2.59 (2 H, J_{H_b,H_c} = 8.0 Hz, $-H_c$), a doublet at 2.86 (2 H, J_{H_d,H_e} = 10.0 Hz, $-H_d$), a doublet at 3.12 (2 H, J_{H_d,H_e} = 10.0 Hz, $-H_e$), and singlets at 7.77 (6 H, external $-CH_3$) and 8.88 (6 H, internal $-CH_3$).

Oxidation of 2d to 16d. A sample of **2d** in perdeuteriotetrahydrofuran was irradiated at −80 °C until the deep orange color of the photostationary state was achieved. When the NMR tube was allowed to warm to 80 °C in the dark, no change in the NMR spectrum occurred. However, when the NMR tube was opened to the air at room temperature, photoproduct **2f** was rapidly converted to **16f**. The NMR spectrum of **16f** showed a singlet at τ 1.75 (2 H, ArH), a doublet at 1.83 (2 H, J_{H_b,H_c} = 8.0 Hz, $-H_b$), a doublet at 2.07 (2 H, J_{H_b,H_c} = 8.0 Hz, $-H_c$), a doublet at 2.23 (2 H, J_{H_d,H_e} = 10.0 Hz, $-H_d$), a doublet at 2.42 (2 H, J_{H_d,H_e} = 10.0 Hz, $-H_e$), a singlet at 7.46 (6 H, external $-CH_3$), and a singlet at 10.00 (6 H, internal $-CH_3$).

Irradiation of 1e in the Presence of Oxygen to Give Thiacoronene. A solution of 5.0 mg of **2e** in perdeuteriotetrahydrofuran was irradiated at room temperature in the presence of oxygen. NMR monitoring showed the rapid disappearance of signals for **1e** and **2e** and the development of the aromatic multiplet from τ 1.20 to 1.45 of thiacoronene. After removal of the solvent, the residue was purified by preparative thin layer chromatography over silica gel using chloroform for elution. This gave a pale yellow solid which, after recrystallization from a benzene–hexane mixture, gave 4.9 mg (100%) of tiny, yellow crystals: mp >350 °C; mol wt calcd for $C_{22}H_{10}S$, 306.050; mol wt found (high resolution mass spectrum), 306.050.

Comparison of the ultraviolet and visible spectrum of this product showed it to be identical with that of an authentic specimen of thiacoronene.[21]

Acknowledgment. We thank the National Science Foundation for their support of this investigation. Dr. Olof Wennerström thanks the Swedish Research Council for fellowship support.

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Synthesis, Structure, and Acetolysis of Some Fused Cyclobutane Derivatives

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Abstract: Syntheses of *exo*- and *endo*-7-hydroxy-6b,7,8,8a-tetrahydrocyclobut[*a*]acenaphthylene (*exo*- and *endo*-**5a**) are described. Several sulfonate esters were prepared from these alcohols. X-ray crystal structure anslyses were carried out on the exo carboxylic acid (*exo*-**5c**) and the endo methanesulfonate (*endo*-**5f**), which both crystallize in the monoclinic system, space group $P2_1/c$, with $Z = 4$ in unit cells of dimensions a = 8.63 (1), b = 20.21 (3), c = 7.35 (1) Å, β = 120.16 (10)°, for *exo*-**5c**, and a = 20.41 (1), b = 5.95 (1), c = 10.88 (1) Å, β = 98.50 (5)°, for *endo*-**5f**. The crystal structures were solved by direct phase-determining procedures and atomic parameters refined to R = 0.123 (1719 reflections from photographic data) for *exo*-**5c** and R = 0.051 (1761 reflections from diffractometer data) for *endo*-**5f**. Kinetic studies of the acetolysis of the exo trifluoromethanesulfonate (*exo*-**5i**) and the exo and endo methanesulfonates (**5f**) showed these to be among the least reactive cyclobutyl derivatives known. The acetates from the exo sulfonate esters were identified as the unrearranged acetate (*exo*-**5e**) and the epimeric, ring-opened *cis*- and *trans*-1-acetoxy-2-vinylacenaphthenes (*cis*- and *trans*-**14b**). The acetate obtained from the endo mesylate was identified as 7-acetoxy-7,8-dihydrocyclohept[*d*,*e*]naphthalene (**18a**). These results are compared with those reported for related cis-fused cyclobutane derivatives, and possible solvolysis pathways are proposed.

Introduction

Carbonium ion reactions of cyclobutane derivatives have been of interest for some time.[1] Those derivatives in which the cyclobutane ring is joined to another ring have attracted particular attention, since in these molecules the four-membered ring is more constrained than in simple cyclobutanes. A variety of compounds with fusion[2-4,5c] and bridging[5] of a four-membered ring to rings of varying sizes has been studied. The conformation of a cyclobutane is of major importance in determining the activity of its derivatives,[2a] since the preferred

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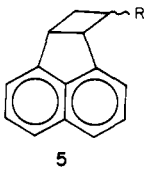
mode of ionization involves overlap of ring bond orbitals with the developing p orbital.[2c,6] Wiberg has discussed the effects that fusion of four-, five-, and six-membered rings to a cyclobutane ring would be expected to have on ring strain and cyclobutane geometry.[2a] Electron diffraction studies have since been reported on the cis-fused molecules **1a**[7] and **2a**.[8] The cyclobutane ring of **1a** is planar, while that of **2a** shows torsion angles of ca. 8°. Compound **3a** would be expected to be less planar still, and **4a** should be nearly as puckered as an unconstrained cyclobutane (torsion angles of about 24°).[9]

In a puckered cyclobutane, assistance to ionization by overlap of ring bond orbitals is possible for an equatorial but not for an axial leaving group.[10] In a fused planar cyclobutane, departure of an endo substituent can be assisted by a disrotatory ring opening in a manner analogous to ionization of cyclopropyl derivatives, while such a ring opening with an exo leaving group would result in increasingly severe strain and steric interactions.[2c,11] Since the geometry of the puckered/equatorial situation is more favorable for orbital overlap than that of the planar/endo situation,[6] the closer the conformation of a cyclobutane comes to planarity, the lower its reactivity would be expected to be.

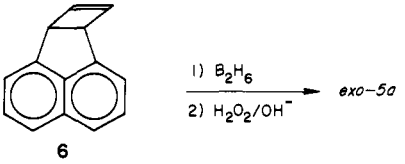
In order to explore these ideas further, endo and exo derivatives of the relatively rigid cyclobutane ring system **5** have been prepared, their crystal structures determined, and their reactivities evaluated.



a: R = OH
b: R = CN
c: R = CO_2H
d: R = $COCH_3$
e: R = $OCOCH_3$
f: R = OSO_2CH_3
g: R = $OSO_2C_6H_4CH_3(p)$
h: R = $OSO_2CH_2CF_3$
i: R = OSO_2CF_3

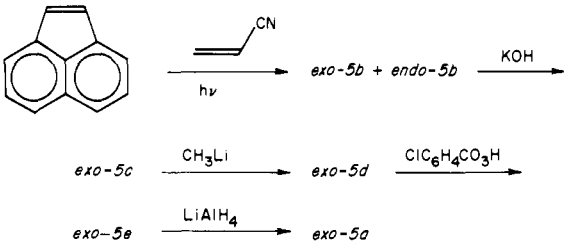
Syntheses

The target compounds were the epimeric alcohols *exo*- and *endo*-**5a**, which could be converted into sulfonate esters for solvolysis studies. The exo alcohol was first prepared by hydroboration/oxidation of the previously described cyclobutene **6**.[12] The low yields associated with the preparation of **6**, however, led us to investigate alternative routes to *exo*-**5a**, as well as to improve the yield of **6** itself.

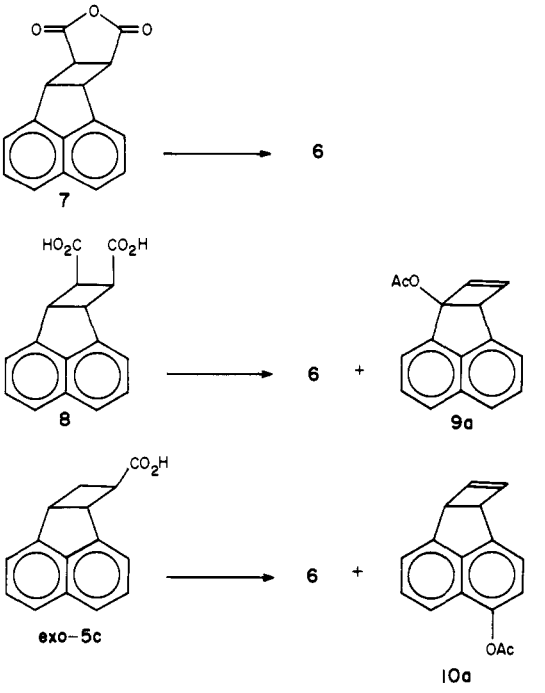


Starting from acenaphthylene, *exo*-**5a** could be obtained in about 18% yield as outlined in Scheme I. The photoaddition of acrylonitrile to acenaphthylene was carried out by a modification of the published procedure.[13] Basic hydrolysis of the resulting mixture of epimeric nitriles in refluxing aqueous ethylene glycol led to good yields of the exo acid. This acid gave the corresponding methyl ketone (*exo*-**5d**) upon treatment with methyllithium. Baeyer–Villiger oxidation of *exo*-**5d** with *m*-chloroperoxybenzoic acid gave the acetoxy compound,

Scheme I



Scheme II



exo-**5e**, though in variable yield. Lithium aluminum hydride reduction of the acetate then gave the desired exo alcohol.

Three of the four reported[12,14,15] preparations of **6** utilize lead tetraacetate bisdecarboxylations of either the anhydride **7** or the corresponding diacid **8** (see Scheme II). The fourth[12] is a low-yield cyclopropane ring expansion sequence. One[14] reports decarboxylation yields of 29% from **8**, and overall yields of **6** from acenaphthylene amounting to 20%. Reproducing the reported conditions for decarboxylation of **8** as closely as possible, however, gave us **6** in less than 2% yield. Varying these conditions gave **6** in yields of up to 7%, along with another product assigned structure **9a** on the basis of its spectral properties and those of the corresponding alcohol **9b**. (In one attempt to determine the origin of **9a**, cyclobutene **6** was submitted to the decarboxylation reaction conditions; no **9a** was produced.) Since simple decarboxylations have been more carefully studied than bisdecarboxylations,[16] and since a convenient route to the exo carboxylic acid was available, conditions utilizing this substrate were investigated. The first experiment, using acetic acid as a cosolvent, gave 12% of **6** along with about 35% of a mixture of acetates, consisting of three to five components. The major component was assigned structure **10a**, based on its spectra and those of its hydrolysis product, **10b**. When the lead tetraacetate, which contained 10% acetic acid, was dried before use, and no acetic acid was added as cosolvent, the yield of **6** rose to 35%. The sequence *exo*-**5c** → **6** → *exo*-**5a** now provides the most convenient route to this exo alcohol.

The corresponding endo alcohol is obtained by lithium aluminum hydride reduction of cyclobutanone **11**, first prepared from *exo*-**5a** by Jones oxidation. (The epimeric alcohols

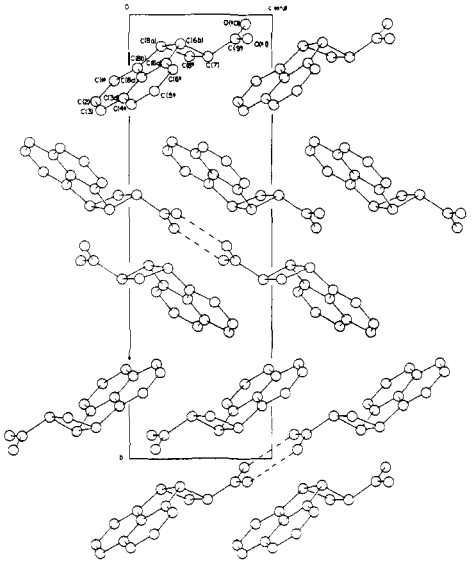


Figure 1. Atom numbering scheme and packing of *exo*-**5c** dimers in the crystal, viewed in projection along the *a* axis; O—H · · · O hydrogen bonds are denoted by broken lines.

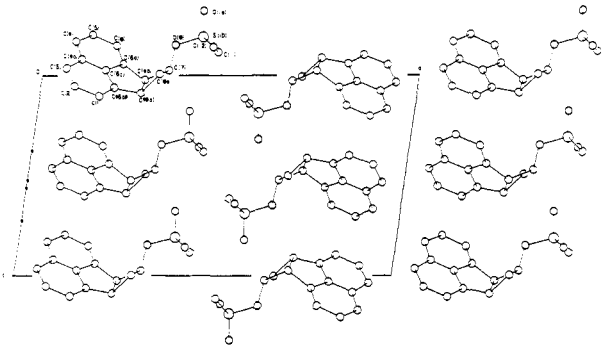
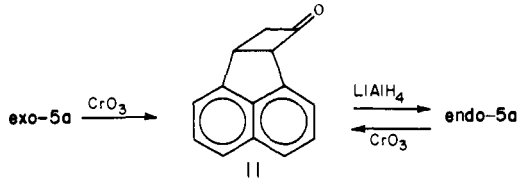
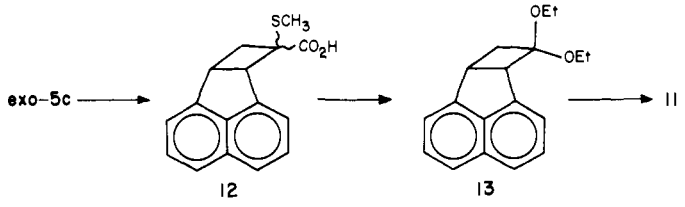


Figure 2. Atom numbering scheme and crystal packing arrangement of *endo*-**5f**, viewed in projection along the *b* axis.

have identical mass spectra, but different infrared and NMR spectra; *endo*-**5a** could be reconverted to **11** by Jones oxidation.)



An improved preparation of **11** which does not consume exo alcohol to produce its endo epimer was suggested by the recent publication of a new route from carboxylic acids to ketones.[17] This technique did in fact provide a convenient path to **11.** Treatment of the dianion of *exo*-**5c** with dimethyl di-



sulfide gave the sulfenylated acid **12** (as a mixture of epimers) in about 70% yield. Diethyl ketal **13** was obtained by treating a bicarbonate-saturated ethanol solution of **12** with *N*-chlorosuccinimide. Hydrolysis to the cyclobutanone was accomplished by vigorously stirring a two-phase ether/dioxane/water mixture containing the ketal and perchloric acid. Lithium aluminum hydride reduction of **11** gave the endo alcohol in 38% overall yield from *exo*-**5c.**

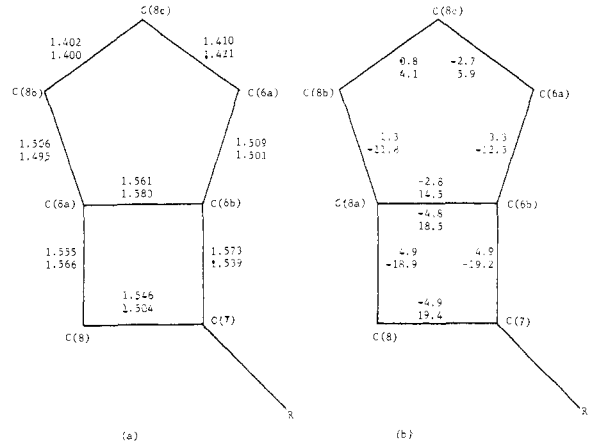


Figure 3. (a) Bond lengths, esd's ±0.005–0.006 Å, and (b) torsion angles, esd's ±0.3–0.4°, in *exo*-**5c** (upper) and *endo*-**5f** (lower).

Four sulfonate esters were prepared from the exo alcohol. These were the mesylate, tosylate, treslate, and triflate (*exo*-**5f–i**). The endo mesylate (*endo*-**5f**) was prepared from the endo alcohol.

Crystal Structures

Single-crystal x-ray analyses were performed on one member of the exo series, *exo*-**5c,** and one member of the endo series, *endo*-**5f.** The conformations and crystal packing arrangements of the exo acid and endo mesylate are illustrated in Figures 1 and 2, respectively; some of the pertinent bond lengths and torsion angles for one enantiomer of each compound are provided in Figure 3. Molecules of the exo acid crystallize as centrosymmetric hydrogen-bonded dimers, O-H···O 2.66 Å, separated by distances which correspond to normal van der Waals type interactions. Within these dimers, the planar carboxyl group is oriented so that the C=O bond lies approximately syn planar [torsion angle C(8)-C(7)-C(9)-O(10) = −2.6°] with respect to the C(7)-C(8) cyclobutane ring bond, a conformation similar to those found for other like compounds.[18] Crystals of the endo mesylate contain discrete molecules separated by van der Waals distances. Thus, in neither case is there any evidence that crystal packing forces exert a significant influence upon the observed solid-state molecular conformations.

The nonplanar cyclobutane rings in *exo*-**5c** and *endo*-**5f** are folded so that their C(7) substituents adopt quasi-equatorial orientations. The differences in the sums of the moduli of the endocyclic torsion angles, $\Sigma|\omega|$, at 19.5° in *exo*-**5c** and 76.0° in *endo*-**5f** reflect the significantly greater degree of puckering which occurs in the cyclobutane ring of the latter. The severe puckering in *endo*-**5f** occurs as a consequence of the outward position of the C-O(mesyl) bond to minimize the combined effects of nonbonded eclipsing interactions between this bond and the C(6a)-C(6b) bond, and between the C(7) substituent and the naphthalene π electrons. Transmission of these conformational differences into the cis-fused five-membered rings and, to a lesser degree, into the naphthalene rings is evident from the endocyclic torsion angles. Thus, in the five-membered ring of *exo*-**5c,** $\Sigma|\omega|$ is only 10.9°, and accordingly the ring atoms deviate by only a small amount from coplanarity. In addition, in the naphthalene ring of this same compound, where the root mean square deviation of the atoms from their least-squares plane is only 0.002 Å, $\Sigma|\omega|$ is 2.8° and not significantly different from the exactly planar value of 0°. In contrast, the

Table I. Product Distribution from Acetolysis of Exo Sulfonates

Reactant	Conditions	Products, % *exo*-**5e**	*cis*-**14b**	*trans*-**14b**	Nonpolar product
exo-**5g**	0.09 M NaOAc, reflux overnight		(5[a])		95[b]
exo-**5h**	0.2 M NaOAc, 105 °C, 5 h	17	17	34	32
exo-**5i**	0.006 M KOAc, 60 °C, 2 h	8	24	50	18

[a] Unseparated mixture of acetates. [b] Identified as vinylacenaphthylene dimer.

Table II. Acetolysis Rate Data

Derivative	Temp, °C	k, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
exo-**5i**	46.2	$8.0 \pm 0.2 \times 10^{-4}$		
	30.3	$1.5 \pm 0.2 \times 10^{-4}$		
	25	7.4×10^{-5} [a]	19.2	−4
	161	5.0×10^{0} [a]		
exo-**5f**	161	2×10^{-3}		
	25	3×10^{-8} [b]		
endo-**5f**	85.3	$2.0 \pm 0.1 \times 10^{-4}$		
	74.8	$6.3 \pm 0.2 \times 10^{-5}$		
	25	5.4×10^{-8} [a]	26.9	+11
	161	2.3×10^{-1} [a]		

[a] Extrapolated value. [b] Calculated from the mesylate/triflate (**1f**/**1i**) ratio of 4×10^{-4} (calculated at 161 °C) applied to the triflate value at 25 °C.

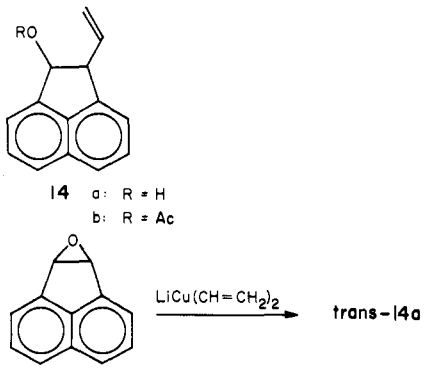
corresponding $\Sigma|\omega|$ for the five-membered ring of *endo*-**5f** is 48.8° and the ring is therefore quite puckered; examination of the individual torsion angles reveals that the ring approximates to a half-chair form in which the C_2 axis passes through C(8c). The root mean square deviation of the naphthalene ring atoms from their least-squares plane at 0.011 Å and the corresponding associated $\Sigma|\omega|$ of 14.8° for the ring torsion angles indicate that the rings are buckled to a small degree.

Bond lengths in the naphthalene rings and at their bonded substituent atoms accord well with those found in naphthalene[19] and other acenaphthene systems.[20] In the cyclobutane rings, however, the mean C–C distances of 1.559 (6) Å in *exo*-**5c** and 1.548 (5) Å in *endo*-**5f** are both increased over the accepted $C(sp^3)$–$C(sp^3)$ bond length[21] (1.537 Å), the greater increase being associated with the smaller degree of ring puckering. Moreover, the bond length increases are more uniformly distributed in *exo*-**5c** (range 1.546–1.573 Å) than in *endo*-**5f** (range 1.504–1.583 Å) where the increases occur in only two bonds, C(8)–C(8a) and C(6b)–C(8a), with the greater increase being in the latter, and the C(7)–C(8) bond at 1.504 Å is actually slightly shorter than normal.

Products and Reactivities

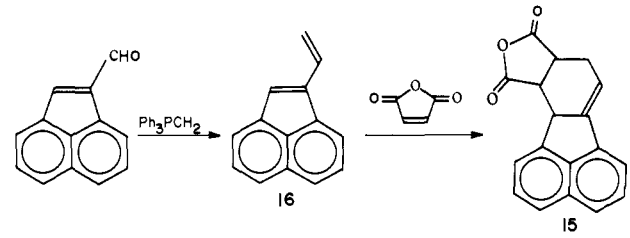
Acetolysis of derivatives of the two epimeric cyclobutanols gave two distinct sets of products, isolated and identified as described below.

From the exo esters, a hydrocarbon fraction and a three-component acetate fraction were obtained.[22] Reduction of the acetates with lithium aluminum hydride gave a mixture of three alcohols which could be separated by TLC. That with the lowest R_f was identical with *exo*-**5a.** The two with higher R_f's appeared to be stereoisomers, since their mass spectra were identical. These alcohols were identified as *cis*-**14a** and



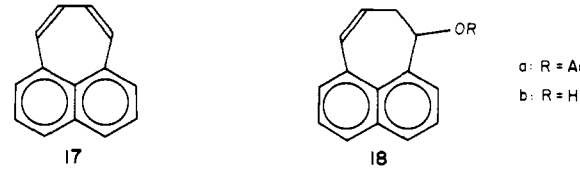
trans-**14a,** chiefly on the basis of spectral evidence, including lanthanide shift reagent experiments. The structure of *trans*-**14a** was confirmed by independent synthesis, via the addition of lithium divinylcuprate to acenaphthylene epoxide.

The hydrocarbon from the acetolysis of the exo tosylate was found to have a molecular weight of 356, corresponding to a dimerized elimination product. When acetolysis of the exo tosylate was carried out in the presence of maleic anhydride, an adduct identical with that formed (**15**) by the addition of maleic anhydride to 1-vinylacenaphthylene (**16**) was obtained.



We presume, therefore, that this hydrocarbon solvolysis product is simply a Diels–Alder dimer of **16.** The distribution of products obtained from each of the exo sulfonate esters is summarized in Table I.

Acetolysis of the endo mesylate (*endo*-**5f**) gave a hydrocarbon identified as pleiadiene (**17**) and a single acetate which



was assigned structure **18a** on the basis of its spectral data and that of the corresponding alcohol, **18b,** obtained by lithium aluminum hydride reduction. (See Experimental Section for further details.)

Kinetic data were obtained conductometrically for the acetolysis of the exo triflate (*exo*-**5i**) and the endo mesylate (*endo*-**5f**). An approximate rate constant was also obtained titrametrically for the exo mesylate (*exo*-**5f**). These results are summarized in Table II.

Discussion

When these kinetic data are compared with those reported for similar systems (see Table III), the low reactivity of the acenaphthylene-fused cyclobutanes is striking. Thus, *endo*-**5f** has a solvolysis rate at least 100 times smaller than that of any other endo mesylates of fused cyclobutanes, and 40 times

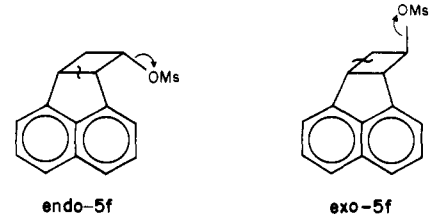


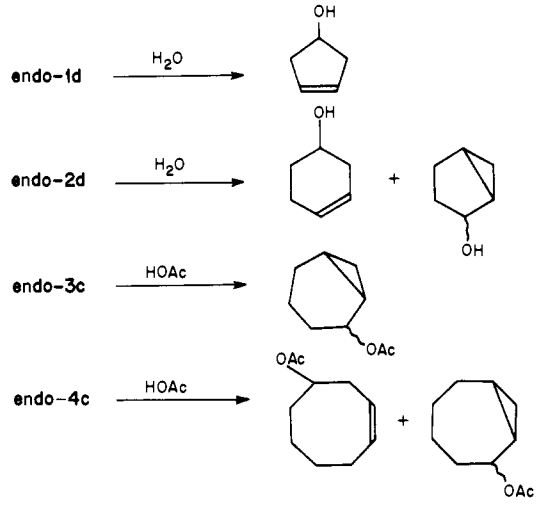
Table III. Relative Rates of Mesylate Acetolysis at 25 °C

Endo ester	k	k_{rel}	Exo ester	k	k_{rel}
5f[a]	5×10^{-8}	2×10^{-2}	**5f**[a]	3×10^{-8}	2×10^{-2}
1b[b]	1×10^{5}	5×10^{10}	**1b**[b]	1×10^{-2}	5×10^{3}
2b[c]	9×10^{0}	4×10^{6}	**2b**[d]	8×10^{-8}	4×10^{-2}
3b[e]	5×10^{-5}	2×10^{1}	**3b**[e]	6×10^{-8}	3×10^{-2}
4b[f]	6×10^{-6}	3×10^{0}	**4b**[f]	6×10^{-5}	3×10^{1}
Cyclobutyl[g]	2×10^{-6}	1			

[a] Present study. [b] Estimated from the rate of solvolysis of the 2,4-dinitrobenzoate in 80% acetone using an approximate factor of 10^7 for the difference in rate between the mesylate in acetic acid and a dinitrobenzoate in 80% acetone (ref 2c). [c] Estimated from the reported (ref 3b) k_{endo}/k_{exo} ratio and the value for *exo*-**2b** (see *d*). [d] Extrapolated from the reported (ref 3a) values for the tosylate at 75 and 90 °C; see note *h*. [e] Extrapolated from the values reported (ref 23) for the tosylates at various temperatures; see note *h*. [f] Extrapolated from the values reported (ref 2b) for the tosylates at various temperatures; see note *h*. [g] Extrapolated from values reported (ref 24) for the tosylate at 70 and 90 °C; see note *h*. [h] The values for tosylates and mesylates were taken to be approximately equal.

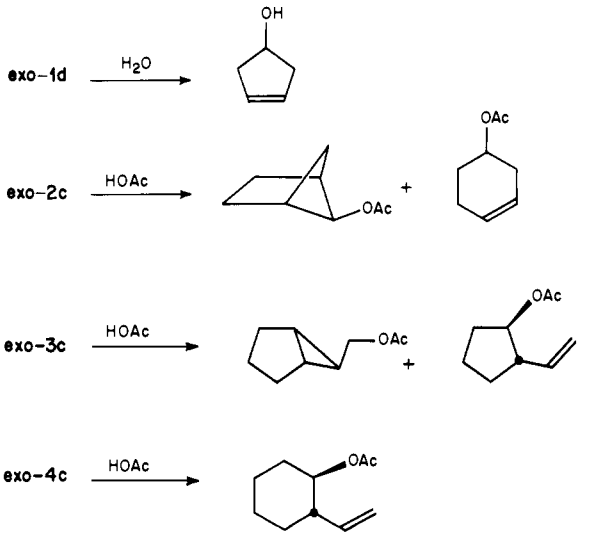
smaller than that of cyclobutyl mesylate itself. The exo mesylate (*exo*-**5f**) is essentially indistinguishable in reactivity from the (highly unreactive) *exo*-bicyclo[3.2.0]hept-6-yl mesylate (*exo*-**3b**), in spite of the fact that *exo*-**5f** contains a β-α-naphthyl substituent trans to its leaving group.

While the reactivities of *exo*- and *endo*-**5f** are very similar (extrapolated to 25 °C), their acetolysis products are totally different. The products obtained from *endo*-**5f** result from cleavage of an "interior" cyclobutane bond, while in the exo isomer it is an "external" cyclobutane bond that cleaves. Similar ring openings occur in related fused systems. Thus, in the endo-substituted compounds shown below, the solvolysis products are derived from cleavage and/or migration of an "interior" cyclobutane bond.



The exo series is less consistent. Of the group of four, only *exo*-**3c** and **4c** give products derived from cleavage of the "external" bond, and even these results differ from those found for *exo*-**5** derivatives in that the products containing vinyl groups are formed with specifically trans stereochemistry.

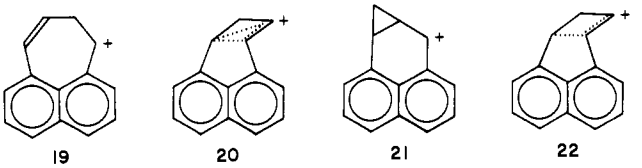
Clearly, it would be of interest to know the precise structures of these cyclobutyl derivatives in order to be able to relate them to the observed reactivities. Electron diffraction analysis of bicyclo[2.1.0]pentane (**1a**) has shown the four-membered ring to be planar within the experimental error.[7] It is likely that derivatives of this ring system also have planar four-membered rings. Interestingly, the cyclobutane rings in bicyclo[2.2.0]-hexane (**2a**) are no longer planar.[8] The torsion angles between the bridging and external C-C bonds were determined to be



8.1 ± 1.3°, and the cyclobutane pucker angle[1] was determined to be 11.5°. Probably exo derivatives of this system have a similar geometry. It is regrettable, however, that an x-ray structure determination has not been carried out on an endo derivative of this system, since the present results suggest that an endo substituent is likely to increase the nonplanarity of the cyclobutane ring. No detailed structural analysis of bicyclo[3.2.0]heptane (**3a**) or an appropriately substituted derivative has been reported.

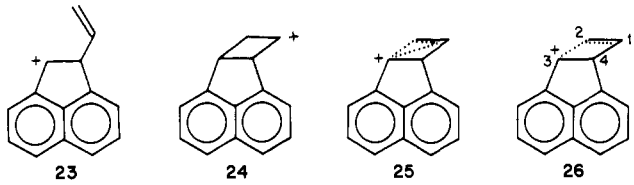
In the present system, the conformations of the cyclobutane rings in both an exo and an endo derivative have been determined. The conformation of the four-membered ring in the exo derivatives (assuming that the structure determined for *exo*-**5c** can be extended to the related sulfonate esters), although not absolutely planar (torsion angles of ~5°), is more nearly planar than that of **2a.** This is not unexpected, since the peri-bridged naphthalene moiety should make the molecule quite rigid. The conformation of the cyclobutane ring of *endo*-**5f,** on the other hand, is surprisingly far from planarity. In fact, it is puckered nearly as much as is an unconstrained cyclobutane. The torsional angles of 19°, compared to 24° in an unconstrained cyclobutane, seem, as noted above, to reflect the distortion of the basic skeleton brought about by nonbonded repulsions involving the endo substituent.

What are plausible mechanisms for the observed acetolyses? The products obtained from *endo*-**5f** seem to be derived from the homoallylic cation **19.** The formation of **19** itself, however,



might involve a variety of pathways. Analogy to related fused cyclobutanes suggests that *endo*-**5f** might ionize first to a delocalized cation such as **20.** Since **20** would be expected to give rise to products corresponding to both **19** and **21,** however, the absence of cyclopropyl carbinyl products, as well as the anomalously slow reaction rate of *endo*-**5f,** makes such an analogy questionable. Ionization of *endo*-**5f** to a less delocalized cationic intermediate such as **22** is a possibility, as is direct ionization to **19.** Determination of the exact nature of the first formed intermediate from *endo*-**5f** must await a more detailed investigation.

The lack of stereospecificity in the formation of the vinyl-substituted products from *exo*-**5** esters is compatible with the intermediacy of the ion **23.** Possible precursor ions of **23** are **24, 25,** and **26.** (Direct ionization to **23** can be ruled out by the



23 24 25 26

formation of *exo*-**5e**, in which the four-membered ring is retained.) It is tempting to suggest that *exo*-**5i** ionizes directly to the classical cyclobutyl cation **24**. But since the solvolysis rates of derivatives of **5** are close to those of the related systems **2** and **3**, and since those systems are proposed[3a] to experience anchimeric assistance, the ionization of *exo*-**5i** would appear to be similarly assisted. This would imply the intermediacy of ion **25** or **26**. As previously mentioned, a planar cyclobutyl geometry is less favorable for orbital overlap than a puckered geometry. The overlap most affected is that between carbon atoms 1 and 3 (see formula **26**). Complete elimination of this 1–3 interaction would result in an ion such as **26**. The near planarity of *exo*-**5** derivatives, as well as the absence of cyclopropyl carbinyl products, disfavors **25**. Ion **26**, therefore, appears to be the most likely possibility for the first-formed intermediate in the solvolysis of *exo*-**5i** and its relatives.

Experimental Section

Melting points, determined either on a Kofler hot stage or Thomas-Hoover capillary apparatus, are not corrected. Infrared spectra were taken on a Perkin-Elmer 257 grating infrared spectrophotometer. Nuclear magnetic resonance spectra were recorded at 60 or 100 MHz on Varian Associates A60A or HA-100 spectrometers, respectively, and are reported in parts per million downfield from internal tetramethylsilane (δ). Ultraviolet spectra were taken on a Cary 14 recording spectrophotometer in 10-mm cells. Mass spectra were determined on an Associated Electrical Industries MS-902 spectrometer.

Gas chromatographic separations were carried out on a Varian Aerograph Model 2100 chromatograph. Analytical thin layer chromatography was performed on Eastman Chromagram plastic sheets, Macherey-Nagel plastic plates, or Analtech glass plates coated with a 250-μm layer of adsorbent. Preparative TLC was performed on Analtech 20 × 20 cm glass plates, having 1000- or 1500-μm layers. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

All reagents are ACS reagent grade unless otherwise noted. Anhydrous ether is from Mallinckrodt. Anhydrous tetrahydrofuran was obtained by distillation from sodium benzophenone ketyl. Hexane is from Fisher, "mixture of isomers". Dimethyl sulfoxide, pyridine, and triethylamine were distilled and stored over 4 Å molecular sieves. *m*-Chloroperoxybenzoic acid is from Aldrich, technical grade (85%). Nitrogen used was "prepurified" grade, dried by passing through a column of silica gel and calcium chloride.

The phrase "dried and concentrated" refers to the procedure of drying the solution (with anhydrous magnesium sulfate unless otherwise stated), filtering the mixture, concentrating the solution on a rotary evaporator, and removing the last traces of solvent under high vacuum (< 1 mm).

7-Cyano-6b,7,8,8a-tetrahydrocyclobut[*a*]acenaphthylene (5b). A mixture of epimers of **5b** was prepared using a modification of the procedure reported by Plummer and Hall.[13] To a water-cooled quartz irradiation vessel equipped with a reflux condenser, nitrogen bubbler, and magnetic stirrer were added 250 mL of freshly distilled methylene bromide (Eastman) and 150 mL of acrylonitrile (Aldrich, "99+%"). After nitrogen had bubbled through the solution for 15 min, a 2.0-g sample of acenaphthylene (Aldrich, Technical) was added and the stirred yellow solution was irradiated with a 450-W Hanovia lamp through a uranium glass filter, while nitrogen was bubbled through. Irradiation was continued until the yellow color had disappeared (about 1 h), at which time another 2.0-g sample of acenaphthylene was added. The procedure was repeated until 8.0 g (0.053 mol) of acenaphthylene had been irradiated (after which time a heavy precipitate of acenaphthylene oligomers is present), and the mixture was concentrated by rotary evaporation. The methylene bromide/acrylonitrile mixture collected from the rotary evaporator was checked for composition (NMR), brought up to the initial ratio and volume by addition of more reagents, and used for another irradiation. The residue from the evaporator was retained for combination with subsequent irradiation residues. The procedure was repeated until a total of 28.0 g (0.184 mol) of acenaphthylene had been irradiated. The combined residues were refluxed with 500 mL of ether for 4 h, the resulting mixture was filtered, and the filtrate was concentrated to give 29.2 g (77%) of **5b** as a yellow, oily solid. The crude product could be purified, with separation of isomers, by column chromatography. Thus, chromatography of about 20 g of crude product on a 4.5 × 77 cm column packed with 700 g of silica gel (Grace grade H, 60–200 mesh) in 15% ether in hexane, eluting first with hexane and then with 15, 30, and finally 70% ether in hexane, gave, in the 30% ether fraction, 12.2 g of *endo*-**5b**, mp 85–86 °C (after recrystallization from hexane/benzene), and in the 70% ether fraction, 3.7 g of *exo*-**5b**. Each isomer had spectral properties (IR, NMR) identical with those previously reported.[13]

exo-6b,7,8,8a-Tetrahydrocyclobut[*a*]acenaphthylene-7-carboxylic Acid (exo-5c). The crude nitrile from the previous reaction was hydrolyzed in two portions. A 15.5-g sample of **5b** was partially dissolved in 250 mL of warm ethylene glycol, then treated with a solution of 15.5 g of potassium hydroxide in 75 mL of water. The resulting mixture was stirred under reflux for 2 h, filtered while hot, cooled, poured into ice, and acidified with concentrated hydrochloric acid. The resulting fine white precipitate was collected on a sintered glass funnel, washed with water, and partially dried by suction. The remaining 13.7 g of **5b** was treated analogously with 230 mL of ethylene glycol, 13.7 g of potassium hydroxide, and 70 mL of water. The two batches of partially dried precipitate were combined and recrystallized once from glacial acetic acid, to give 21.2 g of brown crystals, mp 191–196 °C; yield from acenaphthylene 51%. The same procedure carried out on 5.5 g of purified *exo*-**5b** gave 5.6 g (91%) of acid, *exo*-**5c**, mp 188–194 °C. Further recrystallizations provided colorless crystals: mp 199.5–200.5 °C; IR ($CHCl_3$) inter alia 3200–2400, 1705, 1607 cm^{-1}; NMR ($CDCl_3$) δ 7.53 (m, 6), 4.44 (m, 2), 3.10 (m, 2), 2.16 (m, 1), OH not observed; MS *m/e* 224 (molecular ion). Anal. ($C_{15}H_{12}O_2$) C, H.

exo-7-Acetyl-6b,7,8,8a-tetrahydrocyclobut[*a*]acenaphthylene (exo-5d). To a solution of 5.25 g (23 mmol) of *exo*-**5c** in 150 mL of anhydrous ether was added, dropwise with stirring, 50 mmol of methyllithium in ether. The reactants were stirred for 1 h and then refluxed for an additional 1 h. The reaction mixture was added slowly in small portions with stirring to saturated aqueous ammonium chloride (800 mL). The organic layer was separated and the aqueous phase extracted with ether. The organic extracts were combined, washed once with saturated aqueous ammonium chloride and twice with water, dried, and concentrated, and the residue was sublimed (132 °C, 0.1 mm) to give 3.30 g (65%) of the methyl ketone. Recrystallization from hexane gave a white solid: mp 80–82 °C; IR (CCl_4) inter alia 3050, 2945, 1710, 1601, 1561 cm^{-1}; NMR (CCl_4) δ 7.42 (m, 6), 4.15 (m, 2), 2.92 (m, 2), 2.11 (s, 3), 2.02 (m, 2); MS *m/e* 222 (molecular ion). Anal. ($C_{16}H_{15}O$) C, H.

exo-7-Acetoxy-6b,7,8,8a-tetrahydrocyclobut[*a*]acenaphthylene (exo-5e). Baeyer–Villiger oxidation of 5.98 g (27 mmol) of *exo*-**5d** with 10.5 g (61 mmol) of *m*-chloroperoxybenzoic acid in chloroform (180 mL) was carried out at room temperature. After 16 h, the reaction mixture was filtered and the filtrate concentrated in vacuo. The residue was dissolved in ether and washed three times with saturated aqueous sodium bicarbonate. The aqueous phases were combined and extracted with ether. The combined organic extracts were washed with water and brine and dried over anhydrous sodium sulfate. After the ethereal solution was concentrated, the product was purified by column chromatography (Florisil, F101, 100–200 mesh, 170 g). Gradient elution with hexane (500 mL), 5% ether in hexane (1300 mL), 12% ether in hexane (500 mL), and 20% ether in hexane (250 mL) gave 2.01 g (41% based on recovered ketone) of *exo*-**5e** in the first 1700 mL of eluent. The unreacted ketone (1.39 g) was recovered in the last 850 mL of eluent. The ester was recrystallized from pentane, giving a white solid: mp 91.0–91.5 °C; IR (CCl_4) inter alia 1743, 1228, 1052 cm^{-1}; NMR (CCl_4) δ 7.41 (m, 6), 4.66 (m, 1), 4.18 (m, 2), 2.56 (m, 2), 2.08 (s, 3); MS *m/e* 238 (molecular ion). Anal. ($C_{16}H_{14}O_2$) C, H.

6b,7,8,8a-Tetrahydrocyclobut[*a*]acenaphthylene-7,8-dicarboxylic Anhydride (7). The anhydride (mp 230–231 °C) was prepared in 60% yield by a modification of the method of Shields et al.,[14] utilizing an 8-h irradiation with a 450-W Hanovia lamp through a uranium glass filter.

6b,8a-Dihydrocyclobut[*a*]acenaphthylene (6). A. From Carboxylic

Acid exo-5c. A 10.0-g (44.8 mmol) sample of *exo*-**5c** (mp 191–196 °C) was dissolved in 250 mL of benzene by addition of 25 mL of pyridine, and the solution was purged with nitrogen. Then a 1.00-g (5.0 mmol) sample of cupric acetate was added, followed by 40.3 g (91 mmol) of dried lead tetraacetate (Alfa, 90% $Pb(OAc)_4$/10% AcOH, which had been dried over potassium hydroxide at 0.1 mm overnight), and the mixture heated on an oil bath. When the temperature of the mixture reached about 55 °C, gas evolution became vigorous, the temperature jumped to about 70 °C, and heating was discontinued until gas evolution had subsided. Heating was then resumed and the mixture was refluxed for 45 min. Then 25 mL of ethylene glycol was added and the mixture was washed with water, 10% nitric acid, water, dilute sodium hydroxide, water, and brine, dried, and concentrated to a small volume. Silica gel (10 g) was added, the mixture was evaporated to dryness, and the residue was placed on a silica gel column (150 g, packed in hexane) and eluted with hexane. A total of 2.76 g (35%) of solid was collected in four 1000-mL fractions. Recrystallization from hexane gave colorless crystals, identical in every respect with the cyclobutene 6 previously obtained in these laboratories.[12]

Elution of the silica gel column with benzene then gave a dark, oily residue, which showed one major peak (85%) and several minor peaks by GC (6% OV-1 on Gas Chrom Q, 6 ft × 2 mm, temperature programmed from 100 to 240 °C at 8 °C/min). The major component, **10a,** obtained by preparative GC, was a yellow oil: IR (neat) 3060, 2940, 1756, 1594, 1365, 1204, 1136 cm^{-1}; NMR ($CDCl_3$) δ 7.42 (m, 5), 6.33 (s, 2), 4.67 (m, 2), 2.40 (s, 3); MS *m/e* 236, 194, 168, 165.

A solution of 240 mg of the dark mixture in 15 mL of anhydrous ether was reduced, in standard fashion, using a mixture of 120 mg (3.2 mmol) of lithium aluminum hydride in 15 mL of ether, to give 104 mg (53%) of the corresponding phenol (**10b**), an oil with the following spectral properties: IR (CCl_4) 3620, 3340 (br), 3050, 2950, 1590, 1500, 1425, 1355, 1275, 1215, 1170, 1135, 1115, 1035, 985 cm^{-1}; NMR ($CDCl_3$) 7.80 (d, J = 7 Hz, of d, J = 2 Hz, 1), 7.43 (d, J = 7 Hz, of d, J = 6 Hz, 1), 7.28 (d, J = 6 Hz, of d, J = 2 Hz, 1), 7.22 (d, J = 7.5 Hz, 1), 6.73 (d, J = 7.5 Hz, 1), 6.32 (s, 2), 5.43 (br s, 1), 4.62 (m, 2); UV (50% aqueous methanol) λ_{max} (log ϵ) 218 (4.28), 235 (4.20), 306 (3.65), 330 (3.55); (0.2 N NaOH in 50% aqueous methanol) λ_{max} (log ϵ) 251 (4.13), 343 (3.76).

The ring system in the acetate and phenol is established by the similarity of the upfield NMR absorptions to those of compound **6.** The olefinic protons absorb at δ 6.32 in **6,** 6.33 in **10a,** and 6.32 in **10b,** and the naphthylic cyclobutyl protons absorb at δ 4.61 in **6,** 4.67 in **10a,** and 4.62 in **10b.** The position of the hydroxyl (and corresponding acetoxy) group was determined as follows. They must be on the aromatic ring, since all the nonaromatic absorptions of **6** are still present in **10,** while there are only five aromatic protons in **10** (and **10b** is acidic). The position on the aromatic ring is suggested by the similarity of the aromatic portion of the NMR spectrum of **10b** to that of α-naphthol, and is confirmed by comparison of the change in UV absorption of **10b,** upon addition of base, to that of α- and β-naphthol[25] upon similar treatment. The change exactly mimics that of the α isomer, not of the β.

B. From Anhydride 7. 1. Following the procedure of Shields et al.,[14] an 18.4-g (73.6 mmol) sample of **7** gave 85 mg (0.7%) of **6.**

2. Using the same procedure, but with the addition of 10 mol % cupric acetate to the reaction mixture, a 5% yield of **6** was obtained.

C. From Diacid 8. 1. Lead tetraacetate oxidation of a 9.50-g (35.5 mmol) sample of diacid **8**[14] according to the described procedure[14] gave, after conventional workup, 1.3 g of a brown solid. Chromatography of this residue on silica gel (60 g, packed in hexane) with hexane elution gave 78 mg (1.2%) of **6.**

2. A 6.14-g (23.0 mmol) sample of **8** was dissolved in 160 mL of benzene by addition of 17 mL of dry pyridine. The cooled (ice water bath) solution was treated with 15.2 g (34.5 mmol) of lead tetraacetate and then allowed to warm to room temperature. The resulting precipitate was collected by filtration and dried to give 15.4 g of red-yellow powder. This powder was added to 120 mL of dry dimethyl sulfoxide containing 0.46 g (2.3 mmol) of cupric acetate, and the solution warmed briefly under a heat lamp. After 9 h of stirring with intermittent warming, the mixture was treated with 300 mL of benzene and 150 mL of water, and the benzene layer decanted. Washing the benzene solution with water, 5% hydrochloric acid, water, dilute sodium bicarbonate, water, and brine, followed by drying and concentration, gave 1.04 g of brown residue. Elution through a silica gel column with 1:1 hexane/benzene gave 290 mg (7.2%) of **6.**

Further elution with benzene gave 330 mg of solid which was recrystallized from hexane to give a colorless, crystalline acetate: mp 92–93 °C; IR 3060, 2940, 1740, 1495, 1420, 1370, 1245, 1160, 1040, 800, 780 cm^{-1}; NMR ($CDCl_3$) δ 7.60 (m, 6), 6.67 (d, J = 2.5 Hz, 1), 6.42 (d, J = 2.5 Hz, 1), 4.67 (br s, 1), 2.11 (s, 3); MS *m/e* 236, 194, 176, 165.

This acetate was reduced with lithium aluminum hydride to give 57 mg (87%) of colorless oil: IR (CCl_4) 3610, 3330 (br), 3060, 2950, 1690, 1490, 1270, 1190, 1170, 1070 cm^{-1}; NMR ($CDCl_3$) δ 7.50 (m, 6), 6.33 (s, 2, split into two doublets, each with J = 2 Hz, upon addition of 6 mg of $Eu(fod)_3$), 4.27 (br s, 1), 2.98 (br s, 1) (this signal exhibited the greatest change in chemical shift upon addition of $Eu(fod)_3$).

These compounds were assigned structures **9a** and **9b,** respectively, based on the following reasoning. The retention of the original ring system is suggested by the similarity of the NMR spectra of **9a** and **9b** to that of cyclobutene **6.** Thus, the position of the olefinic absorptions (average δ 6.55 for **9a,** 6.33 for **9b**) compares favorably with the value of 6.32 for **6,** with the downfield shift in **9a** due to the electron-withdrawing acetoxy group. Similarly, the absorption of the naphthylic cyclobutene protons in **6** (δ 4.61) compare favorably with the absorptions at δ 4.67 in **9a** and 4.27 in **9b.** The position of the oxygen substitution is established by the absence of one of the naphthylic cyclobutyl hydrogens.

exo-7-Hydroxy-6b,7,8,8a-tetrahydrocyclobut[*a*]acenaphthylene (exo-5a). A. By Reduction of exo-5e. To a stirred slurry of 1.46 g (38 mmol) of lithium aluminum hydride in anhydrous ether (100 mL) was added, dropwise, a solution of 2.75 g (11 mmol) of *exo*-**5e** in ether (90 mL). After refluxing for 1 h and stirring at room temperature for 9 h, the reaction was quenched by adding successive portions of water (1.5 mL), 15% sodium hydroxide (1.5 mL), and water (4.5 mL). The organic layer was separated and the aqueous portion extracted with ether. The combined organic extracts were dried and concentrated to give 2.11 g (93%) of crystalline material which was recrystallized from hexane, giving colorless needles: mp 113.5–114.5 °C; IR (CCl_4) 3608, 3066, 2969, 1608, 1361, 1073 cm^{-1}; NMR (CCl_4) 7.40 (m, 6), 4.06 (m, 3), 2.45 (m, 3); MS *m/e* 196 (molecular ion). Anal. ($C_{14}H_{12}O$) C, H.

B. By Hydroboration/Oxidation of 6. A 0.178-g (1.00 mmol) sample of cyclobutene **6** was dissolved in 15 mL of anhydrous tetrahydrofuran, cooled in an ice bath, and treated with 1.0 mL of 1.1 M diborane in tetrahydrofuran. After stirring at 0 °C for 0.5 h and room temperature for 1 h, the solution was treated with 5 drops of water, 0.8 mL of 3 N sodium hydroxide, and 0.8 mL of 30% hydrogen peroxide, and stirred on an oil bath (35–45 °C) for 1.3 h. The mixture was then diluted to 75 mL with water and extracted with four 50-mL portions of ether. The ether extract was washed with water and brine, dried, and concentrated to give 0.193 g (99%) of light yellow oil which crystallized on standing. Recrystallization from hexane gave colorless crystals, identical in all respects with the *exo*-**5a** previously obtained.

6b,7,8,8a-Tetrahydrocyclobut[*a*]acenaphthylen-7-one (11). A. By Jones Oxidation of exo-5a. To a cooled (ice–salt bath) solution of 49 mg (0.25 mmol) of *exo*-**5a** in acetone (5 mL) was added, dropwise with stirring, chromic acid solution (freshly prepared from 3.5 g of chromium trioxide, 25 mL of water, and 3mL of concentrated sulfuric acid), until the red color of the reagent persisted. After stirring for 2 h, the mixture was diluted with water and extracted with ether. The ether extract was washed with dilute sodium bicarbonate and water, dried and concentrated to give 21 mg of oily residue. Purification by TLC (alumina, 9:1 pentane/ether development) and recrystallization from pentane gave colorless crystals of **11:** mp 80–81 °C; IR (CCl_4) 3060, 2950, 1785, 1600, 1415, 1365, 1260, 1160, 1055 cm^{-1}; NMR (CCl_4) δ 7.40 (m, 6), 5.03 (m, 1), 4.05 (m, 1), 3.47 (d, J = 18 Hz, of d, J = 9 Hz, of d, J = 3 Hz, 1), 2.67 (d, J = 18 Hz, of d, J = 4 Hz, of d, J = 3 Hz, 1); MS *m/e* (rel abundance) 194 (9), 165 (29), 152 (100).

B. From exo-5c. Following the general procedure of Trost and Tamaru,[17] a 7.0-mL sample of freshly distilled diisopropylamine was added to 140 mL of anhydrous tetrahydrofuran in a 200-mL flask equipped with nitrogen inlet and solid addition apparatus. The solid addition apparatus contained 5.65 g (26.4 mmol) of *exo*-**5c** (mp 191–196 °C). The amine solution was cooled to −15 °C (ice–salt bath) and treated with 33.5 mL of 1.6 M *n*-butyllithium (53.5 mmol). After this mixture was stirred for 30 min, the carboxylic acid was

added, and the resulting mixture was allowed to come slowly to room temperature and stirred under nitrogen for 12 h. The green solution was then cooled to 0 °C and added to a solution of 3.5 mL of dimethyl disulfide in 100 mL of anhydrous tetrahydrofuran at 0 °C, and stirred under nitrogen for 1.5 h at 0 °C and 9 h at room temperature (until the green color had dissipated). The solution was then diluted with 500 mL of 2% potassium hydroxide, washed with chloroform, poured on ice, and acidified with concentrated hydrochloric acid. The resulting precipitate was extracted into ether, which was then washed with 5% hydrochloric acid, water, and brine, dried, and concentrated to give 7.0 g of **12** as an off-white solid. The NMR spectrum (Me_2SO-d_6) of this material showed sharp singlets at δ 2.28 and 1.79 ($-SCH_3$) in the ratio 3:1.

The 7.0 g of sulfenylated acid, without further purification, was dissolved in 500 mL of absolute ethanol which contained an excess of sodium bicarbonate, and treated with 5.0 g of *N*-chlorosuccinimide. Gas evolution ceased after about 45 min, and after stirring for an additional 15 min the mixture was diluted with 300 mL of hexane and washed with water. The aqueous wash was extracted with hexane, and the organic phases were combined and washed with 10% potassium hydroxide, water, 5% hydrochloric acid, water, and brine, dried, and concentrated to give 4.3 g of diethyl ketal **13** as a yellow oil. The NMR spectrum (CCl_4) of the crude product showed ethoxy CH_3 triplets at δ 1.26 and 0.82, integrating to 80% of the aromatic region absorption.

The 4.3 g of crude ketal was dissolved in 100 mL of 1:1 ether/dioxane and treated with 100 mL of 0.5 N perchloric acid. After 5 h of vigorous stirring some ketal was still present (TLC), so 5 mL of 70% perchloric acid was added, and the mixture was stirred for an additional 2 h. The mixture was diluted with ether, then washed with water, saturated sodium bicarbonate, water, and brine, dried, and concentrated to give 3.6 g of brown oil which solidified on standing. Recrystallization from hexane of a portion of this material gave colorless crystals, identical in all respects with the material obtained from Jones oxidation of *exo*-**5a**.

***endo*-7-Hydroxy-6b,7,8,8a-tetrahydrocyclobut[*a*]acenaphthylene (*endo*-5a).** The 3.5 g of crude ketone **11** obtained from the previous sequence was dissolved in 150 mL of anhydrous ether and added, dropwise with stirring, to 250 mL of ether containing 0.72 g of lithium aluminum hydride. After addition was complete the mixture was refluxed for 1 h, then treated with 0.72 mL of water (dropwise), 0.72 mL of 15% sodium hydroxide, and 2.16 mL of water, filtered, and concentrated to give 3.2 of oily, orange solid. Recrystallization from hexane gave 1.90 g (38% from *exo*-**5c**) of yellow crystals, mp 106–109 °C. Further recrystallizations from hexane gave colorless crystals: mp 111–112 °C; IR (CCl_4) 3565 (sh), 3040, 2960, 1600, 1490, 1400, 1360, 1255, 1130, 1090 cm^{-1}; NMR ($CDCl_3$) δ 7.40 (m, 6), 4.52 (m, 2), 3.65 (m, 1), 2.92 (m, 1), 1.85 (s, 1), 1.45 (m, 1); MS indistinguishable from that of *exo*-**5a**. Anal. ($C_{14}H_{12}O$) C, H.

***endo*-7,6b,7,8,8a-Tetrahydrocyclobut[*a*]acenaphthylenyl Methanesulfonate (*endo*-5f).** After a 0.098-g (0.50 mmol) sample of *endo*-**5a** was stirred with 28 mg (0.60 mmol) of 50% sodium hydride in 20 mL of anhydrous ether for 20 min, bubbling had subsided. The mixture was cooled to 0 °C and treated with 0.14 mL of triethylamine and 50 μL (72 mg, 0.53 mmol) of methanesulfonyl chloride. After stirring at 0 °C for 2.5 h and room temperature for 1.5 h, the mixture was diluted to about 50 mL with ether, washed with water, 5% hydrochloric acid, water, and brine (all chilled), dried over sodium sulfate/potassium carbonate, filtered, and concentrated to give 149 mg of nearly colorless oil. Crystallization from hexane gave colorless needles: mp 74–75.5 °C; IR (CCl_4) 3100, 3030, 2990, 1600, 1370, 1350, 1180, 1060, 970, 910, 825 cm^{-1}; NMR ($CDCl_3$) δ 7.40 (m, 6), 5.47 (q, J = 7.5 Hz, 1), 4.57 (br t, J = 7 Hz, 1), 3.10 (m, 1), 2.77 (s, 3), 1.98 (m, 1).

***exo*-7-6b,7,8,8a-Tetrahydrocyclobut[*a*]acenaphthylenyl Methanesulfonate (*exo*-5f).** Analogous treatment of 0.196 g (1.00 mmol) of *exo*-**5a** with 96 mg of sodium hydride, followed by 0.25 mL of triethylamine and 0.15 mL (0.22 g, 1.5 mmol) of methanesulfonyl chloride at 0 °C, gave, after stirring at 0 °C and workup, 0.290 g of yellow oil. Preparative TLC (silica gel, ether development) afforded 200 mg of colorless oil: IR (CCl_4) 3080, 2940, 1610, 1380, 1360, 1185, 960, 890 cm^{-1}; NMR ($CDCl_3$) δ 7.48 (m, 6), 4.45 (m, 3), 2.97 (s, 3), 2.72 (m, 2).

***exo*-7-6b,7,8,8a-Tetrahydrocyclobut[*a*]acenaphthylenyl Trifluoromethanesulfonate (*exo*-5i).** Analogous treatment of 98 mg (0.50 mmol) of *exo*-**5a** with 28 mg of sodium hydride, followed by cooling to −50 °C and treatment with 0.21 mL of triethylamine and 0.20 mL (0.34 g, 1.3 mmol) of trifluoromethanesulfonic anhydride, gave, after stirring for 30 min at −50 °C and workup, 161 mg of nearly colorless oil, which slowly turned dark green on standing at −20 °C. The oil showed the following spectra: IR (CCl_4) 3050, 2960, 1605, 1420, 1200, 1145, 965, 900 cm^{-1}; NMR ($CDCl_3$) δ 7.40 (m, 6), 4.92 (m, 1), 4.28 (m, 2), 2.97 (m, 1), 2.42 (m, 1).

***exo*-7-6b,7,8,8a-Tetrahydrocyclobut[*a*]acenaphthylenyl *p*-Toluenesulfonate (*exo*-5g).** Treatment of 100 mg (0.51 mmol) of *exo*-**5a** in 2 mL of pyridine with 500 mg of *p*-toluenesulfonyl chloride at 4 °C for 3 days, followed by dilution with water, extraction into ether, washing with 15% hydrochloric acid, water, and brine, drying over sodium sulfate/potassium carbonate, and concentrating, gave 330 mg of yellow, oily tosylate, contaminated with tosyl chloride. Recrystallization from hexane gave 124 mg of white crystals: mp 94.5–96.5 °C; IR (CCl_4) 3060, 3000, 2960, 1610, 1498, 1380, 1190, 1189, 1100, 1020, 980, 890 cm^{-1}. Anal. Calcd for $C_{21}H_{18}O_3S$: C, 71.97; H, 5.18. Found: C, 71.83; H, 4.97.

***exo*-7-6b,7,8,8a-Tetrahydrocyclobut[*a*]acenaphthylenyl 2,2,2-Trifluoroethanesulfonate (*exo*-5h).** A 0.52-g sample of *exo*-**5a** was converted into an oily tresylate according to the published procedure.[26] Filtration of a 15% ether/hexane solution of the oil through a short Florisil column and concentration of the eluent gave a solid which was recrystallized from 10% benzene/hexane to give fine white crystals: mp 87.0–88.5 °C; IR (CCl_4) 3090, 2990, 1400, 1330, 1270, 1260, 1185, 1135, 1085, 970, 890 cm^{-1}; NMR ($CDCl_3$) δ 7.45 (m, 6), 4.61 (m, 3), 3.80 (q, J = 9 Hz, 2), 2.79 (m, 2).

Acetolysis Kinetics. A stock solution of potassium acetate was prepared by dissolving 0.294 g (3.0 mmol) of anhydrous potassium acetate in enough dry acetic acid (freshly distilled from acetic anhydride containing a small amount of *p*-toluenesulfonic acid) to make 500 mL of solution.

Conductometric determinations were performed on a continuous recording apparatus constructed by Drs. C. F. Wilcox and R. Winans. A conductivity cell, cell constant $\simeq$0.4 cm^{-1}, volume $\simeq$9 mL, having a tightly sealable metal screw cap assembly with Teflon liner, was utilized. Duplicate runs were made at each of two temperatures. Temperature was controlled to within at least ±0.05 °C. The procedure consisted of making up 25 mL of an approximately 5.0 mM solution of the ester in the acetic acid/potassium acetate solution at 10–20 °C, filling the prerinsed conductivity cell with the solution, placing the cell in a constant-temperature bath, and recording the conductivity as a function of time. About 25 values of conductance (c) and time were taken from each recording for plots in ln ($C - C_\infty$) vs. time. Straight lines were obtained for at least 3 half-lives. The slopes of these lines (rate constants) are presented in Table II.

The tritrimetric determination was performed by the sealed ampule method, at 161 ± 1 °C, titrating with 6.13 mM perchloric acid in acetic acid (made from a measured volume of 70% $HClO_4$, the concentration of which had been determined by titrating against standard sodium hydroxide), using crystal violet (in acetic acid) as the indicator. Ampules were filled at room temperature from a 4.6 mM solution of mesylate (*exo*-**5f**) in the acetic acid/potassium acetate solution. Owing to the unexpected speed of the reaction, only four points were obtained which were within titration error of completion of the reaction. These points (log ($mL_t - mL_\infty$) vs. time, where mL_t is volume of titrant required for neutralization at time t), however, were on a good straight line, having the slope given in Table II.

Acetolysis of exo-5g. A 114-mg (0.35 mmol) sample of *exo*-**5g** was solvolyzed according to the conditions indicated in Table I. The resulting mixture was diluted with water and neutralized with sodium bicarbonate, then extracted with ether. The ether extract was washed with water, dried, and concentrated to give a yellow oil. Preparative TLC (alumina, 9:1 pentane/ether development) of the product yielded 2 mg of a mixture of acetates, not further characterized, and 34 mg of orange-yellow oil: IR (CCl_4) 3160, 2075, 2960, 1695, 1500, 1485, 1050 cm^{-1}; MS m/e 356 (molecular ion).

Identical treatment of a 21-mg sample of *exo*-**5g** with an acetic acid solution containing 14 mg of maleic anhydride yielded 2 mg of a crystalline product after recrystallization from benzene. The compound had mp 234–235 °C; IR (KBr) inter alia 1845, 1785 cm^{-1}; MS m/e (rel abundance) 276 (70), 203 (100), 178 (70), 102 (30). It was identical (spectral data, mixture melting point) with the adduct of maleic anhydride and 1-vinylacenaphthylene (vide infra).

Acetolysis of exo-5h. A 0.72-g (2.1 mmol) sample of *exo*-**5h** was solvolyzed according to the conditions indicated in Table I and worked

up by dilution with water, extraction into petroleum ether, and washing the organic extract with 5% sodium bicarbonate, water, and brine, followed by drying and concentrating the solution. Preparative TLC (silica gel, benzene development) of the product gave 0.35 g of an oil (R_f 0.85) having three acetoxy methyl resonances (NMR) and characteristic acetate IR bands (1743, 1223, and 1052 cm^{-1}), as well as 0.15 g of a nonpolar yellow oil (R_f 1.0) which was composed of five components (GC, 6 ft × 1/8 in. 10% OV-1 on Gas Chrom Q). Although one of the nonpolar components comprised 60% of this fraction, its constitution was not further examined. The acetate mixture was reduced with lithium aluminum hydride and the resulting mixture of alcohols was separated by preparative TLC (silica gel, quadruple development with methylene chloride). Three alcohols, R_f's 0.46, 0.75, and 0.87, were obtained, in the ratio 1:2:1. (Acetylation of a mixture of the alcohols with acetic anhydride in pyridine gave a mixture of acetates identical in GC behavior with the original acetate mixture.)

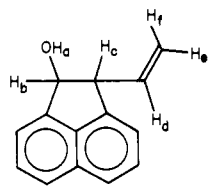
The lowest R_f alcohol was recrystallized from hexane and sublimed (110 °C; 0.3 mm) to give a white solid, mp 111–112 °C, which had IR and NMR spectra identical with those of *exo*-**5a**.

The alcohol with R_f 0.75 was sublimed (110 °C, 0.2 mm) to give a white solid: mp 48–50 °C; IR (CCl_4) inter alia 3666–3100, 3550, 1635, 1602, 910 cm^{-1}; NMR ($CDCl_3$) δ 7.37 (m, 6), 5.88 (m, 1), 5.14 (m, 3), 3.86 (br d, J = 8 Hz, 1), 2.91 (br s, 1); MS m/e 196 (molecular ion). Anal. ($C_{14}H_{12}O$) C, H.

The results of a europium shift reagent experiment are given in Table IV (see paragraph at end of paper regarding Supplementary Material), along with chemical shift assignments. This alcohol was identical in all respects with *trans*-1-hydroxy-2-vinylacenaphthene (*trans*-**14a**, vide infra).

The least polar alcohol was recrystallized from hexane to give white needles: mp 117.5–118.5 °C; IR (CCl_4) inter alia 3555, 1638, 1604, 913 cm^{-1}; NMR ($CDCl_3$) δ 7.45 (m, 6), 6.02 (m, 1), 5.61 (br t, J = 7 Hz, 1), 5.28 (m, 2), 4.32 (t, J = 8 Hz, 1), 1.95 (br d, J = Hz, 1); MS m/e 196 (molecular ion). Anal. ($C_{14}H_{12}O$) C, H.

The mass spectrum of this alcohol was indistinguishable from that of *trans*-**14a**, suggesting the stereoisomeric structure *cis*-**14a**. The most notable difference between the IR spectrum of this alcohol and that of *trans*-**14a** is the absence of the broad hydrogen bonded hydroxyl absorption in the cis isomer. Both the lower polarity and the absence of hydrogen bonding are consistent with the assigned stereochemistry. The results of a europium shift reagent study, given in Chart I, and analysis of coupling constants of the nonaromatic protons led to the assignments shown.



14a

Chart I. Chemical Shift and Europium Shift Data for **14a**

Proton	Chemical shifts, δ		$\Delta\nu$, Hz[a]	
	trans-**14a**	*cis*-**14a**	trans	cis
a	2.91	1.95	238	450
b	5.26	5.61	59	92
c	3.86	4.32	43	23
d	5.88	6.02	5	60
e	5.08	5.28		
f	5.18			

[a] Shift in signal after addition of 15-mg portions of $Eu(fod)_3$.

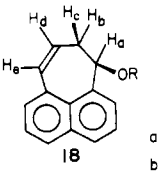
The hydroxyl proton was assigned to the δ 1.95 resonance on the basis of lack of coupling (after dilution) and its large pseudocontact shift. The methine proton α to the OH, H_b, resonates at the expected frequency,[27] and shows the second largest pseudocontact shift. In dilute solution it is coupled only to H_c, with a coupling constant (8 Hz) appropriate for H_b and H_c being cis. H_c is split by both H_b and H_d to the same extent (8 Hz). H_d, however, would be split by three other signals, as is the signal at δ 6.02, with coupling constants of 8 (c, d), 10 (d, e), and 16 Hz (d, f). In addition to the substantial $J_{b,c}$, the large pseudocontact shift of H_d of this alcohol, as compared with that in *trans*-**14a**, further supports the assignment of cis geometry. After addition of 30 mg of $Eu(fod)_3$, the portion of the spectrum showing the H_e and H_f absorptions is simplified and easily interpreted. H_e, a doublet (J = 2 Hz, geminal olefinic methylene) of doublets (J = 10 Hz, cis olefinic), is 20 Hz upfield from H_f. The olefinic proton H_f is a doublet (J = 16 Hz, trans olefinic) with fine splitting, which can be attributed to $J_{e,f}$ = 2 Hz and long-range coupling with H_c.

Acetolysis of exo-5i. A 0.145-g (0.44 mmol) sample of *exo*-**5i** was solvolyzed according to the conditions indicated in Table I and worked up as described for the treslate acetolysis. Preparative TLC (silica gel, benzene development) of the product gave two fractions. The less polar fraction consisted of 13 mg of yellow oil, which was not further characterized. The more polar fraction consisted of 59 mg of a mixture of three acetates (three acetoxy methyl signals in the NMR) which had GC behavior identical with that of acetates from *exo*-**5h**. Reduction of the acetate fraction (vide supra) gave 44 mg of a mixture of alcohols, which were separated into three components. The first component consisted of 4 mg of oily, white solid, which had an IR spectrum and TLC behavior indisinguishable from those of *exo*-**5a**. The second component consisted of 27 mg of colorless oil which had IR and NMR spectra and TLC behavior identical with those of *trans*-**14a**. The last component consisted of 13 mg of white solid, mp 118–120 °C, which had IR and NMR spectra identical with those of the *cis*-**14a** obtained from acetolysis of *exo*-**5h**.

Acetolysis of endo-5f. A 130-mg (0.47 mmol) sample of *endo*-**5f** was solvolyzed according to the conditions indicated in Table I, and worked up as described for the treslate acetolysis. Preparative TLC (silica gel, benzene development) of the product gave two fractions. The less polar fraction consisted of 1 mg of red oil, having an IR spectrum and TLC properties identical with those of an authentic sample of pleiadiene.[12] The second fraction (R_f 0.3) consisted of 51 mg of colorless oil: IR (CCl_4) 3080, 3060, 2960, 1735, 1590, 1510, 1430, 1370, 1245, 1015, 945 cm^{-1}; NMR (CCl_4) δ 7.50 (m, 6), 6.68 (br d, J = 12 Hz, 1), 6.25 (d, J = 6 Hz, of d, J = 2.5 Hz, 1), 5.83 (overlapping d, J = 12 Hz, of q, J = 6 Hz, 1), 3.05 (d, J = 16 Hz, of t, J = 6 Hz, 1), 2.67 (br d, J = 16 Hz, 1), 1.95 (s, 3); UV (cyclohexane) λ_{max} (log ϵ) 312 nm (4.0); MS m/e 238.1005 (calcd for $C_{16}H_{14}O_2$, 238.0993).

Treatment of a 30-mg sample of this acetate with 15 mg of lithium aluminum hydride gave a yellow oil: IR (CCl_4) 3610 (br), 3570, 3060, 3030, 2930, 1590, 1510, 1430, 1405, 1385, 1230, 1195, 1170, 1060, 925 cm^{-1}; NMR ($CDCl_3$) δ 7.55 (m, 6), 6.82 (d, J = 12 Hz, of d, J = 2 Hz, 1), 5.92 (d, J = 12 Hz, of br q, J = 6.5 Hz, 1), 5.17 (m, 1), 2.88 (m, 2, which upon addition of 8.5 mg of $Eu(fod)_3$ separated into two separate signals, a d, J = 16 Hz, of t, J = 6.5 Hz, and a br d, J = 16 Hz), 2.46 (d, J = 9 Hz, 1, exchangeable with D_2O).

These two compounds were assigned structures **18a** and **18b**, respectively, based on the following reasoning. In the NMR, two olefinic protons could be recognized in each of the compounds (δ 6.68 and 5.83 in **18a**, δ 6.82 and 5.92 in **18b**). The hydroxyl group (and therefore the acetoxy group) was seen to be secondary, since the hydroxyl proton of **18b** appears as a sharp doublet before exchanging with D_2O. The results of a europium shift reagent study allow a structure assignment to be made. Thus, a complex two-proton multiplet centered at δ 2.88



18 a: R = $COCH_3$ b: R = H

in **18b** was readily assigned to H_b and H_c, but could not be further evaluated until the individual signals were separated by the addition of $Eu(fod)_3$ to the NMR sample. Addition of this shift reagent caused one proton (H_b) to appear as a broadened doublet and the other (H_c) as a relatively sharp doublet of triplets. The only structure which can have *two* protons α to H_c and situated at approximately equal dihedral angles with respect to H_c (both requirements dictated by the 6-Hz triplet) is structure **18**. Additional evidence in support of this structure include the H_d, H_e coupling constant (12 Hz), which is in the expected range (10–13 Hz) for a cycloheptene,[27] and the indication of extended conjugation provided by the UV absorption of **18a** (λ_{max} 312 nm, cf. 276 nm in naphthalene).

1-Vinylacenaphthylene (16). To a suspension of methylenetriphenylphosphorane, prepared from triphenylphosphonium bromide (1.79 g, 52 mmol) (Aldrich) and phenyllithium (0.42 g, 50 mmol) (Alfa) in 50 mL of anhydrous ether, was added 0.9 g (50 mmol) of 1-formylacenaphthylene.[28] After refluxing overnight, the mixture was filtered and the filtrate concentrated to give a red oil. Chromatography of the pentane-soluble portion of the oil on alumina with pentane elution gave 75 mg of 1-vinylacenaphthylene (**16**) as a bright yellow oil: IR (CCl_4) inter alia 3030, 2910, 1605, 1480, 1460, 1430, 1425 cm^{-1}.

Dimer of 1-Vinylacenaphthalene. A solution of 10 mg of **16** and 7 mg of sodium acetate in 2 mL of acetic acid was refluxed overnight. Workup gave a yellow, oily residue which had an IR spectrum identical with that of the product of solvolysis of *exo*-**5g**.

Adduct of 1-Vinylacenaphthylene and Maleic Anhydride. A solution of 70 mg of **16** and 40 mg of maleic anhydride in benzene (3 mL) was heated under reflux for 2 h. Evaporation of the solvent left 51 mg of solid which was recrystallized to give colorless needles, mp 234–235 °C, having an IR spectrum identical with that of the maleic anhydride adduct of the *exo*-**5g** acetolysis product. Anal. ($C_{18}H_{12}O_3$) C, H.

***trans*-1-Hydroxy-2-vinylacenaphthene (*trans*-14a).** To 2.84 g (19.7 mmol) of cuprous bromide[29] in 75 mL of anhydrous ether was added, dropwise with stirring under nitrogen at −78 °C, 39.4 mmol of vinyllithium solution (Alfa, 1.9 M in tetrahydrofuran). The mixture was stirred until it turned from tan to black (small amount of black precipitate in nearly colorless liquid), then 0.79 g (4.7 mmol) of acenaphthylene 1,2-epoxide[30] in 20 mL of ether was added dropwise. After addition was complete, the cooling bath was allowed to warm to −40 to −45 °C (required about 1 h), and the mixture was stirred at this temperature for 30 min. Then a mixture of 30 mL of 1.0 N hydrochloric acid and 25 mL of 0.5 N ammonium chloride was added, after which the mixture was removed from the cooling bath and stirred for 10 min. The resulting mixture was filtered and the organic phase separated. The aqueous phase was extracted with ether and the organic phases were combined, washed with water, dried, and concentrated to give 5.16 g of a two-phase oil. Chromatography on alumina (3.5 × 10 cm column), eluting with hexane, 10, 20, and 50% benzene in hexane, benzene, and 10, 20, and 50% chloroform in benzene, gave in the 50% chloroform fraction 1.0 g (>100%) of red-orange oil, crude *trans*-**14a**. This material resisted purification, but was converted to the acetate (*trans*-**14b**) (vide infra), purified by TLC, and then reduced back to the alcohol. Thus, reduction of *trans*-**14b** (63 mg) with lithium aluminum hydride gave 47 mg of yellow oil which solidified on standing at −20 °C. Attempted recrystallization (aqueous methanol) yielded only an oil, but sublimation of the oil (110 °C, 0.15 mm, overnight, followed by room temperature, 0.15 mm, 3 days) gave white needles, mp 44–49 °C, which had IR and NMR spectra identical with those of the *trans*-**14a** obtained from acetolysis. The NMR spectrum of this purified material was also indistinguishable from that of the crude product before acetylation.

***trans*-1-Acetoxy-2-vinylacenaphthene (*trans*-14b).** A 74-mg sample of crude *trans*-**14a** was treated with acetic anhydride and pyridine (0.5 mL each) overnight at room temperature. Evaporation of the reagents left a yellow oil which was purified by preparative TLC (silica gel, methylene chloride development) to give 63 mg of light yellow oil, *trans*-**14b**: NMR ($CdCl_3$) δ 7.52 (m, 6), 6.45 (d, J = 2.5 Hz, 1), 6.05 (m, 1), 5.23 (m, 2), 4.25 (br d, J = 7 Hz, 1), 2.12 (s, 3).

Crystal Data. *exo*-**5c**, $C_{15}H_{12}O_2$, mol wt 224.3. Monoclinic, a = 8.63 (1), b = 20.21 (3), c = 7.35 (1) Å, β = 120.16 (10)°, U = 1108 Å^3, d_m (flotation) = 1.34 g cm^{-3}, Z = 4, d_c = 1.344 g cm^{-3}, $F(000)$ = 472. Cu Kα radiation, λ = 1.5418 Å; absorption coefficient for Cu Kα radiation, μ = 8.30 cm^{-1}. Space group uniquely established as $P2_1/c$ (C_{2h}^5) from the systematic absences: $0k0$ when $k \neq 2n$, $h0l$ when $l \neq 2n$.

endo-**5f**, $C_{15}H_{14}O_3S$, mol wt 274.4. Monoclinic, a = 20.41 (1), b = 5.95 (1), c = 10.88 (1) Å, β = 98.50 (5)°, U = 1307 Å^3, d_m (flotation) = 1.38 g cm^{-3}, Z = 4, d_c = 1.394 g cm^{-3}, $F(000)$ = 456. Cu Kα radiation, μ = 21.55 cm^{-1}. Space group uniquely established as $P2_1/c$ (C_{2h}^5) from systematic absences as for *exo*-**5c**.

Crystallographic Measurements. Unit-cell dimensions for *exo*-**5c** were evaluated from precession photographs taken with Mo Kα (λ = 0.7107 Å) radiation. Intensity data from a needle crystal of maximum dimensions ca. 0.86 × 0.28 × 0.30 mm were recorded with Ni-filtered Cu Kα radiation by means of equiinclination, multiple-film Weissenberg photographs of the 0–8kl reciprocal lattice levels. The data, estimated visually by comparison with a calibrated intensity strip, were corrected for spot-shape, Lorentz, and polarization effects to yield 1719 independent structure amplitudes; no corrections were made for the small effects of absorption. Initially, the various layers of data were assumed to be a common scale as each had been given approximately equal exposure times; absolute layer scales were obtained later in the analysis by correlation of $\Sigma|F_o|$ with $\Sigma|F_c|$ at the end of the isotropic refinement cycles.

For *endo*-**5f**, a crystal of dimensions ca. 0.40 × 0.40 × 0.40 mm was oriented on a glass fiber to rotate about the crystal b axis. Preliminary unit-cell dimensions, obtained from precession photographs taken with Mo Kα radiation, were subsequently refined by least-squares treatment of the θ, χ, and Φ angles for 40 widely separated high-order reflections which were accurately centered on an Enraf-Nonius CAD 3 automated diffractometer (Ni-filtered CuKα radiation; 3° takeoff angle). All unique intensity data to θ 67° were recorded by the θ–2θ scanning technique with scan widths (1.00 + 0.50 tan θ)°. Stationary background measurements were made at each end of the scan range for times equal to half the scan period. Instrument and crystal stability, monitored throughout by remeasuring the intensity of a strong standard reflection after each batch of 99 measurements, showed no significant variation. From a total of 2328 such measurements, those 1761 reflections for which $I > 2.0\sigma(I)$, where $\sigma^2(I)$ = (scan count + total background count), were corrected for Lorentz, polarization, and absorption effects, and used in the analysis and refinement.

Structure Analyses. Both crystal structures were solved by direct phase-determining procedures. For *exo*-**5c**, the symbolic addition procedure and tangent formula refinement, as described previously,[31] were employed. An E map generated by use of the set of phase constants, judged to be the best by the criteria given previously,[31] for 359 out of 400 of the largest $|E|$ values yielded all the nonhydrogen atom positions. When structure factors were calculated by use of this model R was 0.290.

The structure of *endo*-**5f** was solved by use of the 251 highest $|E|$ values in MULTAN.[32] An E map evaluated with that set of phases producing the highest figure of merit and lowest residual revealed clearly all of the nonhydrogen atom positions. For structure factors based on these coordinates, R was 0.243.

Full-matrix least-squares adjustment of nonhydrogen atom positional and thermal parameters, at first isotropic and subsequently anisotropic, proceeded smoothly. Hydrogen atom positional and isotropic thermal parameters were varied in the later stages of the refinement processes which converged at R = 0.123 for *exo*-**5c** and 0.051 for *endo*-**5f**. Fractional coordinates and anisotropic thermal parameters for nonhydrogen atoms are in Tables IV and V of the supplementary material;[33] corresponding data for hydrogen atoms are in Table VI. Interatomic distances and angles are reported in Table VII; Table VIII contains complete lists of torsion angles. Displacements of selected atoms from least-squares planes through the naphthalene ring atoms are in Table IX. Lists of observed and calculated structure amplitudes are available upon request.[34]

Scattering factors used in all the structure-factor calculations were those for C, O, and S in the Cromer and Waber[35] compilation; for H the Stewart, Davidson, and Simpson[36] values were used. In the least-squares calculations $\Sigma w\Delta^2(\Delta = |F_o| - |F_c|)$ was minimized, the weights w being assigned according to the scheme $\sqrt{w} = 1$ for $|F_o| < K$, and $\sqrt{w} = K/|F_o|$ for $|F_o| > K$ (K = 5.5 for *exo*-**5c**, 14.0 for *endo*-**5f**). Analyses of these weighting schemes showed no systematic dependence of $\Sigma w\Delta^2$ on $|F_o|$.

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Supplementary Material Available: Tables of atomic coordinates and thermal parameters (Tables IV–VI), interatomic distances and valency angles (Table VII), torsion angles (Table VIII), naphthalene ring least-squares planes (Table IX), and structure factors (35 pages). Ordering information is given on any current masthead page.

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Proton Exchange in Gas-Phase Isopropylation of Benzene and Toluene

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Abstract: In the gas-phase radiolysis of a C_3H_8 (100 mm)–C_6H_6 (5 mm)–C_6D_6 (5 mm) mixture, it has been found that the isopropylbenzene (IPB) produced by the attack of the i-$C_3H_7^+$ ions derived from propane to benzene involves IPB-d_1, -d_2, -d_3, and -d_4 as well as IPB-d_0 and -d_5, and the relative yields of these IPBs increase with increasing degree of the H–D exchange. The result suggests that the proton exchange between the rings of the intermediate complexes, $C_3H_7C_6H_6^+$ and $C_3H_7C_6D_6^+$, and of the reactant benzene molecules occurs. The degree of the H–D exchange decreases with increasing temperature. The H–D exchange during the isopropylation has also been studied in propane–toluene and propane–benzene–toluene systems. The reversible π complex formation between the intermediate complexes and the reactant aromatic molecules followed by the proton exchange has been proposed.

Introduction

In previous papers we reported results for the electrophilic aromatic substitution occurring in gas-phase radiolysis.[1,2] In the reaction the intermediate complex, an arenium ion, formed by the attack of a gaseous ion to an aromatic molecule, exists as a free ion with excess vibrational energy, and interesting features which differ from those in the analogous catalytic reaction in solution (Friedel–Crafts reaction) have been observed. One of them was the thermodynamically controlled isomer distribution of substituted products, which has been revealed by the dominant formation of meta isomers in the isopropylation and benzylation of alkylbenzenes.[1a,b,c]

In the catalytic reaction in solution a counterion acts as a proton acceptor to the intermediate complex giving a neutral product. However, the fate of the intermediate complex in the gas-phase reaction has not been clear, and it is of interest to elucidate the mechanism of the electrophilic aromatic substitution in the absence of a counterion. During the course of our investigations on this subject it was found that the proton exchange between the rings of the intermediate complex and of the reactant benzene occurs in the isopropylation of benzene.[3] In the present study the proton exchange reaction in the isopropylation of benzene and toluene has been investigated in detail in order to obtain information about the fate of the intermediate complex in the gas-phase electrophilic aromatic substitution. The results of the present study have also provided significant information about the gas-phase ion–molecule reactions in aromatic systems which have been studied by many workers using mass and ion cyclotron resonance spectrometric techniques.[4]

Experimental Section

Materials. Benzene and toluene obtained from Wako Pure Chemical Industrial Co. were purified by the usual method. After the extensive distillations using a spinning-band column, the reagents were dried over a sodium mirror and stored in Pyrex tubes equipped with break-seals. Benzene-d_6 and toluene-d_8, obtained from Merck Co.,

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