → **51B** → **50B,** or more simply through **50A** → **50B** (Scheme IV). The scheme is applicable to the 8,8- and

Scheme IV



9,9-dimethyl substitution plans, the dynamic NMR effect arising in the two structures because of "mutual exchange" behavior of the form

$$A_3B_3 \underset{k_R}{\overset{k_F}{\rightleftharpoons}} B_3A_3$$

which operates concurrently at C(8) and C(9). Upon inspection of Dreiding models, it becomes apparent that the flatter, more open forms **49A** and **49B** enjoy a minimum of nonbonded steric interaction and are presumably the more stable. This conclusion receives additional support from two relevant experimental observations. Firstly, the ^{1}H and ^{13}C data for the respective "frozen" conformations ($t < -60$ °C) of the two isomers reveal not only the magnetic nonequivalence of the geminal methyl groups, but show further that the shielding effects operating on the methyl pair in **14** (Δ ^{13}C = 9.17 ppm, Δ ^{1}H = 14 Hz) are significantly more disparate than those prevailing in **15** (Δ ^{13}C = 1.24 ppm, Δ ^{1}H = 12 Hz). These findings are consistent with adoption by **14** and **15** of conformations **52** and **53,** respectively. The key structural feature in

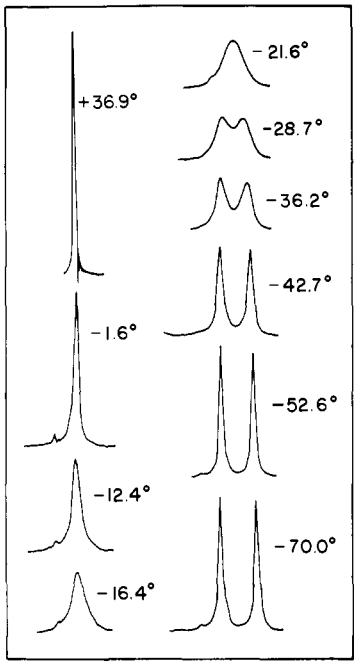


Figure 1. Upfield portions of the 60-MHz spectra of **14** in $CDCl_3$ at various temperatures.

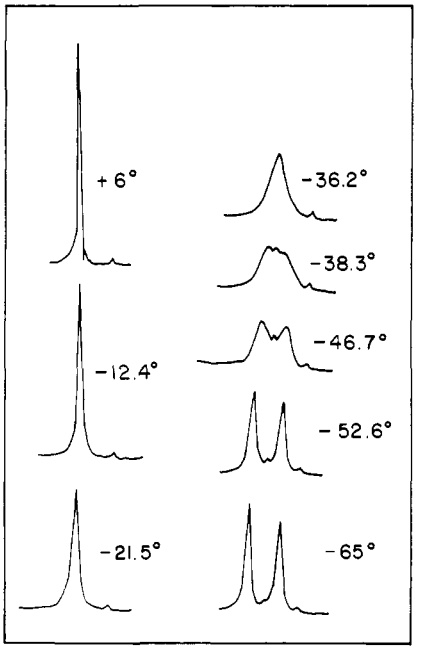
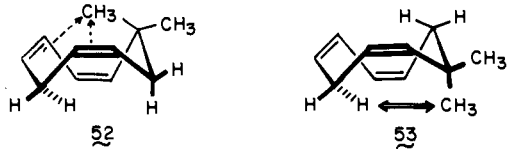


Figure 2. Upfield portions of the 60-MHz spectra in **15** in $CDCl_3$ at various temperatures. The very weak additional signals have a constant line shape over this temperature range and are attributed to an impurity.



52 **53**

52 is the projection of the "inside" methyl group into the shielding region of at least two double bonds. In **53,** the alkyl substituents are positioned in more similar magnetic environments.

The second point concerns the somewhat lower coalescence temperature (~10 °C) exhibited by **15** relative to **14.** This rather small difference (~0.6 kcal/mol) can be viewed to be a reflection of added resistance to attainment of final frozen conformation **53** due to steric compression between endo H(5) and the "inside" C(8) methyl. Additional energy differential could arise because of a decreased barrier to twisting of the $>C(CH_3)_2$ moiety when bonded to the isolated double bond rather than the conjugated diene unit.

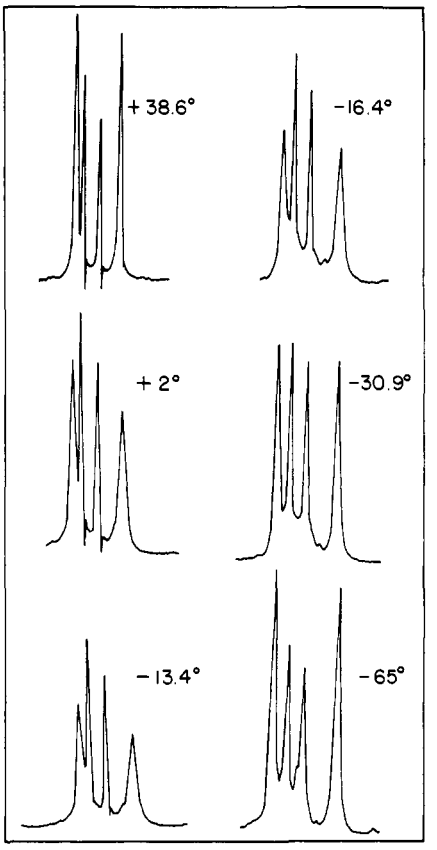


Figure 3. Upfield portions of the 60-MHz ^1H spectra of **6** in $CDCl_3$ at various temperatures.

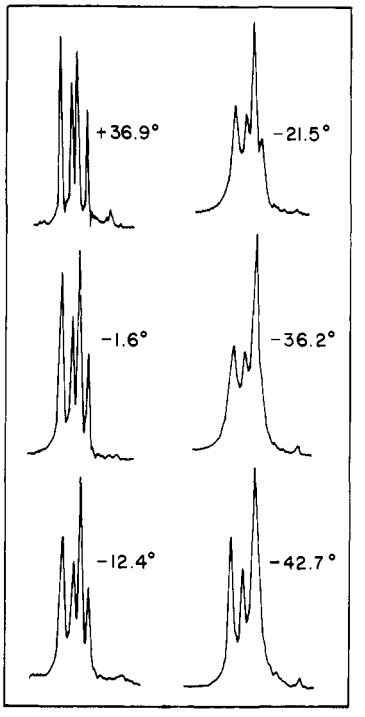


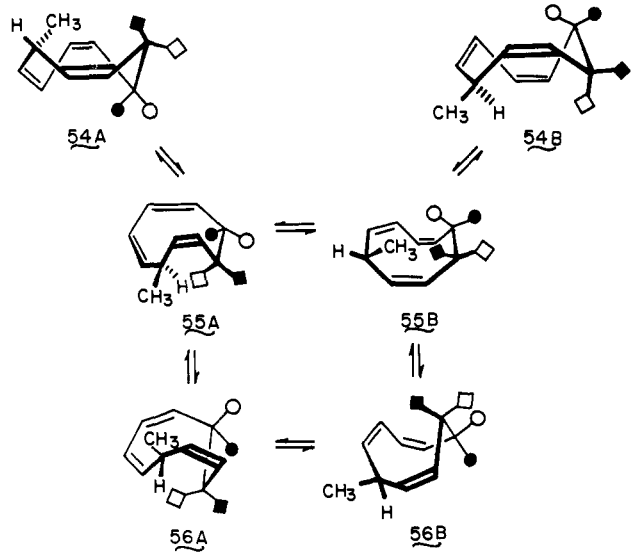
Figure 4. Upfield portions of the 60-MHz spectra of **7** in $CDCl_3$ at various temperatures.

Either ^1H spectrum consists of two singlets which coalesce to one line as the temperature increases and can be treated mathematically as a "two site" exchange process. Since J_{AB} is very small and all A's as well as all B's are magnetically equivalent, this interaction can be ignored. In the present instance, DNMR line shape analysis[31,32] is based on the further assumption that a thermodynamic preference for spin system A_3B_3 does not prevail over B_3A_3 or some other possibility. This condition gains importance in the present instance because of the likelihood that the actual exchange process is more complex than a simple two-site phenomenon (Scheme IV). However, although a six-site exchange may actually be involved, the several rate processes are clearly not comparable in magnitude since only one set of intense signals is encountered in the low-temperature ^1H and ^{13}C spectra. Accordingly, the assumption is made that a single conformational form contributes to the spectrum in each instance.

The computer generated spectra agreed well with those determined experimentally. With the help of the Eyring equation, the $\Delta G^{\ddagger}_{236°}$ for **14** was determined to be 12.9 kcal/mol. For **15,** the magnitude of $\Delta G^{\ddagger}_{236°}$ decreased somewhat to 11.9 kcal/mol.

Assessment of the behavior of trimethyl trienes **6** and **7** (Table I; Figures 3 and 4) immediately reveals that the geminal methyl groups now do not become equivalent over the temperature range examined. This phenomenon results because the presence of a substituent at C(5) precludes the possibility of achieving an identity in magnetic environment (Scheme V).

Scheme V



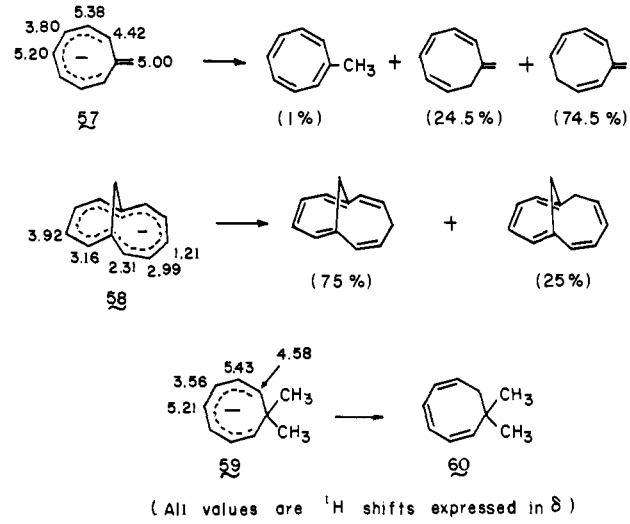
Furthermore, the third methyl introduces steric crowding into a number of the available conformations and imposes certain energy barriers which were not previously of consequence. The presence of these added nonbonded interactions means that the C(5) methyl group exerts some control on the conformational preferences of **6** and **7.**

At +50 °C, the geminal methyl carbons of **6** are separated by 6.86 ppm, and this difference is approximately doubled at −60 °C (12.76 ppm). The ^1H spectra reflect a similar trend: $\Delta\delta$ = 17 Hz at +38.6 °C; $\Delta\delta$ = 25.7 Hz at −65 °C. In contrast, chemical shift changes for C(5) and the 5-methyl group are minimal over this range. On this basis, we conclude that form **54B** which is likely adopted by the molecule at low temperature is thermodynamically favored. The differences in methyl shielding are explainable as before.

Triene **7** does not parallel **6** in its spectral response to temperature effects. At +45 °C, its geminal methyl carbons differ by 3.04 ppm. Upon cooling, this gap is *reduced* to 0.86 ppm because of upfield shifting by the more shielded methyl. Unusual effects prevail in the ^1H spectra where cooling causes both the 5-methyl doublet and the lower field methyl singlet to broaden measurably. But whereas the first of these absorptions is not altered in its chemical shift, the second sharpens upon further cooling and ultimately appears 3.5 Hz to lower field. The higher field methyl singlet remains a sharp signal throughout this entire transition.

Discussion

From a less than systematic investigation of the degree of control that electron density can exert upon the reactivity of cyclic delocalized carbanions, there is seen to prevail a general parallelism between negative charge density and reactivity.[33] For example, the methylenecyclooctatrienyl (**57**)[34] and bicyclo[5.4.1]dodecapentaenyl anions (**58**)[35] both experience



quenching by pentane–water with formation of mixtures dominated by that product arising from protonation at the most electronically shielded carbon atom. But exceptions can be found as, for example, the conversion of the 8,8-dimethylcyclooctatrienyl anion (**59**) chiefly (97%) to **60** (although in low yield).[36]

The behavior of the cyclononatrienyl anions examined in the present study closely parallels that of **57** and **58,** the observed preferential bonding to C(3) and C(5) according fully with the high field positions of the ring protons at these sites (for **3:** δ 3.39; for **4,** 3.23 and 3.06, respectively).[5,7] However, it must be emphasized that attempts to extrapolate regioselectivity considerations beyond this point are not at all justified. Thus, the 7:1 predominance of **15** over **14** which arises upon methanol quenching of **4** could be construed as an indication that site selectivity is fully controlled by the enhanced charge density prevailing at C(5). However, the data do not demand this conclusion, and in fact monomethyl analogue **20** is preferably attacked at C(3) (3:1 selectivity) under comparable conditions.

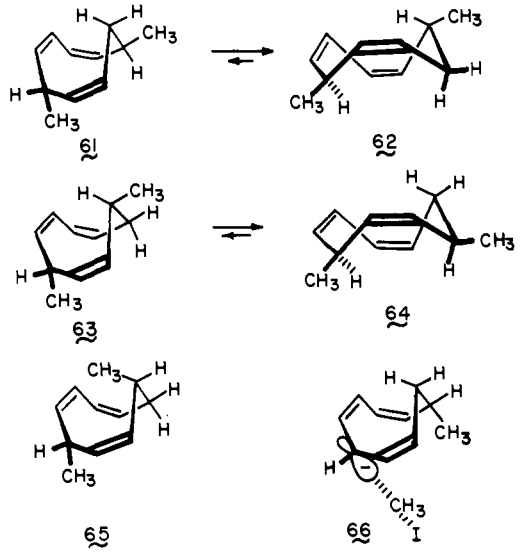
Since both reactions are highly exoenergetic, the transition states will be closer in structure to the carbanions than to the triene products[37] with the possible involvement of thermodynamic control during protonation being rather remote. However, in assessing the source of this experimental dichotomy, it is relevant to consider the rather different conformations which are likely adopted by these carbanions. In the case of **4,** the ^1H NMR data reveal a high degree of twisting about the C(8)–C(9) bond, this torsion conveying to C(3) a degree of untoward steric shielding which cannot be present to the same extent in **20.** Accordingly, the reversal of the reactivities of C(3) and C(5) in these carbanions could owe its origin simply to intrinsic conformational differences.

Methylation of **4** and **20** must occur further along the re-

action coordinate and will expectedly involve a more substantial structural reorganization of the carbanion frames. At the experimental level, the alkylations should therefore reflect closer adherence to thermodynamic control, with product ratios being directed more by steric strain relief, residual $p\pi$ overlap, and the other factors which effect the relative stabilities of the methylated *cis*[3]-1,3,6-cyclononatrienes. As judged from the DNMR behavior of **14** and **15,** the 9,9-dimethyl substitution plan introduces less nonbonded steric congestion in these medium-ring polyolefins than does the 8,8-dimethyl alternative. Since Dreiding models give indication that this energetic discrepancy pervades the great majority of available ground state conformations (Scheme IV; **52** and **53**), we are led to the logical conclusion that **6** enjoys a somewhat greater stability than **7.** If this is correct, the somewhat greater prevalence of **6** in the methylation product mixture (1.97:1) finds adequate explanation in the Hammond postulate.

In a necessarily more intricate extension of this rationale, the conversion of **20** predominantly (40–42%) to **25** can be best understood in terms of the relatively strain-free conformations which can be adopted by this hydrocarbon. Particularly important is the realization that the trans disposition of the two methyl groups likely develops earlier than **62,** and probably at that stage of reaction where product conformation still resembles that of the carbanion, viz. **61** (also consult Scheme V). A cis orientation of the 1,5 substituents is energetically unfeasible in this structural arrangement (given the necessity for "axial" attack) and is reflected in the low percentage composition (5%) of **28** (also see below).

A cis-1,4-dimethyl arrangement as in **26** can similarly be construed from Dreiding models to arise from identical passage through conformation **63** which likewise experiences a minimum of nonbonded strain. Should this be the conformation which develops at the alkylation transition state, the high (22–25%) relative yield of **26** agrees fully with the above thinking. To be consistent, however, our mechanistic rationalization must adopt the further assumption that trans dimethyltriene **27** (found to the extent of 27–33%) is not initially produced in an analogous conformation, but probably results from initial disposition as illustrated by **65**. Although an equivalent possibility exists when the original methyl substituent occupies C(9), the orientation necessarily adopted by this group sterically impedes the requisite approach of methyl iodide from the "underside" (see **66**).



We conclude that the most plausible rationale for the regioselective and stereoselective capture of cyclononatrienyl anions is that which is founded first upon electron density principles, secondly upon the exothermicity of the specific reaction under consideration, and thirdly upon the degree of bonding accessibility to the various low-energy conformations of the carbanion as it begins to experience rehybridization from sp^2 to sp^3 at one of its constituent carbon atoms. Although the present study has provided the most detailed information yet available in this field,[38] it is clear that additional examples must be closely scrutinized to determine the general applicability of these conclusions.

Experimental Section

Melting points and boiling points are uncorrected. Proton magnetic resonance spectra were obtained with Varian A-60A, HA-100, and Bruker HX-90 spectrometers; apparent splittings are given in all cases. Infrared spectra were determined on Perkin-Elmer Model 137 and 467 instruments. Mass spectra were recorded on an AEI-MS9 spectrometer 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.

Reduction of 9,9-Dimethyl-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (5) in Liquid Ammonia. Methyl Iodide Quench. Under a dry nitrogen atmosphere, 1.0 g (6.8 mmol) of **5** was added to a rapidly stirred solution of potassium (0.54 g, 13.8 mg-atom) in anhydrous liquid ammonia (50 ml) cooled to −78 °C. The mixture was stirred for 35 min during which time a red solution of **4** was generated. Methyl iodide (4 ml) was added, ammonia was allowed to evaporate, and the residue was extracted with pentane (3 × 30 ml). The combined organic phases were washed with water (3 × 10 ml), dried, and evaporated. There remained 1.08 g (98%) of pale-yellow oil, VPC analysis of which (18 ft × 0.25 in. 15% XF 1150 on Chromosorb W, 100 °C) indicated the presence of two products in the ratio of 1.97:1. Purification of both components by this technique afforded colorless liquids.

The major component was identified as **6**: ν_{max}^{neat} 3010, 3000, 2965, 2930, 777, 765, and 685 cm^{-1}; $\delta_{Me_4Si}(CDCl_3)$ 5.9–4.9 (m, 6, olefinic), 3.2–2.8 (m, 1, bisallylic), 2.3–1.9 (m, 2, allylic), 1.15 (s, 3, methyl), 1.05 (d, J = 6.5 Hz, 3, methyl), and 0.85 (s, 3, methyl); *m/e* calcd 162.1408, found 162.1410.

Anal. ($C_{12}H_{18}$) C, H.

The minor component proved to be **7**: ν_{max}^{neat} 3005, 2965, 767, 740, and 655 cm^{-1}; $\delta_{Me_4Si}(CDCl_3)$ 5.9–4.75 (m, 6, olefinic), 3.6–3.2 (m, 1, bisallylic), 2.58 (m, 1, allylic), 1.98 (d, J = 6.5 Hz, 1, allylic), 1.22 (s, 3, methyl), 1.10 (s, 3, methyl), and 1.05 (d, J = 6.5 Hz, 3, methyl); *m/e* calcd 162.1408, found 162.1410.

Anal. ($C_{12}H_{18}$) C, H.

Hydrogenation of 6. A solution of 85.8 mg of **6** in methanol (7 ml) containing 10% palladium on charcoal (17 mg) was hydrogenated at atmospheric pressure. After removal of the catalyst, the solution was poured into water (15 ml) and extracted with pentane (2 × 15 ml), and the combined organic layers were dried and evaporated. The residual oil (74.2 mg) was purified by prepatative VPC on the XF-1150 column to give pure **8**: ν_{max}^{neat} 2960, 2940, 2870, 1487, and 1378 cm^{-1}; $\delta_{Me_4Si}(CDCl_3)$ 2.2–1.15 (m, 15), 0.92 (d, J = 6.5 Hz, 3), and 0.83 (s, 6); *m/e* calcd 168.1879, found 168.1882.

Anal. ($C_{12}H_{24}$) C, H.

Hydrogenation of 7. Comparable catalytic reduction of **7** (42.9 mg) furnished 31.1 mg of **9** as a colorless oil: ν_{max}^{neat} 2960, 2925, 2865, 1485, and 1378 cm^{-1}; $\delta_{Me_4Si}(CDCl_3)$ 2.2–1.1 (m, 15), 0.82 (d, J = 6 Hz, 3), and 0.79 (s, 6).

Anal. ($C_{12}H_{24}$) C, H.

2-Acetoxy-6,6-dimethylcyclononanone (11). δ,δ-Dimethylazelaic acid diethyl ester was subjected to the acyloin reaction following the procedure of Blomquist, Wheeler, and Chu.[8] The crude acyloin (6.0 g) was dissolved in pyridine (30 ml) and cooled to 0 °C while acetic anhydride (30 ml) was added dropwise. The resulting mixture was heated at 100 °C for 7 h, poured onto ice, and extracted with ether (3 × 50 ml). The combined ethereal extracts were washed with 10% hydrochloric acid, followed by sodium bicarbonate solution and brine before drying. Chromatography on silica gel (elution with pentane–ether) afforded **11** as a colorless sweet-smelling oil (5.2 g). Further purification was achieved by VPC methods (4 ft × 0.25 in. 15% SF-96 on Chromosorb G, 150 °C); ν_{max}^{neat} 2950, 2863, 1740, 1720, and 1240 cm^{-1}; $\delta_{Me_4Si}(CDCl_3)$ 5.08 (d, J = 4.8 Hz, 1, >CHOAc), 2.7–2.4 (m, 2, $-CH_2CO-$), 2.1 (s, 3, CH_3CO-), 2.0–1.0 (complex m, 10), 0.82 (s, 3, methyl), and 0.79 (s, 3, methyl); *m/e* calcd 226.1569, found 226.1574.

5,5-Dimethylcyclononanone (12).[8] Activated zinc dust (150 g) and mercuric chloride (4.0 g) were added to glacial acetic acid (500 ml) containing 6.3 g (27.8 mmol) of **11**, and the mixture was refluxed under nitrogen for 32 h. The cooled reaction mixture was filtered and neutralized to the extent of 90% with sodium hydroxide solution. Extraction with methylene chloride (3 × 200 ml), followed by washing with water, drying, and evaporation, left 4.5 g (96%) of **12** as a pale-yellow oil. VPC purification of a small sample on the SF-96 column (140 °C) gave pure **12** as a colorless liquid: ν_{max}^{neat} 2925, 2865, 1700, 1478, and 1175 cm^{-1}; $\delta_{Me_4Si}(CDCl_3)$ 2.7–2.2 (m, 4, $-CH_2CO-$), 2.1–1.55 (m, 4), 1.52–1.0 (m, 6), and 0.82 (s, 6); *m/e* calcd 168.1514, found 168.1516.

1,1-Dimethyl-5-methylenecyclononane (13). To a suspension of methyltriphenylphosphonium bromide (2.4 g, 6.71 mmol) in 50 ml of dry tetrahydrofuran was added *n*-butyllithium in hexane (7.0 mmol) with stirring under nitrogen at 0 °C. After 40 min, 5,5-dimethylcyclononanone (1.0 g, 5.94 mmol) was introduced dropwise via syringe. The yellow solution was heated at reflux for 48 h, filtered, and reduced in volume prior to chromatography on silica gel. Elution with pentane furnished 580 mg (58.7%) of **13** as a colorless oil: ν_{max}^{neat} 2957, 2930, and 2860 cm^{-1}; $\delta_{Me_4Si}(CDCl_3)$ 5.93 (s, 1), 5.84 (s, 1), 2.3–1.85 (m, 4), 1.8–1.05 (m, 10), and 0.78 (s, 6); *m/e* calcd 166.1721, found 166.1724.

1,1,5-Trimethylcyclononane (8). A 450-mg sample of **13** in glacial acetic acid (20 ml) was hydrogenated over platinum oxide in a Parr hydrogenator at 3.5 atm overnight. The catalyst was removed by filtration, the filtrate neutralized with sodium hydroxide solution, and the hydrocarbon extracted with pentane (2 × 50 ml). The combined organic layers were washed with brine, dried, and evaporated. The residual clear oil (330 mg) was purified by preparative VPC on the XF-1150 column (80 °C). The spectral properties of **8** were identical with those of the reduction product of **6** and distinctively different from those of **9**.

Reduction of 5 in Liquid Ammonia. Methanol Quench. A 1.0-g (6.85 mmol) sample of **5** was reduced as predescribed. After quenching the resulting monoanion with methanol, there was isolated 995 mg of an oil shown by VPC to consist of two components in a ratio of 1:7. The products were separated on the XF-1150 column at 100 °C.

The more rapidly eluted isomer was characterized as **14**: ν_{max}^{neat} 2965, 2930, and 775 cm^{-1}; $\delta_{Me_4Si}(CDCl_3)$ 6.0–5.2 (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); *m/e* calcd 148.1252, found 148.1254.

Anal. ($C_{11}H_{16}$) C, H.

The major component proved be **15**: ν_{max}^{neat} 3010, 2965, 1470, 1365, 810, 770, 732, and 655 cm^{-1}; $\delta_{Me_4Si}(CDCl_3)$ 5.9–5.15 (m, 6, olefinic), 2.9 (dd, J = 7 and 5 Hz, 2, bisallylic), 2.27 (d, J = 8 Hz, 2, allylic), and 1.18 (s, 6, methyl); *m/e* calcd 148.1252, found 148.1254.

Anal. ($C_{11}H_{16}$) C, H.

Reductions of *syn*- and *anti*-9-Methyl-*cis*-bicyclo[6.1.0]nona-2,4,6-trienes. Methanol Quench. The details of these reductions and the attendant isolation procedure have been previously described.[5]

Reduction of 18 and 19. Methyl Iodide Workup. The procedure is identical beginning with either isomer. The following is illustrative. A 1.0-g sample of **18** (7.6 mmol) was treated with potassium (600 mg, 15.3 mmol) in liquid ammonia (30 ml) in the predescribed fashion. After quenching with methyl iodide (4 ml), processing gave an oil (950 mg) which contained four components by VPC analysis (6 ft × 0.25 in. silver nitrate–glycerol on firebrick, 65 °C) in the ratio 8:4.8:5.2:1. The products were separated on this column, and their spectral properties are given below in the order of elution.

Triene **25**: ν_{max}^{neat} 3000, 2960, 2935, 2875, 1455, 780, 730, and 694 cm^{-1}; $\delta_{Me_4Si}(CDCl_3)$ 5.9–5.03 (m, 6, olefinic), 3.3–2.8 (m, 1, bisallylic), 2.1–1.7 (m, 3, allylic), 1.1 (d, J = 6.5 Hz, 3, methyl), and 1.01 (d, J = 6.5 Hz, 3, methyl).

Anal. ($C_{11}H_{16}$) C, H.

Triene **26**: ν_{max}^{neat} 3050, 2960, 2930, 2875, 1455, 775, 760, 730, and 680 cm^{-1}; $\delta_{Me_4Si}(CDCl_3)$ 5.8–4.9 (m, 6, olefinic), 3.25–2.7 (m, 1, bisallylic), 2.3–1.75 (m, 3, allylic), 1.14 (d, J = 7 Hz, 3, methyl), and 1.0 (d, J = 6.5 Hz, 3, methyl).

Anal. ($C_{11}H_{16}$) C, H.

Triene **27**: ν_{max}^{neat} 3010, 2965, 2935, 2880, 770, 740, and 650 cm^{-1}; $\delta_{Me_4Si}(CDCl_3)$ 5.85–4.8 (m, 6, olefinic), 3.5–3.1 (m, 1, bisallylic), 2.6–1.85 (m, 3, allylic), 1.15 (d, J = 7 Hz, 3, methyl), and 1.06 (d, J = 7 Hz, 3, methyl).

Anal. ($C_{11}H_{16}$) C, H.

Triene **28**: $\delta_{Me_4Si}(CDCl_3)$ 5.8–4.9 (m, 6, olefinic), 3.2–2.7 (m, 1, bisallylic), 2.4–1.7 (m, 3, allylic), 1.10 (d, J = 7 Hz, 3, methyl), and 1.0 (d, J = 6.5 Hz, 3, methyl).

Anal. ($C_{11}H_{16}$) C, H.

Catalytic Hydrogenation of 25–28. General Procedure. A 3–10-mg sample of the triene was dissolved in 1 ml of anhydrous tetrahydrofuran, and 10 mg of platinum oxide was added. This mixture was magnetically stirred under a hydrogen atmosphere at room temperature for 2–8 h. The catalyst was removed by careful filtration, and the filtrate was directly subjected to preparative VPC (15% silanized SE-30, 90 °C). The collected hydrocarbon was examined by Fourier transform ^1H NMR spectroscopy (Table III) and established to be of the proper composition by accurate mass measurement (*m/e* calcd 154.1721). For **29**, found 154.1724; for **31**, 154.1724; for **32**, 154.1724; for **33**, 154.1724.

If reaction times in the case of **26** were abbreviated, the tetrahydro derivative **30** could be readily isolated; $\delta_{Me_4Si}(CDCl_3)$ 5.07 (dd, J = 6.5 and 2 Hz, 2, olefinic), 2.7–2.3 (m, 2, allylic), 1.7–1.2 (m, 10, methylene), and 1.95 (d, J = 6 Hz, 6, methyl); *m/e* calcd 152.1565, found 152.1567.

Conversion of Bicyclo[5.2.1]decan-10-one (34) to Epoxide 35. Sodium hydride (2.16 g of 57% oil dispersion, 0.051 mol) was washed free of oil with pentane (3 × 10 ml aliquots) under a dry nitrogen atmosphere. Dry dimethyl sulfoxide (40 ml) was added, and the mixture was warmed to 60–65 °C for 60 min. Anhydrous tetrahydrofuran (40 ml) was added to the cooled mixture, and the temperature was lowered to −5 °C with external cooling. Trimethylsulfonium iodide (10.4 g, 0.051 mol) was added in small portions during 5 min. After stirring for an additional 2 min, 7.5 g (0.049 mol) of **34** was added by syringe, and reaction was completed by stirring for 90 min at 0 °C. Water (300 ml) was added and the product extracted with pentane (4 × 100 ml). The organic extracts were washed with water (3 × 50 ml), dried, and evaporated to leave a colorless oil. Passage through a short Florisil column [petroleum ether (30/60) elution] gave epoxide **35** (5.3 g, 65%) as a waxy solid: ν_{max}^{neat} 2940, 1480, 1460, 965, 910, 865, and 815 cm^{-1}; $\delta_{Me_4Si}(CDCl_3)$ 2.73 (s, 2, $-CH_2O$), 2.15–1.75 (m, 6), and 1.75–1.25 (m, 10); *m/e* calcd 166.1358, found 166.1360.

10-Aminomethylbicyclo[5.2.1]decan-10-ol (36). An ether solution (15 ml) of **35** (5.0 g, 29.4 mmol) was placed in a glass pressure bottle. The vessel was charged with liquid ammonia (ca. 100 ml), followed by the careful addition of sodium amide (5.9 g, 0.15 mol) under nitrogen. After sealing, the contents were allowed to warm to room temperature where stirring was maintained for 24 h. After cooling to −78 °C, the bottle was opened and water (35 ml) was cautiously added. Ammonia was allowed to evaporate, and the residue was extracted with ether (5 × 50 ml), washed with water (2 × 15 ml), and dried. Removal of solvent gave white needles of **36** (5.05 g, 92%): mp 78–79 °C (from ether); $\nu_{max}(CHCl_3)$ 3700–3000 (br), 2920, 2860, 1475, 1445, and 1100 (br) cm^{-1}; *m/e* calcd 183.1623, found 183.1626.

The *p*-toluenesulfonic acid salt was prepared, mp 185–186 °C [from ethyl acetate/methanol (5:1)].

Anal. ($C_{18}H_{30}NO_4S$) C, H, N.

Deamination of 36. A solution of **36** (3.0 g) in dilute acetic acid (1.3 g of glacial in 30 ml of water) was cooled in an ice–salt bath, and a solution of sodium nitrite (1.5 g) in water (20 ml) was added dropwise during 15 min. The mixture was magnetically stirred at 0 °C for 1.5 h and at the reflux temperature for 30 min. Saturated sodium bicarbonate solution was added to attain neutrality, and the products were extracted with ether (4 × 50 ml). The combined organic layers, upon drying and evaporation, afforded 2.63 g of a waxy solid which was shown to be a mixture of **34** and **37** (ratio 1:2.6) by VPC analysis (5 ft × 0.75 in. 25% SE-30 on Chromosorb G, 170 °C). A small portion of the sample was purified in this manner, and **37** was thereby obtained as a colorless crystalline solid: mp 150–151 °C; ν_{max}^{neat} 2900, 1715, 1450, 1415, 1245, 1145, and 1125 cm^{-1}; $\delta_{Me_4Si}(CDCl_3)$ 2.8–2.2 (m, 4) and 2.2–1.2 (m, 14); *m/e* calcd 166.1358, found 166.1360. The **34** which was concomitantly isolated proved identical with the ultimate starting material.

Hydride Reduction of 37. A solution of ketones **34** and **37** (14.5 g) as obtained from the deamination (ratio 1:2.6) in anhydrous ether (200 ml) was added dropwise to a stirred suspension of lithium aluminum hydride (15.0 g) in ether (150 ml). When the mixture had been stirred at room temperature for 4 h, 10% ammonium chloride solution was cautiously added to destroy the excess hydride, followed by anhydrous magnesium sulfate (10 g). The salts were removed by filtration and washed with copious amounts of dry ether. The combined washings

and filtrate were evaporated to give 13.1 g of a white crystalline product which was used without further purification in the dehydration reaction.

Bicyclo[5.2.2]undec-8-ene (38). This alcohol mixture (9.0 g) in methylene chloride (50 ml) was added dropwise to a cold (0 °C) magnetically stirred solution of *O*-4-methylphenylchlorothioformate[39] (11.8 g, 63 mmol) and pyridine (5.8 g, 73 mmol) in methylene chloride (50 ml). The mixture was stirred overnight at room temperature, quenched by addition of water (50 ml), washed with 10% hydrochloric acid (3 × 50 ml), water (50 ml), and saturated sodium bicarbonate solution (2 × 50 ml), and ultimately dried. Concentration left a dark oil which was passed down a short column of Florisil to give a dark red semisolid (9.0 g). This material was dissolved in 15 ml of tetrahydrofuran, and the resulting solution was introduced dropwise under nitrogen into a heated (380 °C) and partially evacuated (100 mm) glass tube (38 × 2.5 cm) packed with glass helices. The pyrolysate which condensed at −70 °C was taken up in pentane (50 ml), and the organic layer was washed with 15% sodium hydroxide solution and water before drying and careful fractional distillation through a 6-in. jacketed Vigreux column to remove solvent. The residue was subjected to bulb-to-bulb distillation, and there was collected 1.07 g of **38,** bp 95–105 °C bath temperature (25 mm). A small sample was purified by preparative VPC on the 15% silanized SE-30 column; $\delta_{Me_4Si}(CDCl_3)$ 5.83–5.63 (m, 2), 2.72–2.3 (br m, 2), and 2.2–1.2 (br m, 14).

Anal. ($C_{11}H_{18}$) C, H.

***cis*-1,4-Dimethylcyclononane (31).** The above sample of **38** (1.07 g, 7.12 mmol) was dissolved in a mixturg of methanol (30 ml) and methylene chloride (15 ml) and cooled to −70 °C while ozonized. The solvents were carefully removed on a rotary evaporator at 25 °C, and the remaining oil was taken up in glacial acetic acid (15 ml), 30% hydrogen peroxide (15 ml), and 10% sulfuric acid (4 ml). After being heated at reflux for 3 h, this mixture was cooled, treated with 6 ml of 15% sodium hydroxide solution, and carefully evaporated at 25 °C. The residue was taken up in ether and treated with ethereal diazomethane. After 5 min, water (25 ml) was added, the layers were separated, and the organic phase was dried and evaporated to furnish 1.51 g (87.8%) of diester **39a:** ν_{max}^{neat} 1730 cm^{-1}; $\delta_{Me_4Si}(CDCl_3)$ 3.66 (s, 6) and 2.6–1.2 (m, 16).

The unpurified diester (484 mg, 2.0 mmol) was dissolved in dry ether (10 ml) and added dropwise during 10 min to a stirred suspension of lithium aluminum hydride (350 mg, 9.23 mmol) in ether (10 ml). After being stirred at room temperature for 3 h, the mixture was heated at reflux for 1 h, cooled, and worked up as before. Diol **39b** (248 mg, 66%) was obtained as a colorless oil; ν_{max}^{neat} 3400 cm^{-1}.

This diol (124 mg, 0.665 mmol) was dissolved in ice-cold pyridine (2 ml), and methanesulfonyl chloride (229 mg, 2.0 mmol) was added, followed by 2 ml of pyridine. The mixture was stored at 0 °C overnight before pouring into 0.1 N hydrochloric acid and ether. The organic phase was washed again with acid (2 × 20 ml), dried, and evaporated to leave 185 mg (90%) of dimesylate **39c** as a yellowish oil which was not further purified.

To a slurry of lithium aluminum hydride (70 mg) in dry tetrahydrofuran (2 ml) was added dropwise a solution of the crude dimesylate (175 mg, 5.64 mmol) in 2 ml of the same solvent. After 5 h at the reflux temperature, the cooled mixture was treated dropwise with 0.5 ml of 15% potassium hydroxide solution. The salts were removed by filtration and washed with water and pentane. The combined washings and filtrate were separated, and the organic layer was dried and carefully concentrated as above. The *cis*-1,4-dimethylcyclononane (8 mg, 9.2%) which was collected by preparative VPC on the silanized SE-30 column (108 °C) proved identical in all respects with the product or catalytic hydrogenation of **26.**

***trans*-1,4-Dimethylcyclononane.** A pea of sodium metal was allowed to dissolve in 5 ml of dry methanol, and **39a** (1.0 g, 4.12 mmol) in 5 ml of the same solvent was added in one portion. After 24 h, 1 ml of acetic acid was added and the solvent was evaporated. The residue was partitioned between ether and water. The organic phase was dried and concentrated, and the resulting oil was recycled through the equilibrium procedure. There was isolated 640 mg (64%) of diester, ^{1}H NMR analysis of which denoted ca. 30% conversion to **40.**

Reduction of this mixture (320 mg) with lithium aluminum hydride (250 mg) in ether (15 ml) furnished 230 mg (93.5%) of the diol mixture containing **39a** and **41a.** Conversion to the dimesylate as before produced 301 mg (78.8%) of an oily mixture which was reduced directly with lithium aluminum hydride (140 mg) in 8 ml of anhydrous tetrahydrofuran. Preparative VPC on the silanized SE-30 column (95 °C) provided 11 mg (7.3%) of the cis (**31**)/trans (**32**) mixture. The Fourier transform ^{1}H NMR spectrum revealed the minor component (**32**) to be identical with the product of catalytic hydrogenation of **27.**

Conversion of Bicyclo[4.3.1]decan-10-one (42) to Epoxide 43. By a procedure similar to that described for **34,** ketone **42** (2.55 g) was treated with dimethylsulfonium methylide and furnished 2.4 g (84%) of **43** as a waxy solid: mp 105–110 °C; ν_{max}^{neat} 2930, 2850, and 1455 cm^{-1}; $\delta_{Me_4Si}(CDCl_3)$ 2.38 (s, 2) and 2.1–1.2 (m, 16); *m/e* calcd 166.1358, found 166.1360.

10-Aminomethylbicyclo[4.3.1]decan-10-ol (44). Epoxide **43** (3.3 g) when treated with sodium amide in ammonia as previously outlined, gave 3.4 g (93%) of **44:** mp 97–98 °C (from ether at 0 °C); $\nu_{max}(CHCl_3)$ 3600–3100 (br), 2920, 2860, 1450, and 1100 cm^{-1}.

The *p*-toluenesulfonic acid salt was prepared, mp 206–207 °C [from ethyl acetate/methanol (3:1)].

Anal. ($C_{18}H_{30}NO_4S$) C, H, N.

Bicyclo[4.3.2]undecan-10-one (45). Amino alcohol **44** (1.0 g) was dissolved in dilute acetic acid (0.45 g glacial in 10 ml of water), cooled in an ice–salt bath, and treated dropwise with a solution of sodium nitrite (0.5 g) in water (10 ml) during 10 min. The mixture was stirred for 90 min at 0 °C and at room temperature for 1 h before processing as described earlier. There was isolated a waxy solid (750 mg) shown to be a mixture of **42** and **45** in a 1:2 ratio by VPC analysis on the 5% SE-30 column (150 °C). A portion of this mixture was separated by preparative VPC under these conditions, and **45** was obtained as a waxy solid: mp 164–165 °C (sublimed); $\nu_{max}(CCl_4)$ 2910, 1690, 1450, 1290, 1150, and 935 cm^{-1}; $\delta_{Me_4Si}(CDCl_3)$ 2.9–2.1 (m, 4) and 2.1–1.4 (m, 14); *m/e* calcd 166.1358, found 166.1360.

Bicyclo[4.3.2]undec-11-ene (46). A. Pyrolysis of the Thiocarbonate *O*-Ester. A solution of the original ketone mixture (700 mg) in anhydrous ether (10 ml) was added dropwise to a stirred suspension of lithium aluminum hydride (350 mg) in ether (5 ml). After 4 h at room temperature, the customary workup provided 650 mg of a white crystalline product which was utilized without further purification.

A 2.27-g sample (13.5 mmol) of this alcohol mixture was treated in the predescribed manner with 2.79 g (15 mmol) of *O*-4-methylphenylchlorothioformate and 3 ml of pyridine in 25 ml of methylene chloride. The resulting dark brown oil was directly pyrolyzed at 380 °C and 100 mm in the helices packed glass furnace. Workup provided 350 mg of **46** which was identical with the hydrocarbon obtained in the ensuing dehydration.

B. Dehydration with the Burgess Reagent. A sample of the alcohol mixture (650 mg) was dissolved in anhydrous tetrahydrofuran (10 ml), the inner salt (1.2 g) was add added, and the mixture was stirred at room temperature for 18 h. Water (60 ml) was added and the product extracted with pentane (5 × 20 ml). Removal of the solvent using a 6-in. jacketed Vigreux column gave a pale yellow liquid which was purified by preparative VPC on the XF-1150 column (90 °C). There was isolated 136 mg of **46:** ν_{max}^{neat} 2910, 1650, 1470, 1440, 930, 805, 770, and 720 cm^{-1}; $\delta_{Me_4Si}(CDCl_3)$ 6.05–5.6 (AA′BB′ m, 2), 2.8–2.2 (m, 2), and 2.2–1.2 (m, 14).

Anal. ($C_{11}H_{18}$) C, H.

***cis*-1,5-Dimethylcyclononane (33).** A 175-mg sample of **46** was subjected to ozonolysis, and the resulting diacid was esterified with diazoethane to furnish 293 mg (93.3%) of diester **47a.** Reduction of this material with lithium aluminum hydride (350 mg) in ether (20 ml) gave rise to diol **47b** (122 mg, 60.7%) which was directly converted to the oily dimesylate **47c** (74 mg, 36.6%). Exposure of this material to the action of lithium aluminum hydride (50 mg) in refluxing tetrahydrofuran (4 ml) for 6 h and isolation from the silanized SE-30 column (90 °C) furnished 5 mg of pure **33** which proved identical with the product of hydrogenation of **28.**

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An Electron Spin Resonance Study of the Radical Anions of Two Dimethylcyclooctatetraenes

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Abstract: The radical anions of 1,4- and 1,5-dimethylcyclooctatetraene have been generated by electrolysis in DMF at −55 °C, and their ESR spectra have been recorded. These are the first examples of ESR spectra of 1,4- and 1,5-disubstituted :COT radical ions. In 1,5-$Me_2COT^{\cdot -}$ virtually all of the π spin density is localized on the four odd-numbered ring carbons. In complete contrast, the π spin density in 1,4-$Me_2COT^{\cdot -}$ is spread almost equally over all eight ring carbons. These results are shown to provide strong support for symmetry-orbital models of substituted COT radical anions.

Introduction

Reports of ESR spectra of radical ions of benzene and its mono- and polysubstituted derivatives abound in the literature.[2] These studies have provided elegant confirmation of a symmetry-orbital model for the π system of benzene. In contrast, while there have been a number of ESR studies of monosubstituted cyclooctatetraene (COT) radical anions,[3] particularly in the last 2 years, investigations of polysubstituted COT radicals have been limited to two 1,3,5,7-tetrasubstituted derivatives[3d,4a,b] and a single 1,2-disubstituted one.[5] This difference presumably has its origins in the far greater synthetic difficulties inherent in COT chemistry.

Recently the syntheses of 1,4- and 1,5-Me_2COT have been accomplished.[6] The availability of these compounds offered us the opportunity to obtain ESR spectra of the corresponding radical anions, with a view toward exploring further the predictions of symmetry-orbital models of $COT^{\cdot -}$.

Experimental Section

The radical anions of COT and its two dimethyl derivatives were generated by electrolytic reduction of the neutral hydrocarbons in *N,N*-dimethylformamide (DMF) at −55 °C with tetra-*n*-propylammonium perchlorate as electrolyte. The electrolysis was done in a flat quartz cell (Wilmad Glass Co., No. WG-808) small enough to fit inside the Dewar system of the spectrometer. The cathode was a platinum wire passed into the bottom of the cell through a Teflon plug. The platinum anode was brought in through a rubber septum on one arm of a Y-tube at the top of the cell. Outgassed solutions of compound and electrolyte were drawn from a storage flask into a syringe equipped with a Teflon valve and a 10-in. long 26-gauge needle. The solutions were injected into the flat part of the cell through a