Synthesis and Protonation Studies of *syn*- and *anti*-2,4-Bishomotropone. Comparison with the Behavior of Epimeric 2,4-Bishomocycloheptatrienols under Long- and Short-Lived Ionization Conditions

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Abstract: Preparations of *syn*- and *anti*-2,4-bishomotropone (**7** and **11**) as well as the four possible epimeric 2,4-bishomocycloheptatrienols are described. When dissolved in FSO_3H–SO_2ClF below −100 °C, all four alcohols are converted efficiently and rapidly to the *syn*-1,3-bishomotropylium cation (**3**). Under similar conditions, **7** and **11** undergo reversible protonation. However, the conjugate acid of **11** gives indication of extended homoconjugation as denoted by **13**, while protonated **7** does not. The extent of cyclic delocalization in **13** is expectedly attenuated relative to that present in **3**. Protonation of *cis*[3]-2,4,7-cyclononatrienol (**12a**) also gives rise to **3**, thus demonstrating the feasibility of an all-π route to this cation. Solvolyses of the four 2,4-bishomocycloheptatrienyl *p*-nitrobenzoates in 80% aqueous acetone proceeded with clean first-order kinetics, but with a relative rate spread of only 3.2 at 48.9 °C. Methanolysis experiments showed alkyl–oxygen cleavage to be occurring in each of the examples. Products studies showed the anti derivatives **5b** and **6b** to retain their tricyclic structure and the syn derivatives **9b** and **10b** to be converted almost totally (>95%) to monocyclic alcohol **12a**. Deuterium labeling in the first series provided indication of the intervention of a symmetrical allylic cation or a rapidly interconverting pair of unsymmetrical nonplanar cations. Under short-life conditions, these do not experience opening of their cyclopropane rings, although such is possible when thermodynamic control takes over. Because of more favorable electronic factors, derivatives in the syn series appear to proceed from allyl cation intermediates to **3** with only a small energy barrier.

The impressively regiocontrolled electrophilic additions to *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**1**) have elicited much interest in the recent literature.[2-6] Although attack on **1** can in principle occur at C_2, C_3, or C_4, the relative nucleophilicity of C_3 is overwhelmingly dominant, apparently because the resonance-stabilized cation **2** is generated initially. The intervention of **2** has not been demonstrated experimentally. Rather, its involvement has been rationalized on the basis of the nearly perfect alignment of the developing vacant p orbital at C_2 with the internal cyclopropyl bond and the least motion minimal readjustment of bond angles which ensues. The level of delocalization in transoid **2** is understandably uncertain; however, if a closed circuit were to result, the cation would comprise a fascinating double Möbius bishomotropylium network. Presumably in order to achieve enhanced charge dispersal, one of the methylene bridges in **2** is believed to experience subsequent conformational inversion to deliver the more thermodynamically stable and spectroscopically detectable syn isomer **3**. The latter constitutes the only example

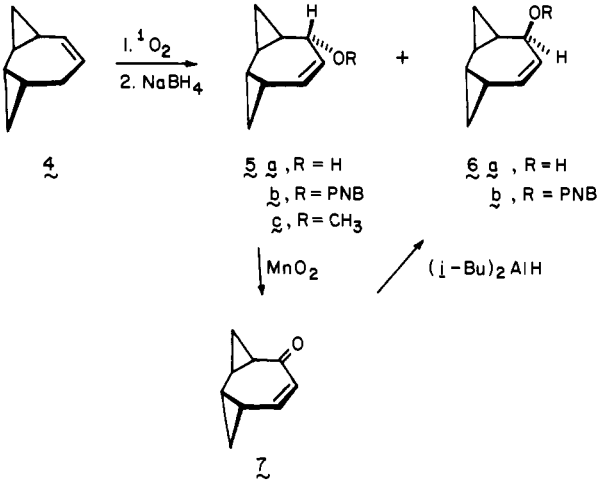
1 **2** **3**

of an *unbridged* 1,3-bishomotropylium cation known to this time.[7] That bonding to **1** occurs stereoselectively from the exo direction with electrophiles larger than D^+ [2,6] has been demonstrated through utilization of various uniparticulate electrophiles.[3,4] The requisite intervention of the folded conformation (as illustrated) was established by examining the reactivity of its *syn*- and *anti*-9-methyl derivatives.[6] The former is prevented by obvious steric factors from attaining a coiled geometry and is unreactive to conditions which rapidly transform the anti stereoisomer to a bishomotropylium species.

Despite the scope of these early investigations, a number of important and fundamental questions have been left unanswered. For example, we remain ignorant of the barrier to bridge flipping in **2**, if such is possible at all. Should the transoid cation prove to be a bona fide intermediate, then an appropriate detailed description of its electronic character is certainly warranted. And what are the limits of ring substitution? Because of our long-standing interest in the question of homoconjugative stabilization, we undertook a study of the preparation and protonation of the *syn*- and *anti*-2,4-bishomotropones, as well as a detailed investigation of the behavior of the four possible epimeric 2,4-bishomocycloheptatrienols under long- and short-lived ionization conditions. By incorporating the desired stereochemical features directly into our substrate molecules, a more precise assessment of the stereoelectronic requirements for σ-homoaromaticity is thereby made possible. The results were expected to provide a test of the importance of geometry to attainment of 1,3-bishomotropylium ion character.[8]

Synthetic Considerations. *anti*-2,4-Bishomotropone (**7**) was conveniently prepared by the sequence outlined in Scheme I. Exposure of the previously described *anti*-3,5-bishomocyclo-

Scheme I



4 **5** a, R = H; b, R = PNB; c, R = CH_3 **6** a, R = H; b, R = PNB **7**

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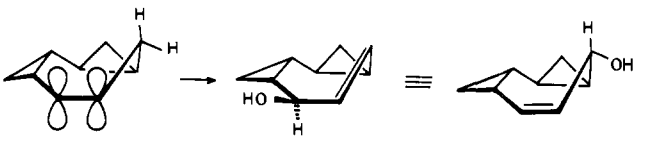
heptatriene (**4**)[9] to singlet oxygen, generated at 0 °C by irradiation (tungsten lamp) of dichloromethane–methanol (9:1) solutions containing rose bengal as sensitizer, and subsequent sodium borohydride reduction of the intermediate hydroperoxides provided a mixture of the epimeric allylic alcohols **5a** (89%) and **6a** (11%). Structural assignment to the major component, which could readily be obtained in pure form by fractional crystallization, is founded upon ^{1}H NMR spectral data, mechanistic considerations, and further chemical modification. Thus, its *H*COH proton appears at δ 4.03, while that in **6a** appears at considerably lower field (δ 4.62). According to the usual shielding parameters associated with epimeric cyclopropylcarbinyl alcohols,[10] that isomer with the more shielded proton α to hydroxyl has this hydrogen disposed syn to the adjacent cyclopropane ring. The structure given **5a** agrees with this generalization.

Furthermore, an examination of molecular models of **4** reveals that the σ bond connecting C_7 to its endo proton is stereoelectronically aligned in plane with the pπ orbitals of the adjacent olefinic linkage as is evident in A.[11] Preferential attack of singlet oxygen on the top face (as drawn) of this conformationally stable hydrocarbon[9] such that this hydrogen is



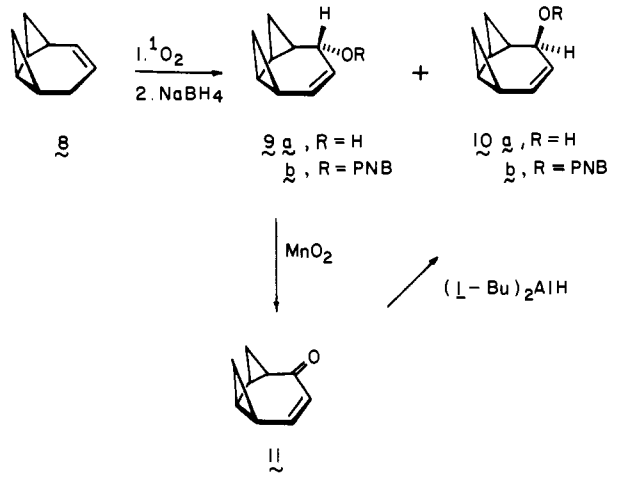
A B B′

eventually abstracted would lead to B (or **5a**) after reduction. As perhaps revealed more clearly in B′, the hydroxyl group in **5a** is equatorially disposed. If these conclusions are correct, then **6a** should carry an axial OH substituent.

Oxidation of the epimeric alcohol mixture with activated manganese dioxide in refluxing cyclohexane gave a single ketonic product identified as **7**. The two olefinic protons of this enone appear as a doublet of doublet of doublets (J = 12, 7, and 1.5 Hz) at δ 6.48 and a broadened doublet at δ 5.38 (J = 12 Hz). Its infrared spectrum shows an intense carbonyl stretch at 1635 cm^{-1} and its electronic absorption spectrum in ethanol features a single maximum at 263 nm (ϵ 4500). Reduction of **7** with diisobutylaluminum hydride in ether at −78 °C[12] gave an 84:16 mixture of **6a** and **5a**, respectively. The dominant alcohol proved to be identical with the minor component of the photooxygenation mixture. As expected, hydride delivery from the less hindered pseudoequatorial surface of **7** projects the hydroxyl group axially into the same face of the molecule as the proximal cyclopropane ring.

Comparable photooxygenation of **8**[9] gave rise to a somewhat more complex mixture of alcohols. High-pressure liquid chromatographic purification of the crude product on Florisil afforded two principal fractions, the more rapidly eluted component of which (80%) contained **9a** and **10a** in a 75:25 ratio (Scheme II).[13] Since the α hydroxyl protons of these epimers have chemical shifts of δ 4.35 and 4.82, respectively, the major constituent was construed to be the anti alcohol. This conclusion receives further substantiation from stereoelectronic considerations which show the anti H_7 proton in **8** to be projected axially in a direction nearly parallel to the plane defined by the π bond (see C). Additionally, manganese dioxide oxidation of the alcohol mixture gave pure **11** whose reduction with diisobutylaluminum hydride returned **9a** and **10a** in a 14:86 ratio. Although **10a** could be isolated in pure form by fractional crystallization of this latter mixture, attempts to obtain **9a** in comparable analytical purity suffered from the proclivity of these alcohols for rearrangement upon column or gas-phase chromatography. However, prior conversion of these alcohols to their *p*-nitrobenzoates made it possible to isolate

Scheme II

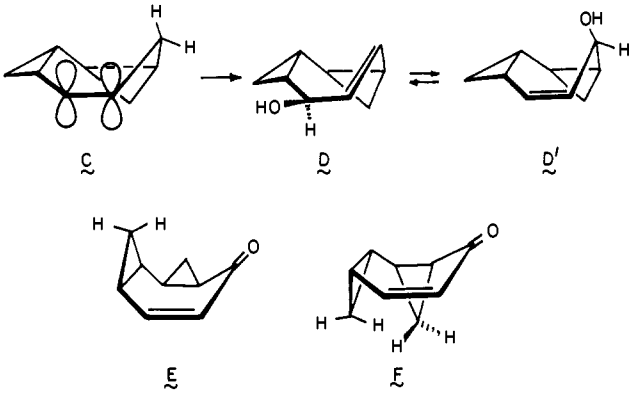


8 9a, R = H; 9b, R = PNB 10a, R = H; 10b, R = PNB 11

quantities of both **9b** and **10b** free of epimeric contaminants.

syn-2,4-Bishomotropone (**11**) displays its olefinic protons as a doublet of doublets at δ 6.33 (J = 12 and 3 Hz) and a doublet of triplets (J = 12 and 0.8 Hz) at 5.61. A carbonyl stretching frequency of 1650 cm^{-1} and an electronic maximum in ethanol at 225 nm (ϵ 5200) round out its spectral profile.

In contrast to the preferred conformation of *anti*-2,4-bishomotropone (**7**) where both cyclopropanes presumably adopt pseudoequatorial positions, syn isomer **11** must necessarily have one pseudoaxial and one pseudoequatorial cyclopropane ring. Molecular models suggest that nonbonded repulsive interactions between the cyclopropyl methylene hydrogens are notably greater in F than in E and that E should



C D D′ E F

consequently be preferred. This conclusion is supported by the DIBAL-H results, where approach of the reducing agent from the pseudoequatorial direction predominates to give chiefly syn alcohol **10a**. Comparable attack on F would deliver **9a** as the major product, but this is not seen.

Additional evidence that **7** and **11** differ in their ground-state conformations is provided by their spectra. Thus, while the chemical shift difference between the olefinic protons in **7** is 1.10 ppm, the comparable $\Delta\delta$ for **11** is only 0.72 ppm. Furthermore, the electronic absorption maximum for **7** appears at 263 nm, substantially more bathochromically shifted than that exhibited by **11** (225 nm). These data suggest that a higher degree of planarity exists in the enone segment of **7**, since conjugative overlap is directly relatable to this parameter.[14]

Experiments Conducted under Long-Life Conditions. When a CD_2Cl_2 solution of **9a** or **10a** was mixed with FSO_3H–SO_2ClF (1:3 v/v) at −140 °C, there was formed a yellowish solution whose NMR spectra (recorded at −100 °C, Table I) proved to be identical with those of **3** previously generated by protonation of **1**.[2,6] The minor shift differences can be attributed to slight alterations in solvent composition as well as to

Table I. NMR Data for 1,3-Bishomotropylium Cation **3**

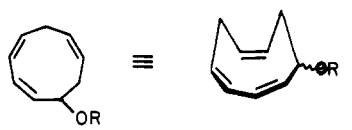
proton	chemical shift[a,b]	carbon	chemical shift[a,c]
H_3	9.08	3	181.4
H_2, H_4	7.98	2, 4	165.9
H_1, H_5	7.18	1, 5	139.2[d]
H_6, H_7	7.00	6, 7	135.2[d]
H_{8_o}, H_{9_o}	3.84	8, 9	29.8
H_{8_i}, H_{9_i}	1.89		

[a] δ, parts per million from Me_4Si. [b] Internal $CHDCl_2$ as standard. [c] External $CHDCl_2$ as standard. [d] Interchangeable values.

the changeover from an internal to an external reference signal.

Having established the susceptibility of this allylic alcohol to rapid and efficient ionization at low temperatures, we proceeded to examine **5a** and **6a** under comparable conditions. The intent here, of course, was to make possible the direct observation of **2**. Individual submission of these anti allylic alcohols to the same treatment with comparable temperature control and direct NMR observation at −100 °C showed the same spectra to be produced in both instances. These were identical with the spectra of **3** obtained by the methods discussed earlier. Clearly, cation **3** is considerably more stable than **2**, the thermodynamic driving force provided by the attainment of *syn*-1,3-bishomotropylium character seemingly being large enough to permit rupture of an internal cyclopropane σ bond and configurational inversion of the two carbons which become disconnected.

Ion **3** can be viewed as the result of strong interaction between a pentadienyl cation segment and an ethylenic moiety. However, this species had thus far been generated rather indirectly: (a) by combination of an allyl cation with two cyclopropane σ bonds as in the protonation-dehydration of **5a**, **6a**, **9a**, or **10a**, or (b) by combination of a pentadienyl cation with one cyclopropane σ bond as in the protonation of **1**. Therefore, it remained to demonstrate the all-π approach to **3** and the behavior of *cis*[3]-2,4,7-cyclononatrienol (**12a**) in magic acid was



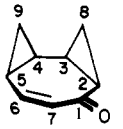
12 a, R = H
b, R = CH_3

examined. Alcohol **12a** was readily prepared by the method of Winstein[15] and subjected to the previously described reaction conditions. Comparably efficient conversion to **3** was observed.

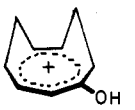
Theory predicts that the majority of the charge within **3** should reside in its pentadienyl segment.[2] Notwithstanding, all attempts to quench this cation with sodium methoxide solutions in methanol at −78 °C returned only polymeric materials.

In anticipation that some distinction between cations of type **2** and **3** might prove feasible through attenuation of the level of charge which is delocalized into the ring, protonation studies of ketones **7** and **11** were subsequently undertaken. The positive charge created by protonation of the carbonyl oxygens is certain to be more highly localized on the enone segments of these molecules.[8,16] We reasoned that as the thermodynamic driving force leading to the bishomoaromatic species is reduced, the tendency for cyclopropane bond rupture and ring inversion in the starting framework should be proportionately decreased. The magnetic resonance spectra of **7**, **11**, and their conjugate acids generated in FSO_3H-SO_2ClF are compared in Tables II and III. The indicated spectral parameters remained unchanged over the temperature range −100 to −65 °C. Also, quenching of these solutions with sodium acetate returned the bishomotropones.

Table II. NMR Data for Neutral and Protonated **11**



11



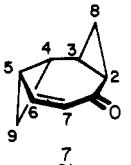
13

proton	chemical shift[a] unprotonated[b]	chemical shift[a] protonated[c]
H_7	6.33	8.39
H_6	5.61	6.84
H_2, H_5	2.08	3.39
H_3, H_4	1.53	2.31
H_{8_o}, H_{9_o}	1.02	2.31, 2.87
H_{8_i}	0.70	1.70
H_{9_i}	0.25	0.76

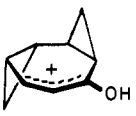
carbon	chemical shift[a] unprotonated	chemical shift[a] protonated	Δδ
C_1	202.3	212.5	10.2
C_6	136.6	168.4	31.8
C_7	127.6	117.8	−9.8
C_2	33.0[d]	35.8[d]	2.8
C_5	19.8[d]	35.8[d]	16.0
C_3	17.1[d]	19.9[d]	2.8
C_8	15.7[e]	12.8[e]	−2.9
C_4	14.4[d]	27.2[d]	12.8
C_9	11.8[e]	12.3[e]	0.5

[a] δ, parts per million from Me_4Si. [b] Internal Me_4Si as standard. [c] External Me_4Si as standard. [d,e] Interchangeable values.

Table III. NMR Data for Neutral and Protonated **7**



7



14

proton	chemical shift[a] unprotonated[b]	chemical shift[a] protonated[c]
H_7	6.48	8.32
H_6	5.38	6.29
H_2, H_5	1.92	2.98, 3.35
H_3, H_4	1.47, 1.70	2.98
H_{8_o}, H_{9_o}	1.33	2.57
H_{9_i}	1.33	2.24
H_{8_i}	0.69	2.24

carbon	chemical shift[a] unprotonated[b]	chemical shift[a] protonated[c]	Δδ
C_1	202.2	213.3	11.1
C_6	143.9	180.3	36.4
C_7	125.0	114.8	−10.2
C_5	28.4	41.3[d]	12.9
C_2	25.8	35.6[d]	9.8
C_9	23.1	36.9[e]	13.8
C_4	23.0	29.0[d]	6.0
C_8	17.9	33.8[e]	15.9
C_3	17.3	22.9[d]	5.6

[a] δ, parts per million from Me_4Si. [b] Internal Me_4Si as standard. [c] External Me_4Si as standard. [d,e] Interchangeable values.

The protonation of **11** is accompanied by substantial increases in the chemical shift separation (Δδ) of both the olefinic protons (0.72 → 1.55 ppm) and the cyclopropyl methylene

pairs H_{8_i}, H_{8_o} (0.32 → 1.17) and H_{9_i}, H_{9_o} (0.77 → 1.55). In the latter instance, the enhanced $\Delta\delta$ values arise chiefly because of substantially increased shielding of the inside protons. Comparison of the ^1H NMR data for **7** and its conjugate acid reveals the separation of the olefinic protons again to increase significantly (1.10 → 2.03), but the $\Delta\delta$ for the cyclopropyl methylene protons to converge to only 0.33 ppm in acid solution. These observations are reconcilable with the following conclusions: (a) the positive charge is somewhat more localized on the protonated enone segment of **14** as compared to **13**; (b) syn isomer **13** possesses a modest ring current while anti isomer **14** does not. In this connection, we see that the $\Delta\delta$'s of inside and outside cyclopropyl methylene protons in **13** (1.17–1.55 ppm) resemble more closely than those in **14** (0.33) the separation observed for the comparable hydrogens in **3** (1.95 ppm).

To achieve effective homoconjugation in **13**, the seven-membered ring must approach at least a shallow boat conformation. In this geometry, the two cyclopropane rings adopt pseudoaxial positions. Since the two inside protons do come into somewhat closer proximity (Dreiding models), one might argue that this increased steric compression will engender van der Waals shielding of H_{8_i} and H_{9_i}[17] and upfield shifting of H_{8_o} and H_{9_o}.[18] Although there may be a small contribution of this sort, the steric interactions are not so severe as to account for the observed magnitudes of the $\Delta\delta$ terms.

The ^{13}C NMR data likewise support the conclusion that **13** partakes of some charge delocalization. Although we cannot dismiss the possibility that conformational differences may affect to a certain extent the $\Delta\delta$ changes noted between the neutral and protonated bishomotropones, several significant differences are seen within the two stereoisomeric series. For example, the conversion of **11** to **13** is accompanied by an increase in the $\Delta\delta$ of C_6 and C_7 amounting to 41.6 ppm (Table II). For the **7** → **14** change, the increase in $\Delta\delta$ is 46.6 ppm, in line with the enhanced localization of positive charge on C_1–C_7–C_6 in **14**. Moreover, cyclopropyl carbons C_8 and C_9 in **14** are deshielded by a total of 30 ppm relative to their position in **7**. In the case of **13**, one of these carbons is actually somewhat shielded as would be expected if charge was dissipated through the seven basal carbons. Unfortunately, unambiguous assignments cannot be made by ^{13}C NMR to C_2–C_5 which might permit better assessment of the magnitude of the ring current. However, the combined ^1H and ^{13}C NMR evidence suggests that **13** is best represented as a hydroxylated 1,3-bishomotropylium cation. It remains important to recognize, however, that the ring current in **13** is markedly diminished relative to that in parent carbocation **3**.

Short-Lifetime Solvolysis Experiments. The divergent topology of the four *p*-nitrobenzoate esters **5b**, **6b**, **9b**, and **10b** provides a richly varied array of structural features for examining possible 1,3-bishomotropylium cation generation under solvolytic conditions. These esters were prepared in conventional fashion and solvolyzed in both 80% aqueous acetone and methanol–tetrahydrofuran (3:1) solution. The results are detailed on an individual basis below. The simplified nomenclature which is utilized here describes the stereochemical relationship of the *p*-nitrobenzoate substituent with the adjacent cyclopropane ring followed by a descriptor for the mutual stereodisposition of the two cyclopropane rings.

The Syn,Anti System. Owing to the orientation of the cyclopropane rings in **6b**, possible anchimeric assistance to departure of the *p*-nitrobenzoate anion is restricted to the flanking three-membered ring. The remote cyclopropane ring is not favorably disposed either for neighboring group participation during solvolysis or for conjugative interaction with the second three-membered ring.

Titrimetric solvolysis rates for **6b** determined in 80% aqueous acetone by the aliquot method showed good first-order behavior throughout (Table IV). Since the infinity titers invariably agreed well with the calculated values, internal return to a less reactive *p*-nitrobenzoate was not an issue. The product mixture was comprised of alcohols **5a** and **6a** in a ratio of 88:12, respectively. Solvolysis of **6b** in methanol–tetrahydrofuran (3:1) gave only the methyl ether **5c**. An independent synthesis of **5c** was realized by methylation of **5a** with sodium hydride and methyl iodide in tetrahydrofuran. The absence of alcohols in the methanolysis experiments is indicative of exclusive alkyl oxygen cleavage in the solvolysis process.

The Anti,Anti System. The mutual stereodisposition of the cyclopropane rings in **5b** is, of course, identical with that which exists in **6b**. However, the altered orientation of the leaving group now allows only for the possibility that the remote cyclopropane ring become involved during the rate-determining step. However, because of ring size constraints, such a transannular interaction was considered rather unlikely.

Ester **5b** was again well behaved kinetically. The rate data show **5b** to undergo ionization twice as fast as **6b** at 48.9 °C. When conducted on a preparative scale, the solvolysis gave an 89:11 mixture of **5a** and **6a**, respectively. Methanolysis led exclusively to **5c**.

The Anti,Syn System. Neither cyclopropane ring in **9b** is favorably aligned to enter directly into participation as the *p*-nitrobenzoate anion departs. However, their syn arrangement is favorable for reasonable conjugative interaction.[19]

The behavior of **9b** in 80% aqueous acetone was of equally good quality. The rate constants denote that its reactivity is only slightly greater than that of **6b** at 48.9 °C (Table IV). The product mixture was composed chiefly (>95%) of an alcohol identified as **12a**. A second minor component was not investigated. Methanolysis afforded a comparable product mixture in which **12b** predominated (>95%).

Table IV. Kinetic Data for *p*-Nitrobenzoate Solvolysis in 80% Aqueous Acetone

compd	temp, °C	k,[a] s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$k_{rel}^{48.9°}$
5b	34.1	5.09×10^{-5}			
	41.6	1.07×10^{-4}	18.8 ± 0.3	−17 ± 1	3.2
	49.9	2.42×10^{-4}			
	48.9	2.18×10^{-4} [b]			
6b	33.9	1.95×10^{-5}			
	40.6	4.49×10^{-5}			
	48.6	9.91×10^{-5}	21.2 ± 0.7	−11 ± 2	1.6
	48.9	1.09×10^{-4} [b]			
9b	34.9	3.03×10^{-5}	22.1 ± 0.4	−7 ± 1	2.3
	48.9	1.53×10^{-4}			
10b	34.9	1.32×10^{-5}			
	42.4	3.34×10^{-5}	22.6 ± 0.6	−8 ± 2	1
	48.9	6.80×10^{-5}			

[a] Average of duplicate runs. [b] Interpolated valued based on the activation parameters.

The Syn,Syn System. The topology of **10b** is seemingly such that both cyclopropane rings appear favorably aligned for potential anchimeric assistance during ionization. From conformational and stereoelectronic considerations alone, **10b** was felt to be the most suitably constructed molecule of the set for attaining maximum conjugative interaction at the onset of solvolysis.

In 80% aqueous acetone, **10b** also exhibited good first-order behavior. However, this *p*-nitrobenzoate was the least reactive of all! The product mixtures realized in aqueous and methanolic solvents were identical with those previously obtained with **9b**.

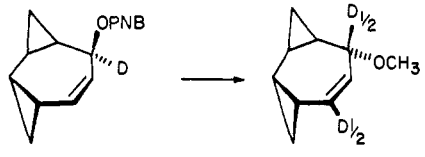
In order to contrast the products of kinetic control with those of thermodynamic control, the four relevant bishomocycloheptatrienols were treated with hydrochloric acid in aqueous tetrahydrofuran. In each instance, the predominant (>95%) product to result was 2,4,7-cyclononatrienol (**12a**).

The kinetic and thermodynamic data in Table IV provide no evidence that cyclopropyl assistance to ionization is important to any of the isomers. The great similarity of the rate constants throughout the series might be accounted for in terms of a leveling effect brought about by the driving force to generate an allyl cation. Wiberg and Nakahira have previously shown, however, that *p*-nitrobenzoate and 3,5-dinitrobenzoate esters of optically active medium-ring allylic alcohols need not proceed to symmetrical cations on solvolysis.[20] These investigators also advanced the somewhat revolutionary idea that olefinic participation may be unimportant in such molecules at the time of C–O bond heterolysis. Interestingly, the kinetic profile for 2-cycloheptenyl *p*-nitrobenzoate[20] is entirely similar to those evaluated experimentally in the present study.

The nearly identical nature of the product mixtures afforded by **5b** and **6b** argues for the intervention of a common intermediate. The C_2 symmetric allylic cation H could be implicated, although the strain introduced when all seven basal carbons are maintained in a coplanar arrangement might cause this structure to be somewhat unattractive energetically. The twisted allyl cations G and I, on the other hand, appear to incorporate significantly lesser levels of strain. Their interconversion would require passage through H as a transition state.

G H I

In order to gain information on this point, **7** was reduced with sodium borodeuteride and the labeled *p*-nitrobenzoate (**15**) was subjected to methanolysis. Conversion to a static



15 16

unsymmetrical cation such as G would generate products with the deuterium localized at the site of solvent capture. Alternatively, the intervention of symmetrical allylic cation H or a rapidly equilibrating pair of unsymmetrical cations (G ⇄ I) would afford products in which the deuterium is virtually equally distributed between the two termini. A 3:1 ratio of olefinic to *H*CO– signal intensities would then be observed. The experimentally determined ratio was 2.7:1. This result is seen to be consistent with dominant intervention of H or G ⇄ I.

The products which arise from **5b** and **6b** agree with either possibility. Although planar species H has four positions available for solvent capture, the two furthest removed from the proximal environment of the cyclopropane rings should be heavily favored and lead chiefly to **5**. For G and I, nucleophilic bonding should occur with greater facility from the pseudoequatorial direction to again deliver predominantly **5**.

The comparable nature of the solvolysis products from **9b** and **10b** also suggests that these epimers pass through a common intermediate upon ionization. Again, an allylic cation is probably generated first and this species may be C_s symmetric

J K L

(K) or unsymmetric (J, L). In contrast to H, the internal bent σ bonds in K project into the same surface above (or below) the basal plane and the development of homoconjugative interactions is geometrically feasible. For H, the development of extended cyclic conjugation would require the cation to have a double Möbius nature. This does not develop under the conditions of solvolysis. Although there is no kinetic evidence for significant rate acceleration with **9b** and **10b**, the products nevertheless must derive from a monocyclic intermediate. The subsequent conversion of K to the product-determining 1,3-bishomotropylium cation (**3**) is consequently impeded by only a small barrier.

It remains possible that the rate data do not provide adequate insight into the nature of the intermediates formed during the solvolysis of **9b** and **10b** and that direct conversion to **3** occurs. This is considered unlikely because of the divergent stereoelectronic factors present at the functionalized carbon (C_1) of these *p*-nitrobenzoates as discussed above.

More enlightening with regard to the generation of 1,3-bishomotropylium ions are the observed conversions of all four bishomocycloheptatrienols to **12a**. These results demonstrate that cation **3** is a thermodynamic sink for the series. Alcohols **5a** and **6a** probably proceed to **12a** by a stepwise route involving two consecutive cyclopropylcarbinyl–homoallyl rearrangements and inversion of one methylene bridge (see below).

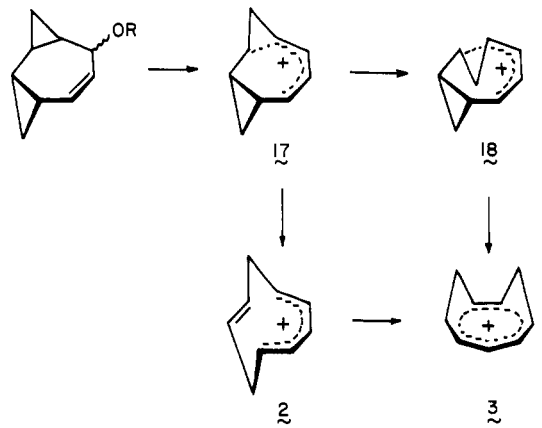
Summary and Conclusions

The principal objectives of this research were to gain evidence for the possible intervention of cation **2**, to elucidate its relationship to **3**, and, if possible, to obtain some information about its electronic character. Through adoption of the σ route to this pair of cations, the consequences of widely divergent orbital arrangements have been made quite clear. As we have seen, solvolysis of syn *p*-nitrobenzoates **9b** and **10b** leads directly to *cis*[3]-2,4,7-cyclononatrienol. Under comparable short-life conditions, the anti *p*-nitrobenzoates undergo alkyl–oxygen cleavage with retention of their tricyclic structure. Other results from deuterium labeling experiments have established that symmetrization of the anti allylic cation does occur during the ionization process prior to solvent capture. Clearly, there exists a deterrent against facile conversion to **2** or its equivalent (see below) when entering the manifold from this direction.

This phenomenon is further revealed in the conjugate acids of bishomotropones **7** and **11**. The extent of homoconjugative delocalization of **13**, although notably less than that prevailing in **3**, is quite good when the usual localizing effect of a carbonyl oxygen is taken into account. In **14**, the positive charge is heavily concentrated on the allyl segment.

Under conditions where thermodynamic control can operate, **5a** and **6a** are likewise converted to **12a**. Inversion of a methylene bridge is required to account for this phenomenon. Al-

though both cyclopropane rings in these molecules are required to experience rupture of their central bonds, our data provide no insight into the timing of these events. It is not plausible to invoke simultaneous cleavage of these bonds. Rather, a stepwise process takes proper account of the structurally enforced orientation of these bent sigmoid orbitals. Initial conversion to **17** is therefore mandated. The positive charge which is thereby relegated to the terminal cyclopropylcarbinyl carbon undoubtedly triggers subsequent opening of the second three-membered ring. However, the question of whether bridge inversion to deliver **18** precedes this final event cannot be determined presently. It will be recalled that NMR analysis at −100 °C and below provided no evidence for the transient



formation either of **17**, **18**, or **2**. Should **17** first isomerize to **18**, then **2** is by-passed completely. Alternatively, passage of **17** to **2** shunts **18** from the mechanistic picture. Clearly, the electronic state of affairs which is present in **2** and **17** is not energetically tolerable. But until either cation can be seen spectroscopically, the details of its charge distribution and the like remain unavailable.

What is no longer in doubt is the feasibility of bridge flipping within these intermediates. Cations **2** or **17** can therefore account for the behavior of *cis*-bicyclo[6.1.0]nonatriene toward electrophilic reagents.

The remaining point to be addressed is the almost identical kinetic behavior of the four *p*-nitrobenzoates whose syn/anti rate ratios differ merely by a factor of 2. If one makes the reasonable assumption that conversion to similar types of allylic cations occurs in each instance, then these data become comprehensible. The charged intermediates may be planar or have folded conformations which are capable of rapid interconversion. Since there is no rate acceleration of any sort, it would seem clear that the cyclopropane rings, whatever their stereochemical relationship to the leaving group, do not provide anchimeric assistance in the rate-determining step. If this is so, then some inductive rate retardation should be evident. This conclusion is consistent with the limited data available.[20] Of course, stereoelectronic factors do enter the picture during subsequent conversion to product.

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 a Bruker spectrometer. Mass spectra were measured on 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.

Photooxygenation of 4. To a solution of 200 mg of rose bengal in 20 mL of methanol was added 1.00 g (8.35 mmol) of **4** dissolved in 180 mL of dichloromethane. The resulting solution was placed in a photolysis vessel equipped with a gas inlet frit at its base. The vessel was immersed in an ice water bath and a slow stream of oxygen was bubbled through the solution. Irradiation of the reaction mixture with a 600-W DYV tungsten projector lamp contained in a quartz well was continued for 11 h at 0 °C. Sodium borohydride (0.76 g, 80 mequiv) was added, and the resulting mixture was allowed to stir for 2 h at room temperature. The organic solution was washed with water (3 × 100 mL), dried over magnesium sulfate containing activated carbon, and concentrated to yield 0.94 g (83%) of a pale yellow oil that proved to be a 6:1 mixture of epimeric alcohols. Recrystallization from low-boiling petroleum ether gave 0.26 g (23%) of **5a** as a white, crystalline solid: mp 65–67 °C; ^{1}H NMR (CCl_4) δ 5.70 (dd, J = 10.5 and 4 Hz, 1 H), 5.38 (d, J = 10.5 Hz, 1 H), 4.03 (m, 1 H), 2.78 (br s, 1 H), 0.98 (m, 6 H), 0.53 (m, 1 H), and 0.05 (m, 1 H); ν_{max} (KBr) 3360, 3070, 3035, 3000, 1650, 1440, 1390, 1300, and 1040 cm^{-1}; *m/e* 136.0890.

***anti,anti*-2,4-Bishomocycloheptatrienyl *p*-Nitrobenzoate (5b).** A 224-mg (1.65 mmol) sample of **5a** was dissolved in 10 mL of pyridine and 400 mg (2.0 mmol) of *p*-nitrobenozyl chloride was added. The resulting mixture was allowed to stir at room temperature for 4 h prior to dilution with 50 mL of water and extraction into ether (2 × 25 mL). The combined ether extracts were washed with cold 10% hydrochloric acid and saturated sodium bicarbonate solutions, dried, and concentrated to yield an off-white, crystalline solid. Recrystallization from hexane yielded 284 mg (60%) of pure **5b**: mp 125.0–125.5 °C; ^{1}H NMR ($CDCl_3$) δ 8.18 (s, 4 H), 5.78–5.25 (series of m, 3 H), 1.67–0.42 (series of m, 7 H), and 0.30 (m, 1 H); *m/e* 285.1003.

Anal. Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.39; H, 5.43; N, 4.89.

***anti*-2,4-Bishomotropone (7).** Activated manganese dioxide (1.74 g, 0.020 mol) was added to a solution of the **5a**/**6a** mixture (0.30 g, 2.2 mmol) in 40 mL of cyclohexane and the resulting slurry was heated at reflux for 24 h. The cooled reaction mixture was filtered through a pad of Celite and concentrated to give 226 mg (76%) of **7** as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 6.48 (ddd, J = 12, 7, and 1.5 Hz, 1 H), 5.38 (br d, J = 12 Hz, 1 H), 2.30–1.00 (series of m, 7 H), and 0.75 (m, 1 H); ν_{max} (neat) 3080, 3000, 1635, 1410, 1355, 1282, 1206, and 942 cm^{-1}; λ_{max} (EtOH) 263 nm (ϵ 4500); *m/e* 134.0733.

Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.42; H, 7.90.

***syn,anti*-2,4-Bishomocycloheptatrienol (6a).** To a solution of **7** (110 mg, 0.82 mmol) in 5 mL of ether cooled to −78 °C was added 0.80 mL of a 25% solution of diisobutylaluminum hydride in heptane. The reaction mixture was allowed to stir for 0.5 h at this temperature before warming to room temperature and addition of 0.5 mL of 1 N sodium hydroxide. After 1 h, the organic solution was decanted, dried, and concentrated to give 98 mg (88%) of a colorless oil composed of **5a** and **6a** (16:84). Crystallization from low-boiling petroleum ether gave 66 mg (60%) of **6a** as a white, crystalline solid: mp 57–58 °C; ^{1}H NMR (CCl_4) δ 5.57 (dd, J = 11 and 5 Hz, 1 H), 5.15 (dd, J = 11 and 3 Hz, 1 H), and 4.62 (m, 1 H), 2.68 (br s, 1 H), and 1.50–0.20 (series of m, 8 H); ν_{max} (KBr) 3240, 3010, 2975, 1665, 1440, 1376, 1278, 1050, 1010, 835, and 728 cm^{-1}; *m/e* 136.0890.

The *p*-nitrobenzoate (**6b**), prepared in the predescribed manner, was obtained as a white, crystalline solid: mp 91.5–92.0 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 8.27 (s, 4 H), 6.08 (m, 1 H), 5.92 (m, 1 H), 5.38 (m, 1 H), and 1.70–0.50 (series of m, 8 H); *m/e* 285.1005.

Anal. Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.26; H, 5.41; N, 4.75.

Photooxygenation of 8. A 1.00-g (8.3 mmol) sample of **8** was photooxygenated as described above for 21 h. The reaction mixture was treated with sodium borohydride (0.76 g, 80 mequiv) at 0 °C before workup as before. Careful HPLC purification on Florisil (elution with 65:35 hexane–ether) gave 0.35 g (44%) of a 3:1 mixture of **9a** and **10a**. This alcohol mixture was dissolved in 15 mL of dry pyridine and 0.74 g (4.0 mmol) of *p*-nitrobenzoyl chloride was added. After stirring for 3 h at room temperature, the reaction mixture was diluted with 50 mL of water and the product was extracted into ether (2 × 25 mL). The combined ether extracts were washed with cold 10% hydrochloric acid and saturated sodium bicarbonate solutions, dried, and concentrated. Recrystallization of the residue from hexane gave pure **9b** (250 mg, 36%) as a white, crystalline solid: mp 99–100 °C; ^{1}H NMR (CCl_4) δ 8.30 (s, 4 H), 6.02 (d, J = 10 Hz, 1 H), 5.83 (m, 1 H), 5.62 (dd, J = 10 and 6.5 Hz, 1 H), 1.70–1.15 (m, 4 H), 1.10–0.35 (m, 2 H), and 0.35–0.00 (m, 2 H); ν_{max} (KBr) 3110, 3070, 3000,

1713, 1605, 1515, 1350, 1280, 1110, 1100, and 710 cm^{-1}; *m/e* 285.1003.

Anal. Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30. Found: C, 67.46; H, 5.18.

***syn*-2,4-Bishomotropone (11).** A 0.54-g (4.0 mmol) sample of the **9a**/**10a** mixture was treated with manganese dioxide (3.5 g, 40 mmol) in 40 mL of cyclohexane as described previously. There was obtained 0.35 g (65%) of **11**: ^1H NMR ($CDCl_3$) δ 6.33 (dd, J = 12 and 3 Hz, 1 H), 5.61 (dt, J = 12 and 0.8 Hz, 1 H), 2.08 (m, 2 H), 1.53 (m, 2 H), 1.02 (m, 2 H), 0.70 (m, 1 H), and 0.25 (m, 1 H); ν_{max} (neat) 3000, 2970, 2930, 2860, 1650, 1405, 1350, 1087, and 885 cm^{-1}; λ_{max} (EtOH) 225 nm (ϵ 5200); *m/e* 134.0733.

Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.72; H, 7.54.

***syn,syn*-2,4-Bishomocycloheptatrienol (10a).** A 250-mg (1.86 mmol) sample of **11** was treated with 2.0 mL of 25% diisobutylaluminum hydride in heptane as described before. Recrystallization of the crude product from petroleum ether afforded 137 mg (54%) of **10a** as a white, crystalline solid: mp 76.5–77.5 °C; ^1H NMR (CCl_4) δ 5.50 (br d, J = 11 Hz, 1 H), 5.05 (br d, J = 11 Hz, 1 H), 4.82 (m, 1 H), 2.35 (br s, 1 H), 1.67–0.55 (series of m, 6 H), and 0.55 to −0.20 (m, 2 H); ν_{max} (KBr) 3400, 3075, 3015, 3005, 2880, 1668, 1450, 1390, 1280, 1040, 1010, 905, 855, 835, and 728 cm^{-1}; *m/e* 136.0890.

The *p*-nitrobenzoate **10b** was isolated as a white, crystalline solid: mp 108–109 °C (from hexane); ^1H NMR ($CDCl_3$) δ 8.30 (s, 4 H), 6.20 (m, 1 H), 5.75 (br d, J = 11 Hz, 1 H), 5.20 (br d, J = 11 Hz, 1 H), 1.65–1.05 (m, 4 H), 1.05–0.0 (series of m, 4 H); ν_{max} (KBr) 1720, 1610, 1530, and 1275 cm^{-1}; *m/e* 285.1005.

Anal. Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.49; H, 5.30; N, 4.92.

General Procedure for Sample Preparation in Superacid Media. A. Proton Spectra. A thin-walled 5-mm NMR tube was immersed in an isopentane–liquid nitrogen slush bath (−140 °C) while being flushed with a stream of dry nitrogen. A 0.10-mL sample of spectrograde fluorosulfuric acid was introduced via pipet into the bottom of the tube where it quickly solidified. Sulfuryl chloride fluoride (0.30 mL) was next added. The organic compound was dissolved in 0.10 mL of dichloromethane-d_2 and placed on top of the sulfuryl chloride fluoride. A thin glass stirring rod was introduced. The NMR tube was allowed to warm until the methylene chloride layer dissolved with stirring. The tube was then stored at −140 °C prior to spectral measurement.

B. Carbon Spectra. A 0.4-mL sample of fluorosulfuric acid was added to a nitrogen-flushed 10-mm NMR tube immersed in a −140 °C slush bath, followed by the addition of 0.5 mL of sulfuryl chloride fluoride. The organic sample was introduced on top of the sulfuryl chloride fluoride. A glass capillary containing dichloromethane-d_2 was inserted and served as lock signal, reference, and stirring rod. The tube was warmed until a homogeneous solution was realized. The sample was stored at −140 °C until recording of the spectrum.

Kinetic Studies. A. Preparation of Reagents. Acetone was prepared by distillation from potassium permanganate. Doubly distilled water was employed. Tetrahydrofuran was prepared by distillation from sodium. Methanol was prepared by distillation from magnesium methoxide. The aqueous acetone and 75:25 methanol–tetrahydrofuran solutions were prepared on a volume to volume basis. Standard 0.0200 N sodium hydroxide was obtained from The Ohio State University Reagents Laboratory.

B. Determination of Data. Solutions of the *p*-nitrobenzoates in 80% aqueous acetone were prepared by weighing the appropriate ester into a 10.0-mL volumetric flask and filling to the mark with 80% aqueous acetone. The concentration of *p*-nitrobenzoate varied from 0.0100 to 0.0200 M over all runs. The resulting solution was divided into eight 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 half-lives. The final ampule was removed after at least 10 half-lives to provide the 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 acetone, and titrated against 0.0200 N sodium hydroxide using phenolphthalein indicator. First-order rate data were determined by measuring the amount of *p*-nitrobenzoic acid generated by solvolysis relative to the experimental infinity point. Duplicate runs agreeing within 5% were made at all temperatures.

General Procedure for Preparative Scale Solvolyses. A. 80% Aqueous Acetone. An 80-mg (0.28 mmol) sample of *p*-nitrobenzoate and 46 mg (0.40 mmol) of tetramethylurea were dissolved in 10 mL of aqueous acetone. The resulting solution was sealed in a glass ampule and immersed in a constant temperature bath for 10 half-lives. The reaction mixture was concentrated, and the residue was taken up in 25 mL of ether. The ether solution was washed with water, dried, and concentrated.

B. Methanol–Tetrahydrofuran (75:25). A 50-mg (0.18 mmol) sample of *p*-nitrobenzoate and 29 mg (0.25 mmol) of tetramethylurea were dissolved in 10 mL of 75:25 methanol–tetrahydrofuran. The solution was sealed in a glass ampule and immersed in a constant temperature bath for an estimated 10 half-lives. The reaction mixture was concentrated and the residue taken up in 25 mL of ether. The ether solution was washed with water, dried, and concentrated.

C. Thermodynamic Products. Samples of each of the alcohols **5a**, **6a**, **9a**, and **10a** (20 mg) were dissolved in 5 mL of tetrahydrofuran–10% hydrochloric acid (70:30). The resulting solution was brought to reflux for 12 h. The reaction mixture was diluted with 20 mL of water and the aqueous solution was extracted with ether. The ether solution was washed with saturated sodium bicarbonate solution, dried over magnesium sulfate, and concentrated. All four alcohols gave identical product mixtures containing >95% of one alcohol identified as **12a**: ^1H NMR (CCl_4) δ 6.0–5.0 (m, 6 H), 4.18 (m, 1 H), 3.0–2.0 (m, 4 H), and 1.77 (br s, 1 H); ν_{max} (neat) 3350, 3020, 2920, 2860, 1630, 1455, 1025, 780, and 720 cm^{-1}; λ_{max} (cyclohexane) 223 nm (ϵ 4400); *m/e* 136.0890.

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.44; H, 9.05.

***anti,anti*-2,4-Bishomocycloheptatrienyl Methyl Ether (5c).** A 24-mg sample of 50% sodium hydride in mineral oil was washed with pentane and dried under a stream of nitrogen. A 38.8-mg (0.286 mmol) sample of **5a** in 4 mL of tetrahydrofuran was introduced and the resulting mixture was brought to gentle reflux for 2 h prior to the addition of methyl iodide (142 mg, 1.00 mmol). After 1 h at room temperature, the reaction mixture was diluted with water (20 mL) and the product was extracted with hexane (30 mL). The hexane solution was washed with water, dried, and concentrated to give 35 mg (82%) of **5c** as a colorless oil: ^1H NMR (CCl_4) δ 5.67 (dd, J = 11.4 Hz, 1 H), 5.40 (d, J = 11 Hz, 1 H), 3.57 (m, 1 H), 3.30 (s, 3 H), 1.60–0.40 (series of m, 7 H), and 0.13 (m, 1 H); ν_{max} (neat) 3075, 3000, 2930, 2820, 1655, 1405, 1105, 830, and 705 cm^{-1}; *m/e* 150.1048.

2,4,7-Cyclononatrienyl Methyl Ether (12b). A 136-mg (1.00 mmol) sample of **12a**[15] was treated with 48 mg (2.00 mmol) of sodium hydride and 300 mg (2.1 mmol) of methyl iodide as described above. There was obtained 120 mg (80%) of **12b** as a colorless oil: ^1H NMR ($CDCl_3$) δ 6.15–5.30 (m, 6 H), 3.72 (m, 1 H), 3.50 (s, 3 H), and 3.20–2.20 (m, 4 H); ν_{max} (neat) 3010, 2920, 1630, 1450, 1090, 905, 780, and 620 cm^{-1}; λ_{max} (cyclohexane) 222 nm (ϵ 3700); *m/e* 150.1048.

***syn,anti*-2,4-Bishomocycloheptatrienol-*1-d* *p*-Nitrobenzoate (15).** Sodium borodeuteride (17 mg, 0.4 mmol) was added to a solution of **7** in 1 mL of methanol-*O-d* cooled to 0 °C. After 1 h, the reaction mixture was diluted with water and the product was extracted into ether. The combined ether extracts were washed with water, dried, and concentrated. The crude product mixture was treated with *p*-nitrobenzoyl chloride (60 mg, 0.3 mmol) in pyridine solution as described above. Recrystallization of the ester from hexane yielded a white, crystalline solid, mp 90–92 °C.

Methanolysis of **15** as before afforded a mixture of methyl ethers **16** displaying a 2.7:1 ratio of olefinic protons to protons α to the methoxyl.

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Synthesis and Reactions of Bicyclo[3.1.0]hexatrienes

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Abstract: The feasibility of inducing two HBr eliminations from 4,6-dibromo-2-bicyclo[3.1.0]hexene (**3**) was explored as a route to bicyclo[3.1.0]hexatriene (**1**). Depending on the base employed **3** was converted to bromobenzene or 6-substituted fulvenes. To elucidate the mechanism by which the fulvene arose, **3** was synthesized specifically labeled with deuterium, ^{13}C, and alkyl groups. The labeling results require the formation of triene **1** as a reaction intermediate. A hidden stereospecific reaction revealed by the labeling studies for the transformation of **1** to fulvenoid products is discussed using frontier orbital considerations. Using ab initio calculations **1** is compared to the isomeric dehydrobenzenes.

The central role of benzene with respect to aromaticity has prompted the synthesis of many perturbations of the parent hydrocarbon. Typically, these approaches fall into two major categories: bending of the ring represented by the cyclophanes or bond fixation by fusion to small rings.[1] The consequences of yet a third approach entailing the introduction of further unsaturation have not been extensively investigated since, of the three isomeric dehydrobenzenes, only *o*-benzyne has been well characterized. In each instance the chemistry of the resulting C_6H_4 entity will reflect both the strain and the resonance energy associated with the 6π electrons. The nature of the electronic interactions arising from the introduction of two additional unsaturated centers will determine whether the resulting π system is resonance stabilized or destabilized.

Numerous theoretical endeavors have focused on the dehydrobenzenes. The reliability of the results varies depending on the assumptions entertained. Even simple Hückel calculations, when applied in conjunction with Hess and Schaad's semiempirical approach,[2] reach relatively reliable conclusions concerning the aromaticity of *m*-benzyne and *p*-benzyne represented as bicyclo[3.1.0]hexatriene (**1**) and bicyclo[2.2.0]hexatriene (**2**), respectively. Using the REPE value of 0.065 for benzene as a standard, REPE for **1** is 0.055 but −0.06 for **2**.[2,3] Thus, replacement of H_1 and H_3 of benzene with a σ bond is predicted to generate an aromatic hydrocarbon, whereas formation of a 1,4 bond would create an antiaromatic hydrocarbon. In agreement with this analysis, more sophisticated calculations predicted **1** to be more stable than **2** by 45–50 kcal after geometry optimization.[4]

1

2

Both *o*- and *p*-dehydrobenzenes have been characterized to varying degrees. The development of a variety of synthetic routes leading to *o*-benzyne has established the chemistry to be that of a strained cyclic acetylene.[5] Moreover, the infrared studies of *o*-benzyne in an argon matrix provided additional confirmation of this bonding arrangement.[6]

The chemistry of *p*-benzyne is not as well established. Two different approaches generated a reactive intermediate possessing quite different properties. Pyrolysis of *cis*-1,2-diethynylethylene produced a symmetrical entity which reacted as a diradical.[7] In contrast, lithium dimethylamide transformed 1-chlorobicyclo[2.2.0]hexadiene into a reactive polyene that was trapped by nucleophiles and dienes.[8] The vigorous conditions required to generate **2** were interpreted to be indicative of a high activation energy associated with formation of an energetically unfavorable species.

Prior to this investigation, *m*-dehydrobenzene had been characterized primarily by computational studies. Early theoretical studies had predicted the singlet–triplet gap of **1** to be small. For example, Hoffmann, using extended Hückel calculations, predicted the ground state to be a singlet.[9] From ab

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