4.62 (m, 2, >CHN<), 1.35–1.9 (br m, 8, methylenes), and 1.30 (s, 6, methyls).

Anal. Calcd for $C_{22}H_{23}N_3O_2$: C, 73.10; H, 6.41; N, 11.63. Found: C, 72.92; H, 6.35; N, 11.60.

N-Phenyltriazolinedione Adduct of 24. Treatment of 200 mg (1.27 mmol) of somewhat impure 1,2-tetramethylenecyclooctatetraene (24) with 443 mg (2.53 mmol) of N-phenyltriazolinedione in ethyl acetate as predescribed afforded after chromatography 350 mg (83%) of **30b**, mp 209–211° (from benzene–hexane): $\delta_{TMS}^{CDCl_3}$ 7.50 (m, 5, aryl), 6.32 (m, 2, olefinic), 5.04 (m, 2, >CHN<), 3.17 (m, 2, 4-ring methine), and 1.3–1.9 (br m, 8, methylenes).

Anal. Calcd for $C_{20}H_{19}N_3O_2$: C, 72.05; H, 5.74; N, 12.61. Found: C, 71.97; H, 5.77; N, 12.64.

Thermal Rearrangement of [4.3.2]Propella-2,4,10-triene (31). An 80-mg sample of 31[31] was pyrolyzed as before at 615° (5 mm) in a stream of nitrogen. Vpc analysis of the pyrolysate revealed two products to be present in a 2:1 ratio and no starting material remaining. Both hydrocarbons were collected from column B at 70°; the major component was characterized as indan (33) on spectral grounds (*m/e* calcd 118.0782, obsd 118.0781) while the minor component was characterized as 1,2-trimethylenecyclooctatetraene (32) by its pmr spectrum.[24,31]

(31) R. K. Russell, full experimental details in preparation.

Directed Syntheses of the Isomeric Dimethylcyclooctatetraenes and a Study of Their Polarographic and Alkali Metal Reduction

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Abstract: The 1,2-, 1,3-, 1,4-, and 1,5-dimethylcyclooctatetraenes have been prepared conveniently in isomerically pure fashion by methods which hold promise of considerable generality. Evidence is presented that these hydrocarbons undergo alkali metal reduction in ND_3 at −50 to −58° with formation of planar or essentially planar dianions. The pmr spectra of these solutions reveal the diatropic nature of these species and show that symmetrical ion pairing prevails. When subjected to polarographic reduction (dry THF, TBAP electrolyte), the polyolefins were found to exhibit reduced electron affinities compared to the parent $(CH)_8$ system because of the inductive contributions from the pair of methyl substituents. The waves were non-Nernstian with n_{app} values between 1 and 2; the irreversibility of the reductions was established by cyclic voltammetry on the 1,5-dimethyl derivative down to −78°. Coulometric studies confirmed the fractional electron uptake. These data point to rapid subsequent reaction of the product of electrochemical reduction. Interestingly, the $E_{1/2}$ values are a linear function of the distance separating the methyl groups. This effect is believed to have its origin chiefly in steric parameters. The significance of these results as well as questions raised by the investigation are discussed.

D iscovery[2] of the clean, unimolecular rearrangement of unsaturated propellanes such as 1 to 1,2-bridged cyclooctatetraenes by way of intramolecular $(_\pi 4_s + _\pi 2_s)$ cycloaddition prompted study of the thermal

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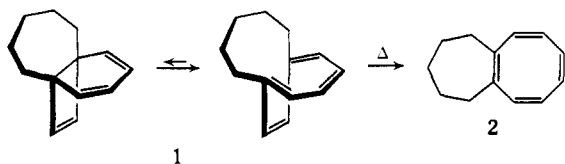
activation of cyclooctatetraenes themselves.[3] To allow for detection of structural bond reorganizations in these COT thermolyses, initial recourse to dialkylated derivatives and specifically to the four possible dimethyl isomers seemed highly desirable.[4] In his recent treatise on COT chemistry, Schröder[5] notes, however, that

synthetic entry to isomeric disubstituted COT's has been realized only in the diphenyl series and this by way of a highly unselective process. Cope and Moore[6] allowed phenyllithium to react with phenylcyclooctatetraene and separated the resulting isomeric tetraenes in very low yield by tedious countercurrent distribution techniques.

Because of anticipated difficulties (subsequently realized, *vide infra*) in separation of the four Me_2COT's, processes of this sort were clearly undesirable and we therefore sought to develop synthetic methodology which would provide each hydrocarbon uncontaminated by isomeric impurities. Simple approaches to these compounds have now been developed which hold promise as general synthetic methods, particularly for 1,3-, 1,4-, and 1,5-functionalized derivatives. In design, the preparative routes avoid the problems engendered by the susceptibility of the cyclooctatetraene ring to rearrangement by approaching the end product in an indirect way and liberating the $(CH)_8$ nucleus in the final step.
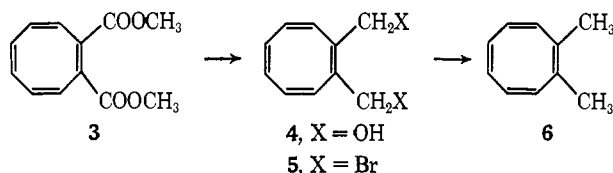
We felt that an examination of the polarography and

(1) University Dissertation Fellow, 1973–1974.

(2) L. A. Paquette and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, 94, 4398 (1972); L. A. Paquette, R. E. Wingard, Jr., and J. M. Photis, *ibid.*, 96, 5801 (1974).

(3) L. A. Paquette, M. Oku, W. E. Heyd, and R. H. Meisinger, *J. Amer. Chem. Soc.*, 96, 5815 (1974).

(4) L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, 94, 9224 (1972); L. A. Paquette and M. Oku, *ibid.*, 96, 1219 (1974).

(5) G. Schröder, "Cyclooctatetraen," Verlag Chemie, Weinheim/Bergstr., Germany, 1965.

(6) A. C. Cope and W. R. Moore, *J. Amer. Chem. Soc.*, 77, 4939 (1955).

alkali metal reduction of these COT's might shed some light on the current controversy surrounding the behavior of the parent hydrocarbon.[7] To the extent that the electron-donating properties of the methyl groups deter electrochemical reduction, the $E_{1/2}$ values will be shifted to more negative potentials. But will the magnitude of this effect be sensitive to positional orientation? Also, if the derived dianions are indeed planar, then one may ask whether the alkali metal ions are symmetrically disposed relative to the organic species. We therefore set out to record the low temperature pmr spectra of the dipotassiocyclooctatetraenides in ND_3 with a view to observing unsymmetrical ion pairing if such exists and interrelating the electrochemical and chemical data if possible.

Results and Discussion

Synthesis. Since the synthesis of 1,2-disubstituted cyclooctatetraenes containing electron-withdrawing groups is readily accomplished by the photocycloaddition of appropriate acetylenes to benzene,[8] an obvious starting point for the preparation of **6** was diester **3**. Reduction to diol **4** was effected by treatment with alane at room temperature.[9] The yields of dibromide **5** in the reaction of **4** with phosphorus tribro-

Figure 1. Pmr spectra (60 MHz) of: (top) dipotassio-1,2-dimethylcyclooctatetraenide (**27**) in ND_3 at $-58°$ (Me_3N present as internal standard; $\delta_{NH_3}^{TMS}$ for Me_3N = 2.135: S. W. Staley and N. J. Pearl, *J. Amer. Chem. Soc.*, **95**, 3437 (1973)); (bottom) 1,2-dimethylcyclooctatetraene (**6**) in $CDCl_3$ at 40°.

mide and pyridine in ether as recommended by Sondheimer[10] were invariably low (16–39%) but could be raised routinely to 69–78% by using triphenylphosphine dibromide in anhydrous dimethylformamide solution. Lithium aluminum hydride reduction of **5** afforded **6**, the infrared spectrum of which proved identical with that published by Cope and coworkers[11] who had earlier gained access to the hydrocarbon by a copolymerization technique. The pmr spectrum of **6** at 40° displays two sharp singlets at δ 1.68 and 1.82 for the methyl groups, with the low field signal being the more intense (Figure 1). As the temperature was raised to 94° (tetrachloroethylene solution), appreciable broadening of these two peaks was observed. At 122°, coalescence to a single sharp peak at δ 1.75 had occurred and the temperature dependency was entirely reversible. This behavior is attributed to bond shift isomerization, the nature of which has been extensively studied with various COT derivatives by other workers.[12]

For the purpose of preparing pure **9**, a pathway involving dimethylation of bridged sulfone **7** and subsequent photoinduced sulfur dioxide extrusion[13] was tested. Although our early preparations of **7** were effected by *m*-chloroperbenzoic acid oxidation of the related sulfoxide,[14] this tedious reaction sequence was quickly supplanted by Huisgen's elegant one-step procedure when the latter made its appearance.[15] Sulfone **7** was readily transformed into its intensely purple colored dianion, the nature of which has been discussed previously,[16] when allowed to react with 2 equiv of *n*-butyllithium in tetrahydrofuran solution at $-70°$. Subsequent treatment with methyl iodide gave **8** in quantitative yield. The structural assignment to **8** follows convincingly from its spectral properties and combustion analysis. Photolysis of **8** dissolved in deaerated ether–acetone (3:1) with a 200-W Hanovia lamp fitted with a Corex filter proceeded readily to furnish isomerically uncontaminated **9** as a clear yellow liquid.

The room-temperature pmr spectrum of **9** shows a pair

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(10) J. A. Elix, M. V. Sargent, and F. Sondheimer, *J. Amer. Chem. Soc.*, **92**, 962 (1970).

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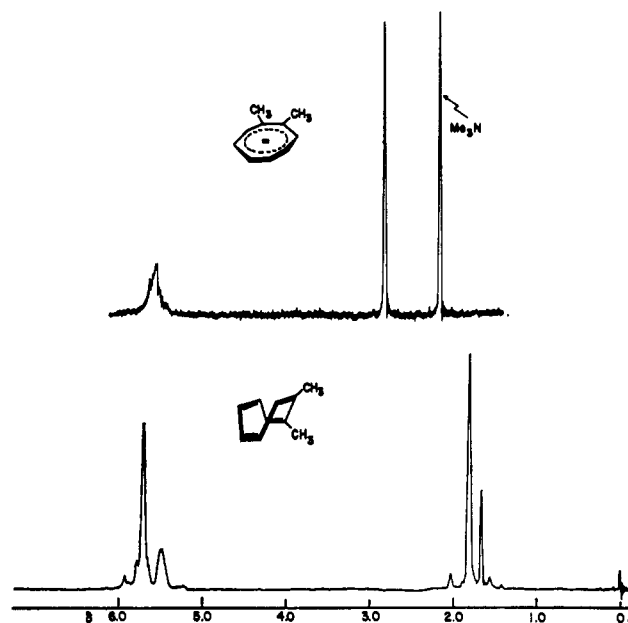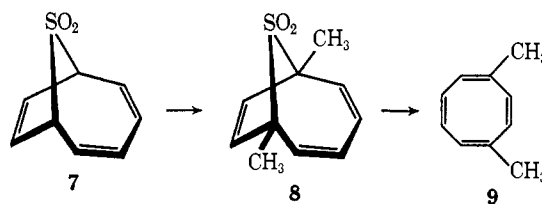
(c) D. E. Gwynn, G. M. Whitesides, and J. D. Roberts, *ibid.*, **87**, 2862 (1965); (d) J. F. M. Oth, R. Merenyi, Th. Martini, and G. Schröder, *Tetrahedron Lett.*, 3087 (1966).

(13) L. A. Paquette, R. E. Wingard, Jr., and R. H. Meisinger, *J. Amer. Chem. Soc.*, **93**, 1047 (1971); L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *ibid.*, **94**, 9224 (1972).

(14) A. G. Anastassiou and Y.-H. Chao, *Chem. Commun.*, 979 (1971).

(15) J. Gasteiger and R. Huisgen, *J. Amer. Chem. Soc.*, **94**, 6541 (1972).

(16) L. A. Paquette, R. H. Meisinger, and R. Gleiter, *J. Amer. Chem. Soc.*, **95**, 5414 (1973).
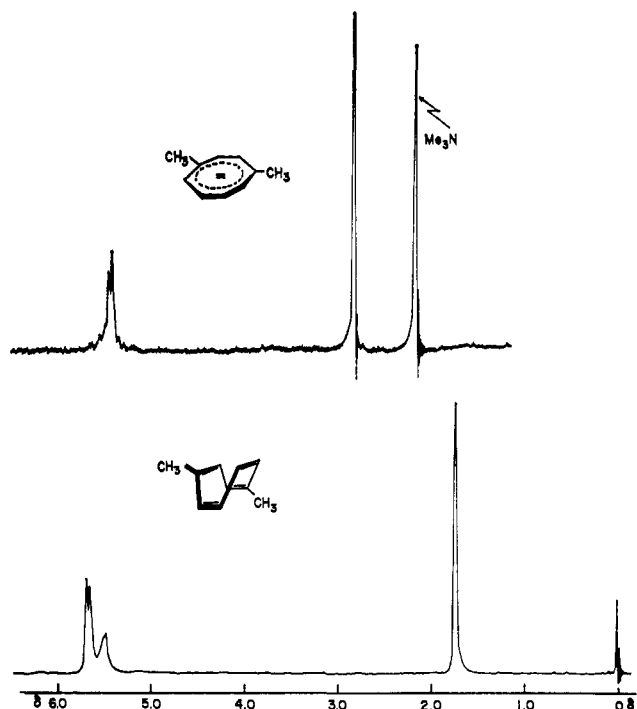
Figure 2. Pmr spectra (60 MHz) of: (top) dipotassio-1,4-dimethylcyclooctatetraenide (**29**) in ND₃ at −58°; (bottom) 1,4-dimethylcyclooctatetraene (**9**) in CDCl₃ at 40°.

of methyl groups as a singlet at δ 1.72, indicating the chemical equivalence of these substituents (see Figure 2).

Because of concern with the possible photorearrangement of **9** during its preparation, a number of preliminary experiments were performed to evaluate the stability of such molecules under the reaction conditions. It will be recalled that low-temperature (−65 to −30°) irradiation of cyclooctatetraene does produce semibullvalene (4%) and benzene (3.5%).[17] In contrast, photoexcitation of the 1,3,5,7-tetramethyl derivative led to no observable amounts of a corresponding semibullvalene either at −65° or at room temperature. In our hands, solutions of both **6** and **9** in acetone were found to be unreactive under the original conditions for up to 100 hr (87–92% recovery). This photochemical stability contrasts in an interesting way with the ready thermal rearrangement of these molecules.[3,4,17]

During the course of this work, an alternative synthesis of **9** was reported by Huisgen and coworkers.[18] Their route involved bromination of bromocyclooctatetraene (**10**), subsequent dehydrobromination of **11** with potassium tert-butoxide to give **12**, and ultimate replacement of bromine by methyl through the agency of lithium dimethylcuprate. Deemphasized by the German group, however, was the fact that the base-induced elimination of HBr from **11** concomitantly provides significant amounts of 1,5-dibromide **13** which is essentially inseparable from **12**. Consequently, when the methylation is effected, a considerable quantity of the 1,5-dimethyl isomer (**14**) is present as undesirable contaminant. Comparable bifurcate behavior has been noted in the bromination–dehydrobromination of methylcyclooctatetraene.[19]

(17) H. E. Zimmerman and H. Iwamura, *J. Amer. Chem. Soc.*, **92**, 2015 (1970).
(18) W. E. Konz, W. Hechtl, and R. Huisgen, *J. Amer. Chem. Soc.*, **92**, 4104 (1970).
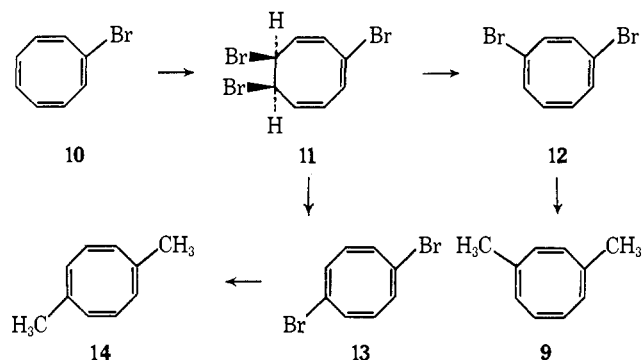
With the recent development of more accessible routes to semibullvalenes[20] arose our interest in the possibility that thermal rearrangement of this class of hydrocarbons to cyclooctatetraenes could be effected at temperatures below those necessary to promote COT isomerization reactions. Our assumptions were substantiated by the finding that semibullvalene itself (**15**) led with good recovery to **17** as the only product when heated in the gas phase (flow system, N₂ diluent, 1–3 sec contact time) at 427° (30 mm).[21] The 1,5-dimethylsemibullvalene molecule (**16**),[20e] in which two carbon atoms of the (CH)₈
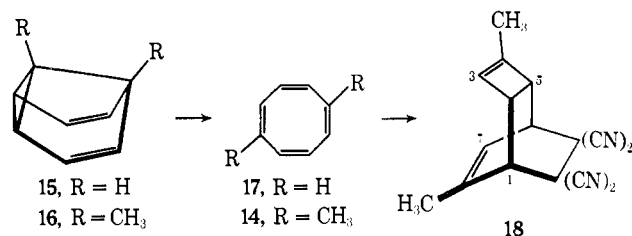
framework are now labeled by virtue of methyl substitution, was similarly pyrolyzed at 390°. In this instance, a lone yellow hydrocarbon was obtained in 71% yield whose pmr spectrum consisted of three absorptions: a pseudosinglet of area 4 at δ 5.68, a narrow multiplet (2 H) at 5.52, and a six-proton singlet at 1.72 (see Figure 3). The ultraviolet and infrared absorptions of this product, although compatible with a dimethylcyclooctatetraene structure, were not those of the 1,2 or the 1,4 derivative. Treatment with tetracyanoethylene in refluxing ethyl acetate gave adduct **18**, pmr analysis of which requires the product to be that derived from (4 + 2) cycloaddition to **14**. Thus, bridgehead proton H₁ appears as a multiplet centered at δ 3.60 whereas H₆ located at 3.80 is seen to be a doublet of doublets (J = 7.0 and 3.0 Hz). The protons at positions 2 and 5 appear as broad overlapping multiplets at 3.13 and the olefinic hydrogens give rise to a doublet (J = 7.0 Hz, 6.00, H₇) and multiplet patterns (5.61, H₃).

A comparable synthesis of **24** required the preparation of 1,3-dimethylsemibullvalene (**23**) as penultimate presursor. To this end, diketone **19**[22] was converted to **20**

(19) L. A. Paquette and K. A. Henzel, *J. Amer. Chem. Soc.*, **95**, 2726 (1973).
(20) (a) J. Meinwald and D. Schmidt, *J. Amer. Chem. Soc.*, **91**, 5877 (1969); (b) H. E. Zimmerman, J. D. Robbins, and J. Schantl, *ibid.*, **91**, 5878 (1969); (c) L. A. Paquette, *ibid.*, **92**, 5766 (1970); (d) R. Askani, *Tetrahedron Lett.*, 3349 (1970); (e) R. Askani, *ibid.*, 447 (1971); (f) R. M. Moriarty, C.-L. Yeh, and N. Ishibe, *J. Amer. Chem. Soc.*, **93**, 3085 (1971); (g) L. A. Paquette, R. E. Wingard, Jr., and R. K. Russell, *ibid.*, **94**, 4739 (1972); (h) L. A. Paquette, D. R. James, and G. H. Birnberg, *ibid.*, submitted for publication.
(21) L. A. Paquette, R. K. Russell, and R. E. Wingard, Jr., *Tetrahedron Lett.*, 1713 (1973).
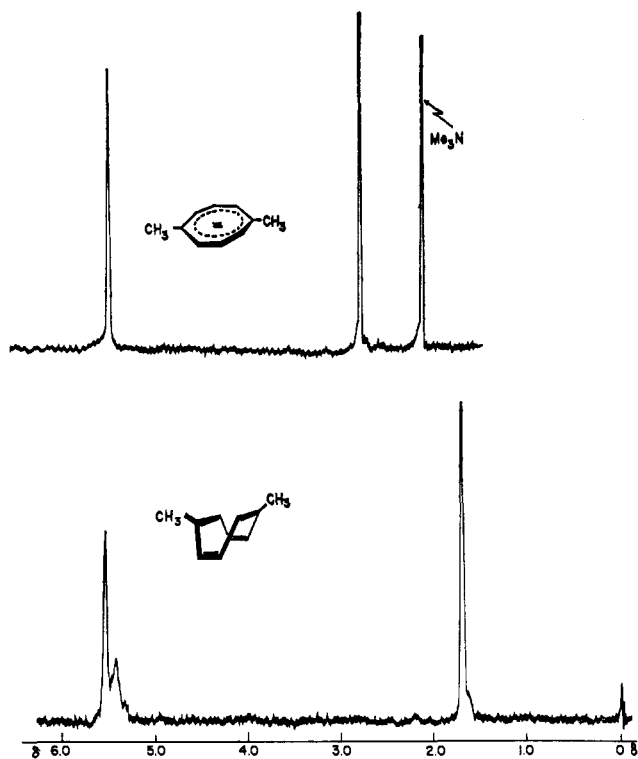(22) U. Weiss and J. M. Edwards, *Tetrahedron Lett.*, 4885 (1968).

Figure 3. Pmr spectra (60 MHz) of: (top) dipotassio-1,5-di-methylcyclooctatetraenide (30) in ND₃ at −50°; (bottom) 1,5-dimethylcyclooctatetraene (14) in CDCl₃ at 40°.

Figure 4. Pmr spectra (60 MHz) of: (top) dipotassio-1,3-di-methylcyclooctatetraenide (28) in ND₃ at −58°; (bottom) 1,3-dimethylcyclooctatetraene (24) in CDCl₃ at 40°.

by condensation with 1 equiv of methyllithium in tetra-hydrofuran at −70°. This crystalline keto alcohol shows in its pmr spectrum two equally intense singlets of area 3 at δ 1.24 and 1.37 in agreement with its homogeneity. Exo attack by the organometallic is assumed. A second hydroxyl group was introduced in quantitative fashion upon lithium aluminum hydride reduction. Subsequent Chugaev elimination afforded a mixture of dienes 22 which after purification were treated sequentially with N-bromosuccinimide and 0.8% lithium amalgam (in ether). The pmr spectrum of 23 exhibits a sharp singlet corresponding to the bridgehead methyl group at δ 1.11, a multiplet of area 3 centered at 1.58 due to the allylic methyl group, and multiplets arising from the time-averaged cyclopropyl and bridgehead protons at 4.33, 4.69, and 5.03.[23] When pyrolyzed as before, 23 underwent 78% conversion to 1,3-dimethyl-cyclooctatetraene (24), a yellow liquid exhibiting three groups of multiplets centered at δ 1.76, 5.40, and 5.62 (Figure 4).

When conducted on a preparative scale, the thermal rearrangements of 16 and 23 represent a convenient and attractive method for the synthesis of the derived [8]-annulenes. This procedure should be generally applicable to other 1,3- and 1,5-disubstituted cyclooctatetraenes, thus providing a direct route to such isomers which has not heretofore been available.

The high level of similarity in the pmr spectra of 9, 14, and 24 (see Figures 1–4 and Table I) removed the possibility that any of these isomers could be identified solely on that basis. Determination of the percentage composition of a mixture of these three hydrocarbons

(23) Full details of the temperature-dependent pmr behavior of 23 will appear elsewhere. For a discussion of substituent-induced equilibrium imbalances in semibullvallenes, consult ref 20g and 20 f.
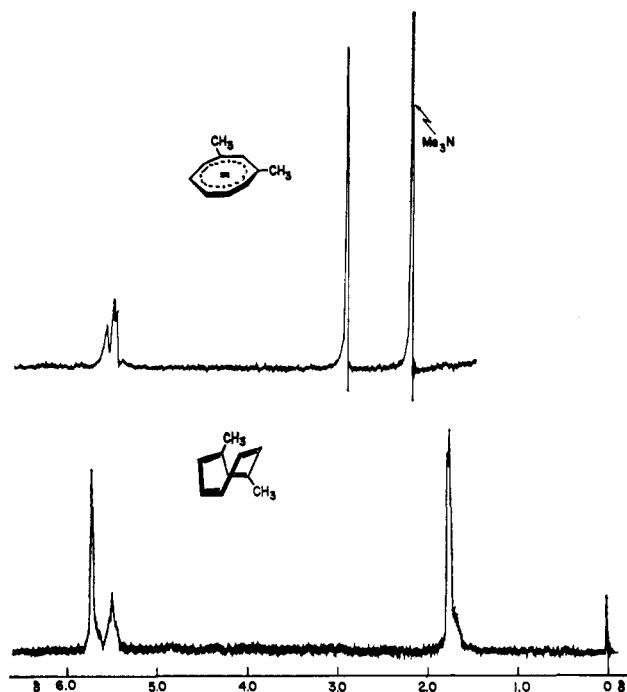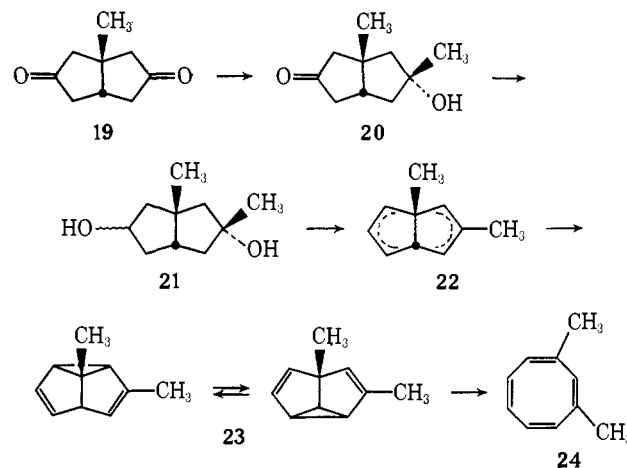

Table I. Summary of Chemical Shift Data (δ, 60 MHz)

Compd	Neutral species (CDCl₃, 40°) Olefinic	Methyl	Dianion (ND₃, −58°)[a,b] Olefinic	Methyl
17	5.7 (s)		5.61 (s)	
6	5.4–6.0 (m)	1.68 (s), 1.82 (s)	5.34–5.8 (m)	2.79 (s)
24	5.4 (m), 5.62 (m)	1.76 (m)	5.3–5.6 (m)	2.86 (s)
9	5.35–5.75 (m)	1.72 (s)	5.35–5.65 (m)	2.81 (s)
14	5.52 (m), 5.68 (m)	1.72 (s)	5.49 (s)	2.80 (s)[c]

[a] Potassium as the counterion. [b] Shifts assigned relative to tri-methylamine (δ$_{TMS}^{NH₃}$ 2.135). [c] Recorded at −50°.

was clearly not possible by this technique. At this point, considerable effort was expended in attempts to realize efficient vapor phase chromatographic separation of the four Me₂COT's. Our most satisfactory results were achieved with a 20 ft × 0.125 in. column packed with 5% PMPE six ring on Chromosorb G operating at 40°. Under these conditions, quantitative

assay of the 1,2 (t_{ret} = 9.58 hr), 1,5 (t_{ret} = 10.66 hr), and combined 1,3/1,4 (t_{ret} = 8.83 hr) ratio proved possible. Also, the four pure isomers exhibited selected fingerprint infrared absorptions which were mutually exclusive of each other: 1,2: 646, 710 (ϵ 370), and 857 cm^{-1}; 1,3: 600, 708 (ϵ 210), and 828 cm^{-1}; 1,4: 655, 701 (ϵ 182), and 844 cm^{-1}; and 1,5: 627, 722 (ϵ 160), and 891 cm^{-1}. As experimental work on the thermal rearrangements of these substances progressed,[3,4] it became increasingly evident that resolution of the crucial composition analysis problem was to rest ultimately on a combination of quantitative vpc and infrared techniques.

Alkali Metal Reduction. Hückel calculations on the hypothetical flat cyclooctatetraene molecule (**17**) indicate a delocalization energy amounting to -1.7β,[24a] but this energy advantage is not realized because of π-electronic instability (a $4n$ system) and adoption of a tub-shaped structure which effectively minimizes pπ overlap (near orthogonal alignment). COT does, however, exhibit a high affinity for electrons to produce a dianion, the delocalization energy of which has been approximated as -3.7β.[25] The pioneering work of Katz on the parent hydrocarbon[26] and the more recent study by Paquette of the 1,3,5,7-tetramethyl derivative[27] confirm that the compressional strain energy which deters flattening of the polyolefin (13–24 kcal/mol[12,9,4b,28]) and the high level of repulsive electron-electron interaction which develops in the dianion[28] are overcome, with the result that a stable, planar species (e.g., **25**) is produced. The two electrons enter non-bonding MO's and generate a filled shell ($4n$ + 2) configuration. Despite the apparent aromaticity of **25**, its concentration in solution is controlled by a disproportionation equilibrium involving reverse electron transfer to **17** with generation of radical anion **26**.[25,26,29]

25   17   26
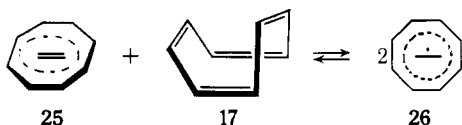
In the case of many benzenoid hydrocarbons, reaction with alkali metals in ether solvents leads to a like equilibrium which, in general, lies very far in the radical anion direction[30] in agreement with theory.[28,31] Notwithstanding the prediction that the conversion of **26** to **17** and **25** should likewise be appreciably endothermic

(91.3 kcal/mol[28]), formation of the dianion is, in contrast, now readily achieved. However, the thermodynamic parameters controlling this equilibrium are a very sensitive function of ion pairing and solvent.[29]

In this connection, Cox[32] has shown that salts of the cyclooctatetraene dianion exist as contact ion pairs in a variety of ether solvents. In diethyl ether, the ring protons are shielded by cation in the order Rb > K > Na > Li, while in both tetrahydrofuran and dimethoxyethane the relative shielding order Rb > Li > K > Na was seen. These data were taken as evidence that all the salts in diethyl ether and the dirubidium, dipotassium, and disodium salts in the other two solvents were of the type in which the cations are bound to the anion as tight contact ion pairs. For the dilithium salt in THF and DME, an equilibrium between two types of contact ion pairs was believed to be operative. Given an ordinary contact ion pair, a change to a more polar solvent normally engenders spectral changes (e.g., upfield pmr shifts) somewhat comparable to those produced by a larger cation. This effect is due to an increase in the average interionic distance caused by weakening of Coulombic attractions[33] and an increase in the fraction of solvent-separated ion pairs.[34] Noteworthy is the findings that the alkali metal salts of COT do not follow these expected trends in a wide range of *ether solvents.*[32]

For the present purposes, we chose to determine the pmr spectra of the dimethylcyclooctatetraene dianions in liquid ND$_3$. The effects of ion pairing are recognized not to be as pronounced in ammonia as they are in ethereal solvents.[35a,b] However, they appear not to be reduced to an insignificant level as gauged by the importance of the counterion on the rate of electron transfer between **25** and **26** in this medium.[22b]
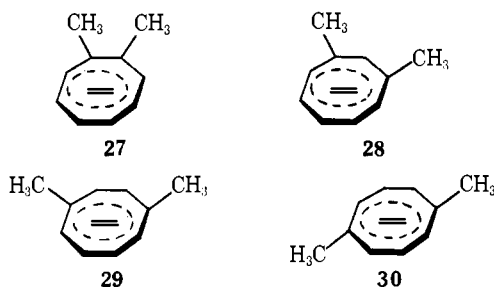
All dianion samples were prepared using high-vacuum techniques.[35c] The ND$_3$ was freshly distilled from a storage reservoir immediately prior to use. Upon reduction of the dimethylcyclooctatetraenes with 2 g-atom equiv of potassium metal, the pmr spectra of the dianions were recorded soon thereafter at -50 to $-58°$. Trimethylamine was present in these solutions as an internal standard. The pmr spectra were consistent with the formation of unique species (Table I and Figures 1–4), the changes in the spectral features reflecting conversion to diatropic[36a] structures endowed with appreciable charge delocalization. Specifically, the pairs of methyl substituents in **27–30** appear at δ 2.79–2.86 as chemically indistinguishable sharp singlets in each instance. As regards the olefinic proton signals, all of the absorptions were seen in the δ 5.3–5.8

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(26) T. J. Katz, *J. Amer. Chem. Soc.*, **82**, 3784, 3785 (1960).

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

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CH₃ CH₃ structures with labels:

CH_3 CH_3 ... **27** CH_3 ... CH_3 **28**

H_3C ... CH_3 **29** H_3C ... CH_3 **30**

region with expected multiplicity differences relatable to the ring positions taken up by the methyl groups. On the basis of the known relationship[36b] between the charge which a carbon atom bears and the chemical shift of a proton attached thereto, reduction of the dimethylcyclooctatetraenes to the respective dianions, with a double negative charge distributed over eight carbon atoms, should be accompanied by a shielding of the olefinic protons to the extent of *ca.* 2.5 ppm. However, the observed net effect in all four instances is a small level of deshielding (Table I) as expected if a substantial ring current exists. The strong deshielding of the methyl groups (*ca.* 1 ppm) also supports this conclusion.

Additionally, the pmr data establish that the dianions are effectively planar on this time scale. These findings accord nicely with X-ray crystallographic studies of the COT dianion (in the complexed state).[37] In detail, **27–30** exhibit lone high field signals of area 6 demonstrating the chemical equivalence of the methyl groups and the absence of *unsymmetrical* tight ion pairing of finite (pmr time scale) duration. Unquestionably the most impressive example of this phenomenon is dianion **30** where the symmetry of the species is reflected in the appearance of only two sharp singlets (Figure 3), this convergence of absorptions demonstrating once again[26,27] that its equilibration with the respective radical anion can be shifted completely to the left (see above). Lastly, we note that the olefinic proton signals of the four dianions are uniformly shifted to higher field as compared to the values reported for dipotassiocyclooctatetraenide in a number of ether solvents (δ 5.75–5.84).[32] The expected increase in the level of solvent-separated ion pair formation would give this effect.

Polarographic Studies. The electrochemical reduction of cyclooctatetraene (**17**) has been the subject of rather extensive investigation for over two decades. Early polarographic studies in aqueous ethanol[38] or 96% dioxane–water[39] revealed the reduction to be a two-electron process. When later examined under aprotic conditions (dry dimethylformamide solution), the actual process was shown to consist of two well-resolved one-electron steps.[40] Interestingly, the rate of the first electron transfer to COT is seen to be unusually slow, while the second is rapid.[40,41] The

relatively slow initial reduction step has been attributed to an activation process which involves energetically demanding transformation of the folded neutral molecule to a planar or nearly planar transition state; under these conditions, a similar conformational distortion is not required for subsequent introduction of the second electron and it occurs with greater facility. More recent results obtained in anhydrous tetrahydrofuran give evidence that the electrochemistry of COT is limited in the accessible potential region to a one-electron reduction and that under commonly employed conditions the radical anion is protonated (*e.g.*, by Hofmann elimination of the quaternary ammonium electrolyte) with subsequent reduction of the radical occurring at a potential slightly more negative than the tetraene itself.[7] Resolution of these widely differing interpretations must await more highly refined measurements.

The electrochemical behavior of methoxy-,[42] benzo-,[43] dibenzo-,[43,44] 1,3,5,7-, and 1,2,4,7-tetraphenylcyclooctatetraenes[45] has also come under scrutiny by various groups. Because the inherent structural features of the derivatives are widely varied and different conditions were employed in certain cases, no simple, direct correlation of structural permutation with half-wave potential, extent of electron transfer, type of electrode process (reversible or irreversible), and the like, is yet possible. Structural changes are recognized to affect polarographic curves in various ways.[46] With the availability of the four Me₂COT's, however, the opportunity for electrochemical study of a series of closely related isomers presented itself. Our initial results in this area follow.

The polarographic behavior of this family of hydrocarbons was examined under standardized conditions employing pure dry tetrahydrofuran (freshly distilled from Na–K alloy) containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as the background electrolyte. The entire series of measurements was conducted under vacuum line conditions with strict exclusion of atmospheric oxygen. The results have been compiled in Table II along with data for COT and its monomethyl derivative for comparison. This solvent system was selected because of recent developments which suggest it to be quite useful for assaying the behavior of the parent COT system.[7]

As regards the electrochemical behavior of the Me₂COT's, the individual half-wave potentials are expectedly more cathodic than COT because of inductive contributions from the methyl substituents. Similar effects have previously been observed in the electrochemical studies of azocines[42] and azulenes.[47] Strikingly, however, the $E_{1/2}$ values appear to be a linear

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Table II. Summary of Polarographic Data

Compd	Concn, mM	$E_{1/2}{}^a$	Slope^b	I	$I\eta^{1/2\ c}$	n_{app}	$E_{1/2}$, second wave	$I\eta^{1/2\ c}$
1,2-Me₂COT	0.048	−2.33	0.030	4.33	2.92	1–2	−3.0	e
(6)	0.335	−2.33	0.031	4.26				
1,3-Me₂COT	0.0945	−2.252	0.0246	4.15	2.77	1–2	−3.07	e
(24)	0.1895	−2.255	0.025	4.00				
	0.308	−2.255	0.0244	4.08				
1,4-Me₂COT	0.0437	−2.20	0.029	5.85	3.84	1–2	−3.02	e
(9)	0.0875	−2.215	0.032	5.96				
	0.146	−2.23	0.026	5.57				
	0.219	−2.222	0.027	5.50				
	0.292	−2.227	0.027	5.44				
1,5-Me₂COT	0.113	−2.145	0.028	5.30	3.60	1–2	−2.95	1.31
(14)								
MeCOT	0.20	−2.125	0.036	5.17	3.62	1–2	−2.88	1.68
	0.325	−2.120	0.0286	5.37				
	0.40	−2.120	0.024	5.45				
COT^d	0.0436	−1.975	0.0274	4.43	3.05 ⎱	2	−2.79	1.34
		−2.14	0.015	1.37	0.93 ⎰		(3rd wave)	
	0.109	−1.98	0.029	4.11	2.80 ⎱	2	−2.80	1.16
		−2.14	0.0188	1.54	1.25 ⎰		(3rd wave)	
	0.218	−1.98	0.033	4.06	2.76 ⎱	2	−2.80	0.91
		−2.145	0.019	2.24	1.52 ⎰		(3rd wave)	

^{a} The $E_{1/2}$ values were obtained vs. AgClO₄|Ag and corrected to sce by adding 0.5 V. ^{b} Slope of graph of E vs. ln $(i/(i_d − i))$. ^{c} Diffusion current constant times square root of the solvent viscosity in μA M^{-1} mg$^{-2/3}$ sec$^{1/2}$ cP$^{1/2}$; the average value is given except for COT. ^{d} The data at the highest concentration compare closely with those in ref 7. ^{e} Values unobtainable (accurately) because of proximity to solvent reduction wave.
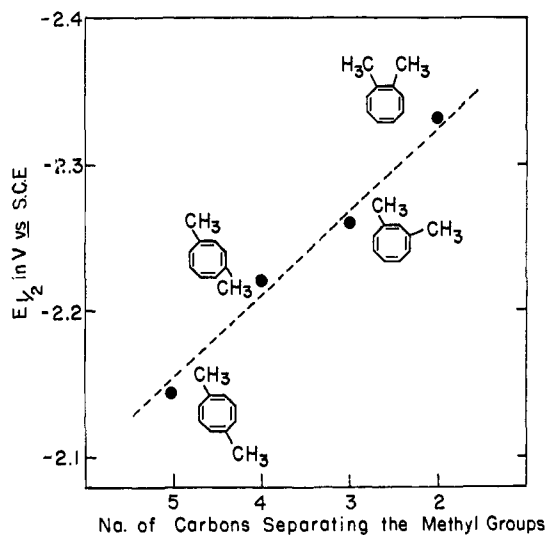
Figure 5. Plot showing the linear relationship between half-wave potential and methyl substitution in 6, 9, 14, and 24.

function of the distance separating the methyl groups (Figure 5)! The major factors controlling the potential at which the first electron is added to a given cyclic polyolefin are the electron affinity (generally considered to be directly relatable to the energy of the lowest unoccupied MO), the compressional energy of ring flattening, solvation, and outer sphere solvent reorganization energies. While these considerations apply specifically to any given depolarizer, comparison of a group of related substances requires that further conditions be fulfilled. Strictly speaking, the mechanism of the electrode processes must be the same for all Me₂COT's involved in the analysis and, particularly for irreversible processes, the value of the transfer coefficient be approximately constant for the entire group.

As concerns the first of these points, the slopes of the reduction waves for all four isomers are such that the

operation of non-Nernstian electron transfer processes is indicated. The irreversibility of the reduction wave was confirmed in the case of the 1,5-dimethyl derivative by cyclic voltammetry at temperatures down to −78° at scan speeds up to 400 mV/sec. No evidence was gained for formation of a reoxidizable product. The addition of 1 M water to the various solutions caused no substantial change in the electrochemistry, as the $E_{1/2}$ values remained the same within ±20 mV and the height of the reduction waves remained unchanged. These findings denote that the lifetimes of the initial products of one-electron transfer are very short, such that appreciable amounts of strong proton donor do not significantly alter the rates at which they undergo subsequent reaction. Because the species produced from all of the Me₂COT's are highly reactive, we have not found it possible to obtain an indication of their identities. The diffusion current constants for all the initial waves are intermediate between the values expected for a one- and two-electron transfer (Table II). Such behavior provides additional convincing evidence for the belief that chemical reaction effectively removes the product of primary electron transfer from the medium as rapidly as it is formed in each example.

Because the polarographic waves for all four hydrocarbons are non-Nernstian, their slopes do not necessarily reflect the relative thermodynamic stabilities of the reduction products. As a result, the values of n_{app} obtained in this fashion may be imprecise measures of electron uptake. To achieve a high level of accuracy, coulometric studies were resorted to. Under the predescribed conditions of solvent and electrolyte, 1,4-Me₂COT (9) exhibited an n_{app} of 1.14, 1,3-Me₂COT (24) an n_{app} of 1.28, and COT a value of 1.99 (measurement made at the potential above the second wave in this case).[48] The fractional electron uptakes do not allow a distinction to be made between a number of possible reaction pathways: for example (a) destruction

(48) We thank Mr. Davis Taggart for these coulometric measurements.

of radical anions according to the scheme Me₂COT·⁻ + H⁺ → Me₂HCOT· → dimer, (b) diffusion of Me₂COT²⁻ out into solution, disproportionation with Me₂COT to give 2Me₂COT·⁻, and subsequent coupling, or (c) yet other possibilities.

Our data indicate a similarity in the slopes of the polarographic waves for the four Me₂COT's (Table II). Since water has little or no effect on the slope and $E_{1/2}$ (<20 mV) in each case, the electron-transfer step is assumed to be rate controlling. Given that the mechanisms of electron transfer are closely similar, then the equal slopes imply similar values for the transfer coefficient α. The changes in $E_{1/2}$ can then be treated as simple functions of the energy changes accompanying each of the four electrode processes (eq 1). Substitution

$$\Delta E_{1/2} = \Delta\left(E° - \frac{RT}{\alpha nF}\ln\left(\frac{i_0}{k_s nF}\right)\right) \approx \Delta\Delta G^{\ddagger} \quad (1)$$

of the thermodynamic interpretation of $\Delta\Delta G^{\ddagger}$ by the Taft treatment of homogeneous reactions[49] leads to eq 2 which covers most substituent effect contributions to the half-wave potentials.[46] Combination of eq 1 and 2 generates eq 3, a form convenient for polarography,

$$\Delta\Delta G^{\ddagger} = \Delta\Delta E_{\sigma}^{\ddagger} + \Delta\Delta E_M^{\ddagger} + \Delta\Delta E_S^{\ddagger} \quad (2)$$

$$\Delta E_{1/2} = P + M_{\pi} + S \quad (3)$$

where the independent variables P, M_{π}, and S comprise the polar, resonance, and steric contributions to the activation energy of electron transfer.

Because of the substitution identity in 6, 9, 14, and 24, the differences in polar and resonance effects are assumed to be essentially constant and therefore canceling for the entire series. As a result, the substituent effect is embodied principally in the steric parameter. In this context, the observed reduction potential of 1,2-dimethylcyclooctatetraene (6, −2.33 V), 360 mV cathodic to the first wave of COT, is considered to reflect the severe methyl–methyl interaction which develops upon ring flattening. The $E_{1/2}$ data of Table II denote an increasing electron affinity with increasing separation of the methyl groups. The rather sizable differences (ca. 55 mV) in the half-wave potentials of the 1,4- and 1,5-dimethyl derivatives cannot be rationalized in terms of increased steric congestion as in 6. A possible explanation may reside in differing outer sphere reorganization energies and the polyolefin orientation at the moment of reduction. Thus, it is possible for 14 to approach the electrode surface from its sterically unencumbered face as in 31; 1,4-dimethyl isomer 9, in contrast, cannot escape the inevitability of projecting one of its alkyl groups toward the electrode surface (see 32).

31   32
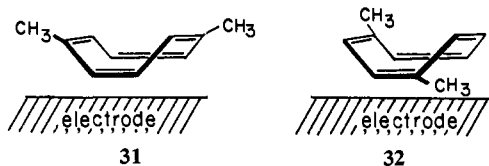
We wish to emphasize that elements of the preceding discussion stand in further need of mechanistic assessment and should not be construed to have acquired credibility from having introduced a semblance of order into this collection of data. Before a detailed mecha-

(49) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956.

nistic analysis of an electrode reaction is possible, knowledge of the mode of particle transport into the inner double layer, of chemical processes preceding the electron transfer proper (if any), of particle orientation at the moment of reaction, of transition state composition and stereochemistry, of reactions subsequent to electron transfer, and of transport of product away from the electrode surface is required. Such complete information about electrode reactions is not available for even a single organic electrochemical process! Although the significance of the reduction potential relationship between the four Me₂COT's goes unquestioned, our rationalization of the causative factors must be viewed as speculative at the present time.

The dimethylcyclooctatetraenes, in common with COT and several of its derivatives, exhibit second waves appearing at very negative potentials. The relevant $E_{1/2}$'s and diffusion current constants are summarized in Table II. These phenomena have been attributed to less conjugated substances, e.g., 1,3,5- and 1,3,6-cyclooctatrienes, produced in situ as a result of protonation reactions following upon the more facile tetraene reduction.

Summary

The sequence involving bridgehead substitution of bicyclic sulfone 7 and subsequent sulfur dioxide extrusion holds considerable promise for the synthesis of 1,4-disubstituted cyclooctatetraenes. In a companion role, the technique of thermal rearrangement of semibullvalenes expands the scope of COT syntheses to permit generation of 1,3- and 1,5-difunctionalized derivatives.

All of the Me₂COT's give rise in demonstrable fashion to stable planar dianions when reduced with potassium metal in liquid ammonia solution at low temperatures. These observations supply added credence to earlier studies with the parent (CH)₈ in tetrahydrofuran and support the idea that varying degrees of alkyl substitution do not deter passage through this manifold despite added charge concentration arising from side-chain inductive contributions.

A number of important questions still remain to be answered about the electrochemical behavior of these systems and particularly about the generation,[50] structure,[51] and fate of COT radical anions under such conditions. For a given isomeric series such as 6, 9, 14, and 24, it is now clear that steric influences do exert effects of major consequence on the half-wave potentials with the observed electron affinity related linearly to the separation of the methyl groups. We hope to provide added insight into these questions at a later date.

Experimental Section

Infrared spectra were recorded with a Perkin–Elmer Model 467 spectrometer. The pmr spectra were determined on Varian A-60A and Jeolco MH-100 instruments and apparent splittings have been cited in all cases. Mass spectra were measured with an AEI MS-9 spectrometer at an ionizing energy of 70 eV. Microanalyses were performed by the Scandinavian Microanalytical Laboratories, Herlev, Denmark.

1,2-Bis(hydroxymethyl)cyclooctatetraene (4). To a mechanically stirred suspension of 4.55 g (0.12 mol) of lithium aluminum hydride

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(51) (a) P. I. Kimmel and H. L. Strauss, J. Phys. Chem., 72, 2813 (1968); (b) J. R. Dodd, Tetrahedron Lett., 3943 (1973).

in 300 ml of ether was added 5.97 g (0.045 mol) of aluminum chloride portionwise under an atmosphere of dry nitrogen at 20°. The white suspension was stirred for 1 hr at room temperature at which time a solution of 12.93 g (0.059 mol) of 3^{8f} in 350 ml of ether was added dropwise with cooling (20–23°, 45 min). The mixture was stirred at room temperature for 3.5 hr, treated cautiously with 40 ml of saturated ammonium chloride solution, and filtered. The insoluble solids were extracted exhaustively with boiling ether. The combined organic layers were dried and evaporated to give 7.9 g (82%) of **4** as a viscous oil whose pmr spectrum was identical with that previously reported.[9]

1,2-Bis(bromomethyl)cyclooctatetraene (5). To a magnetically stirred solution of 51.0 g (0.195 mol) of triphenylphosphine in 400 ml of anhydrous dimethylformamide (freshly distilled from CaH_2) was slowly added under nitrogen 31.2 g (0.193 mol) of bromine. To this reagent was added 8.00 g (48.8 mmol) of **4** in 80 ml of the same solvent during 30 min and the mixture was stirred at room temperature for 2 hr before being poured into 1500 ml of cold water and extracted with ether (3 × 400 ml). The combined organic layers were washed with water and saturated sodium bicarbonate solution, dried, and evaporated. The semisolid so obtained was digested with hot pentane and the pentane extracts were filtered through 20 g of silicic acid to give a yellow solution evaporation of which gave 11.0 g (78%) of **5** as yellow crystals, mp 64–66° (lit.[10] mp 65–66°). This very potent lachrymator exhibited a pmr spectrum identical with that described earlier.[10]

1,2-Dimethylcyclooctatetraene (6). A solution of 9.6 g (0.033 mol) of **5** in 100 ml of ether was added during 25 min to a stirred suspension of 6.3 g (0.165 mol) of lithium aluminum hydride in 150 ml of the same solvent. The mixture was refluxed for 12 hr, cautiously hydrolyzed with 125 ml of saturated ammonium chloride solution, and diluted to 800 ml with dilute hydrochloric acid. After separation of the layers and several extractions with ether, the combined organic layers were washed with saturated sodium chloride solution, dried, and carefully concentrated to a small volume under reduced pressure. The last traces of solvent were removed by distillation at atmospheric pressure. Fractionation of the residue afforded 3.81 g (87%) of **6**, bp 78–80° (45 mm); the infrared spectrum was identical with that reported earlier.[11]

9-Thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-Dioxide (7). To a solution of the sulfoxide (1.485 g, 9.64 mmol), prepared by *in situ* addition of sulfur monoxide to cyclooctatetraene,[14] in 100 ml of methylene chloride was added dropwise with stirring at 0° 1.86 g (89.5% purity, 9.65 mmol) of *m*-chloroperbenzoic acid dissolved in 50 ml of the same solvent. The solution was stirred overnight at ambient temperature at which time it was treated with 0.5 *M* sodium hydroxide solution until alkaline, water until neutral, and saturated brine. The organic layer was dried and evaporated to give white crystals; recrystallization from methylene chloride–ether gave 1.23 g (75%) of **7**, mp 193° (lit.[15] mp 192.5–193°): $\delta_{TMS}^{CDCl_3}$ 3.78–4.15 (m, 2) and 5.80–6.37 (m, 6); ν_{max}^{Nujol} 1100, 1125, and 1290 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 225 (ϵ 2820) and 279 nm (2840); *m/e* calcd 168.0244, obsd 168.0242.

Anal. Calcd for $C_8H_8O_2S$: C, 57.12; H, 4.79. Found: C, 56.90; H, 4.79.

1,6-Dimethyl-9-thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-Dioxide (8). *n*-Butyllithium solution in pentane (2.0 ml, 2.64 mmol) was introduced *via* syringe to a stirred suspension of **7** (170 mg, 1.0 mmol) in 10 ml of tetrahydrofuran cooled to −70° and maintained under nitrogen. The resulting deep purple colored solution was stirred for 5 min at this temperature and treated with a large excess of methyl iodide. The pale yellow solution was allowed to warm to room temperature, the solvent was removed *in vacuo*, and the residue was taken up in methylene chloride. This solution was washed with water, dried, and concentrated to afford a quantitative yield of **8**, mp 149–150° (from methylene chloride–ether): $\delta_{TMS}^{CDCl_3}$ 1.55 (s, 6), 5.60 (s, 2), and 5.50–6.27 (H, 4); ν_{max}^{Nujol} 1120, 1125, 1280, and 1290 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 224 (ϵ 2200) and 278 nm (1530).

Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.19; H, 6.16; S, 16.30. Found: C, 61.13; H, 6.15; S, 16.14.

1,4-Dimethylcyclooctatetraene (9). A solution of 1.00 g (5.10 mmol) of **8** in 100 ml of acetone and 300 ml of ether was irradiated with a 200-W Hanovia lamp fitted with a Corex filter and placed in a quartz immersion well. Prior to irradiation, the solution was deaerated with dry nitrogen for 30 min. After this time, the solution was carefully concentrated to small volume under reduced pressure and the residual solvent was removed by distillation at atmospheric pressure. Isolation of **9** was achieved by preparative vpc techniques (5.5 ft × 0.25 in. 5% SE-30 on Chromosorb G, 125°,

t_{ret} = 5 min); there was obtained 275 mg (41%) of clear yellow liquid. See text for spectral properties.

Anal. Calcd for $C_{10}H_{12}$: C, 90.91; H, 9.09. Found: C, 90.81; H, 9.20.

Pyrolysis of Semibullvalene (15). Freshly prepared semibullvalene (42.8 mg, containing 4.4% **17**) was slowly vaporized into a flow system of nitrogen into a quartz reactor packed with quartz chips[52] heated to 427° (30 mm). The yellow pyrolysate (25.3 mg, 59%) was collected in a Dry Ice–acetone cooled receiver. Pmr and vpc analysis revealed this material to be composed of cyclooctatetraene (95%, $\delta_{TMS}^{CDCl_3}$ 5.75) and semibullvalene (5%, $\delta_{TMS}^{CDCl_3}$ 5.18, 4.20, and 3.00).

Pyrolysis of 1,5-Dimethylsemibullvalene (16). Freshly prepared 16^{20e} (95.1 mg) was pyrolyzed at 390° and 30 min in a nitrogen atmosphere with the above apparatus. The yellow pyrolysate (72.5 mg, 76%) was uniquely the desired 1,5-dimethylcyclooctatetraene (**14**). See text for spectral properties.

Anal. Calcd for $C_{10}H_{12}$: C, 90.91; H, 9.09. Found: C, 90.73; H, 9.12.

TCNE Adduct of 1,5-Dimethylcyclooctatetraene (18). A solution of 12 mg (0.091 mmol) of **14** and 128 mg (1 mmol) of tetracyanoethylene in 3 ml of ethyl acetate was refluxed under nitrogen for 12 hr, cooled, and diluted with ether. Subsequent processing involved washing with 10% sodium bisulfite solution, water, and brine. After drying and evaporation of solvent, the residual crystalline residue was chromatographed on Florisil (methylene chloride elution) to furnish 13.1 mg (55.4%) of **18** as white crystals, mp 179.5–180° (from methylene chloride–ether). See text for pmr data.

Anal. Calcd for $C_{16}H_{12}N_4$: C, 73.83; H, 4.65. Found: C, 73.75; H, 4.71.

1,3-Dimethyl-3-hydroxy-*cis*-bicyclo[3.3.0]octan-7-one (20). To a magnetically stirred solution of 4.65 g (0.03 mol) of 19^{22} in 250 ml of dry tetrahydrofuran cooled to −70° was added dropwise 0.72 g (0.032 mol) of methyllithium (1.30 *M* in ether). After 30 min at this temperature, the reaction was quenched by addition of water. The tetrahydrofuran was evaporated under reduced pressure and the residual aqueous phase was extracted with chloroform. The combined extracts were washed with brine, dried, and evaporated to give 4.85 g (96%) of pale yellow solid. Recrystallization of this material from chloroform–hexane afforded pure **20** as white crystals, mp 83–85°: $\delta_{TMS}^{CDCl_3}$ 1.24 (s, 3), 1.37 (s, 3), and 1.50–2.90 (m, 10); ν_{max} 3305, 2930, and 1727 cm^{-1}.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.72; H, 9.57.

3,7-Dihydroxy-1,3-dimethyl-*cis*-bicyclo[3.3.0]octane (21). To a stirred suspension of 1.80 g (0.04 mol) of lithium hydride in 120 ml of anhydrous ether was added dropwise at 0° a solution of 3.65 g (0.021 mol) of **20** in 30 ml of the same solvent. After being stirred for 20 min at 0° and 1 hr at room temperature, the excess hydride was destroyed by addition of saturated sodium sulfate solution. The inorganic solids were removed by filtration and washed exhaustively with ether. The combined organic layers were washed with brine, dried, and evaporated to give 3.42 g (95%) of white solid, recrystallization of which from chloroform–hexane furnished pure **21**, mp 78.5–81.5°: $\delta_{TMS}^{CDCl_3}$ 1.04 (s, 3), 1.23 (s, 3), 1.50–2.60 (m, 9), 4.05–4.50 (m, 1), and 4.40–5.05 (m, 2, OH); $\nu_{max}^{CHCl_3}$ 3350, 2930, and 1133 cm^{-1}.

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.67; H, 10.69.

1,3-Dimethyl-*cis*-bicyclo[3.3.0]octadienes (22). A 2.00-g (0.0118 mol) sample of **21** was added dropwise with stirring to a suspension of sodium hydride (1.48 g, 0.035 mol. 57% in mineral oil) in 110 ml of dry tetrahydrofuran. The resulting mixture was refluxed for 3 hr, cooled, and treated dropwise with 1.84 ml (0.030 mol) of carbon disulfide. After being heated at reflux for 3 hr, the contents were cooled, treated dropwise with 1.90 ml (0.030 mol) of methyl iodide, again refluxed for 3 hr, and cooled. The excess hydride was decomposed with water, the tetrahydrofuran was evaporated under reduced pressure, and the resulting reddish oil was taken up in chloroform. This solution was washed with water and brine, dried, and evaporated to yield 3.98 g of the dixanthate ester. Pyrolysis of this material at 180–250° (760 mm) afforded a pale yellow pyrolysate which was purified by column chromatography on silica gel (pentane elution). There was obtained 1.09 g (70%) of **22** as a colorless oil which was used directly in the next step:

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(52) For a description of the apparatus, see L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **93**, 2459 (1971).

$\delta_{TMS}^{CDCl_3}$ 1.08 (s, 3), 1.17 (s, 3), 1.63 (m, 3), 1.80–3.20 (br m, 5), and 4.90–5.60 (br m, 3).

1,3-Dimethylsemibullvalene (23). A solution containing 1.09 g (8.3 mmol) of **22** and 2.95 g (16.6 mmol) of *N*-bromosuccinimide in 40 ml of carbon tetrachloride was refluxed for 2 hr and cooled to 0°. The succinimide was removed by filtration and the filtrate evaporated to leave 2.42 g (100%) of a pale yellow lachrymatory oil. This oil was dissolved in 50 ml of ether and 25 g of 0.8% lithium amalgam was added portionwise under argon. After 1.2 hr, the analysis showed no remaining dibromide. The excess amalgam and mercury were separated by decantation and the filtrate was evaporated at atmospheric pressure. The residual liquid was chromatographed on silica gel (pentane elution) to yield 672 mg (61%) of **23** as a colorless liquid. Final purification was achieved by preparatory vpc: $\delta_{TMS}^{CDCl_3}$ 1.11, (s, 3), 1.58 (m, 3), 2.64 (m, 1), 3.06 and 3.28 (m, 1 H each), 4.35, 4.69, and 5.03 (m, 1 H each); *m/e* calcd 132.0939, obsd 132.0940.

1,3-Dimethylcyclooctatetraene (24). Freshly prepared **23** (250 mg, 1.90 mmol) was pyrolyzed as previously described at 445° (35 mm). Vpc analysis of the yellow pyrolysate (195 mg, 78%) revealed a composition of 89% of **24** and 11% of unreacted **23**. Preparative scale isolation (3 ft × 0.25 in 5% OV-11 on Chromosorb G) gave pure **24**; see text for pmr data; *m/e* 132.0939, obsd 132.0940.

Anal. Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 91.10; H, 8.97.

Method for Obtaining Pmr Spectra of Anions in ND_3. Approximately 0.5 ml of ND_3[53] 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 ND_3 during this operation. The cap was replaced and the ND_3 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 standard taper 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 after degassing the sample 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.

Electrochemical Measurements. Polarographic studies in purified, dry tetrahydrofuran solution were carried out on a specially designed vacuum-line electrochemical cell allowing all preparations and measurements to be carried out under conditions of rigorous exclusion of air and moisture.[54] Details of procedure have been previously described.[42] Techniques for purifying solvents and background electrolytes and experimental procedures were identical with those utilized in our earlier work.[42,43,55]

(53) 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 ND_3 were made to guarantee maximum dryness of the solvent; the last transfer was effectively a distillation over elemental sodium.

(54) J. L. Mills, R. Nelson, S. Shore, and L. B. Anderson, *Anal. Chem.*, 43, 157 (1971).

(55) (a) L. A. Paquette, L. B. Anderson, J. F. Hansen, S. A. Lang, Jr., and H. Berk, *J. Amer. Chem. Soc.*, 94, 4907 (1972); (b) L. B. Anderson, M. J. Broadhurst, and L. A. Paquette, *ibid.*, 95, 2198 (1973).

Thermally Induced Degenerate Skeletal Rearrangement and Isomerization Reactions of Cyclooctatetraenes

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Abstract: Thermal rearrangements in the gas phase at 395° and above of various cyclooctatetraenes are herein reported to lead to [8]annulene → [8]annulene isomerization or degenerate rearrangement depending upon substitution. In particular, attention has been given to the four isomeric dimethylcyclooctatetraenes, a doubly labeled (deuterium) derivative of the 1,2-dimethyl compound, benzocyclooctatetraene and its nonaromatic tetrahydro counterpart, various monosubstituted derivatives with wide-ranging electronic demands (R = $COOCH_3$, C_6H_5, CH_3), and the parent hydrocarbon itself (in the form of the 1,4-dideuterio structure). The results are rationalized in mechanistic terms which stress the importance of the valence isomeric bicyclo[4.2.0]octatrienes and orbital symmetry control. The rearrangements are held to occur predominantly through intramolecular Diels–Alder cyclization of the bicyclic trienes with formation and subsequent ($_\sigma 2_s + _\sigma 2_s + _\pi 2_s$) opening of intermediate tetracyclo[4.2.0.0^{2,8}.0^{5,7}]octenes and/or [1,5]-sigmatropic shift within these same trienes. Other possibilities are weighed in light of predicted "one-pass" bond reorganizations and considered less likely or inoperative. The relationship of the various schemes to known thermochemistry is discussed.

T he phenomenon of degenerate structural rearrangement continues to be a source of fascination for chemists. In addition to providing much fundamental information about the structure and behavior of both neutral molecules and ions, processes involving the interchange of constituent atoms and bonds with regeneration of the same gross structure are mechanisti-cally intriguing as well. No generalized reaction scheme accommodates this group of reactions; rather, a broad spectrum of pathways has been uncovered. Bullvalene[1]

(1) G. Schröder and J. F. M. Oth, *Angew. Chem., Int. Ed. Engl.*, 6, 414 (1967); W. von E. Doering, *et al.*, *Tetrahedron*, 23, 3943 (1967); G. Schröder, *Chem. Ber.*, 97, 3140 (1964); W. von E. Doering and W. R. Roth, *Tetrahedron*, 19, 715 (1963).