Neighboring Group Properties of Cyclooctatetraene. Hydrolysis Rate and Mechanism of Ring Contraction of the Chloromethyl Derivative

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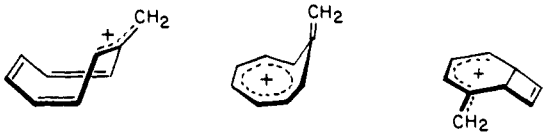
Abstract: To probe the effect of the cyclooctatetraene ring on the stability of an adjacent cationic center, the hydrolysis rate of cyclooctatetraenylcarbinyl chloride in 50% aqueous ethanol was compared with that of the model compound Δ^1-cyclooctenylmethyl chloride. The relative rates of these first-order reactions are such that the COT derivative is five times less reactive at 25°. Both hydrolyses provide major amounts of allylically rearranged alcohols and ethers, although in the methylenecyclooctatriene series the sensitivity of the alcohol to heat, air, and acid precluded its isolation. The mechanism of its facile conversion to *o*-tolylacetaldehyde was examined by making recourse to variously deuterated cyclooctatetraenylcarbinyl chlorides. The fate of the alcohol appears to be protonation of the terminal methylene carbon to give an 8-hydroxyhomotropylium ion which subsequently undergoes two-stage ring contraction. The nature and reactivity of the transient carbonium ions are discussed in light of existing precedent.

The polyolefinic character of cyclooctatetraene (COT), especially evident in its many rearrangement reactions, is due in part to its $4n$ π-electronic character and π-overlap disruptive boat conformation. Though COT is the smallest member of the stable neutral nonaromatic annulenes, the literature contains no report of experiments designed to assess its capability to function as a neighboring group in solvolysis reactions. The hydrolysis of cyclooctatetraenecarbinyl chloride attracted our attention as a consequence of the varied theoretical possibilities for charge delocalization available to the incipient carbonium ion. In addition to customary allylic stabilization as in **1**, the potential for conversion to homotropylium ion **2**, and to several bicyclic cations, e.g., **3**,[1] appeared reasonable. Conversion to **2** finds analogy

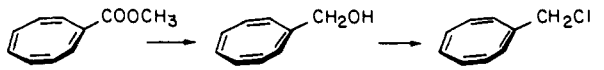


1 **2** **3**

in direct electrophilic additions to COT which lead to comparable six-electron homoaromatic systems.[2] In this connection, the homotropylium ion has been estimated to be 22.3 kcal/mol more stable than a planar cyclooctatrienyl cation.[3] That valence isomerization may precede or be concomitant with ionization and give rise directly to **3** would be analogous to the behavior of 7-cycloheptatrienylcarbinyl derivatives.[4]

If **1** were the cation of kinetic consequence, then the rate of ionization of the chloride should be rather comparable to that of its more saturated counterpart Δ^1-cyclooctenylmethyl chloride, except for the added rate retardation arising from the inductive influences of the additional double bonds.[5] Were **2** involved, it might be argued that a significant rate enhancement would be in evidence.[6] The involvement of **3**, on the other hand, would require overcoming the energy barrier for valence isomerization which is recognized to be on the order of 27 kcal/mol.[7] Consequently, the operation of this pathway might be called to action if both previous processes (and others not considered here) are more energy demanding. Some distinction has now been made at the experimental level. Furthermore, we have now directly attacked the problem of the rearrangement of **6** to *o*-tolylacetaldehyde[1] and provide results and conclusions which do not accord with the earlier hypothesis that aromatization is a direct result of initial ionization. As a result of this new insight, mechanistic correlation of a number of earlier observations in cyclooctatetraene chemistry has been made possible.

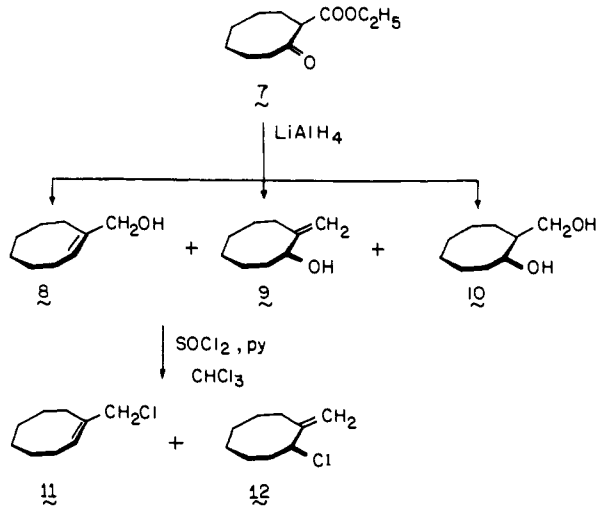
Substrate Syntheses and Kinetics of Hydrolysis. The preparation of cyclooctatetraenecarbinyl chloride (**6**) took advantage of the ready availability of carbomethoxycyclooctatetraene (**4**) by photocycloaddition of methyl propiolate to benzene with 2537 Å light.[8] Lithium aluminum hydride reduction of **4** gave carbinol **5** which with thionyl chloride in pyridine led to **6**. This mode of halogenation af-



4 **5** **6**

forded only 33% yield of the chloride after molecular distillation. Yields of 65–75% were routinely obtained, however, by substitution of $SOCl_2$ with the *N*-chlorosuccinimide–dimethyl sulfide reagent[9] in methylene chloride solution.

The synthesis of Δ^1-cyclooctenylmethyl chloride (**11**) began by hydride reduction[10] of 2-carbethoxycyclooctanone (**7**) to the mixture of alcohols **8–10**. Distillation served to separate **8** and **9** from the diol and preparative VPC was employed to isolate **8** free of **9**. Treatment of **8** with thionyl chloride and pyridine in chloroform afforded a 2:1 mixture of **11** and **12** which again were purified by VPC techniques.



7 **8** **9** **10** **11** **12**

Table I. Buffered (2,6-Lutidine) Hydrolysis Rate Data (H_2O–C_2H_5OH, 1:1)

Compd	Temp, °C	k_1, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
6	25.0	7.77×10^{-6} [a]		
	30.1	1.44×10^{-5}		
	40.0	4.24×10^{-5}	20.7	−12.5
	49.9	1.26×10^{-4}		
11	25.0	3.83×10^{-5} [a]		
	30.1	7.20×10^{-5}		
	40.0	2.16×10^{-4}	21.2	−7.80
	49.9	6.60×10^{-4}		

[a] Extrapolated values based upon the activation parameters.

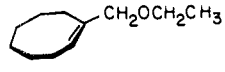
Direct treatment of the distilled mixture of **8** and **9** (1:4) under the same conditions led more conveniently to the same mixture of chlorides.

The hydrolysis rates were determined titrimetrically in 50% aqueous ethanol buffered with 2,6-lutidine. The pseudo-first-order kinetic data and activation parameters for **6** and **11** have been collected in Table I. A serviceable model for use as a basis of comparison would be 1-chloro-2-methyl-2-butene (**13**) which like **11** is a β,γ-dialkyl-substituted allylic chloride. However, the rate of hydrolysis of **13** has not been determined. But because β-methyl substitution is known to give rise to a negligible rate increase,[11] 1-chloro-2-butene (**14**) represents a satisfactory, although

$CH_3CH{=}C(CH_3)CH_2Cl$ (**13**) $\qquad$ $CH_3CH{=}CHCH_2Cl$ (**14**)

somewhat more approximate, model system. Hydrolysis of **14** in 50% aqueous ethanol at 25° proceeds with a rate constant of 1.51×10^{-5} sec^{-1} which indicates that the solvolytic behavior of **11** is rather typical of an allylic chloride containing a γ-alkyl substituent. The finding that **11** exhibits a five-fold rate enhancement over **6** leads one to conclude that the COT ring does not provide demonstrable anchimeric assistance. Furthermore, the results show the rate retardation of **6** to be due to an entropy rather than an enthalpy effect.

Product Results from 6 and 11. Hydrolysis of **11** as above on a preparative scale was seen to proceed with formation of **8** (27%), **9**, (22%), **15** (33%), and **16** (19%) upon direct



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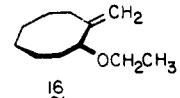

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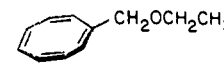
analysis of the product mixture by VPC. The four compounds were separated gas chromatographically and the alcohols were identified by direct comparison with the authentic samples. Their corresponding ethers were identified on the basis of their respective ir, ^1H NMR, and analytical data. The appearance of 41% allylic rearrangement products can be compared with the chlorination reaction of **8** which leads to 33% isomerization.

The initial product studies involving **6** were carried out in analogous fashion. After approximately 5 days at room temperature, the aqueous alcoholic reaction mixture was diluted with water and extracted with ether. To remove residual 2,6-lutidine, the combined organic layers were treated sequentially with water, 3 *N* hydrochloric acid, and saturated sodium bicarbonate solution prior to VPC and ^1H NMR analysis. On this basis, the product was seen to be comprised of 37% of **5**, 17% of structurally retained ether **17**, and 46% of *o*-tolylacetaldehyde (**18**). The identity of **18** was established by independent synthesis involving sequential lithium aluminum hydride reduction and Collins oxidation of commercially available *o*-tolylacetic acid and by



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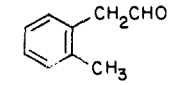


18

19a, R = H
b, R = C_2H_5

comparison of individual spectra, VPC retention times, and semicarbazone derivatives.

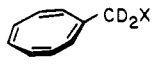
Later direct 100 MHz ^1H NMR examination of the total product mixture subsequent to ether extraction and solvent removal, but prior to exposure to any trace of acid or heat ($t \leq 25°$), failed to provide any indication of the presence of **18.** Rather, from the appearance of intense signals in the δ 5.0–5.25 region, a predominance of **19a** and/or **19b** was inferred (reproducible for several runs). Recourse was next made to VPC analysis on 5% Carbowax columns impregnated with 1–3% KOH at significantly reduced temperatures (105–110°). Under these conditions, two well-defined peaks (area 3:1) of moderate retention times and a minor broad peak of much longer t_{ret} were seen. The major ether peak was collected and identified as **19b** on the basis of its spectra. The infrared curve shows, in particular, intense bands at 892 cm^{-1} characteristic of a terminal methylene group and 1100 cm^{-1} for the antisymmetric C–O–C stretching frequency.[12] Also, the ^1H NMR reveals four main absorption areas ascribable to the olefinic protons (δ 5.5–6.4, m, 6), the exo methylene group together with the doubly allylic hydrogen (5.08–5.22, m, 3), and the ethoxy substituent (3.50, q, J = 7 Hz, 2; 1.22, t, J = 7 Hz, 3) in agreement with the structural features.[13] The less dominant ether and the alcohol were characterized as **17** and **5,** respectively.

With the availability of the ^1H NMR spectra of pure samples of **5, 17,** and **19b,** it became abundantly clear that the 100 MHz spectrum of the total solvolysis mixture could not be duplicated completely by any combined weighting of these three compounds. The signals which remained to be accounted for could be attributed to a second exo methylene derivative, the structure of which was inferred to be rearranged alcohol **19a.** Additional evidence was adduced from the ^1H-decoupled ^{13}C spectrum of this mixture which displays two signals at 112.98 and 112.22 ppm (from TMS) in the chemical shift region anticipated for exo methylene carbon atoms.[14] All attempts to isolate **19a** were frustrated by its blatant instability, its ready polymerization when exposed to air, and its facile conversion to **18** under mildly acidic conditions. This sensitivity to acid is shared by ether analog **19b** but not by **5** and **17.**

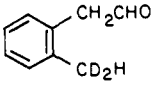
Given the VPC datum that the ratio of **19b** to **17** is 3:1 and the ^1H NMR finding (integration of the methylene singlets) that **17** predominates over **5** by a factor of approximately 2, the best estimate of the actual product composition is 12% of the unrearranged COTcarbinyl derivatives **5** (4%) and **17** (8%), and 88% of the allylic isomers **19a** (66%) and **19b** (22%). The difference in the alcohol/ether ratios **5**/**17** (ca. **19a**/**19b** (ca. 3) is intriguing. The ratio of 3 conforms to the molar ratio of ethanol and water in the mixed solvent and is therefore indicative of the solvent composition. The 0.5 value may reflect in contrast relative nucleophilicities in the competing SN2 reaction and varied solvation factors.

o-Tolylacetaldehyde (**18**) is therefore not directly implicated in the hydrolysis of **6** and is an artifact arising from further rearrangement of the exo methylene products **19** under the original conditions of work-up. To gain further insight into this aromatization process and to more completely analyze the response of **6** to solvolysis as well, extension of this study to include variously deuterated derivatives of the chloride was undertaken.

Deuterium Labeling Studies. Examination of the solvolysis-rearrangement of α,α-dideuterio chloride (**20b**) under the predescribed conditions (direct VPC analysis) provided two relevant observations. First, the resulting aldehyde contained both deuterium atoms in its methyl group (cf. **21**) as



20a, X = OH
b, X = Cl
c, X = OC_2H_5



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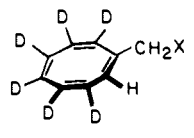
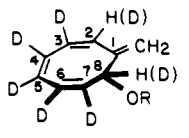
determined by ^1H NMR analysis (see Experimental Section). Also, no apparent loss of isotopic labeling was evidenced by mass spectrometry. In agreement with this latter finding, the reverse experiment, hydrolysis of **6** in D_2O-C_2H_5OD, did not lead to measurable deuterium incorporation. Consequently, the methyl carbon in *o*-tolylacetaldehyde originates from the carbinyl carbon of COT-CH_2Cl. Two of the three appendant hydrogens also come from this source, the third arising not from solvent but from yet a different proton donor.

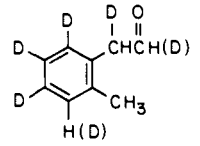
Conversion of the known hexadeuterio alcohol **22a**[8c] to chloride **22b** and its subsequent hydrolysis in buffered (2,6-lutidine or calcium carbonate) 50% aqueous ethanol revealed the ratio of **23b** to **22c** to have remained 3:1. Accordingly, ring substitution by deuterium has no demonstrable effect on product distribution. As concerns the exo methylene products **23**, bond shift isomerization in **22b** would be expected to equalize (discounting isotope effects) the protium distribution at C_2 and C_8 and such was observed (^1H NMR analysis). Deliberate aromatization of the **23a–23b** mixture (VPC column) afforded **24**. The ^1H NMR spectral data for this aldehyde comprised signals of equal area for the aldehyde proton (δ 9.62, 0.5 H) and the aromatic hydrogen (7.12, 0.5 H), a methyl absorption of area 3 at 2.20, and a broadened peak of approximately unit intensity at 3.62 ascribable to the methylene group.[15] From knowledge of the isotopic distribution in **24**, the following additional conclusions can be derived: (1) the third methyl proton is not introduced by migration of a hydrogen (deuterium) away from an existing ring position; (2) the oxygen-bearing carbon (C_8) in **23** serves as the source of the aldehyde group; and (3) in the course of aromatization, C_1 and C_6 appear to become conjoined with simultaneous relegation of C_7 and C_8 to the status of a side chain positioned specifically ortho to the methyl group. Clearly, the rearrangement is deep-seated.



22a, X = OH
b, X = Cl
c, X = OC_2H_5



23a, R = H
b, R = C_2H_5



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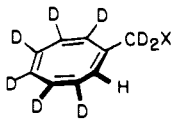
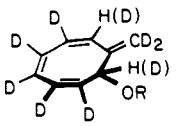
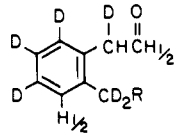
The ultimate in labeling was attained in the d_8 chloride **25b**. Its solvolytic behavior was particularly illuminating owing to the fact that the vinyl region in the ^1H NMR spectrum of the carefully processed reaction mixture now consisted of four "singlets". The overlapping resonances for the lone ring proton in **25a** and **25c** are seen at δ 5.64 and are widely shifted from the coincident signals of the H_2 protons in **26a** and **26b** (6.18). The sp^3-bound H_8 protons in **26a** (5.34) and **26b** (4.96) are likewise distinctive, their combined area equaling the intensity of the 6.18 signal. No aldehyde was present. Subsequent injection of a portion of this total product into a gas chromatograph (95°) and collection of the aldehyde which eluted afforded **27a**. A second portion of the solvolysis mixture was dissolved in THF-D_2O containing one drop of hydrochloric acid and warmed very briefly. Isolation and ^1H NMR analysis showed the resulting aldehyde to be **27b**. Therefore the "third" proton in the methyl group is introduced from the medium during acid-catalyzed rearrangement of the exo methylene isomerization products.



25a, X = OH
b, X = Cl
c, X = OC_2H_5

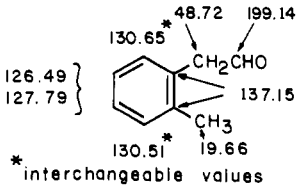


26a, R = H
b, R = C_2H_5



27a, R = H
b, R = D

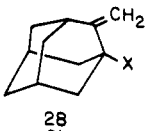
In an attempt to establish unequivocally the position of the residual aryl proton, the ^{13}C NMR spectrum of unlabeled **18** was recorded. However, because the resonances of the two ortho carbons are practically indistinguishable and the presence of three proximate deuterium atoms serves to engender substantial line broadening, this technique proved not to be serviceable. In principle, the four aromatic protons comprise an AA'BB' set if the methyl and acetaldehyde



groups are assumed to be equally perturbing. In such hydrocarbons as *o*-xylene and tetralin, it appears likely that the lower half of the AA'BB' pattern corresponds to H_{ortho},[16] and it seems reasonable that the same order will obtain in the case of **18**. Careful comparison of the ^1H NMR spectra of **18** and its deuterated forms **24**, **27a**, and **27b** indicated the chemical shift of the residual proton in the last two compounds to reside in the downfield half of the aromatic multiplet. That this proton is ortho to methyl rather than the CH_2CHO group is inferred from mechanistic considerations (see Discussion).

Discussion

The rate of hydrolysis of **6**, in tandem with the identity and nature of the product distribution, point to carbocation **1** as the first intermediate reached in the ionization. That k_1 for **6** is only a factor of 5 less than that of **11** follows from the conformational flexibility of the folded COT ring which contrasts with the appreciable rigidity of such molecules as **28**. Rate decelerations on the order of 10^4 have



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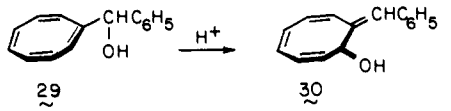
been recorded for such allylic halides.[5] Furthermore, molecular model studies of **1** reveal the developing p orbital to be positioned at an approximate 45° angle with the adjacent nonconjugated π bond. Steric inhibition of pπ interaction is consequently not at its maximum in this species (compare **28**).

The great predominance of allylic rearrangement products **19** is to be compared with the earlier findings of Houghton and Waight who noted the acid-catalyzed isomerization of substituted COTcarbinol **29** to its more stable isomer **30**.[17] The unreactivity of **30** to the acidic conditions



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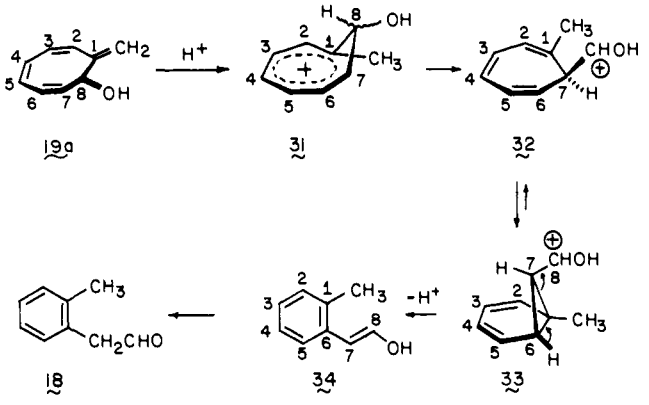
employed by these workers (0.1 *N* HCl in 48% aqueous acetone, room temperature, 6 days) contrasts with our findings and is the likely result of impedance to protonation (contrabenzylic) of the phenyl substituted exocyclic double bond at the terminal carbon (vide infra).

That the hydrolysis of **6** proceeds with a $\Delta H^{\ddagger} = 20.7$ kcal/mol excludes those mechanistic pathways dependent upon valence isomerization. The cyclooctatetraene-bicyclo[4.2.0]octatriene reaction has to overcome $\Delta H^{\ddagger} = 27$ kcal/mol, a barrier height known to be little dependent upon substitution.[7] If such were operating, the half-reaction time would amount to approximately 30 days at 20°. The reactivity of the title compound is notably in excess of this extrapolation (Table I).

On the basis of the existing data, the involvement of homotropylium ion **2** cannot be dismissed. Capture of **2** by solvent would, like **1**, afford the observed products. In this sense, it is an admissable intermediate. Also, if we assume that the ionization of **6** is anchimerically accelerated by a factor of 10^3 but decelerated inductively because of the neighboring double bonds to a comparable extent, **2** then becomes a plausible kinetic intermediate as well. Fundamentally at issue here is the question of whether **1** or **2** is thermodynamically more stable.[18] No homotropylium cations with a trigonal carbon at the bridge position (C_8) are presently known and the possibility remains that such species may be less stable than their cyclooctatrienyl counterparts. However, this need not necessarily be so.

The present work does reveal that protonation of **19a** (and **19b**) does not result in return to that manifold inhabited by the carbonium ion of solvolytic consequence. Rather, isomerization to *o*-tolylacetaldehyde (**18**) is thereby triggered. A direct pathway from **19a** to **18** which conforms in every detail to the consequences of deuterium labeling is outlined in Scheme I. Proton transfer to the exo methylene

Scheme I



19a 31 32 33 34 18

carbon of **19a** triggers formation of 8-hydroxyhomotropylium ion **31** which is expected from an awareness of the behavior of the parent ion[19] to experience conversion to the protonated 7-formylcycloheptatriene (**32**).[20] Should **32** possess the features normally intrinsic to 7-cycloheptatrienylcarbinyl cations, valence isomerization to its norcaradienylcarbinyl tautomer **33** and ultimate deprotonation (as shown) will be rapidly initiated.[4] The development of benzenoid character provides **34**, the enol form of **18**.

For convenience in tracing the structural consequences of this mechanism, the carbon atoms of intermediates **31–34** are numbered. It is seen that requisite bonding of C_1 to C_6 takes place in two stages, by extrusion first of C_8 and then C_7 from the initial eight-membered ring. Concurrent with this sequence of ring contractions, the side chain is constructed in such a manner that the oxygenated carbon (C_8) is necessarily at the terminal position. Entirely comparable mechanistic thinking serves to rationalize convincingly acid and metal ion catalyzed isomerization of COT epoxide and the aqueous $Hg(OAc)_2$-promoted ring contraction of COT to phenylacetaldehyde (two-carbon extrusions),[19-21] the conversion of COT to cycloheptatriene 7-carboxaldehyde dimethylacetal with methanolic mercuric acetate (one-carbon extrusion),[21] and the rearrangement-ring contraction of 2-tropyl-2-phenethyl tosylate to 1,3-diphenylpropene under conditions of acetolysis.[22]

Experimental Section

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 Perkin-Elmer Model 137 and 467 instruments. Mass spectra were recorded on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Preparative VPC work was done on a Varian-Aerograph A90-P3 instrument equipped with a thermal conductivity detector.

Cyclooctatetraenylcarbinol (5). To a suspension of 530 mg (13.95 mmol) of lithium aluminum hydride in 50 ml of ether was slowly added a solution of 2.25 g (13.95 mmol) of ester **4**[8] in 100 ml of ether. The reaction mixture was stirred at room temperature for 2 hr and 0.5 ml of water, 0.5 ml of 10% sodium hydroxide solution, and 1.4 ml of water were added in that order. This slurry was filtered through magnesium sulfate and the filtrate was evaporated to give 1.85 g (99%) of **5**; δ_{TMS} ($CDCl_3$) 5.83 (s, 7, olefinic), 4.02 (s, 2, methylene), and 2.33 (br s, 1, hydroxyl).

The 3,5-dinitrobenzoate was recrystallized from absolute ethanol to give yellow needles, mp 68–69°. Anal. ($C_{16}H_{12}N_2O_6$) C, H.

Cyclooctatetraenecarbinyl Chloride (6). Method A. To a solution of 1.00 g (7.46 mmol) of **5** and 1.6 ml (20.0 mmol) of pyridine in 50 ml of chloroform was slowly added a solution of 1.79 g (15.0 mmol) of thionyl chloride in 5 ml of chloroform. The mixture was stirred at room temperature for 12 hr and quenched by addition of 25 ml of water, and the chloroform layer was separated. The organic phase was washed with water (3 × 50 ml), 3 *N* hydrochloric acid, and saturated sodium bicarbonate solution and dried. Removal of solvent gave a colored oil which was molecularly distilled to give 420 mg (33%) of **6** as a pale yellow liquid: δ_{TMS} ($CDCl_3$) 5.77 (s, 7, olefinic) and 3.92 (s, 2, methylene). Anal. (C_9H_9Cl) C, H.

Method B. To 734 mg (5.5 mmol) of recrystallized *N*-chlorosuccinimide in 20 ml of dry methylene chloride was added at 0° under nitrogen with magnetic stirring 0.44 ml of dimethyl sulfide. After cooling to −30°, a solution of 670 mg (5.0 mmol) of **5** in 5 ml of methylene chloride was introduced via syringe over 10 min. The solution was allowed to warm to 0° and stirred at this temperature for 1 hr before being poured into 30 ml of ice-cold saturated brine. Extraction with ether (3 × 50 ml), washing of the combined organic layers with brine (50 ml), drying, and evaporation of solvent yielded a lemon-colored oil. This was chromatographed directly on silica gel (pentane elution) to give 590 mg (77%) of **6**, spectroscopically identical with the sample prepared above.

Reduction of 2-Carbethoxycyclooctanone. To a suspension of 2.28 g (60.0 mmol) of lithium aluminum hydride in 50 ml of ether was slowly added a solution of 10.0 g (50.4 mmol) of **7**[23] in 50 ml of the same solvent. The mixture was refluxed for 3 hr, cooled, and treated sequentially with 2.3 ml of water, 2.3 ml of 10% sodium hydroxide solution, and 7.0 ml of water. Filtration through magnesium sulfate and evaporation of the combined filtrate and washings gave 7.17 g of residual oil which was distilled to give 4.55 g of a mixture (1:4) of **8** and **9**, bp 75–76° (0.2 mm). These isomers were separated by preparative VPC (6 ft × 0.25 in. 5% Carbowax–1% KOH on Chromosorb G, 140°). For **8**:[24] δ_{TMS} ($CDCl_3$) 5.67 (t, J = 7 Hz, 1, olefinic), 4.06 (s, 2, methylene), 2.20 (br s, 4, allylics), and 1.52 (s, 8, aliphatics). For **9**: δ_{TMS} ($CDCl_3$) 5.01 (m, 1, olefinic), 4.93 (m, 1, olefinic), 4.17 (t, J = 6 Hz, 1, >C*H*-O–), 2.45 (s, 1, hydroxyl), 2,10–2.33 (m, 2, allylic), and 1.33–2.07 (m, 10, aliphatics).

The 3,5-dinitrobenzoate of alcohol **8** was obtained as pale yellow needles, mp 96–97°, from absolute ethanol. Anal. ($C_{16}H_{18}N_2O_6$) C, H, N.

Chlorination of 8. A solution of 595 mg (5.00 mmol) of thionyl chloride in 10 ml of chloroform was introduced slowly into a solution of **8** (340 mg, 2.43 mmol) and pyridine (400 mg, 5.00 mmol) in 50 ml of chloroform. The mixture was stirred at room temperature for 12 hr, diluted with cold water, and extracted with ether. The combined ether extracts were washed with water, 10% hydrochloric acid, and saturated sodium bicarbonate solution, dried, and evaporated. The residual dark oil (375 mg) was chromatographed on silica gel (pentane elution). VPC analysis of the eluate revealed a 2:1 mixture of **11** and **12** to be in hand. These were separated on the predescribed column at 95°. For **11**: δ_{TMS} ($CDCl_3$) 5.72 (t, J = 7 Hz, 1, olefinic), 4.00 (s, 2, methylene), 2.20 (m, 4, allylic), and 1.50 (s, 8, aliphatics). Anal. ($C_9H_{15}Cl$) C, H.

For **12**: δ_{TMS} ($CDCl_3$) 5.14 (s, 1, olefinic), 4.92 (s, 1, olefinic), 4.48 (m, 1, methine), 2.20 (m, 4, methylenes), and 1.52 (br s, 8, methylenes). Anal. ($C_9H_{15}Cl$) C, H.

Kinetics Procedure. A 50% aqueous ethanol solution was prepared by combining an equal volumetric mixture of absolute ethanol and distilled water both of which had been degassed prior to use. A standard solution of aqueous sodium hydroxide was prepared and standardized against potassium hydrogen sulfate. A 0.03 M solution of chloride and 2 equiv of redistilled 2,6-lutidine in 50% aqueous ethanol was prepared. Aliquots of this solution (ca. 1.1 ml) were removed, sealed in glass ampoules, and immersed in a constant temperature bath. After 5 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 from the ampoule with an automatic pipet, treated with a drop of a saturated solution of phenolphthalein indicator in ethanol, and titrated with standard sodium hydroxide solution. A Fisher Accumet pH meter with microprobe combination electrode was used to determine the titrimetric end point. 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 before to give the infinity titer. The rate constants, activation parameters, and extrapolated rate constants were calculated by least-squares treatment of the data (Wang electronic calculator).

Product Studies. Hydrolysis of 11. A solution of 325 mg (2.31 mmol) of **11** and 247 mg (2.31 mmol) of 2,6-lutidine in 25 ml of 50% aqueous ethanol was stirred at room temperature for 5 days. The reaction mixture was added to 100 ml of water and extracted with ether. The combined ether portions were washed with water, 3 N hydrochloric acid, and saturated sodium bicarbonate solution, dried, and evaporated in vacuo to give 275 mg of colorless liquid. Analysis by VPC using the above column showed the mixture to be composed of **8** (27%), **9** (22%), **15** (33%), and **16** (19%). These were separated and the alcohols were shown to be identical with the original samples.

For ether **15**: δ_{TMS} ($CDCl_3$) 5.56 (t, J = 7 Hz, 1, olefinic), 3.80 (s, 2, allylic, $-CH_2O-$), 3.38 (q, J = 7 Hz, 2, $-OCH_2-$), 2.16 (br s, 4, allylic), 1.48 (s, 8, aliphatics), and 1.14 (q, J = 7 Hz, 3, methyl). Anal. ($C_{11}H_{20}O$), C, H.

For ether **16**: δ_{TMS} ($CDCl_3$) 4.98 (s, 2, olefinic), 3.68 (m, 1, methine), 3.22 (m, 2, methylene), 2.20 (m, 2, allylic), 1.52 (br m, 10, aliphatics), and 1.14 (t, J = 7 Hz, 3, methyl). Anal. ($C_{11}H_{20}O$) C, H.

Hydrolysis of 6. Procedure A. A solution of 330 mg (1.95 mmol) of **6** and 2.4 mg (2.00 mmol) of 2,6-lutidine in 25 ml of 50% aqueous ethanol was stirred at room temperature for 116.5 hr. The reaction mixture was added to 100 ml of water and extracted with ether. The combined ether portions were washed with water, 3 N hydrochloric acid, and saturated sodium bicarbonate solution and dried over magnesium sulfate. Removal of the ether in vacuo gave 250 mg of yellow oil which was analyzed by VPC on a 6 ft × 0.25 in. column packed with 10% QF-1 on Chromosorb G. The three components were collected and identified as **5** (37%), **17** (17%), and **18** (46%). The last two substances were synthesized independently and the relevant spectra were superimposable.

Cyclooctatetraenylmethyl Ethyl Ether (17). A. To a solution of 350 mg (2.61 mmol) of **5** and 285 mg (2.61 mmol) of ethyl bromide in 20 ml of tetrahydrofuran was added 292 mg (2.61 mmol) of potassium *tert*-butoxide. The reaction mixture was stirred at room temperature for 6 hr, diluted with water, and extracted with ether. The combined ether portions were washed with 25 ml portions of water, 3 N hydrochloric acid, and saturated sodium bicarbonate solution and dried. Removal of the ether in vacuo gave 300 mg (75%), of **17,** which was purified by VPC on the 6 ft 5% Carbowax–1% potassium hydroxide–Chromosorb G column at 135: δ_{TMS} ($CDCl_3$) 5,80 (s, 7, olefinic), 3.86 (s, 2, allylic $-CH_2O-$), 3.48 (q, J = 7 Hz, 2, $-OCH_2-$), and 1.18 (t, J = 7 Hz, 3, methyl). Anal. ($C_{11}H_{14}O$) C, H.

B. To a solution of sodium ethoxide (from 100 mg of sodium metal) in 25 ml of absolute ethanol was added 400 mg (2.0 mmol) of cyclooctatetraenecarbinyl bromide in absolute ethanol (2 ml). This solution was stirred at room temperature for 12 hr, diluted with water, and processed as above to give 315 mg (95%) of **17.**

***o*-Tolylacetaldehyde (18).** To a suspension of 0.635 g (0.017 mmol) of lithium aluminum hydride in 50 ml of ether was slowly added a solution of 250 mg (0.017 mmol) of *o*-tolylacetic acid in 50 ml of the same solvent. The mixture was stirred at room temperature for 2 hr and an alkaline work-up was used (sequential addition of 0.65 ml of water, 0.65 ml of 10% sodium hydroxide solution, and 2.0 ml of water). The mixture was filtered through magnesium sulfate and the solvent was evaporated in vacuo to give 220 mg of 2-(*o*-tolyl)ethanol: δ_{TMS} ($CDCl_3$) 6.78 (s, 4, aryl), 4.05 (br s, 1, hydroxyl), 3.40 (t, J = 7 Hz, 2, $-CH_2O-$), 2.52 (t, J = 7 Hz, 2, benzylic), and 1.96 (s, 3, methyl).

To a solution of 100 mg (0.736 mmol) of the alcohol in 50 ml of methylene chloride was added 1.16 g (7.36 mmol) of Collins reagent. The solution was stirred at room temperature for 24 hr and the solvent was removed in vacuo. The residue was taken up in 100 ml of ether, washed with 50 ml portions of water, 10% hydrochloric acid, and saturated sodium bicarbonate solution, and dried. Removal of the solvent in vacuo gave 100 mg of colorless liquid, VPC purification (6 ft × 0.25 in. column of 5% Carbowax–1% potassium hydroxide on Chromosorb G at 130°) of which afforded pure **18**: δ_{TMS} ($CDCl_3$) 9.60 (t, J = 2 Hz, 1, CHO), 7.12 (s, 4, aryl), 3.62 (d, J = 2 Hz, 2, methylene), and 2.24 (s, 3, methyl). A semicarbazone of **18** was prepared in the usual manner and recrystallized twice from 95% ethanol to give a crystalline product, mp 176–177°. A mixture melting point proved it to be identical with the derivative prepared from the sample isolated above. Anal. ($C_{10}H_{13}NO$) C, H, N.

Hydrolysis of 6. Procedure B. Chloride **6** (405 mg, 2.7 mmol) and 2,6-lutidine (286 mg, 5.4 mmol) were dissolved in 50 ml of 50% aqueous ethanol and stirred in the absence of light at room temperature for 5 days. No **6** remained. The solvolysis mixture was well extracted with ether (3 × 100 ml) and the combined extracts were rapidly filtered, dried, and evaporated below 25°. The resulting yellowish oil (350 mg) was then examined directly by 100 MHz ^1H NMR. The predominance of **19a** and **19b** in this mixture could readily be inferred (see text for discussion) from the appearance of intense absorption at δ 5.0–5.25. VPC analysis on a 10 ft × 0.125 in. 5% Carbowax 20M–Chromosorb P column gave evidence for the presence of **17, 19b,** and **5.** These were collected by preparative VPC on the KOH–Carbowax column (100°). For **19b**: ν_{max} (CCl_4) 3010, 2979, 2870, 1700, 1600, 1440, 1380, 1335, 1300, 1155, 1100, 892, and 645 cm^{-1}; δ_{TMS} ($CDCl_3$) 5.5–6.4 (m, 6, ring olefinics), 5.08–5.22 (m, 3, exo methylene and $>CHO-$), 3.50 (q, J = 7 Hz, 2, $-OH_2-$), and 1.22 (t, J = 7 Hz, methyl). Anal. Calcd for $C_{11}H_{14}O$: m/e 162.1045. Found: m/e 162.1047.

Cyclooctatetraenecarbinyl Chloride-α,α-d_2 (20b). Reduction of 2.60 g (16.0 mmol) of **4** with 675 mg (16.0 mmol) of lithium aluminum deuteride as predescribed afforded 1.66 g (76%) of alcohol **20a**: δ_{TMS} ($CDCl_3$) 5.82 (s, 7, olefinic) and 2.52 (br s, 1, hydroxyl).

A solution of 1.66 g (12.2 mmol) of **20a,** 1.98 g (25.0 mmol) of pyridine, and 2.38 g (20.0 mmol) of thionyl chloride in 55 ml of chloroform was stirred at room temperature for 12 hr and processed as before to give 660 mg (35%) of **20b**: δ_{TMS} ($CDCl_3$) 5.82 (m, olefinic). Anal. Calcd for $C_9H_7D_2Cl$: m/e 154.0518. Found: m/e 154.0519.

Hydrolysis of 20b. A solution of 1.16 g (6.79 mmol) of **20b** and 750 mg (7.00 mmol) of 2,6-lutidine in 75 ml of 50% aqueous ethanol was stirred at room temperature for 7 days and worked up according to procedure A. VPC analysis gave evidence for the pro-

duction of **20a** (37%), **20c** (17%), and **21** (46%). These compounds were purified on a preparative scale by this technique for characterization purposes. For **20a**: Anal. Calcd for $C_9H_8D_2O$: *m/e* 136.0857. Found: *m/e* 136.0859.

For **20c**: δ_{TMS} ($CDCl_3$) 5.76 (s, 7, olefinic), 3.46 (q, J = 7 Hz, 2, $-OCH_2-$), and 1.18 (t, J = 7 Hz, 3, methyl). Anal. Calcd for $C_{11}H_{11}D_2O$: *m/e* 164.1170. Found: *m/e* 164.1173.

For **18**: δ_{TMS} ($CDCl_3$) 9.62 (t, J = 2 Hz, 1, CHO), 7.12 (m, 4, aryl), 3.64 (d, J = 2 Hz, 2, methylene), and 2.20 (br s, 1, CD_2H). Anal. Calcd for $C_9H_8D_2O$: *m/e* 136.0857. Found: *m/e* 136.0859.

Cyclooctatetraenecarbinyl Chloride-*3,4,5,6,7,8-d*$_6$ (22b). A 1.0 g (6.5 mmol) sample of **22a**[8c] was allowed to react with *N*-chlorosuccinimide (1.09 g, 7.5 mmol) and dimethyl sulfide (0.65 ml) in 30 ml of dry methylene chloride as previously outlined. There was obtained 650 mg (60%) of the chloride: δ_{TMS} ($CDCl_3$) 5.82 (br m, 1, olefinic) and 3.96 (s, 2, methylene).

Hydrolysis of 22b. The chloride (650 mg, 3.9 mmol) in 1:1 aqueous ethanol (65 ml) buffered with calcium carbonate (1.0 g) was stirred at room temperature for 120 hr in the absence of light. Work-up and product examination were conducted as previously described for the undeuterated material, and as detailed in the text.

The deuterated derivatives **23a, 23b, 24, 25c, 26a, 26b, 27a,** and **27b** resulting from the solvolytic and acid-catalyzed reactions were characterized by the coincidence of their residual ^1H resonances with the appropriate ones in their undeuterated counterparts.

Cyclooctatetraenecarbinyl Chloride-*α,α,3,4,5,6,7,8-d*$_8$ (25b). Reduction of carbomethoxycyclooctatetraene-*3,4,5,6,7,8-d*$_6$[8] (1.0 g, 60 mmol) with lithium aluminum deuteride (220 mg, 60 mmol) gave alcohol **25a** in >95% yield. Conversion to **25b** with *N*-chlorosuccinimide and dimethyl sulfide proceeded in 65% yield: δ_{TMS} ($CDCl_3$) 5.82 (br).

Hydrolysis of 25b. The above chloride (600 mg) was hydrolyzed in 50:50 aqueous ethanol (50 ml) (buffered with calcium carbonate) at room temperature, in the absence of light for 120 hr. Work-up and product examination were conducted as already detailed and discussed in the text.

VPC-Promoted Rearrangement. Direct ^1H NMR examination of the total solvolysis product of **6** revealed the absence of **18**. Injection of a sample onto a preparative VPC instrument (injector, 95°; column, 80°, detector, 80°; collector, 70°) equipped with a 2 ft × 0.25 in. SE-30 column, collection of the total eluate, and subsequent 100 MHz ^1H NMR analysis indicated gross changes in that **18** was now present in substantial proportions along with **19b** and small amounts of **5** and **17**. A freshly prepared 2 ft × 0.25 in. SE-30 column liberally treated with hexamethyldisilazane at 200° before use failed to suppress this rearrangement.

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References and Notes

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