

**DEGENERATE AND NONDEGENERATE ISOMERIZATIONS OF
8,8-DIMETHYL BENZOHOMOTROPYLIUM CATIONS**

**To My Parents and
My Husband Siva**

**DEGENERATE AND NONDEGENERATE REARRANGEMENTS IN
8,8-DIMETHYLBENZOHOMOTROPYLUM CATIONS**

By

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ABSTRACT

Investigations on the stability and reactions of various isomers of the benzohomotropylium/bridged [11]-annulene system are presented in this thesis. As 1,6-methano-[11]-annulenium cations are isomeric with benzohomotropylium cations in principle it is possible for these systems to be interconverted by a circumambulatory migration of the 'bridging' methano group. If this reaction were to proceed to equilibrium it would allow the examination of the thermodynamic stability of the various isomers.

Homotropylium cations with two methyl groups at C₈ are known to undergo facile circumambulatory rearrangements. Thus in this work the 1-hydroxy 8,8-dimethyl-2,3-benzohomotropylium and 1-hydroxy 8,8-dimethyl-4,5-benzohomotropylium cations have been prepared by protonation of the corresponding 2,3- and 4,5-benzohomotropones in FSO₃H. On the basis of their ¹H NMR spectra it is concluded that they can properly be regarded as homoaromatic cations. The thermal isomerizations of these cations have been studied in detail. The thermal isomerization of these cations led to the formation of a

series of products but does not yield the corresponding [11]-annulenium isomer. In addition the barriers to ring inversion in these cations were found to be much lower than those of other homotropylium cations. This suggests that the former cations have a very open structure. Besides this experimental approach, the relative stability of these isomers has been explored using MNDO calculations. The calculated heats of formation (ΔH_f) showed that the 1-benzohomotropylium cation is more stable than the corresponding [11]-annulenium ion by 21 kcal/mol.

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INTRODUCTION

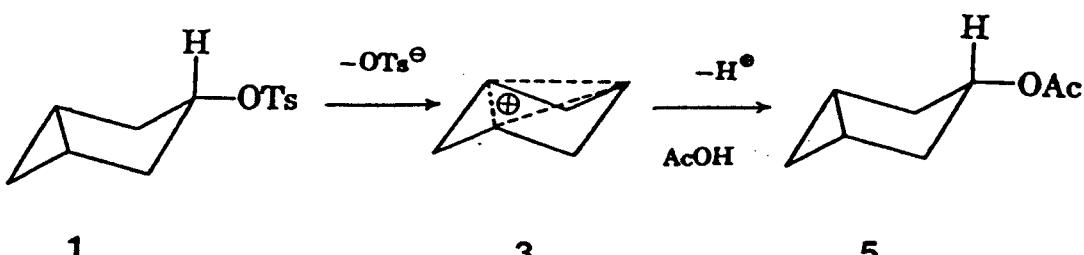
CHAPTER 1

I. HOMOAROMATICITY

a. Historical Background

Saul Winstein first introduced the concept of homoaromaticity in a generalized way in 1959.^{1,2} Since that time there has been an impressive amount of work in this area and a large variety of systems have been considered to be homoaromatic.

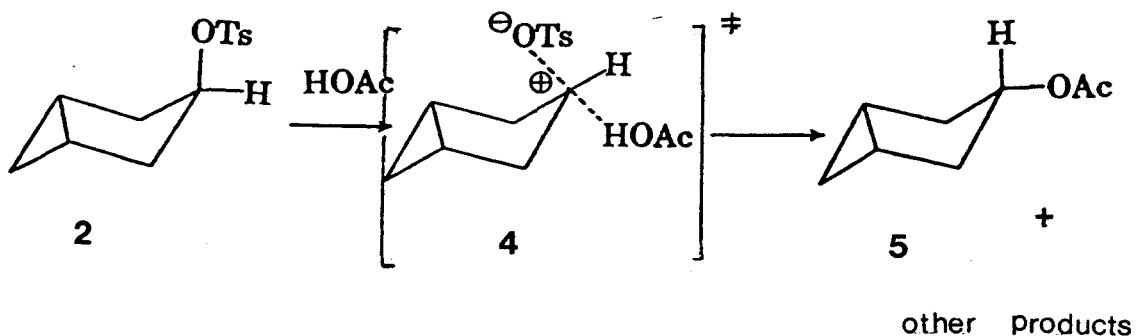
The first homoaromatic species was proposed by Winstein³⁻⁵ to account for the unusual solvolytic behaviour of the cis and trans-bicyclo[3.1.0]-hexyl-toluenesulfonates 1 and 2 respectively. In acetolysis the cis-toluenesulfonate 1 is substantially more reactive than the trans epimer. The product obtained from 1 is exclusively the cis-acetate 5 with no accompanying olefin. The trans-toluenesulfonate gives rise to 5 but also with the formation of considerable amounts of related olefins.



1

3

5



The enhancement in the rate of solvolysis of 1 as compared to 2 suggests that ionization of the cis toluene-sulfonate 1 is somewhat anchimerically accelerated with the involvement of a unique carbenium ion intermediate 3. This cation was considered to be homoaromatic and the term "tris-homocyclopropenyl" has been suggested by Winstein. On the other hand 2 was presumed to ionize classically.

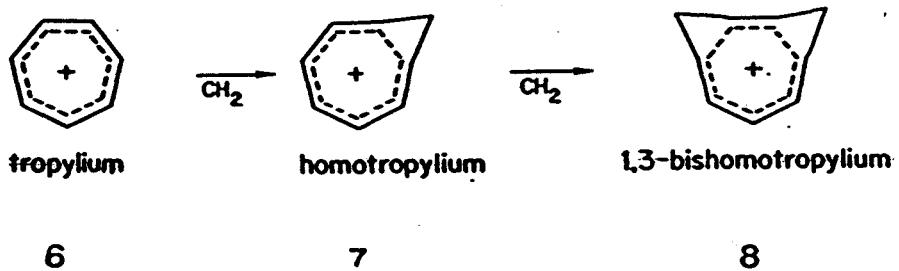
Since this original work the concept of homoaromaticity has been expanded to encompass a range of other systems. It continues to remain an extraordinarily rich area of chemistry.

b. General Concept and Nomenclature

Homoaromatic molecules or ions are cyclic unsaturated systems in which the π -system is interrupted at one or more points by a methylene bridge.

Homoaromatic systems can in principle be classified as neutral, cationic or anionic. The σ skeleton of an aromatic species may be interrupted on one,

two or three sides and thus one can conceive of mono-, bis-, and tris-homoaromatic species. It is important to note that the designations such as mono-, bis- and tris- are based on the number of sides where the σ backbone is removed or lengthened and not on the number of methylene groups inserted on any particular side. For example the monohomotropylium ion 7 can be derived by the insertion of a CH_2 group into the seven membered ring of the tropylium ion 6, likewise bishomotropylium ions can be derived by the insertion of two CH_2 groupings.



6

7

8

The important feature of these homoaromatic systems is that the aromatic properties of the parent system are maintained. In other words the orbital interactions between the noncontiguous π centers flanking the bridging methylene group are maintained. The extent of this interaction may be reduced in a homoaromatic systems such as 7 as compared to the corresponding

aromatic analogue 6.

Homoaromatic delocalization is particularly important with medium ring cations. A few examples of homoaromatic cations are listed in Table 1. Of the monohomoaromatic cations, the homotropylium cation 7 has received more attention than any other homoaromatic molecule or ion. Some homologues of the tropylium cation are summarized in Figure 1.

II. HOMOTROPYLIUM CATIONS

1. Early Studies

a. Structure

Development of homotropylium cation chemistry began with Pettit's observation that treatment of cyclooctatetraene, 16, with strong acids generated a carbocation which showed an unusual ^1H NMR spectrum. (Equation 1).^{20,25} This cation was also isolated as a solid salt $\text{C}_8\text{H}_9^+ \text{SbCl}_6^-$, by treatment of 16 with HCl and SbCl_5 .²⁰

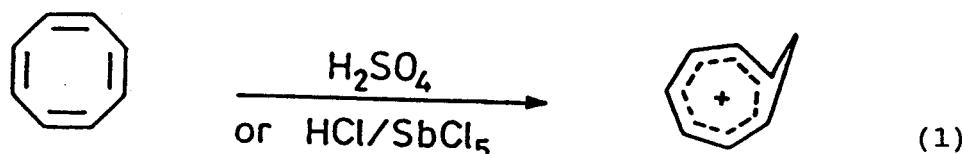
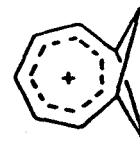


Table 1

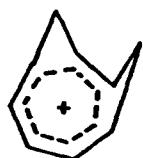
Examples of Homoaromatic Cations



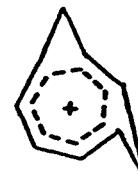
homotropylium
cation 7



1,1-bishomotropylium
cation 11



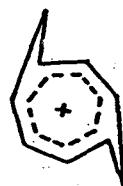
1,3-cis-bishomotropylium
cation 9



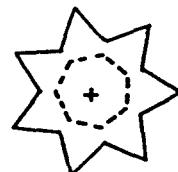
1,3-trans-bishomo-
tropylium cation 12



1,4-cis-bishomotropylium
cation 13



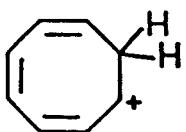
1,4-trans-bishomo-
tropylium cation 14



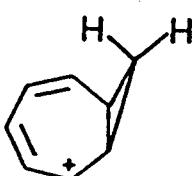
heptahomotropylium
cation 15

Figure 1. Some Homologues of Tropylium Cation.

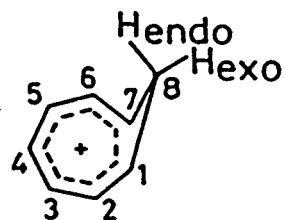
The ^1H NMR spectrum of the cation obtained was found to consist of four distinct multiplets with the chemical shift values of δ 8.6, 6.6, 5.2 and -0.6 ppm and relative areas 5:2:1:1, respectively. Pettit considered three possible structures 7, 17 and 18 for the cation but favoured structure 7.



17



18



7

The key evidence used to propose its structure was the ^1H NMR spectrum.²¹ The resonances corresponding to the two protons of the methylene group were separated by 5.80 ppm with one resonance occurring at δ -0.60 ppm, a strikingly high-field position for a proton on a carbocation. The resonances corresponding to the two hydrogens on C₁ and C₇ occur as a multiplet at δ 6.6 which is lower than normally expected for a hydrogen on a cyclopropane. On the basis of this NMR spectrum, Pettit ruled out the classical cyclooctatrienyl cation 17. The remarkably large chemical shift difference ($\Delta\delta$) between the exo and endo protons suggested that there is an induced ring current present in this cation and Pettit represented this

ion as 7 to indicate that the delocalization was cyclic and involved six electrons.

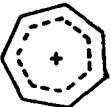
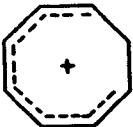
Subsequent work of Winstein and coworkers enhanced the earlier suggestions for the electronic structure of the homotropylium ion.⁷ High-field ¹H NMR and ¹³C NMR studies of the homotropylium ion have been reported.^{21,24,26-27}

The direct evidence for the existence of an induced ring current comes from the volume diamagnetic susceptibility measurements reported by Dauben and coworkers.²⁸ The homotropylium cation clearly shows significant exaltation of diamagnetic susceptibility, like that of benzene and the tropylium cation (Table 2).

Further insight into the electronic structure of the homotropylium ion is provided by its ultraviolet spectrum.^{29,32} The long wavelength absorption of the homotropylium ion occurs at considerably shorter wavelengths than would be expected for the cyclooctatrienyl cation 17. Instead the UV spectrum resembles more closely to that of the tropylium ion 6 (Table 2). On the basis of the long wavelength absorption bond and HMO treatment of the homotropylium ion, Winstein estimated the 1,7 bond order to be 0.56 which can be compared to a π bond order of 0.64 for the tropylium ion.

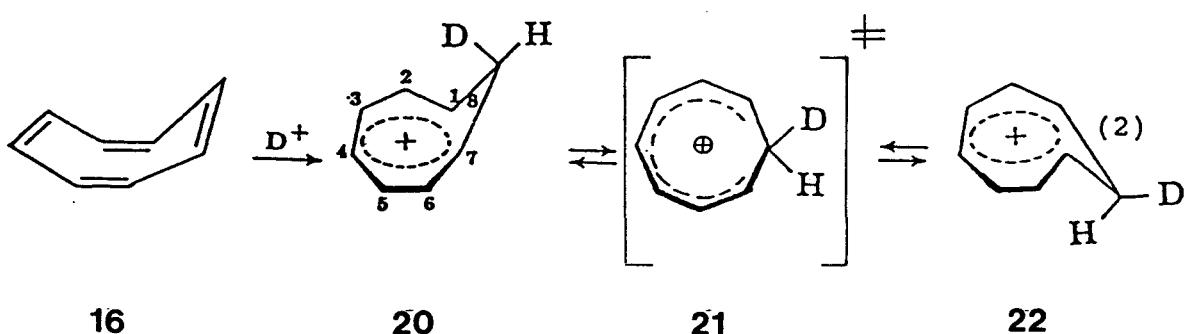
Table 2.

Ultraviolet Absorption and Diamagnetic Susceptibility
data

Compound	$\lambda_{\text{max}}^{\text{nm}}$ (Log ϵ)	Diamagnetic Susceptibility Exaltation (-10^{-6} cm 3 /mole)
	217.0 (4.61) 273.5 (3.63)	19.5
6		
	232.5 (4.52) ^{30,31} 313.0 (3.48)	18.0
7		
	Ca 470 ³²	-
17		
	-	13.7
19		

b. Stability

Winstein and coworkers showed that the addition of D⁺ to cyclooctatetraene 16 in D₂SO₄ at -10°C occurs predominantly (80%) from the inside of the cyclooctatetraene tub conformation to give the cation 20.



Continued NMR observation of the cation 20 revealed that the intensities of the inside and outside proton signals approached a value corresponding to half a proton in each position. Winstein suggested that this equilibration of the exo and endo positions of C₈ occurred via a ring inversion process. Presumably this involves a planar cation 21.²⁹ The first order rate constant for this process was found to be 9.8 × 10⁻⁴ sec⁻¹ at ca. 37°C, ΔG[‡] = 22.3 kcal/mol. It was assumed that 21, representing the energy maximum of this inversion process, was 22.3 kcal/mol higher in energy than 20.²⁹

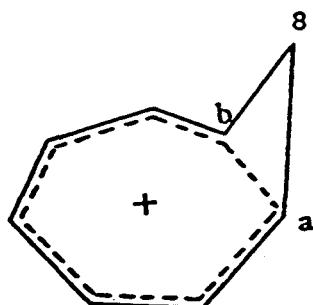
2. Further Studies on Homotropylium Cations

a. Structure

Two complementary approaches have been used to determine the structure of homotropylium cations. One of the approaches involves theoretical calculations.³³⁻³⁶

There have been several reports of theoretical treatment of the homotropylium systems. The most complete examination of the homotropylium energy surface is that reported by Haddon.³³

Haddon in his earlier calculations used a perturbational molecular orbital approach and predicted that in the case of homotropenyl cation the attachment of the pentadienyl unit to a cyclopropane ring leads to the removal of electron density from the a-b bond in 7 hence a lengthening of the cyclopropane bond would be expected leading to an "open" cyclopropane unit.³⁷⁻³⁸



7

Later Haddon reinvestigated the equilibrium geometry of 7 using MINDO/3 with full geometry

optimization. The results obtained from these calculations are summarized in Tables 3 and 4.

Table 3 shows the MINDO/3 geometries for 7 which were obtained at two levels of optimization: planar(all atoms were constrained to the plane of the "seven membered" ring with the exception of the hydrogen atoms of the homoconjugate linkage and the bridging methylene group), and nonplanar. Table 4 shows the MINDO/3 energies with C-H bond length optimization.

Table 3

Calculated Geometries of the Homotropenylium Cation ^{7c}

Bond Lengths (a-b) ^a Bond Angles (a-b-c) ^b .	STO-3G Planar	MINDO/3 Planar	MINDO/3 Nonplanar
1-7	1.512	1.579	1.621
1-2	1.471	1.465	1.449
2-3	1.361	1.380	1.387
3-4	1.438	1.416	1.412
1-8	1.510	1.502	1.498
< 2-1-7	127.6	124.4	122.8
< 1-2-3	128.5	131.8	133.9
< 2-3-4	126.7	128.4	128.5
< 3-4-5	134.5	130.9	129.5
< 1-8-7	60.1	63.4	65.5

^a In angstroms^b In degrees^c Taken from R.C.Haddon, Tetrahedron Lett, 2797 (1974).

Table 4.

Calculated Energies for the MINDO/3 geometries of the homotropylium cation 7

	ΔH_f kcal/mol	Relative energies kcal/mol
planar (C-H opt)	213.43	3.27
nonplanar (C-H opt)	210.16	0.00

The energy minimum corresponding to this non-planar geometry was found to be 3 kcal/mol lower than that for the geometry with a planar seven membered ring. The elongation of the homoconjugate linkage (1.621 Å) is consistent with an open cyclopropane structure 7.

Later Haddon, in a detailed theoretical investigation of the homotropylium cation, has concluded that there are two minima on the potential energy surface.³³ The lowest energy of these, has a calculated homoconjugate internuclear distance of 1.621 Å. The second energy minimum, was calculated to be some 6-10 kcal/mol less stable than the former conformation and has a very long C₁-C₇ homoconjugate distance of 2.303 Å.

Very recently Haddon has performed a high level Hartree-Fock (HF/6-31G+5D level of theory) geometry optimization on homotropylium cation 7 and again found that the same two minima are located on the potential energy surface (Figure 2).⁴⁸ The homoconjugate bond distances were 1.660 and 2.290 Å which agreed well with the

previous calculations and the x-ray structure determinations. However as seen in figure 2 the potential energy surface is completely transformed by the inclusion of electron correlation effects in the wave function (MP2 and MP3) and a single minimum results in both cases with an $R_{1,7}$ value of 1.7-2.0 Å. The ring current exhibited a maximum value around $R_{1,7} = 1.8$ Å. However the calculated ring current is surprisingly large over the whole range of $R_{1,7}$ values and even at $R_{1,7} = 2.6$ Å, the ring current is 39% of that of the tropenylum cation.

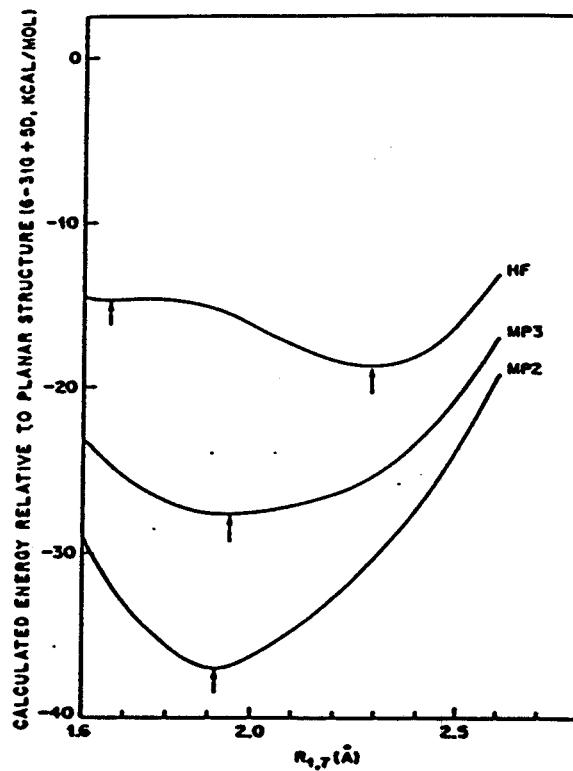
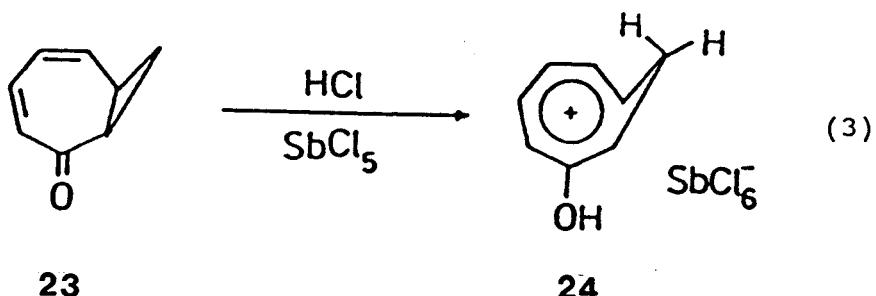


Figure 2. Energies for homotropylium cation at HF optimized geometries obtained with the 6-31G+5D basis set as a function of the homoconjugate distance.

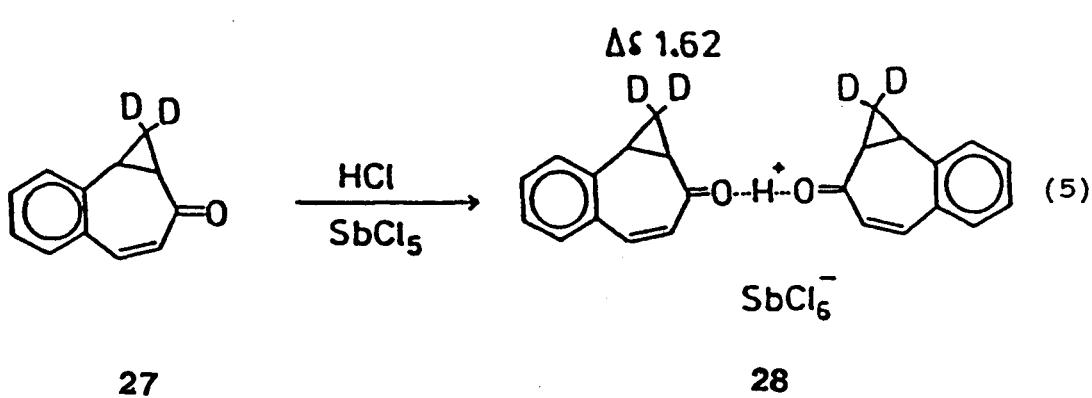
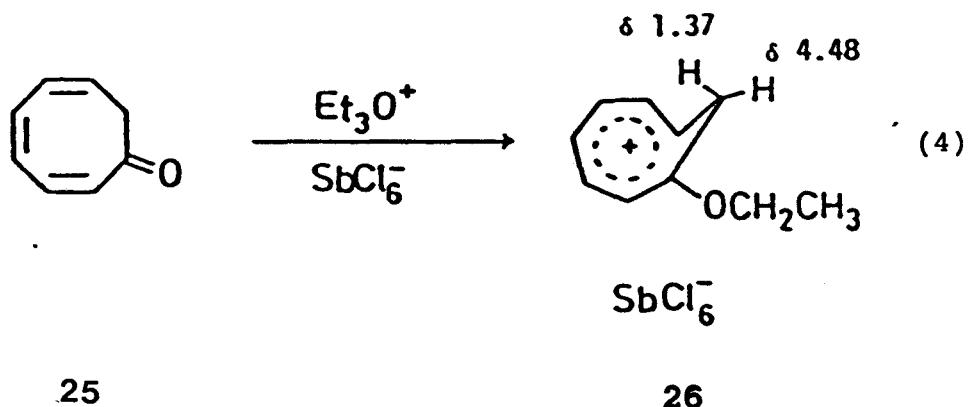
The other approach used to investigate the structure of the homotropylium cation involves the experimental approach of x-ray diffraction techniques applied to isolated salts.

Recently Childs and coworkers succeeded in structurally characterizing salts of the 2-hydroxyhomotropenyl cation 24 (Equation 3)³⁹ and the 1-ethoxyhomotropylium cation, 26 (Equation 4).⁴⁵ The ion 24 exhibits a similar type of ¹H NMR spectrum to that of the parent ion although the chemical shift difference between the C₈ exo and endo protons is only 3.10 ppm. The reduction in the chemical shift difference of the C₈ protons results from a partial removal of the positive charge from the ring system onto the oxygen atom. The C₁-C₇ bond distance was found to be 1.626 Å which is significantly longer than that of a normal cyclopropane (1.510 Å),³⁹⁻⁴⁴ but in good agreement with Haddon's calculation.

$$\Delta\delta = 3.10 \text{ ppm.}$$



The ^1H NMR spectrum of 26 shows the chemical shift difference between the C_8 exo and endo protons is 3.12 ppm. The C_1-C_7 bond distance of 26 was found to be 2.284 Å which is very much greater than the comparable internuclear distance of 24.⁴⁵ This indicates that the cation 26 has adopted an open conformation as was predicted as the second energy minimum by Haddon.³³



The structure of a further homotropylium cation has also been determined by Childs and coworkers.^{46,47} In this case the situation is somewhat more complex in as

much as a dimeric species was isolated (Equation 5).

The presence of the deuteriums in this cation reflect material availability. In this case the "key" internal cyclopropane bond length (C_1-C_7) is only 1.544 Å which is much shorter than the corresponding bond length of 1.626 Å observed in 24 and is not significantly different from that of free cyclopropane (1.510 Å). It was suggested that 28 cannot be regarded as a homotropylium cation and that the extent of homoaromatic delocalization occurring in 28 must be small.

b. Energetics

Molecular energetics are a further widely used criterion of aromaticity. In the case of the homotropylium cation one approach is to compare the energy of the non-planar ground state of the cation to its planar, non aromatic cyclooctatrienyl cation.^{46,49} From the study of Winstein and coworkers on the bridge flipping process in the homotropenyl cation this energy difference was found to be 22.3 kcal/mol.

Ab initio STO-3G and 4-31G calculations on the STO-2G optimized structures lead to energy differences of 25.2 and 10.0 kcal/mol, respectively between the ground state and planar forms. Haddon suggested a new and unexpected minimum on the potential surface of 7 which is termed as cyclooctatrienyl cation 29 with the 1,7

interatomic distance of 2.303 Å. However the most recent calculations show that the potential energy surface is extremely flat with the inclusion of electron correlation effects. If Figure 2 is taken at face value, there is only one minimum on the potential surface of 7 with a homoconjugate bond length intermediate between those found previously.

In a more direct approach to measuring the energies of homoaromaticity in homotropylium ions, Childs et al. have measured the heats of protonation of a series of unsaturated ketones.⁴⁹ The heats of transfer (ΔH_{tr}) from CCl₄ to FSO₃H of some seven-membered ring ketones are summarized in figure 3. As can be seen in this series addition of the third double bond to the seven membered ring, i.e 32 —> 33, produced a substantial increase in ΔH_{tr} . This discontinuity in behaviour reflects the aromaticity of 33H. A similar pattern is observed with 32 —> 23.

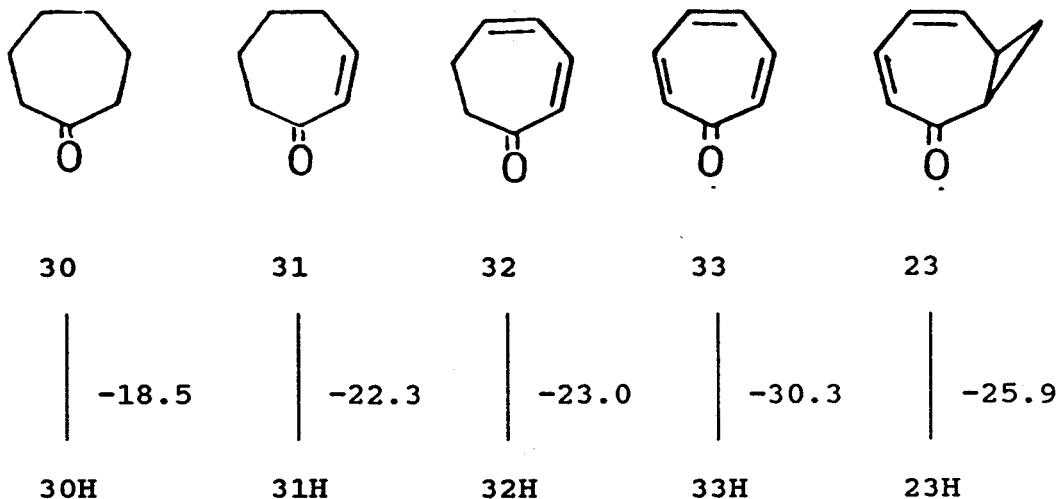


Figure 3: Heats of transfer of various ketones from CCl_4 to FSO_3H

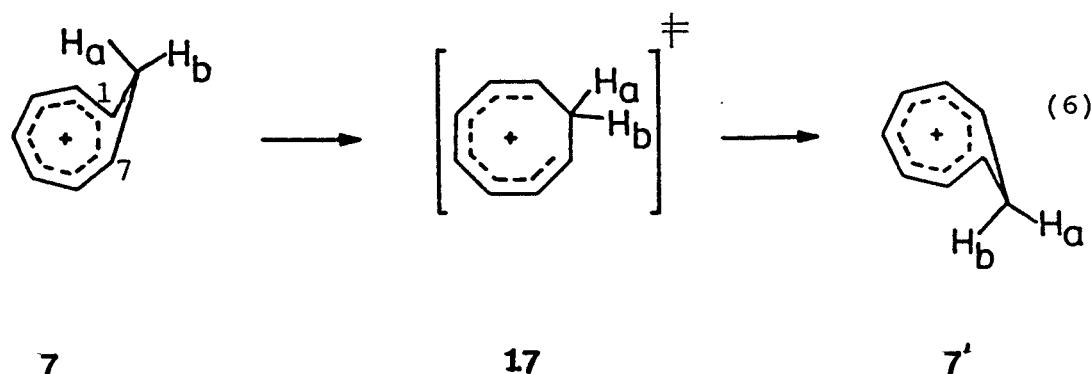
The magnitude of the increase in ΔH_{tr} on introduction of the cyclopropyl ($32 \longrightarrow 23$) is about 40% of that observed between 32 and 33. This is a good evidence for the "extra" stability of 23 resulting from the cyclic delocalization in this cation, however homoaromaticity does not seem to be as important a factor as aromaticity itself.

3. Reactions of homotropylium cations

In addition to the obvious reactions with nucleophiles and deprotonation, homotropylium cations undergo two degenerate rearrangements as well as a variety of irreversible isomerizations. The first degenerate

rearrangement is the ring inversion process that has been mentioned earlier (Equation 6). A second is the circumambulation of C₈ around the "seven-membered" ring of these cations.

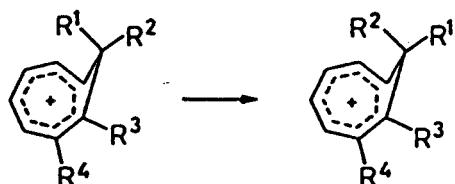
a. Ring Inversion



As mentioned earlier the ring inversion was first observed by Winstein in the deuteration studies on cyclooctatetraene. The barrier for this reaction is substituent dependent with electron donating substituents at C_1 lowering the energy barrier whereas electron donating substituents at C_2 and C_4 raise the energy barrier for inversion as compared to the parent system. Substituents at the C_8 position have little effect on the activation barrier indicating that little change in the fraction of positive charge at this carbon occurs during the isomerization.

Table 5.

Examples of ring inversion process in homotropylium cations.



System	Activation barrier ΔG^\ddagger (kcal/mol)	Reference
17. $R_1=D; R_2=R_3=R_4=H$	22.3	29
19. $R_2=D; R_1=R_3=R_4=H$		
34. $R_3=OH; R_1=R_2=R_3=H$	>20	52
35. $R_3=OCH_3; R_1=D; R_2=R_4=H$	19.6	53
36. $R_3=OCH_3; R_2=D; R_1=R_4=H$		
37. $R_3=OH; R_1=CH_3; R_2=R_4=H$	17.1	40, 41
38. $R_3=OH; R_2=CH_3; R_1=R_4=H$		
39. $R_4=OH; R_1=CH_3; R_2=R_3=H$	>27	40, 41
40. $R_4=OH; R_2=CH_3; R_1=R_3=H$		

Bulky substituents at C₈ normally prefer to be in the exo position due to the steric interactions.^{40,41,50,51}

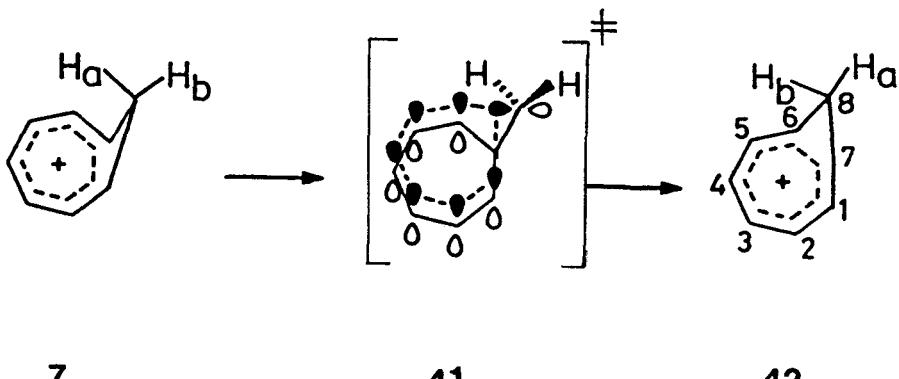
Some examples of the ring inversion process and the corresponding activation barriers are listed in Table 5.

b. Circumambulatory Rearrangements

A circumambulatory rearrangement is a process in which a substituent atom or group of atoms migrates around the periphery of a ring such that it can become bonded to any of the ring carbons.⁵⁴ This atom or group may be joined to one or more of the ring atoms.

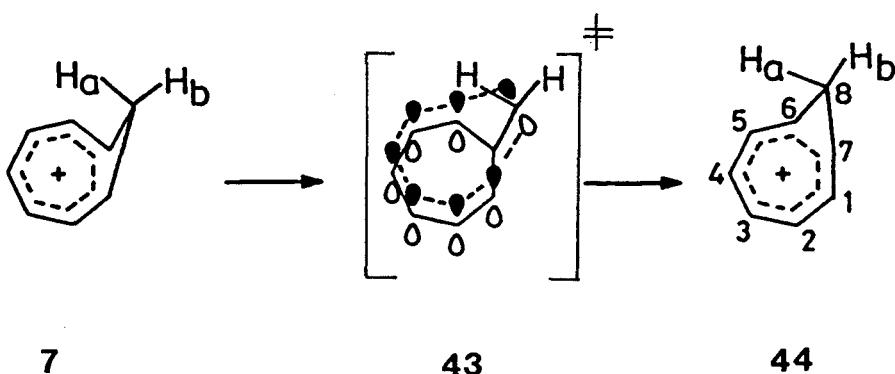
Berson and coworkers attempted to detect circumambulation in the homotropylium cation using deuterated derivatives. No circumambulation was found and the barrier to such a migration must be greater than 26 kcal/mol.⁵⁵ Circumambulation in a homotropylium cation involves a suprafacial [1,6] sigmatropic shift and as such this rearrangement would be expected to proceed thermally with retention of configuration at C₈. For a concerted migration there are two possible geometries for the transition state.^{56,57} The bisected transition state 43 which involves inversion at the migrating carbon is orbital symmetry forbidden but least motion allowed process in the ground state. The alternate eclipsed transition state 41, involving retention at the migrating

carbon, is orbital symmetry allowed but least motion disallowed process in the ground state.⁵⁸⁻⁶⁰



eclipsed transition state

symmetry allowed

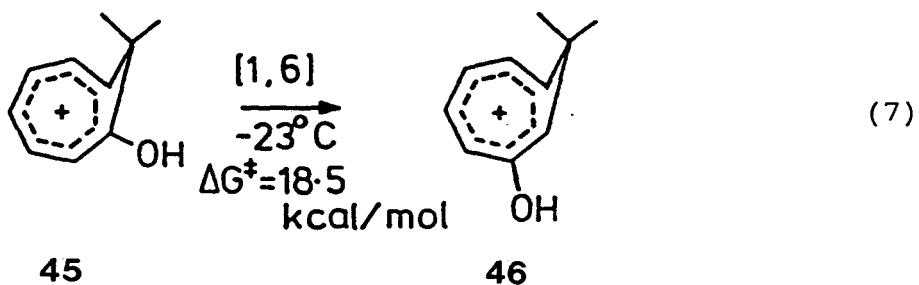


bisected transition state

symmetry forbidden

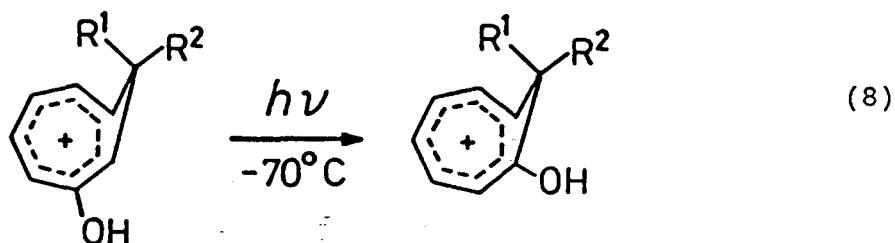
Childs and coworkers have shown that one way of facilitating circumambulation in homotropylium cations is to place electron donating substituents at C₈ which will stabilize the transition state.⁴⁰ This is in line with Hehre's ab initio STO-3G calculations.^{34,35,61}

Childs and coworkers observed circumambulatory rearrangements in 8,8-dimethyl-1-hydroxyhomotropylium cations (Equation 7) and pointed out the ease of ground state circumambulation in C₈ dimethyl substituted homotropylium cations.^{40,41} No comparable isomerization occurs with the 1-hydroxyhomotropylium cation lacking the methyl substituents at C₈. Scott and Brunsvold have observed a circumambulatory rearrangement with a ring-fused homotropylium cation.⁶²



Childs and colleagues have also observed circumambulatory migration in the excited state of homotropylium cations (Equation 8). The irradiation of the 2-hydroxyhomotropylium cations led to the formation of the corresponding 1-hydroxy isomers. The reactions proceed with overall retention of stereochemistry but with inversion at C₈, e.g. 40 → 37. As was mentioned above, migration with retention of configuration, formally the thermally allowed process, involves a large twisting

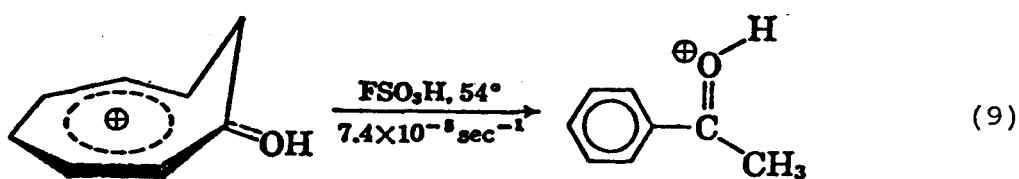
motion of C₈ and difficult on geometric grounds. In contrast the photochemically allowed migration should involve inversion of configuration at the migrating carbon and thus should be a least motion reaction.



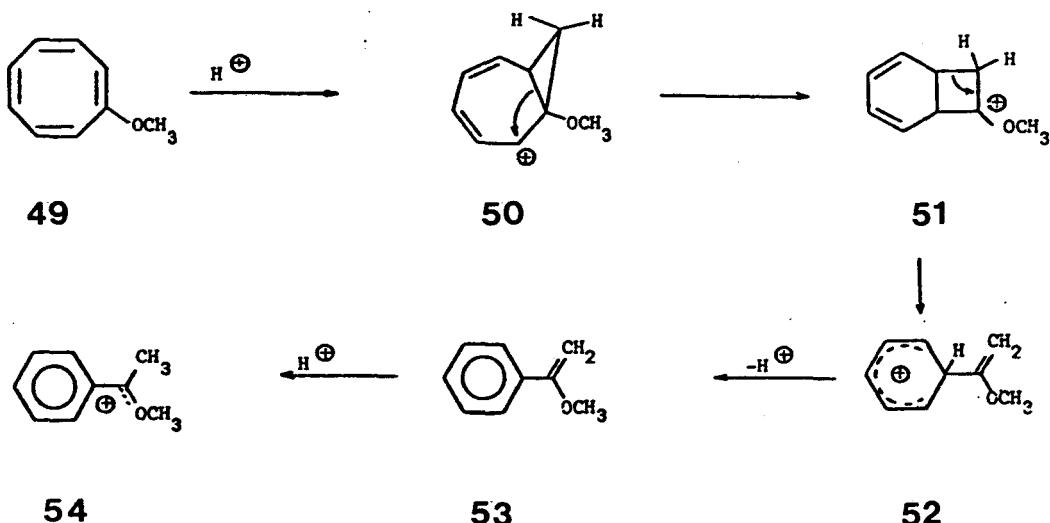
47	R ₁ =R ₂ =H	34
40	R ₁ =CH ₃ ; R ₂ =H	37
39	R ₁ =H; R ₂ =CH ₃	38
46	R ₁ =R ₂ =CH ₃	45

c. Ring contraction and Ring opening reactions

Winstein and coworkers reported the thermal rearrangement of 1-hydroxyhomotropylium cation to protonated acetophenone.⁶⁵

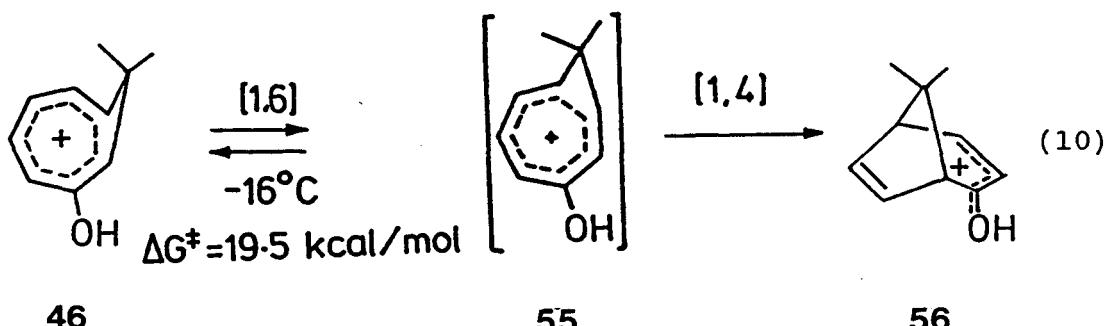


Brookhart and Atwater observed a comparable thermal rearrangement of ion 50 to the phenylmethylmethoxy carbonium ion 54.⁶⁶ These workers proposed that these rearrangements proceed via the mechanism outlined below in Scheme 1.

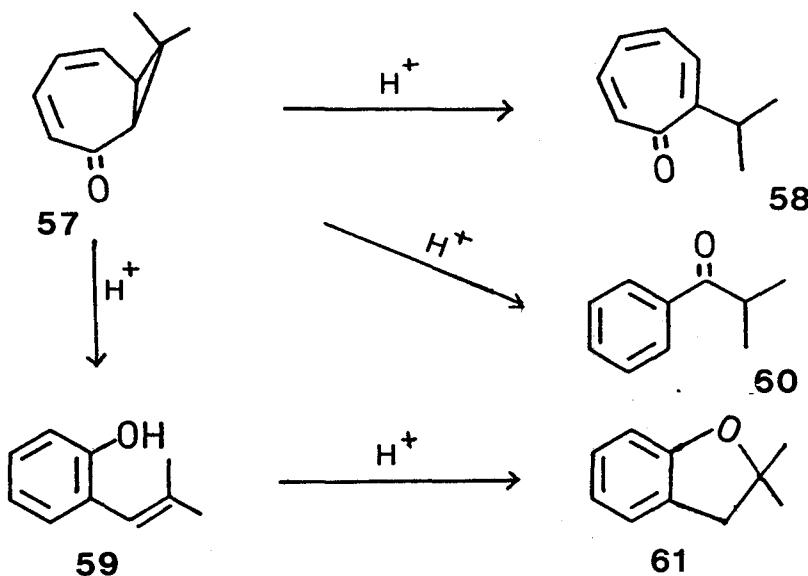


Scheme 1.

Childs and Rogerson showed that the 2-hydroxy homotropylium cation 46 undergoes an irreversible isomerization to the non aromatic cation 56 (Equation 10).⁴⁰

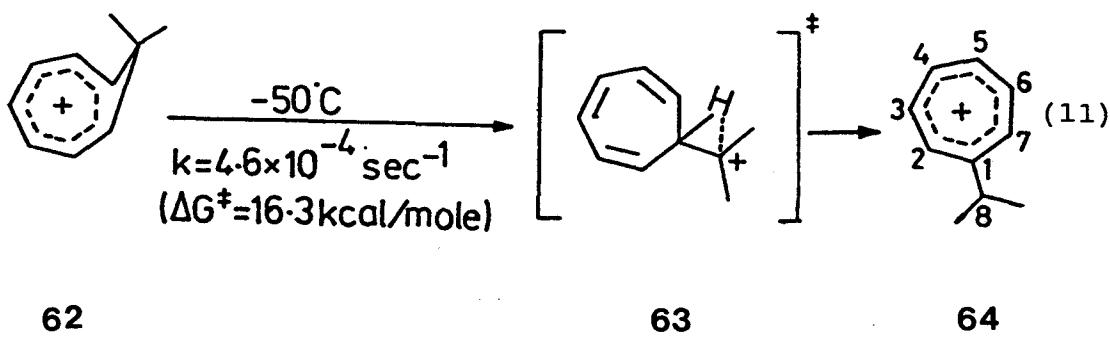


Recently Childs and Varadarajan have studied the acid catalysed rearrangement of 8,8-dimethyl-2,3-homotropone 57, reaction which appears to involve the formation of the corresponding 2-hydroxyhomotropylium cation.⁶⁷ The results are summarized in Scheme 2.

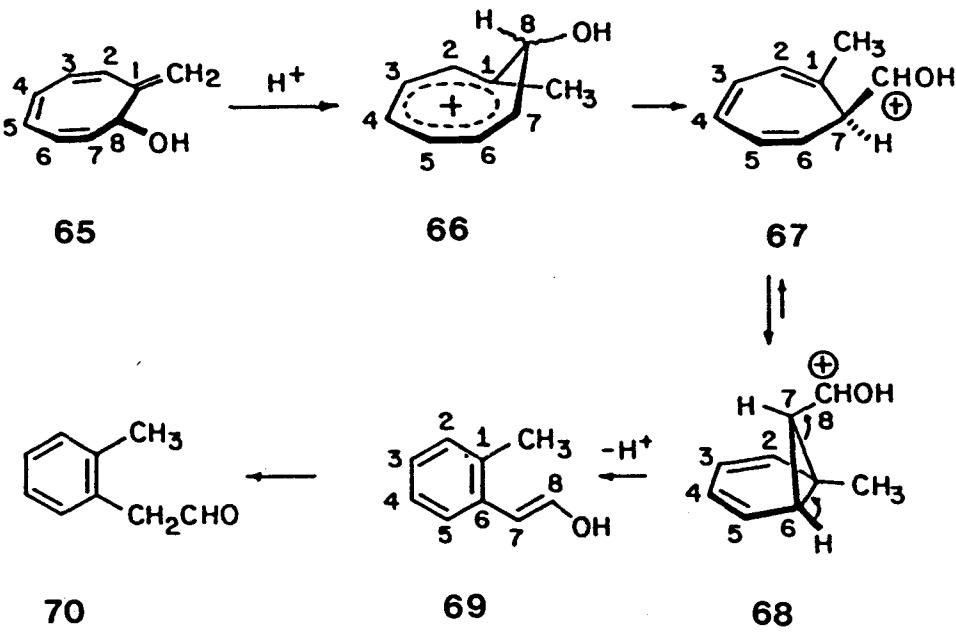


Scheme 2

These workers have also observed the following irreversible isomerization process in 8,8-dimethylhomotropylium cation (Equation 11).⁶³

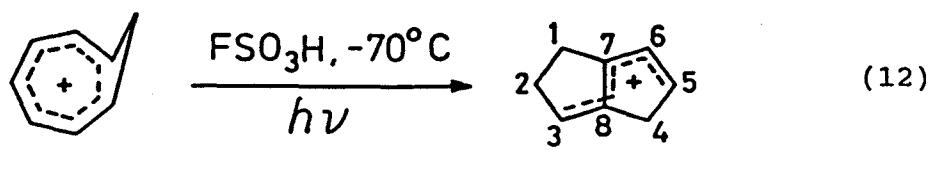


Paquette and coworkers have observed that proton transfer to the exo methylene carbon of 65 triggers formation of O-tolylacetaldehyde 70.⁹⁸ The mechanism proposed is outlined in Scheme 3.



Scheme 3.

In contrast to these thermal isomerizations the irradiation of homotropylium cation itself gave 1,2-dihydro-4H-pentalenyl cation 71 (Equation 12).^{68,69} The mechanism for this reaction is uncertain.



Electrophilic additions to cyclooctatetraene often yield ring contraction products. Electrophilic addition to cyclooctatetraene gives rise to 8-substituted homotropylium cation which then undergoes ring contraction followed by nucleophilic capture to give products.⁹⁹

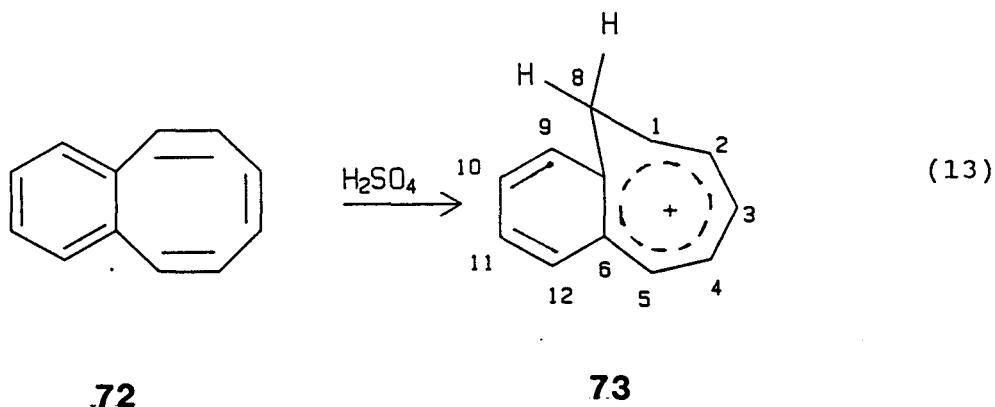
III. BENZOHOMOTROPYLIUM CATIONS

a. Preparation and characterization

Pettit and Merk have studied the protonation of benzocyclooctatetraene 72.⁷⁰ The NMR spectrum of benzocyclooctatetraene in H₂SO₄ consists of a doublet at δ 10.04 (1H), a complex set of bands in the range 7.92-9.30 (8H), a quartet at 5.36 (1H) and a triplet at 1.50 (1H). The data are consistent with the formation of the benzo-homotropylium cation 73. It is interesting that both simple perturbation MO theory and SCF MO theory predict that protonation of benzocyclooctatetraene should give the cation 73.⁷⁰

Three independent features point to a homoaromatic structure for 73. First the large difference in chemical shift between protons H_a and H_b (3.9 ppm) suggests the presence of a ring current. Second the coupling constant between H_a and H_b in 73 is in an intermediate range between fully formed cyclopropyl systems and acyclic methylenes. Finally as the data in Table 6 show the UV spectrum of the cation 73 bears a very strong similarity

to that of the benzotropylium cation 74. The chemical shift difference $\Delta\delta$ between exo and endo protons in 73 is 3.86 ppm. This decrease in $\Delta\delta$ from the value observed for the parent homotropylium cation 7 is attributed to a dampening of the extent of homoallyl interaction by the presence of the benzene ring.



.72

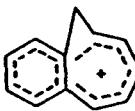
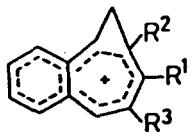
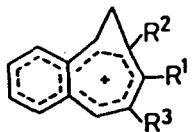
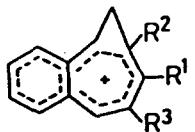
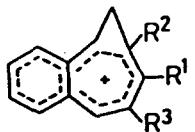
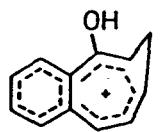
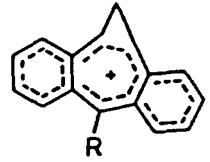
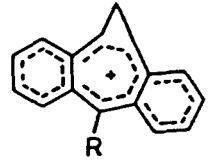
73

Table 6.
UV spectral date for compounds 73 and 74

Compound	λ_{max} (m μ) (log ϵ)
Benzotropylium cation, 74	233 (4.25)
	280 (3.91)
	315 (3.38)
	400 (3.43)
Benzohomotropylium cation, 73	234 (4.30)
	282 (4.74)
	338 (3.54)
	426 (3.25)

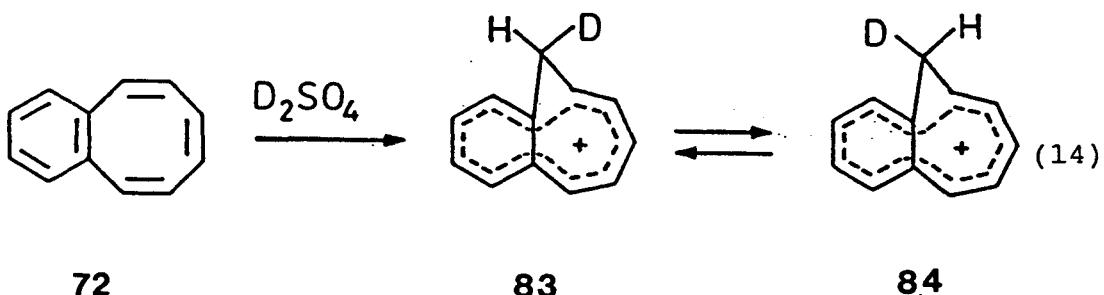
A variety of substituted benzohomotropylium cations have been reported. Some of these are listed in Table 7.

Table 7.
Benzannelated derivatives of homotropylium cations

Compound	Chemical shift difference ($\Delta\delta$)	Reference	
73		3.86	70
75		5.34	71
76		2.41	71, 72
77		2.29	72
78		-	73
79		2.30	74
80		4.67	75, 76
81		3.96	75, 76
82		3.20	77

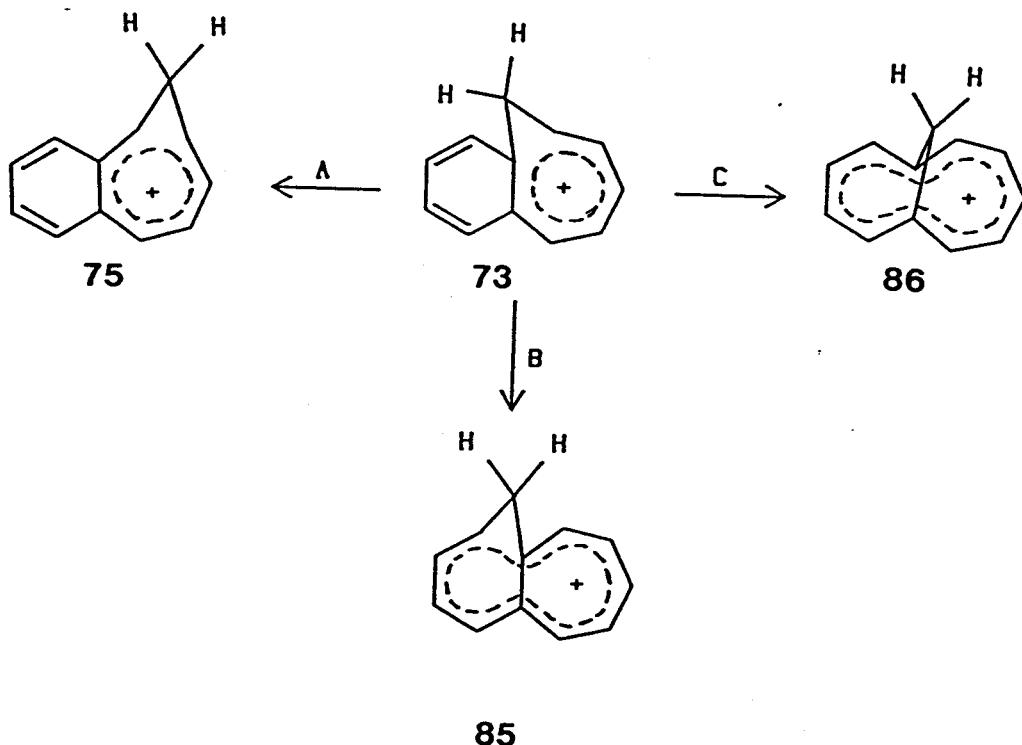
b. Ring Inversion Reactions

As was observed in the parent homotropylium cation a ring inversion process also occurs in benzohomotropylium cation 73 (Equation 14)⁷⁰. Using the deuterated cation 83, Pettit showed that this process occurs at room temperature.



No other reactions of benzohomotropylium cation have been reported.

While no circumambulation rearrangements of benzohomotropylium cation 73 have been reported it is interesting to note that if such a reaction were to occur then three different products could be formed. The first of these, giving cation 75 is unexceptional. The second to form 85, moves the bridge to the six-membered ring. The third rearrangement moves the bridge to the two atoms common to both rings forming 86.



This third possibility is particularly interesting in that such an ion is well known. It is in fact bridged [11]-annulene, first described by Vogel and coworkers.⁷⁹

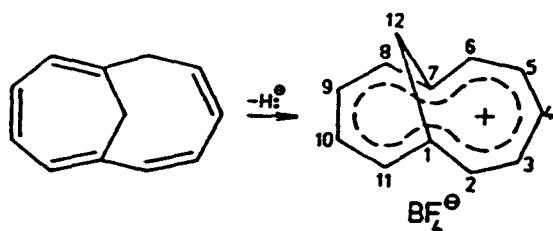
IV. BRIDGED [11]-ANNULENES

a. Relationship to benzohomotropylium cations

Annulenes are completely conjugated monocyclic polyenes. The ring size of the annulene is indicated by a number in brackets. Many of these systems show aromatic character when they possess a $(4n+2)\pi$ electron configuration. Despite their aromatic properties,

annulenes such as [10]-annulene are highly reactive molecules. Their reactivity would seem to stem from the difficulty of getting them to adopt a planar geometry as a result of the bond angle strain. Vogel showed that this geometric problem can be overcome by joining atoms 1 and 6 of [10]-annulene with a CH_2 group.⁸⁴ These bridged annulenes are stable, aromatic systems. The resonances of the bridge protons in annulenes experience a shift to higher field due to the ring current in the molecule. Some of the substituted derivatives of [11]-annulenium cation which have been prepared are summarized in Table 8.

Vogel and coworkers have also synthesized the bicyclo[5.4.1]dodecapentaenylium cation 86 by treatment of 87 with triphenylmethyltetrafluoroborate.^{79,85}



87

86

The exact structure of bicyclo[5.4.1]dodecapentaenylium cation has been a matter of some debate. Vogel and coworkers formulated the ion in terms of a perturbed [11]-annulenium system 86.⁸⁰ On the other hand Masamune

and coworkers have suggested a benzohomotropenylum structure from their ^{13}C NMR spectra.^{82,83}

b. Molecular Geometry

A single crystal x-ray diffraction study of bicyclo [5.4.1]dodecapentaenylium hexafluorophosphate was carried out by Simonetta and coworkers.⁸⁶ They concluded that 86 has a relatively open structure similar to that of the neutral bridged [10]-annulenes with a C₁-C₆ distance of 2.299 Å.

The main features of the cation geometry are represented in Figure 4. The structure would appear to have minimal orbital overlap between the C₁- and C₆-positions or the system can be considered to be a [11]-annulene system.

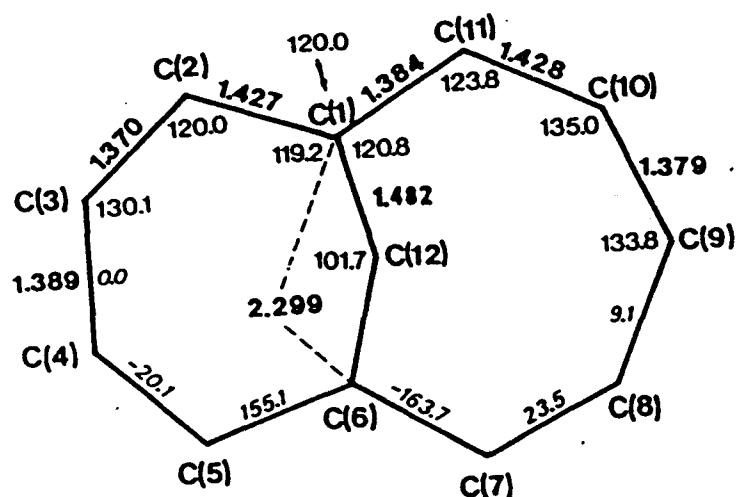


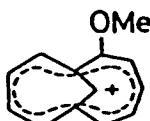
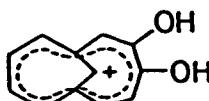
Figure 4. A Schematic representation of the bicyclo [5.4.1]dodecapentaenylium cation geometry.⁸⁶

c. Electronic Structure

Haddon has studied the structure of 86 using perturbational molecular orbital (PMO) theory.⁸⁷ He suggested that the homo interaction is less important in the [11]-annulenium cation than 1,6-methano [10]-annulene 88. This probably results from the differing angles between the $p\pi$ orbitals at the C₁, C₆- positions in the two molecules. The dihedral angles of the bonds to the 1,6 atoms are 34.0° in [1,6] methano-[10]-annulene but only 24.9° and 16.3° in 1,6 methano-[11]-annulenium cation 86. Thus in the case of 88 the $p\pi$ -orbitals will overlap more effectively at these positions than in 86.

Table 8.

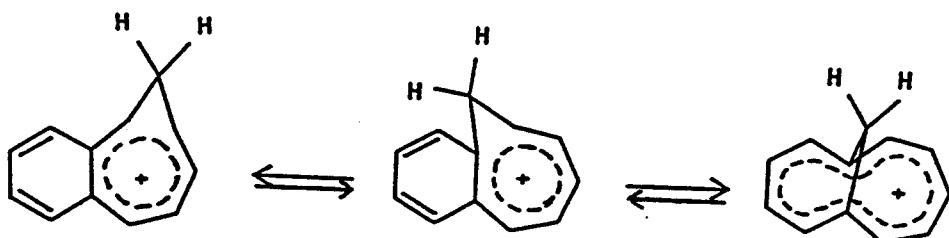
Bridged [11]-annulenium cation derivatives

System	Bridge protons ($\Delta\delta$ ppm)	Reference
	-0.2, -0.6 (J=11.0Hz).	84, 85
89		
	-	85
90		
	-0.3, -1.8	88
91		
	-1.05, 0.13 (J=10.7Hz).	81
92		

V. OBJECTIVES OF THE PRESENT STUDY

As 1,6-methano-[11]-annulenium cations are isomeric with benzohomotropylium cations in principle it is possible for these systems to be inter converted by a circumambulatory migration of the 'bridging' methano group. No circumambulatory rearrangements of benzohomotropylium cations have yet been reported.

Homotropylium cations with two methyl groups at C₈ have been shown to undergo facile circumambulatory rearrangements. For example such rearrangements have been well established in the case of 8,8-dimethyl-hydroxyhomotropylium cations. As a result it would be of interest to prepare examples of benzohomotropylium cations which would possess two methyl groups at the bridge position. The purpose of the work described here was to prepare such benzohomotropylium cations and investigate the possibility of these isomers undergoing circumambulatory rearrangements to give a bridged [11]-annulene.



75

73

86

The results of these studies are discussed in detail in the succeeding chapters.

In addition to this experimental approach, the relative stability of these isomers has been explored using theoretical calculations. In particular it was hoped that the relative stability of these benzohomotropylium cations might be modified by the suitable placement of additional ring substituents.

RESULTS AND DISCUSSION

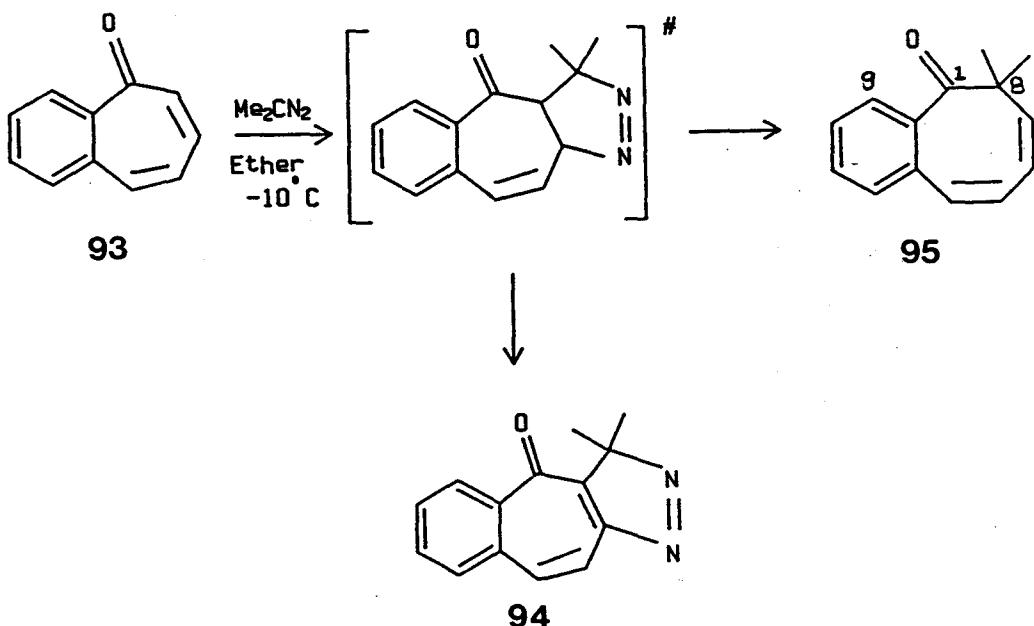
CHAPTER 2

I. REARRANGEMENT STUDIES ON 8,8-DIMETHYL-1-HYDROXY-2,3-BENZOHOMOTROPYLIUM CATIONS

The main aim of this project is to examine the relationship between the bridged [11]-annulenium and benzohomotropylum cations. The 8,8-dimethyl compounds were chosen for study because of the ease of the circumambulatory rearrangements of similar cations.

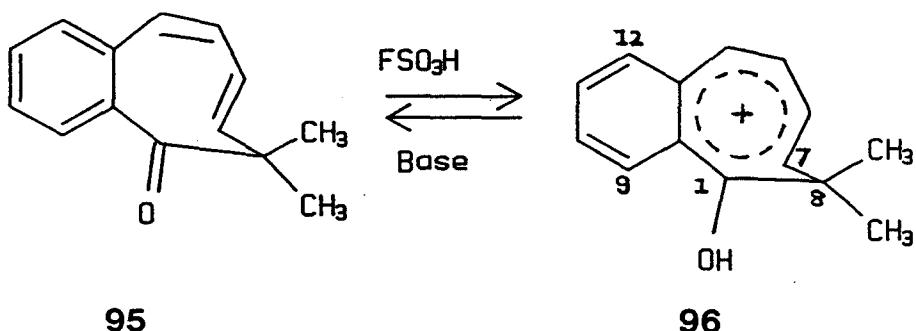
1. Preparation and protonation of 8,8-dimethyl-2,3-benzohomotropone

The 8,8-dimethyl-2,3-benzohomotropone 95 was prepared by the procedure of Franck-Neumann and Martina.⁸⁸ The addition of diazopropane to 2,3-benzotropone 93, gave 94 and 95 via a pyrazolotropone intermediate. Compounds 94 and 95 were isolated and purified by flash column chromatography. The ¹H and ¹³C NMR spectral data for these compounds (Tables 9 and 10 respectively) are in agreement with those reported in literature.



Dissolution of 95 in FSO_3H at -78°C gave the corresponding 1-hydroxy benzohomotropylium cation 96. The ^1H and ^{13}C NMR spectra of the cation obtained at low temperatures (Figure 6) were in agreement with the assigned structure (Tables 9 and 10 respectively).

The 500 MHz ^1H NMR spectrum of 96 exhibited resonances at δ 0.38 and δ 1.87 corresponding to the two methyl groups attached to C_8 of the eight membered ring. The proton resonance at δ 5.31 corresponded to H-7 and the other ring protons appeared from δ 7.08 to 7.99 ppm .



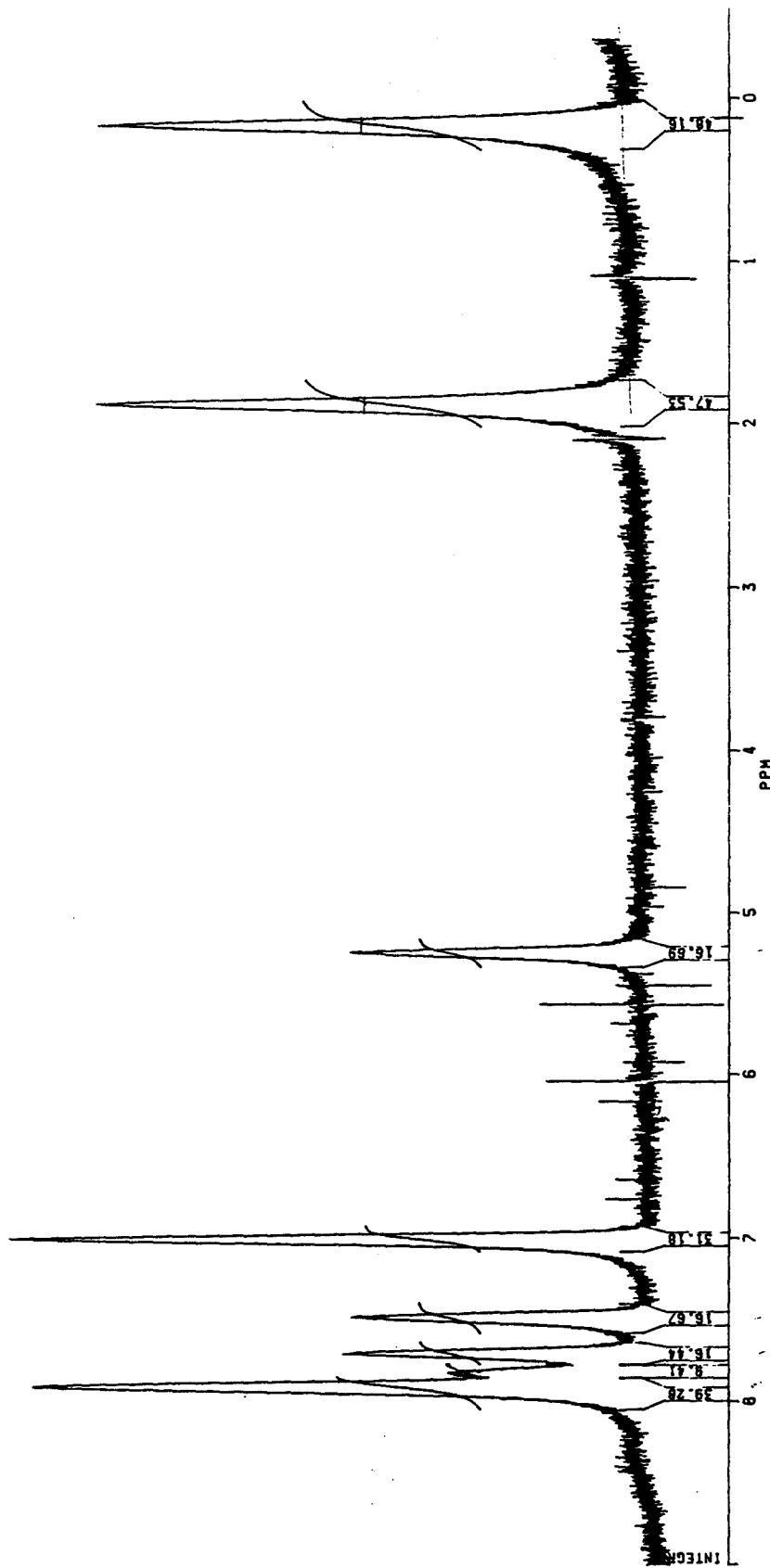
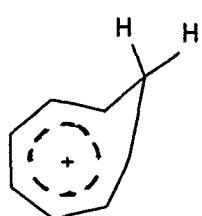


Figure 5 : ^1H NMR spectrum of cation 96 at -78 °C

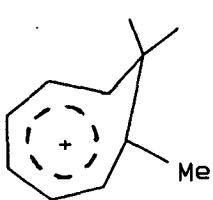
The resonances of the methyl groups on C₈ of 96 have distinctly different chemical shifts indicating that they are in different magnetic environments. If the 8-membered ring of 96 is non planar with C₈ tilted up out of the plane of the other ring atoms, just as has been found with other homotropylium ions (eg 7) then one of the methyls will be over the ring and the other in an exo position.

It has been suggested that one measure of cyclic delocalization in homoaromatic systems has been the magnitude of the chemical shift difference of resonances of the exo and endo substituents on the bridging carbon in the NMR spectrum of a system.⁴⁰ The chemical shift difference ($\Delta\delta$) of the C₈ substituent resonances of a range of homotropylium species are shown in Figure 7.1,^{40,70}

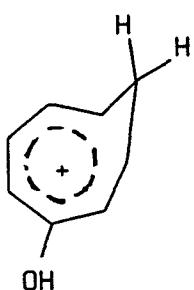
As can be seen by comparing 7 with 34 or 47 the chemical shift difference between the two C₈ proton resonances is attenuated by about a factor of 2 on introduction of the hydroxy group onto C1 or C2 of the homotropylium cations.¹ Nevertheless, the chemical shift difference for 34 ($\Delta\delta = 3.1\text{ppm}$) is still appreciable. The decrease in $\Delta\delta$ in 73 as compared to 7 is attributed to a dampening of the homo-interaction by the presence of the benzene ring.⁷⁰

$\Delta\delta = 5.8$ 

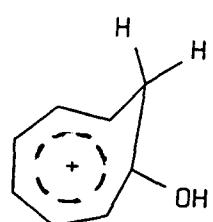
7

 $\Delta\delta = 5.0$ 

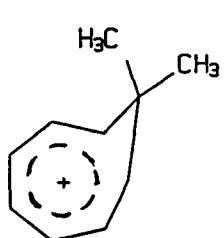
97

 $\Delta\delta = 3.1$ 

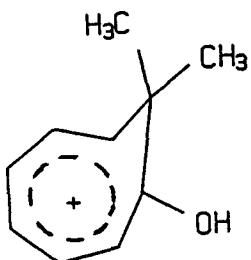
47

 $\Delta\delta = 3.1$ 

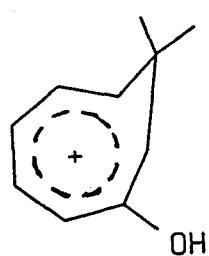
34

 $\Delta\delta = 2.8$ 

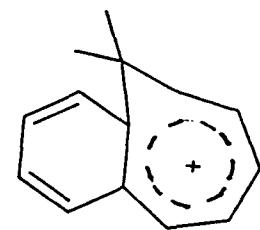
62

 $\Delta\delta = 2.0$ 

45

 $\Delta\delta = 1.2$ 

46

 $\Delta\delta = 3.9$ 

73

Figure 6: Differences in ^1H Chemical Shifts of the Exo and Endo Substituent Resonances.

The chemical shifts of hydrogens at C₈ are more sensitive to an induced ring current than those for methyl groups which are located further away from the centre of the ring. Thus the chemical shift difference, $\Delta\delta$, for the C₈ methyl substituents of 62 is attenuated by approximately 3 as compared to the corresponding C₈ protons of 7. Introduction of a hydroxy substituent on the ring of 62 (eg 45 or 46) again reduces the chemical shift differences between the C₈ methyl groups.

Examination of the results obtained here for 96 show that $\Delta\delta$ is 1.47 ppm. This observed chemical shift difference is smaller than that observed for 73 or 45 as would be expected. Overall it would appear that the hydroxy group on C₁ of a benzohomotropylium cation reduces but by no means eliminates cyclic delocalization. Using the criterion for homoaromaticity of the presence of an induced ring current 96 may be classified as an homoaromatic cation.

The ¹³C NMR spectra (Table 6) of solution of these compounds in FSO₃H are also in accord with the assigned cationic structures.

Table 9.

¹H NMR Spectral data for 94, 95 & 96.

Comp	Solv	Temp	Chemical Shifts (δ ppm.) ^b										
			°C		H4	H5	H6	H7	H8	H9	H10	H11	H12
94	CDCl ₃	30	7.27	7.11	-	-	1.16	8.16	7.24	7.24	7.24		
			(d)	(d)			(s)	(d)	(m)	(m)	(m)		
95	CDCl ₃	30	6.63	6.04	5.76	5.64(1.39)	7.18	7.32 ^a	7.38 ^a	7.10			
			(d)	(dd)	(ddd)	(d)	(s)	(dd)	(td)	(td)	(td)		
96	FSO ₃ H	-58	7.56	7.08	7.08	5.31(1.85) (0.38)	7.78	7.99	7.99	7.99			
			(d)	(bd)	(bd)	(d)	(s)	(d)	(m)	(m)	(m)		
Coupling constants (Hz)													
Compd			J _{4,5}	J _{5,6}	J _{6,7}	J _{9,10}	J _{10,11}	J _{11,12}					
94			11.5	-	-	7.5	-	-					
95			12.2	4.5	12.2	-	7.6		7.5				
96			9.9	-	8.0	-	-	-	6.9				

^a Assignments may be reversed

^b All Chemical shifts referred to tetramethylsilane (CDCl₃ solvent) or internal CH₂Cl₂ taken as δ 5.3 (FSO₃H solvent), s: singlet; d:doublet; t:triplet; m:multiplet; values in parenthesis represent methyl groups.

Table 10
¹³C NMR Chemical Shifts data for 94, 95 and 96.

Compd	Solv	Temp °C	Chemical Shifts (ppm)		
			C ₁	C ₂ - C ₁₂	8-CH ₃
94 ^b	CDCl ₃	30	-	122.8, 131.7, 132.0, 133.4 136.1, 136.4, 139.3, 141.9	20.8
95 ^a	CD ₂ Cl ₂	29.4	212.5	125.4, 125.6, 127.2, 127.7 128.5, 129.3, 130.8, 133.5 139.7, 143.3, 50.2	26.1
96 ^a	FSO ₃ H	-78.1	194.0	127.1, 127.5, 128.8, 130.2 130.6, 135.7, 135.9, 136.3 136.4, 136.9, 137.9	22.5 16.1

^a Relative to CDCl₃ internal standard (δ 77.6) .

^b Relative to CD₂Cl₂ internal standard (δ 53.6) .

2. Reactions of benzohomotropylium cation

a. Ring inversion

1) ^1H NMR studies

The ^1H NMR spectrum of 96 displayed both a reversible and an irreversible temperature dependence. At temperatures up to -10°C a reversible averaging process was observed in which the signals of the two methyl resonances at δ 0.38 and δ 1.87 ppm, first broadened then coalesced and formed a sharp singlet at 1.10 ppm (Figure 7). The resonances of the other protons were not affected by this averaging process of the methyl resonances. This temperature dependent behaviour can best be explained in terms of a ring inversion or bridge flipping process involving C₈, the bridging carbon, that has the effect of interchanging the exo and endo C₈ substituents. A comparable ring inversion reaction in the parent benzohomotropylium cation has been reported by Pettit and coworkers.⁷⁰

2) Energy barrier and comparison with other systems

The rates of reaction for this ring inversion process in 96 were determined by simulating spectra for a range of different rate constants using the DNMR3 computer program. The computer was programmed to calculate the position and intensities of the ^1H NMR signals undergoing

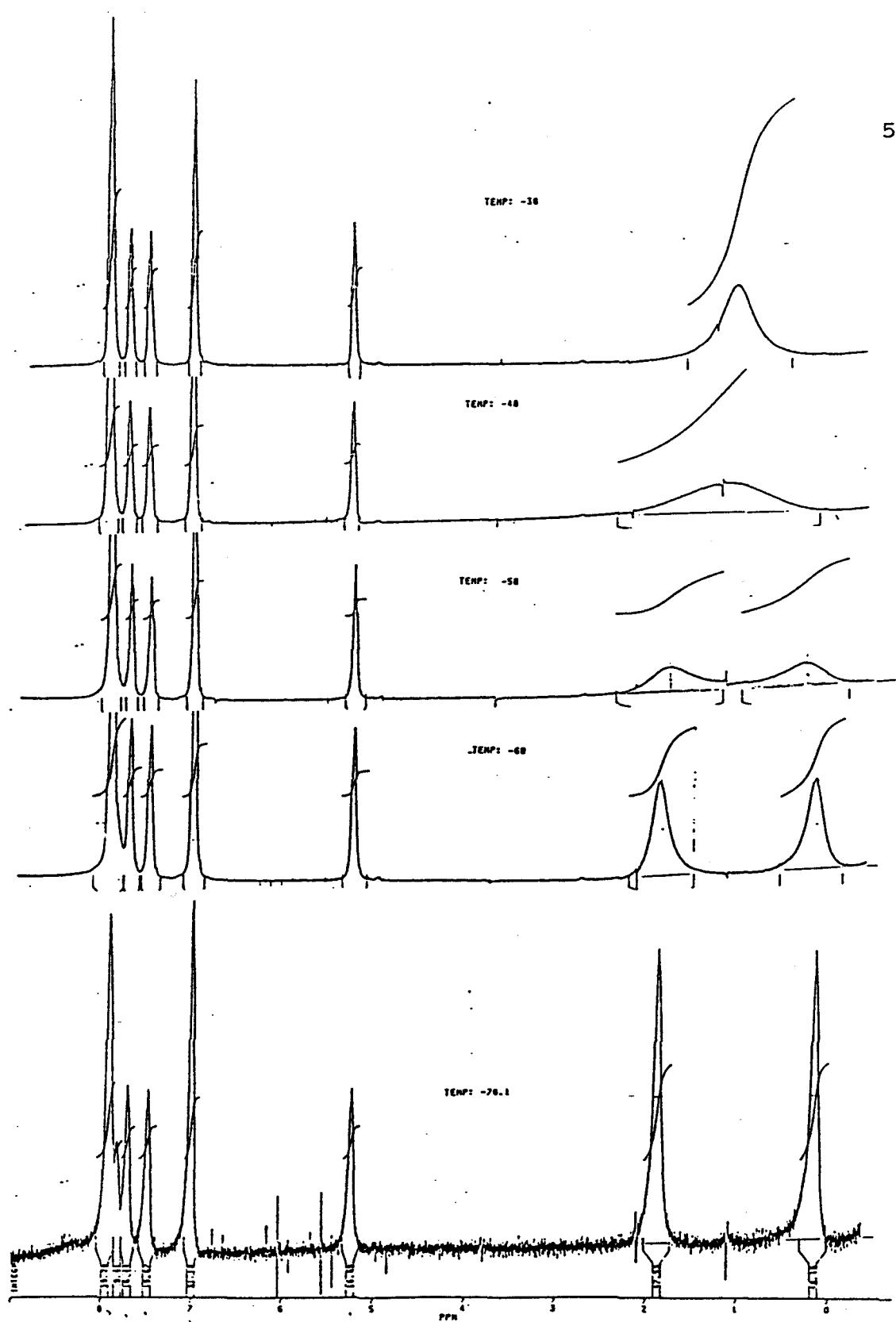


Figure 7: Variable Temperature ^1H NMR spectra of 96 from -78°C to -38°C

averaging with a given rate constant. The rate of migration was established when a good agreement between the experimental temperature dependent ^1H NMR spectra of 96 and calculated computer simulated spectra was obtained, Table 11. The ΔG^\ddagger values were then calculated by using the following equation 14.

$$\Delta G^\ddagger = -RT \ln [K_{\text{obs}} h / K_b T] \quad (14)$$

Where K_b : Boltzmann constant

$$(1.38 \times 10^{-23} \text{ J K}^{-1})$$

h : Planck's constant

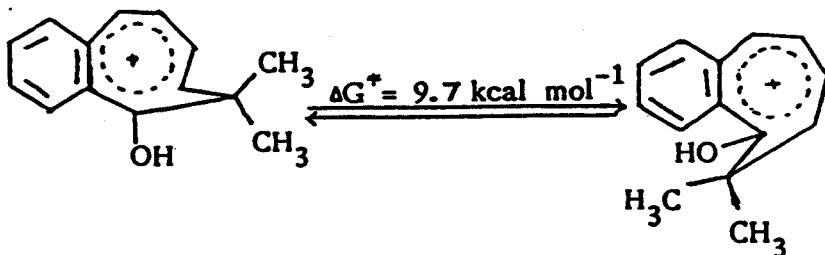
$$(6.626 \times 10^{-34} \text{ J S})$$

T : Temperature in k.

K_{obs} : Rate constant obtained from DNMR3 program.

R : Gas constant

$$(8.314 \text{ J. K}^{-1} \text{ mol}^{-1})$$



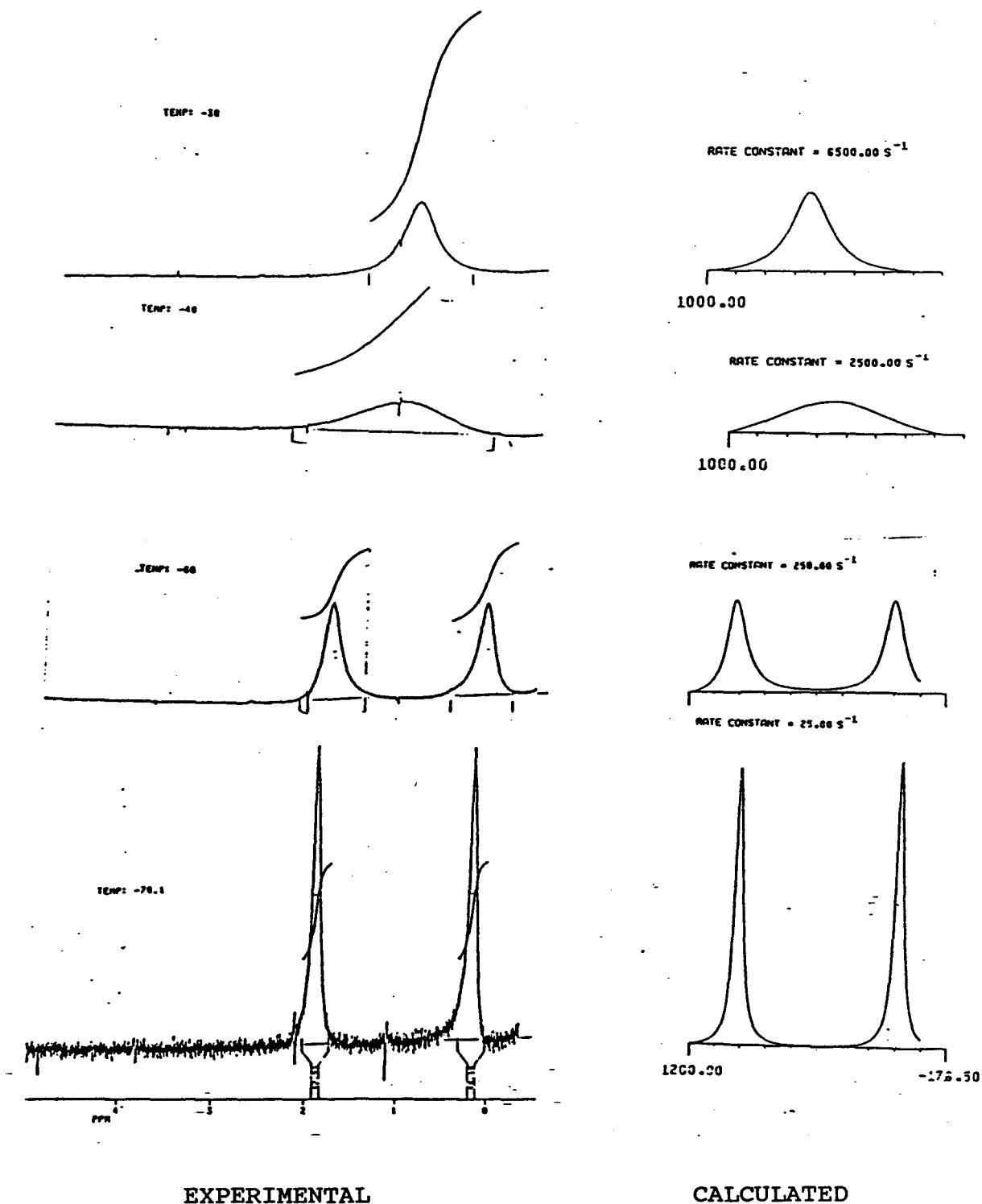


Figure 8: ${}^1\text{H}$ NMR Spectra of 96

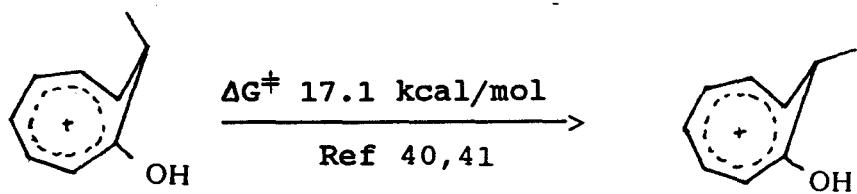
Table 11

Rate constants for the degenerate rearrangement of 96

Rate constant sec ⁻¹	Temperature °C	ΔG [#] kcal/mol
25	-78.1	10.1
250	-68	9.6
2500	-48	9.5
6500	-38	9.5

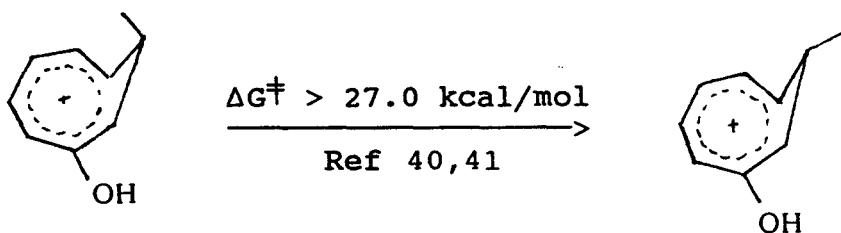
The ΔG[#] for the ring inversion process of 96 was estimated as (9.7 ± 0.25) kcal/mol. The barrier to inversion in 96 is considerably lower than observed for the parent homotropylium cation ($\Delta G^{\ddagger} = 22.3$ kcal/mol).

The variation in the barrier to inversion can be understood in terms of the degree of "openness" of the "homo bond" in the homotropylium cation. For example, consideration of the resonance structures in scheme 7, in the case of the 1-hydroxyhomotropylium cation 34, it can be seen that stabilization of the positive charge by the hydroxy substituent can only be achieved in the "open" form of the homotropylium cation. Inversion involves breaking the C₁-C₇ bond in the homotropylium cation and, substituents such as a 1-OH group which favors the open form will lower the barrier to inversion as compared to the parent system. The opposite effect is seen with a 2-OH substituent.



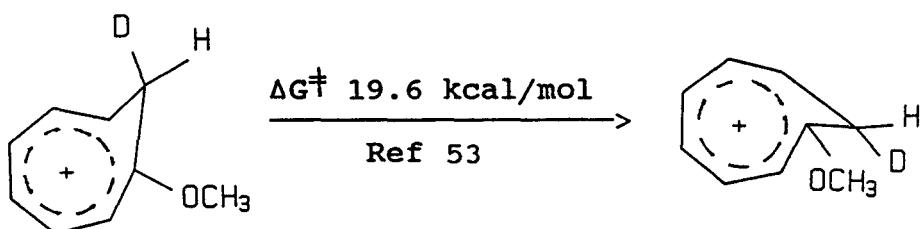
37

38



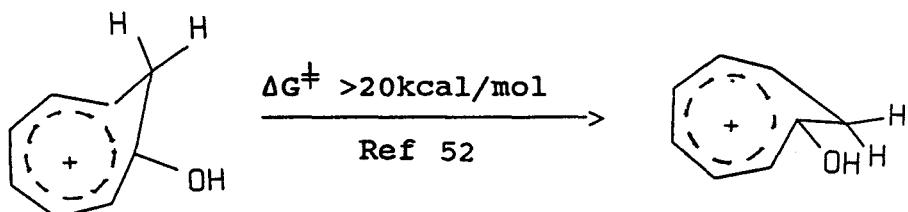
39

40



35

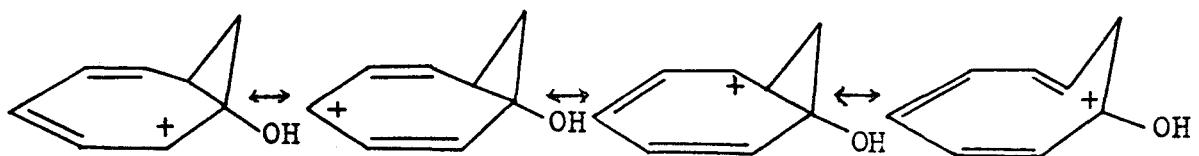
36



34

34

The much lower barrier to inversion in 96 as compared to even the 1-OH system of 34 suggests that 96 has an even more open structure than 34. It would thus seem that the fused benzene ring in 96 reinforces the effect of the 1-OH substituent.



Resonance Structures for the 1-Hydroxy homotropylium Cation (34)

34a

34b

34c

34d

b. Circumambulatory Rearrangements

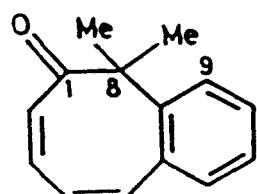
1) NMR Studies and identities of new cations

An irreversible isomerization process was observed when acid solutions of 96 were heated to temperatures above -8°C. As is shown in Figure 9, four new peaks in the methyl region of the spectrum were found to appear at δ 0.80(s), 1.74(s), 2.17(s) and 2.89(s) ppm which sandwich the original averaged peak at δ 1.10 ppm(s). Since each peak would seem to correspond to one methyl group and each product should have two methyl groups there should be two new compounds formed. In addition new peaks were formed in the aromatic hydrogen region.

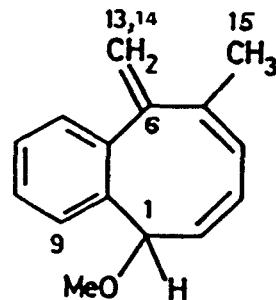
As it was difficult to assign these new peaks in

the proton spectrum of the rearranged material, the acid solution was quenched in $\text{NaHCO}_3\text{-MeOH}$ in ether at -78°C and the neutral products obtained were analyzed. The products of this irreversible isomerization were separated by centrifugal chromatography and, as will be shown below, were found to be 98 and 99 in a ratio of 2:1. The structural assignments of the products rests largely on their spectroscopic properties. The rate constant for the circumambulation of 96 was found to be $1.05 \times 10^{-3} \text{ sec}^{-1}$ and the corresponding $\Delta G^\ddagger = 20.3 \text{ kcal/mol}$.

The major product 98 was identified by its ^1H , ^{13}C NMR, UV, IR and MS spectra. The mass spectral analysis at both high and low resolution showed that this major compound has the same molecular weight as the starting ketone 95. The ir spectrum indicated that the carbonyl group was still present in 98. However, the NMR spectrum was different from that of the starting material. The ^1H and ^{13}C NMR spectra obtained for these compounds are reported in Tables 12 and 13 respectively.



98



99

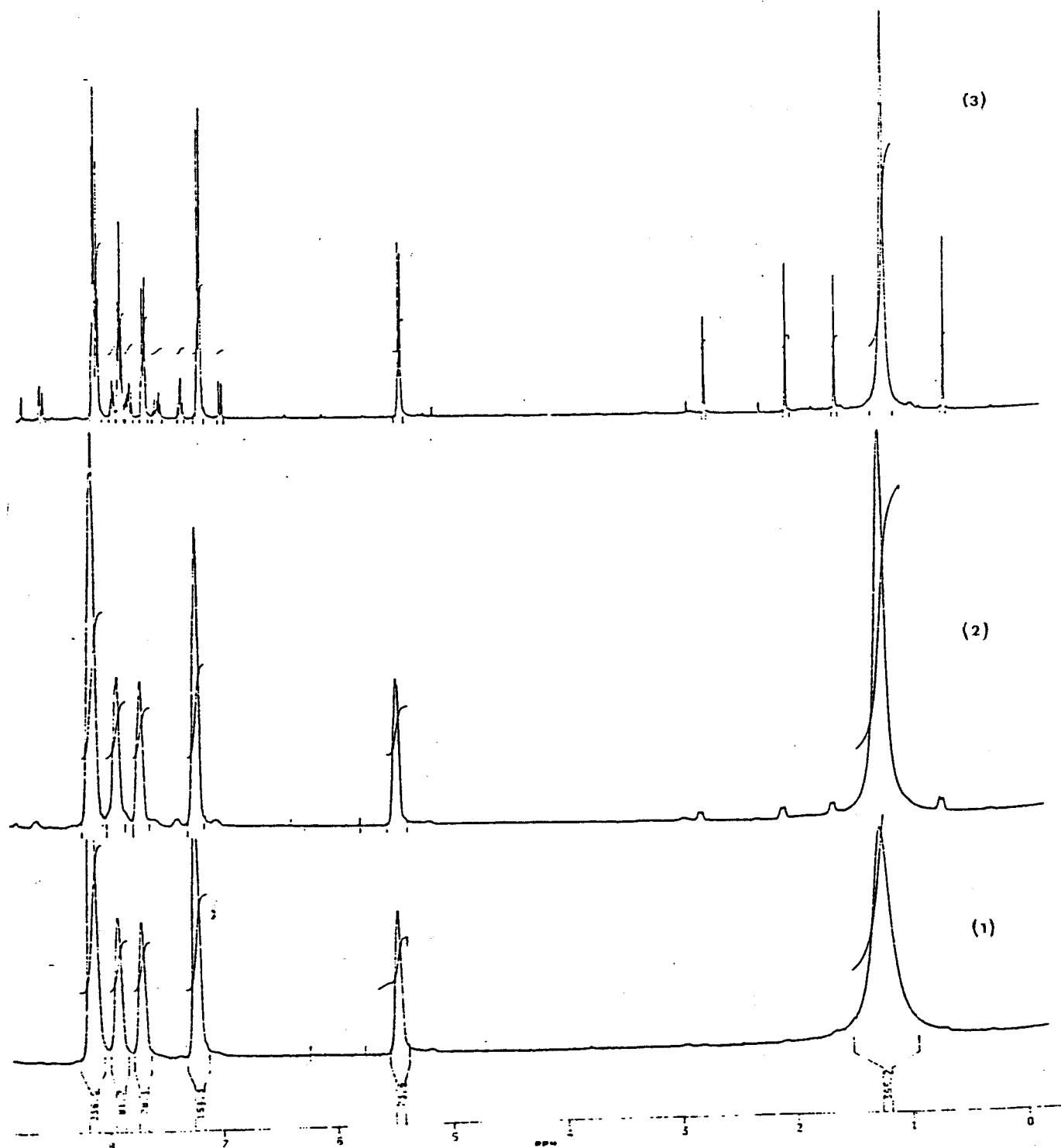


Figure 9: ^1H NMR Spectra of 96 (1) at -28°C (2) at -18°C
(3) at -8°C after 1 hour

Table 12
 ^1H NMR Spectral Data

Compd	98 ^a	99 ^a	101 ^b	103 ^b
Protons	Chemical Shifts (δ ppm)			
H-1	-	3.94(d)	-	9.61(d)
H-2	6.23(m)	5.72(dd)	7.11(d)	8.82(t)
H-3	6.23(m)	5.90(dd)	7.97(dd)	9.13(d)
H-4	6.23(m)	6.53(dd)	7.46(dd)	8.76(d)
H-5	7.14(m)	-	8.69(d)	-
H-6	-	-	-	-
H-7	-	-	-	-
H-8	1.53(s)	-	2.17(s) 0.80(s)	-
H-9	7.42(d)	7.44(d)	7.89(d)	9.11(t)
H-10	7.26(t)	7.34(t)	8.05(t)	8.62(t)
H-11	7.14(m)	7.13(td)	7.64(td)	8.62(t)
H-12	7.12(d)	7.34(t)	7.92(d)	8.86(d)
H-13	-	5.15(s) 5.13(s)	-	5.88(s) 5.35(s)
H-14	-	1.99(s)	-	2.43(s)
OMe	-	3.50(s)	-	

^a Chemical shifts referred to tetramethylsilane ($\delta=0$).
 s: singlet; d: doublet; t: triplet; m: multiplet,
 values in parenthesis represent methyl groups.

^b CH_2Cl_2 internal reference (δ 5.3 ppm)

Table 13
 ^{13}C NMR Spectral Data for 98, 99, 101 and 103.

Compd	solvent	Chemical Shifts (ppm)					
		C1	C2 - C12	δCH_3	OMe	C13	C14
98 ^a	CCl ₄	200.5	126.4, 127.6 127.9, 129.1 130.7, 130.8 135.6, 136.4 137.9, 52.6	25.6	-	-	-
99 ^a	CCl ₄	79.4	121.2, 121.8 124.1, 124.8, 128.2, 128.3, 131.8, 133.6, 139.8, 145.6, 146.7	-	56.8 116.2 22.5		
101 ^b	FSO ₃ H	169.0	156.1, 153.5, 23.7 150.8, 145.5, 17.8 141.6, 141.1, 140.1, 129.7, 126.4, 122.4, 121.3	-	-	-	-
103 ^b	FSO ₃ H	-	136.3, 139.6 139.7, 140.3 140.8, 142.9 143.7, 145.9 147.4, 157.9 161.4, 178.1	-	-	120.4	25.6

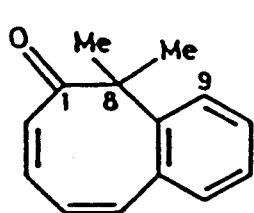
^a Relative to CCl₄ internal standard (δ 96.7 ppm)

^b Reference internal CD₂Cl₂ (δ 53.6 ppm)

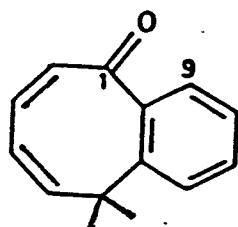
In the 500 MHz ^1H NMR spectrum of 98 the resonances of the two methyl groups appeared as a singlet at δ 1.53. The proton resonances at δ 6.23-7.14 (m) ppm correspond to H₂-H₅ protons and the other benzene ring protons appeared at δ 7.12-7.42 (m).

Examination of the proton resonances of 98 reveals that the coupling constants of the four spin system (H₂-H₅) is very similar to that of the 8-methyl cyclooctatriene-2,4,6-one previously reported by A.B.Holmes⁹⁶ indicating that C₂-C₅ is part of an eight membered ring.

The ^1H NMR spectrum of 98 was recorded in the presence of Eu(dpm)₃ shift reagent. The largest downfield paramagnetic shift observed of any of the hydrogens was for C₈ methyl protons, establishing its location nearest the carbonyl group. These data are consistent with 98, and rule out 100 from consideration.



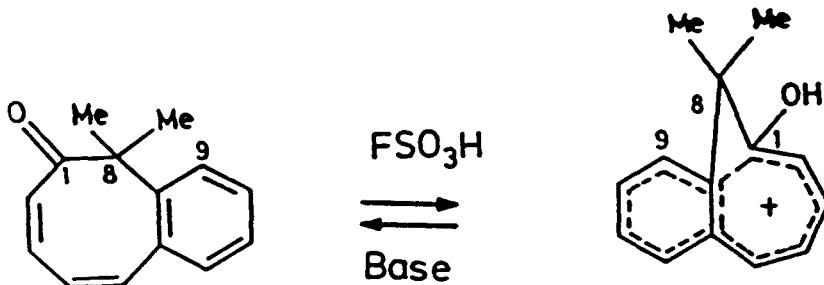
98



100

Extraction of 98 from CH₂Cl₂ into FSO₃H led to the formation of the corresponding hydroxy cation 101. This

cation was stable below 0°C and was quenched in Et₂O-HCO₃⁻ at -78°C to give the original ketone 98 in quantitative yield.



98

101

$$J_{2,3} = 12.1$$

$$J_{3,4} = 9.2$$

$$J_{4,5} = 12.1$$

$$J_{9,10} = 8.0$$

$$J_{10,11} = 7.5$$

$$J_{11,12} = 8.0$$

The 500 MHz NMR spectrum of cation 101 (Figure 10) clearly indicates that the signals due to all the protons experience a downfield shift as compared to those of 98.

The ¹H NMR spectrum of 101 showed resonances appearing as doublets at δ 7.11, 8.69, 7.89 and 7.92 ppm corresponding to H-2, H-5, H-9 and H-12, respectively (Figure 10). Proton resonances appeared at δ 8.05 and 7.64(t) correspond to H-10 and, H-11, respectively.

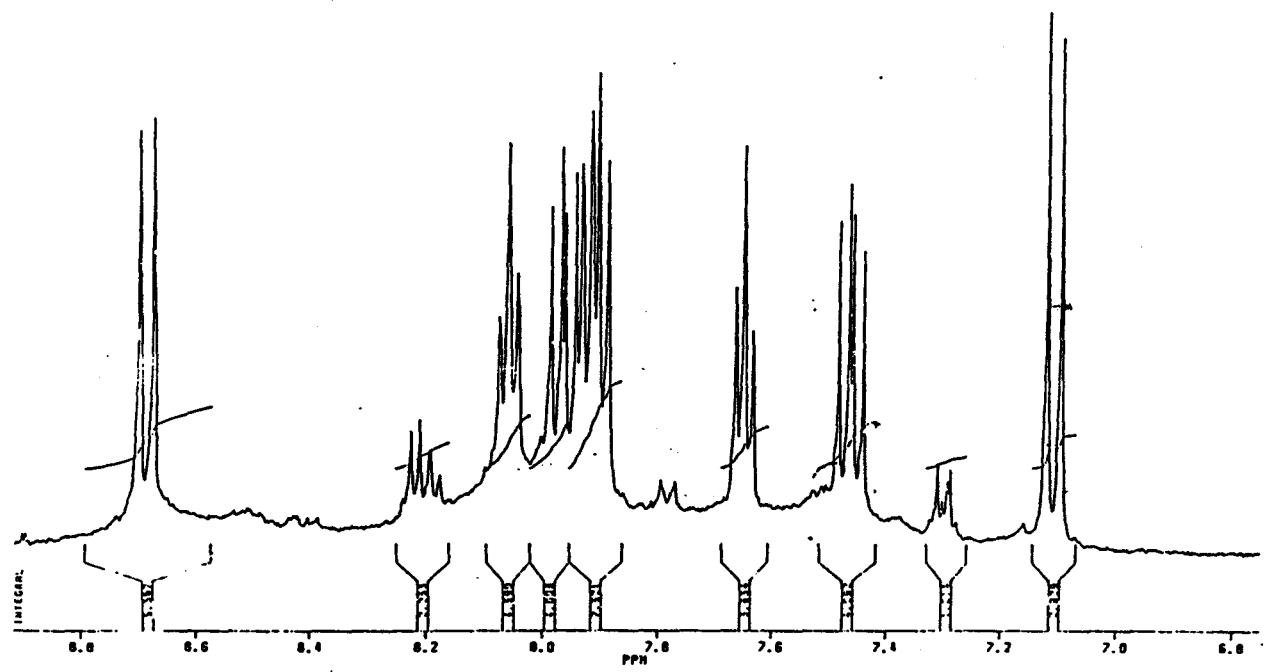
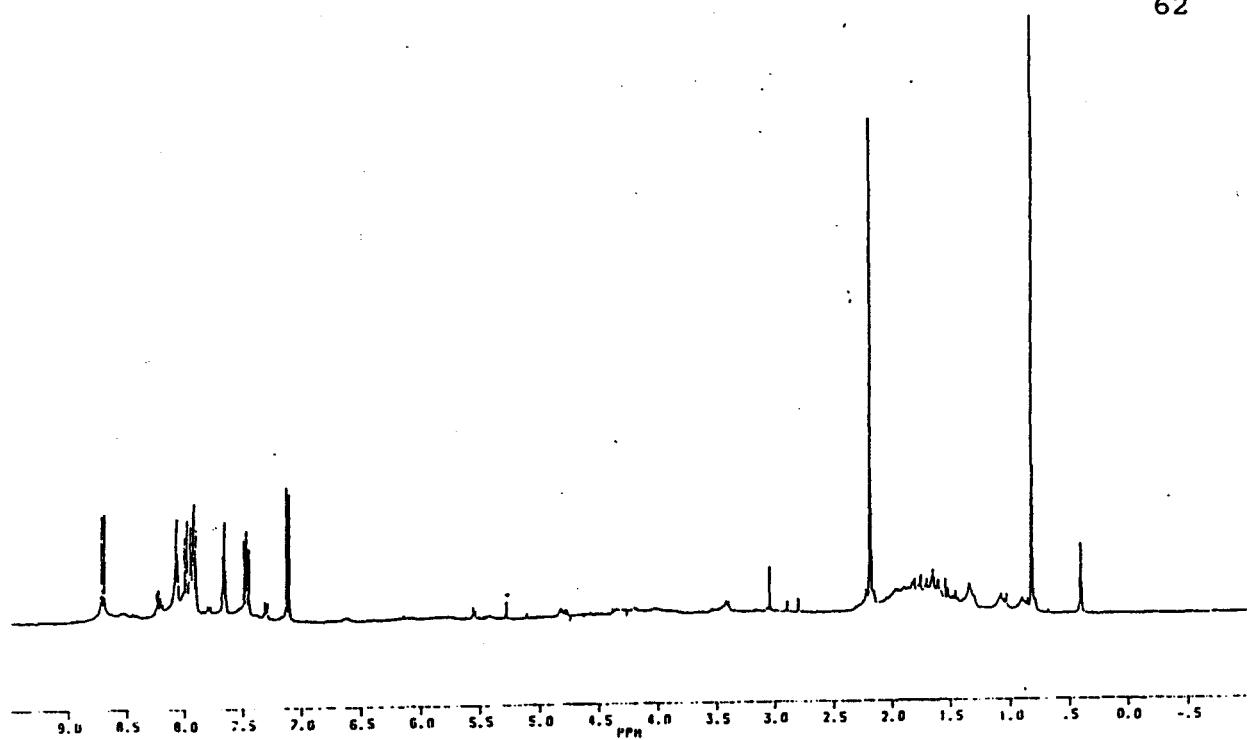


Figure 10: ^1H NMR Spectra of 101

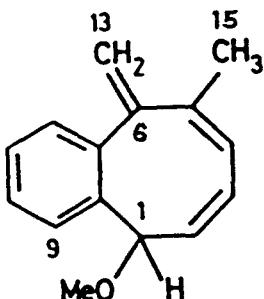
The other ring protons H-3 and H-4 appeared as quartets at δ 7.97 and 7.46 ppm respectively indicating that they each had two neighboring protons. Proton resonances at δ 2.17 and 0.80 ppm are correspond to the methyl groups attached to C₈. The chemical shift difference δ = 1.37 ppm between "endo" (8-CH_3) and "exo" (8-CH_3) signals is somewhat smaller than the value obtained in the 8,8-dimethyl-1-hydroxy 2,3-benzohomotropylium cation 96 (δ = 1.47 ppm). The deshielding of all the ring protons and the chemical shift separation of the methyl resonances suggest that 101 is a benzohomotropylium cation.

After neutralization of the FSO₃H acid the second product of the rearrangement of 96 was identified as 99.

The mass spectral analysis at both high and low resolution showed that this minor compound had a molecular weight of 212 which is 15 units higher than the starting material 95. This indicated that a CH₃ group had been added to 95 after the rearrangement. The ir spectrum indicated that the carbonyl group was lost from the original molecule. In addition the infrared spectrum showed, in particular, the presence of a band corresponding to a (=CH₂) group.

The ¹H NMR spectrum of 99 showed two resonances at δ 1.99 and 3.50, which correspond to methyl groups. The chemical shift of the latter of these resonances is in

such a position to correspond to methyl bonded to oxygen. The resonance at δ 5.13, 5.15 correspond to H-13, H-14 protons which correspond to an exocyclic double bond. The resonances at δ 7.13-7.44, 3.94, δ 5.72-6.53 ppm correspond to benzene ring protons, H-1, and vinyl protons of the eight membered ring respectively.



99

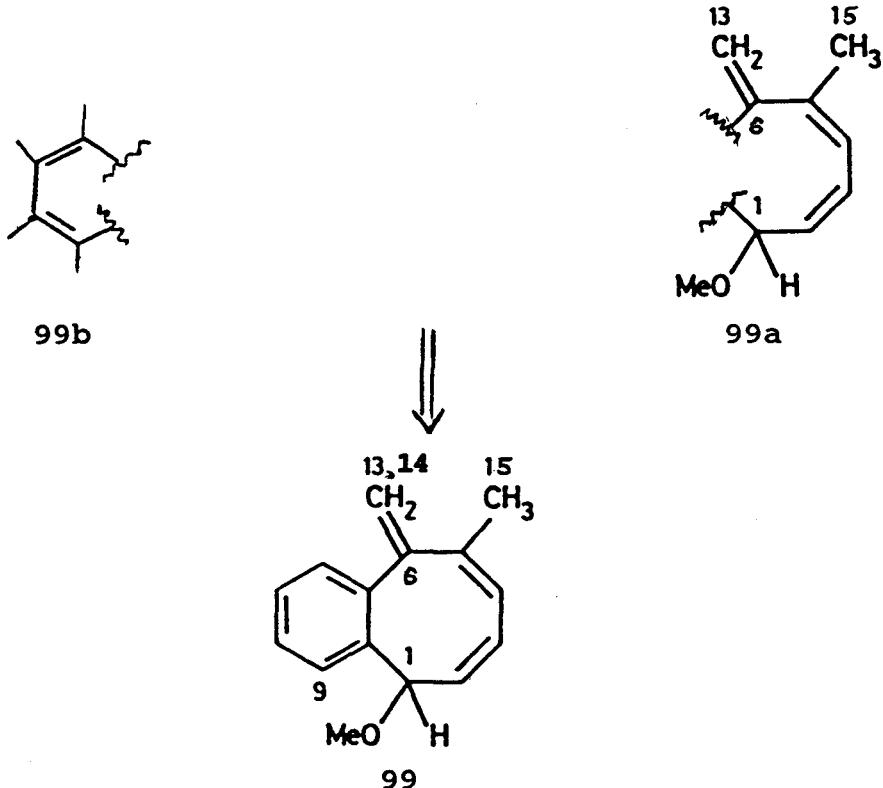
$J_{2,3} = 10.1$	$J_{9,10} = 7.6$
$J_{3,4} = 5.3$	$J_{9,11} = 1.2$
$J_{2,4} = 0.9$	$J_{10,11} = 7.5$
$J_{1,3} = 2.0$	$J_{13,14} = 1.4$
$J_{1,2} = 4.4$	

NOE measurements and homonuclear COSY techniques were used to locate the positions of the substituents on the eight numbered ring.

The pattern of couplings between the protons was deduced from the diagonal and cross peaks of the COSY spectrum. Beginning with the exomethylene protons H₁₃/H₁₄ ($J_{13,14} = 1.4$ Hz) which resonate at δ 5.13 and 5.15, it was noted that one of these protons shows a coupling to

three protons resonating at δ 1.99 ppm, which can be assigned as H₁₅. Similarly connectivities are also observed that correlate H₁ with H₂ which resonates at δ 5.72 ppm, H₂ with H₃ which resonates at δ 5.90, and H₃ with H₄ which resonates at δ 6.53 ppm. There are no connectivities beyond this point in this direction either as expected from the structure. Thus, from this series of operations, it is possible to assemble a rather large piece of the structure of 99 as represented by 99a.

In similar fashion, beginning with the H-9 benzene proton, correlations can be established to the H₁₀ proton H₁₀ and H₁₁ which resonate at δ 7.13 ppm. From the H₁₁ proton the H₁₂ protons, which resonate at δ 7.34 can also be assigned, reaching a termination point in the assignment process again as a consequence of the structure. The structural fragment thus assembled is shown by 99b.



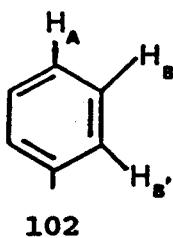
In summary, for 99, the COSY experiment provides two substantial structural fragments, 99a and 99b which would be a significant piece of information in establishing the structure of the molecule 99.

In addition nuclear Overhauser enhancements (nOe) confirm the relationship of H₁₅ and exomethylene protons. Irradiation of the H₁₅ resonance at δ 1.99 ppm gave significant positive nOe's at H₁₄ and H₄ resonating at δ 5.13 and 6.53 ppm respectively.

The irradiated resonance is indicated with a large arrow in Figure 11. It was already mentioned that H₁₄ is due to one of the exocyclic double bond proton resonances, hence the methyl group should be located adjacent to the

exocyclic double bond. Proceeding outward from these assignments, additional evidence was adduced from the ^{13}C NMR spectrum of 99 which displayed peaks at δ 22.5 and δ 116.2 ppm as expected for C_{15} and $=\text{CH}_2$, respectively (Figure 11).⁹² The peak at δ 56.8 is due to the $-\text{OMe}$ group and the other ring carbons appeared from δ 121.2 to 146.7 ppm.

A detailed examination of the ^1H NMR spectrum and coupling constants in 99 reveals further evidences regarding the structure of 99. The geminal coupling constant $J_{13,14} = 1.4$ Hz is in the normal range of such exomethylene protons.⁸⁹ The three spin system (H_2-H_4) coupling constants are very similar to those of the appropriate moiety in an eight membered ring.⁹⁰ Similarly, the four spin system (H_9-H_{12}) coupling constants in 99 are in the range of benzene 102.⁹⁰



$$J_{A,B} = 7-10 \text{ Hz.}$$

$$J_{A,B} = 2-3 \text{ Hz.}$$

Examination of models, clearly showed that the eight membered ring is not planar hence the H-1 proton will be placed in the shielding region of the eight membered ring depending on the stereochemistry of $-\text{OMe}$.

The above observations unambiguously assigned the structure 99 as indicated.

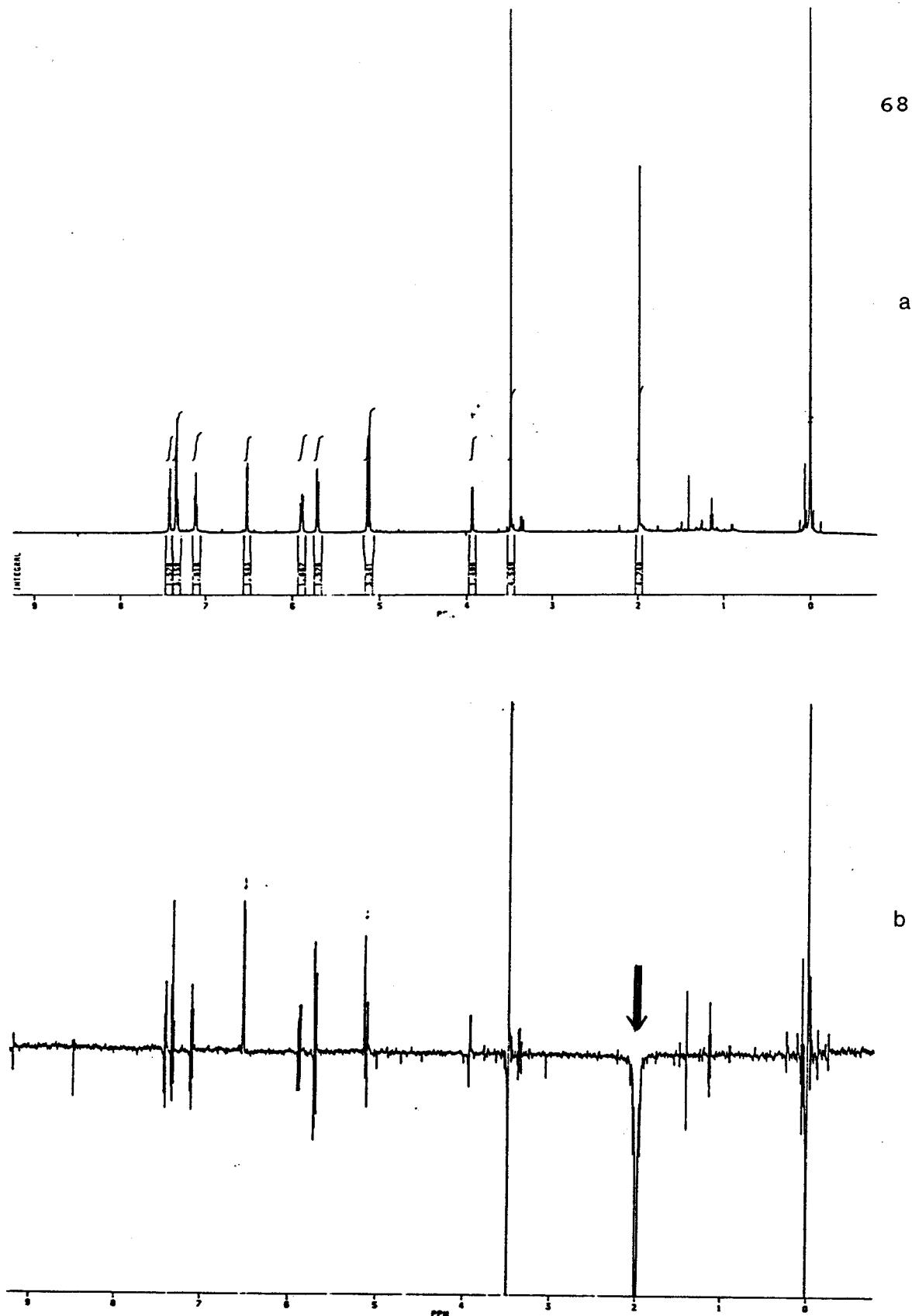


Figure 11: NOE Difference Spectrum of CH_3 at 1.99 ppm a) before irradiation b) after irradiation



a



b

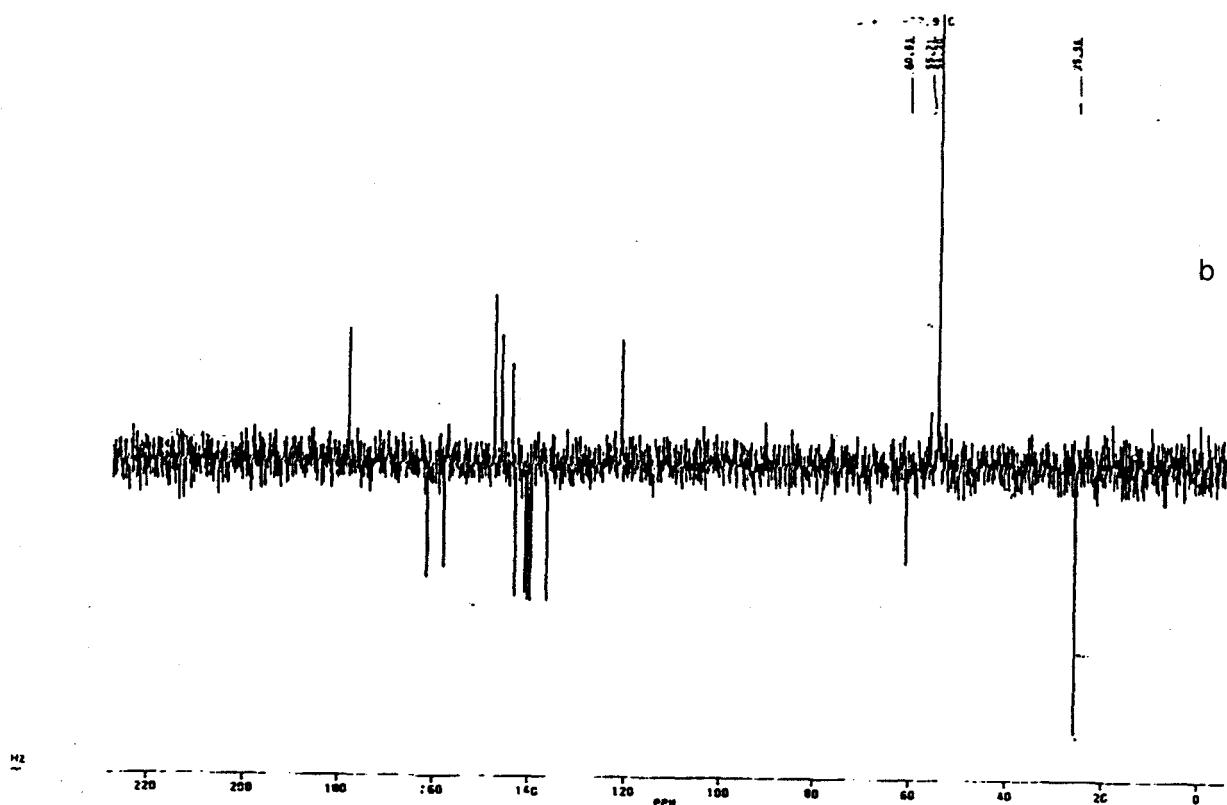
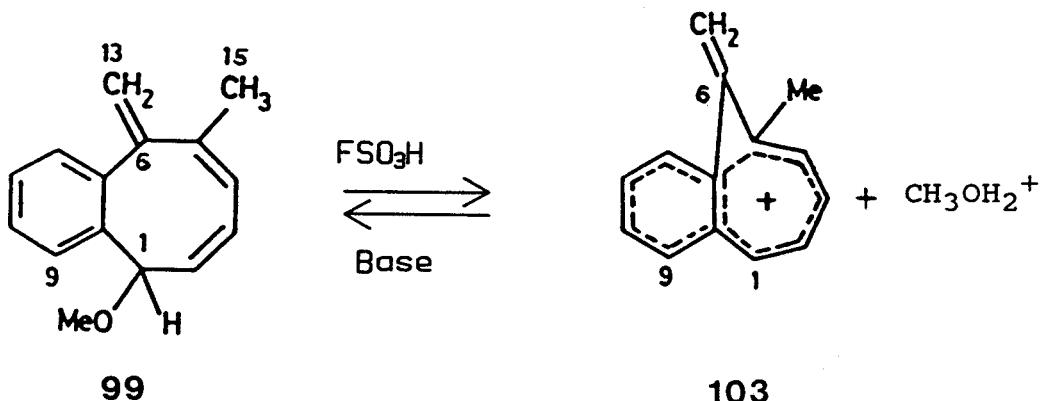


Figure 12: ^{13}C NMR Spectra of 99 and cation 103
(Spin Sort Experiment)

(a) 99 (b) 103

Extraction of 99 from CH_2Cl_2 into FSO_3H at low temperature (-78°C) would seem to give the unique homotropylium ion 103 that bears a vinyl substituent at C_6 . The cation 103 was stable below 30°C and could be quenched in $\text{MeOH}-\text{HCO}_3^-$ at -78°C to give the original methoxy ether 99. It is important to note that 103 is not present in the original rearrangement mixture of 96.



$$J_{1,2} = 10.0$$

$$J_{2,3} = 9.9$$

$$J_{3,4} = 10.0$$

$$J_{9,10} = 7.5$$

$$J_{10,11} = 7.2$$

$$J_{11,12} = 7.4$$

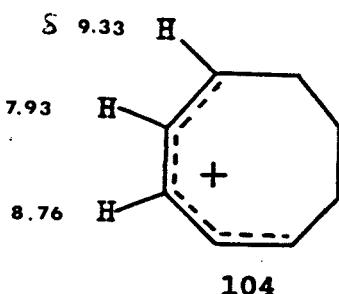
The ^1H NMR spectral data of solutions of 103 are given in Table 12. At 500 MHz most of the proton resonances of 103 were resolved and it was possible to obtain the proton/proton coupling constants. One feature of the spectrum is that, with the exception of the methoxy

signal at 3.50 ppm, the resonances of 103 have a similar pattern to those of the corresponding resonances of the neutral compound 99 but with all the proton resonances shifted downfield. In addition a peak was also observed at δ 4.3 ppm which corresponded to protonated CH_3OH_2^+ .

There are three major factors supporting the formation of the structure of 103 as being homoaromatic. First the position of the exocyclic proton resonances. Second the substantial downfield shifts of the vinyl proton resonances. Third the disappearance of the signal in the MeO^- region and the substantial downfield shift of the H_1 proton.

The exocyclic protons H_{13} and H_{14} were shifted ca 0.6 ppm downfield in comparison with that of the precursor 99. No coupling was observed between H_{13} and H_{14} (J_{gem})

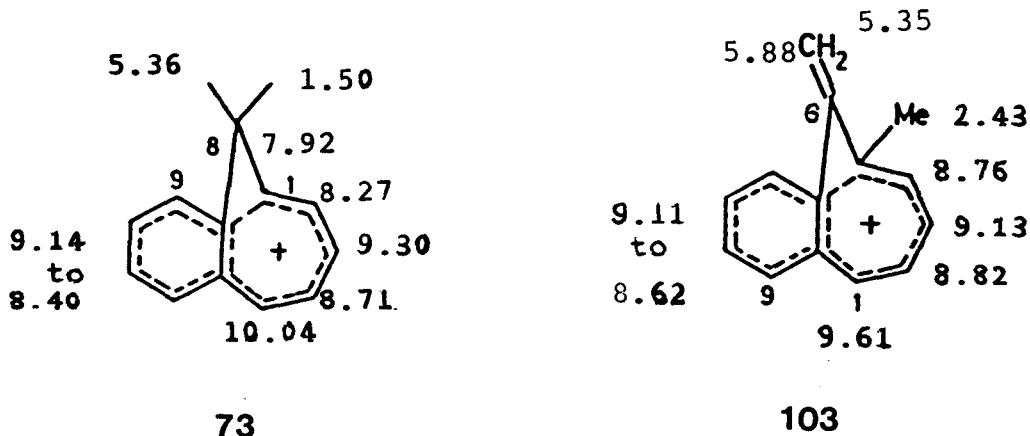
The downfield shifts of the resonances attributable to $\text{H}_1\text{-H}_4$ are particularly large and these protons occur further downfield than the corresponding resonances of cyclooctadienyl cation 104, scheme 4. 91



Scheme 4: The ^1H NMR Spectra of the Cyclopentadienyl Cation 104.

The downfield positions of the H1-H4 resonances in 103 are suggestive of the presence of an induced ring current indicating that the electronic structure of 103 may be represented as a benzohomotropylium cation.

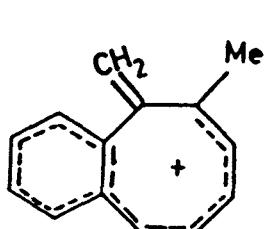
Pettit has reported the NMR spectrum of 73 in H_2SO_4 . Comparing the data obtained with Pettit's data strongly supports the homoaromatic character of the central ring. The most significant feature is that the H₁ (δ 9.61) experiences a similar deshielding as the corresponding proton H₅ in the cation 73 (δ 10.04).



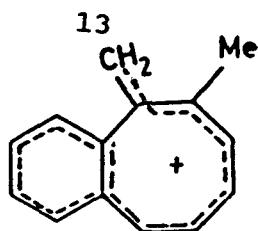
It should be noted that the C₅C₆C₇ bond angle should be close to 120° as C₆ is an Sp² hybridized carbon. As substantial angle strain is involved on going from 120° → 60°, it is very unlikely to have a closed cyclopropane structure. Consequently the C₅-C₇ internuclear distance will be long.

Compounds with long internuclear distances have been deemed homoaromatic. Childs et al in their analysis of the 1-ethoxy-homotropylium cation 26 concluded that even though 26 can best be regarded as a linear 1-ethoxy octatrienyl cation on structural grounds, the NMR reveals that 26 sustains an induced ring current.⁴⁵ In this case the C₁,C₈,C₇ bond angle and the C₁-C₇ bond distance were found to be 101.1° and 2.3 Å respectively. Haddon in his latest geometry optimizations of the molecular structure of homotropylium cation found that the ring current is 39% of the tropylium ion at R_{1,7} = 2.6 Å. The above observations support the homoaromatic nature present in 103.

Additional evidence for the structure of 103 was adduced from the ¹³C NMR spectrum of 103. It can be seen that the resonances of all the carbon atoms are shifted downfield on protonation. The exomethylene carbon atom (=CH₂) of 99 which displayed a signal at 116.2 ppm⁹⁷ was also experience small deshielding on protonation (4 ppm). That exclude the possibility of 105 being 103. Since in 106 a methylene group is at a charge centre as in various benzyl cations, an upfield shift would be expected for C₁₃ protons. Conversely all the protons moved downfield on protonation. This strongly indicates that no significant hybridization change is occurring at C13. This rules out the possibility of 106 being 103.



105

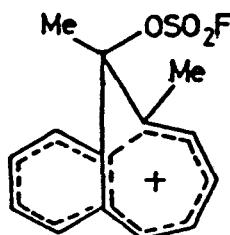


106

In conclusion, it is quite clear from these results that this cation 103 is homoaromatic, and can best be regarded as a benzohomotropylium cation. However the structural studies performed so far rely heavily on the NMR data and further studies of homotropylium cations such as x-ray studies or thermochemical properties will be more informative to support a homoaromatic formulation present in 103.

The precursor for the formation of 99 in the original solution obtained after rearrangement of 96 in FSO_3H could possibly be cation 107. Compound 99 was isolated and characterized spectroscopically. Protonation of 99 gives 103 and as has been mentioned above, this is not the same cation as observed in original rearrangement. As the 500 MHz ^1H NMR spectrum of the rearranged mixture of 96 was complex, all the individual peaks associated with 107 could not be assigned specifically. The signals which could be unambiguously assigned were those due to the methyl resonances at δ 1.74 and δ 2.89 ppm. The

remainder of the spectrum consisting of aromatic protons was a complex array of resonances ranging from δ 7.1 to δ 8.9 ppm. On the basis of the mechanism outlined in Scheme 6, 107 could be considered as a logical structure.

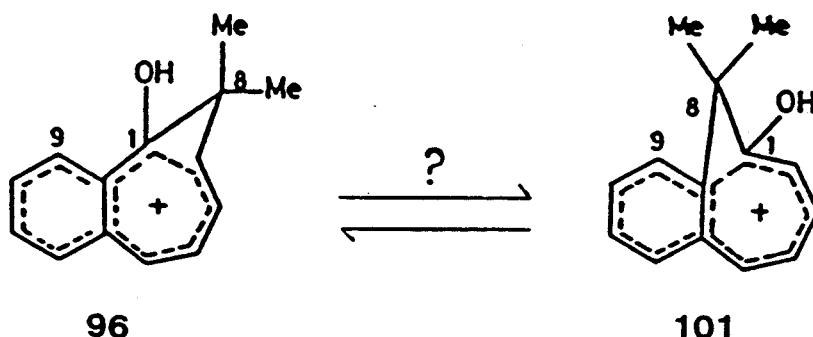


107

Homotropylium cations with similar substituents as those in 107 have been reported by Paquette and coworkers.⁹² A cation such as 107 would be expected to lose a FSO_3H molecule to give 99 on neutralization.

It is interesting to note that 103 rearranged to a new cation at room temperature. In this new cation the original methyl resonance at δ 2.89 ppm started to diminish, however due to the small quantity obtained after neutralization its characterization could not be carried out.

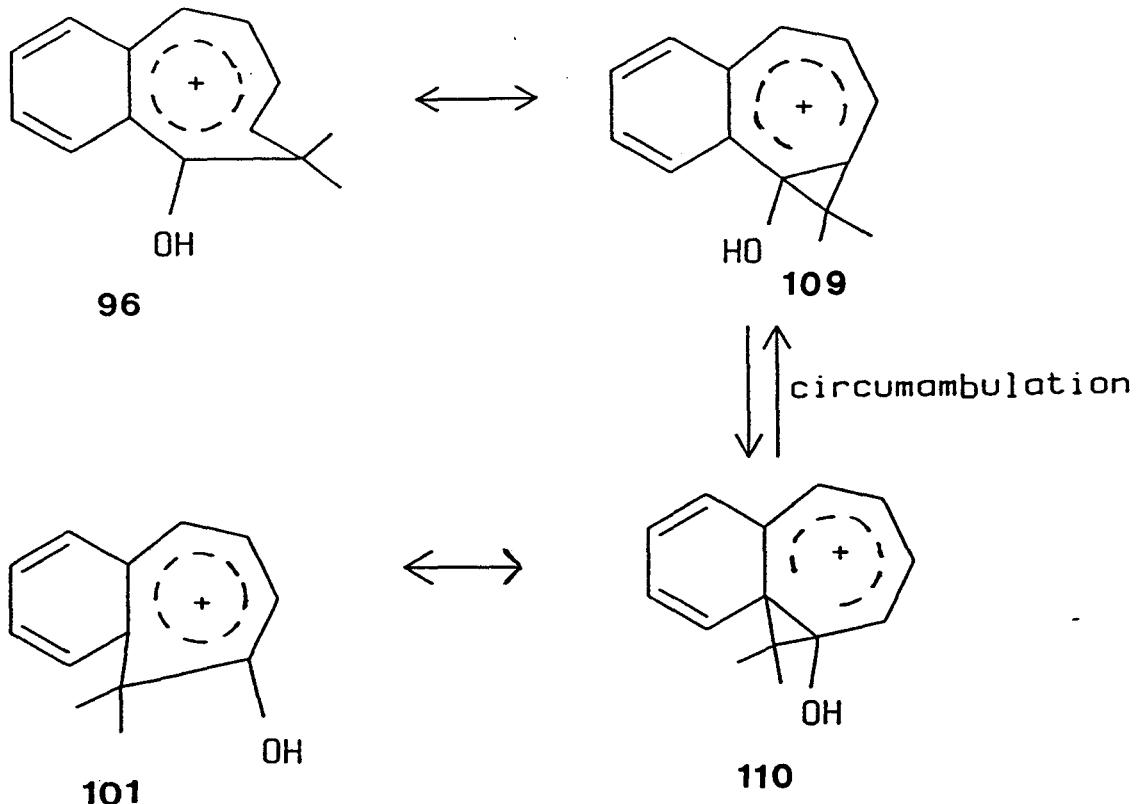
Attempts were made to establish an equilibrium between 96 and 101 in order to investigate the free energy difference between the two isomers. However this approach was unsuccessful.



While the solutions of the protonated ketone 101 in FSO_3H were stable up to 0°C , they underwent general decomposition without the formation of any characterizable materials on warming to higher temperatures. Neither protonated 8,8-dimethyl 2,3-benzohomotropone 96 nor [11]-annulene isomer 108 were detected under any of these conditions.

c. Possible mechanisms for the isomerization of 96.

The formation of 101 from 96 can be understood in terms of circumambulatory migration of the C_8 carbon around the periphery of the "seven membered" ring (Scheme 5). Analogous rearrangements have been observed by Childs and coworkers in the 1-hydroxy substituted 8,8 dimethyl homotropylium cations.⁶⁴ These circumambulatory shifts in homotropylium cations become energetically possible when C_8 bears charge stabilizing groups, as suggested by Childs and Hehre.¹⁰



Scheme 5: Formation of 101

The formation of 107 from 96 likely involves a methyl shift followed by protonation and loss of the hydroxy group to yield a benzocyclooctatetraene dication 113, (Scheme 6). This could then collapse with FSO_3^- to yield 107. Brouwer and Van Doorn have reported a similar 1,2-methyl shift and the loss of the carbonyl oxygen in the rearrangements of protonated 3,3 dimethylcyclo-pentanone and -hexanone.⁹³ Attempts to observe 113 using stronger acid media such as 4:1 $\text{FSO}_3\text{H-SbF}_5$ have thus far failed.

II. PHOTOISOMERIZATIONS

Protonated 8,8-dimethyl 2,3 benzohomotropone, 96 exhibits intense long wavelength absorptions at ca. λ_{394} nm (Table 14). Irradiation of FSO_3H solutions of 96 at low temperature with broad spectrum light for 32 hours led to the formation of complex mixtures of products. Due to the small amount of products obtained after neutralization with base, their characterization could not be carried out. Similarly 101 was irradiated in FSO_3H solution at 78°C with broad spectrum light for 16 hours. A complex mixture of products was obtained and due to the difficulty in assigning signals in the complex NMR spectrum, definite structures could not be assigned for the species formed. No signals were observed upfield of 0 ppm, which would correspond to the methyl groups on a bridged annulenium cation.

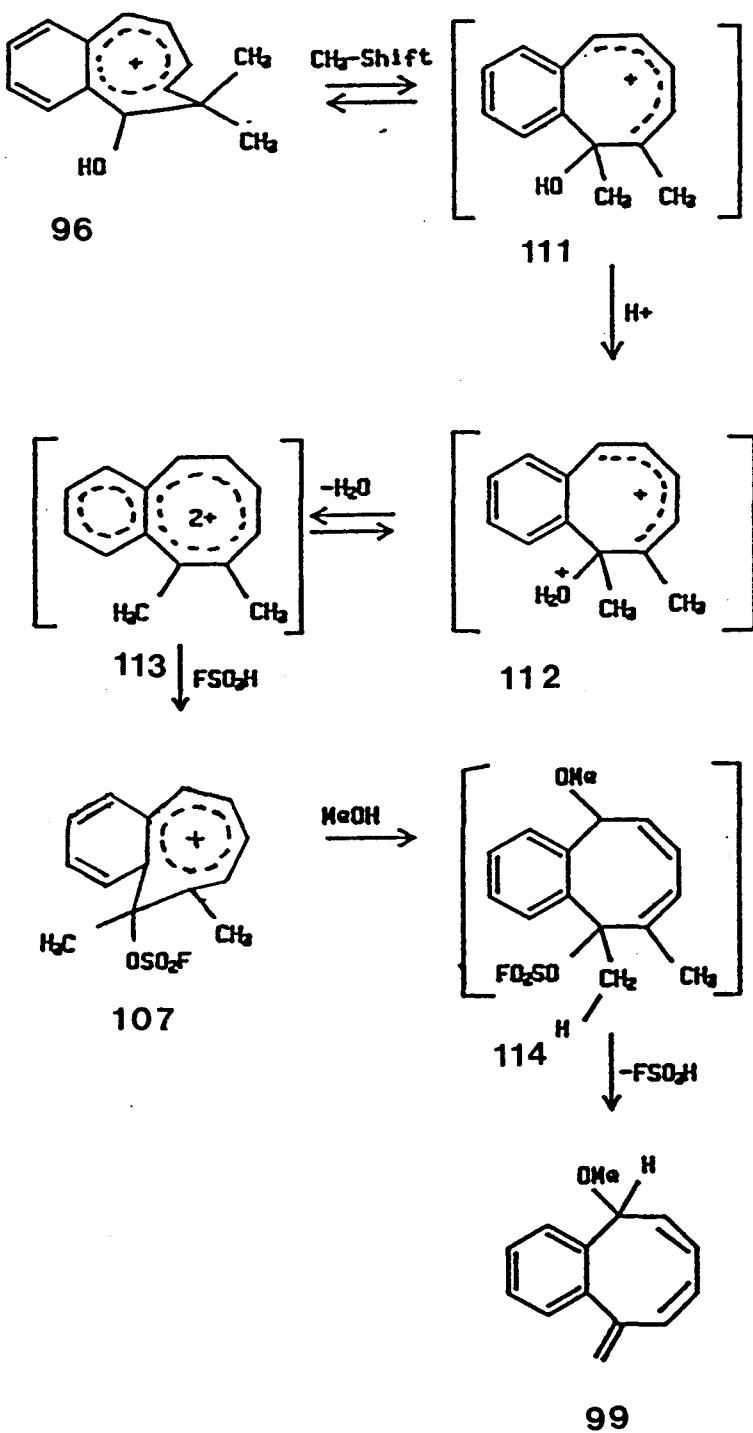
Table 14

U.V. Spectral Data

Compound	λ_{max} (n.m)
96	308, 394 ^b
98	212, 298 ^a
101	316, 418 ^b
99	274 ^a

^a spectra obtained in cyclohexane

^b spectra obtained in FSO_3H .



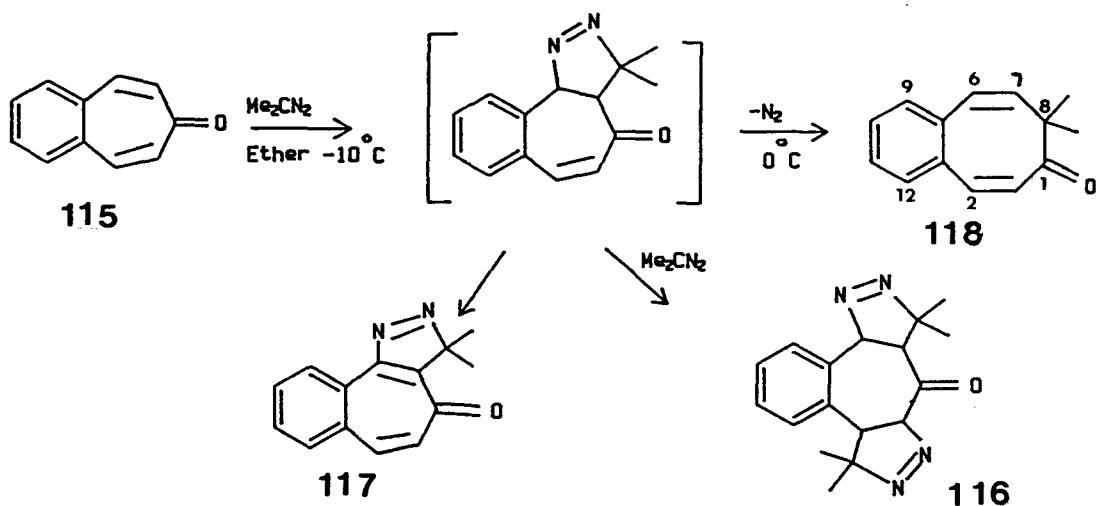
Scheme 6: Possible mechanism for the formation of 99

III. STUDIES ON THE REARRANGEMENT IN 8,8-DIMETHYL-1-HYDROXY-4,5-BENZOHOMOTROPYLIUM CATION

As the relative position of ring substituents could alter the relative energies of these systems the rearrangement reactions of the 8,8-dimethyl-1-hydroxy-4,5-benzohomotropylium cation were examined.

1. Preparation

The 8,8-dimethyl-4,5-benzohomotropone 118 was prepared by the method of Franck-Neumann and Martina.⁸⁸ Cycloaddition of diazopropane to 4,5 benzotropone 115 gave compounds 116, 117 and 118 via a pyrazolotropone intermediate. These products were separated by flash column chromatography and characterized by their spectroscopic properties (Table 15).



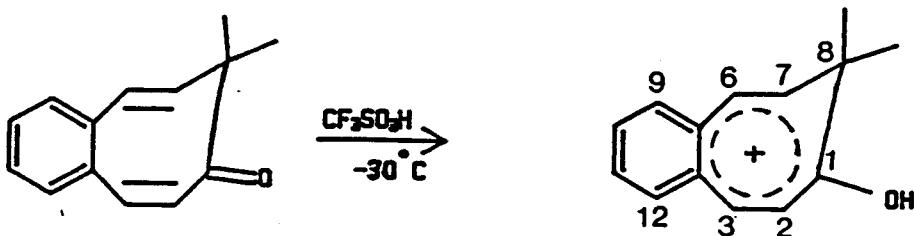
2. Characterization of the cation 119

Extraction of 118 into FSO_3H at -78°C gave the corresponding 4,5 benzohomotropylium cation 119. (The

same cation was obtained using $\text{CF}_3\text{SO}_3\text{H}$ as the acid medium at -30°C). The 500 MHz NMR spectrum of 119 (Figure 13) consists of singlets at δ 0.45 and δ 1.92 which correspond to the two methyl groups attached to the C₈ of the eight membered ring. The peak at δ 5.76(d) was assigned to H-7, and the series of resonances from δ 7.9 to 8.1 to the protons attached to benzene ring. The proton resonance at δ 7.2, 7.7 and 8.6 ppm corresponded to H-2, H-6 and H-3, respectively.

The ^1H NMR spectrum of the cation 119 clearly indicates that the signals due to all the protons experience a downfield shift. These can only be interpreted in terms of a cyclic delocalization existing in the molecule. The chemical shift difference

$\delta = 1.47$ ppm between "endo" and "exo" methyl signals is comparable to the value obtained in the 1-hydroxy 2,3-benzohomotropylium cation 96, suggesting the presence of a ring current. In addition the coupling constant $J_{2,3} = 12.7$ Hz is comparable to that of the 4,5-benzo-2,3 homotropylium cation previously reported by Childs and Corver.⁹⁴



118

119

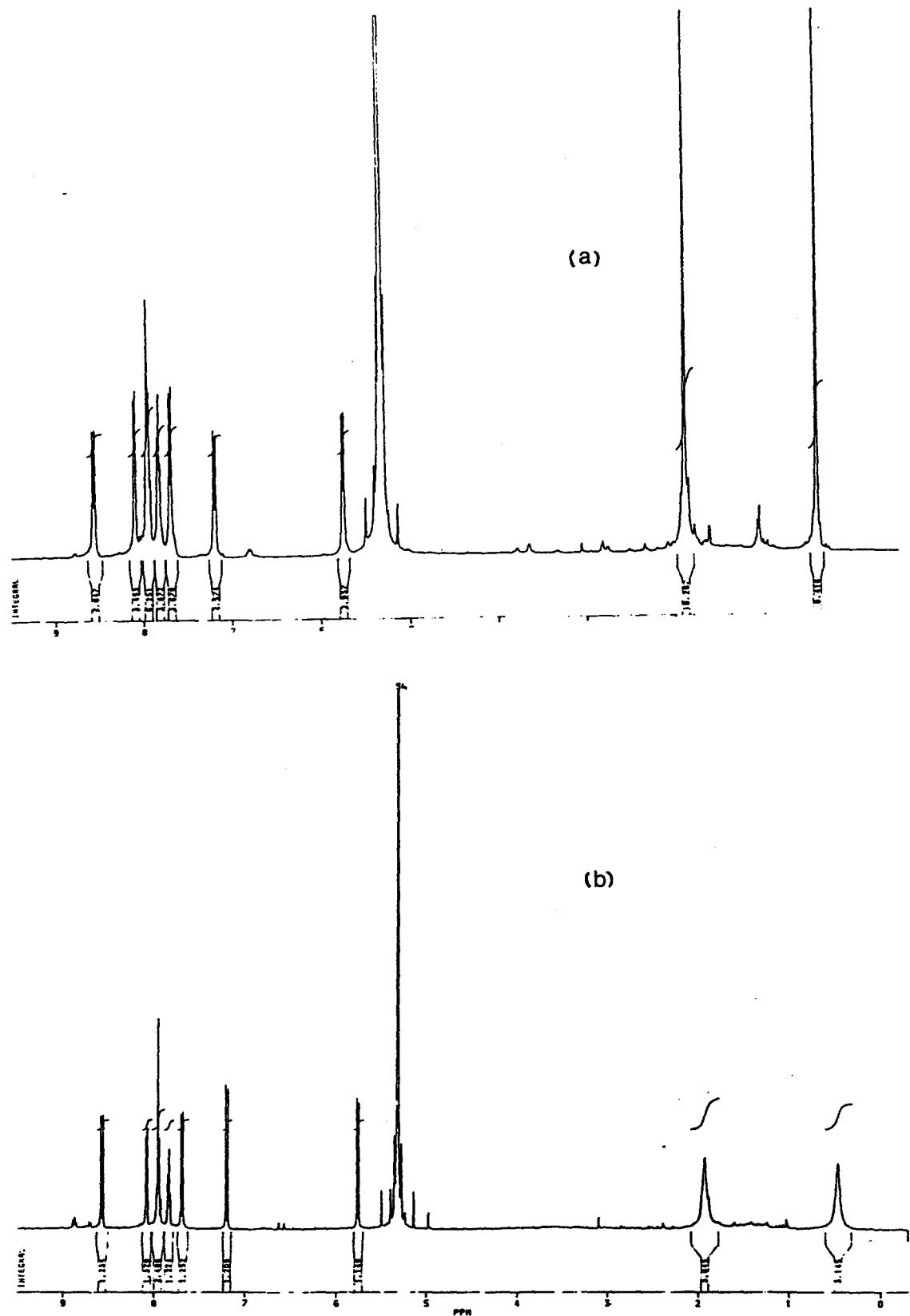


Figure 13: ^1H NMR Spectra of cation 119 in $\text{F} \text{ SO}_3\text{H}$

(a) at -78°C (b) at 34°C

Table 15

¹H NMR spectral data for 118 119 120 and 121.

Compd	118 ^a	119 ^b	120 ^c	121 ^a
Proton	Chemical Shift (δ ppm) ^d			
H-2	6.2(d) ^e	7.2(d)	8.7(d)	6.7(d)
H-3	6.9(d) ^e	8.6(d)	9.2(d)	7.1(d)
H-6	6.7(d) ^e	7.7(d)	9.2(d)	3.9(d)
H-7	5.6(d) ^e	5.8(d)	8.7(d)	5.7(d)
H-9	7.3(bs)	7.9(d)	6.1(s)	4.9(s) ^e
H-10	7.3(bs)	7.8(t) ^e	6.0(s)	5.0(s) ^e
H-11	7.3(bs)	8.0(t) ^e	2.3(s)	1.9(s)
H-12	7.3(bs)	8.1(d)	8.4(m)	7.2(d) ^e
H-13	1.1(s)	-	8.5(m)	7.2(t)
H-14	1.1(s)	-	8.5(m)	7.3(t)
H-15	-	-	8.4(m)	7.4(d) ^e
H-16	-	-	-	3.5(s)
8-CH ₃	-	(0.45) (s) (1.92) (s)	-	-
Coupling Constants (Hz)				
J _{2,3}	14.5	12.7	11.0	11.7
J _{6,7}	12.0	11.0	11.0	4.7
J _{9,10}	7.8	7.9	-	-
J _{10,11}	8.3	7.8	-	-
J _{11,12}	8.2	7.9	-	-
J _{12,13}	-	-	9.15	7.8
J _{13,14}	-	-	9.27	7.3
J _{14,15}	-	-	-	7.8

^aReference for CCl₄ (TMS = 0). ^bCH₂Cl₂ internal reference (δ 5.3 ppm). ^cReference for triflic acid at δ 10.5 ppm.

^dValues in parenthesis represent methyl groups,

s: singlet, d: doublet, t: triplet, m: multiplet

^eAssignments may be reversed

Table 16
 ^{13}C NMR Chemical Shift Data

Compd	Solv	Temp °C	Chemical Shifts (ppm)		
			C1	C2-C12	δ -CH ₃
119 ^a	FSO ₃ H	-78.3	199.6	159.8, 139.8 139.5, 137.9 135.7, 135.6 135.3, 130.9 129.8, 120.4 48.8	24.7 16.9
120 ^b	CF ₃ SO ₃ H	34	159.7	152.9, 140.6 140.1, 139.9 139.2, 138.5 132.7, 129.6 127.9, 116.2 57.4, 22.0	24.3

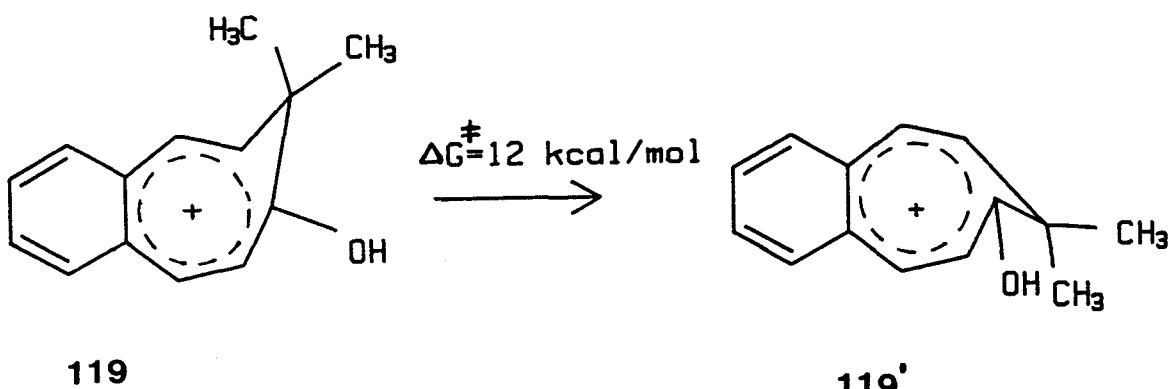
^a Relative to CH₂Cl₂ (Internal standard δ 53.8 ppm)

^b Relative to CF₃SO₃H at δ 120 ppm.

3. Thermal isomerization of 119.

The ^1H NMR spectrum of 119 in FSO_3H at -78°C is shown in Figure 13. When the temperature of the NMR sample was raised the two methyl resonances at δ 0.45 and δ 1.92 ppm started to broaden at 30°C . On cooling the sample this broadening was reversed. No other signals, in the ^1H NMR spectrum of 119 were broadened at room temperature. A complete average spectrum could not be obtained due to rearrangement of 119.

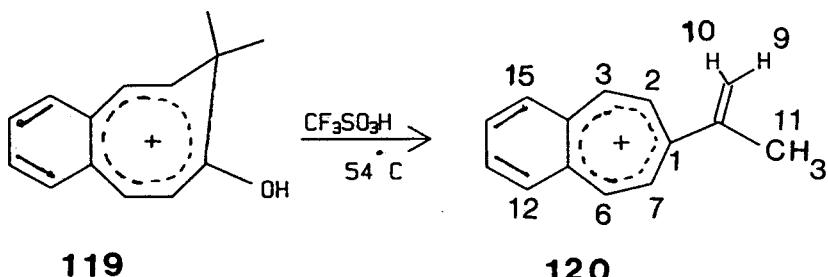
The averaging of the signals of the methyl groups can be explained in terms of a ring inversion process. The rate of the ring inversion of 119 was determined using DNMR3 computer program. The results obtained were matched with the experimental values and the corresponding ΔG^\ddagger was calculated as mentioned before.



The ΔG^\ddagger for the ring inversion process was found to be (12 ± 0.25) kcal/mol. This barrier is larger than that of 96 measured previously.

4. Irreversible isomerization of 119

Cation 119 was found to be thermally stable up to room temperature in $\text{CF}_3\text{SO}_3\text{H}$. At higher temperatures it rearranged irreversibly to a new cation, identified as 120, in a quantitative yield. The same product was obtained when FSO_3H was used as the protonating acid, but in this case isomerization occurred at a lower temperature. The first order rate constant for the isomerization of $119 \rightarrow 120$ in FSO_3H at 42°C was found to be $(2.35 \pm 0.3) \times 10^{-4} \Delta G^\ddagger = 23.4 \text{ kcal/mol}$.



The 500 MHz NMR spectrum of 120, (Figure 14) obtained at 54°C consisted of five resonances (Table 15). The proton resonances at δ 8.7 and δ 9.2 ppm correspond to H_2/H_7 and H_3/H_6 protons respectively. It also exhibited a methyl resonance at δ 2.3 and the olefinic protons at δ 6.1 ppm. In addition the benzene ring protons appeared as a multiplet at δ 8.4-8.5 ppm. The small peaks in the nmr spectrum of 120 is due to the presence of 119 in the sample. These peaks were also present in the spectrum of 119 and are due to incomplete purification of the starting material.

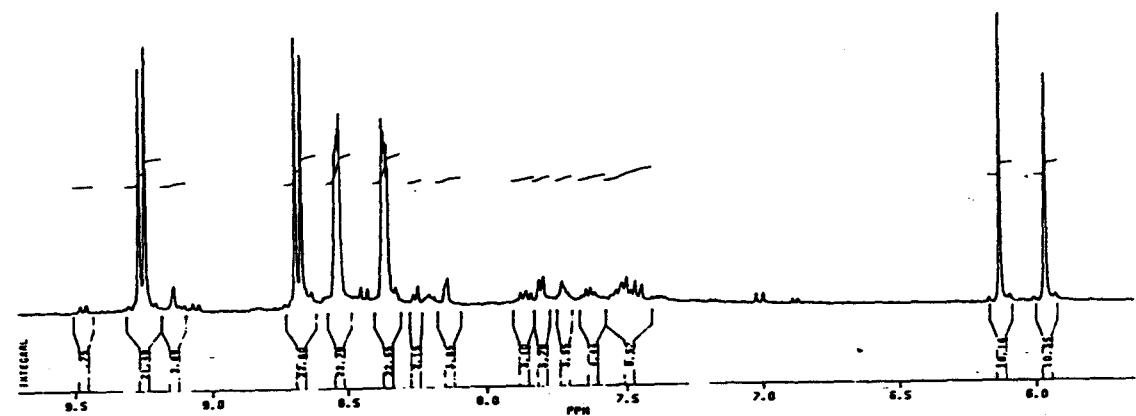
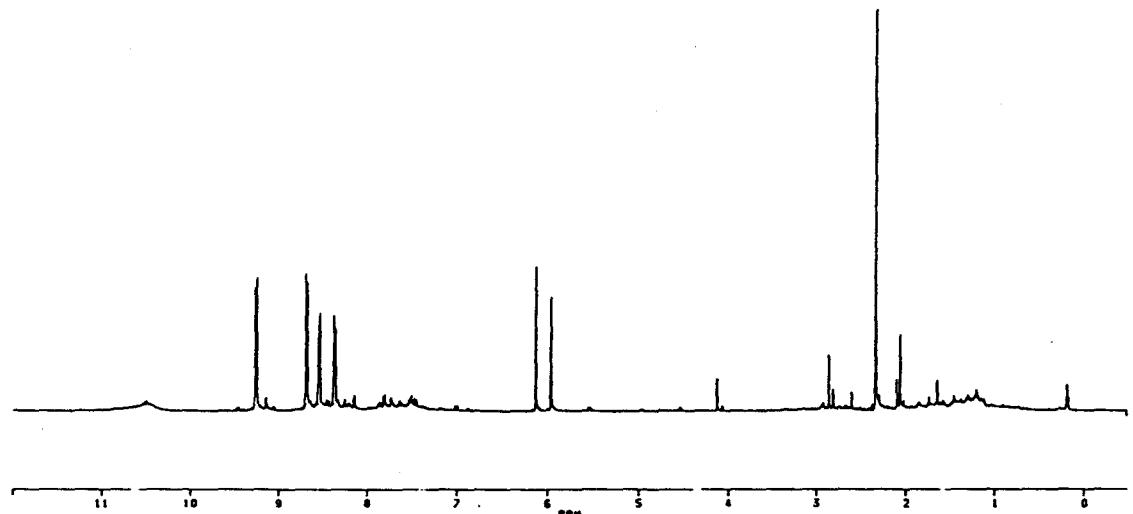
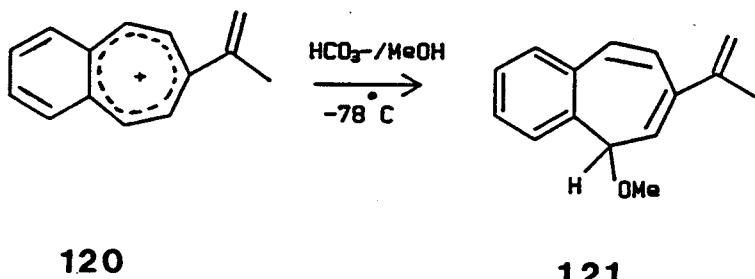


Figure 14: ^1H NMR Spectra of 120

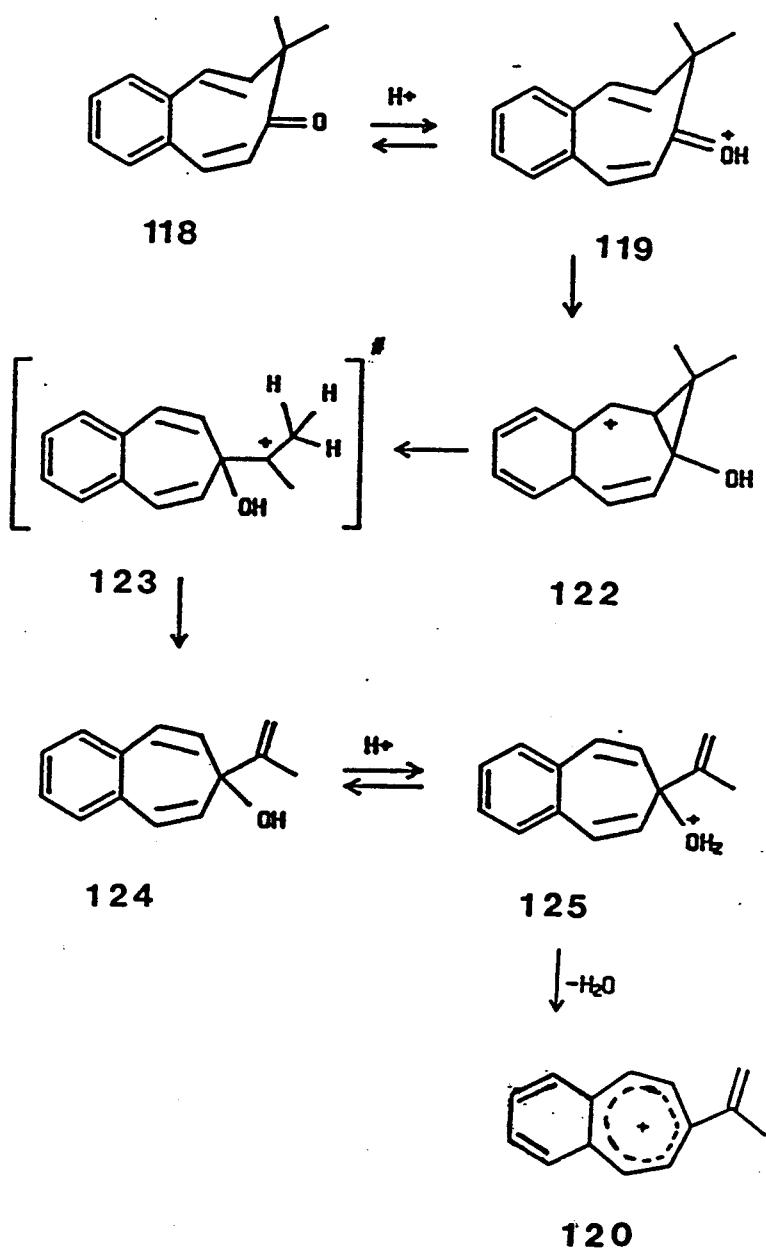
Several features emerge from the analysis of the nmr spectrum regarding the structure of 120. First the symmetrical pattern exhibited by the proton resonances clearly indicate that 120 has a plane of symmetry, passing through the C₁ carbon atom and bisecting the 4,5 carbon bond. Second the examination of the coupling constants J_{2,3} and J_{6,7} show that H₂H₃/H₆H₇ are part of the seven membered ring.⁹⁵ Third the substantial downfield shift of the vinyl proton resonances H₂-H₇ from the neutral compound 121 show that extensive delocalization of the positive charge is occurring in cation 120. It is informative to compare the NMR spectra of 120 with those of the benzotropylium cation. A similarity in the position and the pattern of the chemical shift resonances were observed in both the cations. The odd-numbered proton resonances being further downfield than those of the even-numbered protons.

The cation 120 was quenched in MeOH-HCO₃⁻ at -78°C to give the methoxy ether 121 in quantitative yield. Comparison of the ¹H NMR data (Table 15) of 121 to the similar compound 1,2-benzocycloheptatriene-7-methyl ether reported by D. Bertelli and W. Rossiter indicate that these compounds are very similar spectroscopically.⁹⁷



The proton NMR signals for 121 were fully consistent with the assigned structure (Table 15). The resonance for the OMe substituent on the seven membered ring appeared at δ 3.5 and the proton resonance of H-3 at δ 3.9 ppm. The significant upfield shift of the H-3 proton resonance proves the position of the OCH_3 at C₆. All the other resonances moved somewhat further upfield than that observed in 120. Due to the small amount of quantity obtained after neutralization its ¹³C NMR spectrum could not be obtained.

As shown in scheme 6 the formation of 120 from 119 could be considered to proceed via 123, followed by deprotonation to yield 124. Subsequent protonation of 124 followed by removal of water could result in the formation of 120. This reaction could be compared with the rearrangement of 62 studied by Childs and coworkers. They observed that 8,8-dimethylhomotropylium 62 rearranged to the corresponding 1-isopropylbenzotropylium cation 64.



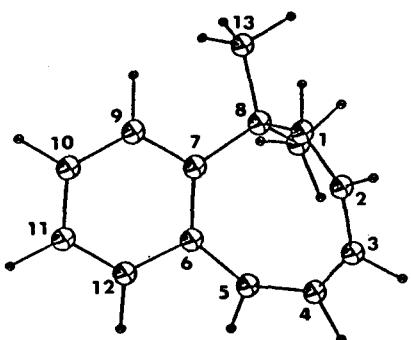
Scheme 6 : Possible Mechanism for formation of 120

IV. THEORETICAL CALCULATIONS

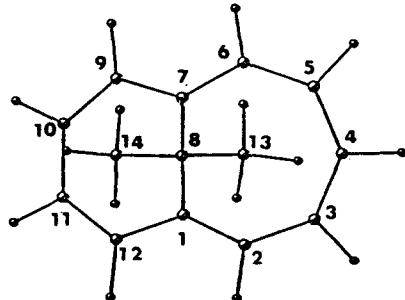
The selection of a theoretical technique for the quantitative assessment of the structures and energies of potentially homoaromatic molecules is critical. In order to achieve a good description of the energetic aspects of the potential energy surface the inclusion of electron correlation effects was found to be mandatory; to obtain quantitatively reliable data the energies had to be evaluated at a high level of theory.

In the present study, MNDO calculations were performed on the species under consideration in an attempt to put these experimental observations in more quantitative terms.

The AMPAC semi-empirical electronic structure program was used to carry out both MNDO and AM1 calculations on 126 (8,8-dimethyl-2,3-benzohomotropylium cation) and 127 ([11]-annulenium ion). Geometrical optimization of all internal coordinates was performed to locate the structures of 126 and 127.



126



127

Table 17

MNDO optimized geometries of 8,8-dimethylbenzohomotropylium cation, [11]-annulenium ion, and its hydroxy derivatives

Atomic dis. (Å)	THEORETICAL			
	96	128	Structures 134	136
C ₁ -C ₇	2.52	2.33	2.51	2.33
C ₁ -C ₂	1.33	1.34	1.44	1.35
C ₁ -C ₈	1.49	1.52	1.50	1.51
C ₂ -C ₃	1.45	1.45	1.35	1.47
C ₃ -C ₄	1.34	1.35	1.45	1.35
C ₄ -C ₅	1.46	1.45	1.41	1.45
C ₄ -C ₁₂	-	-	1.40	-
C ₅ -C ₆	1.41	1.43	1.46	1.43
C ₅ -C ₉	-	1.40	1.40	-
C ₅ -C ₁₂	1.40	-	-	1.39
C ₆ -C ₇	1.46	1.41	1.33	1.41
C ₆ -C ₉	1.41	-	-	1.41
C ₆ -C ₁₂	-	1.42	-	-
C ₇ -C ₈	1.51	1.48	1.49	1.48
C ₈ -C ₁₃	1.53	1.52	1.53	1.52
C ₈ -C ₁₄	1.54	1.53	1.54	1.53
C ₉ -C ₁₀	1.39	1.40	1.39	1.39
C ₁₀ -C ₁₁	1.40	1.41	1.40	1.40
C ₁₁ -C ₁₂	1.39	1.39	1.39	1.40

Table 17 (continued)

Table 17 (continued)

Atomic dis. (Å)	THEORETICAL							
	101	126	127	129	Structures	131	133	135
C ₁ -C ₇	2.47	2.39	2.23	2.33	2.33	2.23	2.38	2.61
C ₁ -C ₂	1.45	1.36	1.38	1.44	1.44	1.37	1.35	1.34
C ₁ -C ₈	1.51	1.49	1.50	1.50	1.50	1.51	1.49	1.49
C ₂ -C ₃	1.35	1.41	1.40	1.36	1.41	1.42	1.41	1.43
C ₃ -C ₄	1.45	1.38	1.38	1.43	1.37	1.42	1.39	1.42
C ₄ -C ₅	1.34	1.38	1.40	1.43	1.42	1.37	1.41	1.35
C ₅ -C ₆	1.46	1.43	1.39	1.36	1.36	1.36	1.41	1.45
C ₆ -C ₇	1.41	1.42	1.39	1.44	1.44	1.36	1.42	1.41
C ₆ -C ₁₂	1.40	1.43	-	-	-	-	1.43	1.42
C ₇ -C ₈	1.51	1.51	1.51	1.50	1.50	1.51	1.51	1.51
C ₇ -C ₉	1.41	1.40	1.43	1.37	1.38	1.45	1.40	1.41
C ₈ -C ₁₃	1.53	1.54	1.53	1.53	1.54	1.54	1.54	1.54
C ₈ -C ₁₄	1.54	1.53	1.53	1.53	1.53	1.53	1.52	1.55
C ₉ -C ₁₀	1.38	1.39	1.36	1.43	1.42	1.35	1.39	1.39
C ₁₀ -C ₁₁	1.41	1.40	1.43	1.36	1.37	1.44	1.40	1.39
C ₁₁ -C ₁₂	1.39	1.38	1.36	1.43	1.43	1.35	1.38	1.38
C ₁₂ -C ₁	-	-	1.44	1.37	1.37	1.45	-	-

EXPERIMENTAL^a

Atomic distances	86
C ₁ -C ₇	2.299
C ₄ -C ₅	1.379
C ₅ -C ₆	1.428
C ₆ -C ₇	1.384
C ₇ -C ₉	1.427
C ₉ -C ₁₀	1.370
C ₁₀ -C ₁₁	1.389
C ₁ -C ₁₂	1.482

^aTaken from M. Simonetta et al J. Am. Chem. Soc., 98, 1999 (1976).

The MNDO structures of 126 and 127 show a fully delocalized cation moiety with the C₁-C₇ interatomic distances of 2.390 Å and 2.266 Å respectively (Table 17).

Examination of the structure of 127, shows that the C₁-C₇ bond distance is significantly longer than that of a normal cyclopropane bond

The structure of the [11]-annulenium ion has been determined by Simonetta and coworkers.⁸⁶ The C₁-C₆ bond distance was found to be 2.299 Å (Table 17) which is comparable to that found in 127 using the MNDO calculations.

The heats of formation calculated using MNDO for 126, and 127 were found to be 236.9 and 258.0 kcal/mol

respectively. These calculations indicate that the 1-benzohomotropylium cation is more stable than the corresponding [11]-annulenium ion by 21 kcal/mol.

Among the 8,8-dimethyl benzohomotropylium cations, the stability decreases in the order 126 > 128 > 127. In other words this would represent that 1-benzohomotropylium cations are the most stable ions among their other isomers. This analysis can be extended to the protonation studies of unsubstituted benzohomotropylium of Pettit, and on reflection it is not at all difficult to see why these workers detected only the 1-benzohomotropylium isomers in the protonation of benzocyclooctatetraene.⁷⁰

The relative stability of these cations should depend on the ring substitution pattern. In this work the effect of -OH substituent at various positions has been examined. The results obtained are summarized in Table 18. As can be seen from this data the heats of formation of 129, 130 and 131 were found to be 211.9, 211.0 and 210.3 kcal/mol respectively. This indicates that there is no dependence on position of -OH on ΔH_f . In other words these results suggest that charge density is carried equally at all three positions.

The ΔH_f values for 96 and 101 were found to be 187 and 193 kcal/mol respectively a difference of 6 kcal/mol. This order is inconsistent with the experimental results, however, it should be noted that the

difference is small and likely reflects the precision expected from this type of calculation. One should also note as was mentioned above, that in the case of the parent cations 126 is more stable than 128. The smaller energy difference between 96/101 as compared to 126/128 shows that electron donating substituents do have a stabilizing effect on these benzohomotropylium cations, however it is clear the effect is not large enough to make the annulenium cation to be more stable than the benzohomotropylium cations. The heats of formation for 101 and 133 were found to be 193.3 and 197.9 kcal/mol respectively. It is seen that the cation with the -OH in "4" position is a little less stable than the "1" position. The experimental results of Childs et al show that 1-hydroxydimethylhomotropylium cations are slightly less stable than the 4-hydroxy isomer.⁶³ The energy difference between 134 and 135 (11.8 kcal/mol) indicates that "1-OH" isomer is more stable than "3-OH" isomer. These results are quite consistent with the experimental results observed by Childs and coworkers.

In summary the calculated gas phase heats of formation (ΔH_f) for these cations can serve as a guide for the relative stability of these cations in solution. In solution some degree of attenuation of this difference can be anticipated due to the difference in the solvation energies of these cations.

Conclusion :

From these calculations the various site preferences for the substituent can be obtained. In the case of 129 the charge stabilizing hydroxy substituent has no effect on the stability of -OH. However the -OH substituent still has some effect on the stability of benzohomotropylium cation isomers. For example the energy difference between 96 and 128 shows that the -OH substituent has a pronounced effect at the C-1 position.

The energy difference between 131 and 133 (12.4 kcal/mol) suggests that it may be possible to interconvert 133 to the corresponding [11]-annulenium ion photochemically, however based on these results a facile conversion of 126 to 127 would not be expected.

Table 18

Calculated heats of formation obtained from MNDO calculations

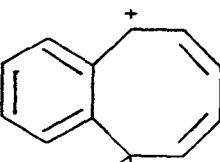
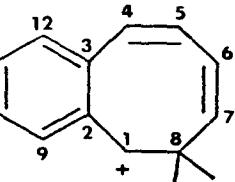
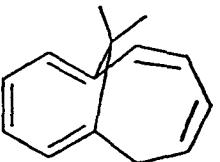
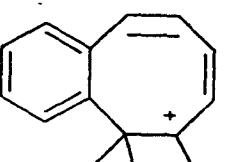
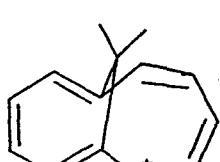
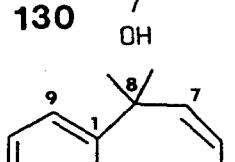
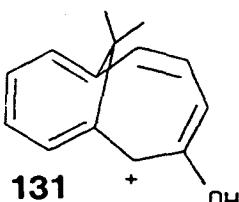
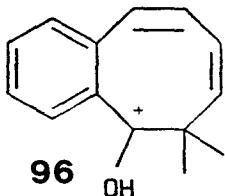
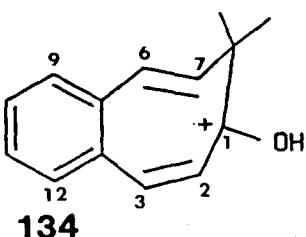
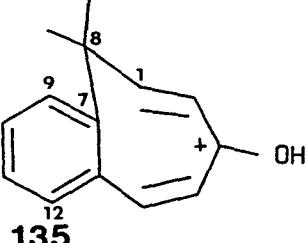
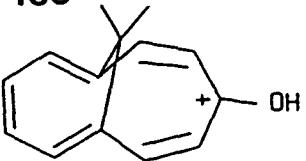
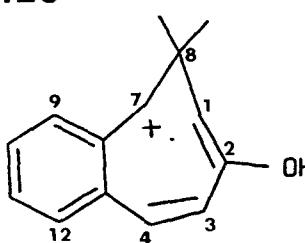
Compound	ΔH_f (kcal/mol)
 126	236.9
 128	249.7
 127	258.0
 101	193.6
 130	211.0
 133	197.9

Table 18 (continued)

Table 18 (continued)

Compound	ΔH_f (kcal/mol)
	210.3
	186.8
	187.3
	199.1
	211.9
	208.8

CONCLUDING REMARKS

Despite the fact that benzohomotropylium cations have already received considerable attention, the work presented in this thesis is the first reported approach to study circumambulatory migrations in such systems.

It has been suggested in chapter 1 of this thesis that these circumambulatory rearrangements proceed via the single-step migration of C₈ around the "seven-membered ring" in a [1,6]-sigmatropic shift, and that by placing electron donating substituents at C₈ of the homotropylium cation the activation energy for the migration can be reduced, thus allowing thermally induced migrations to occur. The results presented and discussed in chapter 2 show that protonated 8,8-dimethyl benzohomotropones do indeed undergo the similar circumambulatory processes to the homotropylium cations. However, the circumambulatory rearrangements of 8,8 dimethylbenzohomotropylium cations do not yield the corresponding bridged [11]-annulenium ions.

The formation of the tropylium cation derivative which was formed as a final product in the rearrangement of 1-hydroxy 4,5-benzohomotropylium cation indicates that the homoaromatic systems are thermodynamically less stable than the aromatic tropylium ions.

The low thermal barrier to inversion in 96 show that this cation have a very open structure. As can be seen from a comparison of the barriers to ring inversion of 96 ($\Delta G^\ddagger = 9.7$ kcal/mol) and 119 ($\Delta G^\ddagger = 12$ kcal/mol), the ground state properties of the 2,3- and 4,5- benzo-1-hydroxyhomotropylium cations are quite different. Such differences in behaviour can most reasonably be attributed to the effect of the benzene group has on the "degree of openness" of the internal "cyclopropane" bond of these systems.

In order for a photochemically induced circumambulatory rearrangement to occur, it must be possible to write an intermediate in which a full sigma bond is formed across the bridging methylene group. It was already noted that the C1-C7 interatomic distance between these two atoms was very large, consequently it is very difficult to form a sigma bond across the bridging carbons. This could be a possible reason for the failure of 96 or 101 to photoisomerize to give 130. Determination of the C1-C7 interatomic distance (eg:by x-ray diffraction techniques) in the benzohomotropylium cation and a number of other substituted homoaromatic systems could provide evidence to support a correlation between this distance and the ease of inducing a photochemical rearrangement. It could be the subject of further investigation.

EXPERIMENTAL

CHAPTER 3

EXPERIMENTAL METHODS

1. Instrumental Techniques

Proton magnetic resonance (^1H NMR) spectra were recorded on a Varian EM- 390 spectrometer, and low temperature spectra were recorded on a Bruker AM - 500 spectrometer. The chemical shifts ($\Delta\delta$) are reported in parts per million (ppm). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were obtained on the Bruker AM-500 spectrometer. The reference signals used to measure the chemical shifts are indicated with the data.

Infrared (IR) spectra were obtained on a Perkin-Elmer model 283 spectrophotometer. Only major and diagnostic bands are reported.

Ultraviolet (UV) spectra were obtained from a Hewlett Packard 8451A Diode Array spectrophotometer using cyclohexane and FSO_3H as solvents for neutral compounds and cations respectively.

Mass spectra (MS) were recorded on a VG 70-70F double focussing and a VG ZAB-E triple focussing mass-spectrometers operating at an ionization potential of 70 eV.

Centrifugal chromatography was performed on the model 7924T chromatotron, fitted with a silica (Merck, Kieselgel 60 PF₂₅₄) coated glass plate. The absorbent thickness is 2.0 mm. The solvent mixtures used for all separations were ether in petroleum ether (bp. 30-60°C) at various proportions.

Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected.

2. Purification of solvents and reagents

Fluorosulfuric acid (FSO₃H) was distilled from a small quantity of sodium fluoride (NaF) through an eight inch Vigreux column into a nitrogen filled round bottom flask from which it was transferred to clean dried glass ampoules in approximately 1 ml quantities. No grease was used on the joints. In a typical distillation 75-100 ml FSO₃H was distilled from 1.0g of NaF discarding the first 15-20 ml. The next 30-40 ml were collected and transferred to the ampoules. The rest was discarded by quenching slowly in Na₂CO₃⁻ water slurry. Fresh anhydrous ether was used without any further purification. Deuterated methylene chloride (CD₂Cl₂) was taken directly from the glass ampoules as supplied in 1 ml quantities from Merch-Sharpe and Dohme.

3. Synthetics

Some of the compounds used in this work have been reported previously. In these cases the literature methods were used to prepare the samples and their purity was checked by ^1H NMR spectroscopy. The following is a list of such compounds along with the literature references for their preparation. Acetone hydrazone,¹⁰⁰ diazopropane,¹⁰¹ 2,3- benzotropone,¹⁰² 2,7 dicarbo-methoxy-4,5-benzotropone,¹⁰³ 2,7-dicarboethoxy-4,5-benzotropone,¹⁰³ 2,7-dicarbohydroxy-4,5-benzotropone.¹⁰³ Benzosuberone, O-phthalaldehyde, dimethyl-3-oxo-glutarate and lithium aluminumhydride were obtained commercially and were used without any further purification. The preparation of the other compounds is described below.

a. Preparation of 8,8-dimethyl-2,3-benzocycloocta-4,6-dienone 95.

This procedure is essentially the same as that used by Franck-Neumann. Diazopropane (generated from 3g of acetone hydrazone) and 2,3-benzotropone (2g) were allowed to react in (ca 50ml) ethyl ether at -78°C (in acetone dryice bath). The mixture was shaken and left in an ice salt bath (0°C) for 3 hours and then in the fridge overnight at 0°C.

The ether was removed in vacuo to give a brown oil. Flash column chromatography on silica gel using

ethyl ether/petroleum ether (3:7 ratio) gave pure 8,8-dimethyl 2,3-benzohomotropone (200 mg; <30%). The product was examined by ^1H NMR spectroscopy. The results obtained are discussed in the text.

b. Preparation of 8,8-dimethyl-2,3 benzocycloocta 2,3-benzocycloocta 4,6-dienone cation 96.

The FSO_3H was (about 1 ml) transferred to the nmr tube by capillary dropper from a freshly opened ampoule. Care was taken to ensure no acid is left on the side of the NMR tube. The NMR tube was immersed into a small Dewar of dry ice acetone (-78°C). The 8,8-dimethyl-2,3-benzocycloocta-4,6-dienone (0.5g) was dissolved in Ca 0.3-0.5 ml CH_2Cl_2 (CD_2Cl_2) and the solution was cooled in ice for 5 minutes. Then the solution was transferred to the cooled NMR tube containing the acid via capillary dropper.

Some cooling of the CH_2Cl_2 solution was obtained by allowing the solution to run down the sides of the nmr tube.

An homogeneous mixture of protonated ketone was obtained by mixing the CH_2Cl_2 layer and FSO_3H layer using a thin pyrex rod (1.5 m.m.). The pyrex rod was precooled by quickly immersing it in liquid nitrogen before mixing. A reddish black acid layer was observed in the lower part of the nmr tube with a colorless CH_2Cl_2 layer above it

after the nmr tube solution was allowed to settle, for some time. Prior to being transferred to the precooled nmr probe the nmr tube was dipped in a Dewar containing dry-ice acetone. The NMR tube was then transferred to the precooled NMR probe and spectra were recorded after slowly warming the nmr probe to the desired temperature, starting at -78°C.

Neutralization of 8,8-dimethyl-2,3-benzohomotropylium 96.

The neutralization procedure used in this work involved adding the acid solution via a cooled (-78°C) capillary dropper to the stirring quench media. Typically NaHCO₃ was added to ether (30ml) and MeOH (15ml) in a 100 ml Erlenmeyer flask. The contents of the flask were cooled in a dry ice acetone bath and were stirred using a magnetic stir bar. The contents of the NMR tube were taken up in a capillary tube and were added quickly to the cooled stirring quench media. After completion the Erlenmeyer flask was removed from the dry ice acetone bath and allowed to warm to room temperature. Then water was added and the stirring was continued for another 15 minutes. The quench solution was then poured into a separating funnel and the aqueous methanol layer was extracted with two lots of ether and the combined ether layers were further extracted by water (ca 3x50 ml) and dried over anhydrous Na₂SO₄. The dried ether layer was

decanted from the Na₂SO₄ and the ether was removed under vacuum. The resulting solution was chromatographed on silica gel using ethylether/petroleum ether (3:7 ratio).

The product were examined by ¹H NMR spectroscopy. The NMR spectra of the residue indicated the formation of two compounds one of which is the methoxy ether. Samples for ¹³C NMR spectra were prepared using the same conditions described above.

Separation of the products:

The mixture was separated by centrifugal chromatography using ether/petroleum ether (3:7 ratio) as the solvent. The products were collected separately and the solvent was removed in vacuo. The residue which was dissolved in CH₂Cl₂ was subjected to ¹H NMR analysis.

c. Preparation of the 2,2-dimethyl-3,4-benzocycloocta-5,7-dienone cation 101.

The 2,2-dimethyl-3,4-benzocycloocta-5,7-dienone 98 was extracted from CH₂Cl₂ into an NMR tube and cooled in ice for few minutes. The FSO₃H was then transferred (ca 0.5 ml) dropwise to the NMR tube and the tube was cooled in dryice acetone bath. The ketone was added to the FSO₃H by a capillary dropper and the resulting mixture was mixed with a thin quartz rod. The NMR tube was transferred to the precooled NMR probe and the ¹H NMR

spectra taken immediately at -78°C.

d. Preparation of cation 103.

The methoxy ether compound 99 was extracted from a minimum volume of CH_2Cl_2 and cooled in ice. FSO_3H (ca 0.5-1.0ml) was taken in an NMR tube and cooled in an acetone dry icebath (78°C). The compound was then added to FSO_3H and the solutions were mixed with a thin quartz rod. The ^1H NMR spectra were then recorded at -78°C and the temperature was raised to room temperature by slowly warming the NMR probe and the spectra recorded at room temperature. The ^1H NMR data are given in table 11.

Similar procedure was used to protonate the methoxy ether using 20% SbF_5 , FSO_3H and SO_2 . The tube was sealed and quickly transferred to NMR probe which was precooled and the spectra run immediately at -78°C.

Quenching of cation 103.

The neutralization procedure used to quench cation 106 was identical to that used in reaction 3b.

e. Preparation of 4,5-Benzocycloocta2,6-dienone 118.

2,7-Dicarboxylic acid-4,5-benzotropone (20.0g) and 0.5% hydrochloric acid (300ml) were heated in a Parr bomb at 200-210°C for 5 hrs. The bomb was cooled to room temperature and the pressure released. The bomb

contents were poured into a 1 litre separating funnel and the dark brown oil separated from the aqueous layer. The aqueous layer was extracted with ether (three 50ml portions) and the combined ether extracts and oil washed initially with 15% sodium bicarbonate (two 15ml portions) and then with a saturated sodium chloride solution (two 20ml portions). The ether extract was dried over anhydrous Na_2SO_4 , and the ether was removed in vacuo. The pale brown solid was recrystallised using heptane to give pale yellow crystals (11g; 87%), which were identical to that previously reported.

mp 66.5-67.0°C. ^1H NMR(CCl_4) δ 7.64-7.42 (m, 4, ArH), 7.27 (dt, 2, vinyl H, J=12.5 Hz, 1.2 Hz), 6.60 (dt, 2, vinyl H, J=12.5 Hz, 1.2 Hz)

f. Reaction of 4,5-Benzotropone 118 with Diazopropane

This procedure was essentially the same as that used by Franck-Neumann. 4,5-Benzotropone (1.05g) and diazopropane (generated from 1.5g of acetone hydrazone) were allowed to react in ethyl ether (ca 100ml) at -78°C (in acetone dry ice bath). The mixture was shaken and left in an ice salt bath (0°C) for 3 hours then in the fridge at 0°C for 3 days. The ether was removed in vacuo to give a brown liquid. The resulting liquid was subjected to flash column chromatography on silica gel using 50% ethylether-petroleum ether mixture which gave

pure 8,8-dimethyl 4,5-benzohomotropone (0.27g; 20%). The spectral properties were identical to those previously reported.

Compound 120: clear crystals IR $\bar{\nu}$ (C=O) 1730 cm⁻¹, $\bar{\nu}$ (N=N) 1555cm⁻¹ UV λ_{max} 331 nm. ¹H NMR δ (CH₃) 4 singlets at 0.93;1.28;1.36 and 1.68 ppm. The ¹H NMR spectra of the other products obtained were reported in Table 14.

g. Preparation of 8,8-dimethyl-4,5-bencycloocta 2,6-dienone cation 119.

The 8,8-dimethyl-4,5-benzocycloocta-2,6-dienone 97 was dissolved in minimum volume methylene chloride and cooled in ice for 5 minutes. The FSO₃H was (ca 1ml) was transferred from a freshly opened ampoule to an NMR tube which was precooled in dry ice acetone bath. The ketone was added to FSO₃H and an homogeneous mixture was obtained by mixing the solution using a thin pyrex rod. The pyrex rod is precooled by quickly immersing it in liquid nitrogen before mixing. Then the NMR tube was quickly transferred to the precooled NMR probe and spectra recorded at various temperatures starting at -78°C.

h. Preparation of 1-Isopropenyl benzocyclohepta 2,4,6-trienylium ion 120.

The 8,8-dimethyl-4,5-benzocycloocta 2,6-dienone 113 was dissolved in minimum volume of d-methylene

chloride. The $\text{CF}_3\text{SO}_3\text{H}$ (ca 0.8-1.0 ml) was transferred to the NMR tube by capillary dropper, and the NMR tube was immersed into a small Dewar containing dry ice acetone (78°C). The NMR tube was raised and warmed by placing a finger on the frozen section until solution occurs. The ketone solution was added to the cooled NMR tube containing the acid and transferred to an ice bath at 0°C . An homogeneous mixture was obtained by mixing the CD_2Cl_2 and $\text{CF}_3\text{SO}_3\text{H}$ layers using a glass rod. Then the mixture was warmed to 54°C and the reaction monitored by ^1H NMR spectroscopy. The results obtained are summarized in Table 14.

Neutralization of the cation 120.

After 2-3 hours at this temperature, the reaction mixture was quenched by following the same procedure as employed in the quenching of 8,8-dimethyl 4,6-benzohomo-tropylium ion 119. The ^1H NMR data are given in Table 14.

i. Measurement of Rate constants

The rate constants for conversion of 96 to 101 and the conversion of 119 to 120 in FSO_3H are reported on pages 58 and 81. The kinetics for these processes were followed by measuring the ratio of the peak heights of a particular proton signal in the starting cation to those of another proton signal in the product at various time

intervals. This ratio was used as a unit free concentration term [C]. A constant temperature bath was used throughout the reaction.

The first order rate constant k was measured from the formula,

$$\ln C_t = kt + \ln C_0$$

Where C_0 was the concentration at time t_0
 C_t was the concentration at time t.

The reaction was followed until they were greater than 80% complete. The temperature of the NMR probe was measured before and after a kinetic run, and the average value was taken.

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