Buffered Acetolyses of β-Cyclooctatetraenylethyl Brosylates. Isomerization to Tetrahydroazulenoid Products in Response to Homoallylic Electron Deficiency[1]

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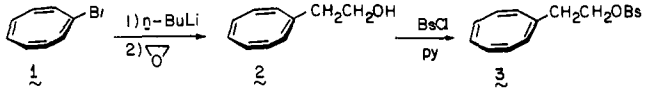
Abstract: Evidence is presented that β-cyclooctatetraenylethyl brosylates undergo solvolysis with participation by the double bond of the homoallylic system to give initially spiro[7.2]nonatrienyl cations. The rate of acetolysis of the parent system (**3**) has been compared with those of β-(Δ¹-cyclooctenyl)ethyl (**7b**) and β-cyclooctylethyl brosylates (**8b**) and the relative order of reactivity was 5:260:1, respectively. The products of ionization have been isolated throughout the series. Whereas **7b** and **8b** behave in predictable fashion, **3** experiences deep-seated rearrangement with formation of a tetrahydroazulenyl acetate. Deuterium labeling of the side chain and methyl substitution of the medium ring attest to symmetrization of both moieties during the novel ring contraction sequence. A mechanistic rationalization in full agreement with all the available data is presented. The structural question surrounding the spiro[7.2]nonatrienyl cation intermediate is discussed briefly.

The ideal electronic stability of benzene is recognized not to lend itself readily to protonation because of requisite passage to the benzenonium ion and destruction of the aromatic sextet. With superacids such as hydrogen fluoride–antimony pentafluoride in SO_2ClF, proton addition to the arene can be made to occur at low temperatures,[2] but weaker acids are notably less effective. An interesting contrast is found in the susceptibility of cyclooctatetraene (COT) to protonation. Owing to the lack of significant resonance stabilization in COT[3] and its conversion upon electrophilic attack to stabilized homotropylium cations, its propensity for protonation far exceeds that of its lower $(CH)_n$ homolog.[4] Concentrated sulfuric acid is now adequate to the task.

Despite the energy disadvantage associated with benzenonium ion generation, β-phenethyl derivatives seemingly do solvolyze by way of intermediate σ-bridged phenonium ions.[5] However, the latent potential of COT to function as a like neighboring group, perhaps with formation of related homotropylium ions, remained to be examined. We now describe a novel series of rearrangements which operates upon ionization of β-COTethyl derivatives.[6]

Results

Synthesis. The preparation of β-cyclooctatetraenylethanol (**2**) was effected in 60% yield by lithiation of bromoCOT (**1**) followed by reaction with excess ethylene oxide.[7] The derived brosylate **3** was obtained as a low melting pale yellow crystalline solid.



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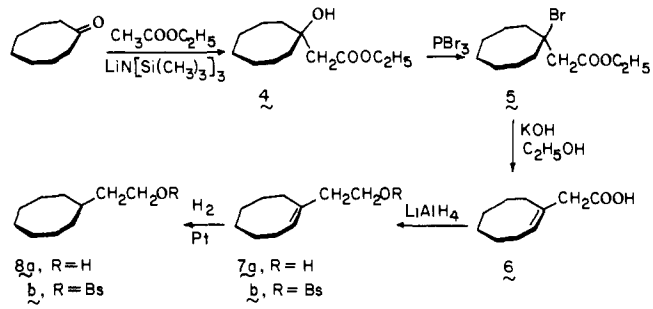
Access to model compounds was gained by treating cyclooctanone with lithium bis(trimethylsilyl)amide and ethyl acetate according to Rathke's procedure.[8] This method was found to be less tedious and more efficient in the production of **4** than the Reformatsky procedure (95% vs. 45%). When the hydroxy ester was treated with phosphorus tribromide and the bromo ester so produced (**5**, 99%) exposed directly to the action of ethanolic potassium hydroxide, we were gratified to observe high yield formation of Δ¹-cyclooctenylacetic acid (**6**) free of the conjugated exocyclic isomer. Less satisfactory methods included, for example, the reaction of triphenylphosphine dibromide with **5** in dimethylformamide at 100°. Under these conditions, ester hydrolysis was not operational, but 33% contamination by the conjugated ester was noted. Hydride reduction of **6** gave alcohol



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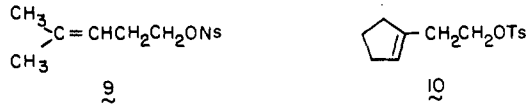
7a which also served as the ultimate precursor to the known **8a**.[7]

Solvolysis Rates and Products. Table I lists the pertinent kinetic data for acetolysis of **3**, **7b**, and **8b** in acetic acid buffered with sodium acetate. Good first-order behavior was evidenced in all three instances. When the ratio of the rate constants for **7b** and **8b** (260) is compared to the k_{unsat}/k_{sat} value (350) reported for the acetolysis of 4-methyl-3-pentenyl β-naphthylsulfonate (**9**),[9] a rather similar quantitative relationship is seen. For comparison, the k_{unsat}/k_{sat} for acetolysis of **10** is only 40[10] and signals the impact



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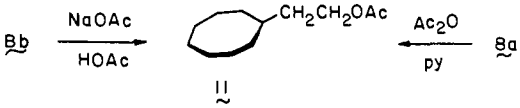
which strain and ring size effects can exert on homoallylic solvolysis. On this basis, the β-(Δ¹-cyclooctenyl)ethyl system gives indication of anchimeric assistance to ionization. Comparison with the primary homoallylic brosylate **7b** suggests that the β-cyclooctatetraenylethyl example **3** is only moderately reactive, its solvolytic behavior being more closely allied to that of the fully saturated **8b**. However, this simple comparison may be unreliable (see Discussion).

The saturated brosylate **8b** was solvolyzed for 10 half-lives (7 days) at 85° in acetic acid containing sodium acetate. The sole product, identified as **11** on the basis of its



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unequivocal synthesis from **8a**, was isolated in greater than 90% yield. No elimination product(s) could be detected by VPC or ^1H NMR analysis.

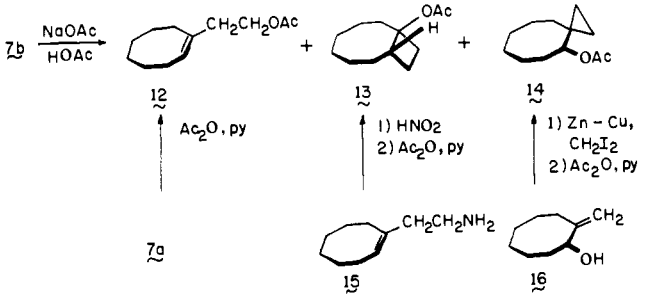
Similar solvolysis of **7b** at 50° using a tenfold molar excess of sodium acetate gave rise to the trio of acetates **12**

Table I. Buffered (NaOAc) Acetolysis Rate Data

Brosylate	Temp, °C	k_1, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Rel rate, 65°
3	55.00 ± 0.02	1.91×10^{-6}			
	65.00 ± 0.03	6.58×10^{-6}	25.3	−7.9	5
	75.00 ± 0.03	1.87×10^{-5}			
7b	45.00 ± 0.02	3.43×10^{-5}			
	55.00 ± 0.03	1.25×10^{-4}	24.9	−0.78	260
	65.00 ± 0.03	3.74×10^{-4}			
8b	65.0	1.43×10^{-6}[a]			
	75.00 ± 0.03	4.69×10^{-6}			
	85.00 ± 0.03	1.16×10^{-5}	24.9	−11.8	1
	95.00 ± 0.03	3.25×10^{-5}			

[a] Extrapolated value based on the activation parameters.

(34%), **13** (10%), and **14** (55%).[11] These products were separated by gas chromatographic methods and characterized by means of their ir and ^{1}H NMR spectra and independent preparation. The action of acetic anhydride in pyridine on **7a** gave the primary acetate **12.** The alternative route to tertiary acetate **13** took advantage of the fact that deamination of amine **15** leads to 1-hydroxybicyclo[6.2.0]decane in



addition to **7a.**[11] Acetylation of this bicyclic alcohol provided authentic **13.** Secondary acetate **14** was identical in all respects with the material obtained from sequential Simmons–Smith cyclopropanation and acetylation of **16.**[12]

As expected,[13] reduction in the amount of buffer effected changes in the product composition. With only a 10% molar excess of sodium acetate, for example, **13** was found to comprise 41% of the product mixture while **14** accounted for the remaining 59%. Apparently, the inevitable SN2 component observed originally as a consequence of the excessive concentration of acetate ion utilized was now reduced to a nondetectable level. The exclusive production of rearranged products under these conditions points up the importance of double bond participation in the course of ionization. The possibility that acetates **12–14** were capable of solvolysis in their own right was also assessed. At 50° under the original reaction mixture, **13** rearranged exclusively to **12** while **14** isomerized (less readily) with formation of both **12** and **13** (4:1). Acetate **12** proved insensitive to further change.

Similar acetolysis (75°) of **3** resulted in conversion to **17, 18,** and, at low buffer concentrations, 1,2-dihydronaphthalene (**19**), naphthalene (**20**), and tetralin (**21**). As summarized in Table II, evidence gathered from several runs has denoted again a significant variation in product ratio as a function of NaOAc concentration. Moreover, independent treatment of **18** with *p*-toluenesulfonic acid in acetic acid

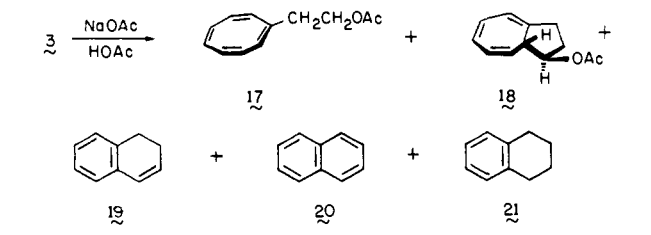
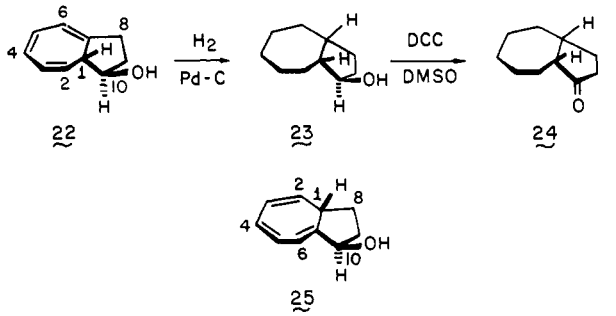


Table II. Product Variation during Acetolysis of 3

Run	Molar proportion NaOAc	Concn, *N*	Product composition, % 17	18	19	20	21
A	1	0.1			86	7	7
B	10	0.2	19	69	12		
C	10	2.0	49	48	3		

resulted in almost complete conversion to **19.** Accordingly, the real possibility exists that **18** and **19** arise from a common cationic intermediate with formation of **18** being favored in a medium containing high levels of acetate ion.

The hydrocarbon products were identified by comparison of their spectral data and VPC retention times with those of authentic samples. Acetate **17** was readily accessible from the acetylation of **2.** The structural elements inherent in **18** were established by suitable chemical correlation with *cis*-perhydro-1-azulenone in tandem with spin decoupling and Eu(fod)$_3$ shifting of the ^{1}H NMR spectrum of alcohol **22** obtained by lithium aluminum hydride reduction of this acetate. Thus, catalytic hydrogenation of **22** provided **23,** oxidation of which by the Moffatt procedure gave **24.** Direct



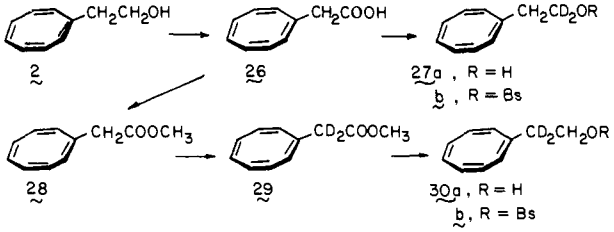
comparison of spectral data[14] and identity of the semicarbazone derivatives (mp 220–221°)[14] confirmed this ketone to be the cis isomer and eliminated *trans*-perhydro-1-azulenone[15] from further consideration.

Our inability to oxidize **22** successfully was invariably thwarted by its facile dehydrative rearrangement to **19.** Pursuit of the necessary distinction between **22** and its tautomer **25** then followed a course of spin decoupling studies. A first suggestion that the alignment of the three conjugated double bonds accorded uniquely with structure **22** came from the finding that the pair of C_8 methylene hydrogens appear at δ 2.37–2.70 significantly downfield of the H_9 signal (2.03–2.28) and in the normal allylic region of the spectrum. A comparable chemical distinction between positions 8 and 9 is not present in **25.** Furthermore, H_1 is coupled uniquely to the adjacent olefinic proton H_2 (J = 4 Hz), no spin interaction with an adjacent sp^3 C–H being evident at 100 MHz. This observation agrees with expected adherence to the Karplus correlation,[16] the H_1, H_2 and H_1, H_{10} dihedral angles in **22** approximating 120 and 90°, respectively. In contrast, molecular models of **25** reveal H_1 to be positioned 20 and 95° out of plane to the pair of hydrogens bonded to C_8. Although a negligible coupling constant would be expected where the angle is 95°, a dihedral angle of 20° should give rise to a large (ca. 7 Hz) spin interaction term. However, this was not observed.

Differentiation of these two structures was made possible on a more convincing basis by lanthanide induced shifting of the ^{1}H NMR spectrum. In **22,** the vicinal cis relationship of H_1 to the hydroxyl group should be reflected in a rapid downfield shift of this proton upon incremental addition of Eu(fod)$_3$. In **25,** the 1,3 relationship of H_1 to the site of complexation should be evidenced by relatively greater

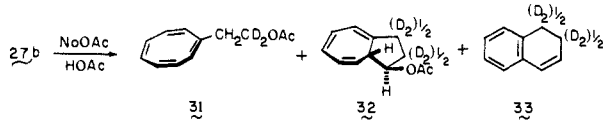
downfield shifting of *syn*-H_9. The experimental facts can be summarized in terms of the relevant ΔEu values[17] for the various protons which are seen to decrease in the order: -OH (−121), H_{10} (−24.2), H_1 (−18.7), H_{9s} (−16.9), H_{8s} (−14.1), H_{9a} (−9.15), H_{8a} (−8.71), H 2(−6.99), H_3 (−5.69), H_4 (−3.61), H_6 (−3.17), and H_5 (−2.99). Protons situated geminally to a hydroxyl function are known to give rise to ΔEu values in the range of −21.7 to −26.7 ppm.[17] Vicinal protons have been found to experience deshielding effects of −8.8 to −19.2 ppm depending upon the dihedral angle separating the -OH group from the proton under consideration.[17] A linear relationship also exists between ΔEu and R, the vector distance involved. In structure **25**, the R for H_1 is approximately 4.5 Å which would correspond to a ΔEu of approximately −6 ppm. In **22**, the R value is decreased to 3 Å and a much stronger ΔEu (>−15 ppm) should be observed as a result. Our data are reasonably consistent only with structural assignment **22**, and consequently with tetrahydroazulenyl acetate **18** as the major acetolysis product of **3**.

Deuterium Labeling of the Side Chain in 3. Subsequent to the identification of **18**, the question of the origin of **17** and **18**, and particularly knowledge of whether these acetates arose from a common cationic intermediate, became the mechanistic issue. That the precursors to **17** and **18** are in fact nonidentical was revealed upon acetolysis of **27b** and **30b**. The α,α-dideuterio brosylate was prepared by Jones oxidation of **2**, reduction of the carboxylic acid so produced (**26**) with lithium aluminum deuteride, and reaction with *p*-bromobenzenesulfonyl chloride in pyridine. Synthesis of the β,β-dideuterio isomer (**30b**) was achieved by diazo-



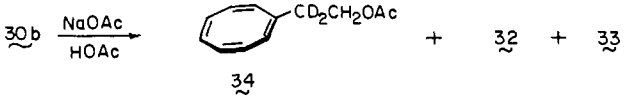
methane esterification of **26**, isotopic exchange of the pair of α-carbonyl protons with sodium methoxide in CH_3OD, and repetition of the previous sequence but with $LiAlH_4$. ^1H NMR analysis of **30b** denoted an isotopic purity greater than 95%.

Solvolysis of **27b** under so-called B conditions (Table II), followed by preparative VPC separation of the three products, revealed three relevant facts. First, unrearranged acetate **31** had not suffered deuterium scrambling: the signal at



δ 4.13 anticipated for the $-CH_2O-$ functionally was lacking and the absorption at 2.37 due to the allylic methylene group was of undiminished intensity (area 2). Comparable ^1H NMR analysis of **32** gave evidence that the deuterium atoms were equally distributed between C_8 and C_9.[18] Also, the isolated 1,2-dihydronaphthalene had undergone an entirely comparable deuterium scrambling at C_1 and C_2, an unsurprising result in view of the preexisting knowledge that this hydrocarbon is a secondary product arising from further rearrangement of the tetrahydroazulenyl acetate.

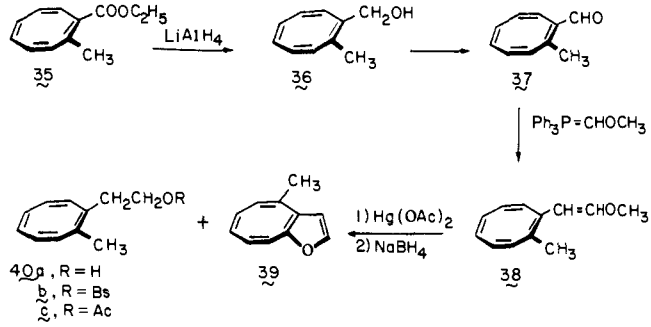
Acetolysis of **30b** gave an entirely comparable result with **34** exhibiting no deuterium scrambling and the other two



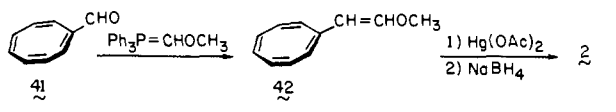
products showing equivalent levels of isotopic substitution at their individual methylene groups.

Because the β-cyclooctatetraenylethyl acetate in both instances did not undergo positional transposition of deuterium, the genesis of this product may consequently be accounted for simply in terms of SN2 behavior. As regards the formation of **32**, the results implicate a symmetrical carbocation precursor. However, mechanistic considerations (see Discussion) require that symmetrization of the two-carbon side chain be accompanied by attainment of equivalency by certain pairs of the COT ring carbons (C_2,C_8; C_3,C_7; C_4,C_6). This point was next established.

Substitution of the Cyclooctatetraene Ring. Because particularly facile synthetic entry to 1,2-disubstituted cyclooctatetraenes can be gained by the photocycloaddition of suitable acetylenes to benzene,[19,20] consideration was initially given to brosylate **40b**. Starting ester **35**, prepared from



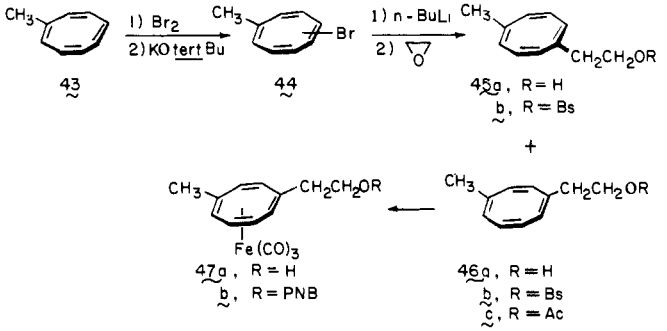
ethyl tetrolate as described by Anet,[19i] was subjected in turn to hydride reduction and oxidation with "active" manganese dioxide on carbon following Carpino's general procedure.[21] This aldehyde reacted readily with methoxymethylenetriphenylphosphorane with formation of vinyl ether **38** in 82% yield. This substance proved to be rather unstable and was seen to undergo considerable polymerization upon standing for 24 hr at room temperature. Moreover, its hydrolysis proved to be difficult since the usual protic acids were seen to preferentially attack the COT ring rather than the side chain. Reaction of **38** with mercuric acetate and sodium borohydride in base did comprise a mild, clean method for conversion to **40a**, but this alcohol comprised only one-third of the reaction mixture. The major product (58% isolated) was identified as 2-methylcycloocta[*b*]furan (**39**) on the basis of its spectral features (see Experimental Section). This heterocycle comprises the first member of this class of compounds, only the isomeric cycloocta[*c*]furan having been previously reported.[22] We have been puzzled by the preliminary finding that comparable two-stage reduction of vinyl ether **42** gave **2** in almost quantitative yield



without any indication for production of desmethyl **39**. The separation of **39** and **40a** was effected conveniently by column chromatography. Solvolysis of **40b** in the predescribed manner afforded unrearranged acetate **40c** exclusively. Consequently, a methyl group at position 2 appears to be a sufficient structural perturbation to preclude solvolytic rearrangement along that reaction channel which provides tetrahydroazulenoid product.

Efforts were then directed to the preparation of an isomeric brosylate where the methyl group would be positioned more remotely from the solvolysis center (but not at C_5). Konz, Hechtl, and Huisgen had previously reported the synthesis of 1,4-dibromoCOT by the bromination-dehydrobromination of bromoCOT.[23] Although subsequent

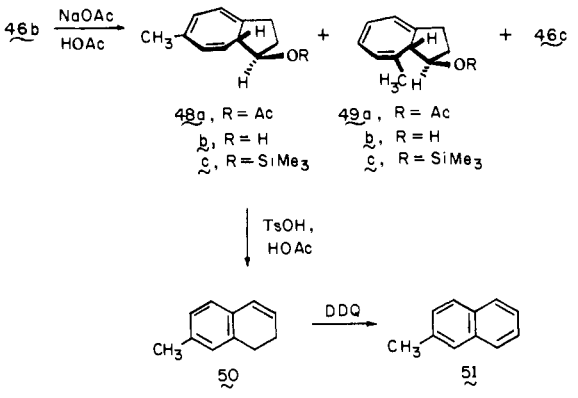
work in this laboratory revealed that significant quantities of the 1,5 isomer were produced as well in this reaction,[20] it remained clear that the 1,4-dibromide predominated. Should methylCOT (**43**) behave in a phenomenologically comparable way, then 1-bromo-4-methylCOT (**44**) could be acquired with minimal difficulty. In actuality, when **44** was



synthesized in this manner and treated with *n*-butyllithium and ethylene oxide, there was obtained a 1:3 mixture of the 5-methyl- (**45a**) and 4-methyl-β-COTethanol (**46a**) isomers, These alcohols could be separated with great loss by VPC; their brosylates have significantly different melting points although their ^{1}H NMR spectra are nearly identical.

For the purpose of structural elucidation, **46a** was treated with iron enneacarbonyl in ether and the resulting $Fe(CO)_3$ complex (**47a**) was converted to its *p*-nitrobenzoate for three-dimensional X-ray crystal structure analysis. 1,4-Placement of the substituents was thereby unequivocally established.[24]

The acetolysis of **46b** gave an inseparable mixture of **48a** and **49a** (ca. 1:1) in 80% yield together with **46c** (20%) and a trace of a methyldihydronaphthalene. Acetates **48a** and **49a** were characterized by spectral analysis preceding (as



the mixture) and subsequent to hydride reduction, trimethylsilylation, and VPC separation. The ^{1}H NMR spectra of pure **48c** and **49c** were distinctively different with the most distinguishing features seen in the vinyl region. In **49c,** the peak at δ 4.8 ascribable to H_2 is lacking and the chemical shifts for both H_3 and H_{10} are notably deshielded compared with the related signals in both **18** and **48c.** For **48c,** the H_4 proton is lacking and the remainder of the spectrum is compatible with the structural assignment (see Experimental Section).

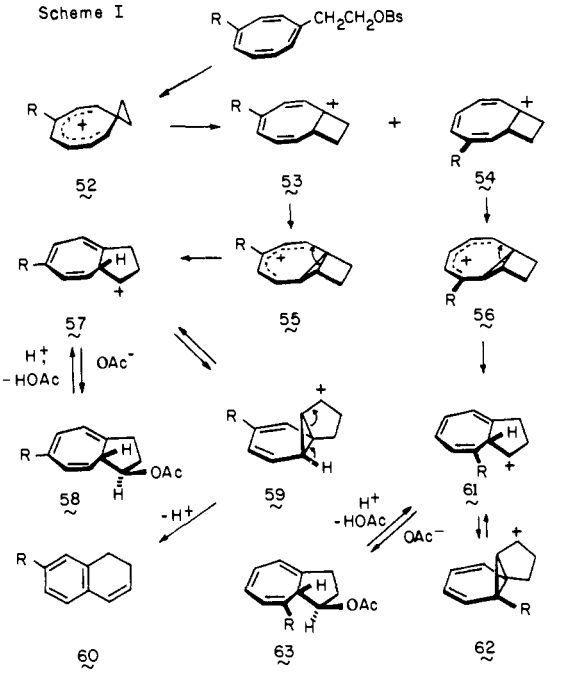
Once separated, the trimethylsilyl ethers were hydrolyzed back to the corresponding alcohols[25] and each was subsequently treated with a trace of *p*-toluenesulfonic acid in anhydrous acetic acid at 50°. In the case of **48b,** rearrangement occurred to give exclusively methyldihydronaphthalene (**50**) which was transformed to β-methylnaphthalene (**51**) when exposed to DDQ. As expected, **49b** did not aromatize under the same acidic conditions (see Discussion).

We infer from these results that ring contraction of the cyclooctatetraene nucleus during conversion to tetrahydroazulenoid products operates in a manner such as to render equivalent the C_4 and C_6 atoms. Although the similar convergence of C_2,C_8 and C_3,C_7 remains untested by experiment, consideration of the most direct reaction pathway indicates that these pairs of carbon atoms share a similar fate.

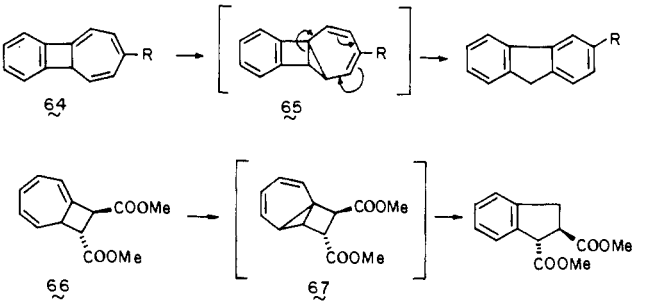
Discussion

The intriguing rearrangement of **3**,[26] its dideuterio derivatives **27b** and **30b,** and its methyl congener **46b** as delineated above imposes a number of mechanistic limitations which are satisfied by Scheme I. Ionization of the title bro-

Scheme I



sylates is viewed as proceeding with participation by the double bond of the homoallylic systems with generation of the intermediate spiro[7.2]nonatrienyl cation **52** which when R = H is a species of C_s symmetry. As required by the data therefore, such a homoallyl–cyclopropylcarbinyl interconversion eventuates in symmetrization of both the ring and side chain (R = H). Passage to cyclobutyl cations **53** and **54**[9a] triggers bond relocation, presumably via **55** and **56,** respectively, thereby providing access to the cycloheptatrienyl–norcaradienylcarbinyl cation pairs **57** $\rightleftarrows$ **59** and **61** $\rightleftarrows$ **62**.[27] The conversion of **53** and **54** to their respective bicyclopentane-containing isomers **55** and **56** would appear at first to be energetically awkward steps. Yet, somewhat related structural types, e.g., **65** and **67,** have been similarly



invoked in explanation of the rearrangement of **64** (R = H and $COOC_2H_5$) to the isomeric indenes and of the concurrent ring contraction (7 → 6) ring expansion (4 → 5) of **66**.[29,30] The operation of simple 1,2-hydride shifts in **57** and **61** to yield stable tropylium ions does not gain importance,

likely because of the overwhelming preference of such species to exist as norcaradienylcarbinyl cations (see **59**).[27] At high acetate ion concentrations, **57** and **61** experience charge annihilation with formation of **58** and **63.** Alternatively, these acetates could arise by direct nucleophilic attack at the appropriate bridgehead carbons in **55** and **56.** When the acetate levels are low, the favored[31] tricyclic cations **59** and **62** can be expected to gain importance. In the case of **59,** deprotonation with formation of dihydronaphthalene **60** should be facile. In contrast, the position of the R group in **62** prohibits such aromatization. On this basis, therefore, it is not surprising that alcohol **49b** is stable to acid-catalyzed rearrangement under mild conditions.

An important aspect of this mechanistic scheme concerns the nature of cation **52.** Two reasonable possibilities exist. In the first, the species can be viewed as a rather classical cyclopropylcarbinyl cation system in which the eight-membered ring retains its tub conformation (**68**); meaningful de-

68

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localization of positive charge by the cyclooctatrienyl system is thereby impeded and inductive rate deceleration should be in evidence, Alternatively, a flattening of the ring could be realized at the rate-determining ionization step which would permit extensive homoaromatic charge stabilization (**69**). The 52-fold rate deceleration of **3** relative to **7b** is not immediately conducive to the notion that anchimeric assistance with direct intervention of **69** does operate. Ideally, one should know the rate of nonassisted acetolysis of **3,** but this, of course, is impossible to assess. Perhaps **7b** is not a suitable model compound! One should recall that the bare system, allylcarbinyl tosylate, undergoes solvolytic cyclization in formic acid only 3.7 times faster than *n*-butyl tosylate, notwithstanding the intervention of the "bicyclobutonium" ion.[32] As usual, the problem is compounded by the innate difficulty of examining the structures of short-lived ions, and the still greater task of examining transition states. Accordingly, the question of whether **52** partakes of homoaromatic delocalization under conditions of kinetic control must remain open until such time as future detailed investigations address the problem.

Experimental Section

Melting points are corrected while boiling points are uncorrected. Proton magnetic resonance spectra were obtained with Varian A60-A and Jeolco MH-100 spectrometers; apparent splittings are given in all cases. Infrared spectra were determined with a Perkin-Elmer Model 137 instrument. 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.

β-Cyclooctatetraenylethanol (2). To a solution of 3.85 g (32.0 mmol) of **1**[33] in 100 ml of dry ether under nitrogen at −60° was added 26 ml of 1.5 *M* *n*-butyllithium (38.0 mmol) by means of a syringe. The resulting orange solution was stirred at this temperature for 2 hr to complete the halogen–metal exchange and used directly. Ethylene oxide (3.13 g, 71 mmol) was introduced at −60° and after 30 min at this temperature the solution was allowed to warm to room temperature. The mixture was washed with two 100-ml portions of 10% hydrochloric acid followed by two 50-ml portions of saturated sodium chloride solution. The ether layer was removed, dried, and concentrated in vacuo. The residue (3.1 g) was distilled to yield 2.8 g (60%) of **2**: bp 80–85° (0.5 mm); $\nu_{max\ (neat)}$ 3310 and 1020–1050 cm^{-1}; $\delta_{TMS\ (CDCl_3)}$ 5.77 (s, 7, olefinic), 3.62 (t, J = 6.5 Hz, 2, $-CH_2O-$), 2.27 (t, J = 6.5 Hz, 2, allylic), and 2.09 (s, 1, OH). Anal. ($C_{10}H_{12}O$) C, H.

The 3,5-dinitrobenzoate was obtained as yellow needles, mp 69–70°, from absolute ethanol (lit.[7] mp 67–67.8°).

Brosylate **3** was obtained in 91% yield as pale yellow needles, mp 41–42°, from absolute ethanol: $\delta_{TMS\ (CDCl_3)}$ 7.75 (s, 4, aryl), 5.75 (s, 7, olefinic), 4.17 (t, J = Hz, 2, $-CH_2O$), and 2.42 (t, J = 7 Hz, 2, allylic). Anal. ($C_{16}H_{15}BrO_3S$) C, H, S.

Methyl 1-Hydroxycyclooctylacetate (4). A. To a 100-ml three-necked flask fitted with condenser, nitrogen inlet tube, and serum stopper, and containing 25 ml of dry ether, was added 9.5 ml (45.1 mmol) of hexamethyldisilizane. To this solution was slowly added 30 ml of *n*-butyllithium in pentane (1.5 *M*, 45.1 mmol). Gas evolution was immediately apparent. The mixture was refluxed for 30 min and cooled to room temperature, and the solvent was removed in vacuo to give a white solid residue. To this solid was added 20 ml of tetrahydrofuran and the resulting solution was cooled to −70°. A syringe was used to add 3.3 ml (39.7 mmol) of ethyl acetate and the reaction mixture was stirred for 15 min at −70°, at which time a solution of 5.00 g (39.7 mmol) of cyclooctanone in 20 ml of tetrahydrofuran was introduced. The reaction mixture was stirred for 10 min and acidified with 20 ml of 10% hydrochloric acid. The solution was allowed to warm to room temperature at which point the organic layer was separated, washed with water and saturated sodium bicarbonate solution, and dried. Removal of the solvent in vacuo gave 8.10 g (95%) of **4** as a colorless liquid: bp 93–94° (0.02 mm); $\nu_{max\ (neat)}$ 3550 and 1710 cm^{-1}; $\delta_{TMS\ (CDCl_3)}$ 4.23 (q, J = 10.5 Hz, 2, $-OCH_2-$), 3.46 (s, 1, OH), 2.49 (s, 2, $-CH_2COO-$), and 1.1–2.2 (complex m, 17). Anal. ($C_{12}H_{22}O_3$) C, H.

B. Approximately 5 g (79 mg-atoms) of mossy zinc was first activated by adding it to a warm solution of 5% sulfuric acid and washing with water, methanol, acetone, and ether. The zinc was heated in a vacuum oven at 110° for 30 min and placed in a three-necked flask fitted with overhead stirrer, condenser to which was attached a nitrogen inlet, and dropping funnel. A solution of 10.0 g (79.4 mmol) of cyclooctanone and 13.3 g (75.4 mmol) of ethyl bromoacetate in 100 ml of dry ether was placed in the dropping funnel and a 3-ml aliquot was added slowly to the zinc. The mixture was heated until reaction began and the remainder of the solution was then added at a rate necessary to maintain reflux. After the addition was complete, the solution was refluxed for 4 hr, cooled to room temperature, and treated slowly with 50 ml of 10% sulfuric acid with vigorous stirring. The layers were separated and the ether layer was washed with 5% sulfuric acid, 10% sodium carbonate solution, and water. The combined aqueous layers were extracted with ether and the combined ether layers were washed with saturated sodium chloride solution and dried. The ether was removed in vacuo and the residue was distilled at a pressure of 0.02 mm to give 5.32 g (31%) of 95% pure **4**, bp 93–94°, as well as an additional 3.23 g (19%) of 75% pure **4,** bp 81–82°, to give a total yield of 45%.

Ethyl 1-Bromocyclooctylacetate (5). To 5.32 g (24.8 mmol) of **4** at 0° was slowly added 6.9 ml (19.5 g, 72.0 mmol) of phosphorus tribromide. The solution was stirred at room temperature for 24 hr, at which time the mixture was added very slowly, with stirring, to 25 ml of ice–water. (Rapid addition resulted in ignition of the solvent.) The aqueous solution was extracted with ether, and the organic layer was subsequently washed with a saturated sodium chloride solution and dried. The ether was removed in vacuo to give 6.70 g (99%) of crude **143** which was not distilled. TLC analysis showed the presence of one component: $\nu_{max\ (neat)}$ 1720 cm^{-1}.

Δ^1-Cyclooctenylacetic Acid (6). The crude bromide **5** (6.70 g, 24.2 mmol) was added to a solution of 8.0 g of potassium hydroxide in 30 ml of ethanol and stirred overnight at room temperature. The ethanol was removed in vacuo and 25 ml of ether was added to the residue. The ethereal solution was subsequently washed with water and saturated sodium carbonate solution, and dried. Upon removal of solvent, the residue was distilled to give 4.0 g (96%) of cyclooctenylacetic acid: bp 108–110° (0.1 mm): $\nu_{max\ (neat)}$ 1720 cm^{-1}; $\delta_{TMS\ (CDCl_3)}$ 5.60 (t, J = 8.0 Hz, 1, olefinic), 3.03 (s, 2, methylene), 1.9–2.3 (br s, 4, allylic), and 1.50 (br s, 8).

β-(Δ^1-Cyclooctenyl)ethanol (7a). A slurry of 0.313 g (2.20 mmol) of lithium aluminum hydride and 10 ml of ether was placed in a 100-ml three-necked flask fitted with reflux condenser, magnetic stirrer, and addition funnel. To this mixture was added a solution

of 0.50 g (2.98 mmol) of **6** in 10 ml of ether. The mixture was refluxed for 24 hr and the usual work-up was used (0.4 ml of water, 0.4 ml of 15% sodium hydroxide solution, and 1.2 ml of water). After filtration, the ether solution was dried and evaporated. Distillation of the residue gave 0.43 g (98%) of **7a**: bp 121° (16 mm); $\delta_{TMS\,(CDCl_3)}$ 5.33 (t, J = 8.0 Hz, 1, olefinic), 3.72 (t, J = 6.5 Hz, 2, $-CH_2O-$), 2.62 (s, 1, OH), 1.9–2.5 (complex m, 6, allylic), and 1.51 (br s, 8).

The 3,5-dinitrobenzoate was obtained as white crystals, mp 55–56°, from ethanol. Anal. ($C_{17}H_{20}N_2O_6$) C, H, N.

Brosylate **7b** was obtained in 67% yield as a colorless oil which was purified by low-temperature recrystallization: $\delta_{TMS\,(CDCl_3)}$ 7.73 (s, 4, aryl), 5.37 (t, J = 8 Hz, 1, olefinic), 4.17 (t, J = 7 Hz, 2, $-CH_2O-$), 2.33 (t, J = 7 Hz, 2, allylic methylene), 2.05 (br m, 4, allylic ring protons), and 1.42 (br s, 8).

β-Cyclooctylethanol (8a). To a solution of 950 mg (6.17 mmol) of **7a** in 30 ml of methanol was added 3 ml of acetic acid and 100 mg of platinum oxide. Hydrogenation was carried out at room temperature in a Parr hydrogenator (50 psi) for a period of 24 hr. The reaction mixture was filtered through Celite and 25 ml of water was added to the filtrate. The filtrate was extracted with ether and the combined ether extracts were washed with water, saturated sodium bicarbonate solution, and saturated sodium chloride solution and dried. Removal of the solvent in vacuo left 680 mg of a colorless liquid. Distillation at 0.05 mm gave a forerun (bp 40–41°) which was identified as ethylcyclooctane as well as 577 mg (60%) of **8a**; bp 101–102° [lit.[7] bp 78–79° (0.02 mm)]; $\delta_{TMS\,(CDCl_3)}$ 3.63 (t, J = 7 Hz, 2, $-CH_2O-$) and 1.53 (br m, 17).

Brosylate **8b** was obtained as a colorless oil which was purified by low-temperature recrystallization techniques: $\delta_{TMS\,(CDCl_3)}$ 7.75 (s, 4, aryl), 4.12 (t, J = 7 Hz, 2, $-CH_2O-$), and 1.50 (br m, 17).

Kinetics Procedure. Anhydrous acetic acid was prepared by refluxing a solution of acetic anhydride in glacial acetic acid overnight and subsequent fractional distillation in a dry atmosphere. Standard perchloric acid solutions in acetic acid were prepared by dilution of an accurately weighed quantity of standard 70% perchloric acid with anhydrous acetic acid to a known volume. Sodium carbonate which had been heated over an open flame and cooled in a desiccator was accurately weighed and diluted to a known volume with anhydrous acetic acid to prepare the standard sodium acetate solutions; the water of neutralization was not removed.

Standard solutions of brosylate in the sodium acetate solution were prepared. Aliquots of this solution (ca. 1.1 ml) were removed, sealed in glass ampoules, and immersed in a constant-temperature bath. After 10 min, the first ampoule was removed, an accurate timer started, and the ampoule quickly cooled in an ice–water bath. The ampoule was then placed in a vessel of water at room temperature. After 5 min, exactly 0.923 ml of solution was removed with an automatic pipet, treated with 1 drop of a saturated solution of Bromophenol Blue indicator in acetic acid, and titrated with standard perchloric acid using a Fisher Accumet pH meter with microprobe combination electrode to determine the endpoint potentiometrically. The remaining ampoules were removed at appropriately timed intervals, immediately cooled in ice–water, and titrated as previously described. In each case one ampoule was allowed to remain in the heated bath for a period of at least 10 half-lives. The sample was then titrated as above to give the infinity point. The rate constants were calculated using a STAT-6 program for the least-squares treatment of the data.

Solvolysis of 8b. A solution of 0.725 g (1.93 mmol) of **8b** was placed in 8 ml of 0.10065 N sodium acetate–acetic acid and heated at 85° for a period of 10 half-lives (7 days). The solution was cooled and 10 ml of water added. The resulting solution was extracted with ether and the combined ether portions were washed with water, saturated sodium bicarbonate solution, and saturated sodium chloride solution and dried. Removal of the ether in vacuo gave 350 mg of yellow residue. VPC analysis on a 6 ft × 0.25 in. column of 5% Carbowax on Chromosorb C showed **11** to be the only product. A quantity of this acetate was isolated from this column at 140° for spectral comparison with an authentic sample prepared as described below.

β-Cyclooctylethyl Acetate (11). A solution of 180 mg (1.15 mmol) of **8a** and 550 mg (5.59 mmol) of acetic anhydride in 0.5 ml of pyridine was stirred at room temperature for 24 hr. Ice was added and the mixture was extracted with ether and the combined ether portions washed with water, 10% hydrochloric acid, and saturated sodium bicarbonate solution, dried, and evaporated to give 205 mg (91%) of **11**. Purification was achieved on a 5 ft × 0.25 in. 5% SF-96 column on Chromosorb G at 120°: $\delta_{TMS\,(CDCl_3)}$ 4.08 (t, J = 7 Hz, 2, $-CH_2O-$), 2.00 (s, 3, methyl), and 1.53 (br m, 17). Anal. ($C_{12}H_{22}O_2$) C, H.

Solvolysis of 7b. A solution of 1.00 g (2.68 mmol) of **7b** in 150 ml of 0.1954 N sodium acetate–acetic acid was heated at 50° for a period of 10 half-lives (30 hr). The reaction mixture was added to ice and the resulting solution was extracted with ether. The combined ether portions were washed with water, saturated sodium bicarbonate solution, and saturated sodium chloride solution, dried, and evaporated to give 0.43 g of yellow residue. A VPC analysis of the mixture was performed on a 10 ft × 0.25 in. column of 10% XF-1150 on Chromosorb W and the following product ratio was found: **12** (34%), **13**, (10%), and **14** (56%). These products were isolated from the same column and their NMR spectra were found to be identical with those of authentic samples.

β-(Δ¹-Cyclooctenyl)ethyl Acetate (12). Acetylation of 300 mg (1.95 mmol) of **7a** with 550 mg (5.39 mmol) of acetic anhydride in 0.5 ml of pyridine in the predescribed manner afforded 382 mg (100%) of **12**. Purification on the SF-96 column at 120° gave the analytical sample: $\delta_{TMS\,(CDCl_3)}$ 5.42 (t, J = 8 Hz, 1, olefinic), 4.13 (t, J = 7 Hz, 2, $-CH_2O-$), 2.00 (s, 3, methyl), 1.83–2.53 (m, 6, allylic), and 1.48 (br m, 8). Anal. ($C_{12}H_{20}O_2$) C, H.

1-Acetoxybicyclo[6.2.0]decane (13). Ten milliliters of 15% perchloric acid solution was adjusted to a pH of 3.5 by adding 2 N sodium hydroxide solution at 5°. To this was added 2.0 g (13.08 mmol) of **15**.[11] To this solution was added 0.20 g of sodium nitrite in 10 ml of water, while 15% perchloric acid solution was added simultaneously to maintain a pH of 3.5. After the addition was complete, the reaction mixture was heated at 60° for 3 hr, cooled, and treated with 20 ml of saturated sodium chloride solution. The mixture was extracted with ether and the combined ether phases were washed with water and saturated sodium chloride solution, dried, and evaporated. The yellow residue (140 mg) showed two components upon VPC analysis. The mixture was separated on a 6 ft × 0.25 in. column of 5% Carbowax–1% potassium hydroxide on Chromosorb G at 150°. The two components were shown to be the desired 1-hydroxybicyclo[6.2.0]decane as well as **7a**. A phenylurethane derivative of the bicyclic alcohol was obtained as a white crystalline solid, mp 148–149° (lit.[11] mp 139–142°).

Acetylation of 50.0 mg (0.325 mmol) of the alcohol in 0.14 ml of pyridine containing 0.16 ml (1.65 mmol) of acetic anhydride gave 45 mg of **13**. An analytical sample was obtained by purification on the XF-1150 column: $\delta_{TMS\,(CDCl_3)}$ 2.09 −2.42 (m, 7, cyclobutyl protons and CH_2COAc), 2.00 (s, 3, methyl), and 1.25–1.92 (m, 10). Anal. ($C_{12}H_{20}O_2$) C, H.

1-Acetoxyspiro[2.7]decane (14). A fresh zinc–copper couple[34] was prepared by adding 7 g of zinc dust to a hot, rapidly-stirred solution containing 0.4 g of cupric acetate monohydrate in 10 ml of glacial acetic acid. After approximately 5 min, the copper was deposited on the zinc and the mixture was shaken for 1 min. The acetic acid was decanted and the Zn–Cu couple was washed with two 10 ml portions of acetic acid and filtered. The couple was washed with acetone and ether and dried in vacuo prior to further use.

A mixture of 110 mg (2.00 mmol) of this couple, 40 mg (1.50 mmol) of methylene iodide, and 0.2 ml (2 mmol) of glyme in 5 ml of ether was refluxed for 30 min. To this mixture was added a solution of 100 mg (0.71 mmol) of **16**[12] in 5 ml of ether. The resulting solution was refluxed for 8 hr, cooled, and treated with 10 ml of saturated ammonium chloride solution. The ether layer was decanted into a separatory funnel and the aqueous layer was extracted with ether. The combined ether layers were washed with saturated sodium chloride solution, dried, and evaporated to give the cyclopropanated alcohol as a colorless residue which was isolated pure from a 6 ft × 0.25 in. column of 5% Carbowax–1% potassium hydroxide on Chromosorb G: $\delta_{TMS\,(CDCl_3)}$ 2.95 (m, 1, $>CH-O-$), 2.07 (br m, 2), and 1.25–1.95 (m, 11). The phenylurethane was isolated as a white solid, mp 67–68°. Anal. ($C_{17}H_{23}N_2O$) C, H.

Acetylation of 17 mg (0.11 mmol) of this alcohol with 0.05 ml of acetic anhydride and 0.06 ml of pyridine as before gave 22.4 mg of **14**: $\delta_{TMS\,(CDCl_3)}$ 4.33 (t, J = 6 Hz, 1, $>CH-O-$), 2.02 (s, 3, methyl), 1.42–1.83 (m, 12), and 0.25–0.67 (m, 4, cyclopropyl).

Control Experiments, For 12: A solution of 53.5 mg (0.27 mmol) of **12** in 1.5 ml of 0.1945 N sodium acetate–acetic acid was heated

at 50° for 30 hr. The reaction mixture was added to 5 ml of water and extracted with ether. The customary work-up led to isolation of 50.0 mg of a colorless residue. VPC analysis (10 ft × 0.25 in. column of 10% XF-1150 on Chromosorb W) showed one peak, subsequently identified after collection as starting material.

For 13, A solution of 75 mg (0.38 mmol) of acetate **13** in 40 ml of 0.10065 *N* sodium acetate-acetic acid was heated at 50° for 30 hr. The solution was poured over ice and subsequently extracted with ether. Work-up as before gave 62.2 mg of residual oil. VPC analysis of the mixture (10 ft × 0.25 in. column of 10% XF-1150 on Chromosorb W) showed 52% of unchanged **13** and 48% of **12** to be present.

For 14, A solution of 22 mg (0.11 mmol) of acetate **14** in 30 ml of 0.10065 *N* sodium acetate-acetic acid was heated at 50° for 30 hr. The solution was poured over ice, subsequently extracted with ether, and processed in the predescribed manner to give 30.6 mg of a mixture of acetates which were identified by VPC (10% XF-1150) as recovered **14** (61%), **12** (31%), and **13** (8%).

Acetolysis of 3, A solution of 1.00 g (2.73 mmol) of **3** was placed in 135 ml of 0.1945 *N* sodium acetate-acetic acid and heated at 75° for a period of 10 half-lives (103.5 hr). The reaction mixture was cooled and added to 100 ml of ice-water. This aqueous solution was extracted with ether and the combined ether portions were washed with water and saturated sodium bicarbonate solution, dried, and evaporated to give 500 mg of dark residue which was first chromatographed on silica gel (pentane elution) to remove gross impurities. The components of the mixture were then purified on the 5% XF-1150 column at 140°. The most volatile component was identified as 1,2-dihydronaphthalene (**19**, 12%) by ir and NMR comparison with the spectra of an authentic sample.[35] The second component was shown to be **17** (19%) and the final acetate was identified as **18**; $\delta_{TMS\ (CDCl_3)}$ 6.28–6.57 (m, 2, H_4 and H_5), 5.87–6.28 (m, 2, H_3 and H_6), 5.20–5.45 (m, 1, H_{10}), 5.02 (d of d, J = 4.5 and 2.5 Hz, 1, H_2), 2.37–2.70 (m, 2, H_8), 2.03–2.28 (m, 3, H_1 and H_9), and 1.90 (s, 3, methyl). Anal. ($C_{12}H_{14}O_2$) C, H.

β-Cyclooctatetraenylethyl Acetate (17), To a solution of 500 mg (3.38 mmol) of **2** in 1.5 ml of pyridine was added 1.6 ml (17.0 mmol) of acetic anhydride. The solution was stirred at room temperature for 24 hr and worked up in the usual manner to give 610 mg (95%) of **17** as a colorless liquid. Purification on a 6 ft × 0.25 in. column of 5% SF-96 on Chromosorb G (115°) provided the analytical sample: $\delta_{TMS\ (CDCl_3)}$ 6.78 (s, 7, olefinic), 4.13 (t, J = 7 Hz, 2, $-CH_2O-$), 2.37 (t, J = 7 Hz, 2, allylic), and 2.02 (s, 1, O*H*). Anal. ($C_{12}H_{14}O_2$) C, H.

1-Hydroxy-1,2,3,4-tetrahydroazulene (22), To a suspension of 27 mg (0.70 mmol) of lithium aluminum hydride in 5 ml of ether was slowly added a solution of 125 mg (0.70 mmol) of **18** in 10 ml of ether. The mixture was refluxed for 3 hr and a standard basic work-up was used. The mixture was filtered through magnesium sulfate and the ether was evaporated in vacuo to give 100 mg of alcohol which was purified by chromatography on silica gel (elution with 10% ether in pentane): $\delta_{TMS\ (CDCl_3)}$ 6.33–6.63 (m, 2, H_4 and H_5), 5.92–6.33 (m, 2, H_3 and H_6), 4.98 (d of d, J = 4.5 and 2.5 Hz, 1, H_2), 4.39 (d of d, J = 3.0 and 1.0 Hz, 1, H_{10}), 2.42–2.90 (m, 3, H_8 and OH), and 1.67–2.20 (m, 3, H_1 and H_9).

1-Hydroxyperhydroazulene (23), A solution of 272 mg (1.84 mmol) of **22** in 5 ml of methanol was hydrogenated at atmospheric pressure using 25 mg of 10% Pd/C catalyst. The hydrogenation was allowed to proceed for 5 hr when no further uptake of hydrogen was observed. The reaction mixture was filtered through Celite and the methanol was removed in vacuo to give 111 mg of **23** which was chromatographed on silica gel (elution with 10% ether in pentane) prior to oxidation: $\delta_{TMS\ (CDCl_3)}$ 3.70 (m, 1, >C*H*-O-) and 0.83 (m, 15).

***cis*-1-Perhydroazulenone (24)**, To a solution of 25 mg (0.162 mmol) of **23** in 15 ml of dry benzene was added 0.5 ml of dimethyl sulfoxide, 0.02 ml of pyridine, 0.01 ml of trifluoroacetic acid, and 97 mg (0.486 mmol) of dicyclohexylcarbodiimide. The mixture was stirred at room temperature for 15 hr and added to 5 ml of water. The aqueous solution was extracted with ether and the ether portion was subsequently washed with water and saturated sodium chloride solution, dried, and evaporated to give 45.1 mg of oily material. Ketone **24** was isolated in pure form from a 6 ft × 0.25 in. column of 5% SE-30 on Chromosorb G at 125°: $\delta_{TMS\ (CDCl_3)}$ 0.92–2.58 (br m with spikes at 1.57, 2,10, and 2.12). The ir and ^1H NMR spectra of this ketone were superimposable upon those of an authentic sample.[14]

The semicarbazone was obtained as white crystals, mp 220–221°, from absolute ethanol (lit.[14] mp 220–221°).

Cyclooctatetraenylacetic Acid (26), To a solution of 2.00 g (13.5 mmol) of **2** in 200 ml of acetone at 5° was slowly added 9.0 ml (19.1 mmol) of Jones' reagent (2.01 *M*). After the addition was complete, a red color persisted and the solution was allowed to warm to room temperature and neutralized with 10% sodium hydroxide solution. Filtration followed by evaporation of solvent left an oily residue which was dissolved in 200 ml of ether and washed with saturated sodium bicarbonate solution. Evaporation of the ether gave 0.80 g of liquid residue which contained some starting material and some COTacetaldehyde. This liquid was reoxidized to give 0.40 g (20%) of **26**, The bicarbonate solution was acidified, extracted with ether, and dried over magnesium sulfate to give an additional 0.90 g (61% combined yield) of **26** as a yellow oil. All attempts to induce crystallization were unsuccessful: $\delta_{TMS\ (CDCl_3)}$ 7.92 (s, 1, carboxyl), 5.73 (s, 7, olefinic), and 3.07 (s, 2, methylene).

β-Cyclooctatetraenylethanol-α,α-d_2 (27a), To a slurry of 0.88 g (21.0 mmol) of lithium aluminum deuteride in 25 ml of ether was slowly added 3.70 g (21.0 mmol) of **26** in 50 ml of ether. The mixture was gently refluxed for 2 hr and stirred at room temperature for 7 hr. Following an alkaline work-up, the filtrate was dried and evaporated to leave 1.92 g (61%) of **27a**; bp 49–50° (0.02 mm). The ^1H NMR spectrum showed 95% isotopic purity: $\delta_{TMS\ (CDCl_3)}$ 5.77 (s, 7, olefinic), 3.15 (br s, 1, O*H*), and 2.27 (s, 2, allylic).

Brosylate **27b** was obtained as a yellow oil which could not be made to crystallize: $\delta_{TMS\ (CDCl_3)}$ 7.72 (m, 4, aryl), 5.68 (s, 7, olefinic), and 2.37 (s, 2, allylic).

Methyl Cyclooctatetraenylacetate (28), A solution of excess diazomethane in ether was carefully added to a solution of 4.35 g (26.9 mmol) of **26** in 50 ml of ether. This solution was stirred at −5° for 15 min and allowed to warm to room temperature where it was stirred for an additional 30 min. The solution was dried over magnesium sulfate and the ether was evaporated to give 3.89 g (81%) of crude ester. The ester was purified for analysis by twofold preparative VPC isolation (6 ft × 0.25 in. 10% SE-30 followed by 6 ft × 0.25 in. 10% SF-1150 columns): $\delta_{TMS\ (CDCl_3)}$ 5.85 (s, 7, olefinic), 3.68 (s, 3, methyl), and 3.08 (s, 2, methylene). Anal. ($C_{11}H_{12}O_2$) C, H.

β-Cyclooctatetraenylethanol-β,β-d_2 (30a), Into 400 mg (17.0 mmol) of CH_3OD was placed 4 mg of sodium metal, and 150 mg (0.85 mmol) of **28** was next introduced. The solution was heated at 50° for 12 hr and cooled to room temperature, and the solvent was removed in vacuo. The residue was taken up in pentane and washed with saturated sodium chloride solution. Removal of solvent gave 89.6 g of **29** as a yellow liquid which was purified by molecular distillation: $\delta_{TMS\ (CDCl_3)}$ 5.82 (s, 7, olefinic) and 3.68 (s, 3, methyl).

To a suspension of 0.285 g (7.75 mmol) of lithium aluminum hydride in 50 ml of dry ether was slowly added a solution of 1.38 g (7.75 mmol) of **29** in 25 ml of ether. The mixture was refluxed for 4 hr and a basic work-up was employed. The mixture was filtered through magnesium sulfate and the ether removed in vacuo to give 1.05 g of yellow liquid which was purified by molecular distillation. For **30a**: $\delta_{TMS\ (CDCl_3)}$ 5.77 (s, 7, olefinic), 3.62 (s, 2, $-CH_2O-$), and 2.13 (s, 1, O*H*).

Brosylate **30b** was isolated as a noncrystallizable yellow oil: $\delta_{TMS\ (CDCl_3)}$ 7.75 (m, 4, aryl), 5.72 (s, 7, olefinic), and 4.05 (s, 2, $-CH_2O-$).

Solvolysis of 27b, A solution of 1.10 g (3.00 mmol) of **27b** in 150 ml of 0.1945 *N* sodium acetate-acetic acid was heated at 75° for a period of 10 half-lives (103.5 hr). The mixture was cooled and added to 100 ml of ice-water. The aqueous solution was extracted with ether and the combined ether portions were washed with water and saturated sodium bicarbonate solution and dried over magnesium sulfate. Removal of the ether in vacuo gave 550 mg of dark residue which was first chromatographed on silica gel (elution with pentane). The three-component mixture was separated by making recourse to a 6 ft × 0.25 in. 5% XF-1150 column on Chromosorb G at 140°. The ^1H NMR spectra of the three components showed deuterium to be distributed in the manner outlined in the formulas.

Solvolysis of 30b, A solution of 1.00 g (2.75 mmol) of **30b** in 30

ml of 1.0 *N* sodium acetate–acetic acid was heated at 75° for a period of 10 half-lives (103.5 hr). The mixture was then cooled, added to 100 ml of ice–water, and worked up as before to give 420 mg of dark residue. Separation as above and ^{1}H NMR analysis of the three purified components showed deuterium to be distributed as indicated by the formulas.

1-Carboethoxy-2-methylcyclooctatetraene (35). A solution of 15 ml of ethyl tetrolate[36] and 500 ml of benzene was placed in a quartz tube fitted with a glass stopper and irradiated for a total of 32 hr in a Rayonet reactor fitted with 2537 Å lamps. The quartz vessel was treated with cleaning solution (potassium dichromate in sulfuric acid) after each 8-hr photolysis period. After a total reaction time of 32 hr the benzene and remaining ethyl tetrolate were removed by distillation (33° (140 (140 mm)) and the residue was distilled (61° (0.075mm)) to give a 45% yield of **35.** The ^{1}H NMR spectrum was found to be in full agreement with that reported in the literature.[19i]

1-Hydroxymethyl-2-methylcyclooctatetraene (36). To a slurry of 1.55 g (40.75 mmol) of lithium aluminum hydride in 75 ml of ether was slowly added a solution of 7.74 g (40.75 mmol) of **35** in 50 ml of ether. The mixture was refluxed gently for 5 hr, cooled, and worked up in the customary alkaline fashion. The mixture was filtered through magnesium sulfate and the solvent was removed in vacuo to give 5.81 g (96%) of **36** as a yellow liquid: $\delta_{TMS\ (CDCl_3)}$ 5.80 (s, 6, olefinic), 4.12 (s, 2, methylene), 2.47 (s, 1, O*H*), and 1.85 (s, 3, methyl).

2-Methylcyclooctatetraenecarboxaldehyde (37). To a solution of 2.40 g (16.2 mmol) of **36** in 160 ml of chloroform was added 35 g of "active" manganese dioxide on carbon.[21] The slurry was stirred at room temperature for 24 hr and filtered through Celite, and the filtrate was evaporated to give 2.20 g (93%) of **37** as a clear yellow liquid: $\nu_{max\ (neat)}$ 1695 cm^{-1}; $\delta_{TMS\ (CDCl_3)}$ 6.82 (d, J = 2 Hz, 1, H_8), 6.05 (m, 2, olefinic), 5.80 (m, 3, olefinic), and 1.83 (s, 3, methyl).

The 2,4-dinitrophenylhydrazone was obtained as dark red crystals, mp 204–205°, from methanol and chloroform–pentane. Anal. ($C_{16}H_{14}N_4O_4$) C, H, N.

1-(2-Methoxyvinyl)-2-methylcyclooctatetraene (38). A solution of sodium ethoxide in ethanol was prepared by adding 920 mg (40 mg-atoms) of sodium metal to 100 ml of absolute ethanol. After all the sodium had reacted, this solution was slowly added to a solution of 13.7 g (40.0 mmol) of methoxymethyltriphenylphosphonium chloride[37] in 50 ml of ethanol. The mixture was stirred for 4 hr and the solvent was removed in vacuo to leave a white solid. The crystalline ylide was taken up in 50 ml of ether and this solution was slowly added to 2.14 g (12.5 mmol) of **37** dissolved in 25 ml of ether. The mixture was refluxed for 1 hr, cooled, and filtered through alumina. The solvent was removed in vacuo and the residue was triturated twice with pentane and the precipitated triphenylphosphine oxide was removed by filtration. The ethereal solution was concentrated to give 2.14 g (82%) of a yellow liquid which was purified by passage through a 6 ft column of 5% Carbowax on Chromosorb G at 135°. The vinyl ether (two bond shift isomers) proved to be extremely unstable and polymerized upon standing for more than 24 hr: $\delta_{TMS\ (CDCl_3)}$ 6.50 (d, J = 13 Hz, 1, =C*H*-OCH$_3$), 5.70 (m, 6, ring olefinics), 5.52 (d, J = 13 Hz, 1, vinyl), 3.55 (s, 3, methoxyl), 1.88 (s, 2, 0.67 of methyl), and 1.75 (s, 1, 0.33 of methyl). Anal. Calcd for $C_{12}H_{14}O$: *m/e* 174.1045. Found: *m/e* 174.1041.

Hydrolysis of 38. To a solution of 3.58 g (12.3 mmol) of mercuric acetate in 50 ml of 50% aqueous tetrahydrofuran was added 2.14 g (12.3 mmol) of **38.** The mixture was stirred for 1 min at room temperature, then treated with 20 ml of 15% sodium hydroxide solution and 467 mg (12.3 mmol) of sodium borohydride in 20 ml of 15% sodium hydroxide solution. The reaction mixture was filtered through Celite and the filtrate was neutralized with 3 *N* hydrochloric acid. This solution was extracted with ether and the combined ether layers were washed with 50-ml portions of water and saturated sodium bicarbonate solution, dried, and evaporated to give 1.70 g of residue which was chromatographed on silica gel. Elution with pentane gave 1.10 g (56%) of **39**, while elution with 20% ether in pentane gave 520 mg (28%) of **40a**.

For **39**: $\lambda_{max\ (C_2H_5OH)}$ 235 nm (ϵ 31,400); $\delta_{TMS\ (CDCl_3)}$ 7.40 (d, J = 2 Hz, 1, =C*H*-O-), 6.20 (d, J = 2 Hz, 1, furan β-proton), 6.05 (br s, 2, olefinic), 5.65 (br s, 3, olefinic), and 1.87 (s, 3, methyl). Anal. ($C_{11}H_{10}O$) C, H; *m/e*: calcd, 158.0731; found, 158.0728.

For **40a**: $\delta_{TMS\ (CDCl_3)}$ 5.80 (s, 4, olefinic), 5.65 (s, 2, olefinic), 3.60 (t, J = 7 Hz, 3, CH_2O*H*), 2.38 (t, J = 7 Hz, 2, allylic methylene), 1.80 (s, 2, 0.67 of methyl), and 1.68 (s, 1, 0.33 of methyl).

Brosylate **40b** was obtained in 88% yield as pale yellow needles, mp 74–75°, from ethanol: $\delta_{TMS\ (CDCl_3)}$ 7.82 (s, 4, aryl), 5.78 (s, 4, olefinic), 5.63 (s, 2, olefinic), 4.15 (t, J = 7 Hz, 2, -CH_2O-), 2.52 (t, J = 7 Hz, 2, allylic methylene), 1.75 (s, 2, 0.67 of methyl), and 1.65 (s, 1, 0.33 of methyl). Anal. ($C_{17}H_{17}BrO_3S$) C, H, S.

Solvolysis of 40b. A solution of 560 mg (1.47 mmol) of **40b** in 50 ml of a 0.20 *N* solution of sodium acetate in acetic acid was placed in a preheated oil bath at 75° for 104 hr. At this time the solution was cooled and poured into 100 ml of water. The resulting solution was extracted with ether and the combined ether solutions were washed with water and saturated sodium bicarbonate solution, dried, and evaporated. The colored residue was chromatographed on a short column of silica gel (elution with pentane) to give 270 mg (92%) of a yellow liquid. NMR and VPC analysis showed the presence of only the unrearranged acetate **40c**: $\delta_{TMS\ (CDCl_3)}$ 5.65 and 5.52 (m, 6, olefinic), 3.97 (t, J = 7 Hz, 2, -CH_2O-), 2.32 (t, J = 7 Hz, 2, allylic), 1.85 (s, 3, OCH_3), and 1.68 (s, 3, methyl).

Cyclooctatetraenecarboxaldehyde (41). To a solution of 710 mg (5.30 mmol) of **2** in 50 ml of chloroform was added 10 g of "active" manganese dioxide on carbon.[21] The mixture was stirred at room temperature for 5 hr and filtered through Celite and magnesium sulfate, and the solvent was removed in vacuo to give 600 mg (85%) of **41** as a yellow liquid: $\delta_{TMS\ (CDCl_3)}$ 7.65 (s, 1, C*H*O) and 5.92 (m, 7, olefinic).

2-Methoxyvinylcyclooctatetraene (42). A solution of sodium ethoxide in ethanol was prepared by adding 185 mg (8.0 mg-atom) of sodium metal to 15 ml of absolute ethanol. After all the sodium had reacted, this solution was slowly added to a solution of 2.75 g (8.0 mmol) of methoxymethyltriphenylphosphonium chloride in 20 ml of ethanol. The reaction was stirred for 4 hr and the solvent was removed in vacuo to give a white solid. The crystalline Wittig reagent was taken up in 25 ml of ether and slowly added to a solution of 500 mg (3.75 mmol) of **41** in 10 ml of ether. The mixture was refluxed for 1 hr, cooled, and filtered through alumina. The solvent was removed in vacuo and the residue was triturated twice with pentane. The precipitated triphenylphosphine oxide was removed by filtration and the ethereal solution was concentrated to give 570 mg (94%) of vinyl ether **42** which was used immediately.

Hydrolysis of 42. To a solution of 1.03 g (3.25 mmol) of mercuric acetate in 50 ml of 50% aqueous tetrahydrofuran was added 520 mg (3.25 mmol) of unpurified 42. The mixture was stirred for 1 min at room temperature whereupon 10 ml of 15% sodium hydroxide together with 123 mg (3.25 mmol) of sodium borohydride dissolved in 10 ml of 15% sodium hydroxide solution were added. Filtration through Celite was followed by neutralization with 3 *N* hydrochloric acid. The neutral solution was extracted with ether and the combined ether layers were washed with 50-ml portions of water and saturated sodium bicarbonate solution and dried. Removal of solvent gave 430 mg (91%) of **2**.

1-Bromo-4-methylcyclooctatetraene and 1-Bromo-5-methylcyclooctatetraene (44). A solution of 13.7 g (0.116 mmol) of **43** in 200 ml of methylene chloride was cooled to −70° under nitrogen. To this was slowly added a solution of 6.4 ml of bromine (0.116 mmol) in 100 ml of methylene chloride. After the addition was complete, the mixture was stirred at −70° for 1 hr. An Erlenmeyer flask containing 16.8 g (0.15 mmol) of potassium *tert*-butoxide was affixed to the flask by means of a Gooch tube and approximate 1-g portions of base were added to the mixture at 15-min intervals. After addition was complete, the mixture was again stirred for 1 hr at −70° and then allowed to rise slowly to room temperature. A solution of 20 ml of acetic acid in 200 ml of saturated sodium chloride solution was added to the mixture and stirred thoroughly. The organic layer was separated, washed with 100-ml portions of water, and saturated sodium bicarbonate solution, dried, and evaporated. There was obtained 15.5 g of dark residue which was chromatographed on silica gel and eluted with pentane to give 10.5 g (50%) of yellow liquid which was used directly. VPC analysis of this oil showed impurities to be present and this was supported by the ^{1}H NMR spectrum.

β-(4- and 5-Methylcyclooctatetraenyl)ethanols (45a and 46a). To 10.5 g (53.3 mmol) of unpurified **44** in 200 ml of ether cooled to −70° under nitrogen was introduced a solution of 26 ml of *n*-butyllithium in pentane (2.34 *N*, 60.0 mmol). After the addition

was complete, a large excess of ethylene oxide (100 g) was added and the mixture was stirred at −70° for an additional 2 hr before the temperature was allowed to rise to room temperature. The solution was acidified with 3 *N* hydrochloric acid and the ether portion was separated, washed with 100 ml portions of water and saturated sodium bicarbonate solution, dried, and evaporated. There was isolated a red-orange oil which was distilled at 55–56° (0.02 mm) to give 3.28 g (38%) of a clear, yellow liquid. VPC analysis on a 6 ft × 0.25 in. column of 5% Carbowax-1% potassium hydroxide on Chromosorb G at 138° showed a 3:1 mixture of the 1,4- (**46a**) and 1,5-isomers (**45a**).

For **45a**: $\delta_{TMS\ (CDCl_3)}$ 5.70 (s, 4, olefinic), 5.52 (s, 2, olefinic), 3.54 (br s, 2, $-CH_2O-$), 2.62 (s, 1, O*H*), 2.23 (t, J = 7 Hz, 2, allylic), and 1.67 (s, 3, methyl).

The brosylate was obtained as a pale yellow crystalline solid: mp 47–48°; $\delta_{TMS\ (CDCl_3)}$ 7.71 (d, J = 2 Hz, 4, aryl), 5.66 (s, 4, olefinic), 5.51 (s, 2, olefinic), 4.08 (t, J = 7 Hz, 2, $-CH_2O-$), 2.35 (t, J = 7 Hz, 2, allylic), and 1.70 (s, 3, methyl).

For **46a**: $\delta_{TMS\ (CDCl_3)}$ 5.80 (s, 4, olefinic), 5.62 (s, 2, vinyl), 3.53 (br s, 2, $-CH_2O-$), 2.25 (t, J = 7 Hz, 3, allylic and O*H*), and 1.69 (s, 3, methyl).

Brosylate **46b** was isolated as a pale yellow crystalline solid: mp 34–35°; $\delta_{TMS\ (CDCl_3)}$ 7.66 (d, J = 2 Hz, 4, aryl), 5.62 (s, 4, olefinic), 5.46 (s, 2, olefinic), 4.02 (t, J = 7 Hz, 2, $-CH_2O-$), 2.31 (t, J = 7 Hz, 2, allylic), and 1.72 (s, 3, methyl). Anal. ($C_{17}H_{17}BrO_3S$) C, H, S.

Iron Tricarbonyl Complex of 46a (47a). To a solution of 225 mg (1.39 mmol) of unpurified **46a** in 20 ml of ether was added 1.09 g (3.00 mmol) of iron enneacarbonyl. The mixture was refluxed gently for 2 hr, cooled, and removed of solvent in vacuo. The residue was chromatographed on silica gel (elution with 10% ether–pentane) to give 120 mg of a red oil which was used directly: $\delta_{TMS\ (CDCl_3)}$ 4.40–5.80 (br m, 6, olefinic), 3.64 (s, 2, $-CH_2O-$), 2.28 (t, J = 7 Hz, 2, allylic), and 1.86 (s, 4, methyl and O*H*).

β-(4-Methylcyclooctatetraenyl)ethanol *p*-Nitrobenzoate·Fe(CO)$_3$ (47b). To a solution of 120 mg (0.40 mmol) of unpurified **47a** in 10 ml of pyridine cooled to 0° was added 110 mg (0.80 mmol) of recrystallized *p*-nitrobenzoyl chloride. The mixture was stirred at 0° for 1 hr and 50 ml of water was introduced. The aqueous mixture was extracted with ether and the combined ether portions were washed with 50-ml portions of water, 3 *N* hydrochloric acid, and saturated sodium bicarbonate solution, dried, and evaporated. There was obtained 100 mg of a red oil which was crystallized from ethanol to give 81 mg (45%) of **47b** as a red crystalline solid: mp 82–83°; $\delta_{TMS\ (CDCl_3)}$ 8.20 (d, J = 2 Hz, 4, aryl), 4.40–5.80 (m, 6, olefinic), 3.46 (t, J = 7 Hz, 2, $-CH_2O-$), 2.62 (t, J = 7 Hz, 2, allylic), and 1.90 (s, 3, methyl). Anal. ($C_{21}H_{17}FeNO_7$) C, H, N.

Acetolysis of 46b. A solution of 540 mg of **46b** in 75 ml of 0.20 *N* sodium acetate in acetic acid was placed in a preheated oil bath at 75° for 104 hr. The mixture was processed as with **3** to give 300 mg of a slightly colored liquid. VPC analysis (6 ft × 0.25 in. column of 5% SE-30 on Chromosorb G at 125°) showed a 20% conversion to **46c** and an 80% mixture of **48a** and **49a** (ca. 1:1). All attempts to separate these isomers by gas chromatographic methods were unsuccessful. Mass spectral analysis of this mixture showed a parent ion at *m/e* 204.1148 (calcd 204.1150).

β-(4-Methylcyclooctatetraenyl)ethyl Acetate (46c). To a solution of 50.0 mg (0.309 mmol) of **46a** in 0.25 ml (3.10 mmol) of dry pyridine was slowly added 3.16 mg (3.10 mmol) of acetic anhydride. The reaction mixture was stirred at room temperature for 5 hr and quenched with 10 ml of water. Work-up as before gave 55 mg of yellow liquid which was purified on a 6 ft × 0.25 in. 5% SF-96 column (Chromosorb G) at 140°: $\delta_{TMS\ (CDCl_3)}$ 5.68 (m, 6, olefinic), 4.09 (t, J = 7 Hz, 2, $-CH_2O-$), 2.34 (t, J = 7 Hz, 2, allylic), 2.04 (s, 3, CH_3CO), and 1.74 (s, 3, methyl). Anal. ($C_{13}H_{16}O_2$) C, H.

Reduction of the Acetate Mixture. To a suspension of 57 mg (1.50 mmol) of lithium aluminum hydride in 50 ml of ether was slowly added a solution of 300 mg (1.47 mmol) of acetate mixture in 50 ml of ether. The mixture was stirred at room temperature for 2 hr when 0.06 ml of water, 0.06 ml of 10% sodium hydroxide solution, and 0.20 ml of water were added. The reaction mixture was filtered through magnesium sulfate and the solvent was removed in vacuo to give 200 mg (84%) of alcohol mixture **46a, 48b,** and **49b.**

Trimethylsilyl Ethers 48c and 49c. To a solution of 200 mg (1.23 mmol) of alcohol mixture in 1.0 ml of pyridine (12.4 mmol) was added a solution of 1.35 g (12.3 mmol) of trimethylchlorosilane in 5 ml of ether. This solution was stirred at room temperature for 1 hr and quenched with water. The ether layer was separated, washed with 5-ml portions of water, 2 *N* hydrochloric acid, and saturated sodium bicarbonate solution, dried, and evaporated to give 242 mg (85%) of product. The ethers were separated on a 6 ft × 0.25 in. column of 10% QF-1 on Chromosorb G at 125° to give isomerically pure **48c** (40%) and **49c** (40%). For **48c**: $\delta_{TMS\ (CDCl_3)}$ 6.32 (m, 2, H_4 and H_5), 6.02 (m, 2, H_3 and H_6), 5.00 (m, 1, H_2), 4.40 (br s, 1, H_{10}), 2.20–3.00 (m, 5, H_1, H_8 and H_9), 2.10 (s, 3, methyl), and 0.28 (s, 9, trimethylsilyl).

For **49c**: $\delta_{TMS\ (CDCl_3)}$ 6.40 (m, 1, H_5), 6.08 (m, 2, H_3 and H_6), 4.80 (br s, 1, H_{10}), 2.20–3.00 (m, 5, H_1, H_8, and H_9), 2.08 (s, 3, methyl), and 0.28 (s, 9, trimethylsilyl). Anal. Calcd for $C_{14}H_{22}OSi$: *m/e* 234.1440. Found: *m/e* 234.1436.

Hydrolysis of 48c. To a solution of 30.8 mg (0.132 mmol) of **48c** in 10 ml of 50% aqueous tetrahydrofuran was added 30 mg of *p*-toluenesulfonic acid. The mixture was stirred at room temperature for 5 hr and the product was extracted with ether. The combined ether portions were washed with 10-ml portions of water and saturated sodium bicarbonate solution, dried, and evaporated. There was obtained 20 mg of **48b.**

2-Methyl-7,8-dihydronaphthalene (50). To a solution of 20 mg of **48b** in 2 ml of acetic acid was added 25 mg of *p*-toluenesulfonic acid. The solution was heated at 50° for 12 hr, cooled, and diluted with 10 ml of water. This aqueous solution was extracted with ether and the combined ether portions were washed with 10-ml portions of water and saturated sodium bicarbonate solution, dried, and evaporated to give 15 mg of **50**; $\delta_{TMS\ (CDCl_3)}$ 7.16 (s, 4, aryl), 6.64 (m, 1, olefinic), 6.18 (m, 1, olefinic), 2.96 (t, J = 8 Hz, 2, benzylic), and 2.54 (br s, 5, allylic and methyl).

β-Methylnaphthalene (51). To a solution of 15.0 mg (0.104 mmol) of **50** in 2 ml of benzene was added 82 mg (0.366 mmol) of DDQ. The mixture was stirred at room temperature for 1 hr and passed though an alumina column (elution with pentane). The solvent was carefully removed in vacuo to give a colorless residue which was identified at γ-methylnaphthalene by comparison of its NMR and VPC retention time with that of an authentic sample: $\delta_{TMS\ (CDCl_3)}$ 7.06–7.70 (m, 7, aryl) and 2.38 (s, 3, methyl).

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Tetracyanoethylene Addition to Iron Tricarbonyl Complexes of Substituted Cyclooctatetraenes. Regioselectivity Considerations during Formation of the 2,3,4,10-Tetrahapto Adducts

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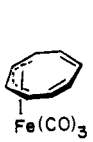
Abstract: The cycloaddition of tetracyanoethylene to a number of cyclooctatetraeneiron tricarbonyls occurs via an unusual 1,3 bonding process with formation of η^4 products in which the iron atom is both σ and π bonded. Although the reaction gives every indication of being general, the site of initial attack by the uniparticulate electrophile is markedly influenced by electronic factors. Thus, methylcyclooctatetraeneiron tricarbonyl is shown to yield two complexes arising from attack at the γ (71%) and δ (21.5%) ring carbons (relative to the substituent). For the phenyl case, attack at the α position (39%) is seen to be competitive with bonding at the γ (16%) and δ (23%) sites. As concerns carbomethoxyl substitution, this electron-withdrawing group directs the electrophile preferentially α (23%) and β (64%). The inference to be drawn from the methoxyl example is that bonding to the γ carbon is kinetically preferred. In benzocyclooctatetraeneiron tricarbonyl, the carbon atom adjacent to the site of benzo fusion is attacked exclusively as it is in protonation. Oxidation of the adducts with ceric(IV) ion furnishes dihydrotetracyanotriquinacenes in high yield and this route will likely be serviceable for the convenient preparation of unusually substituted triquinacenes. A tentative mechanistic scheme which rationalizes all of the data is presented.

The manner in which the chemical properties of cycloolefinic ligands are modified through coordination to a metal center has been the subject of intensive investigation during the last two decades since the discovery of ferrocene. This high level of interest has been fostered by the numerous unique transformations which have been uncovered, some mechanistic implications of which continue to challenge both inorganic and organic chemists. Sometimes discoveries of new and novel reactions are not without the attendant problems of proper visualization and analysis of the events. As a direct consequence, improper or erroneous interpretations are occasionally advanced. Cyclooctatetraeneiron tricarbonyl (**1**) is a case in point. Several conflicting claims surrounded the early investigations of the chemistry of **1** subsequent to its initial synthesis in 1959.[2] For example, its protonation was first studied by Rausch and Schrauzer and the resulting species was considered to be the monocyclic structure **2**.[3] This assignment was quickly corrected by Wilkinson and coworkers who established by ^{1}H NMR techniques that the bicyclo[5.1.0]octadienyliron tricarbonyl cation **3** is actually formed under these conditions.[4] More recent work by Brookhart has revealed that low-temperature (−120°) protonation of **1** in FSO_3H-SO_2F_2 does in fact lead initially to the ring opened cyclooctatrienyliron tricarbonyl cation (**2**);[5] upon warming of such solutions, clean first-order electrocyclization to **3** occurs with a $\Delta F^{\ddagger}_{-60°}$ of 15.7 kcal/mol. Proton attack trans to the iron atom is kinetically preferred, with the entering hydrogen (deuterium) ultimately occupying the endo H_8 position in **3**.[4] Protonation of cyclooctatetraene itself is now recognized to lead to a homotropylium ion in which the electrophile is similarly endo oriented.[6] Interestingly, these results contrast with the exo stereochemistry attending protonation of cyclooctatetraenemolybdenum tricarbonyl,[7] and with the



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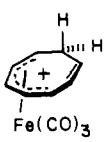

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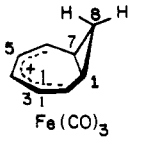

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