Stereoisomeric Bishomo-3,5-cycloheptadienyl *p*-Toluenesulfonates as Probes of the Geometric and Conformational Dependence to Long-Range Cyclopropyl Interaction during Acetolysis

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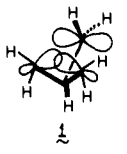
Abstract: Acetolysis of *syn,anti*-3,5-bishomocycloheptadienyl tosylate (6) produces *anti*-bicyclo[6.1.0]non-5-en-3-yl acetate (**12**) in >98.5% yield. Comparable solvolysis of its d_2- (**19**) and d_4-labeled derivatives (**24**) demonstrated that product formation is the result of dual cyclopropane ring cleavage with concomitant reconstruction of a different three-membered ring and solvent capture from the face opposite that utilized by the leaving group. Importantly, C(3)–C(4) bond cleavage must occur exclusively in the first phase of the rearrangement to account for the lack of deuterium scrambling and the ultimate location of the isotopic label. The involvement of a symmetrical cation is accordingly precluded. When syn,syn isomer **7** was subjected to acetolysis, *syn*-bicyclo[6.1.0]non-5-en-3-yl acetate (**27**) was formed almost exclusively (>98.5%). In this instance, attack by solvent occurs stereospecifically on the same surface from which tosylate ion is lost, such behavior being diametrically opposed to that exhibited by 6. Recourse to the d_4 derivative **28b** provided independent demonstration that the course of rearrangement was otherwise identical. Since anti,anti tosylate **8** underwent acetolysis to give four products, this epimer clearly does not ionize to an identical cation. The rate constants and thermodynamic parameters for all three isomers were determined experimentally. These kinetic studies show the relative reactivity gap at 40 °C to be a factor of 18.7. The mechanistic schemes which can be delineated on the basis of these data, particularly as they pertain to direct anchimeric assistance by the C(3)–C(4) cyclopropane ring, are presented.

Progression from the cyclopropylcarbinyl cation (**1**) to homologous β-cyclopropylethyl systems (**2**) is accompanied by a dramatic alteration in the geometry adopted to achieve maximum conjugative overlap. The spatial requirement in **1**



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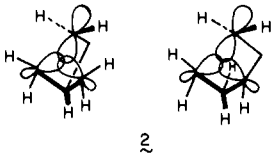

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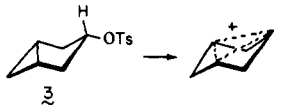
is a bisected structure which necessitates that the remote carbon–carbon bond of the three-membered ring be aligned "anti periplanar" to the leaving group.[2-4] In rigid molecules where such an arrangement is unattainable, direct conjugative assistance is absent and pronounced kinetic deceleration is seen because of sizable inductive contributions[5] by the proximate three-membered ring. When homoconjugated transition states such as **2** are involved, kinetic effects are frequently not as pronounced. In actuality, rate comparisons have been of least value in this area since formation of a delocalized intermediate need not necessarily give rise to an enhanced rate.[6] Tosylates **3** and **4** serve as useful contrasts. Thus, **3** exhibits little rate



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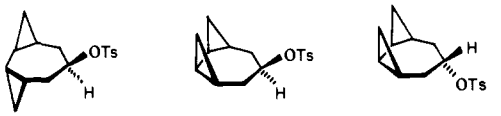
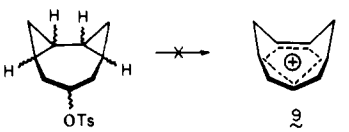
4 **5**

acceleration, presumably because the conformation necessary for participation is not preferred,[7] while the conformationally rigid and strained **4** is highly reactive toward ionization.[8] The early controversy concerning the extent of cyclopropyl participation operating during ionization of parent brosylate **5**[9] further accentuates the difficulty in establishing definitively whether the cyclopropyl group anchimerically assists in formation of the carbonium ion or interacts with the cationic center only after it is formed. As noted by Haywood-Farmer,[4] studies of long-range interactions in β-cyclopropylethyl systems have been surprisingly few in number despite the inherent fascination of the subject. The difficulties mentioned above have apparently comprised a major deterrent to many potential investigators.

Herein we report details of the solvolytic behavior of the isomeric bishomo-3,5-cycloheptadienyl tosylates **6–8,** three



6 **7** **8**



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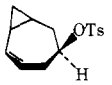
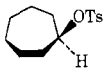
molecules which incorporate structural features particularly well suited for elucidation of long-range cyclopropyl participation. The special characteristic unique to each of these molecules is detailed on an individual basis below. It is emphasized here that the thrust of this research was *not* the possible generation of tetrahomocyclopentadienyl cations of type **9**. Because such intermediates clearly should suffer from thermodynamic destabilization, even when geometry is favorable, participation by the pair of cyclopropyl groups in this fashion was considered highly unlikely from the outset. Rather, our objective was to gain extra kinetic evidence for the existence or absence of homoconjugative cyclopropyl participation during ionization by the simple expedient of symmetry-based structural design.

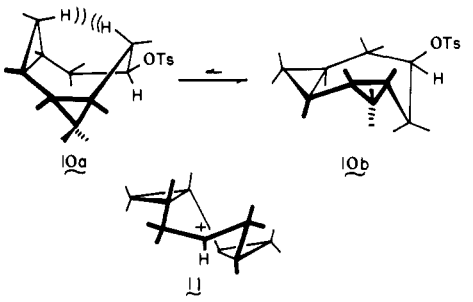
Results

***syn,anti*-3,5-Bishomocycloheptadienyl System.** Stereochemically pure **6**-OH, the synthesis of which was described in the preceding paper,[10] and its crystalline tosylate derivative (**6**) can exist in the two conformationally distinctive forms **10a** and **10b**. In saddle geometry **10a,** the proximity of "axial" H_2

Table I. Kinetic Data for Acetolysis in Buffered Acetic Acid

Compd	Temp, °C	k, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$k_{rel}^{40°C}$
6	79.7	3.50×10^{-4}	24.8 ± 0.6	−4.5 ± 1.8	1
	63.4	5.43×10^{-5}			
	40.0	3.46×10^{-6}			
7	51.1	2.63×10^{-4}	23.9 ± 0.5	−1.3 ± 1.5	18.7
	40.0	6.48×10^{-5}			
	28.4	1.49×10^{-5}			
8	79.7	6.38×10^{-4}	24.1 ± 1.2	−5.0 ± 3.6	2.1
	66.4	2.09×10^{-4}			
	50.0	3.06×10^{-5}			
	40.0	7.41×10^{-6}			
	40.0	4.43×10^{-5}[a,b]	21.9 ± 0.5	−8 ± 4	12.8
	40.0	1.95×10^{-5}[c,d]	23.3	−5.7	5.6

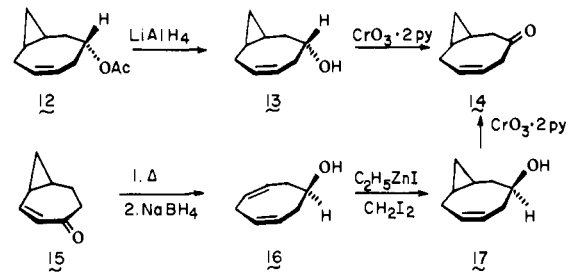
[a] Interpolated value based on the activation parameters. [b] J. B. Lambert, A. P. Jovanovich, J. W. Hamersma, F. R. Koeng, and S. S. Oliver, *J. Am. Chem. Soc.*, 95, 1570 (1973). [c] Extrapolated value based on the activation parameters. [d] H. C. Brown and G. Ham, *J. Am. Chem. Soc.*, 78, 2735 (1956).



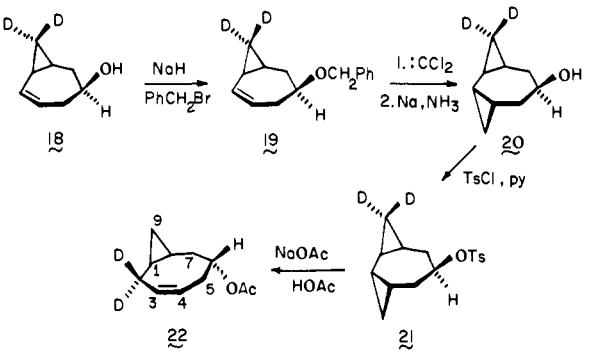
to the endo proton of the 5,6 bridge gives rise to transannular nonbonded repulsions and, as a consequence, extended form **10b** is considered to be thermodynamically favored. Furthermore, the two cyclopropane rings in **10b** are projected in the equatorial plane in contrast to their axial disposition in **10a**. The possibility that **10a** and **10b** interconvert is, of course, not ruled out. However, neither cyclopropyl group in **10a** is properly aligned for long-range anchimeric assistance to ionization (see **2**). In **10b**, only the syn cyclopropane ring has its internal bond suitably oriented to provide neighboring group assistance. Accordingly, should cyclopropyl participation gain importance during the ionization of this system, interaction is necessarily restricted to the syn three-membered ring for geometric reasons. On the other hand, if such direct involvement is lacking at the solvolytic transition state, secondary carbocation **11** could intervene. Because **11** possesses axial symmetry and is constructed such that either cyclopropane ring can now participate with equal probability in charge delocalization, the earlier restriction of unique syn cyclopropyl involvement is no longer strictly applicable. On this basis, the extent of cyclopropyl assistance during and after ionization could be indicated by the extent to which the anti three-membered ring has experienced appropriate perturbation while going to product(s). The possible operation of "memory effects" [11] (now considered to be the result of unsymmetrical ion pairing[12]) has not been taken into consideration in the above analysis (vide infra).

Titrimetric solvolysis rates for **6** were measured in sodium acetate buffered (0.0510 M) acetic acid by the aliquot method and good first-order behavior was exhibited throughout. The kinetic data and activation parameters are summarized in Table I. Since the infinity titers invariably agreed well with the calculated values, internal return to a less reactive tosylate was not an issue. The product mixture was comprised of a single acetate to the extent of >98.5%. The remaining 1.5% appeared to be a mixture of hydrocarbons and was not further investigated. The structure of the nearly exclusive product was es-

Scheme I



Scheme II



tablished as **12** by sequential lithium aluminum hydride reduction to **13** and oxidation of this alcohol to bicyclic enone **14**. The independent synthesis of **14** took advantage of the facile thermal rearrangement of **15** to 3,6-cyclooctadienone,[13] which afforded **16** upon treatment with sodium borohydride.[13,14] Controlled Simmons–Smith cyclopropanation of **16** led to **17**, the epimer of **13**, which was likewise transformed to **14** when treated with the chromium trioxide dipyridine complex (Scheme I).

A mechanistically plausible rationalization of the conversion of **6** to **12** considers initial homoconjugative interaction of one of the cyclopropane rings to generate a cyclopropylcarbinyl cation intermediate which is trapped by solvent as its homoallylic equivalent. Due to the unsymmetrical nature of **12**, it becomes possible by suitable deuterium labeling to establish not only cyclopropane ring enters into which phase of this reaction, but also the extent to which these cyclopropyl interactions are specific. The pursuit of this objective was made possible by the synthetic sequence outlined in Scheme II. Treatment of 3,5-cycloheptadienol with diiodomethane-d_2 and zinc–silver couple gave **18** admixed with lesser quantities of

Table II. ^{1}H NMR Spectra of the Isomeric Bicyclo[6.1.0]non-3-en-6-yl Acetates and Their Deuterated Derivatives (δ, $CDCl_3$, 90 MHz)

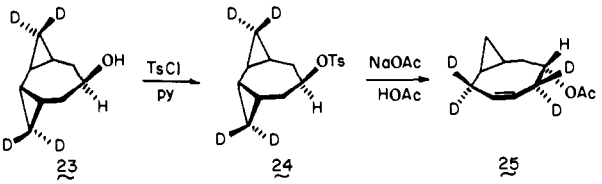
Compd	H_3	H_4	H_6	H_{2a},H_{5a}[a]	H_{2s},H_{5s},H_{7a}[a]	CH_3	H_{7s}	H_1,H_8,H_{9exo}	H_{9endo}
12	5.63 (d of d of d)	5.47 (d of d of d)	4.95 (d of t)	3.16–2.50 (m)	2.25–1.92 (m)	2.04 (s)	1.20 (m)	1.1–0.5 (m)	−0.1 (m)
22	5.63 (d)	5.47 (d of d of d)	4.95 (d of t)	2.92 (m, 1 H)	2.25–1.92 (m, 2 H)	2.04 (s)	1.20 (m)	1.1–0.5 (m)	−0.1 (m)
25	5.63 (d)	5.47 (d)	4.98 (br s)		2.15 (m, 1 H)	2.05 (s)	1.20 (m)	1.1–0.5 (m)	−0.1 (m)
Compd	H_3	H_4	H_6	H_{2a},H_{2s},H_{5a},H_{5s},H_{7a}[a]		CH_3	H_{7s}	H_1,H_8,H_{9exo}	H_{9endo}
27	5.84 (d of t)	5.58 (d of d of d)	4.73 (q of t)	2.67–2.08 (m)		2.00 (s)	1.40 (q of t)	1.0–0.5 (m)	0.05 (m)
29	5.84 (d)	5.58 (d)	4.74 (d of d)	2.34 (d of t, 1 H)		2.01 (s)	1.40 (q of t)	1.0–0.5 (m)	0.05 (m)

[a] The subscripts a and s are sterochemical descriptors and refer to the syn or anti orientation of the proton relative to the cyclopropane ring.

the two biscyclopropanated tetradeuterio alcohols. Conversion to benzyl ether **19** followed by reaction with dichlorocarbene under phase transfer conditions and sodium/ammonia reduction provided **20**. The assignment of stereochemistry to **20** is based reliably on the synthetic method[10] which is known[15] to introduce the first cyclopropane ring onto 3,5-cycloheptadienol stereoselectively from the syn direction. Therefore, there exists no question that the syn cyclopropane ring in tosylate **21** carries the pair of deuterium substituents. When subjected to acetolysis as before, **21** was converted to acetate **22**.

The labeling pattern assigned to **22** follows principally from comparisons of its ^{1}H NMR spectrum with that of **12** (Table II). In the case of **12**, the noteworthy spectral features are: (1) the doublet of doublet multiplicity of each olefinic proton arising from mutual coupling and spin interaction with the adjoining methylene groups; (2) the deshielded nature of anti H_2 and H_5 (δ 3.16–2.50) caused by their spatial proximity to the acetate substituent; and (3) the rather similar chemical shifts of syn H_2, syn H_5, and anti H_7 which give rise to a series of overlapping multiplets at 2.25–1.92. In dideuterio derivative **22**, the complex signals at 3.16–2.50 and 2.25–1.92 are both decreased in intensity by the relative area 1. While this feature alone does not constitute proof of the loci of deuterium substitution, the emergent patterns of the remainder of the spectrum suggest the structure to be **22**. Thus, while the 5.63 absorption due to H_3 experiences simplification to a doublet (J = 11 Hz) and the multiplet at 1.1–0.5 is somewhat altered in appearance, the remainder of the signals do not lose their original character. Consequently, acetate **22** must be substituted with two deuteriums at C(2).

Further confirmation of this assignment was derived from an examination of the solvolytic behavior of **24** under compa-

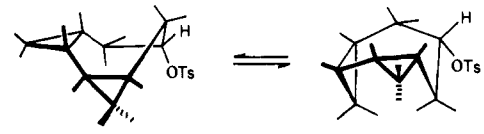


23 24 25

rable conditions. Prepared from alcohol **23**, a product of the cyclopropanation of 3,5-cycloheptadienol with CD_2I_2, this tosylate underwent ready conversion to **25**. The revealing aspects of its spectrum include the collapse of both olefin signals to doublets, the total absence of the δ 3.16–2.50 multiplet, and reduction in relative intensity of the next upfield absorption (2.15) to area 1 combined with its simplification. These data are uniquely compatible with the indicated 2,2,5,5-tetradeuterio substitution plan.

Once attention is called to the overlapping nature of the H_{2a} and H_{5a} signals, it is clear that a direct measure of the "leakage" of deuterium from H_{2a} to H_{5a} during acetolysis is not feasible. Fortunately, an indirect assessment of this question is possible. When the multiplicities of the α-acetoxy (H_6) and olefinic protons (H_3 and H_4) in well-resolved spectra of **22** are examined closely, two points emerge: (a) relative to their appearance in unlabeled acetate **12**, the H_6 and H_4 patterns are not permuted; (b) no vestiges of the original multiplicity of the δ 5.63 signal (due to H_3) are visible, it being replaced by a doublet showing additional narrow long range coupling ($J \approx$ 1 Hz). Based on these observations, the deuterium would appear to be localized very heavily, and perhaps exclusively, at C(2). Consequently, to the level of accuracy accorded by this analysis, the question of cyclopropyl participation is resolved in favor of the syn three-membered ring.

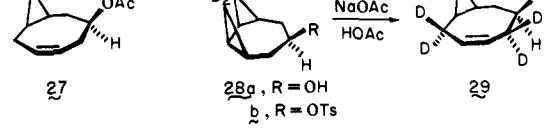
Cationic Rearrangement of *syn,syn*-3,5-Bishomocycloheptadienyl Tosylate 7. Conformational analysis of **7** reveals that the molecule can exist as the two interconvertible forms **26a** and **26b**. In either structure, one axial and one equatorial cy-



26a 26b

clopropyl ring is projected from the tub-shaped cycloheptane frame. From models, the steric interaction prevailing between the endo axial cyclopropane and transannular "axial" proton pair in these conformers seemingly causes a greater degree of flattening of the medium ring than found, for example, in **10b**. Although the axial three-membered rings cannot provide anchimeric assistance to ionization, this restriction does not apply to their equatorial counterparts. But since both **26a** and **26b** possess a cyclopropyl group properly oriented for participation and because the activation energy for ionization should exceed the barrier to their interconversion, solvolysis will likely occur from both conformers.

Determination of the acetolysis rate constant revealed **7** to be well-behaved kinetically and to be almost 19 times more reactive than **6** at 40 °C (Table I). When conducted on a preparative scale, the solvolysis led to an oil shown to be composed of a single acetate (>98.5%) identified as **27** by its reduction

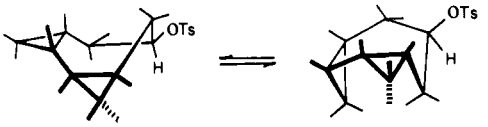


27 28a, R = OH; b, R = OTs 29

to alcohol **17**. Therefore, the ionizations of **6** and **7** proceed with like skeletal rearrangement but with high levels of contrasting selectivity. The absence of crossover between intermediate ions is thereby demonstrated. Although an intermixing of rearrangement pathways is difficult to imagine as long as the reactive species are tricyclic, these results establish that merging

of the rearrangement manifolds does not occur at a later stage during the evolution of bicyclic character. This aspect of the problem gains importance in view of the independent demonstration that acetolysis of **28b** leads ultimately to cleavage of both original cyclopropane rings before delivery of acetate product. As revealed previously by the conversion of **24** to **25**, the syn,syn and syn,anti series share this common reactivity pattern. The comparative spectral features of **27** and **29** are detailed in Table II.

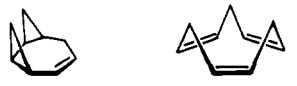
Acetolysis of *anti,anti*-3,5-Bishomocycloheptadienyl Derivative 8. Heating of 7-OH with aluminum isopropoxide in a 2-propanol–acetone solvent system resulted in epimerization and gave **8**-OH as the major component (58%). Isomer separation was achieved by chromatography on silica gel, and the composition of the mixture (58:42) was established as the equilibrium distribution by similar reaction of the pure anti,anti alcohol. In contrast to **7** where the quasi-axial functional group is predisposed for anchimeric assistance by the equatorial cyclopropane ring, similar neighboring group participation appears less likely for **8**. If the prevailing conformations are indeed **30a** and **30b**, then neither internal cyclopropane



30a 30b

bond attains a geometric relationship relative to the tosylate group which permits realization of that orbital orientation (cf. **2**) necessary to aid departure of the leaving group. However, long-range cyclopropyl participation in **8** would not be altogether precluded if a more shallow tub conformation were adopted. On this basis, operation of the presumed low-energy pathways open to **6** and **7** would not necessarily be fully deterred, but the possibility exists that solvolytic pathways not encountered in the earlier examples could now become operational. One of these may, of course, merely be preliminary ionization to the unrearranged secondary carbocation.

The acetolysis of **8** proceeded as smoothly as that of its isomers, the rate constants denoting a reactivity level at 40 °C approximately double that of **6** (Table I). Four products were generated in high yield, two of which were hydrocarbons and the others acetates. The spectra of the acetates require that they be 7-OAc (9%) and **27** (55%). The hydrocarbons were similarly readily identified as *syn*-3,5-bishomocycloheptatriene (**31**, 25%)[10] and *cis*[3]-1,4,7-cyclononatriene (**32**, 11%).[16]



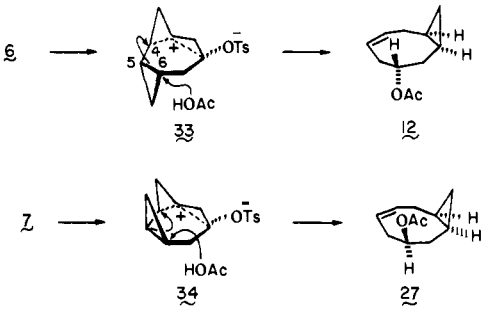
31 32

This product distribution clearly discounts the possibility that tosylate **8** ionizes to exactly the cationic intermediate formed from **7**.

Discussion

The solvolytic conversions of the *syn,anti*- and *syn,syn*-3,5-bishomocycloheptadienyl tosylates **6** and **7** to the epimeric acetates **12** and **27** are, within the limits of our analytical method, completely stereospecific. As little as 0.3% intercontamination could have been detected but was not. In both instances, complete stereochemical control is maintained during twofold cyclopropane ring cleavage with solvent capture occurring from the *opposite* and *same* surfaces, respectively, as that utilized by the departing tosylate ion. These findings are consistent with, but do not by themselves require, utilization of the secondary C(3)–C(4) bonding cyclopropane electrons

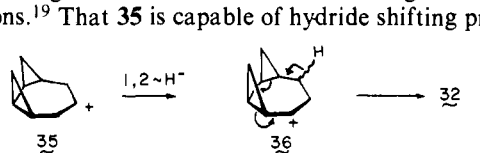
Scheme III



in synchronous backzide participation. What is strictly demanded is that no rotation or other conformational perturbation occur about C(4) prior to rupture of the C(5)–C(6) bond and charge annihilation at C(6). This would certainly be reasonable if molecular rigidity were gained by long-range interaction to C(4), to be followed by stereospecific rearrangement of the rather unique cyclopropylcarbinyl cations **33** and **34**. Scheme III illustrates simplified versions of this analysis.

From the nature of the acetate obtained from solvolysis of deuterium labeled tosylate **21**, it is clear that the *syn,anti*-3,5-bishomocycloheptadienyl system does not undergo rate-controlling ionization to secondary cation **11**. Rather, the stereospecific formation of **22** supports intervention of bishomoallyl cation **33**[16] rather than evolution of this symmetrical intermediate. A not unreasonable assumption is that contributions from unsymmetrical ion pairing may also retard full equilibration to **11**. Since **6** ionizes at about the same rate as **8** whose geometry is not particularly conducive to anchimeric assistance, rigorous analysis of the kinetic data is made somewhat complicated. There is little doubt that the ground states of both **7** and **8** are thermodynamically less stable than that of **6** because of the structurally enforced requirement that one of their cyclopropyl appendages be projected axially. This factor may be chiefly responsible for the somewhat reduced $\Delta H^{\ddagger}$ values of **7** and **8** as compared with **6**. But if **6** and **7** do solvolyze with anchimeric assistance (permissible on the basis of product formation), how is the $k_{\text{acetolysis}}$ for **8** to be assessed?

The ionization of **8** seemingly does lead in part (55% of **27**) to a cation similar to **34** but with anti tosylate departure. This reaction channel could reflect cyclopropyl participation from a rather shallow tub conformation as previously discussed. The nature of the other three products indicates that delocalized intermediates of comparable type are unimportant in their formation and that a classical electron-deficient species (**35**) probably intervenes. Direct solvent capture from the less hindered backside surface now provides 7-OAc,[18] while β proton loss leads to olefin **31**. The formation of 1,4,7-cyclononatriene (**32**) may be attributed to a 1,2-hydride shift process generating **36** which by well-precedented electronic reorganization can release strain with simultaneous introduction of alternating single and double bonds. Cyclononatriene **32** may also arise from subsequent protonation of **31** during acetolysis. However, this question was decided in the negative when **31** was recovered unchanged after resubmission to the original reaction conditions.[19] That **35** is capable of hydride shifting provides



important insight into the level of electron deficiency which builds up at C(1). In particular, this specific transformation demonstrates by its absence during acetolysis of **6** and **7** that structural factors present in the latter tricyclic systems deny

comparable development of cationic character at C(1). On pragmatic grounds, direct bishomoallyl cation intervention concisely rationalizes this dichotomy.

If the above analysis is valid, then the acetolysis rate constant for **8** becomes a composite of k_Δ and k_s terms.[20] The extent to which **27** is produced (55%) can be taken to indicate that k_Δ is the dominant component. On this basis, the relative kinetic ordering of **8** (Table I) becomes comprehensible. Since differences in activation energies comprise the sum of ground state and transition state inequalities, the k_Δ for **8** should parallel rather closely in magnitude the value experimentally determined for **7**. This state of affairs arises because **7** and **8** are merely epimeric at C(1) and the anchimerically assisted transition states (cf. **34**) are closely similar. Accordingly, one is tempted to conclude that cyclopropyl participation operates in all three isomeric systems, although to a reduced extent in **8** because of adverse orbital geometry factors.[21] Importantly, the presence of two *noninteracting* cyclopropane rings in **6–8** would be expected to reduce their rates of ionization significantly below that of cycloheptyl tosylate due to adverse inductive effects, but this is not observed (Table I).

These findings cause the converse viewpoint which would argue that all three tosylates solvolyze without anchimeric assistance and that cyclopropyl participation, if operative, occurs only during rate-limiting ionization to be less than convincing. Under these terms, the single feature which would preclude **6** from becoming fully symmetric (cf. **11**), and the reaction manifolds of **7** and **8** from fully merging, is oriented ion pairing with solvent relaxation occurring more slowly than possible molecular skeletal vibrations. Although ion pairing is known to gain importance in amine deamination processes,[12] it has not acquired comparable prominence in acetolysis reactions.[22] But because the importance of metastable unsymmetrically solvated intermediates cannot be directly assessed, their role cannot be dismissed. We note, however, that because capture of acetate ion occurs at C(6) and not in the immediate vicinity of tosylate departure, counterion control of stereospecificity becomes rather unlikely. This conclusion is supported by the stereochemical crossover observed with **6** and **7** (compare **33** and **34**). A further relevant issue concerns whether the counterion is responsible for the inability of **11** to become symmetric and of **35** (as generated from the two epimeric tosylates) to relax fully to a common geometry. In the latter instance, it is also obligatory that the level of charge buildup at C(1) also be controlled by solvation factors. Although the completely symmetric conformations of **11** and **35** may not coincide with the minima in the vibrational potential curves, there can be no doubt that these structures would be attained during a given molecular vibration. It therefore becomes necessary for solvent to trap these nascent cations in less than $\sim 10^{-13}$ s. To the extent that this criterion is unlikely, the hypothesis of direct cyclopropyl participation gains credence. The problem reduces to one of how the symmetry properties of nonisolable intermediates are to be construed in mechanistic studies.

There remains the need to consider the possibility that both cyclopropane rings open simultaneously. It is instructive to consider first the syn,anti derivative **6**. Molecular models (see **10**) indicate that the prevailing geometry is rather unfavorable for full cyclopropane delocalization because the relevant orbitals are canted to opposite surfaces of the molecule. Such geometry has previously been recognized not to be conducive to efficient electronic interaction.[23] In the **7** and **8** examples, an almost coplanar arrangement of the inner cycloheptane core is necessitated. Such conformations can indeed be attained and extended cyclopropane–cyclopropane interaction seemingly gains meaningful importance during the ionizations of **7** (but not **8**) if the results described in the ensuing paper[24] provide serviceable analogy.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. The ^{1}H NMR spectra were determined with Varian A-60A and Bruker HX-90 instruments and apparent splittings are given in all cases. The ^{13}C spectra were also run on the Bruker spectrometer. Mass spectra were measured with an AEI-MS9 spectrometer at an ionizing energy of 70 eV. Preparative scale VPC separations were performed on a Varian Aerograph Model A-90-P3 instrument equipped with thermal conductivity detectors. Microanalytical determinations were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

***syn,anti*-3,5-Bishomocycloheptadienyl Tosylate.** A solution of *syn,anti*-3,5-bishomocycloheptadienol (360 mg, 2.6 mmol)[10] and *p*-toluenesulfonyl chloride (1.0 g, 5.2 mmol) in pyridine was Kept at −20 °C for 24 h, poured into ice water, and extracted with ether (3 × 25 ml). The combined ether extracts were washed with cold 10% hydrochloric acid and saturated sodium bicarbonate solutions before drying, evaporation, and recrystallization of the residue from pentane. There was obtained 470 mg (62%) of 6 as a white solid, mp 70.5–71.5 °C; $\delta_{Me_4Si}^{CCl_4}$ 7.70 (d, J = 8 Hz, 2), 7.42 (d, J = 8 Hz, 2), 4.62 (m, 1), 2.40 (s, 3), 2.22 (m, 2), 1.30 (m, 2), 0.68 (m, 6), and −0.05 (m, 2); *m/e* 292.1138 (292.1133).

Anal. Calcd for $C_{16}H_{20}O_3S$: C, 65.72; H, 6.89; S, 10.97. Found: C, 65.73; H, 7.06; S, 11.11.

***syn,syn*-3,5-Bishomocycloheptadienyl Tosylate (7).** Reaction of 500 mg (3.6 mmol) of the alcohol[10] with 1.50 g (7.8 mmol) of *p*-toluenesulfonyl chloride in pyridine (7 ml) as above afforded 675 mg (64%) of **7** as colorless crystals, mp 53–54 °C, from pentane; $\delta_{Me_4Si}^{CCl_4}$ 7.73 (d, J = 8 Hz, 2), 7.27 (d, J = 8 Hz, 2), 4.73 (m, 1), 2.43 (s, 3), 2.33 (d of t, J = 16 and 5 Hz, 2), 1.65 (m, 2), 1.05 (m, 2), 0.70 (m, 4), and 0.13 (m, 2).

Anal. Calcd for $C_{16}H_{20}O_3S$: C, 65.72; H, 6.89; S, 10.97. Found: C, 65.48; H, 6.97; H, 11.02.

***anti,anti*-3,5-Bishomocycloheptadienol.** A mixture of *syn,syn*-3,5-bishomocycloheptadienol (690 mg, 5.0 mmol), aluminum isopropoxide (4.1 g, 20 mmol), and acetone (0.1 ml) in 10 ml of 2-propanol was sealed in a heavy-walled glass ampule and heated at 130 °C for 72 h. The cooled contents were poured into cold 10% hydrochloric acid, and the product was extracted with ether (3 × 20 ml). The combined organic extracts were washed with saturated sodium bicarbonate and sodium chloride solutions, dried, and concentrated. NMR analysis showed the anti,anti isomer to dominate by a factor of 58:42. Careful silica gel chromatography gave pure anti,anti alcohol (220 mg, 32%) as a white solid: mp 54–56 °C; $\delta_{Me_4Si}^{CDCl_3}$ 3.58 (quint, J = 6 Hz, 1), 1.97 (m, 4), 1.50–0.30 (m, 6), and 0.0 (m, 2); ν_{max}^{heat} 3340 cm^{-1}; *m/e* 138.1047 (138.1045).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.01; H, 10.47.

***anti,anti*-3,5-Bishomocycloheptadienyl Tosylate (8).** From 186 mg (1.4 mmol) of the alcohol and 344 mg (1.8 mmol) of *p*-toluenesulfonyl chloride in 4 ml of pyridine, there was obtained 240 mg (61%) of **8** as a white solid, mp 58–59 °C, from pentane; $\delta_{Me_4Si}^{CDCl_3}$ 7.70 (d, J = 8 Hz, 2), 7.25 (d, J = 8 Hz, 2), 4.37 (m, 1), 2.40 (s, 3), 2.40–1.40 (m, 4), 1.40–0.25 (m, 6), and −0.08 (m, 2).

Anal. Calcd for $C_{16}H_{20}O_3S$: C, 65.72; H, 6.89; S, 10.97. Found: C, 65.55; H, 7.07; S, 11.10.

Preparative Scale Acetolysis of 6. A 900 mg (3.1 mmol) sample of 6 was dissolved in 25 ml of 0.3 M sodium acetate in acetic acid and sealed in a glass ampule. The ampule was heated at 65 °C for 6 h and cooled before pouring the contents into 60 ml of ice water. The aqueous solution was extracted with ether (3 × 20 ml), and the combined organic layers were washed with saturated sodium bicarbonate solution prior to drying and concentration in vacuo. Molecular distillation of the residue yielded 390 mg (71%) of acetate **9** as a colorless oil shown by VPC analysis to be 99% pure. See text for ^{1}H NMR data.

This material was dissolved in dry ether (5 ml), and this solution was added dropwise to a stirred slurry of lithium aluminum hydride (63 mg) in dry ether (7 ml). The resulting mixture was refluxed gently for 1 h and hydrolyzed by addition of 63 μl of water, 50 μl of 10% sodium hydroxide solution, and 63 μl of water. The ether solution was decanted from the white solids which were then washed with ether. The combined organic phases were dried and evaporated to give 200 mg (86%) of **13** as a colorless oil: $\delta_{Me_4Si}^{CDCl_3}$ 5.63 (m, 2), 3.90 (m, 1), 3.17–0.60 (m, 6), 2.10 (s, 1, −OH), and −0.03 (m, 1); *m/e* 138.1047 (138.1044).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.95; H, 10.38.

***cis*-Bicyclo[6.1.0]non-3-en-6-one (14).** Chromium trioxide (90 mg, 0.9 mmol) was introduced under nitrogen to a magnetically stirred solution of pyridine (144 mg, 1.8 mmol) in 3 ml of methylene chloride. After 30 min, 12.5 mg (0.09 mmol) of **13** was introduced via syringe. After 15 min, the solution was decanted and evaporated. The solid residue was washed with ether (2 × 8 ml) and the combined organic extracts were shaken with 10% hydrochloric acid and saturated sodium bicarbonate solutions, dried, and concentrated. There was obtained 6 mg (60%) of ketone **14** as a colorless oil; $\delta_{Me_4Si}^{CDCl_3}$ 5.67 (m, 2), 3.5–1.3 (series of m, 6), 1.2–0.5 (m, 3), and 0.10 (m, 1); *m/e* 136.0890 (136.0888).

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 78.85; H, 9.33.

Cyclopropanation of 3,6-Cyclooctadienol (16). Diiodomethane (440 mg, 1.64 mmol) was added under nitrogen to 10 mmol of ethylzinc iodide in ether. The resulting solution was heated at reflux for 30 min at which point 100 mg (0.81 mmol) of **16**[13,14] was added via syringe. After an additional 3 h of heating, the solution was poured into 20 ml of cold 10% hydrochloric acid. The ether layer was washed with brine, dried, and evaporated. Preparative scale VPC isolation of the major component (6 ft × 0.25 in. 5% SE-30 on Chromosorb G, 150 °C) furnished 33 mg (30%) of **17**: $\delta_{Me_4Si}^{CDCl_3}$ 5.65 (m, 2), 3.70 (m, 1), 2.8–0.3 (series of m, 9), 2.48 (s, 1, −O*H*), and −0.02 (m, 1); *m/e* 138.1047 (138.1046).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.11; H, 10.39.

Oxidation of this alcohol in the predescribed manner led exclusively to formation of **14.**

Diiodomethane-d_2. Under a nitrogen atmosphere, sodium (2.3 g, 0.01 g-atom) was added in small pieces to deuterium oxide (50 g, 2.5 mol) with vigorous stirring. Diiodomethane (48 g, 0.18 mol) was added, and the mixture was heated overnight at the reflux temperature. The diiodomethane was separated and added to fresh NaOD-D_2O (24 h). The recovered halide was dried and distilled to give 36.4 g (76%) of colorless liquid, bp 81–85 °C (10 mm). ^1H NMR analysis indicated the material to be 99% dideuterated.

***cis*-Bicyclo[5.1.0]oct-2-en-5-ol-*8,8*-d_2 (18).** The zinc–silver couple was prepared by addition of zinc powder (6.2 g, 91 mg-atoms) to 0.5 g of silver acetate in hot acetic acid with vigorous stirring. The acetic acid was decanted, and the couple was washed several times with ether. Dry ether (50 ml) was added followed by 18.0 g (67 mmol) of CD_2I_2 and after 30 min of heating 3,5-cycloheptadienol (1.20 g, 11.0 mmol) dissolved in 10 ml of dry ether was added dropwise. Heating was continued for 48 h at which time the solution was decanted into 100 ml of cold 10% hydrochloric acid. The organic phase was washed further with the acid (2 × 50 ml) and then with saturated sodium bicarbonate solution before drying and evaporation. The product mixture was separated into its three components by preparative VPC at 150 °C (12 ft × 0.25 in. 5% DEGS in Chromosorb G): 327 mg (21%) of **28a**, 160 mg (10%) of **23**, and 211 mg (15%) of **18.**[15]

For **28a**: $\delta_{Me_4Si}^{CDCl_3}$ 4.05 (m, 1), 2.37 (d of t, *J* = 15 and 5.5 Hz, 2 H), 1.48 (m, 2), 1.3–0.4 (m, 4), and 1.08 (s, 1); *m/e* 142.1298 (142.1295).

For **23**: $\delta_{Me_4Si}^{CDCl_3}$ 3.97 (m, 1), 2.25 (m, 2), 1.58 (s, 1), and 1.5–0.3 (m, 6).

***syn,anti*-3,5-Bishomocycloheptadienyl Tosylate-d_2 (21). Reaction of 100 mg (0.794 mmol) of 18** with 41.3 mg (1.0 mmol) of 57% sodium hydride and 96 μl (0.80 mmol) of benzyl bromide as described previously[10] furnished 165 mg (96%) of ether **19.** This material was added to 3 ml of 50% sodium hydroxide solution, 300 μl of benzene, and 0.03 g of triethylbenzylammonium chloride with vigorous stirring. Chloroform (400 μl, 5 mmol) was introduced dropwise via syringe, and the mixture was stirred at room temperature for 2 h before pouring it into water (15 ml). Workup led to isolation of 219 mg (96%) of the dichlorocarbene adduct which was reduced as predescribed[10] with 460 mg of sodium in 5 ml of ammonia containing 370 mg of *tert*-butyl alcohol. The usual processing gave 65 mg (64%) of pale-yellow oil. The crude alcohol was further purified by VPC (150 °C, 5% SE-30 column); 30 mg (29%) of pure **20** was thereby obtained.

Reaction of this material (21 mmol) with 100 mg (0.52 mmol) of *p*-toluenesulfonyl chloride in 1.5 ml of dry pyridine as above afforded 20 mg (33%) of **21,** mp 70–72 °C, after three recrystallizations from pentane.

Acetolysis of 21. The tosylate (20 mg, 0.068 mmol) was dissolved in 1.5 ml of 0.0510 M sodium acetate in acetic acid, heated at 100 °C for 1 h, and poured into cold water. Customary processing provided 12 mg of a colorless oil that was comprised almost solely (>98%) of **22**; $\delta_{Me_4Si}^{CDCl_3}$ 5.63 (d, *J* = 9 Hz, 1), 5.47 (d of d, 1), 4.95 (d of t, 1), 2.92 (m, 1), 2.25–1.92 (m, 2), 2.04 (s, 3), 1.20 (m, 1), 1.1–0.5 (m, 3), and −0.10 (m, 1); *m/e* 182.1279 (182.1276).

***syn,anti*-3,5-Bishomocycloheptadienyl Tosylate-d_4 (24). *p*-Toluenesulfonyl chloride (130 mg, 0.68 mmol) was added to a cooled solution of 23** (60 mg, 0.42 mmol) in 2 ml of dry pyridine. After 48 h at −20 °C, there was obtained a solid which was recrystallized three times from pentane: 25 mg (20%), mp 69–71 °C.

Acetolysis of 24. The above tosylate (25 mg, 0.084 mmol) was dissolved in 1.7 ml of 0.0510 M sodium acetate in acetic acid, heated to 100 °C for 1 h, and worked up as above to give 14 mg (90%) of a colorless oil containing >98% of a single product identified as **25**: $\delta_{Me_4Si}^{CDCl_3}$ 5.63 (d, *J* = 12 Hz, 1), 5.47 (d, *J* = 12 Hz, 1), 4.98 (br s, 1), 2.15 (m, 1), 2.05 (s, 3), 1.33–0.50 (m, 4), and −0.10 (m, 1); *m/e* 184.1403 (184.1401).

Preparative Scale Acetolysis of 7. An 840 mg (2.88 mmol) sample of **7** dissolved in 12 ml of 0.3 M sodium acetate in acetic acid was sealed in a glass ampule and heated at 85 °C for 2 h. Workup in the predescribed fashion and molecular distillation yielded 340 mg (66%) of a colorless oil that contained >99% of a single product. This substance (**27**) was dissolved in dry ether (5 ml) and added dropwise to a stirred slurry of lithium aluminum hydride (50 mg) in dry ether (7 ml). The resulting mixture was gently refluxed for 1 h prior to hydrolysis. There was isolated 200 mg (87%) of **17.**

Acetolysis of 28b. Reaction of **28a** (115 mg, 0.81 mmol) with *p*-toluenesulfonyl chloride (230 mg, 1.2 mmol) in dry pyridine (−20 °C, 24 h) furnished 105 mg (44%) of pure **28b,** mp 55–56 °C. When solvolyzed as before (0.0510 M NaOAc in HOAc, 100 °C, 1 h), there was isolated 46 mg (70%) of a colorless oil containing >98% of acetate **29**; $\delta_{Me_4Si}^{CDCl_3}$ 5.84 (d, *J* = 11 Hz, 1), 5.58 (d, *J* = 11 Hz, 1), 4.74 (br d of d, *J* = 10 Hz, 1), 2.34 (br d of t, *J* = 14 and 3 Hz, 1), 2.01 (s, 3), 1.37 (m, 1), 1.0–0.5 (m, 3), and 0.08 (m, 1); *m/e* 184.1403 (184.1401).

Preparative Scale Acetolysis of 8. A 100-mg (0.31 mmol) sample of **8** dissolved in 10 ml of 0.0510 M sodium acetate in acetic acid was sealed in a glass ampule and heated at 80 °C for 1 h. Product analysis on a 12 ft × 0.25 in. 10% XF-1150 on Chromosorb P column (155 °C) indicated four products to be present in the ratio of 25:11:55:9. The first hydrocarbon isolated proved identical in all respects with *syn*-3,5-bishomocycloheptatriene (**31**).[10] The second hydrocarbon displayed spectral properties identical with those reported for 1,4,7-cyclononatriene (**32**).[25] The major acetate proved to be **27** while the minor acetate was identical with **7**-OAc.

***syn,syn*-3,5-Bishomocycldheptadienyl Acetate (7-OAc).** A solution containing 40 mg (0.29 mmol) of **7**-OH[10] in 2 ml of dry pyridine was added to 300 mg (2.9 mmol) of acetic anhydride and allowed to stand overnight. The mixture was poured into water (20 ml) and the product extracted with ether. Molecular distillation of the oil so obtained provided 38 mg (73%) of **7**-OAc as a colorless oil; ν_{max}^{neat} 1730 cm^{-1}; $\delta_{Me_4Si}^{CDCl_3}$ 5.07 (m, 1), 2.37 (d of t, *J* = 15 and 5 Hz, 2), 2.00 (s, 3), 1.55 (d of t, *J* = 15 and 7 Hz, 2), 1.4–0.4 (m, 6), and 0.20 (m, 2); *m/e* 180.1154 (180.1150).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.41; H, 8.95.

Kinetic Studies. A. Preparation of Reagents. Dry acetic acid was prepared by distillation of glacial acetic acid from acetic anhydride. Perchloric acid (70%) was standardized against sodium hydroxide with phenolphthalein indicator. Standard perchloric acid in acetic acid was prepared by weighing the standard perchloric acid into a volumetric flask and filling to the mark with dry acetic acid.

Standard sodium acetate in acetic acid was prepared by weighing dry sodium carbonate (flame dried and allowed to cool in a desiccator) into a volumetric flask and filling to the mark with dry acetic acid. The water of neutralization was not removed. After standing for 1 week, the sodium acetate in acetic acid solution was standardized against the perchloric acid in acetic acid solution using bromophenol blue indicator.

B. Determination of Data. Solutions of tosylates **6**, **7**, and **8** in buffered acetic acid were prepared by weighing the appropriate tosylate into a 10.0-ml volumetric flask and filling to the mark with 0.0510 *M* sodium acetate in acetic acid. The concentration of tosylate varied from 0.0114 M to 0.0224 M over all runs. The resulting solution was divided into nine glass ampules which were sealed under partial

vacuum. All ampules were simultaneously immersed into a constant temperature bath. After 5 min, one ampule was removed from the rate bath and placed in an ice water mixture. A timer was started upon removal of the first ampule. The remaining ampules were removed and cooled at appropriate intervals covering 2 to 3 half-lives. The final amuple was removed after at least 10 half-lives to give an infinity point. The individual ampules were allowed to warm to room temperature, at which point a standard aliquot was removed, diluted with 1 ml of dioxane, and titrated against 0.0192 M perchloric acid in acetic acid using one drop of bromophenol blue indicator. First-order rate data was determined by measuring consumption of tosylate by acetolysis relative to the experimental infinity point. Duplicate runs agreeing within 3% were made at all temperatures.

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The Fate of Bishomocycloheptadienyl Cations Generated by Deamination

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Abstract: Preparations of *anti*- and *syn*-3,5-bishomocycloheptadienone tosylhydrazones (**10b** and **11b**) together with the anti- and syn-2,5-bishomo isomers (**14b** and **17b**) are described. Photodeamination of **10b** in methanol gave olefin **19** (3%) and ethers **20** (19%) and **21** (78%). Under similar conditions, **11b** was converted to olefin **22** (12%) and a mixture of eight ethers. Seven of these have been identified: **21** (3%), **23** (19%), **24** (11%), **25** (22%), **26** (6%), **27** (22%), and **28** (2%). The ninth component (3%) remains uncharacterized. The anti-2,5-bishomo tosylhydrazone **14b** was more well behaved, giving **12** (11%), **21** (24%), **28** (11%), and **46b** (54%), while **17b** upon comparable deamination returned only ether **25** (99%) and a trace of olefin **15**. The product distributions in aqueous alkaline solution were also examined. The various interconversions, which differ appreciably from those encountered in acetolysis of the corresponding tosylates, are explained in terms of vertical ionization concepts. These arguments are supported by the solvolytic behavior of the tosylates in the common solvent methanol. The varied degrees of complexity arise because of the critical interdependence of the mutual geometry of the cyclopropane rings and the developing cationic center which in turn dictates the level of molecular rearrangement, the extent and stereochemistry of solvent capture, and the possibility of deprotonation. Thermodynamic considerations also gain importance in certain cases, although they never seem to dominate over kinetic control.

The *anti*- and *syn*-3,5-bishomocycloheptadienyl cations (**1** and **2**) have evoked interest in connection with the questions of the extent and stereochemical dependence of long-range cyclopropane participation. Acetolysis of tosylate **3** resulted in efficient conversion (>98.5%) to **4a** via a deep-seated rearrangement involving rupture of both original cyclopropyl groups and ultimate reconstruction of a third, different three-membered ring.[2] Acetolysis of **5a** revealed the operation of an identical bond reorganization; however, the stereochemical outcome was now diametrically opposite (>98.5%