

STEREOCHEMICAL REQUIREMENTS FOR

BISHOMOAROMATICITY

STEREOCHEMICAL REQUIREMENTS FOR  
BISHOMOAROMATICITY

by

HANS A. CORVER, ASSOC. IN PURE CHEM.

A Thesis

Submitted to the School of Graduate Studies  
in Partial Fulfilment of the Requirements

for the Degree

Doctor of Philosophy

McMaster University

(November) 1973

DOCTOR OF PHILOSOPHY (1973)  
(Chemistry)

McMASTER UNIVERSITY  
Hamilton, Ontario.

TITLE: Stereochemical Requirements for  
Bishomoaromaticity

AUTHOR: Hans A. Corver, Assoc. in Pure Chem.  
(Western Australian  
Institute of Technology)

SUPERVISOR: Professor R.F. Childs

NUMBER OF PAGES: xiv, 173

ABSTRACT OF THE DISSERTATION  
Stereochemical Requirements for  
Bishomoaromaticity

To investigate the stereochemical requirements for bishomoaromaticity it was necessary to develop a synthetic scheme that would give suitable precursors in which the stereochemistry could be unambiguously assigned. Arguments are presented in this thesis to suggest that, if bishomoaromaticity is to be detected when the two methylene bridges are trans with respect to each other, the 1,4-bishomotropylium system is more favourably orientated for cyclic delocalization than the 1,3-bishomotropylium system.

By reacting benzotropone ethylene ketal with phenyl mercuric trichloromethane, followed by removal of the chlorines and protecting group, it was possible to synthesize the trans-4,5-benzo-2,3:6,7-bishomotropone. The cis-4,5-benzo-2,3:6,7-bishomotropone was synthesized by the action of dimethyloxosulfonium methylide on benzotropone. The stereochemistry in the cis and trans isomers was unambiguously established by examining the nmr spectra of the derived alcohols.

To determine the effect of the benzene ring in these homoaromatic systems it was necessary to synthesize 4,5-benzo-2,3-homotropone. By reacting benzotropone with dimethyloxo-

sulfonium methylide it was possible to obtain a high yield of 4,5-benzo-2,3-homotropone.

The low temperature nmr spectra of protonated 4,5-benzo-2,3-homotropone and the derived alcohol clearly showed that the benzene ring did not decrease the homoaromatic nature in these systems. The hydroxy substituent, however, had a marked effect on the homoaromatic nature.

The low temperature nmr spectra of the protonated cis and trans-4,5-benzo-2,3:6,7-bishomotropones showed that the trans hydroxy cation could be best interpreted as a cyclopropylcarbinyll delocalized system and the cis hydroxy cation as a bishomoaromatic species.

The low temperature nmr spectrum of the trans-4,5-benzo-2,3:6,7-bishomotropylium cation also supported the cyclopropylcarbinyll delocalization in this system. In contrast to the hydroxy-substituted system, however, the unsubstituted system was not equilibrating between the two possible equivalent boat conformations. This was attributed to the hydroxy substituent effect on the transition state of the boat-boat equilibrium.

In conclusion, arguments are presented that would suggest that the trans-1,3-bishomotropylium cation is not a bishomoaromatic cation as previously reported, but that it can be best represented as a cyclopropylcarbinyll delocalized system.

To Val, Richard

and

Deborah

## ACKNOWLEDGEMENTS

I wish to express my deep appreciation to Professor Ron Childs for his inspirational guidance and continued encouragement throughout this work.

I would like to thank the members of our research group for the many informative discussions and in particular B. Sayer who obtained many of the nmr spectra.

Appreciation is also extended to the Ontario Government, National Research Council of Canada and McMaster University for their financial assistance.

I am grateful especially to Val, my wife, who typed this manuscript and without whose love and patience this work could not have been completed.

## TABLE OF CONTENTS

Descriptive Note.....	ii
Abstract of the Dissertation.....	iii
Preface.....	v
Acknowledgements.....	vi
Table of Contents.....	vii
List of Tables.....	xiii
List of Figures.....	xiv

### A. INTRODUCTION AND GENERAL DISCUSSION

#### SECTION ONE

HISTORICAL BACKGROUND.....	2
AROMATICITY.....	3
HOMOAROMATICITY - GENERAL CONCEPT AND NOMENCLATURE.....	6

#### SECTION TWO

MONOHOMOAROMATICITY.....	11
(a) Monohomotropylium Cation.....	11
Coupling Constants in the Homo- Tropylium Cation.....	16
(b) Substituted Homotropylium Cations.....	21
1-Methyl- and 1-Phenylhomotropylium Cations.....	21
1-Hydroxy- and 1-Methoxyhomotropylium Cations.....	23

2-Hydroxy- and 4-Hydroxyhomotropylium Cations.....	25
Application and Validity of the Johnson Bovey Equation.....	27
8-Substituted Homotropylium Cations.....	28
Benzo- and Dibenzohomotropylium Cations.....	33

### SECTION THREE

BISHOMOAROMATICITY.....	41
(a) 1,4-Bishomotropylium Cations.....	41
Kinetic Evidence.....	48
(b) 1,3-Bishomotropylium Cation.....	52
(c) Comparative and Theoretical Treatment of the Tropylium, Homotropylium and Bishomotropylium Cations.....	55

## B. RESULTS AND DISCUSSION

### SECTION ONE

STATEMENT OF THE PROBLEM.....	59
GENERAL SYNTHETIC CONSIDERATIONS.....	63
(a) Nature of Precursor.....	63
(b) Potential Methods for the Cyclo- propanation of Benzotropone.....	64
Addition of Methylene Using Diazo Compounds.....	66
Simmons-Smith Reagent.....	67
Dimethyloxosulfonium Methylide and Dimethylsulfonium Methylide as Methylene Transfer Agents.....	68
Generation and Addition of Dihalo- carbenes to Olefinic Bonds.....	70

(a) Preliminary Experiments.....	72
(b) Preparation of 4,5-Benzotropone Ethylene Ketal.....	74
(c) Dihalocarbene Addition to the Ethylene Ketal of 4,5-Benzotropone.....	79
(d) Reaction of Dimethyloxosulfonium Methylide with 4,5-Benzotropone.....	80

## SECTION TWO

NMR SPECTRA OF <u>CIS-</u> AND <u>TRANS-</u> 4,5-BENZO- 2,3:6,7-BISHOMOTROPONES.....	83
STEREOCHEMISTRY.....	87

## SECTION THREE

GENERATION AND OBSERVATION OF THE MONO- AND BISHOMOTROPYLIUM CATIONS.....	90
(a) The 4,5-Benzo-2,3-Homotropylium Cation.....	90
(b) The 1-Hydroxy-4,5-Benzo-2,3-Homo- tropylium Cation.....	95
(c) 220 MHz Nmr Spectrum of the 2-Hydroxy- homotropylium Cation.....	97
(d) Protonated <u>Cis</u> and <u>Trans</u> -4,5-Benzo- 2,3:6,7-Bishomotropones.....	99
(e) Protonation of <u>Cis-</u> and <u>Trans-</u> <u>Alcohols 111-OH and 112-OH</u> .....	104
(f) Conclusions and General Discussion.....	108

## C. EXPERIMENTAL

GENERAL PROCEDURES.....	114
Nuclear Magnetic Resonance Spectra (nmr).....	114
Methylene Chloride.....	115
Carbon Tetrachloride.....	115

Infrared Spectra.....	116
Mass Spectra.....	116
Melting Points.....	116
GENERATION, OBSERVATION AND QUENCHING OF CATIONS.....	116
Protonations.....	117
Method A.....	117
Method B.....	118
Quenching of Cations.....	119
SYNTHESIS	
2,7-Dicarbomethoxy-4,5-Benzotropone.....	121
2,7-Dicarboethoxy-4,5-Benzotropone.....	121
2,7-Dicarboxylic Acid-4,5-Benzotropone.....	122
4,5-Benzotropone (110).....	122
Reaction of 4,5-Benzotropone (110) with Diazomethane in Ether.....	123
Reaction of 4,5-Benzotropone (110) with Phenyl Mercuric Trichloromethane.....	123
Reaction of 4,5-Benzotropone (110) with the Simmons-Smith Reagent.....	124
7-Hydroxy-3,4-Benzocycloheptatriene.....	125
Reaction of 7-Hydroxy-3,4-Benzocycloheptatriene with the Simmons-Smith Reagent.....	125
Reaction of 4,5-Benzotropone (110) with Ethylene Glycol.....	126
1-Ethoxy-4,5-Benzotropylium Fluoborate Salt (130).....	127
4,5-Benzotropone Ethylene Ketal (125).....	127
Reaction of 4,5-Benzotropone Ethylene Ketal (125) and Phenyl Mercuric Tribromomethane.....	128
Reaction of 4,5-Benzotropone Ethylene Ketal (125) and Phenyl Mercuric Trichloromethane.....	129

<u>Trans</u> -4,5-Benzo-2,3:6,7-Bishomotropone Ethylene Ketal (138).....	131
<u>Cis</u> -4,5-Benzo-2,3:6,7-Bishomotropone Ethylene Ketal (137).....	132
<u>Trans</u> -8,8,9,9-Tetradeutero-4,5-Benzo 2,3:6,7-Bishomotropone Ethylene Ketal (138-D).....	132
<u>Cis</u> -8,8,9,9-Tetradeutero-4,5-Benzo- 2,3:6,7-Bishomotropone Ethylene Ketal (137-D).....	132
<u>Trans</u> -4,5-Benzo-2,3:6,7-Bishomotropone (112).....	133
<u>Trans</u> -8,8,9,9-Tetradeutero-4,5-Benzo- 2,3:6,7-Bishomotropone (112-D).....	134
<u>Cis</u> -4,5-Benzo-2,3:6,7-Bishomotropone (111).....	134
4,5-Benzo-2,3-Homotropone (124).....	134
8,8-Dideutero-4,5-Benzo-2,3-Homotropone (124).....	136
<u>Cis</u> -4,5-Benzo-2,3:6,7-Bishomotropone (111).....	137
<u>Cis</u> -8,8,9,9-Tetradeutero-4,5-Benzo- 2,3:6,7-Bishomotropone (111-D).....	138
<u>Trans</u> -7-Hydroxy-2,3-Benzotricyclo [6.1.0.0 <sup>4,6</sup> ] nonane (112-OH).....	138
<u>Trans</u> -5,5,9,9-Tetradeutero-7-Hydroxy-2,3- Benzotricyclo [6.1.0.0 <sup>4,6</sup> ] nonane (112-OH(D)).....	139
<u>Trans</u> -7-Deutero-7-Hydroxy-2,3-Benzotricyclo [6.1.0.0 <sup>4,6</sup> ] nonane (112-OH ( $\alpha$ D)).....	139
<u>Cis</u> -7-Hydroxy-2,3-Benzotricyclo [6.1.0.0 <sup>4,6</sup> ] nonane (111-OH).....	139
<u>Cis</u> -5,5,9,9-Tetradeutero-7-Hydroxy-2,3- Benzotricyclo [6.1.0.0 <sup>4,6</sup> ] nonane.....	140
<u>Cis</u> -7-Deutero-7-Hydroxy-2,3-Benzotricyclo [6.1.0.0 <sup>4,6</sup> ] nonane (111-OH( $\alpha$ D)).....	140
7-Hydroxy-2,3-Benzobicyclo [5.1.0] oct-4- <b>ene</b> (124-OH).....	140

8,8-Dideutero-6-Hydroxy-2,3-Benzobicyclo [5.1.0]oct-4-ene (112-OH(D)).....	141
6-Deutero-6-Hydroxy-2,3-Benzobicyclo [5.1.0]oct-4-ene (124-OH( $\alpha$ D)).....	141
2,3-Homotropone (38).....	142
SPECTRA.....	143
BIBLIOGRAPHY.....	164

LIST OF TABLES

I	Ultraviolet Absorption and Electron Distribution Data for Various Carbonium Ions	19
II	Volume Diamagnetic Susceptibilities	20
III	Nmr Comparison Between 8-exo- substituted Homotropylium Ions and the Compounds CH <sub>3</sub> -X	32
IV	Nmr Chemical Shifts ( $\tau$ ) for Various Substituted Bicyclo [4.3.1] deca-2,4,7-trienyl Cations	47
V	Solvolysis Rates for Various Allylic Systems in 80% Aqueous Acetone	50
VI	Comparison of Various Homoaromatic Cations	55
VII	Nmr Parameters for the Protonated <u>Trans</u> Alcohols <u>146</u> and <u>146-D</u>	105

## LIST OF FIGURES

1.	Typical Cyclopropyl Coupling Constants	17
2.	Resonance Structures for the 1-Hydroxy Homotropylium Cation	24
3.	Plot of $\delta$ vs $\Delta$ for Homotropylium Systems	28
4.	Charge Distribution and Delocalization Energies for a Variety of Carbonium Ions	57

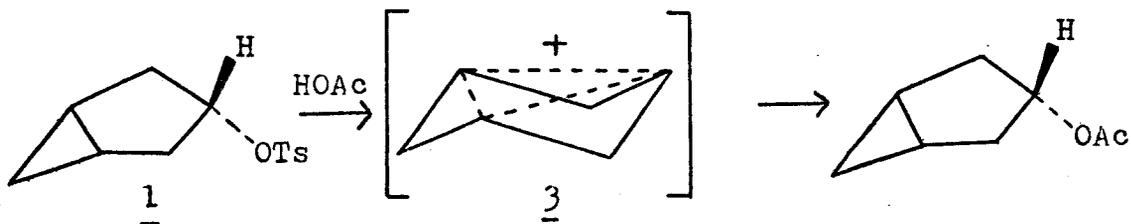
A. INTRODUCTION AND GENERAL DISCUSSION

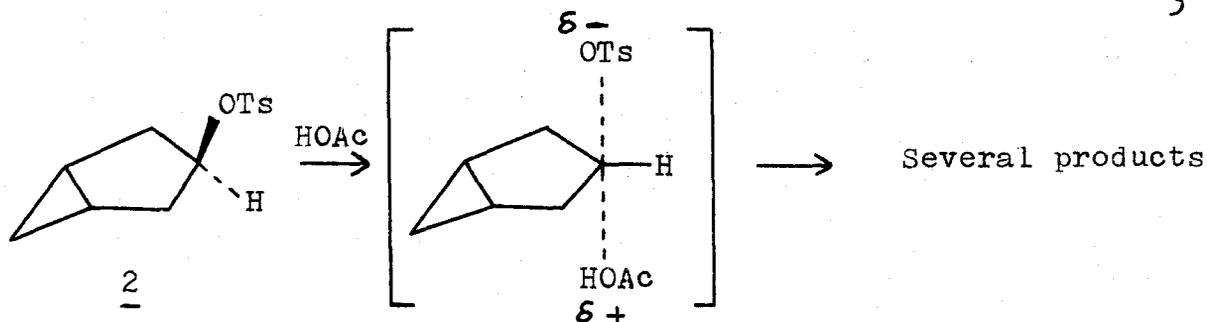
SECTION ONE

HISTORICAL BACKGROUND

For more than one decade, a preoccupation of numerous chemists has been the study of homoaromaticity, first postulated by Winstein<sup>1</sup> in 1959. In many respects the concept of homoaromaticity closely resembles the concept of homoconjugation<sup>2</sup>, but the extrapolation to homoaromaticity took more than a decade.

The first homoaromatic species was proposed by Winstein<sup>3</sup> to explain the marked difference in rate of solvolysis of the cis- and trans-bicyclo[3.1.0]hexyl-toluene-sulfonates, 1 and 2 respectively. The kinetic data were interpreted in terms of anchimerically assisted ionization of 1 to give the non-classical cation 3. This cation was considered to be homoaromatic and termed the "trishomocyclopropenyl cation". On the other hand, 2 was presumed to ionize classically. The factors contributing to the stability of 3 were not readily accepted and numerous publications have appeared to dispute<sup>4</sup> and support<sup>5</sup> the claim of a symmetrical non-classical intermediate in the solvolysis of 1.





Since this initial controversy, the concept of homoaromaticity has found ample fulfillment in the many homoaromatic systems which have been prepared and studied<sup>6</sup>.

### AROMATICITY

Although this thesis deals with the question of homoaromaticity, it must be noted that controversy still exists on the definition and criteria of aromaticity<sup>7</sup>. Originally the concept of aromaticity developed as a means of characterizing certain types of organic molecules. Thus, aromatic compounds undergo substitution reactions and not addition reactions. It has been known for some time that aromatic compounds possess typical physical properties, such as the anisotropy of diamagnetic susceptibility<sup>8</sup>. However, the emphasis has been on chemical reactivity rather than on the physical properties.

With the advent of quantum chemistry the experimental findings were given theoretical grounding. The valence bond method and molecular orbital methods<sup>9</sup> were developed, thus permitting the calculation of the resonance energy<sup>10</sup>. There has thus been a continuous process of transforming the meaning of aromaticity from the chemical definition to the

physical viewpoint.

The leading role in the theory of aromatic compounds has been played by Hückel's " $4n + 2$ " rule<sup>11</sup>. Although the theoretical foundations for the HMO method are weak, it has had remarkable success in explaining the vast variety of observed facts and predicting new ones<sup>12</sup>. For example, when  $n = 0$  the cyclic system contains  $2\pi$ -electrons and the predicted stability has been confirmed by the preparation of stable cyclopropenium salts by Breslow<sup>13</sup>. The well known aromatic sextet,  $n = 1$ , is found in 5-, 6-, and 7-membered rings. Thus, the stability of the cyclopentadienide ion 4, benzene 5 and tropylium ion 6 are well documented<sup>14</sup>.



4



5



6

A definition which is dependent on the electronic structure of the molecule or ion in question, has recently been formulated by Badger<sup>7a</sup>, "an unsaturated cyclic or polycyclic molecule or ion (or part of a molecule or ion) may be classified as aromatic if all the annular atoms participate in a conjugated system such that, in the ground state, all the  $\pi$ -electrons (which are derived from atomic orbitals having axial orientation to the ring) are accommodated in bonding molecular orbitals in a closed annular shell".

While a definition such as Badger's is easy to apply it tells nothing of the "degree" of aromaticity or stability of the system in question. One of the earliest quantitative approaches was by the determination of the resonance energy of a molecule. However, difficulties encountered with the resonance energy criterion prompted the idea of defining aromaticity by the ring current concept<sup>15</sup>. An aromatic compound would be defined as a compound which will sustain an induced ring current in a constant applied external magnetic field. The magnitude of the ring current, which is a function of the delocalization of the  $\pi$ -electrons around the ring, is reflected in the deshielding of the hydrogens attached to the aromatic ring. The deshielding of the aromatic hydrogens is thus a quantitative measure of the aromaticity of the compound.

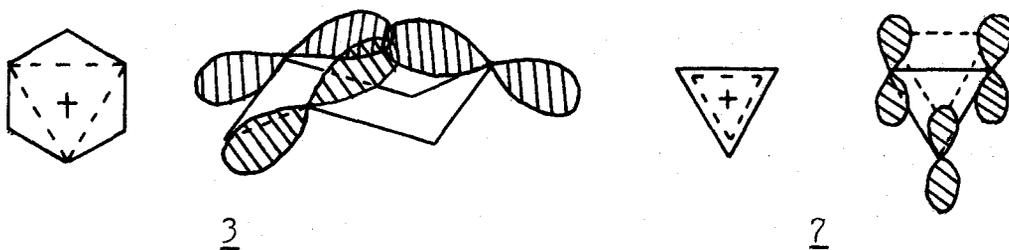
This concept, however, has been criticized by Musher<sup>16</sup> who argued that the chemical shift of aromatic hydrogens, generally attributed to  $\pi$ -electron ring currents, can be correctly represented as a sum of contributions from localized electrons of both  $\sigma$  and  $\pi$  character. Pople<sup>17</sup>, on the other hand, has demonstrated that the shift to lower field of the ring protons, of an aromatic molecule, compared to the protons of the respective ethylene is predominantly due to the ring current, although local induced atomic currents also contribute to the total effect. The controversy is still unsettled. Moreover, it must be realized that the aromatic ring current is not directly linked either to the resonance energy or to

the reactivity of the molecule<sup>18</sup>.

Dauben<sup>19</sup> proposed diamagnetic susceptibility exaltation as a criterion for aromaticity, since it unequivocally reflects the presence of appreciable cyclic  $\pi$ -electron delocalization. The importance of this criterion lies in the fact that it is related to a theoretically well-defined quantity, the London diamagnetism.

### HOMOAROMATICITY - GENERAL CONCEPT AND NOMENCLATURE

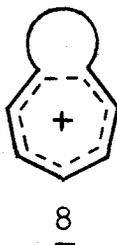
The non-classical bicyclo [3.1.0] hexyl cation 3 is related to the cyclopropenyl cation 7 by interposition of a  $\text{CH}_2$  group between the CH groups on all three sides of the molecule. It was because of this analogy that Winstein referred to 3 as the "trishomocyclopropenyl cation". There are however, some basic differences in the mode of electron delocalization in 3 and 7. Thus, it can be seen that the



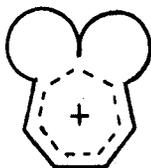
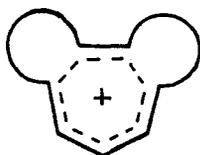
overlap in 3 is not  $\pi$  but intermediate between  $\sigma$  and  $\pi$ . Also, overlap and exchange integrals are 1,3 rather than 1,2. While the two cations have the same pattern of molecular orbital energy levels<sup>20</sup>, the resulting delocalization energy

is smaller for 3 than for 7.

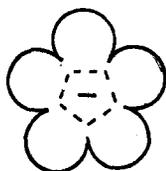
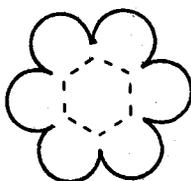
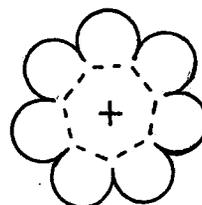
The ideas of homoaromaticity, developed with the trishomocyclopropenium, were later generalized. For example, the sigma backbone of an aromatic system may be interrupted in one, two, three or more sides and so give mono-, bis-, tris- and polyhomoaromatic species. By having one interruption in an aromatic system such as the tropylium ion, the monohomotropylium ion would be obtained. Because of the presence of only one homo-interaction, there exists only one principal type, symbolized by structure 8.



With two homo-interactions, several bishomoaromatic systems can be derived from the tropylium ion 6. Depending on the relative position of the two bridges in these bishomotropylium ions, we can distinguish three principal types, symbolized with structures 9, 10 and 11. All three ions have a sextet of electrons and are potentially aromatic species. They are named 1,2-, 1,3- and 1,4-bishomotropylium ions, respectively.

91011

These generalities can be extended to include homo counterparts of other aromatic systems. Thus, the pentahomocyclopentadienide 12, hexahomobenzene 13 and heptahomotropylium 14 can be considered as the homo counterparts of 4, 5 and 6, respectively.

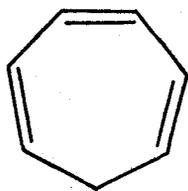
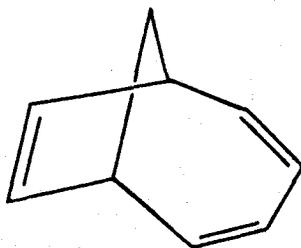
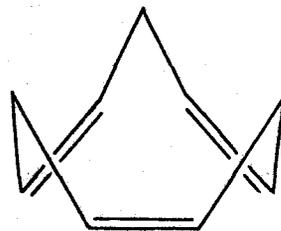
121314

It is important to note that the designations mono-, bis-, tris- and polyhomoaromatic refer to the number of sides where the sigma backbone is removed and not on the number of methylene groups inserted at a particular site.

More recently the concept of homoaromaticity has been treated using symmetry arguments<sup>21</sup>. Thus, the monohomoaromatic system can be envisaged as a single ribbon\* in which two termini are linked through a saturated centre. This array

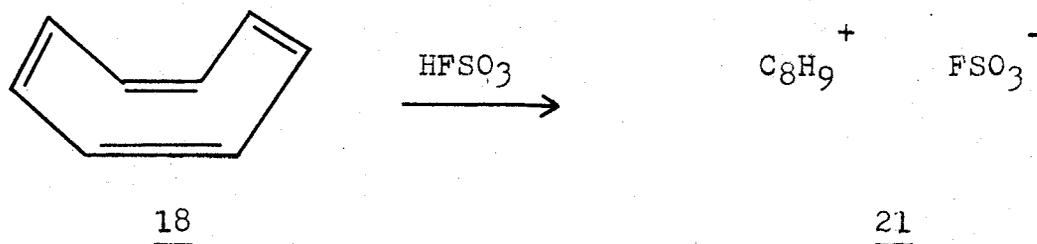
\* A ribbon constitutes an intact conjugated polyene segment.

of ribbon(s) constitutes the pericyclic topology<sup>21b</sup>. Treated in this manner, stabilization of such ribbons can only occur if the ribbon contains  $4n + 2 \pi$  electrons<sup>21b</sup>. An important quantitative difference, between the neutral-neutral ribbon interactions which stabilize molecules and the neutral-charged ribbon interactions which stabilize ions, is that the ion-stabilizing interaction operates over a smaller energy gap than does either of the two interactions which stabilize neutral molecules. Since the magnitude of any interaction is inversely related to the size of such an energy gap, it follows that the stabilization of ions should exceed those of neutral molecules<sup>22</sup>. Indeed, the stabilization of neutral, incompletely conjugated polyenes has so far been experimentally detected only in a uniquely favourable case, namely the 1,3,5-cycloheptatriene 15<sup>23</sup>. The pseudo-aromatic structure for 15 suggested by Doering<sup>24</sup> can be termed monohomobenzene. Where two or more interruptions are involved such as in the bicyclo[4.2.1]nona-2,4,7-triene 16 and 1,4,7-nonatriene 17 no stabilization has been detected, either by heats of hydrogenation measurements<sup>25</sup>, or by photoelectron spectroscopy<sup>26</sup>. Clearly, if homoaromaticity is to be detected, charged species would be the most favourable systems to investigate.

151617

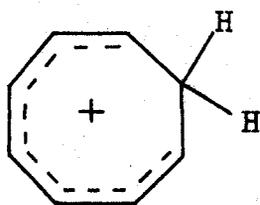
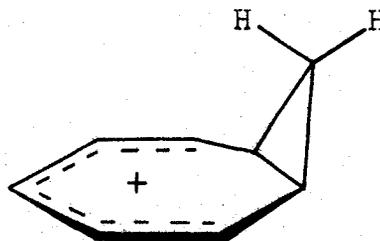
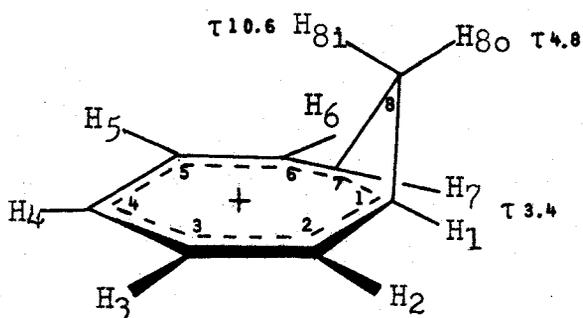
SECTION TWOMONOHOMOAROMATICITY(a) Monohomotropylium Cation

Pettit and coworkers<sup>27</sup> protonated cyclooctatetraene 18 in concentrated H<sub>2</sub>SO<sub>4</sub> and obtained a carbonium ion, that was surprisingly stable. Similar results were later obtained by Winstein<sup>28</sup> upon protonation of 18 in HFSO<sub>3</sub>.



Three possible structures were considered for this C<sub>8</sub>H<sub>9</sub><sup>+</sup> carbonium ion, each having different electron configurations.

1. The planar classical cyclooctatrienyl cation 19.
2. The bicyclic form 20, which can be visualized as a pentadienyl cation with "normal" cyclopropyl conjugation.
3. A fully six-electron delocalized structure 21, which would be expected to exhibit homoaromaticity.

192021

$$\Delta = 5.8 \text{ ppm}$$

$$H_2-H_6 = \tau 1.4$$

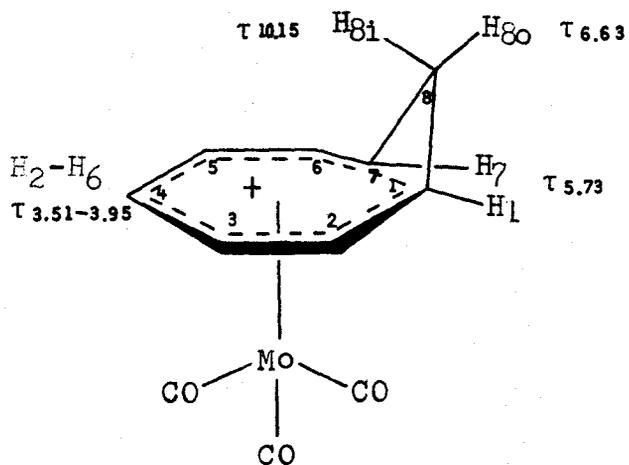
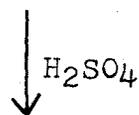
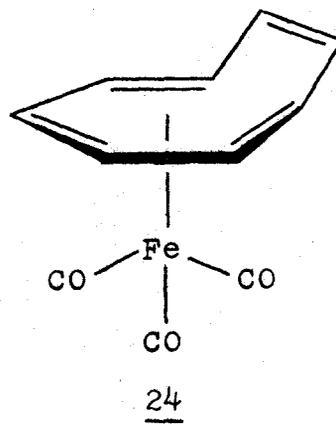
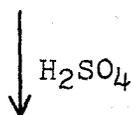
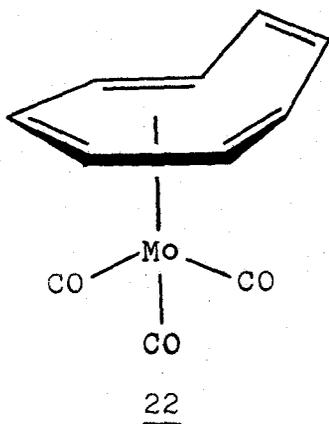
The planar classical cation 19 is completely inconsistent with the observed nmr, since the hydrogens on  $C_8$  are equivalent. While structures 20 and 21 differ only in the mode of cyclopropyl delocalization, the nmr data would suggest that the monohomoaromatic ion 21 better represents the structure of the  $C_8H_9^+$  cation. Thus, the chemical shift of the protons  $H_2-H_6$  in 21 are very similar to the position of the ring protons in the tropylium ion 6. The most significant feature however, is the large chemical shift difference,  $\Delta = 5.8$  ppm, between the protons on  $C_8$ . Both research groups concluded that under certain conditions the cyclopropane ring behaves as a carbon-carbon double bond. Consequently, the p-orbital component on  $C_1$  and  $C_7$  may interact

with the p-orbital on the adjacent carbon atoms  $C_2$  and  $C_6$ . Under these conditions, the cyclopropane sigma bond is delocalized, resulting in this case in a  $4n + 2$  Hückel system.

Examination of models of 21 clearly shows that  $H_{81}$  is in a position over the ring, while  $H_{80}$  is almost coplanar with the ring. In a constant applied external magnetic field, for example in an nmr experiment, the six-delocalized electrons would sustain an induced diamagnetic ring current. Thus,  $H_{81}$  would experience a shielding effect and  $H_{80}$  a deshielding effect.

Deno<sup>29</sup> has examined a variety of cyclopropyl carbonium ions and in all cases the chemical shift difference between the four cyclopropyl hydrogens was ca 0.6 ppm. In marked contrast, the four cyclopropyl hydrogens in the  $C_8H_9^+$  cation differ by 7.2 ppm. Despite this large difference, Deno<sup>30</sup> concluded that the properties of the  $C_8H_9^+$  cation are in accord with "normal" cyclopropyl conjugation and can be best represented by the bicyclic form 19.

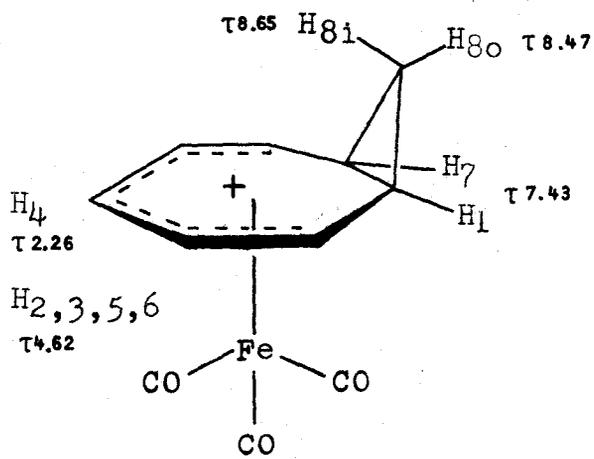
Using the cyclooctatetraene metal complex  $C_8H_8Mo(CO)_3$  22, in which the olefin is bound to the metal by six  $\pi$ -electrons on six carbon atoms ( $6\pi - 6C$ ), Winstein<sup>31</sup> elegantly confirmed the homoaromatic nature of 21. Protonation of 22 in  $H_2SO_4$  and examination of the resultant cation 23 by nmr, shows that the  $C_8$  hydrogens in 23 differ by 3.42 ppm. In contrast, the nmr spectrum of  $C_8H_8Fe(CO)_3$  24 in  $H_2SO_4$  25 shows that the  $C_8$  hydrogens differ by only



$$J_{181} = J_{781} = 10 \text{ Hz}$$

$$J_{180} = J_{780} = 7.5 \text{ Hz}$$

23



$$J_{180} = J_{780} = 8.0 \text{ Hz}$$

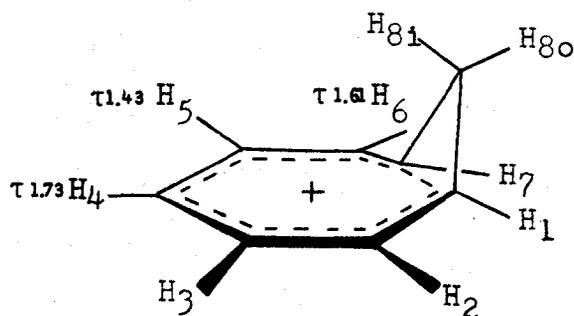
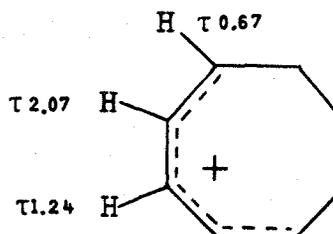
$$J_{181} = J_{781} = 4.5 \text{ Hz}$$

25

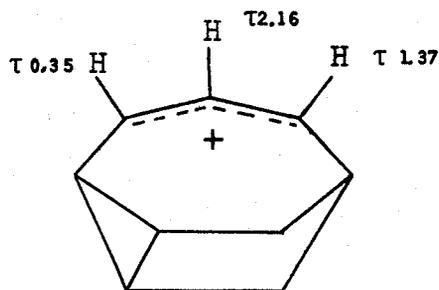
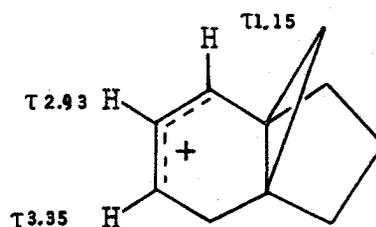
0.2 ppm<sup>32</sup>. The ( $4\pi - 5C$ ) preference of an Fe atom is consistent with 25 having an electron configuration in which there is little or no delocalization of the internal cyclopropyl sigma bond. Thus, 25 would not be expected to sustain an induced ring current. That this is indeed the case, is reflected in the near identical chemical shift of the C<sub>8</sub> hydrogens.

The 60 MHz nmr spectrum of the homotropylium cation 21 obtained by Pettit and Winstein could not resolve the low field multiplet assigned to the five ring protons. Warner<sup>33</sup> has re-examined the nmr of 21 using a 251 MHz spectrometer. Under higher resolution the olefinic protons exhibit three distinct triplets at  $\tau$  values, 1.61, 1.43 and 1.73 of relative areas 2, 2, and 1, respectively. This permitted the complete assignment of all the protons in 21.

Comparing the charge distribution in 21 with the cyclooctadienyl cation 26, it can be seen that the greatest amount of positive charge is located at the extremity of the pentadienyl unit (C<sub>1</sub>, C<sub>5</sub>) in 26 whilst in 21 most of the positive charge is located at the  $\beta$ -carbon atom (C<sub>3</sub>, C<sub>5</sub>).

2126

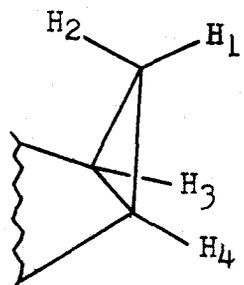
To compare the charge distribution in 21 and 26 may not be valid, since it can be argued that the cyclopropane ring may have some influence on the charge distribution in 21. However, examining compounds 27<sup>34</sup> and 28<sup>35</sup> which have an allyl moiety conjugated with a cyclopropane ring in a symmetrical or near symmetrical bisected fashion<sup>36</sup> shows that this is not so. In these systems again, most of the charge is located at a carbon atom adjacent to the cyclopropane ring. This evidence strongly supports the homoaromatic nature of 21.

2728

### Coupling Constants in the Homotropylium Cation

Examination of the coupling constants in cyclopropyl carbonium ions and other cyclopropyl derivatives revealed that  $J_{gem}$  (4.5-5.0 Hz) is very small. In addition, the  $J_{cis}$  (ca 8.0 Hz) is larger than  $J_{trans}$  (ca 4.5 Hz)<sup>29,37</sup>. This is illustrated in Fig. I.

The protonated complex  $C_8H_8Fe(CO)_3$  25 shows the pattern expected for a normal cyclopropane ring and strongly supports the previous conclusions. On the other hand, for the homotropylium ion 21 the coupling constant pattern is



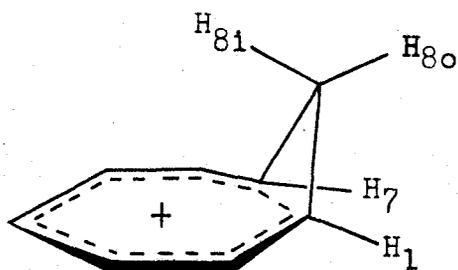
$$J_{12} = J_{\text{gem}} \text{ ca } 4.5\text{-}5.0 \text{ Hz}$$

$$J_{13}, J_{14} = J_{\text{cis}} \text{ ca } 8.0 \text{ Hz}$$

$$J_{23}, J_{24} = J_{\text{trans}} \text{ ca } 4.5 \text{ Hz}$$

Fig. 1 Typical Cyclopropyl Coupling Constants

quite different. Not only is the  $J_{\text{trans}}$  larger than  $J_{\text{cis}}$ , but  $J_{\text{gem}}$  has increased. The same pattern of coupling constants is exhibited in the protonated  $\text{C}_8\text{H}_8\text{Mo}(\text{CO})_3$  complex 23. The in-



21

$$J_{\text{gem}} = J_{8081} = 7.2 \text{ Hz}$$

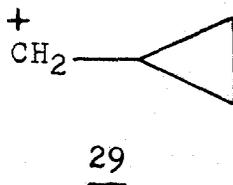
$$J_{\text{cis}} = J_{180} = J_{780} = 7.2 \text{ Hz}$$

$$J_{\text{trans}} = J_{181} = J_{781} = 9.8 \text{ Hz}$$

crease in the geminal coupling constant is attributed to a more open cyclopropane ring in the homoaromatic structures 21 and 23, than in the cation 25.

A further qualitative difference between a simple cyclopropylcarbinyl ion 29 and the homotropylium ion 21 can be obtained by examining the  $J_{13\text{CH}}$  coupling constant of the methylene group. The  $J_{13\text{CH}}(\text{CH}_2) = 180 \text{ Hz}$  in 29<sup>38</sup> is much

larger than the average  $J_{13\text{CH}}(\text{CH}_2) = 159$  Hz in 21. Since 29 is a degenerate system, the coupling constant measured



is the average of two desired types and one where the "CH<sub>2</sub>" is the methylene group at a charge centre. When a methylene group is at a charge centre, as in various benzyl cations, a value of ca 169 Hz would be expected for  $J_{13\text{CH}}$ <sup>39</sup>. Thus the  $J_{13\text{CH}} = 180$  Hz obtained for 29 represents a lower limit for a cyclopropyl coupling constant. Although the factors contributing to the  $J_{13\text{CH}}$  are complex, gross changes can be primarily attributed to the "s" character in the carbon-hydrogen bond<sup>40</sup>. The value of  $J_{13\text{CH}} = 159$  Hz for 21 strongly indicates that no significant hybridization change is occurring at C<sub>8</sub> due to increased lengthening of the C<sub>1</sub>C<sub>7</sub> carbon-carbon bond. In addition little charge is developed at C<sub>8</sub>, since the value for  $J_{13\text{CH}}$  is within experimental error of the value for a normal cyclopropane ring<sup>41</sup>.

Further insight into the electronic structure of the monohomotropylum ion 21 was provided by its ultraviolet spectrum<sup>42</sup>. Table I

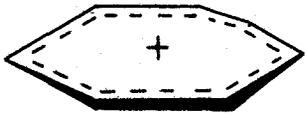
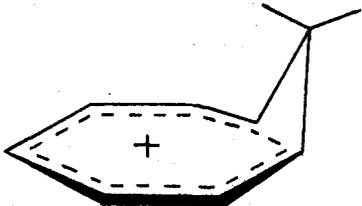
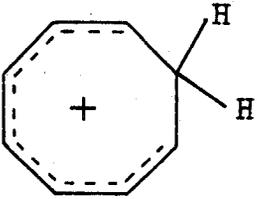
<u>Compound</u>	<u><math>\lambda_{\max}</math> nm</u> <u>(log <math>\epsilon</math>)</u>	<u>H<sub>2-6</sub> (<math>\tau</math>)</u>	<u><math>\beta_{17}</math></u>	<u>Bond Order</u>
 <u>6</u>	217.0 (4.61) 273.5 (3.63)	1.0	$\beta_0$	0.64
 <u>21</u>	232.5 (4.52) 313.0 (3.48)	1.5	$0.73\beta_0$	$\beta_{1,7} = 0.56$
 <u>19</u>	ca 470 <sup>43</sup>	-	$0.765\beta_0$	0

Table I

Ultraviolet Absorption and Electron  
Distribution Data for Various  
Carbonium Ions

It has been demonstrated that for a large number of carbonium ions a reasonably good correlation exists between the HMO excitation energy and the frequency of the longwave length absorption<sup>44</sup>. For the homotropylium ion 21 to fit such a correlation the HMO excitation energy must be approximately  $1.45\beta$  compared to the value of  $1.69\beta$  for the tropylium ion 6. This value results in a  $\beta_{17} = 0.73$  for 21. With this  $\beta_{17}$  the 1,7 bond order is 0.56 by HMO treatment and compares favourably with a value of 0.64 for the  $\pi$  bond order for the tropylium ion 6.

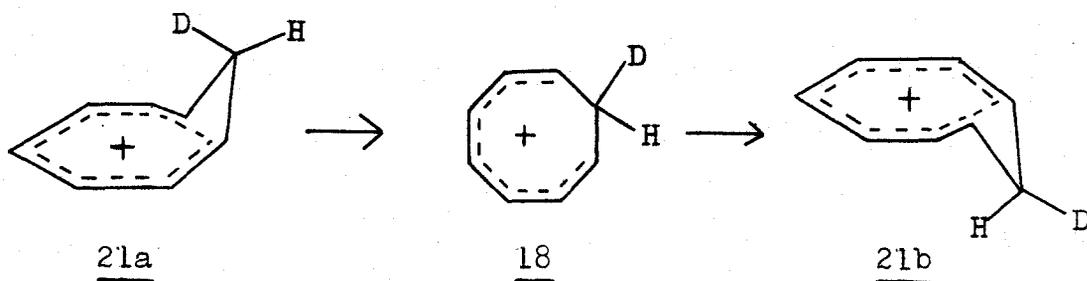
Volume diamagnetic susceptibility data obtained by Dauben and coworkers<sup>6,45</sup> provide more direct evidence for the presence of an aromatic ring current in the monohomotropylium ion 21. The cation 21 shows an exaltation compared to the calculated non-aromatic value, almost as large as that of the tropylium ion 6. Comparison of the exaltation per unit area of the ring would indicate that the homotropylium ion 21 is just as aromatic as 6, or indeed benzene itself.

Table II.

	<u>Benzene</u>	<u>Tropylium</u>	<u>Mono-homotropylium</u>
$\bar{\chi}_m$ Obs	54.8	$66.4 \pm 2.0$	$78 \pm 4$
Calc	41.1	46.9	60.0
Exhaltation $\Lambda$	13.7	19.5	18.0
$\Lambda/S$	2.69	2.68	2.53

Table II    Volume Diamagnetic Susceptibilities

When cyclooctatetraene 18 is dissolved in  $D_2SO_4$  at  $-10^\circ$  and the nmr observed rapidly, considerable tendency towards stereospecificity in the protonation step is evident<sup>42</sup>. The initial nmr shows that 80% of the incoming deuterium occupies the inside ( $H_{81}$ ) position. After a short period of time, the intensities of  $H_{81}$  and  $H_{80}$  become equal thus permitting the evaluation of a first-order rate constant for the isomerization of 21a  $\rightarrow$  21b. This is  $9.8 \times 10^{-4} \text{ sec}^{-1}$  at  $37^\circ$  and  $6.1 \times 10^{-4} \text{ sec}^{-1}$  at  $32^\circ$  and corresponds to a  $\Delta F^\ddagger$



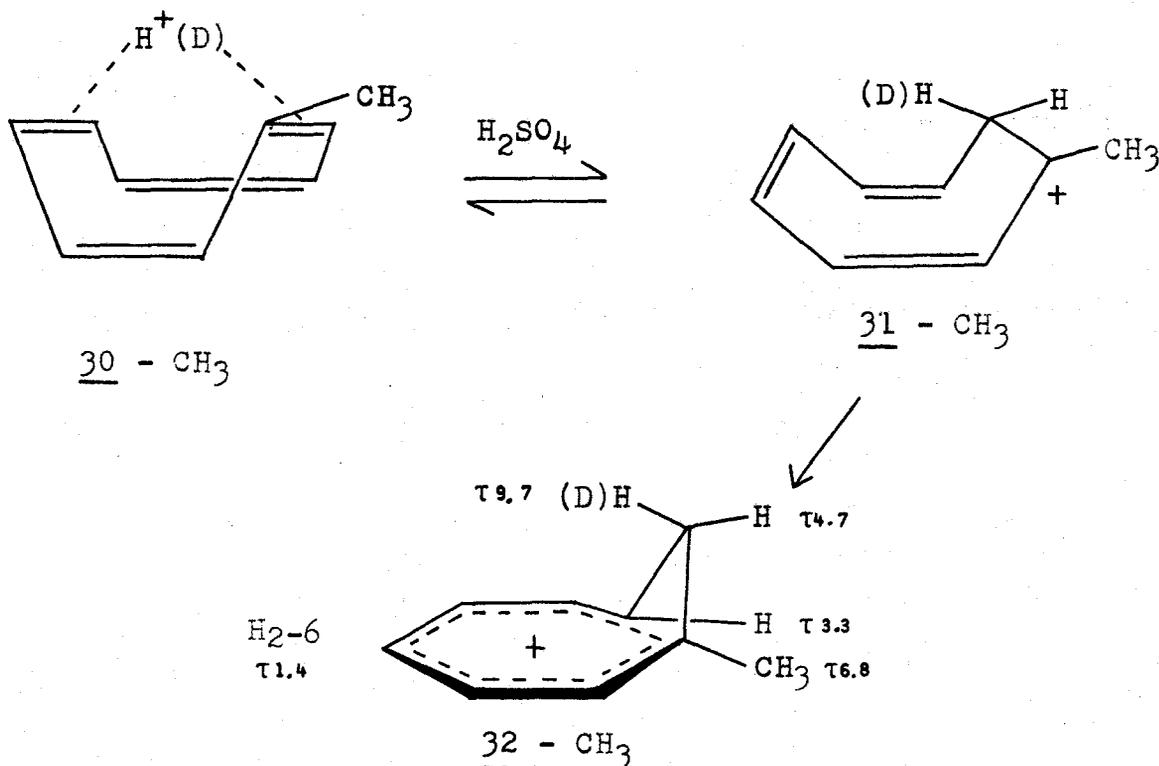
of  $22.3 \text{ kcal mole}^{-1}$ . If the isomerization is visualized to proceed by ring inversion<sup>42</sup> through the planar cyclooctatrienyl cation 18, then the free energy of 18 must be  $22.3 \text{ kcal mole}^{-1}$  higher than that of the homotropylium ion 21.

## (b) Substituted Homotropylium Cations

### 1-Methyl- and 1-Phenylhomotropylium Cations

Protonation of methyl and phenyl cyclooctatetraene provided a more complete understanding of the protonation process leading to the formation of the monohomotropylium ion 21<sup>46</sup>. Thus methylcyclooctatetraene 30 on protonation could conceivably lead to six isomeric methyl-homotropylium cations. However, both the methyl and phenylcyclooctatetraene

show the formation of only one isomer. The formation of



the methylhomotropylium cation 32, can be rationalized by considering the incoming proton to interact initially with the opposite  $\pi$ -clouds of methylcyclooctatetraene. Subsequent formation of the most stable classical carbonium ion 31, followed by a low energy conformational change results in the exclusive formation of 32.

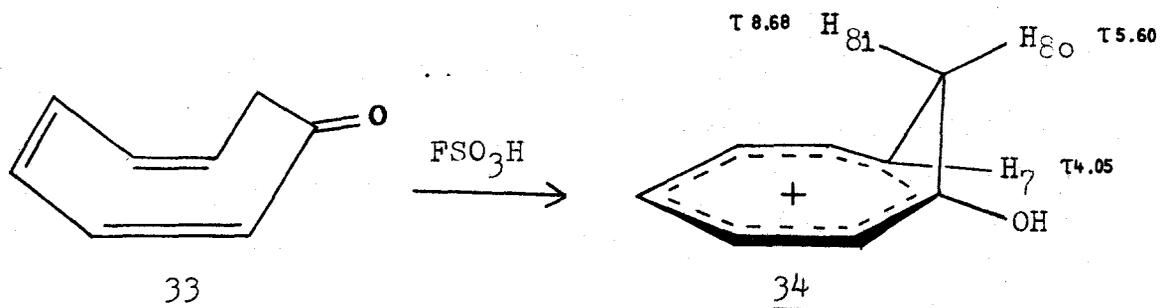
Dissolution of 30 in D<sub>2</sub>SO<sub>4</sub> and examination of the nmr spectrum, showed that the gross pattern is the same as in H<sub>2</sub>SO<sub>4</sub>. However, the signals at  $\tau$  4.7 and  $\tau$  9.7, previously of equal intensity, now had a relative intensity of 0.75 to 0.25 respectively. Thus the endo preference, observed in the protonation of cyclooctatetraene, is also observed for 30. Protonation of phenylcyclooctatetraene shows a similar stereospecificity.

In this particular communication Pettit did not indicate any equilibration of the deuterium. If indeed the planar cation 18 is the intermediate for ring inversion, a lower energy of activation would be expected based on the positive charge stabilizing effect of the methyl substituent.

A detailed examination of the nmr spectrum reveals that the coupling pattern for 32 is similar to 21. Thus,  $J_{\text{gem}}$  ( $J_{80,81} = 8.0 \text{ Hz}$ ) is large and  $J_{\text{trans}}$  ( $J_{7,81} = 10.0 \text{ Hz}$ ) is larger than  $J_{\text{cis}}$  ( $J_{7,80} = 7.5 \text{ Hz}$ ).

#### 1-Hydroxy- and 1-Methoxyhomotropylium Cations

Winstein and coworkers<sup>47</sup> protonated cyclooctatrienone 33 at low temperature and obtained the 1-hydroxyhomotropylium cation 34. Examination of the nmr spectrum of 34 shows that the chemical shift difference  $\Delta$ , between  $H_{81}$  and  $H_{80}$  is 3.4 ppm. This decrease in  $\Delta$  for 34 compared to 21, indicates the reduced homoaromatic nature of 34 due to the presence of the hydroxy substituent. In contrast the low temperature



( $-73^\circ$ ) nmr of 33 shows a chemical shift difference between the methylene protons of only 0.42 ppm.

Examination of the coupling constants in 34 reveals that  $J_{gem}$  ( $J_{80,81} = 10.8$  Hz) is significantly larger than for the homotropylium cation 21 ( $J_{gem} = 7.2$  Hz). This increase in  $J_{gem}$  can at least be partly attributed to a widening in the  $C_1-C_8-C_7$  bond angle. In terms of valence bond theory it can be argued that the resonance structure where the charge is localized on the carbon atom containing the hydroxy function, contributes a greater fraction to the

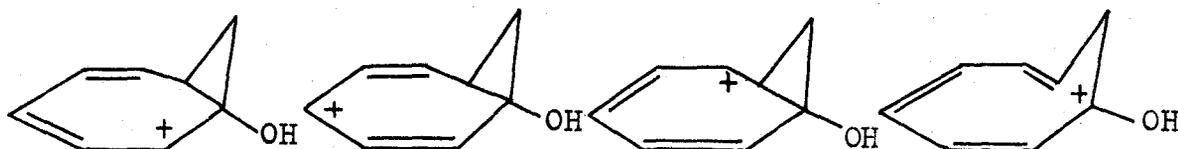


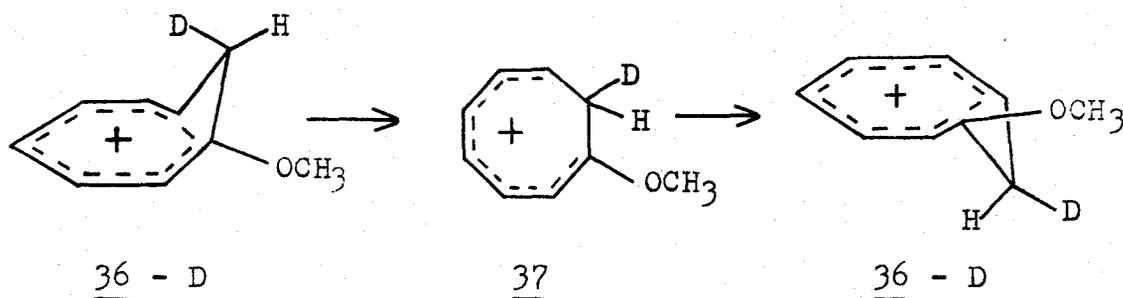
Fig. 2 Resonance Structures for the 1-Hydroxy homotropylium Cation (34)

overall structure. (Fig 2.) The increased  $C_1-C_8-C_7$  bond angle results in  $C_8$  approaching a "normal methylene" carbon atom, for which the  $J_{gem}$  is in the range from 12.0 - 14.0 Hz. For 34 a  $J_{trans}$  ( $J_{7,81} = 9.2$  Hz) larger than  $J_{cis}$  ( $J_{7,80} = 7.7$  Hz) is the same as is observed in the homotropylium cation 21.

As in the homotropylium cation 21 diamagnetic susceptibilities confirm the homoaromatic character of 34<sup>6</sup>.

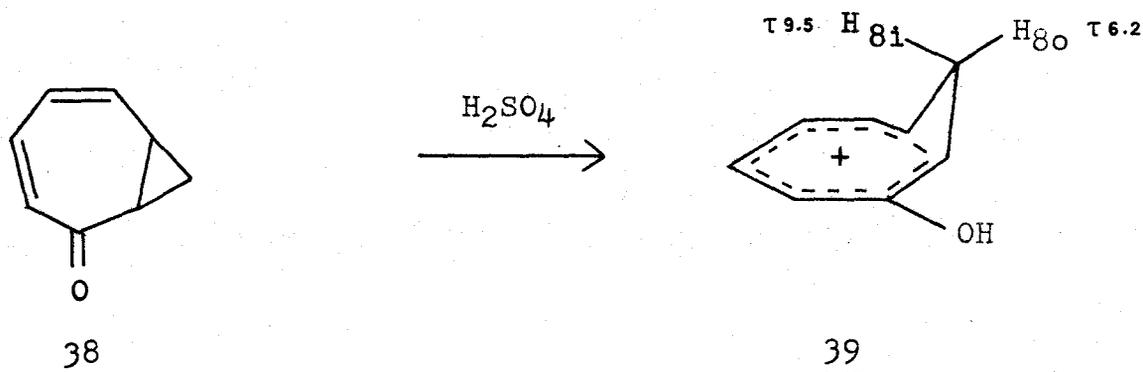
Brookhart<sup>48</sup> obtained the 1-methoxyhomotropylium cation 36 by protonation of methoxycyclooctatetraene 35. The nmr spectrum of 36 closely resembles that of 34. Using  $D_2SO_4$  again resulted in the preferential formation of the endo-D cation 36-D.

The activation energy for the ring inversion process in 36 corresponds closely to Winstein's value obtained for 34. However, for 34 and 36 the energy barrier is significantly lower than the energy barrier for the unsubstituted homotropylium cation 21. If the transition state for the ring inversion process is considered to be the planar non-classical cation 37 the hybridization at  $C_1$  and  $C_7$  must change from a value between  $sp^3$  and  $sp^2$  to a hybridization approximating  $sp^2$ . The electron donating methoxyl and hydroxyl substituents would stabilize the transition state relative to the ground state, thus lowering the energy barrier to ring inversion.



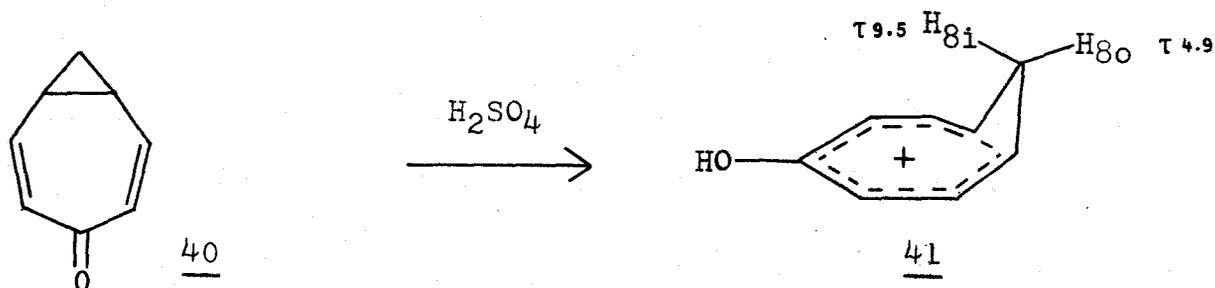
#### 2-Hydroxy- and 4-Hydroxyhomotropylium Cations

Dissolving 2,3-homotropone 38 in sulfuric acid and examining the nmr spectrum of the resulting cation 39 fully confirms the homoaromatic nature of 39<sup>49</sup>. Again, the chemical shift difference  $\Delta$ , is reduced due to the decrease in ring current. No details of the coupling constants were reported by the authors, so that any variation due to the



position of the substituent could not be determined.

Protonation of 4,5-homotropone 40 in sulfuric acid results in the formation of the 4-hydroxyhomotropylium



cation 41<sup>50</sup>. No details of the nmr spectrum were reported. It is significant however, that the chemical shift difference between  $\text{H}_{81}$  and  $\text{H}_{80}$  is 4.6 ppm, which is considerably larger than for the 1-hydroxy and 2-hydroxyhomotropylium cations 34 and 39 respectively. No reason for this difference was given by the authors.

From Warner's<sup>33</sup> data for the parent homotropylium cation 21 it can be seen that of the olefinic carbon atoms ( $\text{C}_2 - \text{C}_6$ ),  $\text{C}_4$  bears the least amount of positive charge. Since the hydroxy substituent is a powerful electron donating substituent, it would be expected to assert its smallest

influence at the least positive centre. Consequently, 41 would have a greater ring current than 34 resulting in a larger chemical shift difference.

Application and Validity of the Johnson Bovey Equation.

Johnson and Bovey<sup>51</sup> deduced that in a constant applied magnetic field, the chemical shift ( $\delta$ ) of a proton due to the presence of a ring current, is given by the expression  $\delta \propto I \times f(X,Y,Z)$  .....(1) where  $I$  is the magnitude of the ring current and  $f(X,Y,Z)$  is a function of the coordinates of the position of the proton relative to the plane of the ring.

Thus for a series of related structures, such as the homotropyliums, in which the geometry of the carbon skeleton remains fixed, it follows from equation 1 that for differing values of the size of the ring current there should exist a linear relationship between  $\delta$ , the chemical shift of one proton and  $\Delta$ , the difference in the chemical shift between the two protons.

Pettit<sup>52</sup> plotted the relevant data for a number of substrates, whose structures are closely related to the monohomotropylium cation 21. These data are shown in Fig. 3. The linear plots obtained by Pettit strongly support the homoaromatic nature of the various substituted monohomotropylium ions. Winstein<sup>31</sup> considered these linear plots as fortuitous and misleading, since ring currents are not the only factor

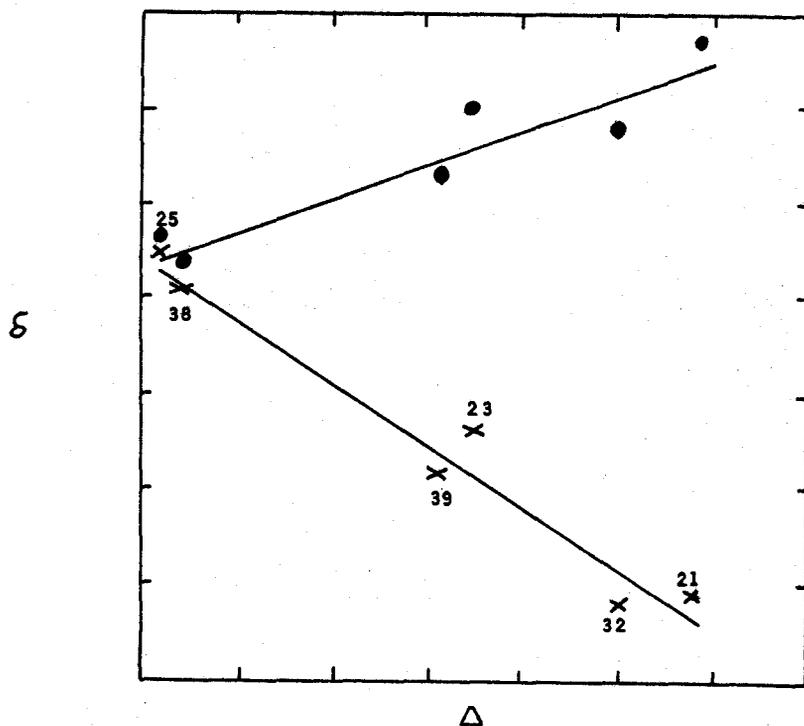
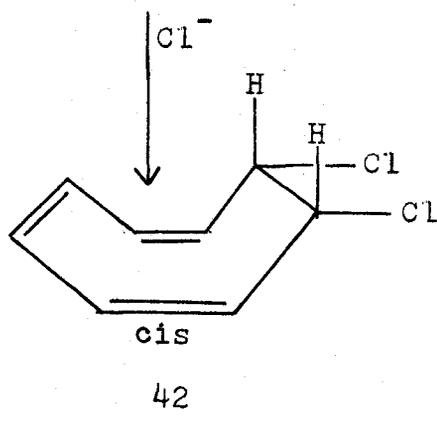
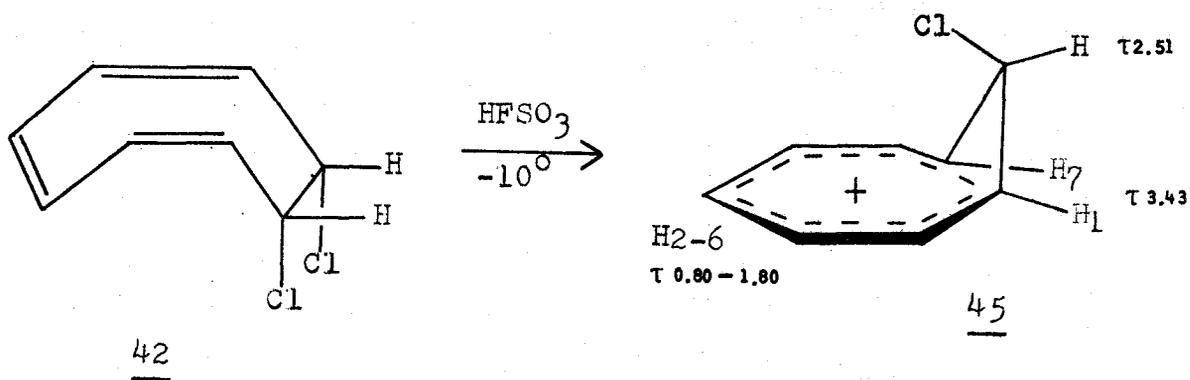
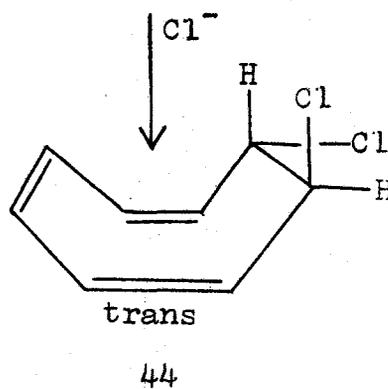
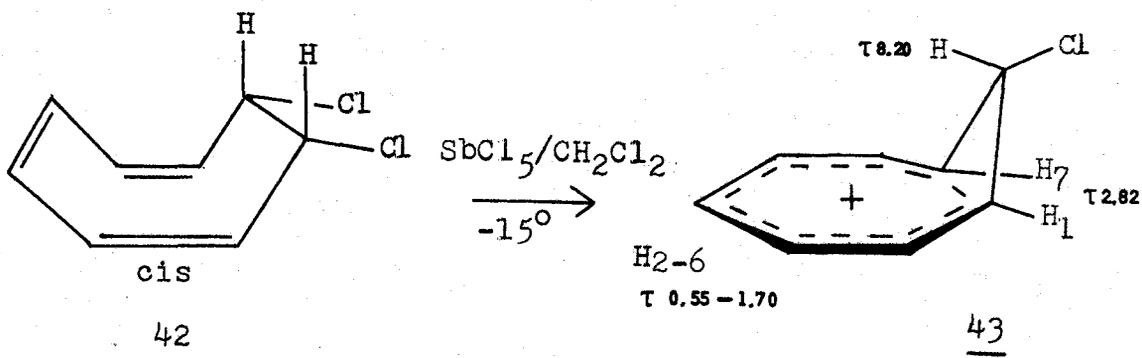


Fig. 3 Plot of  $\delta$  vs  $\Delta$  for Homotropylium Systems

causing variations in  $\delta$ . Variation of charge at  $C_8$  is also an important contributing factor. Clearly charge delocalization at  $C_8$  would invalidate the conclusions of Pettit, but the  $J_{13CH}$  data obtained subsequently by Warner<sup>33</sup> suggest that little charge is delocalized to  $C_8$ . Thus, Pettit's conclusions must be considered valid.

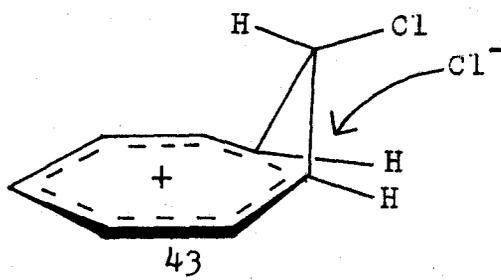
#### 8-Substituted Homotropylium Cations

Huisgen and coworkers<sup>53</sup> have made a careful study of 8-substituted homotropylium cations in an attempt to unravel the mechanistic details involved in the chlorination of cyclooctatetraene. From the viewpoint of homoaromaticity, several enlightening details have been disclosed by this study.



The exo-8-chlorohomotropylum ion 43, prepared by reacting cis-7,8,-dichlorocycloocta-1,3,5-triene 42 with  $\text{SbCl}_5$ , can be quenched with chloride ion to give trans-7,8-dichlorocycloocta-1,3,5-triene 44. Alternatively, the endo-8-chlorohomotropylum ion 45, prepared by reacting 42 with  $\text{HFSO}_3$ , can be quenched with chloride ion, to give the cis-7,8-dichlorocycloocta-1,3,5-triene 46.

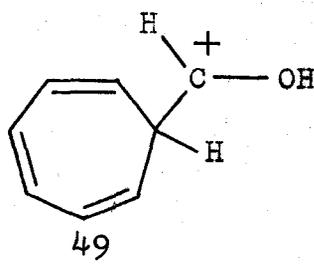
These results indicate that both the 8-chlorohomotropylum ions 43 and 45 suffer preferential endo attack by  $\text{Cl}^-$  ion. This is illustrated for 43.



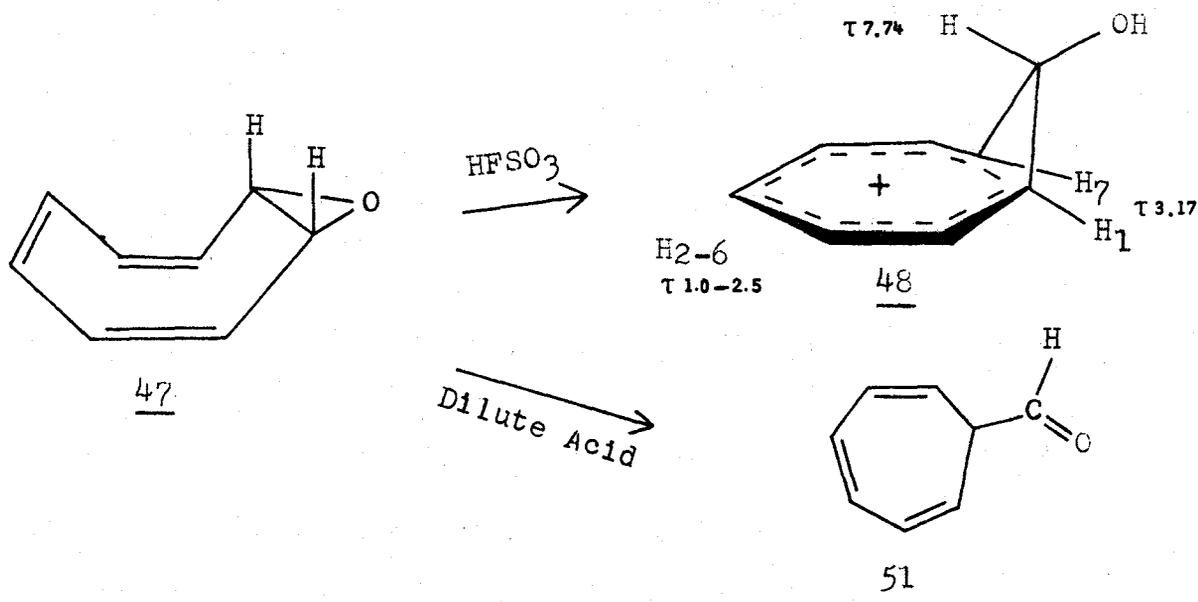
The high stereospecificity exhibited in the collapse of these homotropylum ions was explained on the following basis. Between  $\text{C}_1$  and  $\text{C}_7$  carbons of the homotropylum system there is an asymmetrical electron distribution, each carbon atom being somewhere between  $\text{sp}^3$  and  $\text{sp}^2$  hybridized with the greatest electron density being on the opposite side of the "seven-membered ring" to the bridging group. The attacking nucleophile approaches  $\text{C}_1$  ( $\text{C}_7$ ) on the side of the atom which has the least electron density.

The exo-8-hydroxyhomotropylum ion 48 can be generated by treating 7,8-epoxycycloocta-1,3,5-triene 47 with  $\text{HFSO}_3$  at low temperature<sup>54</sup>. Huisgen contends that some

interesting conclusion can be reached by examining the nmr data of the various 8-substituted homotropylium cations, compared to the unsubstituted homotropylium cation 21. In the various 8-substituted homotropylium cations the substituents shift the 8-hydrogen triplet to lower field. The substituent effect corresponds qualitatively but not quantitatively to the substituent effect observed for simple  $\text{CH}_3\text{-X}$  compounds<sup>55</sup>. The low chemical shift of the 8-hydrogen resonance for 48 suggested to the authors some contribution from the hyperconjugated structure 49. The authors



also contend that this is supported by the observation by Pettit<sup>56</sup> that 47 is converted to the 7-formylcyclohepta-1,3,5-triene 51 under acid catalysed conditions.



Any contribution from the hyperconjugated structure 49 implies that not only the internal, but also the external bond, of the cyclopropane ring is delocalized in 48. This results in an increased positive charge at C<sub>8</sub>.

The change in resonance frequency  $\delta$  is often difficult to separate from the change due to altered bulk susceptibility, yet this distinction must be made if any valid conclusions about polarity and charge development are to be made<sup>57</sup>.

In the compounds CH<sub>3</sub>-X, the change in chemical shift of the methyl hydrogens when X = OH from X = H is 3.18 ppm to lower field. This is attributed to the electronegativity of the hydroxy function. For the 8-exo-hydroxyhomotropylium ion the corresponding change is 2.99 ppm. Even neglecting any medium effects (hydrogen bonding and other weak bonds between groups capable of independent existence), the difference between the two classes of compounds is small (ca 0.2 ppm).

	<u>exo-H</u>	<u>exo-I</u>	<u>exo-Br</u>	<u>exo-Cl</u>	<u>exo-OH</u>
endo-8-H	10.73	9.0	8.76	8.51	7.74
$\Delta\tau$ (ppm)	1.73	0.24	0.25	0.77	
	<u>CH<sub>3</sub>-H</u>	<u>CH<sub>3</sub>-I</u>	<u>CH<sub>3</sub>-Br</u>	<u>CH<sub>3</sub>-Cl</u>	<u>CH<sub>3</sub>-OH</u>
CH <sub>3</sub> -X	9.78	7.81	7.31	6.95	6.60
$\Delta\tau$ (ppm)	1.97	0.50	0.36	0.35	

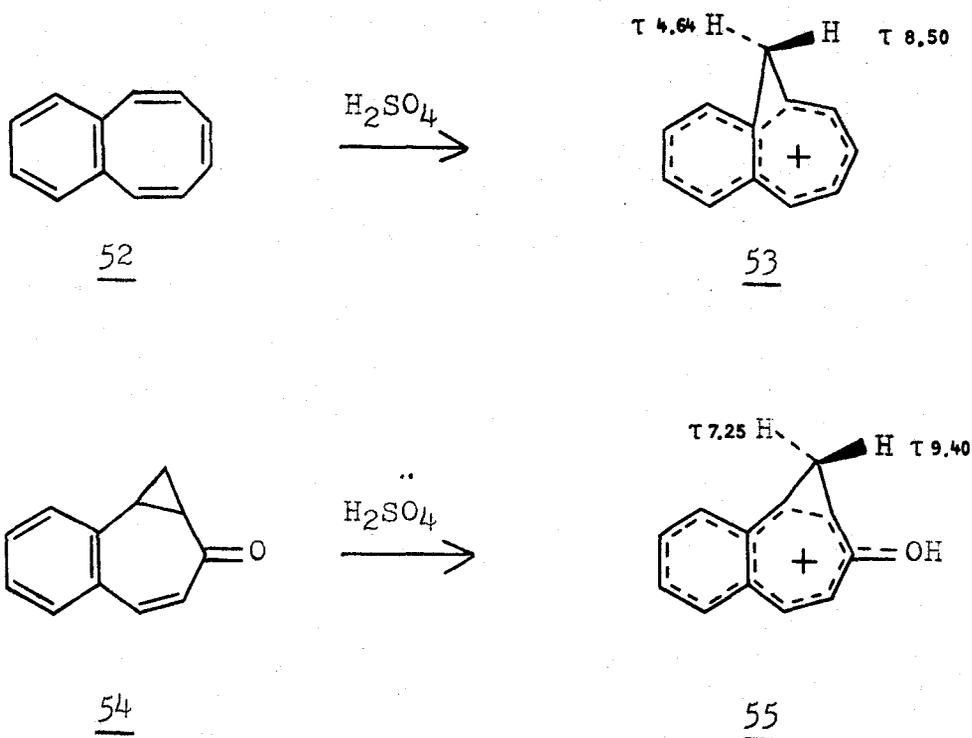
Table III      Nmr Comparison Between 8-exo-substituted Homotropylium Ions and the Compounds CH<sub>3</sub>-X

It must thus be concluded that the predominant (if not the only) effect exerted by the hydroxy function at C<sub>8</sub>, is inductive and not hyperconjugative as proposed by Huisgen.

Thus the earlier evidence (*vide supra*) showing little charge development at C<sub>8</sub> in monohomoaromatic systems with no substituents at C<sub>8</sub> is strongly supported.

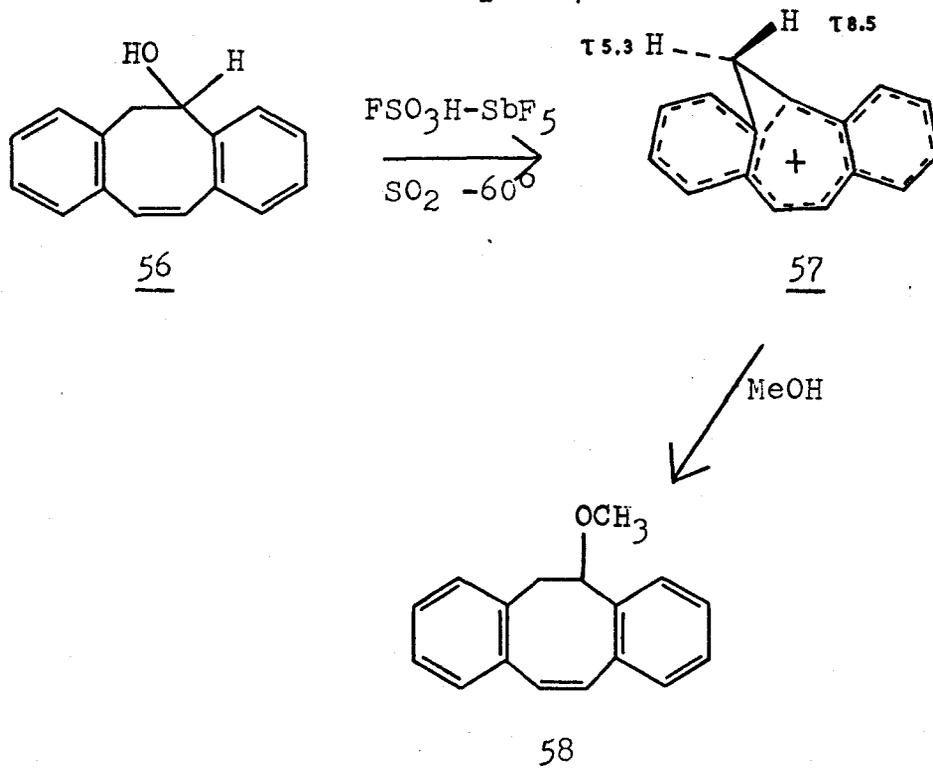
### Benzo- and Dibenzohomotropylium Cations

Protonation of benzocyclooctatetraene 52<sup>58</sup> and 4,5-benzohomotropone 54<sup>59</sup> have been reported to give the corresponding cations 53 and 55 respectively.



Nmr investigations of the cations 53 and 55 fully confirm the cyclic delocalization. The chemical shift difference  $\Delta$ , between inside ( $H_{81}$ ) and outside ( $H_{80}$ ) protons in 53 is 3.9 ppm. This decrease in  $\Delta$ , from the value observed for the parent homotropylium cation 21, is attributed to a dampening of the homo-interaction by the presence of the benzene ring. For 55  $\Delta$  is only 2.20 ppm, reflecting again the attenuating effect of the hydroxy function.

The geminal coupling constant ( $J_{gem} = 10.4$  Hz) in 53 is larger than the value of a fully formed cyclopropane ring (ca 5.0 Hz) and smaller than the value for normal nonstrained methylene protons (ca 12 - 15 Hz). It is significant, however, that  $J_{gem}$  in 53 is considerably larger than in the unsubstituted homotropylium ion 21 ( $J_{gem} = 7.2$  Hz), indicating substantial increase in  $C_1 - C_7$  bond length.



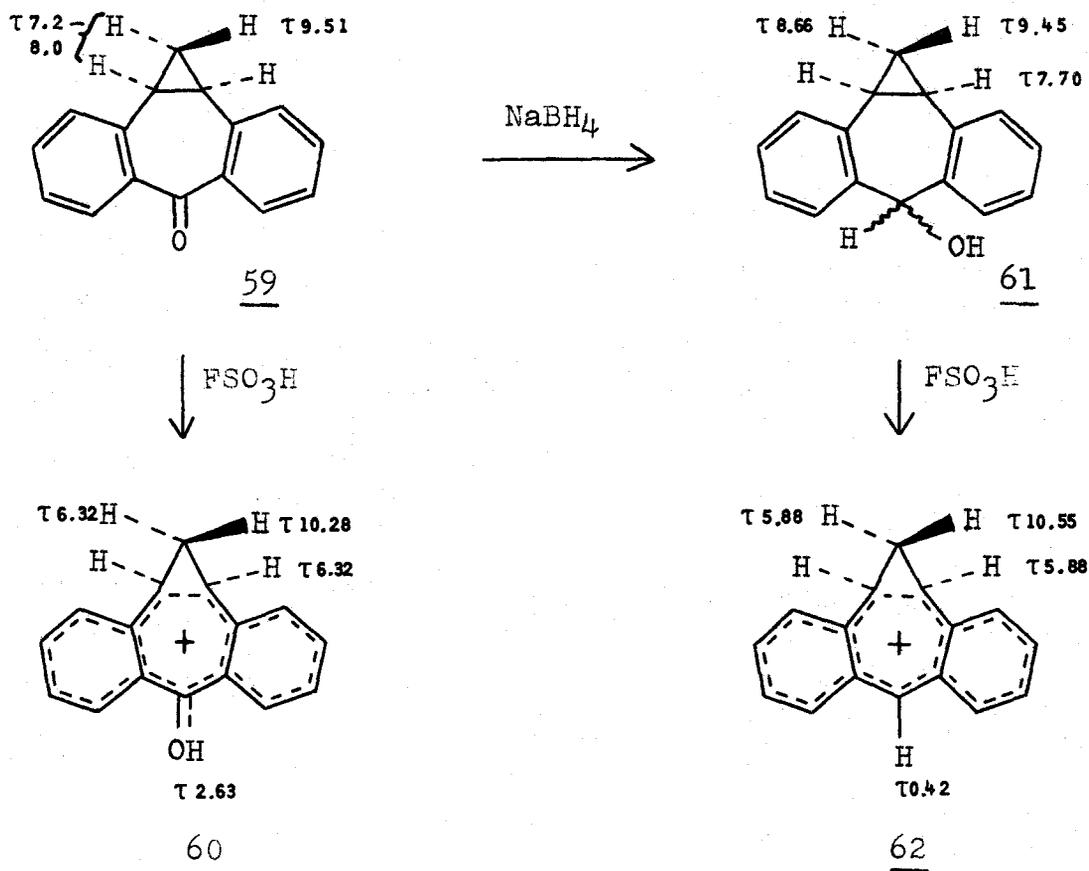
Olah and coworkers<sup>60</sup> reported the formation of a dibenzohomotropylium cation 57 by protonating the precursor 56. The nmr spectrum is only consistent with a homoaromatic structure. Coupling constant data shows a large geminal (8.6 Hz) and the trans (11.4 Hz) larger than the cis (8.6 Hz), which resembles the parent homotropylium cation.

Childs and coworkers<sup>61</sup> performed one of the more detailed studies to determine the importance of homoconjugation in cyclic systems. The system chosen for the investigation was the dibenzohomotropylium cation 62, the homocounterpart of the dibenzotropylium ion 60.

Protonation of the precursor alcohol 61 resulted in the formation of 62. The nmr spectrum showed a chemical shift difference between inside and outside protons,  $\Delta = 4.7$  ppm. This value is considerably larger than the value reported by Olah,  $\Delta = 3.2$  ppm for cation 57.

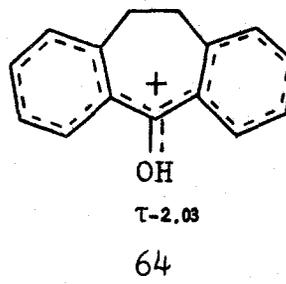
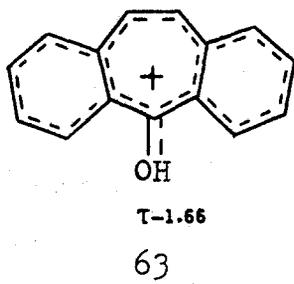
The chemical shift difference, however, is dependent on the relative positions of the inside ( $H_{81}$ ) and outside ( $H_{80}$ ) hydrogens with respect to the "seven membered" ring and the size of the induced ring current. Examination of models of 57 and 62 showed that orientation of  $H_{81}$  and  $H_{80}$  with respect to the "seven membered" ring is quite different. Consequently, the difference in  $\Delta$ , between 57 and 62 may be due to orientation and not due to any variation in the size of the induced ring current. No definite conclusion can be reached at this time.

As expected the dibenzohydroxyhomotropylum cation 60 obtained by protonation of the appropriate ketone 59 shows a significant decrease in  $\Delta$  due to the attenuating effect of the hydroxy function.



The greater the ability of the group or groups which are attached to the carbonyl to stabilize the positive charge, the more the protonated carbonyl becomes a hydroxy cation, and the position of the O-H resonance reflects this change<sup>62</sup>. At  $-90^\circ$  a broad singlet was detected at  $\tau$  -2.63 for 60 which was attributed to the OH function. This value is lower than the corresponding absorption for protonated dibenzotropone

63 and dibenzocycloheptadienone 64 which occur at  $\tau$  -1.66 and  $\tau$  -2.03 respectively. The results indicate that there



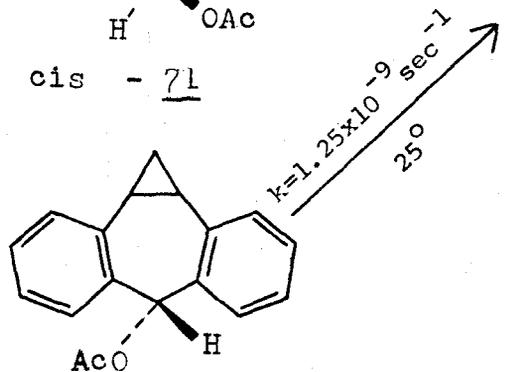
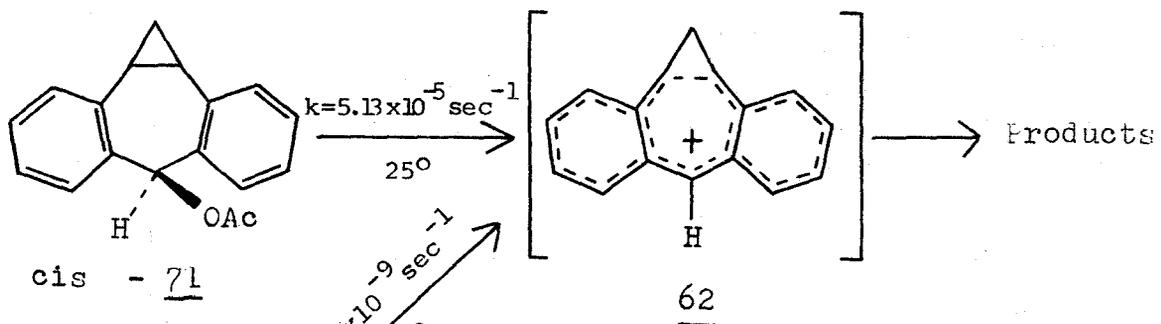
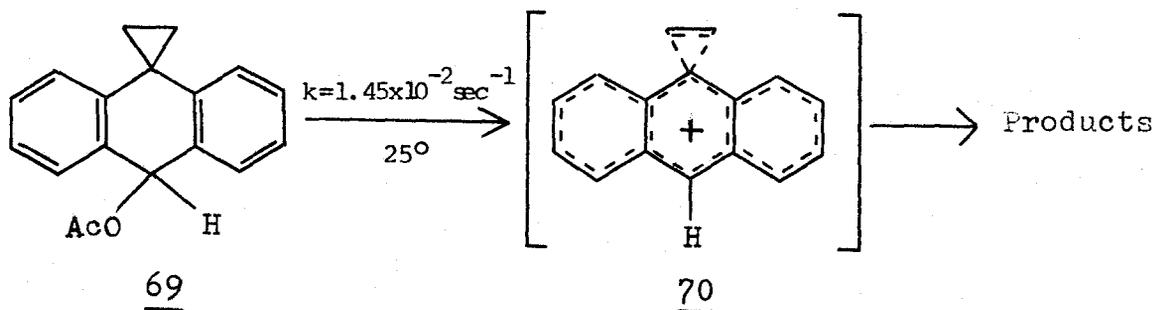
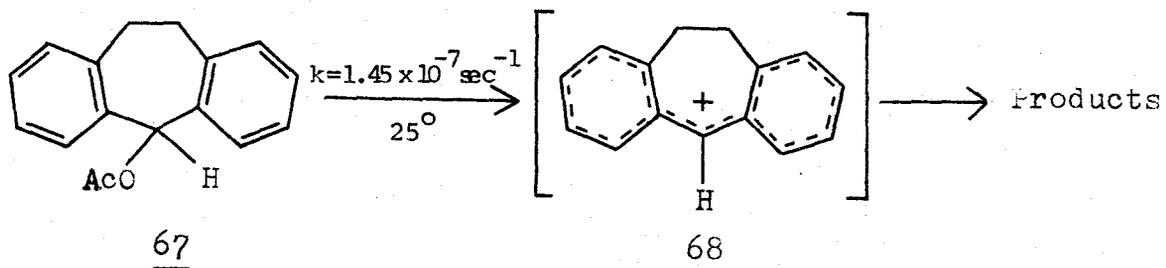
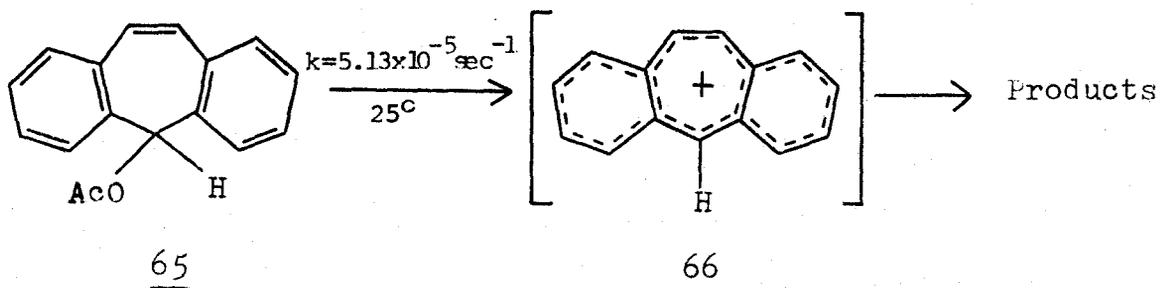
is less tendency to delocalize the charge into the dibenzohomotropyl system. However, as pointed out by the authors, the choice of model compounds is questionable. Conformational differences and the absence of a ring current in 64 could affect significantly the deshielding experienced by the hydroxy proton.

Kinetic investigations by the authors show that :

(i) the cyclopropane in dibenzohomotropyl system is less rate enhancing than the olefinic group of dibenzotropylium system or the spiro cyclopropane group of 69, and

(ii) the cis-acetate 71-OAc solvolyzed some  $10^2$  times faster than the trans-acetate 72-OAc in the dibenzohomotropyl system.

It is significant that the difference in rate between cis-acetate 71 and the trans-acetate 72 is also reflected in the products. Thus, the cis:trans methoxy ether ratio (71-OMe:72-OMe) derived from either precursor is ca  $10^2$ .



Rel. Rate

cis:trans :: 240:1

This contrasts the thermodynamic equilibrium ratio of close to 1.

The cation 62 was quenched in methanol-bicarbonate to give products with a cis to trans ratio of 94.8 to 5.2. This value is in agreement with the product ratio obtained in the methanolysis of the acetates. Clearly, the cation obtained during solvolysis of both the cis and trans acetates is the dibenzohomotropylum cation 62 and its selectivity in collapse must arise from some intrinsic property.

The stereochemical control exhibited by a cyclopropyl ring during formation and collapse of a carbonium ion is well documented. Systems investigated include the formation of allyl cations upon heterolysis of suitable cyclopropyl derivative<sup>63</sup>, cyclopropylcarbinyl systems, particularly when the stereochemistry is kept rigidly fixed<sup>64</sup>, and remote cyclopropyl as, for example, the trishomocyclopropenium cations<sup>5</sup>. The dibenzohomotropyl system is somewhat different than these in that there is involvement and stereochemical control by a remote cyclopropane which is acting through a  $\pi$ -system.

One view considered in the dibenzohomotropyl system is that the unsymmetrical electron distribution between  $C_1$  and  $C_7$  of the cation 62 is reflected at  $C_4$ , with the greater electron density being maintained upon the side of the seven membered ring away from the bridging group. This is analogous to the high degree of stereospecificity reported in the collapse

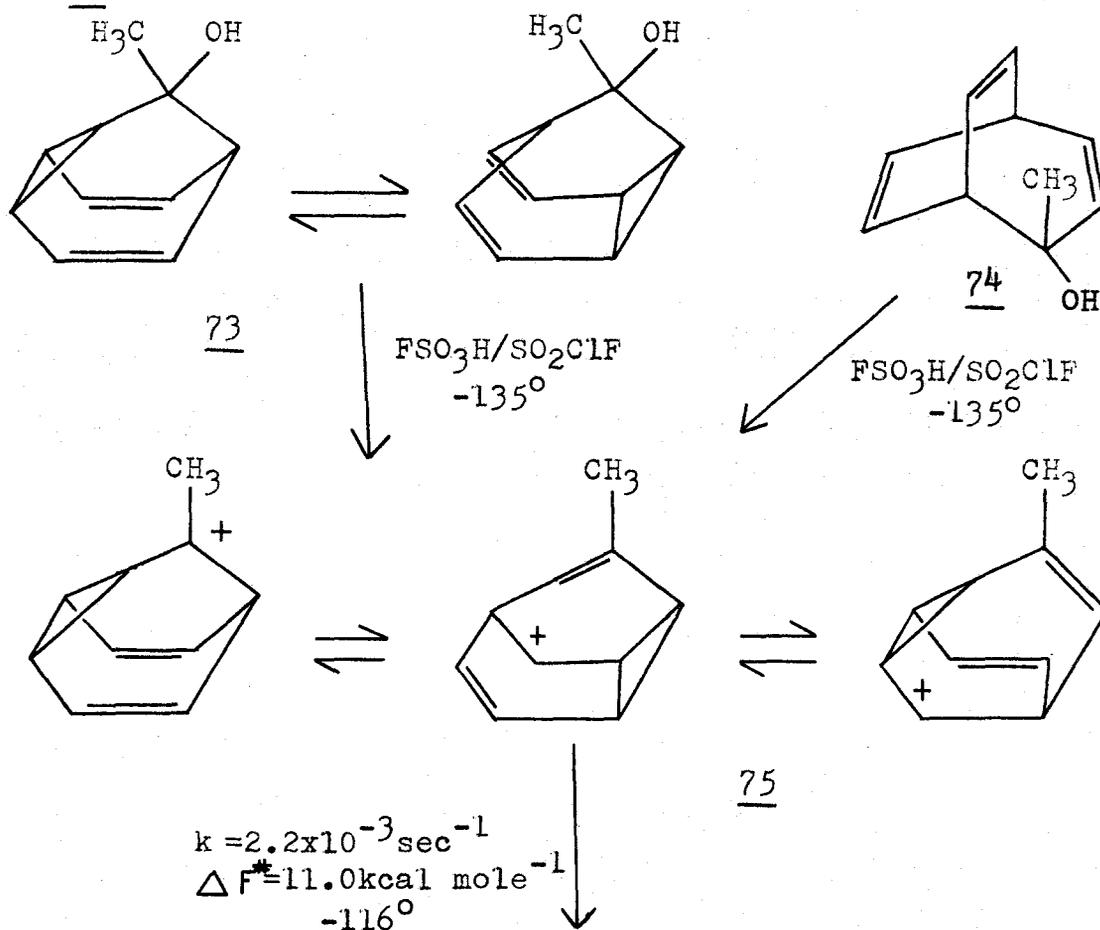
of the 8-chlorohomotropylium cations (vide supra).

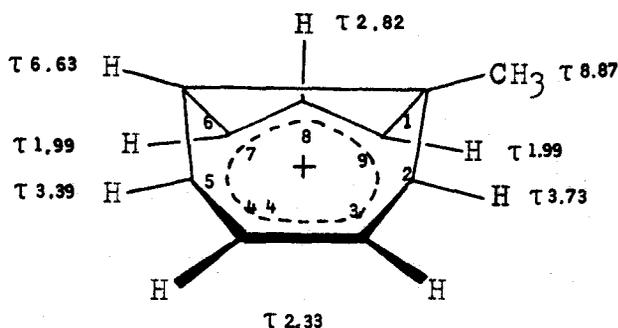
Alternatively, steric interactions could result in 62 adopting a shallow boat conformation giving rise to an asymmetric  $\pi$ -electron distribution at C<sub>4</sub>. As a result greater electron density will be trans to the methylene bridge. As such, the nucleophile would be expected to attack C<sub>4</sub> cis to the C<sub>8</sub> bridge.

## SECTION THREE

BISHOMOAROMATICITY(a) 1,4-Bishomotroproylium Cations

The 9-methyl-9-barbaralyl cation 75 was prepared by protonation of 73 or 74 at  $-135^{\circ}$ .<sup>65</sup> As the temperature was increased 75 underwent a rapid non-Cope degenerate rearrangement and at higher temperatures rearranged to a new carbonium ion 79.<sup>66</sup>





J	2,3	2,4	2,5	2,9	3,4	3,5	3,6
Hz	8.9	0.1	0.0	small	6.7	1.7	small
J	4,5	4,6	5,6	5,7	6,7	7,8	8,9
Hz	7.7	small	4.9	small	2.0	4.0	4.0

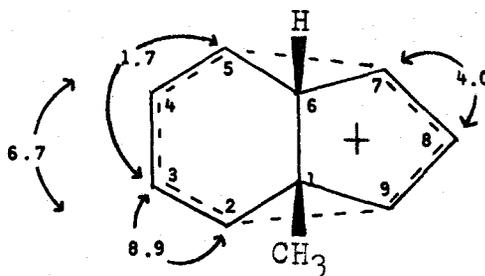
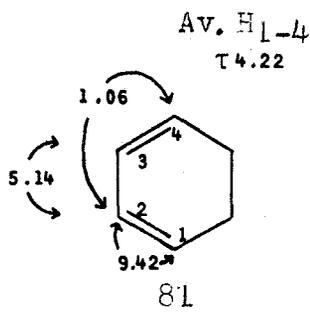
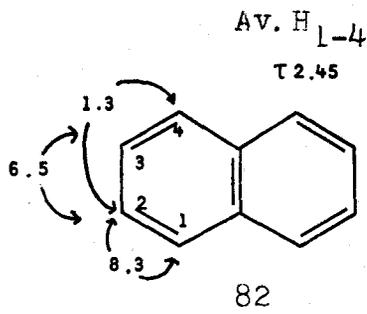
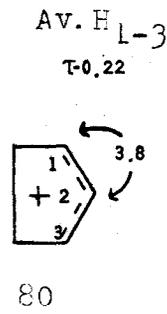
79

Examination of the nmr spectrum of 79 reveals that the three spin system ( $H_7 - H_9$ ) coupling constants are very similar to those of the cyclopentyl cation 80, indicating that  $C_7 - C_9$  is part of a five-membered ring. Similarly, the four spin system ( $H_2 - H_5$ ) coupling constants in 79 are close to those of the appropriate moiety in cyclohexadiene 81 and naphthalene 82. (Scheme 1). From these data, the authors concluded that the skeletal structure of 79 is as indicated.

Comparison of the appropriate chemical shifts of 79 to the chemical shifts in 80, 81 and 82 shows that ( $C_7 - C_9$ ) is not an isolated allylic cation, but instead a considerable amount of the positive charge has been donated from ( $C_7 - C_9$ ) to the "butadiene" moiety ( $C_2 - C_5$ ). The total deshielding\*

\* The total deshielding refers to the difference in the average chemical shift of the ( $C_2 - C_5$ ) portion in 79 compared to a model compound.

of the "butadiene" portion of 79 relative to 81 is ca 5 ppm. This deshielding is accompanied by a total shielding of ca 7 ppm in the "allylic" portion of 79 relative to the same resonances in 80.

79818280

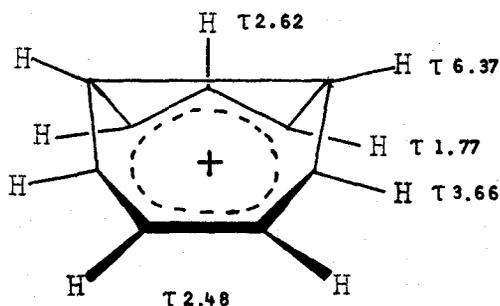
Scheme I      Coupling Constants (Hz) and Chemical Shifts ( $\tau$ )  
for 1-Methylbicyclo[4.3.0]nonatrienyl Cation 79  
and some Model Compounds

This transfer of charge in 79 indicated the presence of homo-interactions between  $C_2$  and  $C_9$  and  $C_5$  and  $C_7$ . Thus, the electronic structure of 79 is best represented as a 1,4-bis-homotropylium cation.

By taking into account probable shielding

of the protons bonded to C<sub>2</sub>, C<sub>5</sub>, C<sub>7</sub> and C<sub>9</sub> due to rehybridization, the authors concluded that ca 0.5 unit positive charge has been delocalized into the "butadiene" part from the "allylic" part in 79.

The unsubstituted cation 83 has also been observed at low temperature.<sup>67</sup> The nmr spectrum is similar except the dissymmetry due to the methyl group in 79 is now removed.

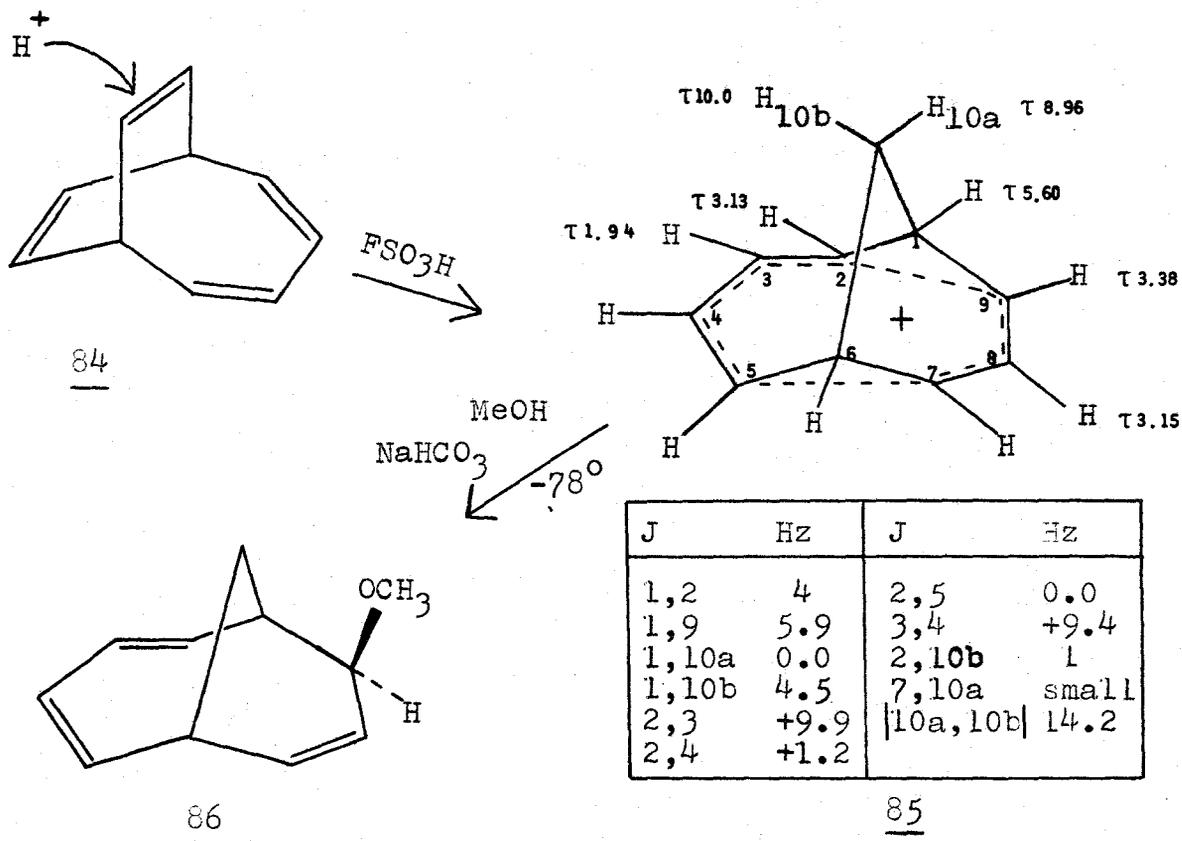


J	2,3(4,5)	3,4(3,5)	2,4	3,4	7,8(8,9)	1,3(4,6)
Hz	8.4	0.9	0.0	6.7	3.9	0.8

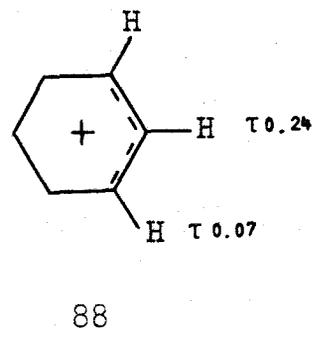
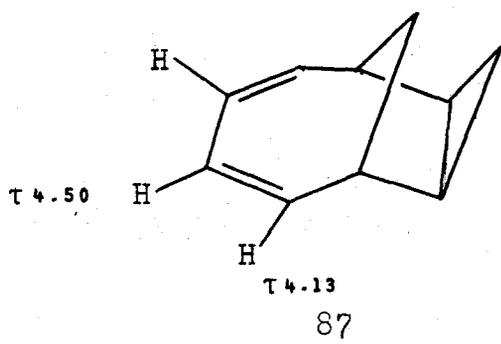
83

A further more informative skeletal structure to investigate 1,4-bishomoaromaticity is the bicyclo [4.3.1] deca-2,4,7-trienyl cation, independently synthesized by winstein<sup>34</sup> and Schröder<sup>68</sup>. In the previously reported 1,4-bishomotropylium cations, the evidence for cyclic delocalization depended primarily on charge delocalization. The bicyclo [4.3.1] skeleton, however, contains a methylene group which lies over the plane of the ring and thus offers a probe to test for a ring current.

Extraction of a solution of bicyclo [4.2.2.] deca-2,4,7,9-tetraene 84 in  $\text{CD}_2\text{Cl}_2$  into  $\text{HFSO}_3 - \text{SO}_2\text{ClF}$  at  $-128^\circ$  resulted in the formation of the cation 85, which was stable



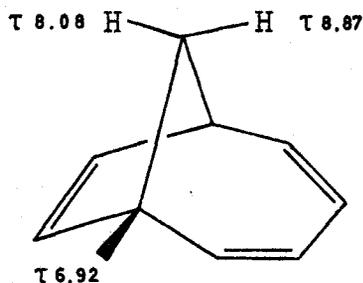
to  $+20^\circ$ . The cation 85 could be quenched in  $\text{MeOH}-\text{NaHCO}_3$  at  $-78^\circ$  to give 86. Using similar arguments, the authors concluded that the "butadiene" moiety in 85 is deshielded by a total of ca 7 ppm relative to the model compound 87. The "allylic" protons are shielded ca 7.7 ppm relative to the cyclohexyl cation 88. Thus, the authors estimate the ca 0.7 unit positive charge has been donated to the "butadiene" moiety in 85 compared to ca 0.5 in 83.



The chemical shifts of H<sub>10a</sub> and H<sub>10b</sub> are at  $\tau$  10.00 and  $\tau$  8.96 respectively, with a geminal coupling constant of 14.2 Hz. Using 16 as a model compound it is clear that the C<sub>10</sub> hydrogens are on the average shielded by ca 1.0 ppm due to the induced ring current. Consistent with the ring current model is the observation that the bridgehead protons H<sub>1</sub> and H<sub>6</sub> resonances appear 1.3 ppm to lower field than those in 16. From molecular models it is clearly shown that H<sub>1</sub> and H<sub>6</sub> project outside the seven membered ring and would be in a deshielding area.

It may be questionable to use 16 as a model compound for detecting ring currents, since the possibility exists that 16 itself can support an induced ring current. However, as pointed out earlier in this thesis ( Page 9 ) no stabilization due to delocalization has been detected for 16.

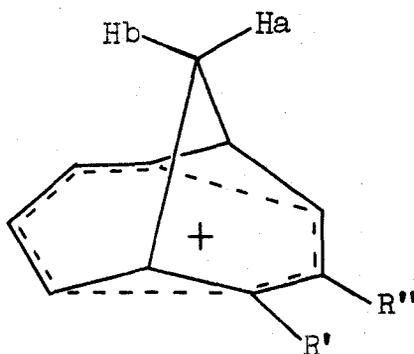
Schroder and coworkers<sup>69</sup> have synthesized a variety of substituted bicyclo[4.3.1]deca-2,4,7-trienyl cations 89 and utilized the average chemical shift of the C<sub>10</sub> hydrogens to



16

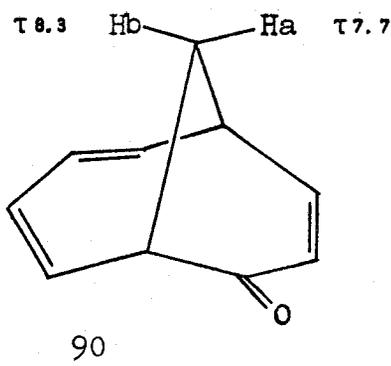
probe the substituent effect on the cyclic delocalization. The relevant nmr parameters are shown in Table IV. In this case  $\Delta$  is the change in chemical shift of the  $C_{10}$  protons relative to a suitable model ketone 90.

89

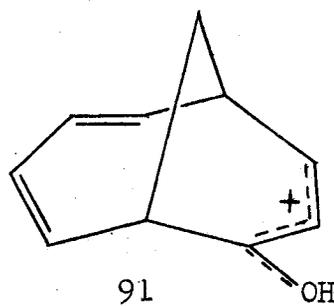


<u>Cation</u>	<u>H<sub>10a</sub></u>	<u>H<sub>10b</sub></u>	<u><math>\Delta</math>(ppm)</u>
R' = Br, R'' = H	8.2	9.4	0.8
R' = H, R'' = Br	8.9	9.9	1.4
R' = CO <sub>2</sub> CH <sub>3</sub> , R'' = H	8.7	9.6	1.0
R' = H, R'' = CO <sub>2</sub> CH <sub>3</sub>	8.8	9.8	1.2
R' = CH <sub>3</sub> , R'' = H	8.5	9.65	0.9
R' = OH, R'' = H	7.7	8.3	0.0
R' = H, R'' = H	8.96	10.0	1.5

Table IV      Nmr Chemical Shifts ( $\tau$ ) for Various Substituted  
Bicyclo [4.3.1] deca-2,4,7-trienyl Cations

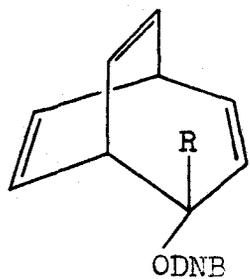


The most significant feature is that for the 7-hydroxybicyclo [4.3.1] decatrienyl cation 89-OH,  $\Delta$ , is zero. The authors interpreted this to indicate that 89-OH does not support an induced ring current and can be best represented as a "non-interacting" carbonium ion 91.

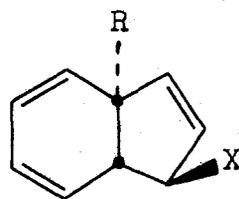


### Kinetic Evidence

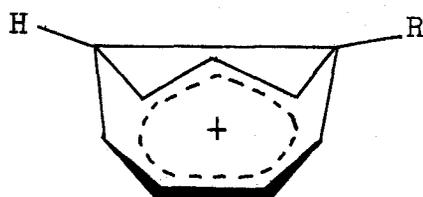
Although several precursors 92-95 were subjected to kinetic investigation, no conclusive evidence to support the intermediacy of a 1,4-bishomoaromatic ion was found<sup>70</sup>. Solvolysis of both exo- and endo-7-bicyclo [4.3.1] deca-2, 4,8-trienyl *p*-nitrobenzoates 96 however, showed a significant rate difference between the two isomers<sup>71</sup>. Table V lists the kinetic data for 96 together with suitable model compounds.



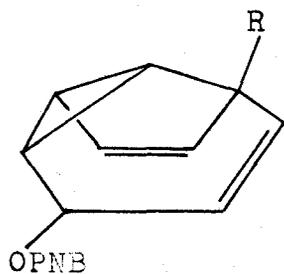
92 R = H



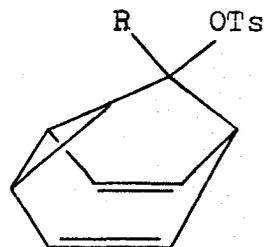
93 a. X=Cl, R=Ph  
b. X=ODNE, R=H



79



94 R = H



95 R = D

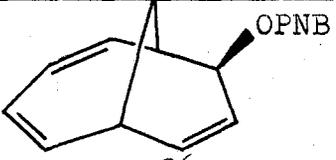
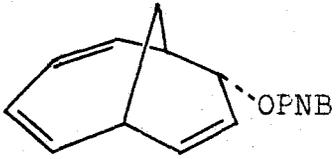
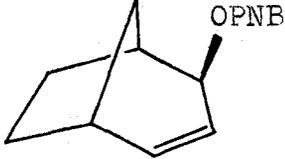
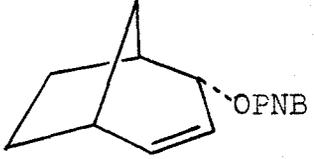
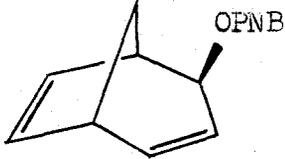
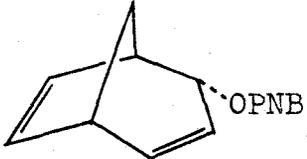
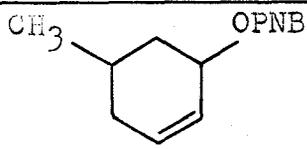
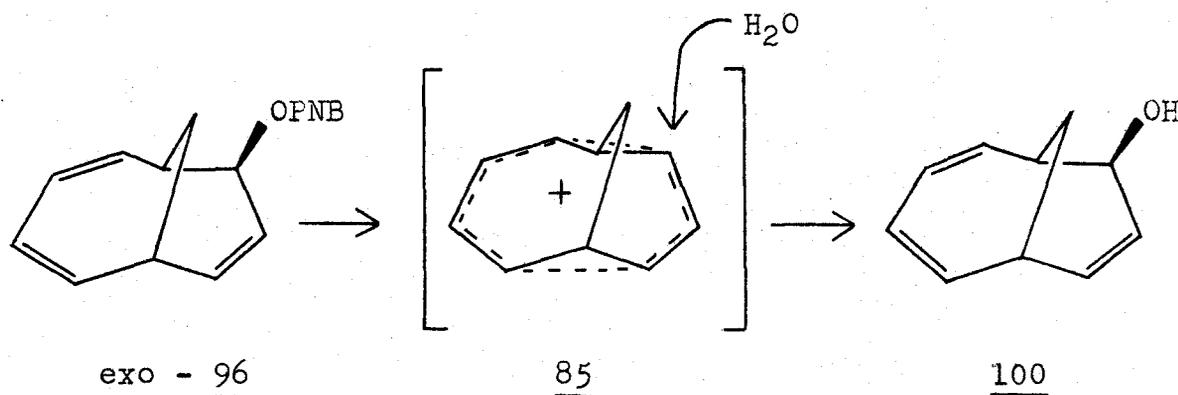
Compound	$k \times 10^7 \text{sec}^{-1} (100^\circ)$	$k_{\text{rel}} (100^\circ)$
 <u>exo - 96</u>	$3.5 \times 10^6$	$1.2 \times 10^6$
 <u>endo - 96</u>	6.6	2.3
 <u>exo - 97</u>	176	63
 <u>endo - 97</u>	47	17
 <u>exo - 98</u>	2.8	1
 <u>endo - 98</u>	2.7	1
 <u>99</u>	37	13

Table V      Solvolysis Rates for Various Allylic Systems  
in 80% Aqueous Acetone

By taking the exo-97<sup>72</sup> as a standard for rate of solvolysis of allylic systems in fused six-membered rings, it is clear that the introduction of a second double-bond in exo-98, has a rate-retarding effect. The butadiene moiety in exo-96, while it would be expected to be inductively retarding, actually enhances the rate of solvolysis by a factor of  $10^3$ . Furthermore, the rate ratio of exo-96 and endo-96 indicates that exo-96 solvolyses with anchimeric assistance, since backside participation would not be expected in endo-96. These results are only consistent with the intervention of a bishomotropylium cation 85 in which there is cyclic delocalization. The only product from solvolysis

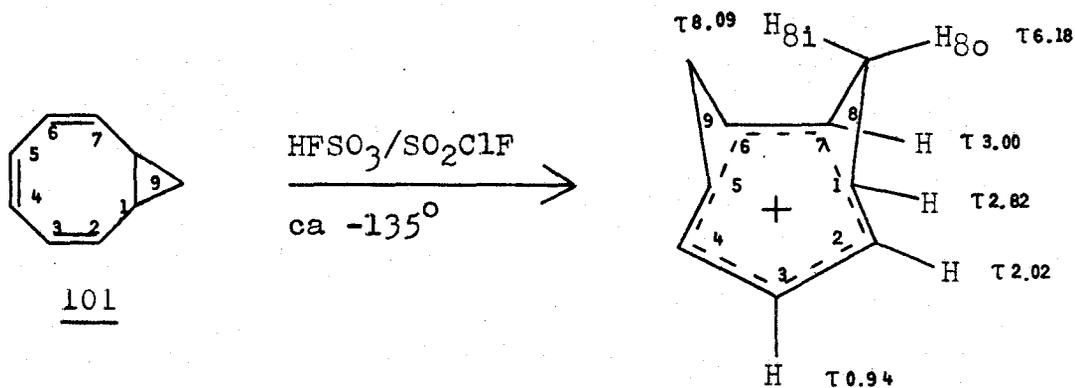


was the exo alcohol 100. It is significant that the quench of 85 in MeOH gave only the exo-OMe 86.

The results strongly support the unsymmetrical electron distribution above and below the plane of the "seven membered ring", with the incoming nucleophile approaching the ion or ion pair from the side of least electron density.

(b) 1,3-Bishomotropylium Cation

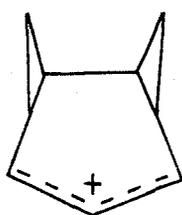
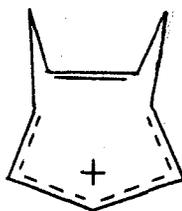
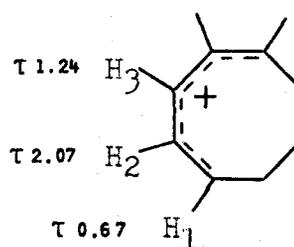
Warner and Winstein<sup>73</sup> protonated cis-bicyclo [4.1.0] nona-2,4,6-triene 101 using conventional methods and obtained the carbonium ion 102.



$J_{23}$	$6.0 \pm 0.5$ Hz	$J_{12}$	$9.0 \pm 0.5$ Hz
$J_{180}$	$9.0 \pm 0.5$ Hz	$J_{780}$	$9.0 \pm 0.5$ Hz
$J_{181}$	$11.0 \pm 0.5$ Hz	$J_{781}$	small
$J_{8081}$	$12.0 \pm 0.5$ Hz		

102

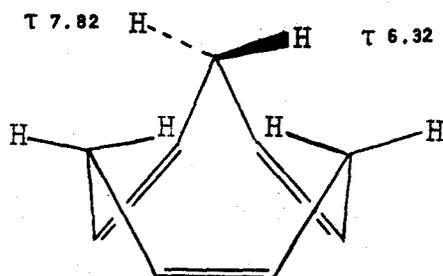
Protonation at  $C_2$ ,  $C_3$  or  $C_4$  would result in either a 1,2-, 1,3- or 1,4-bishomotropylium ion. The authors concluded that the nmr spectrum is only consistent with  $C_3$  protonation. The cation 103 is not an adequate representation since  $J_{\text{gem}} (J_{8081}) = 12.0$  Hz is too large for a normal cyclopropane ring.

103104105

Examination of the charge distribution in 102 showed that it is opposite to that which would be expected for a normal pentadienyl cation 105. Thus, 102 is not adequately represented by structure 104. The upfield shift of  $H_1$  and  $H_5$  signals in 102 compared to those in 105 reflects the charge delocalization from the "pentadienyl" portion to the "ethylene" part. That this is indeed the case is shown by the corresponding downfield shifts of the  $H_6$  and  $H_7$  resonances compared to a suitable model compound, namely cyclohexene ( $\tau$  4.41).

On the premise that  $J_{trans} > J_{cis}$  for homoaromatic systems (vide supra) the authors identified the methylene hydrogens  $H_{80}$  ( $H_{90}$ ) and  $H_{81}$  ( $H_{91}$ ). Examination of models clearly indicates that the repulsion between  $H_{81}$  and  $H_{91}$  forces the methylene carbons apart, whereby the proper dihedral angle ( $\angle 781 = 120^\circ$ ) required for a small coupling constant is achieved. This fact accounts for the one small trans coupling constant ( $J_{781}$ ).

The chemical shift difference  $\Delta$ , between inner and outer methylene protons is 1.9 ppm. However, the nmr spectrum of 1,4,7-cyclononatriene 17 revealed that the inner proton resonances are at lower field than the outer proton resonances. For 102 the situation is reversed. Thus a more reasonable measure for  $\Delta$ , in 102 would be  $1.9 + 1.5 = 3.4$  ppm. Thus 101 can be best described as a 1,3-bishomotropylium cation sustaining an induced ring current.

17

$$\begin{aligned}
 J_{\text{gem}} &= 12.5 \pm 0.5 \text{ Hz} \\
 J_{\text{trans}} &= 9.0 \pm 0.5 \text{ Hz} \\
 J_{\text{cis}} &= 6.3 \pm 0.5 \text{ Hz}
 \end{aligned}$$

The conclusions made by the authors concerning the existence of a ring current in 102 are not compelling for two reasons. Firstly, the inner and outer protons were only identified on the basis of their coupling constants. Secondly, it is well possible that the two cyclopropane bridges could be trans with respect to each other and this would negate the chemical shift argument of the authors.<sup>74,75</sup>

(c) Comparative and Theoretical Treatment of the Tropylium, Homotropylium and Bishomotropylium Cations.

Since the deshielding of the ring protons in aromatic systems is a measure of the ring current,<sup>15</sup> nmr data can be used to obtain a qualitative comparison between various homoaromatic and bishomoaromatic systems. From the nmr data in Table VI it can be seen that the average deshielding of the ring protons is in the order  $\underline{6} > \underline{21} > \underline{102} > \underline{85} > \underline{83}$ . Although these data are complicated by shielding effects which accompany the rehybridization of the homo-interacting carbon atoms, the trend indicated still allows for a qualitative comparison. Thus, it can be seen that tropylium  $\underline{6}$  has a greater ring current than monohomotropylium  $\underline{21}$  which in turn has a greater ring current than the bishomotropylium cations. It is interesting that these data indicate that the 1,3-bishomotropylium cation  $\underline{102}$  has a greater ring current than either of the 1,4-bishomotropylium cations  $\underline{83}$  and  $\underline{85}$ .

<u>Ion</u>	<u>Average Chemical Shift for Seven Ring Protons (<math>\tau</math>)</u>
Tropylium $\underline{6}$	0.76
Monohomotropylium $\underline{21}$	2.12
1,3-bishomotropylium $\underline{102}$	2.23
1,4-bishomotropylium $\underline{83}$	2.62
1,4-bishomotropylium $\underline{85}$	2.70

Table VI      Comparison of Various Homoaromatic Cations

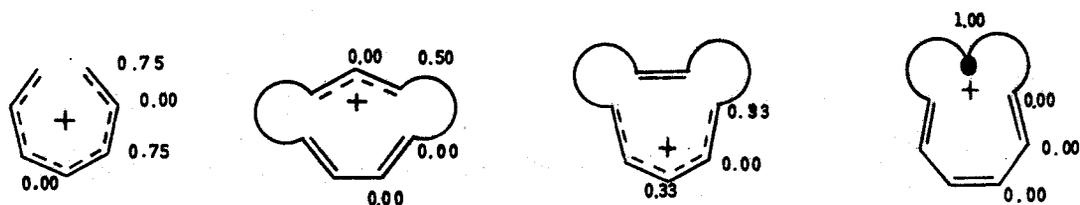
The UV spectrum of an ion, in combination with the HMO method has been used to calculate the charge distribution in a variety of ions.<sup>75</sup> Fig. 4.

Application of this method to the 1,4-bishomotropylium ion 85 results in an excitation energy of ca  $1.50 \beta_0$ , which corresponds to  $\beta_{29} = \beta_{57} = 0.70 \beta_0$ .<sup>75</sup> Using this value in a HMO calculation, with neglect of overlap, a charge distribution as shown in Fig. 4 was obtained. In total 0.50 unit of the positive charge is delocalized away from the "allylic" moiety to the "butadiene" part of the ion. This value is to be compared to ca 0.7 unit positive charge estimated from the total deshielding of the "butadiene" hydrogen resonances in the nmr spectrum.

Since the UV spectrum could not be obtained for the 1,4-bishomotropylium ion 83 and the 1,3-bishomotropylium ion 102, a  $\beta' = 0.70 \beta_0$  was used in the HMO calculations. Thus, for 102 the HMO method indicates that 0.24 unit positive charge has been transferred from the "ethylene" moiety to the "pentadienyl" part of the ion, Fig. 4. This is in agreement with ca 0.30 unit positive charge obtained from the nmr data.

The delocalization energies (DE) for the ions with no homointeractions, 105, 106 and 107, vary considerably but in an expected way. In contrast, the DE of the bishomotropylium ions 85, 102 and 103 is almost the same, when  $\beta' = 0.70 \beta_0$ . The difference in the DE between the heptatrienyl cation 104 and the tropylium cation 6 is almost the same as the difference between the cations 105 and 85. Thus, the estimated gain of DE through

homointeractions is larger in bishomotropylium ions than in the monohomotropylium ion.



D.E 2.055

1.301

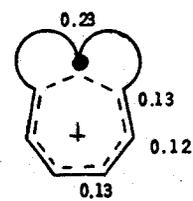
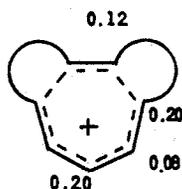
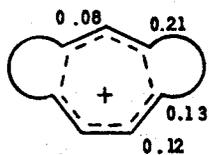
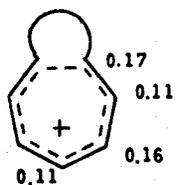
1.464

0.988

104105106107

$$\beta' = 0.73\beta^\circ$$

$$\beta' = 0.70\beta^\circ$$

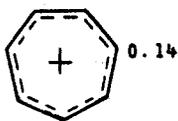


D.E 2.662

2.268

2.286

2.235

2185102103

D.E 2.988

6

Fig. 4

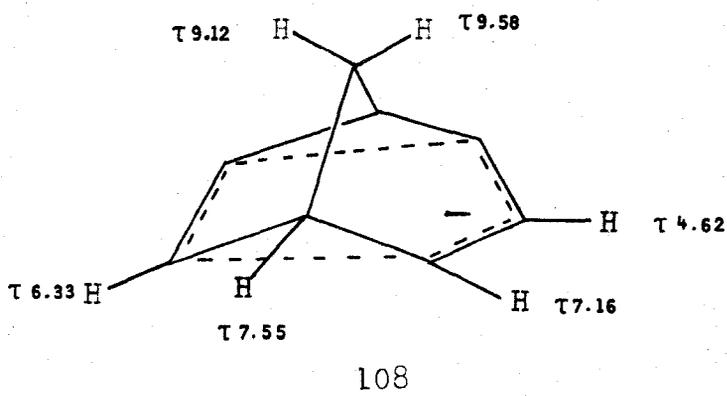
Charge Distribution and Delocalization Energies  
for a Variety of Carbonium Ions

## B. RESULTS AND DISCUSSION

SECTION ONE

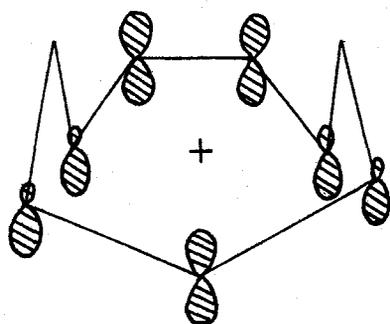
STATEMENT OF THE PROBLEM

At the inception of this work, the general concept of homoaromaticity had been verified for a number of substituted monohomoaromatic systems, however, only one bishomoaromatic species 108 had been proposed in the literature<sup>76</sup>. The 1,3-bishomocyclopentadienide anion 108 was proposed to explain the enhanced kinetic acidity of the precursor bicyclo [3.2.1] octa-2,6-diene compared to suitable model compounds. Subsequent nmr studies<sup>77</sup> fully confirmed the six-electron delocalization in 108. During the course of this study several bishomotropylium cations 83<sup>67</sup>, 85<sup>34,68</sup> and 102<sup>73</sup> were reported and their electronic structure extensively discussed.

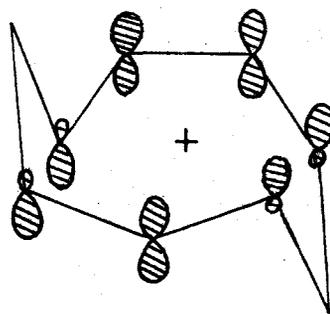


In a bishomoaromatic system an additional parameter which must be considered, is the possibility of having the two bridges in a different orientation

with respect to each other. Thus, for the 1,4-bishomotropylium cations, the two methylene bridges can adopt two distinct geometric arrangements, either cis or trans with respect to each other.

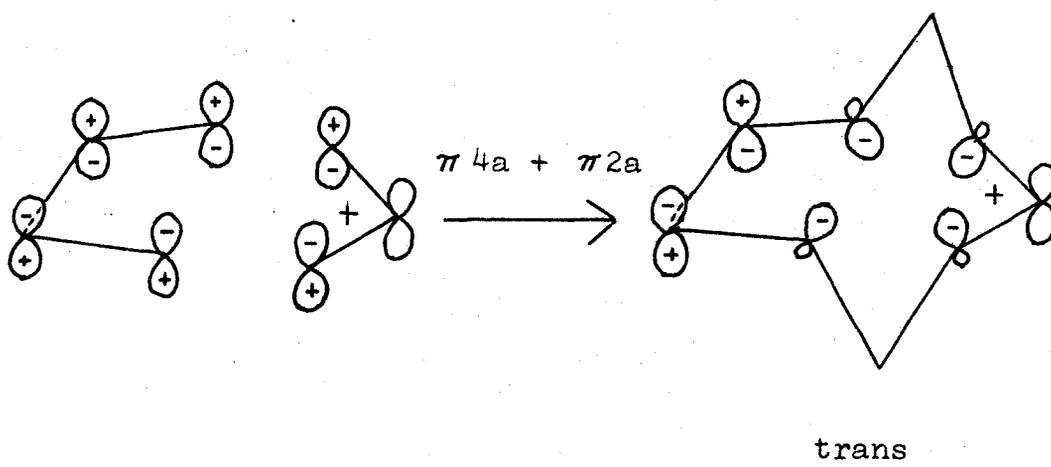
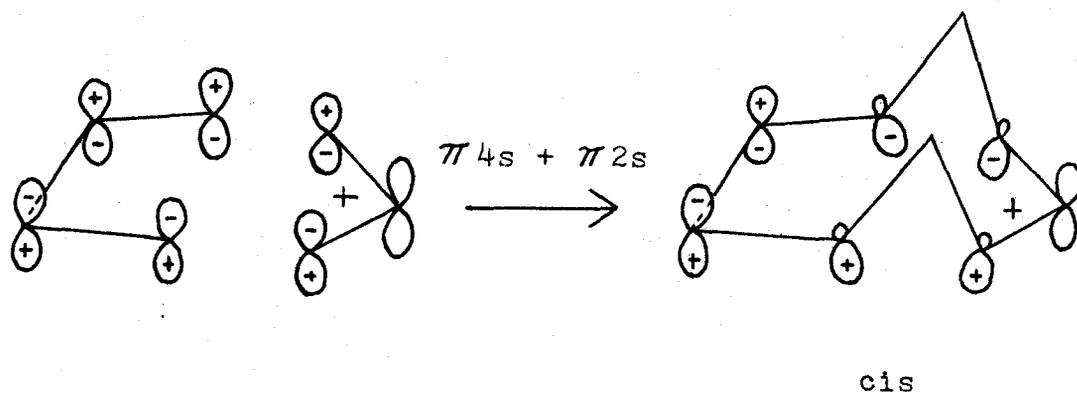


cis



trans

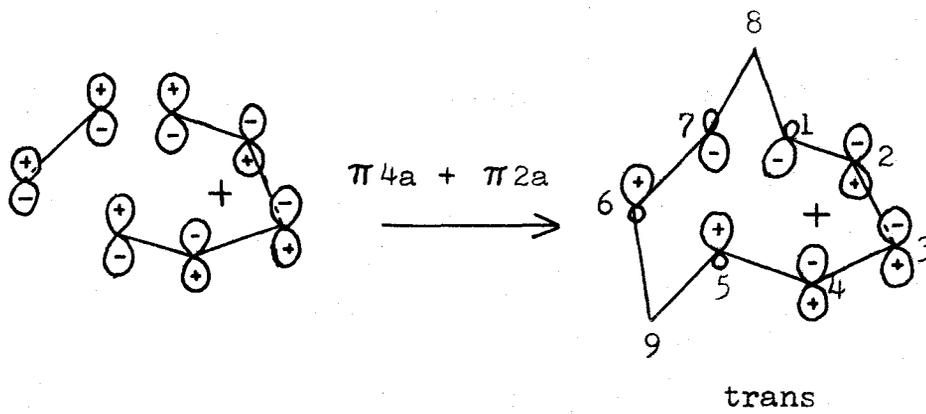
By arbitrarily choosing the symmetry of the basis set of atomic orbitals, it can be seen that the two isomers have an even number of sign inversions (0,2,4....) and are therefore Hückel type systems. Alternatively, extending the inter-relationship of orbital symmetry and homoaromaticity<sup>78</sup>, the two isomers can be considered the "transition state" for the cycloaddition of an allyl cation and a 1,3-diene. Regarded as such, the cis isomer can be viewed as the "transition state" for a  $\pi 4s + \pi 2s$  cycloaddition and the trans isomer as the "transition state" for a  $\pi 4a + \pi 2a$  cycloaddition.



It is clear that in the cis isomer, continuous overlap between adjacent  $p$  atomic orbitals, is only possible on the side opposite the two bridges. In the trans isomer however, the overlap between adjacent  $p$  atomic orbitals is partly distributed above and below the plane of the "seven membered ring".

Although this discussion has centred on the 1,4-bis-homotropylium cations, the arguments presented are equally

valid for the 1,3-bishomotropylium cations. In this system however, the two isomers can be considered the "transition state" for the cycloaddition of ethylene and a pentadienyl cation.

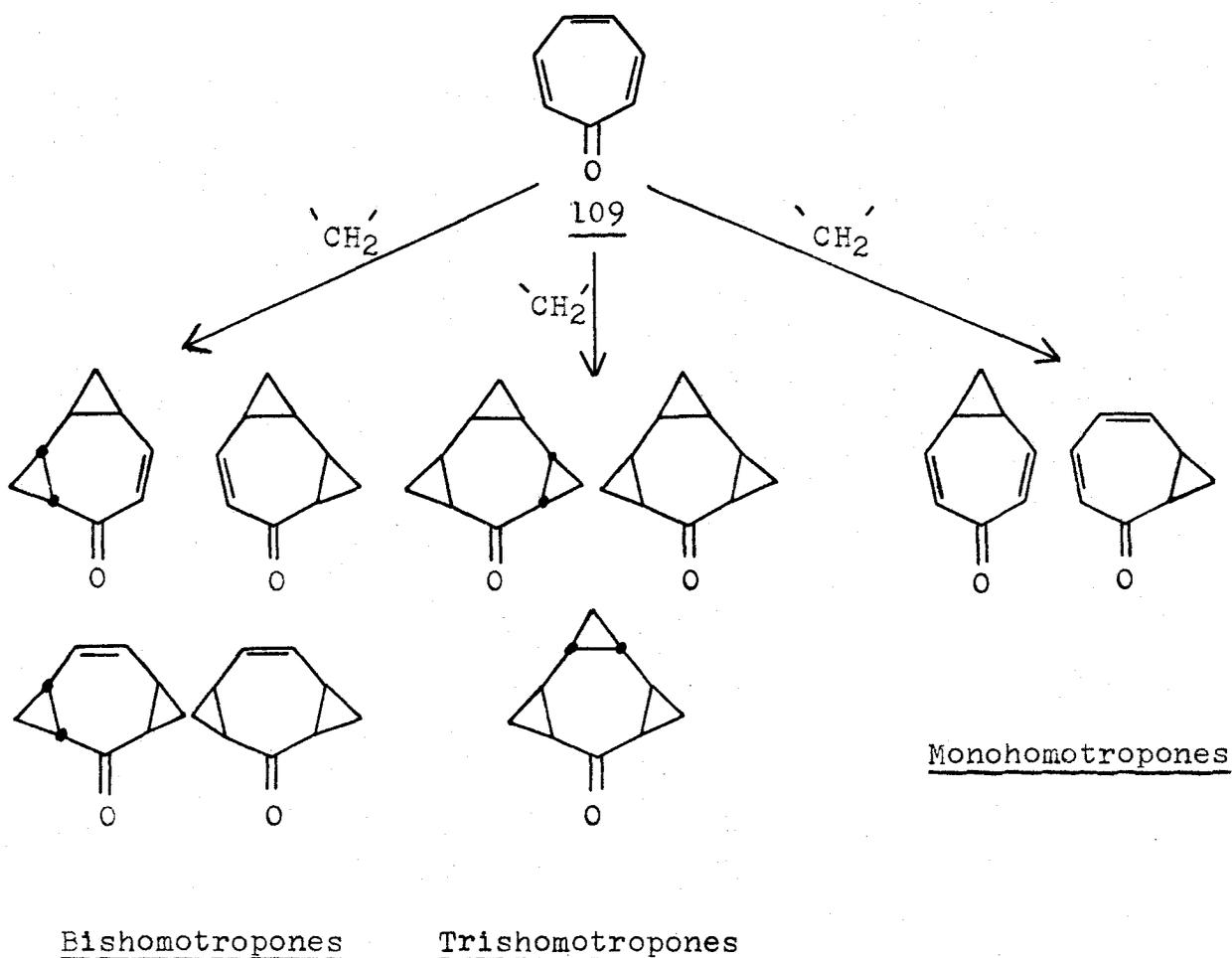


A comparison of the trans-1,4-bishomotropylium cation with the trans-1,3-bishomotropylium cation showed that in the 1,3-bishomotropylium cation, considerable twisting of the 6,7-double bond is required to obtain good overlap of the  $p$  atomic orbitals. From this point of view, if homoaromaticity is to be detected in the trans configuration, the 1,4-bishomotropylium cation appears to be the more favourable system to investigate.

It is proposed to examine the importance of the relative geometry of the two methylene bridges by synthesizing the cis and trans-1,4-bishomotropylium cations from suitable precursors in which the stereochemistry is rigorously defined.

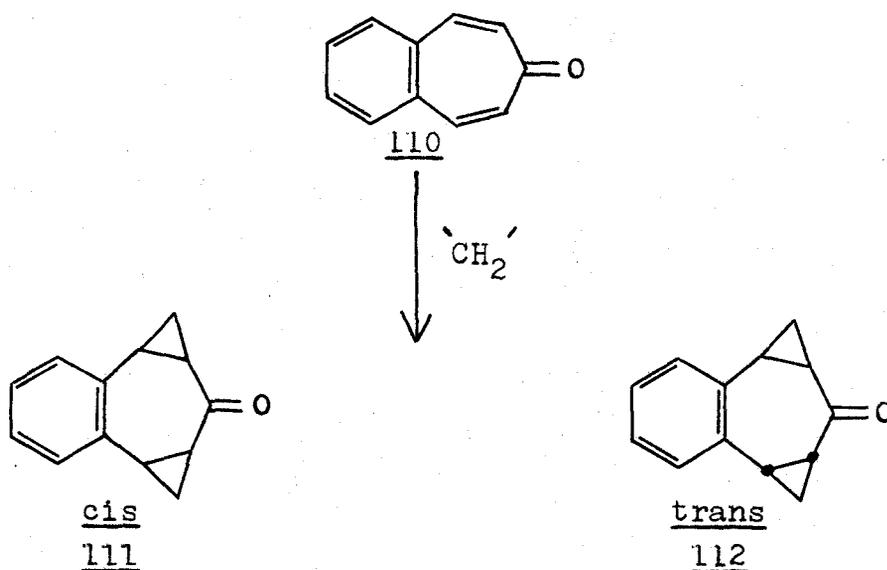
GENERAL SYNTHETIC CONSIDERATIONS(a) Nature of Precursor

The addition of methylene to tropone 109 could conceivably result in four possible bishomotropones, and their separation and identification could pose considerable difficulty. In addition to the bishomotropones, two monohomotropones and several trishomotropones are possible. Thus, 109



did not appear to be an attractive starting material for the synthesis of the 1,4-bishomotropones.

Alternatively, the addition of methylene to the two double bonds of 4,5-benzotropone 110 can only result in the formation of the cis and trans-4,5-benzo-2,3:6,7-bishomotropones 111 and 112 respectively. Although the presence of



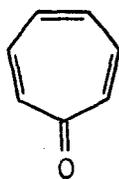
the benzene ring introduces a further perturbation, the fact that the desired 1,4-bishomotropones appear to be more readily attainable, makes 110 the more attractive precursor.

(b) Potential Methods for the Cyclopropylation of Benzotropone

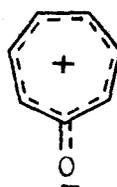
From a synthetic point of view, the question of whether the seven membered ring in 110 is aromatic or not becomes significant, since this factor will influence the chemical reactivity of the carbon-carbon double bonds. To gain insight into this question it is instructive to examine the electronic

structure of tropone.

Tropone is generally considered to be a representative nonbenzenoid aromatic compound<sup>79</sup>. The aromatic character of tropone is a consequence of significant ground-state contribution of the cyclic delocalized resonance structure 109b. The characterization stems primarily from



109a



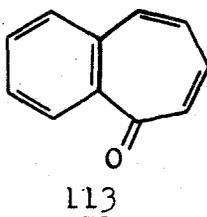
109b

the empirical resonance energy<sup>80</sup>, planarity<sup>81</sup>, diamagnetic susceptibility<sup>82</sup>, and dipole moment<sup>83</sup> of this molecule. The ultraviolet spectrum, infrared<sup>84</sup> spectrum  $\nu(\text{C}=\text{O}) = 1638 \text{ cm}^{-1}$  and high basicity<sup>84</sup> further support the aromatic nature of 109.

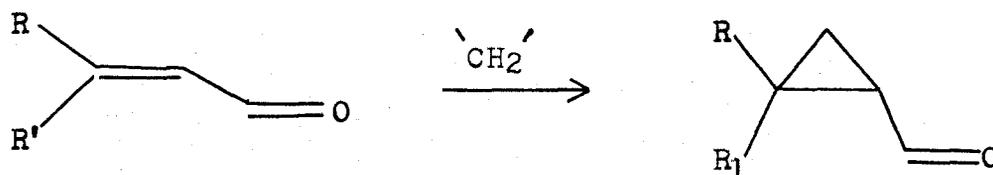
Bertelli<sup>85</sup> has recently challenged this view of the aromatic nature of tropone and has suggested on the basis of dipole moments in conjunction with CNDO/2 molecular orbital calculations, that it can be best represented as a conjugated dienone. Analysis of the nmr coupling constants of tropone also support a non-delocalized structure<sup>85</sup>.

Buchanan<sup>86</sup> has examined the properties and reactions of 2,3-benzotropone 113 and concluded that there is little evidence of aromatic character in the seven membered ring.

The properties of 4,5-benzotropone 110 would be expected to be similar to 113.



A search of the literature reveals that there are several methods available for the cyclopropanation of olefinic bonds<sup>87</sup>. More directly related to this particular synthetic problem, is the cyclopropanation of the carbon-carbon double bond in an  $\alpha\beta$ -unsaturated ketone.



#### Addition of Methylene Using Diazo Compounds

Diazo compounds ( $RR'C = N_2$ ) constitute one of the principal class of carbene precursors and the parent compound diazomethane has been extensively employed to cyclopropanate a variety of olefinic bonds<sup>88</sup>.

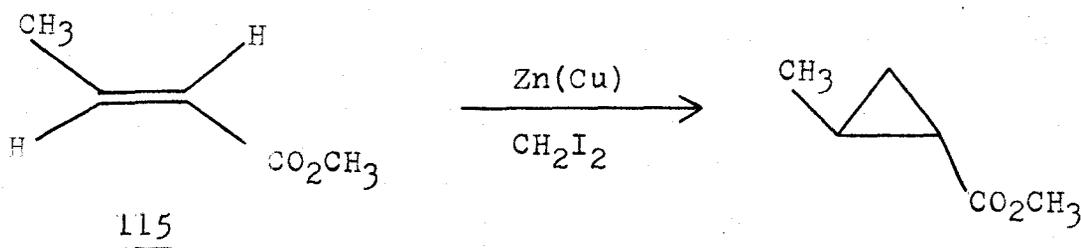
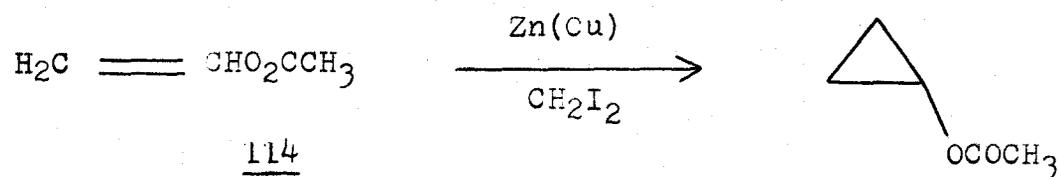
If the methylene is generated photochemically an extremely reactive carbene results, which reacts to give not only cyclopropanes, but in addition, C-H insertion products. With  $\alpha\beta$ -unsaturated ketones formation of epoxides has been reported<sup>87</sup>. Alternatively diazomethane in ether reacts with

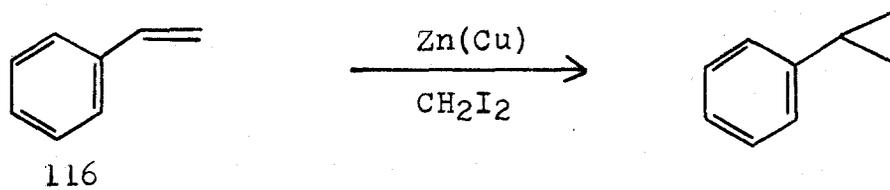
$\alpha\beta$ -unsaturated ketones at  $0^{\circ}\text{C}$ , to give predominantly cyclopropane products<sup>89</sup>.

The catalytic decomposition of diazo compounds with copper or copper salts<sup>90</sup> leads to carbene-copper complexes, which are less energetic than the free carbene. These complexes have been reported to add stereospecifically to carbon-carbon double bonds.

#### Simmons-Smith Reagent

The Simmons-Smith reaction<sup>91</sup> is considered to be one of the most versatile methods available for the formation of cyclopropanes from olefins. The intermediate iodomethyl zinc iodide complex reacts in a bimolecular process with the olefin in the methylene transfer step. From the evidence, it is clear that intermediate complex behaves as an electrophile towards the olefinic bond. Thus, vinyl acetate 114, methylcrotonate 115 and styrene 116 all react to give the corresponding cyclopropane products.





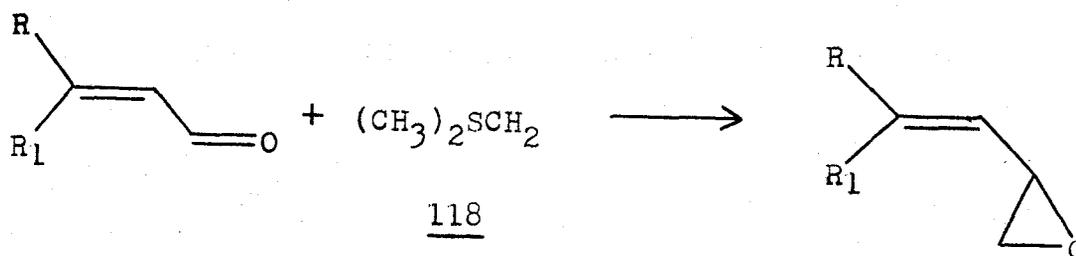
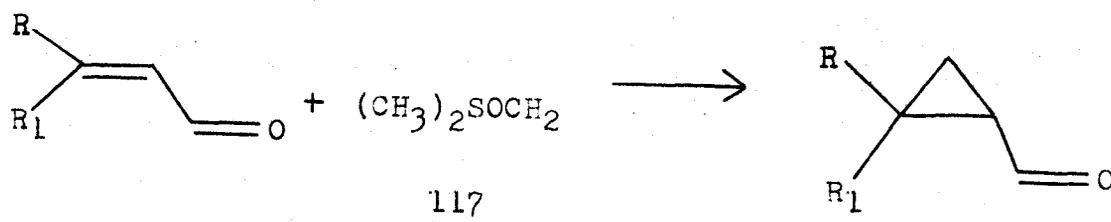
Numerous publications<sup>92</sup> have appeared that use the basic Simmons-Smith procedure, but many involve a variation in the preparation of the Zn(Cu) couple. The reproducibility of Zn(Cu) couple is undoubtedly one of the limiting factors in this synthetic procedure.

One of the more useful synthetic applications of the Simmons-Smith reagent is in the reaction with allylic and homoallylic alcohols<sup>93</sup>. The hydroxyl group not only imparts a rate-enhancing effect compared to simple olefins, but in addition accounts for the stereospecificity of the addition reaction.

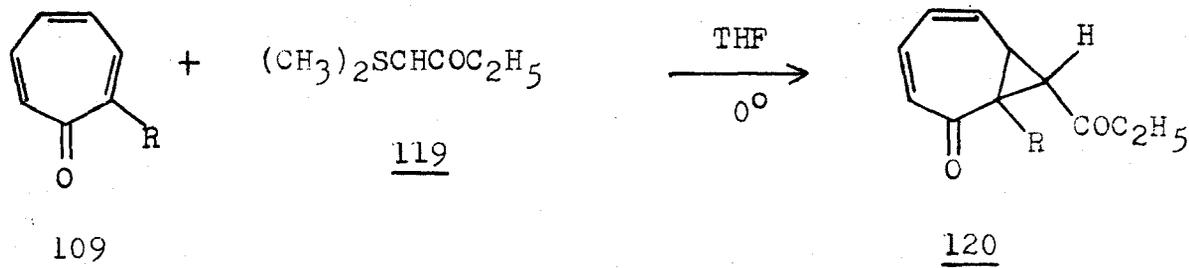
Dimethyloxosulfonium Methylide and Dimethylsulfonium Methylide as Methylene Transfer Agents

Corey and coworkers<sup>94</sup> have extensively investigated the chemistry of dimethyloxosulfonium methylide ((CH<sub>3</sub>)<sub>2</sub>SOCH<sub>2</sub>) 117 and dimethylsulfonium methylide ((CH<sub>3</sub>)<sub>2</sub>SCH<sub>2</sub>) 118 with particular emphasis on their synthetic utility. Both ylids are nucleophiles and both function to transfer methylene to certain electrophilic unsaturated linkages, including C=O, C=N, C=S and in certain cases C=C. Of particular interest is the reaction of these ylids with ketones and  $\alpha\beta$ -unsaturated ketones. The oxosulfonium ylid 117 interacts with the carbonyl function of aromatic ketones and nonconjugated aldehydes and ketones to form oxiranes and with  $\alpha\beta$ -unsaturated

ketones, which are Michael receptors to form cyclopropyl ketones. In contrast, the sulfonium ylid reacts with the same substrates, even  $\alpha$ -unsaturated carbonyl systems to give exclusively oxiranes.

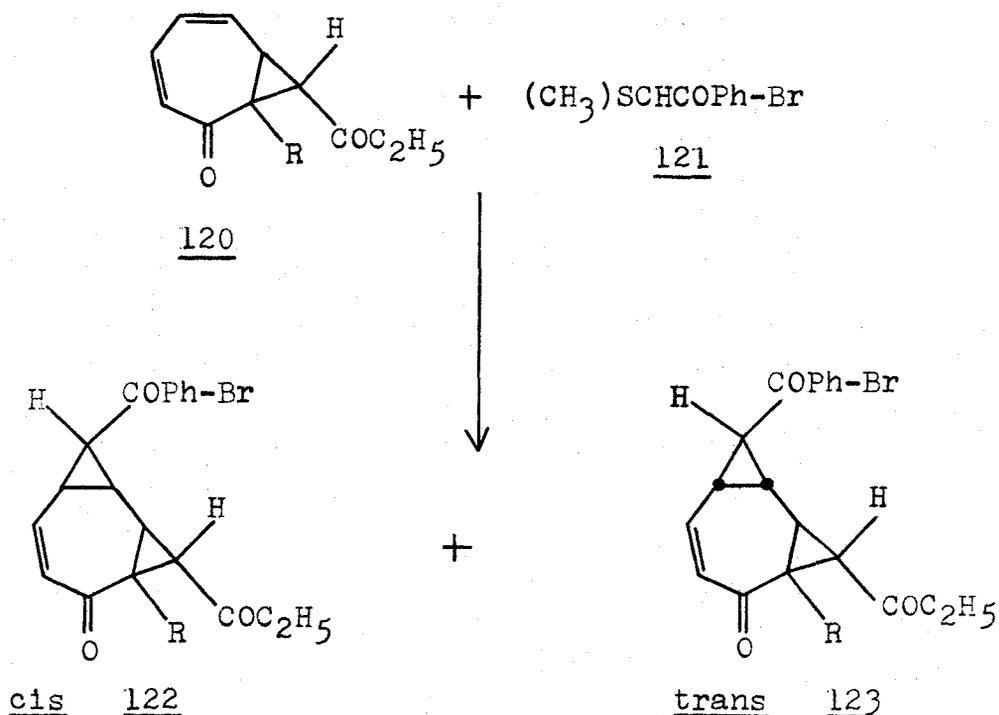


Sugimura<sup>95</sup> has synthesized several 2,3,-homotropone derivatives 120 by reacting substituted tropones with the ethoxycarbonyl ylid 119 in THF at low temperatures. However, addition to only one carbon-carbon double bond was



achieved. Reacting 120 with *p*-bromophenacyl ylid

121 in benzene at 80°C gave two isomers which were reported to be the cis- and trans-1,3-bishomotropone derivatives 122 and 123 respectively.

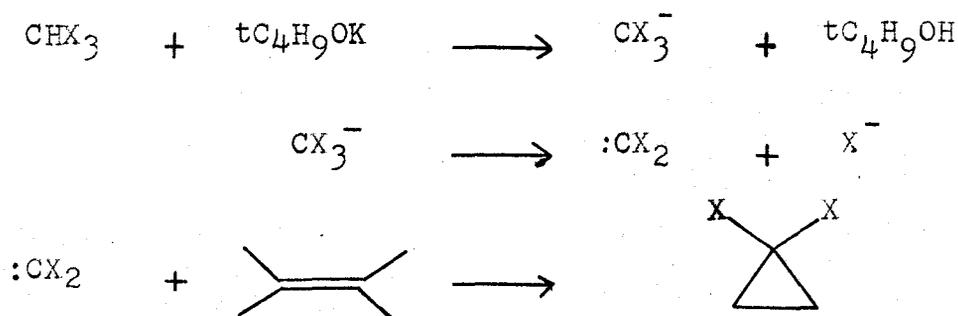


Although this reaction shows considerable potential for obtaining the cis- and trans-1,4-bishomobenzotropones 111 and 112, there still exists the problem of removing the ethoxycarbonyl and phenylacyl substituents in 122 and 123 respectively.

#### Generation and Addition of Dihalocarbenes to Olefinic Bonds

Several routes are available for generating dihalocarbenes and it is apparent that their reactivity towards olefinic substrates is at least partly dependent on the mode

and medium of generation<sup>87</sup>. Among these methods, the generation of dichlorocarbene by the action of aqueous alkali on chloroform in the presence of triethylbenzylammonium chloride has attracted considerable attention<sup>96</sup>. This method has been found superior to other methods in the synthesis of 1,1-dichlorocyclopropanes from less reactive olefins. In fact, several cationic micellar agents catalyze this reaction<sup>96b</sup>. The generation of dihalocarbenes from chloroform or bromoform however, is limited to substrates which are not susceptible to basic media.

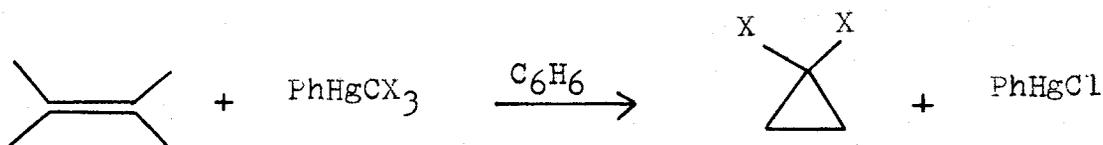


The preparation of gem-dihalocyclopropanes by the thermal decomposition of alkali metal trihaloacetates<sup>97</sup> avoids the basic reaction conditions. With weakly nucleophilic olefins **however**, a reaction between the carbene and trihaloacetate ion serves to intercept much of the carbene resulting in low product yields.

A further route to gem-dichlorocyclopropanes is one based on prior formation of trichloromethyl lithium,  $\text{LiCCl}_3$ , at low temperature<sup>98</sup>. It has been claimed that this reagent reacts directly and rapidly with olefins to give gem-dichloro-

cyclopropanes, but allenes are frequently produced as well.

Over the last decade Seyferth<sup>99</sup> has reported the synthesis of a variety of phenyl(trihalomethyl)-mercury compounds which have proven to be useful dihalocarbene transfer agents. Their utility lies in the fact that base-sensitive and/or weakly nucleophilic olefins can be readily converted to dihalocyclopropanes.



The addition of dichloro and dibromo carbene to a variety of olefinic substrates has been reported to proceed in high yield<sup>99</sup>. The subsequent removal of the halogens by tri-n-butyl tin hydride<sup>100</sup> or potassium/t-butanol/tetrahydrofuran<sup>101</sup>, K/tBuOH/THF is readily accomplished.

## SYNTHESIS

### (a) Preliminary Experiments

The direct methylation of 4,5-benzotropone 110 using diazomethane in ether resulted in no cyclopropane products being produced. The original ketone 110 was recovered in quantitative yield.

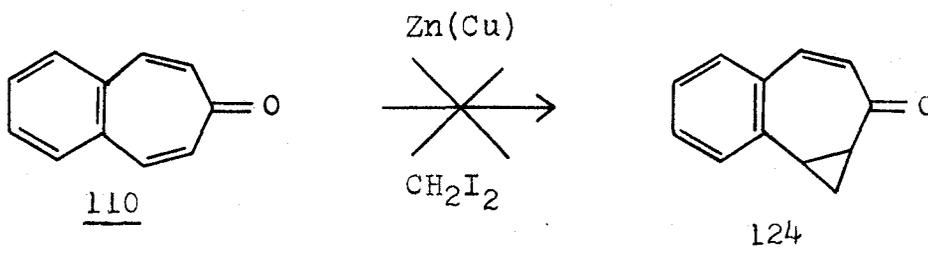
The reaction of phenyl (trichloromethyl) mercury with 110 in refluxing benzene resulted in extensive decomposition.

The reaction mixture showed the presence of the original ketone 110 and small amounts of unidentified product. The unidentified product did not have a carbonyl function as was indicated by its ir spectrum.

The Simmons-Smith reagent did not react with ketone 110, even though a variety of methods were used to generate the Zn(Cu) couple.

These preliminary investigations clearly suggest that the olefinic bonds in 110 are not readily susceptible to electrophilic attack by carbene or carbene-complex species. This is undoubtedly due to the extensive delocalization of the  $\pi$  electrons, and consequently 110 will have to be synthetically modified to decrease the extent of delocalization. Protecting the carbonyl function is a plausible approach to this problem.

Reduction of the ketone 110 by  $\text{NaBH}_4$  and reaction of the resultant alcohol with the Simmons-Smith reagent did not produce the expected cyclopropane product. Even the rate-enhancing effect of the hydroxy function<sup>93</sup> was not sufficient to cause methylation of the olefinic bond(s).

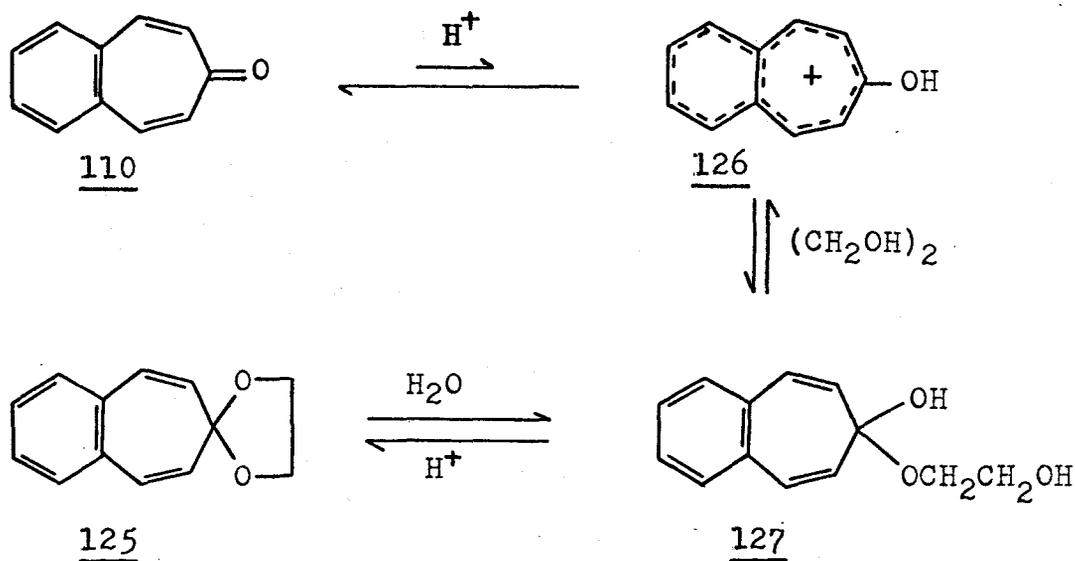


At this point, the primary objective of this work was directed towards the synthesis of the ethylene ketal of 4,5-benzotropone 110

(b) Preparation of 4,5-Benzotropone Ethylene Ketal

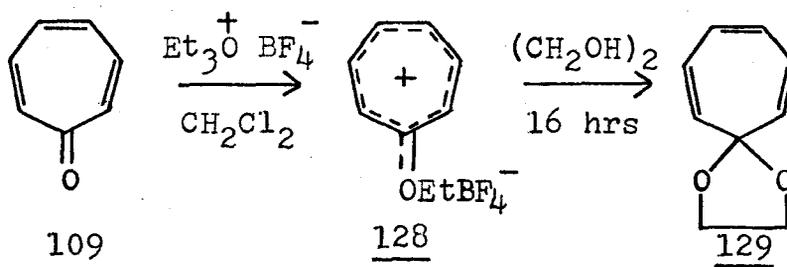
As is evident in the literature pertaining to the preparation of steroidal cyclic ketals<sup>102</sup>,  $\alpha\beta$ -unsaturated ketones do not ketalize as readily as simple ketones. More often than not low yields are reported and double bond isomerization occurs readily. Examination of the experimental procedures revealed inexact instructions in specifying the amount of *p*-toluenesulfonic acid monohydrate catalyst required to perform the reaction. The amount specified varies from "a trace"<sup>103</sup>, "a crystal"<sup>104</sup> to "a few crystals"<sup>105</sup>, frequently resulting in non-reproducible reactions. A recent article points out that 1% acid catalyst was required to obtain unrearranged ketal from 4-cholestene-3-one<sup>102a</sup>.

The reaction of 4,5-benzotropone 110 with ethylene glycol in refluxing benzene using a Dean-Stark water take off method resulted in approximately 10-15% of the ethylene ketal 125 in the final mixture. Even if the equilibrium concentration of the hydroxy cation 126 is small one would predict the collapse of this cation with ethylene glycol to be rapid, resulting in the formation of the hemiketal 127. From the equilibria in the reaction sequence 110  $\rightarrow$  125, one would predict that removal of the water would drive the reaction

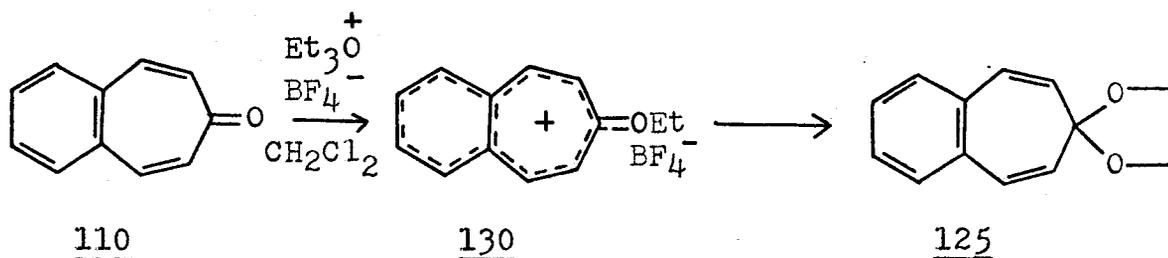


in favour of 125. Any water present in the refluxing medium, however, would drive the reaction back to the starting ketone 110. Under the reaction conditions it is probable that all the water was not removed, consequently 126 was not formed in significant amounts.

Simmons<sup>106</sup> has reported the synthesis of tropone ethylene ketal 129 by quenching the ethoxytropylium fluoroborate salt 128 in ethylene glycol.



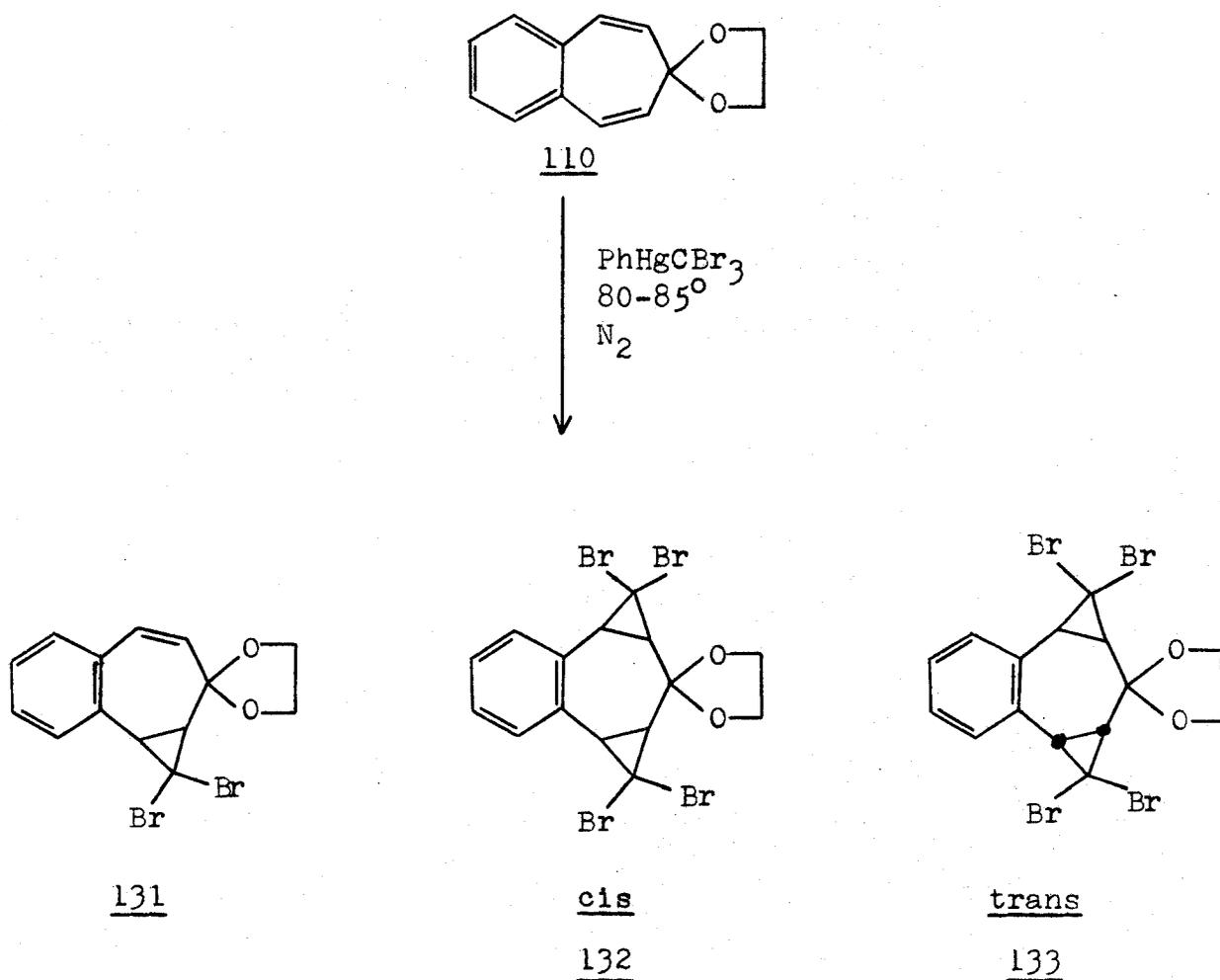
A solution of 4,5-benzotropone in  $\text{CH}_2\text{Cl}_2$  was reacted with triethyloxonium fluoroborate resulting in the formation of the corresponding 1-ethoxy-4,5-benzotropylium fluoroborate salt 130, which could be readily isolated. The salt was quenched in sodium ethylene glycolate/ethylene glycol to give the 4,5-benzotropone ethylene ketal 125 in quantitative yield. The ketal was purified by column chromatography using basic alumina.



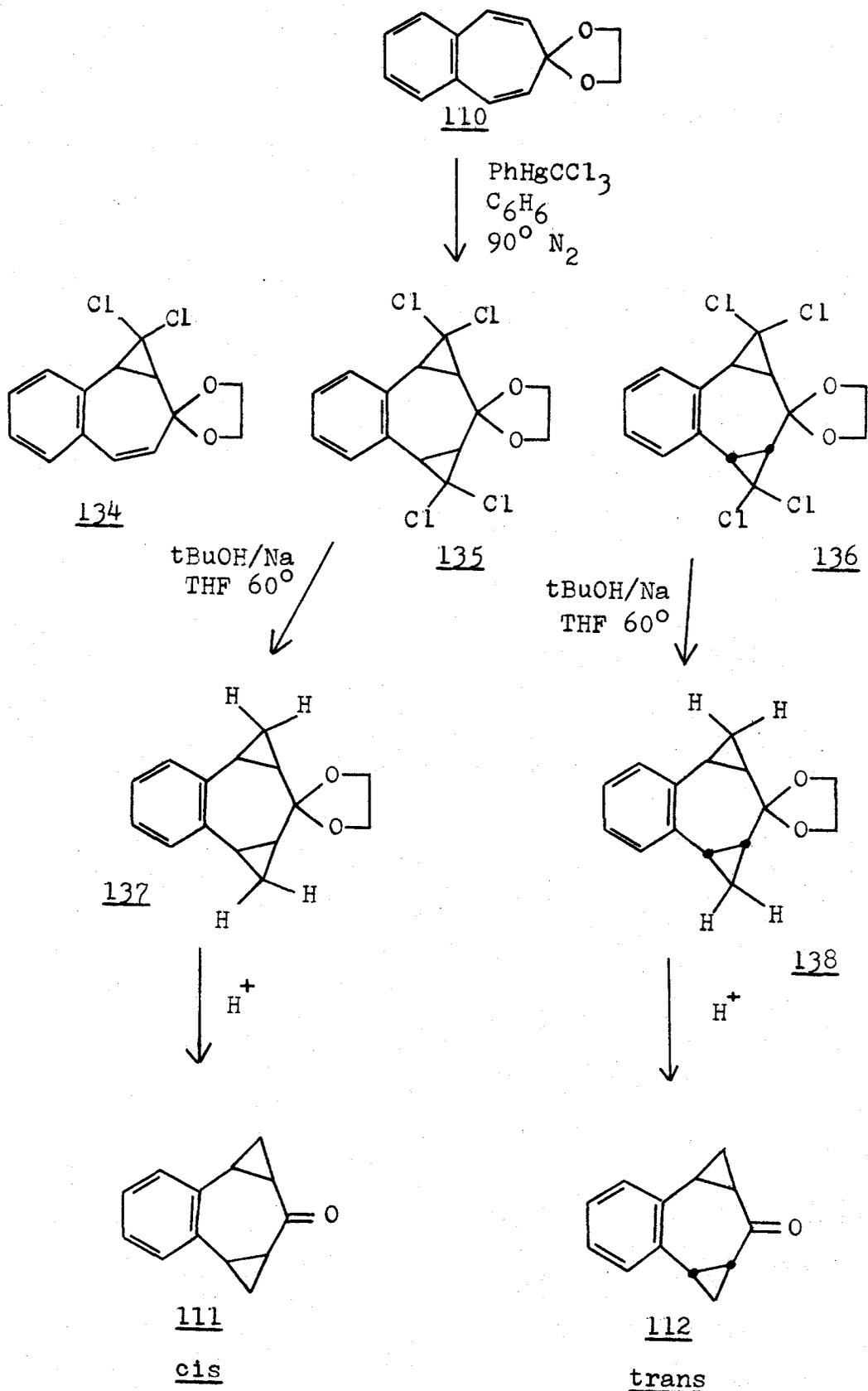
(c) Dihalocarbene Addition to the Ethylene Ketal of 4,5-Benzotropone

A two-fold excess of  $\text{PhHgCBr}_3$  in benzene, was heated in the presence of 125 to give three dibromo adducts. These were separated by column chromatography using basic alumina. They were fully characterized by examining their nmr spectra and shown to be the mono-dibromo adduct 131 and the two bis-dibromo adducts 132 and 133 respectively. Since the mono-dibromo adduct 131 was

the predominant product in the reaction mixture, the  $\text{PhHgCBr}_3$  was increased to a four fold excess, but this modification did not increase the yields of 132 and 133 significantly. Alternatively, pure 131 was reacted with two-fold excess of  $\text{PhHgCBr}_3$  in refluxing benzene, but again the yield of 132 and 133 was small. In each case the reaction was accompanied by extensive decomposition.



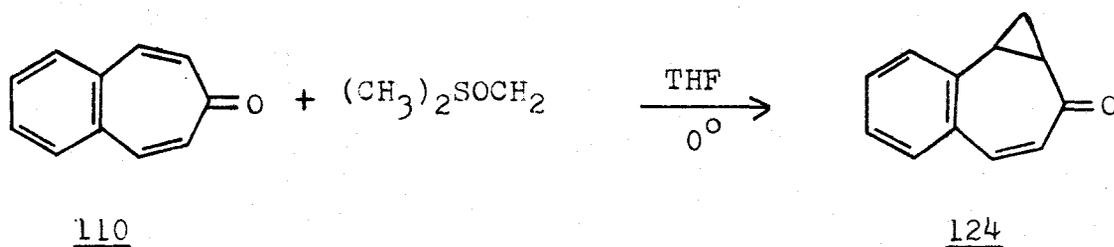
The use of the less reactive  $\text{PhHgCCl}_3$  reagent as a dichloro carbene precursor resulted in increased yields of the bis dichloro adducts 135 and 136 as well as the mono dichloro adduct 134. With a four-fold excess of  $\text{PhHgCCl}_3$  and reacting this with 110 in benzene at  $90-100^\circ$  for several days gave predominantly the two bis-dichloro adducts 135 and 136. Removal of the halogens from the two bis adducts 135 and 136 gave the corresponding ethylene ketals 137 and 138 respectively. The ketals were fully characterized by their spectral and analytical data and will subsequently be shown to have the stereochemistry indicated. Acid hydrolysis of 137 and 138 gave the corresponding cis and trans 4,5-benzo-2,3:6,7-bishomotropones 111 and 112 respectively. The relative stereochemistry of 111 and 112 was unambiguously assigned by examining the nmr spectra of the derived alcohols. (page 87)



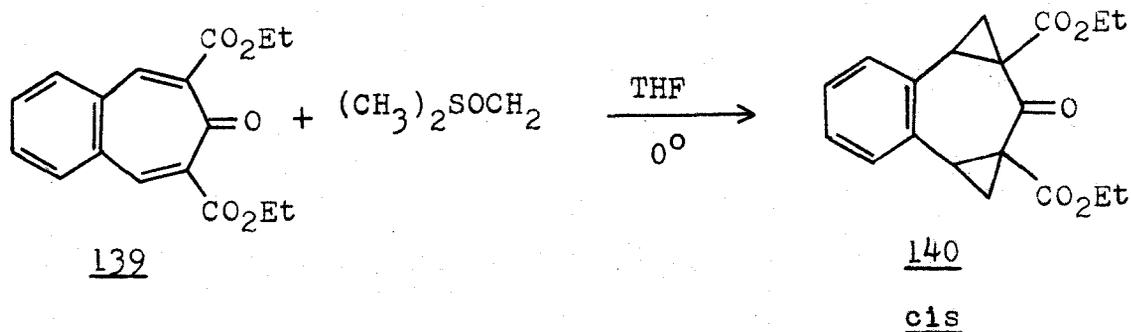
(d) Reaction of Dimethyloxosulfonium Methylide with 4,5-Benzotropone

Although the *cis* and *trans* isomers 111 and 112 could be synthesized via dichloro carbene addition, yields of the *cis* isomer 111 were very low. This is not surprising, since the addition of dichloro carbene to 125 to give the *cis* isomer 135 imposes severe steric interaction between the two inside chlorine atoms. Consequently, an alternative method to synthesize 111 was examined.

Sugimura<sup>59</sup> reported that the reaction of 4,5-benzotropone 110 and dimethyloxosulfonium methylide 117 in tetrahydrofuran, THF at 0° gave the 4,5-benzo-2,3-homotropone 124 in high yield. No 4,5-benzo-2,3:6,7-bishomotropones were obtained by this procedure. However, the reaction of 2,7-diethoxycarbonyl-

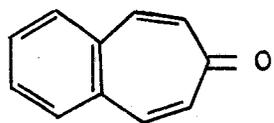


4,5-benzotropone 139 under analogous reaction conditions, resulting in the formation of exclusively *cis*-2,7-diethoxy-4,5-benzo-2,3:6,7-bishomotropone. Clearly, the activating effect of the carboethoxy groups was sufficient to cause cyclopropylation



of the second olefinic bond. Although potentially useful, removal of the carboethoxy groups under conditions that will not destroy the cyclopropane rings is a difficult task.

To increase the reactivity of 117 it was prepared in DMSO and subsequently reacted with 4,5-benzotropone 110. At room temperature for 24 hours this gave only the mono isomer 124. A two-fold excess of 117 in DMSO reacted with 110 at  $50^\circ$  gave the mono isomer 124, and another product which was subsequently identified to be the cis 4,5-benzo-2,3:6,7-bishomotropone 111. Although 111 was produced in relatively small yields it could be easily separated from 124 by column chromatography using neutral alumina. Since this synthetic procedure is more direct than the previous method discussed, it represents the more practical pathway for obtaining 111. However, the dichloro carbene pathway must still be used to obtain the trans isomer 112.



110

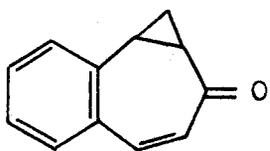
+

$(\text{CH}_3)_2\text{SOCH}_2$   
(2-fold excess)



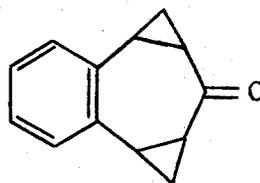
Dimethylsulfoxide  
(DMSO)

50°



124

+



111

SECTION TWONMR SPECTRA OF CIS- AND TRANS-4,5-BENZO-2,3:6,7-BISHOMOTROPONES

With respect to the seven membered ring, the two ketones 111 and 112 appear to be conformationally mobile structures, capable of interconversion between two boat conformations. In the cis isomer 111 the two boat conformations are not equivalent since interconversion of these two conformers interchanges the spatial relationship of the two inside methylene hydrogens. The boat conformation that places the two cyclopropyl rings in a pseudo axial position 111a will result in a severe steric interaction between the inside methylene hydrogens. Alternatively, the boat conformation which places the two cyclopropyl rings in a pseudo equatorial position 111e will result in no steric interaction between the two inside methylene hydrogens.

In the trans ketone, the two boat conformations are equivalent, with one cyclopropyl ring in a pseudo axial position and the other cyclopropyl ring in a pseudo equatorial position. Consequently, no non-bonded interactions between the inside methylene hydrogens are present.

The nmr spectra of 111 and 112 (spectra 1 and 4 respectively) both exhibit highly symmetrical patterns for the cyclopropyl resonances. In the case of the cis ketone 111 this can be interpreted on the basis of either boat conformation but it is clear the conformation 111e will be preferred.

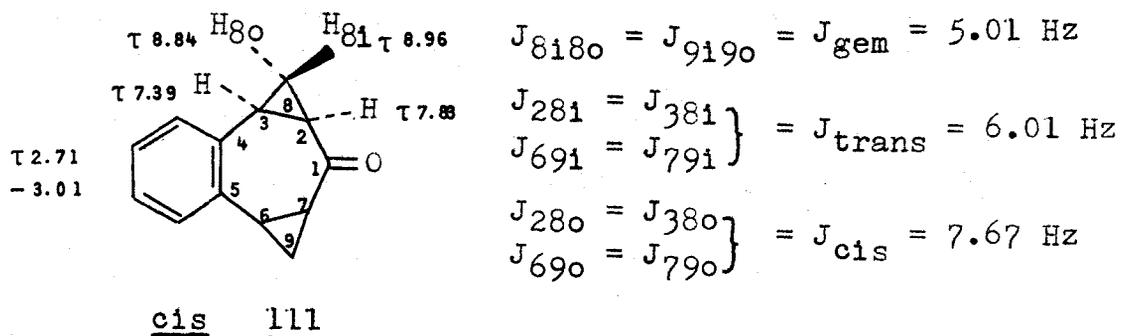
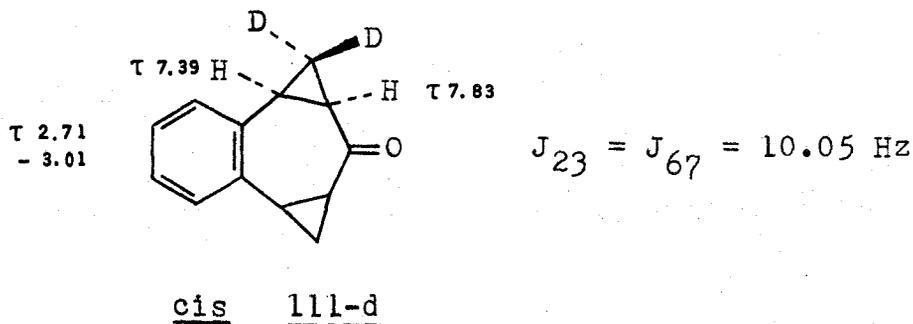
The symmetry exhibited by the trans ketone 112 can be interpreted on the basis of either a planar structure or a rapidly inverting non-planar structure. Anet<sup>107</sup> has shown that the activation energy for the inversion process in 1,3,5-cycloheptatriene is 6.3 kcal mole<sup>-1</sup>. It is thus reasonable to assume that the trans ketone 112 is also a rapidly interconverting non-planar structure at room temperature.

The 100 MHz nmr spectrum of cis-4,5-benzo-2,3:6,7-bishomotropone 111 (spectrum 1) in CCl<sub>4</sub> exhibits multiplets at  $\tau$  2.86(4), 7.39(2), 7.83(2) and 8.90(4). By utilizing deuterated dimethyloxosulfonium methylyde and reacting this with 110 in DMSO d<sub>6</sub> the ketone 111-d is obtained in which the C<sub>8</sub> and C<sub>9</sub> methylene protons have been replaced by deuterium. The 100 MHz spectrum of 111-d in CCl<sub>4</sub> showed no absorption at  $\tau$  8.93, and the absorptions previously at  $\tau$  7.39 and  $\tau$  7.85 now appear as part of an AB multiplet (J=10.05 Hz). Since the seven membered ring in 111 adopts a shallow boat conformation, H<sub>3</sub> and H<sub>6</sub> will be placed in the deshielding zone of the benzene ring and thus are assigned as indicated.

Under higher resolution (220 MHz) (spectrum 3) the resonance at  $\tau$  8.90 was resolved into two distinct resonances from which the chemical shifts and coupling constants were obtained. These data used in conjunction with a simulated spectrum (spectrum 2) generated using a LAOCN III nmr program<sup>108</sup> resulted in the complete analysis of the nmr spectrum.

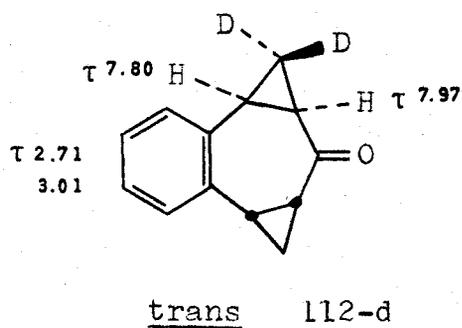
For normal cyclopropane rings it is well documented that  $J_{cis} > J_{trans}$ ,<sup>29,37</sup> and consequently H<sub>81</sub> (H<sub>91</sub>) and

$H_{80}$  ( $H_{90}$ ) were unambiguously assigned as indicated.

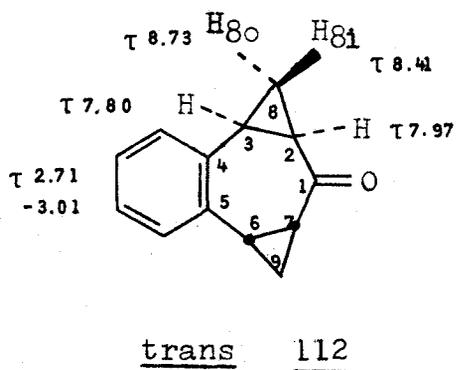


The 100 MHz spectrum of trans-4,5-benzo-2,3:6,7-bis-homotropone 112 in  $CCl_4$  (spectrum 4) exhibits multiplets at  $\tau$  2.86(4), 7.89(4), 8.41(2) and 8.73(2). As already discussed the symmetry of the multiplets is accounted for on the basis of a rapidly inverting non-planar structure (page 84). By using t-BuOD in place of t-BuOH in the appropriate synthetic step,

it was shown that the methylene hydrogens resonated at  $\tau$  8.41 and  $\tau$  8.73. Coupling constants were obtained by generating a simulated spectrum (spectrum 5) using the LAOCN III nmr program. The "inside" and "outside" methylene proton signals were differentiated on the basis that  $J_{cis} > J_{trans}$  for normal cyclopropane rings.



$$J_{23} = J_{67} = 9.59 \text{ Hz}$$



$$J_{8081} = J_{9091} = J_{gem} = 4.92 \text{ Hz}$$

$$J_{281} = J_{381} = J_{trans} = 5.96 \text{ Hz}$$

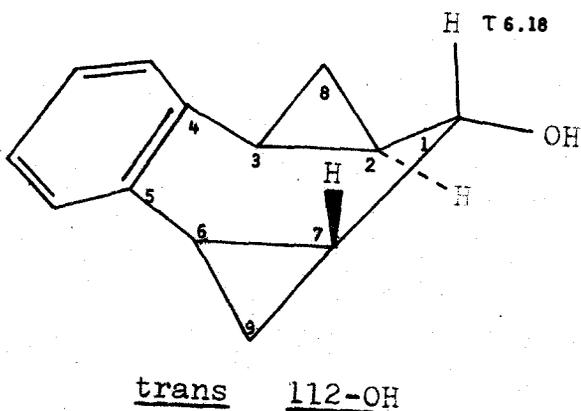
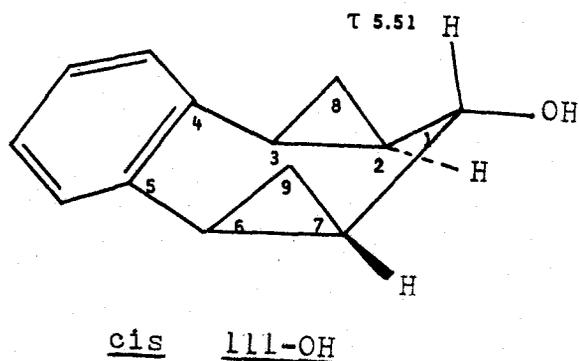
$$J_{691} = J_{791}$$

$$J_{280} = J_{380} = J_{cis} = 8.57 \text{ Hz}$$

$$J_{690} = J_{790}$$







$$J_{12} = J_{17} = 4.0 \text{ Hz}$$

$$J_{12} = 6.5 \text{ Hz}; \quad J_{17} = 1.0 \text{ Hz}$$

passing through the carbonyl carbon atom and bisecting the 4,5 carbon bond. Regardless which isomeric alcohol is obtained from the reduction of the cis ketone 111, the alcohol 111-OH with the stereochemistry indicated is the only one that can account for the observed symmetry in the nmr spectrum. Thus, it would appear that the ketone 111 has the two cyclopropyl rings cis with respect to each other and the ketone 112 has the two cyclopropyl rings trans with respect to each other.

More direct evidence regarding the relative stereochemistry of 111 and 112 was obtained by examining the multiplicity of the  $\alpha$ -hydrogen signals in their derived alcohols 111-OH and 112-OH respectively. The signal attributed to the  $\alpha$ -hydrogen in 111-OH was a symmetrical triplet ( $J=4.0\text{Hz}$ ) while the corresponding signal in 112-OH appeared as a doublet of doublets ( $J=6.5$  and  $1.0$  Hz). Only when the two cyclopropanes are cis with respect to each other are  $H_2$  and  $H_7$  equivalent. Thus, 111 must be the cis ketone and 112 the trans ketone.

SECTION THREEGENERATION AND OBSERVATION OF THE MONO- AND BIS-HOMOTROPYLIUM CATIONS

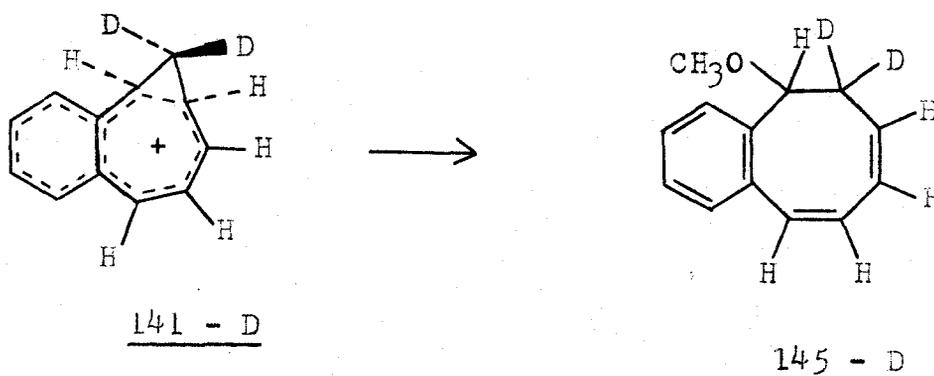
The question whether or not cis and trans geometries in suitable 6  $\pi$ -electron systems, such as 111 and 112, can exhibit bishomoaromaticity can be evaluated by examining the nmr spectra of the derived cations. As was discussed earlier in this thesis, (page 64) the benzene ring could impose a perturbation<sup>8</sup> which must be determined before any definite conclusions can be reached. To determine the effect of the benzene ring, if any, the 4,5-benzohomotropylium cation was generated and examined in detail.

(a) The 4,5-Benzo-2,3-Homotropylium Cation

Reduction of 4,5-benzo-2,3-homotropone 124 with  $\text{NaBH}_4$  gave the corresponding alcohol 124-OH. Although it is possible to obtain two isomeric alcohols in the reduction, only one isomer was present in the reaction mixture (>95%). The chemical shifts and coupling constants as shown, were obtained by suitable deuterium incorporation. Thus, the methylene proton signals were positively assigned by using deuterated trimethylsulfoxonium methyllide in the appropriate synthetic step and the  $\alpha$ -hydrogen signal was identified by carrying out the reduction using  $\text{LiAlD}_4$ .



Extraction of the 1-hydroxy-4,5-benzo-2,3-homotropone 124-OH from  $\text{CD}_2\text{Cl}_2$  into  $\text{FSO}_3\text{-SO}_2\text{ClF}$  (1:3v/v) at  $-80^\circ$  gave the corresponding cation 141. The cation was stable below  $-20^\circ$  and was quenched in  $\text{MeOH-NaOCH}_3$  at  $-78^\circ$  to give the methoxy ether 145 in quantitative yield. The methylene hydrogens and  $\alpha$ -hydrogen in 141 were identified by protonating the appropriately



deuterated precursor. The complete assignment of the chemical shifts and the evaluation of the coupling constants was made by generating the simulated spectrum using a LAOCN III nmr program (spectrum 10).

The nmr spectrum of the cation 141 ( spectrum 9) clearly indicates that the signals due to all the protons except one experience a downfield shift. One signal actually experiences a shielding of 2.75 ppm. These observations can only be inter-

preted in terms of a cyclic delocalised structure involving 6  $\pi$ -electrons. Thus, 141 can only be described as a monohomoaromatic system. The chemical shift difference  $\Delta = 5.34$  ppm between "inside" ( $H_{81}$ ) and "outside" ( $H_{80}$ ) signals is comparable to the value obtained in the homohomotropylium cation 21<sup>27,28</sup> ( $\Delta = 5.80$  ppm). Clearly, in this case the benzene ring is not significantly attenuating the homoaromaticity of 141<sup>58</sup>.

Examination of the coupling constants in 141 and comparing these to the corresponding coupling constants in the precursor alcohol 124-OH (spectrum 8) reveals several features regarding the electronic structure of 141.

Both  $J_{67}$  and  $J_{23}$  decrease significantly in value from their respective values in 124-OH. The value of  $J_{23} = 3.0$  Hz is comparable to the value of 1.0 Hz obtained for the homotropylium cation 21<sup>33</sup>. This decrease in  $J_{23}$  reflects the increased delocalization of the  $C_2-C_3$   $\sigma$  bond.

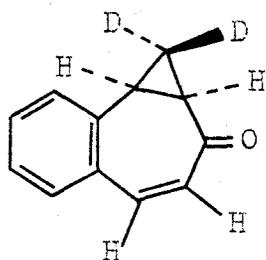
The geminal coupling constant ( $J_{8081}$ ) in 141 has increased to 5.5 Hz from 4.8 Hz in 124-OH. It is interesting that  $|J_{gem}|$  in 141 is smaller than the value obtained for the monohomotropylium cation 21 ( $|J_{gem}| = 6.5$  Hz)<sup>27,28</sup>. The value of  $|J_{gem}|$  is critically dependent on the dihedral angle ( $H_{80}-C-H_{81}$ ) and the amount of charge developed at  $C_8$ , but it is often difficult to separate these two contributing but opposing factors<sup>33</sup>. However, from the chemical shift of  $H_{81}$  it would appear that no significant amount of charge is delocalized at  $C_8$ . Thus, the small, but real increase in

$|J_{\text{gem}}|$  is consistent with  $C_2C_3$  bond lengthening in this homotropylium cation.

In an earlier section of this thesis (page 16) it was shown that homotropylium cations exhibit a trans coupling constant which is greater than the cis coupling constant. This pattern is reversed in "normal" cyclopropane rings<sup>29,37</sup>. In the cation 141 it is clear that  $J_{\text{trans}} > J_{\text{cis}}$ , but the two trans coupling constants are not equivalent ( $J_{381} = 11.5$  Hz;  $J_{281} = 7.5$  Hz). From the chemical shifts of  $H_2$  and  $H_3$  it is clear that  $C_3$  bears more positive charge than  $C_2$ , which results in a different hybridization at  $C_2$  and  $C_3$ . This in turn will effect the dihedral angles ( $\angle 281$ ,  $\angle 280$ ,  $\angle 381$  and  $\angle 380$ ) in the cyclopropyl ring. While dihedral angles cannot be precisely related to coupling constants<sup>109</sup> it is clear that the dihedral angle  $\angle 381$  must increase significantly from the "normal" value of  $144^\circ$ <sup>37</sup> towards  $180^\circ$ , while the dihedral angle  $\angle 281$  only increases by a small amount. The geometric changes associated with the hybridization changes at  $C_2$  and  $C_3$  will also be reflected in the cis coupling constants. For normal cyclopropanes the dihedral angles  $\angle 280$  and  $\angle 380$  are  $0^\circ$ <sup>109</sup> and any deviation from this value will decrease the value of the cis coupling constant. It is evident from the Karplus equation<sup>109</sup> that changes in dihedral angles in the range  $0-20^\circ$  do not change the value of the coupling constant by a significant value. Consequently, the cis coupling constant  $J_{280}$  and  $J_{380}$  in 141 only decrease by a small amount and any small difference that there may be between  $J_{280}$  and  $J_{380}$  is not readily observed.

(b) The 1-Hydroxy-4,5-Benzo-2,3-Homotropylum Cation

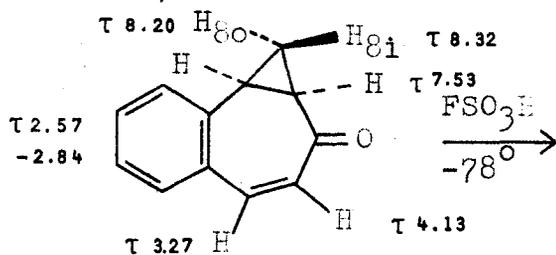
The nmr spectrum (spectrum 11) of 4,5-benzo-2,3-homotropone 124 in  $\text{CCl}_4$  could be completely assigned by suitable deuterium incorporation, and the coupling constants determined by generating a simulated spectrum (spectrum 12) using a LAOCN III nmr program. The chemical shifts and coupling constants in 124 compare closely with the nmr spectrum previously reported by Sugimura<sup>59</sup>.

124 - D

$$J_{23} = \text{not available} \\ \text{coincident}$$

$$J_{67} = 13.3 \text{ Hz}$$

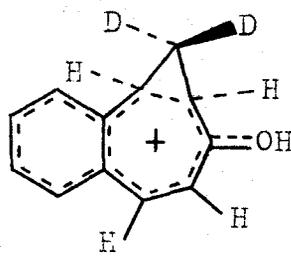
$$J_{27} = 1.0 \text{ Hz}$$



$$J_{\text{gem}} = J_{8081} = 4.37 \text{ Hz}$$

$$J_{\text{trans}} \begin{Bmatrix} J_{281} \\ J_{381} \end{Bmatrix} = 8.92 \text{ Hz}$$

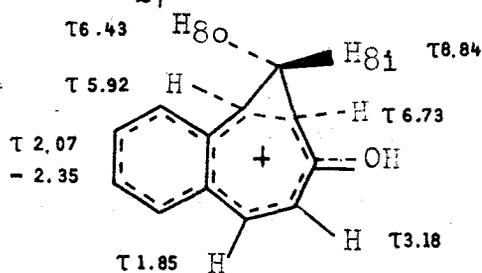
$$J_{\text{cis}} \begin{Bmatrix} J_{280} \\ J_{380} \end{Bmatrix} = 6.95 \text{ Hz}$$

124142 - D

$$J_{23} = 7.0 \text{ Hz}$$

$$J_{67} = 12.5 \text{ Hz}$$

$$J_{27} = 2.5 \text{ Hz}$$



$$J_{\text{gem}} = J_{8081} = 4.73 \text{ Hz}$$

$$J_{\text{trans}} \begin{Bmatrix} J_{281} \\ J_{381} \end{Bmatrix} = \begin{Bmatrix} 6.09 \text{ Hz} \\ 9.42 \text{ Hz} \end{Bmatrix}$$

$$J_{\text{cis}} \begin{Bmatrix} J_{280} \\ J_{380} \end{Bmatrix} = 8.52 \text{ Hz}$$

142

Extraction of 124 from  $\text{CD}_2\text{Cl}_2$  into  $\text{FSO}_3\text{H}$  at  $-60^\circ$  gave the corresponding hydroxy cation 142. The cation was stable below  $-20^\circ$  and could be quenched in  $\text{Et}_2\text{O}-\text{HCO}_3^-$  at  $-78^\circ$  to give the original ketone 124 in high yield. The protonated ketone 142 shows analogous shifts of the "inside" and "outside" protons, but the magnitude of the difference between these two is now much less,  $\Delta = 2.4$  ppm, reflecting the decreased homoaromaticity in 142 due to the presence of the hydroxy function. (Spectrum 13 and 14)

The value of  $\Delta$  in 142 is less than reported for the 2-hydroxyhomotropylium ion 39<sup>49</sup> ( $\Delta = 3.1$  ppm), 1-hydroxyhomotropylium ion 34<sup>47</sup> ( $\Delta = 3.4$  ppm) and significantly less than the value for the 4-hydroxyhomotropylium ion 41<sup>50</sup> ( $\Delta = 4.6$  ppm). It is evident that the position of the hydroxy substituent has a marked effect on the value of  $\Delta$ . However, the chemical shift difference,  $\Delta$ , observed in 142 is comparable to the value obtained for the 2-hydroxyhomotropylium ion 39 which is the only meaningful comparison.

Sugimura<sup>59</sup> has also reported the nmr spectrum of 142 in  $\text{D}_2\text{SO}_4$ . Comparing the data obtained with Sugimura's data reveals that the chemical shifts obtained in this work are uniformly shifted ca 0.6 ppm downfield. In addition, the authors report no coupling constants for the cation 142.

The coupling constant pattern for the cation 142 shows comparable trends to those in the cation 141. Thus, the cis coupling constants ( $J_{280}$ ,  $J_{380}$ ) decrease from their original value in the ketone 124, but the changes exhibited by the trans

coupling constants ( $J_{281}$ ,  $J_{381}$ ) upon protonation are more complex than in 141. Whereas in 141 both trans coupling constants increase, although by different amounts, in 142  $J_{381}$  increases significantly (6.95 Hz to 9.42 Hz), while  $J_{281}$  decreases slightly (6.95 Hz to 6.09 Hz). The increase in the value of  $J_{381}$  is consistent with the arguments advanced for the cation 141, but the small decrease in the value of  $J_{281}$  is difficult to rationalize. It is clear, however, that the dihedral angle  $\angle 281$  does not increase and in fact could possibly decrease due to the presence of the hydroxy substituent.

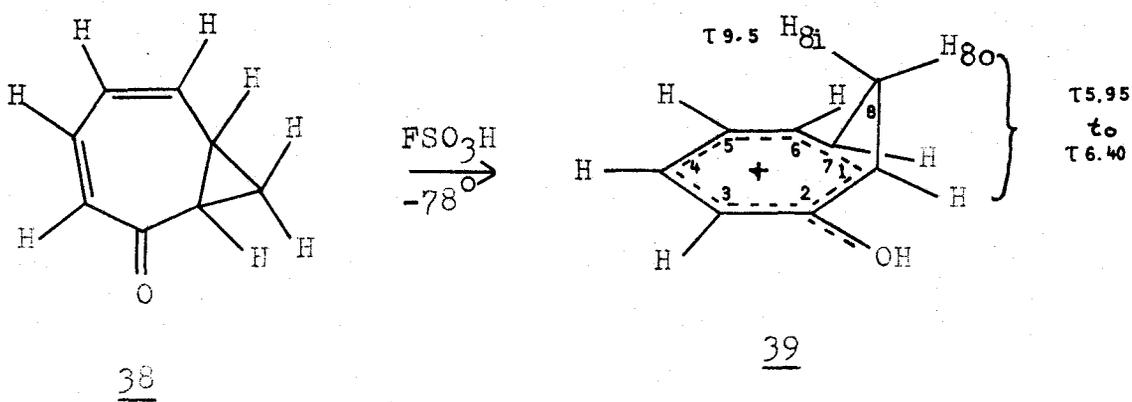
The most significant feature is the small increase in the geminal coupling constant (4.37 Hz to 4.73 Hz) which can be attributed to an increased length of the  $C_2C_3$  bond. This increase however, is significantly different from the value reported for the 1-hydroxyhomotropylum cation <sup>47</sup> 34 ( $|J_{gem}| = 10.8$  Hz). A more meaningful comparison would be to compare the geminal coupling constant in 142 with the value in the 2-hydroxyhomotropylum cation 39, but Pettit's <sup>49</sup> communication dealing with the nmr spectrum of 39 does not include a detailed analysis. To determine if the position of the hydroxy function has any effect on the geminal coupling constant in such systems, 2,3-homotropone was synthesized by Houk's <sup>110</sup> procedure and subsequently protonated.

(c) 220 MHz Nmr Spectrum of the 2-Hydroxyhomotropylum Cation

Extraction of 38 from  $CD_2Cl_2$  into  $FSO_3H$  at  $-78^\circ$  gave cleanly the 2-hydroxyhomotropylum cation 39. The cation

was stable at the temperature of the nmr probe ( $+37^{\circ}$ ) and was quenched in  $\text{Et}_2\text{O}-\text{HCO}_3^-$  to give the original ketone 38.

A complete analysis of the nmr spectrum (Spectrum 15) was not possible because of the complex pattern due to the overlapping multiplets attributed to  $\text{H}_{1,}$   $\text{H}_7$  and  $\text{H}_{80}$ . Decoupling experiments however, indicated that the value of  $|J_{\text{gem}}|$  is in the range of 5.0 - 6.0 Hz. This value is comparable to the value obtained for 142 and is significantly less than the value for the 1-hydroxyhomotropylium cation 34. Clearly, the position of the hydroxy substituent has a marked influence on the geminal coupling constant in homotropylium systems.



$$J_{8081} = \text{ca } 5.0 - 6.0 \text{ Hz}$$

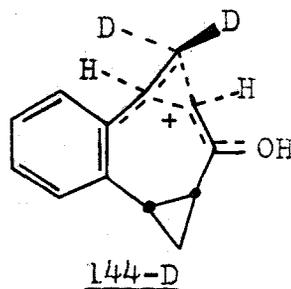
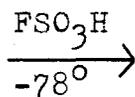
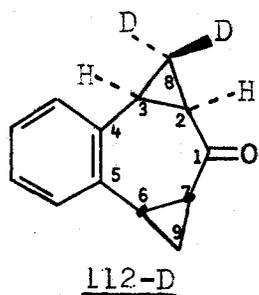
(d) Protonated Cis- and Trans-4,5-Benzo-2,3:6,7-Bis-Homotropones

Extraction of 111 and 112 from  $CD_2Cl_2$  into  $FSO_3H$  at  $-78^\circ$  gave cleanly the corresponding hydroxy cations 143 and 144 respectively. (Spectrum 16 and 18). The acid solutions of 143 and 144 were stable below  $-20^\circ$  and were quenched in  $Et_2O-HCO_3^-$  at  $-78^\circ$  to give recovered 111 and 112, respectively, in high yield.

The methylene protons in 143 and 144 were identified by protonating the deuterated compounds 111-D and 112-D respectively. In both systems the coupling constants were evaluated by obtaining simulated spectra (Spectrum 17 and 19 respectively) using a LAOCN III nmr program.

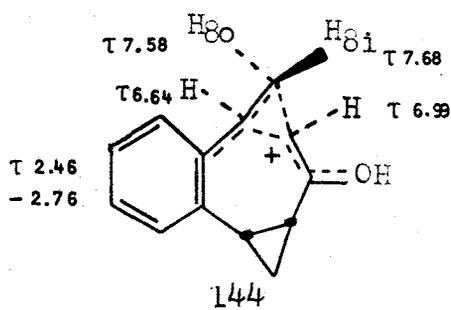
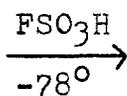
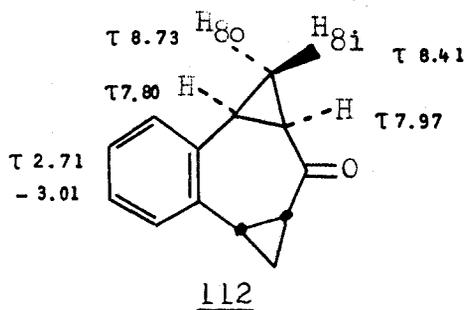
The deshielding of all the proton resonances of 112 upon protonation is indicative of substantial charge delocalization in the trans cation 144. While the symmetry displayed by the cyclopropyl resonances is compatible with a planar structure there is virtually no difference in the chemical shifts of the "inside" and "outside" methylene protons ( $\Delta = 0.1$  ppm). Using the difference in chemical shift of these protons as a criterion of homoaromaticity it must therefore be concluded that 144 is not bishomoaromatic.

Symmetrical cyclic delocalization in 144 can only occur when the seven-membered ring is planar. In such a conformation the internal cyclopropyl bonds are not in the most favourable orientation for overlap with the electron deficient centre at  $C_1$ . Deviation from a planar structure results in the formation of one of two equivalent boat con-



$$J_{23} = J_{67} = 9.59 \text{ Hz}$$

$$J_{23} = J_{67} = 8.99 \text{ Hz}$$



$$J_{\text{gem}} = J_{8o8i} = 4.92 \text{ Hz}$$

$$J_{\text{gem}} = J_{8o8i} = 5.78 \text{ Hz}$$

$$J_{\text{trans}} \begin{cases} J_{28i} \\ J_{38i} \end{cases} = 5.96 \text{ Hz}$$

$$J_{\text{trans}} \begin{cases} J_{28i} = 7.22 \text{ Hz} \\ J_{38i} = 9.18 \text{ Hz} \end{cases}$$

$$J_{\text{cis}} \begin{cases} J_{28o} \\ J_{38o} \end{cases} = 8.57 \text{ Hz}$$

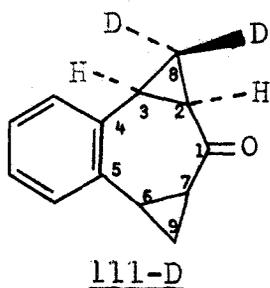
$$J_{\text{cis}} \begin{cases} J_{28o} \\ J_{38o} \end{cases} = 7.66 \text{ Hz}$$

TRANS SYSTEM

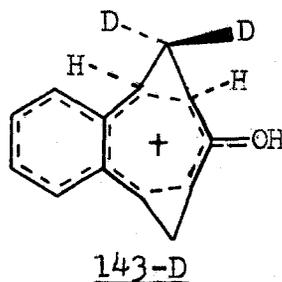
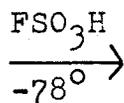
formations in which one cyclopropyl adopts the highly preferred bisected conformation<sup>36</sup> and the other is perpendicular to the  $\pi$  system. It would seem that the spectrum of 144 can best be described in terms of a rapid interconversion of these two boat conformations.

The cis cation 143 also exhibits a nmr spectrum that is symmetrical and which is indicative of substantial charge delocalization. It differs from the nmr spectrum of 144 in that there is a difference between the "inside" and "outside" methylene proton signals of 0.7 ppm. In 143 the bisected conformation of the cyclopropyls with respect to  $C_1$ , the geometry demanded for effective delocalization, is only realized when the seven membered ring becomes a shallow boat with the cyclopropanes in pseudo-axial positions. Such a geometry can only be attained at the expense of a severe steric interaction between the two "inside" protons, and the gain in cyclic delocalization must be mitigated against this increased steric compression. The close proximity of the two "inside" protons ( $H_{81}$ ,  $H_{91}$ ) will result in each being deshielded and for similar systems the magnitude of the van der Waal's deshielding<sup>111</sup> has been estimated at ca 1.5 ppm. Thus a better estimate of the difference between the "inside" and "outside" protons would be  $0.7 + 1.5 = 2.2$  ppm which is comparable to that shown for 142 and would strongly suggest a bishomoaromatic type delocalization in 143.

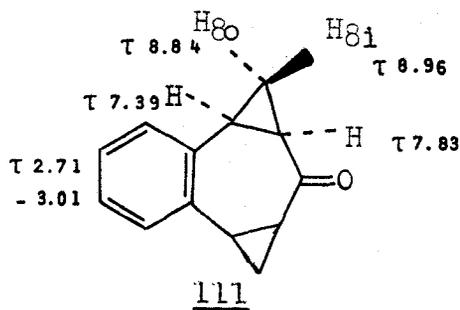
The assignment of "inside" and "outside" methylene proton resonances in 143 and 144 is based on an analysis of the coupling constant pattern, and comparing the pattern with that obtained for



$$J_{23} = J_{67} = 10.05 \text{ Hz}$$



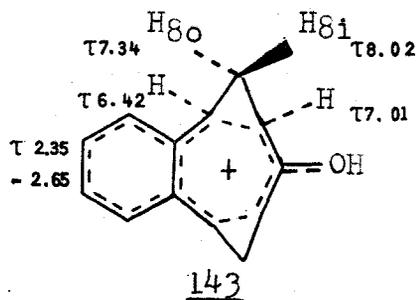
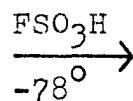
$$J_{23} = J_{67} = 8.34 \text{ Hz}$$



$$J_{\text{gem}} = J_{8081} = 5.01 \text{ Hz}$$

$$J_{\text{trans}} \begin{Bmatrix} J_{281} \\ J_{381} \end{Bmatrix} = 6.01 \text{ Hz}$$

$$J_{\text{cis}} \begin{Bmatrix} J_{280} \\ J_{380} \end{Bmatrix} = 7.65 \text{ Hz}$$



$$J_{\text{gem}} = J_{8081} = 6.34 \text{ Hz}$$

$$J_{\text{trans}} \begin{Bmatrix} J_{281} = 6.16 \text{ Hz} \\ J_{381} = 8.59 \text{ Hz} \end{Bmatrix}$$

$$J_{\text{cis}} \begin{Bmatrix} J_{280} \\ J_{380} \end{Bmatrix} = 8.31 \text{ Hz}$$

CIS SYSTEM

the 4,5-benzo-2,3-homotropylium cation 141 and 1-hydroxy-4,5-benzo-2,3-homotropylium cation 142. For the cations 141 and 142 the following general trends were observed :

1. The geminal coupling constant only increases by 0.7 to 1.0 Hz.
2. The two trans coupling constants do not change to the same extent, thus  $J_{381}$  increases by ca 4.0 Hz while  $J_{281}$  is almost invariant.
3. Both cis coupling constants decrease by the same amount but the decrease is small, ca 0.5 Hz.

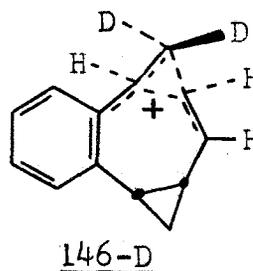
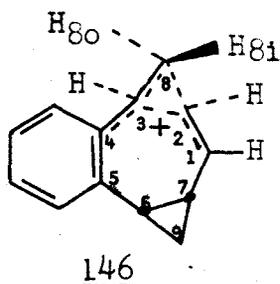
These observations are primarily associated with the increased delocalization of the  $C_2C_3$  carbon bond and resultant hybridization change at  $C_2$  and  $C_3$ . In both the cations 143 and 144 the  $C_2C_3$  and  $C_6C_7$  carbon bond lengths increase, consequently the coupling constant pattern exhibited by 143 and 144 should show these general trends. However, in the cis cation 144 the cis coupling constants increase from their original value in 143. Although the reason for this increase is not obvious, the general conclusions regarding the assignment of "inside" and "outside" methylene protons are valid. Therefore, it is not possible to reconcile the conclusions obtained with a reversed assignment of the methylene hydrogens.

(e) Protonation of Cis- and Trans Alcohols 111-OH and 112-OH.

Extraction of a solution of the trans alcohol 112-OH in  $CD_2Cl_2$  into  $FSO_3H-SO_2ClF$  (1:3 v/v) at  $-125^\circ$  resulted in the formation of the carbonium ion 146. The nmr spectrum (spectrum 20) of 146 was recorded at  $-75^\circ$ , since above this temperature rapid decomposition was evident. Repeated attempts to quench the acid solution in  $MeOH-NaOCH_3$  at  $-78^\circ$  were unsuccessful.

From the nmr data in Table VII it is clear that considerable charge has been delocalized into the benzene ring. Furthermore, the nonsymmetrical pattern exhibited by the cyclopropyl resonances clearly indicate that the seven-membered ring is non-planar and consequently the seven-membered ring must adopt a shallow boat conformation. Molecular models reveal that in a boat conformation, one cyclopropyl ring is in a quasi-equatorial position and the other cyclopropyl ring in a quasi-axial position. Only the cyclopropyl ring in the quasi-axial position is in the bisected conformation with respect to the  $\pi$ -system and therefore suitably aligned for delocalization<sup>36</sup>. The other cyclopropyl ring is in the perpendicular conformation with respect to the  $\pi$ -system and is thus inductively electron withdrawing<sup>36</sup>.

That this is indeed the case, is supported by examination of the coupling constants. While a complete analysis

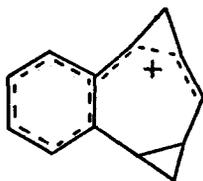


Proton(s)	Chemical Shift ( $\tau$ )	Multiplicity (JHz)	
		<u>146</u>	<u>146-D</u>
ArH	0.68, 1.11	m	m
H <sub>3</sub>	1.36	m	broad s ( $J_{23}$ ca 2 Hz)
H <sub>1</sub>	1.39	d ( $J_{12} = 10$ Hz) ( $J_{23} = 2$ Hz)	d ( $J_{12} = 10$ Hz) ( $J_{17} = \text{small}$ )
H <sub>2</sub>	2.66	m	d ( $J_{12} = 10$ Hz)
H <sub>6</sub>	3.68	m	d ( $J_{67} = 9$ Hz)
H <sub>7</sub>	3.98	m	t ( $J_{67} = 9$ Hz) ( $J_{17} = \text{small}$ )
H <sub>81</sub> H <sub>80</sub> } H <sub>91</sub> H <sub>90</sub> }	three H 6.08-7.10	m	-
	one H 8.46	m	-

Table VII      Nmr Parameters for the Protonated  
Trans Alcohols 146 and 146-D

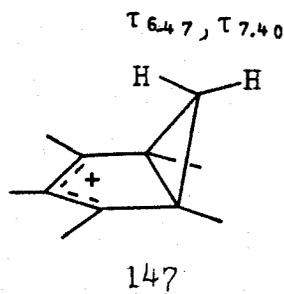
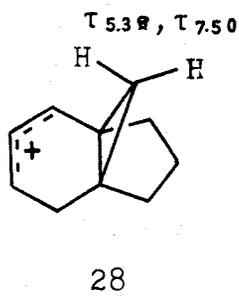
of the cyclopropyl coupling constants was not possible because of the overlapping multiplets and some viscosity broadening the deuterated system 146-D clearly indicated that  $J_{23} = \text{ca } 2.0 \text{ Hz}$ , while  $J_{67} = 9.0 \text{ Hz}$ . These values can be compared to that obtained for the 4,5-benzo-2,3-homotropylium cation 141 ( $J_{23} = 3.0 \text{ Hz}$ ) and a normal cis cyclopropyl coupling constant ( $J_{67} \text{ ca } 8-9 \text{ Hz}$ ) respectively<sup>29,37</sup>.

The low field resonances of  $H_2$  and  $H_3$  compared to  $H_6$  and  $H_7$  further indicates that only the cyclopropyl ring containing  $C_8$  is conjugatively delocalized. Furthermore, it is clear that in 146 the  $H_2$  and  $H_3$  signals have shifted downfield significantly, while the  $H_{81}$  and  $H_{80}$  signals have not moved downfield to the same extent compared to their value in the original alcohol 112-OH. This is attributed to the extensive delocalization of internal cyclopropyl bond  $C_2C_3$  compared to the external cyclopropyl bond  $C_2C_8$ . Thus, there is a significant contribution from the homoallylic delocalized structure 153

153

In the carbonium ion 146 there is no equilibration between the two possible boat conformations, contrasting the observation for the hydroxy substituted cation 144. This is attributed to the strong electron donating influence of the hydroxy substituent in 144, which would decrease the free energy for interconversion of the two equivalent boat conformations.

The observation that the chemical shift difference between "inside" and "outside" methylene proton signals of one cyclopropyl ring in 146 differ by ca 1.80 ppm is intriguing. Examination of models, clearly showed that if the seven-membered ring adopts a boat conformation, one cyclopropyl ring (containing C<sub>8</sub>) is in a quasi-axial position while the other cyclopropyl ring (containing C<sub>9</sub>) is in a quasi-equatorial position. Thus, the relative position of H<sub>81</sub> and H<sub>91</sub> and H<sub>80</sub> and H<sub>90</sub> will be markedly different. Indeed, H<sub>81</sub> will be "over" the seven-membered ring while H<sub>80</sub>, H<sub>90</sub> and H<sub>91</sub> will be "outside" the seven-membered ring. For similar systems 28<sup>35</sup> and 147<sup>112</sup>, which can be considered possible model systems for cyclopropyl rings adjacent to a  $\pi$  system, the direct field effects<sup>113</sup> of the  $\pi$  system on the exo and endo methylene hydrogens can result in a difference of 1.5 - 2.0 ppm. In the absence of specific deuterium labelling, however, it is not possible to assign which proton (H<sub>80</sub> or H<sub>81</sub>) appears at lower fields.



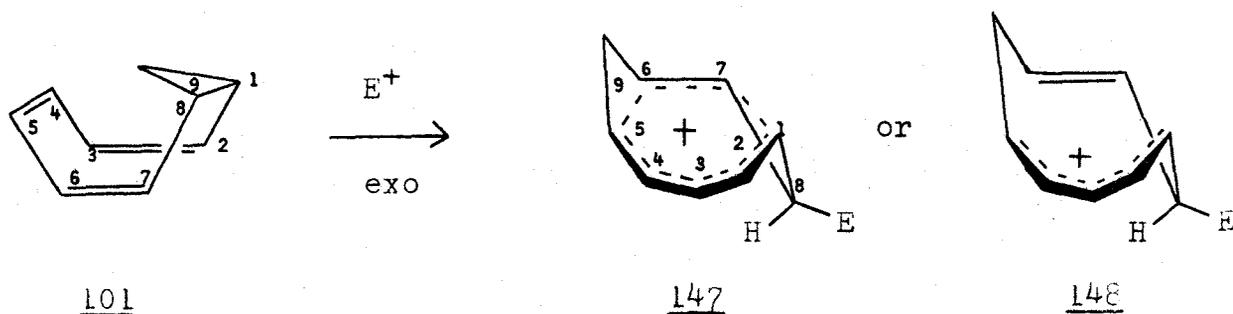
Repeated attempts to protonate cis-1-hydroxy-4,5-benzo-2,3:6,7-bishomotropone 111-OH in the range of temperatures  $-78^{\circ}$  to  $-125^{\circ}$  were unsuccessful. In the cis-alcohol the two cyclopropyl rings are both in a quasi-equatorial position, the geometry least favourable for interaction with a  $\pi$ -orbital at C<sub>1</sub>. To obtain the bisected conformation, the cyclopropyl rings must adopt a quasi-axial position, resulting in severe steric interaction between the "inside" methylene protons. This factor undoubtedly contributes to the difficulty in obtaining a clean protonation.

(f) Conclusions and General Discussion

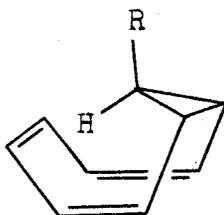
Despite the fact that bishomotropylium ions have already received considerable attention (vide supra), the work in this thesis is the first reported<sup>114</sup> systematic approach to evaluate the stereochemical requirements in such systems. The results show that in a 1,4-bishomotropylium system when the two cyclopropyl rings are trans with respect to each other, the cation is not bishomoaromatic. On the other hand, when the two cyclopropyl rings are cis with respect to each other, the cation is best represented as a bishomoaromatic system. It is interesting to extrapolate the results of this work to that published in the literature.

Warner<sup>73</sup> has reported the protonation of cis bicyclo [4.1.0] nona-2,3,6-triene 101 and concluded that a 1,3-bishomotropylium ion 102 was formed, which has the two methylene bridges cis with respect to each other. Paquette's<sup>74</sup> work

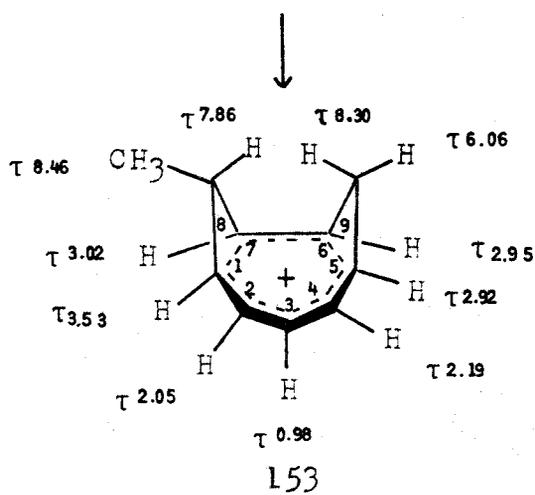
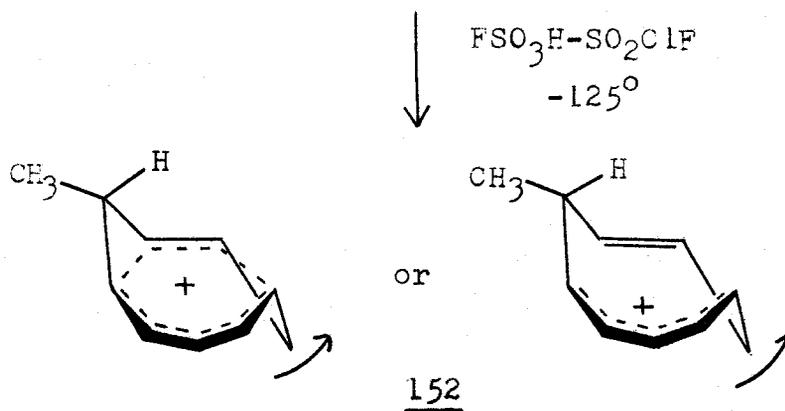
involving chlorosulfonyl isocyanate ( $\text{ClSO}_2\text{N}=\text{C}=\text{O}$ ) addition to 101 clearly showed exo attack on 101, followed by internal collapse of the trans-1,3-bishomotropylium intermediate 147 to product. Consequently, some uncertainty was raised concerning the assignment of "inside" ( $\text{H}_{81}$ ,  $\text{H}_{91}$ ) and "outside" ( $\text{H}_{80}$ ,  $\text{H}_{90}$ ) protons reported by Warner. Paquette<sup>74,115</sup> has also investigated the electrophilic addition to a number of methylated derivatives 101-CH<sub>3</sub> but the results can readily be accommodated by the formation of a carbonium ion in which most of the charge is on the pentadienyl unit. That is, a non-interacting cation 148.



More recently Paquette and Warner<sup>116</sup> have conducted a more intensive investigation of the protonation of 101 and several methyl derivatives 149, 150 and 151. Protonation of the syn-methyl derivative 149 and the dimethyl derivative 151 gave only polymeric material. Protonation of the anti-methyl derivative 150, on the other hand, gave a carbonium ion whose nmr spectrum is only consistent with either a cis-1,3-bis-



101, R=H

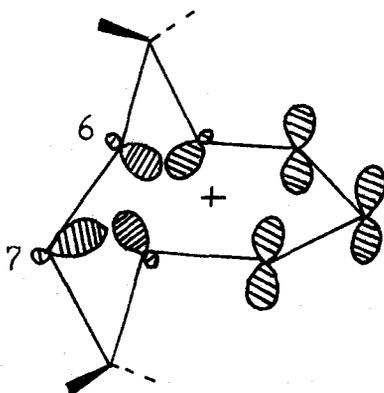
150, R=CH<sub>3</sub>

J	J <sub>12</sub>	J <sub>23</sub> , J <sub>34</sub>	J <sub>45</sub>	J <sub>59i</sub>	J <sub>59o</sub>	J <sub>69o</sub>
Hz	9.5	6.0	9.0	11.0	9.5	10.0
J	J <sub>69i</sub>	J <sub>181</sub>	J <sub>67</sub>	J <sub>781</sub>	J <sub>909i</sub>	
Hz	0	11.0	8.0	0	12.0	

homotropylium ion 152 or a trans-1,3-bishomotropylium ion 153. The coupling constant pattern (more specifically  $J_{\text{trans}} > J_{\text{cis}}$ ) indicates that the resultant carbonium ion has the two methylene bridges cis with respect to each other, that is 153. In addition, the homoaromatic nature of 153 is supported by the observation that charge is transferred from the pentadienyl unit to the ethylene unit and the charge distribution in the pentadienyl unit is not what would be expected for cyclopropyl carbonyl delocalization (page 16). The remarkable dichotomy in behaviour between the syn-methyl 149 and the anti-methyl 150 indicates that protonation in these systems at  $C_3$  must occur from the folded conformation, resulting in the methyl group being placed outside the ring. Consequently the initially formed cation must be the trans oriented system which subsequently undergoes a bridge flipping (of the less substituted side) to give the cis-1,3-bishomotropylium ion 153. In conclusion the authors state that the trans-1,3-bishomotropylium ion is reasonably rigid, fairly strain free and certainly less demanding than the comparable 1,4-bishomotropylium system<sup>116</sup>.

Molecular models clearly show that a slight twisting of the  $C_1-C_5$   $\pi$  system in the trans-1,3-bishomotropylium system places both cyclopropyls in the bisected conformation, so that simultaneous overlap of the internal cyclopropyl bonds with the  $p$ -orbital at  $C_2$  and  $C_4$  is possible. However, it is difficult to see how the  $p$ -component of the orbitals at  $C_6$  and  $C_7$  can be properly aligned for overlap. To obtain

significant cyclic delocalization in the trans-1,3-system would thus require severe twisting of the  $C_6C_7$  bond and consequently it is difficult to rationalize the statement that the trans-1,3-system is "fairly strain free and less demanding than the trans-1,4-system".



Trans-1,3-System

In view of this, it is unlikely that significant cyclic delocalization will occur in the trans-1,3-system, but no definite conclusions regarding the electronic structure in such systems can be reached until suitable precursors of known stereochemistry are synthesized.

C. EXPERIMENTAL

## GENERAL PROCEDURES

### Nuclear Magnetic Resonance Spectra (nmr)

Room temperature spectra were taken on a Varian HA-100 or ER-220 Spectrometer in standard thin walled nmr tubes. Chemical shifts ( $\tau$ ) are reported in parts per million (ppm) downfield from tetramethylsilane (TMS  $\tau$ 10.0) using internal  $\text{CH}_2\text{Cl}_2$  as a secondary standard, set at  $\tau$ 4.70.

Low temperature spectra were recorded on a Varian HA-100 Spectrometer equipped with a variable-temperature probe. Probe temperature was measured with a methanol sample utilizing the temperature dependence of the hydroxyl proton chemical shift. The separation between hydroxyl and methyl resonances had been previously correlated with temperature<sup>117</sup>. Reproducibility of temperature readings was  $\pm 2^\circ$  and spectra were recorded in the temperature range  $-20^\circ$  to  $-80^\circ$ .

In all cases the nmr spectra were recorded several times and the chemical shifts had a reproducibility of  $\pm 0.07$  Hz.

For each protonation a fresh vial was opened and the acid transferred by means of a capillary dropper. Care was taken to ensure that the acid did not come into contact with the air for any extended period since it readily hydrolyzes to HF and  $\text{H}_2\text{SO}_4$ .

Simulated spectra<sup>108</sup> were obtained using a LAOCN III nmr program. The program has the capability of generating a table of frequencies and intensities of the lines expected

in the nmr spectrum from an arbitrarily chosen set of chemical shifts and coupling constants. The program can also cause the computer to perform an iterative calculation by means of which the calculated frequencies of assigned lines are brought as close as possible (by the least squares criterium) to the corresponding observed lines in the actual nmr spectrum. The chemical shifts and coupling constants which yield the best fit are then printed out together with the expected errors in them. Tables of observed and calculated line frequencies, calculated intensities and errors in fitting the frequencies of observed lines are also printed out.

The calculated line frequencies and intensities are then used in conjunction with a plotting program<sup>118</sup> from which the simulated spectra were obtained. In all cases the maximum error in chemical shifts and coupling constants was  $\pm 0.05$  Hz.

#### Methylene Chloride

Fisher reagent grade methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) was dried over anhydrous potassium hydroxide (KOH) pellets and used without further purification. Deuterated methylene chloride ( $\text{CD}_2\text{Cl}_2$ ) was taken directly from the glass ampoules as supplied in 1 ml quantities from Merck-Sharpe and Dohme.

#### Carbon Tetrachloride

Mallinckrodt analytical reagent grade carbon tetrachloride ( $\text{CCl}_4$ ) was distilled through a Vigreux column and the middle third taken and stored in glass stoppered bottles over KOH pellets. This was used for the nmr spectra without further purification.

### Infrared Spectra

Infrared spectra were recorded on a Perkin-Elmer Model 521 grating spectrometer, normally as 10-15% solutions in carbon tetrachloride ( $\text{CCl}_4$ ) although some were recorded as potassium bromide (KBr) discs.

### Mass Spectra

Mass spectra were recorded on a CEC 21-110B high resolution mass spectrometer.

### Melting Points

Melting points were determined using a Kofler Hot-stage thermopan and are uncorrected.

### GENERATION, OBSERVATION AND QUENCHING OF CATIONS

Fluorosulfuric acid ( $\text{FSO}_3\text{H}$ ) was obtained commercially from Allied Chemical in 2 lb. glass bottles. The acid was distilled from sodium fluoride ( $\text{NaF}$ ) through an eight inch Vigreux column into a nitrogen filled round bottom flask from which it was transferred to clean oven dried glass ampoules in approximately 1 ml quantities. No grease was used on the joints, since this is rapidly attacked by the  $\text{FSO}_3\text{H}$ . In a typical distillation 75 ml  $\text{FSO}_3\text{H}$  was distilled from 1.0 g of  $\text{NaF}$  discarding the first 15-20 ml. The next 30-35 ml were collected in three flasks and transferred to the ampoules. The residual 20-25 ml was discarded by quenching slowly in water.

## Protonations

Because of their relatively high stability, protonated ketones are more easily prepared than carbonium ions. In general Method A was used to prepare the protonated ketones and Method B for the preparation of carbonium ions.

### Method A

A clean, dry, thin walled nmr tube is held in a one-holed clamped rubber stopper and is flushed with nitrogen. The nitrogen initially enters the nmr tube near the bottom by placing the capillary tube near the base of the nmr tube. After a few minutes the flow of nitrogen is reduced and the capillary tube placed so that the lower extremity of the capillary tube is approximately one-third from the top of the nmr tube. Approximately 0.8 ml of  $\text{FSO}_3\text{H}$  is then transferred to the nmr tube by capillary dropper from a freshly opened ampoule. Care is taken to ensure no acid is left on the side of the nmr tube. The nmr tube is now immersed into a small Dewar of dry ice acetone ( $-78^\circ$ ).

The precursor ketone (20-25 mg) is dissolved in ca 0.3 ml  $\text{CH}_2\text{Cl}_2$  ( $\text{CD}_2\text{Cl}_2$ ) and the solution transferred to the cooled nmr tube containing the acid via capillary dropper. Some cooling of the  $\text{CH}_2\text{Cl}_2$  solution is obtained by allowing the solution to run down the side of the nmr tube.

An homogeneous mixture of protonated ketone is obtained by mixing the  $\text{CH}_2\text{Cl}_2$  layer and  $\text{FSO}_3\text{H}$  layer using a thin pyrex rod (1.5 mm). The pyrex rod is precooled by quickly immersing it in liquid nitrogen before mixing. The nmr

solution is allowed to settle at which time a pale yellow acid layer is observed in the lower section of the nmr tube with a colourless  $\text{CH}_2\text{Cl}_2$  layer above it. The nmr tube containing the protonated ketone is then removed from the one-holed rubber stopper, capped and placed in a Dewar containing liquid nitrogen. Prior to being placed in the precooled nmr probe the nmr tube is dipped in a Dewar containing dry ice - acetone and the acetone on the outside removed by using a tissue. The nmr spectra are then recorded after slowly warming the nmr probe to the desired temperature.

#### Method B

A clean dry thin walled nmr tube is held in a one-hole clamped rubber stopper and is flushed with nitrogen. The nitrogen initially enters the nmr tube near the bottom by placing the capillary tube near the base of the nmr tube. After a few minutes the flow of nitrogen is reduced and the capillary tube placed so that the lower extremity of the capillary tube is approximately one-third from the top of the nmr tube. The nmr tube is then transferred to a Dewar containing dry ice acetone and  $\text{SO}_2\text{ClF}$  ( 0.6 ml ) slowly distilled into the base of the cooled nmr tube directly from a lecture bottle. The amount of  $\text{SO}_2\text{ClF}$  is controlled by allowing the level to reach a precalibrated mark on the nmr tube.  $\text{FSO}_3\text{H}$  (0.2 ml) is now placed into the nmr tube via a capillary dropper and the  $\text{SO}_2\text{ClF}$  and  $\text{FSO}_3\text{H}$  completely mixed using a 1.5 mm pyrex glass rod. The solution is allowed to settle and the nmr tube then transferred to a petroleum ether

nitrogen bath (ca  $-120^{\circ}$ ). Approximately 0.1 ml of  $\text{CH}_2\text{Cl}_2$  ( $\text{CD}_2\text{Cl}_2$ ) is then placed on top of the  $\text{SO}_2\text{ClF}-\text{FSO}_3\text{H}$  layer.

The precursor alcohol is dissolved in  $\text{CH}_2\text{Cl}_2$  ( $\text{CD}_2\text{Cl}_2$ ) (ca 0.2 ml) and the solution slowly transferred to the cooled nmr tube containing the acid solution. If the alcohol- $\text{CH}_2\text{Cl}_2$  solution freezes out on the side of the nmr tube, the tube is raised and warmed by placing a finger on the frozen section until solution occurs. The  $\text{CH}_2\text{Cl}_2$  ( $\text{CD}_2\text{Cl}_2$ ) layer serves the purpose of ensuring the alcohol is cooled to some degree so that a clean protonation is obtained.

The acid solvent system is now mixed using a 1.5 mm pyrex glass rod which is precooled by dipping it in liquid nitrogen. In most protonations an orange-red homogeneous solution is obtained because the  $\text{SO}_2\text{ClF}$  renders the  $\text{CH}_2\text{Cl}_2$  ( $\text{CD}_2\text{Cl}_2$ ) soluble in the acid layer. No spectral differences are apparent due to the presence of the  $\text{CH}_2\text{Cl}_2$  ( $\text{CD}_2\text{Cl}_2$ ) in the acid solvent system. The nmr tube is now removed from the one-holed rubber stopper, capped and then placed in the precooled nmr probe.

#### Quenching of Cations

Protonated ketones are best quenched in ether-sodium bicarbonate ( $\text{Et}_2\text{O}-\text{HCO}_3^-$ ) slurries at  $-78^{\circ}$ , while carbonium ions are best quenched in methanol sodium methoxide ( $\text{MeOH}-\text{NaOCH}_3$ ) solutions at  $-78^{\circ}$ .

The quench procedure used in this work involved adding the acid solution via a cooled ( $-78^{\circ}$ ) capillary dropper to the stirring quench media. Typically,  $\text{NaHCO}_3$  (5 g) was

added to ether (15 ml) in a 50 ml Erlenmeyer flask. The contents of the flask were cooled in a dry ice acetone bath and the contents stirred rapidly by means of a magnetic stir bar. The contents of the nmr tube were taken up in a capillary tube which had the top reservoir cooled by jacketing the tube with dry ice. The contents of the capillary tube were added slowly to the cooled, stirring quench media. At the completion of the quench the Erlenmeyer flask was removed from the dry ice acetone bath and allowed to warm to room temperature. The ether was then decanted into a separating funnel containing water (25 ml). The  $\text{NaHCO}_3$  was washed three times with 15 ml of ether and the combined ether extracts washed with water until the water was neutral to litmus paper (ca three 15 ml washes). The ether was then removed and dried over anhydrous  $\text{K}_2\text{CO}_3$ . The ether was decanted from the  $\text{K}_2\text{CO}_3$  layer into a 100 ml round-bottom flask and the ether removed in vacuo. The nmr spectra of the residue was identical to the original ketones.

For carbonium ions the cooled acid solution was added slowly to a solution containing  $\text{NaOCH}_3$  (5 g) in 15 ml of  $\text{CH}_3\text{OH}$  at  $-78^\circ$  using an identical procedure. The quench solution was then poured into a separating funnel containing water (20 ml). The aqueous methanol layer was extracted with three lots of ether (25 ml) and the combined ether layers washed with water until neutral to litmus (ca three 15 ml washes). The ether was removed and dried over anhydrous  $\text{K}_2\text{CO}_3$ . The dried ether layer was decanted from the  $\text{K}_2\text{CO}_3$  into a 100 ml

round-bottom flask and the ether removed in vacuo. The nmr spectra of the residue indicated the formation of the methoxy ether.

### SYNTHESIS

#### 2,7-Dicarbomethoxy-4,5-Benzotropone

o-Phthalaldehyde (40 g), dimethyl-3-oxoglutarate (52.4 g), glacial acetic acid (1 ml) and piperidine (1 ml) were heated in benzene (600 ml) in a 1 litre 3-neck flask fitted with a stirrer and a Dean and Stark water take-off. The mixture was refluxed (80-85°) for 20 hr and then cooled in an ice bath. The resulting crystals were filtered, washed with cold benzene (two 50 ml portions) and dried in a dessicator under vacuum. The resulting white **crystalline** product (36.7 g; 45%) with the identical properties to that previously reported<sup>119</sup>: mp 183.5-184.5°; nmr (CDCl<sub>3</sub>)  $\tau$  1.82 (s, 2, vinyl H), 2.14-2.36 (m, 4, ArH), 6.05 (s, 3, OCH<sub>3</sub>).

The material was used directly in the next stage.

#### 2,7-Dicarboethoxy-4,5-Benzotropone

o-Phthalaldehyde (21.5 g), diethyl-3-oxoglutarate (32.5 g) glacial acetic acid (0.75 ml) and piperidine (0.75 ml) were heated in benzene (500 ml) in a 1 litre 3-neck flask fitted with a stirrer and a Dean and Stark water take-off. The mixture was refluxed (80-85°) for 15 hr and then cooled in an ice bath. The resulting crystals were filtered, washed with cold benzene (two 50 ml portions) and dried in a desicator under vacuum.

The resulting white crystalline product (47.3 g; 59%) was identical to that previously reported<sup>119</sup>: mp 94-95°; nmr (CDCl<sub>3</sub>)  $\tau$  1.93 (s,2,vinyl H), 2.12-2.34 (m,4,ArH), 5.63 (q,2,CH<sub>2</sub>), 8.53 (t,3,CH<sub>3</sub>).

The material was used directly in the next stage.

#### 2,7-Dicarboxylic Acid-4,5-Benzotropone

2,7-Dicarbomethoxy-4,5-benzotropone (36 g) or (2,7-dicarboethoxy-4,5-benzotropone) was heated in 20% sulfuric acid (400 ml) in a 1 litre 2-neck flask fitted with a stirrer and reflux condenser. The mixture was refluxed (100-110°) with stirring for 12 hr and then cooled to room temperature. The resulting crystals were filtered off, washed twice with water (two 50 ml portions) and dried. The resulting pale yellow powder (36.7; 94%) was identical to that previously reported<sup>119</sup>: mp 210-215°.

This material was used directly in the next stage.

#### 4,5-Benzotropone (110)

2,7-Dicarboxylic acid-4,5-benzotropone (20.0 g) and 0.5% hydrochloric acid (300 ml) were heated in a Parr bomb at 200-210° for 5 hr. 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 50 ml portions) and the combined ether extracts and oil washed initially with 15% sodium bicarbonate (two 15 ml portions), and then with a saturated sodium chloride solution

(one 20 ml portion). The ether extract was dried over potassium carbonate, and the ether was removed in vacuo. The pale brown solid was taken up in boiling heptane and recrystallized to give pale yellow crystals (11.2 g; 87%) which were identical to that previously reported<sup>119</sup>: mp. 66.5-67.0°; nmr. (CCl<sub>4</sub>)  $\tau$  2.36-2.58 (m, 4, ArH), 2.73 (dt, 2, vinyl H, J=12.5 Hz, 1.2 Hz) 3.40 (dt, 2, vinyl H, J=12.5 Hz, 1.2 Hz); ir. (KBr) 3015 1620 1580 1410 1289 857 (broad) 764 cm<sup>-1</sup>.

Reaction of 4,5-Benzotropone (110) with Diazomethane in Ether

4,5-Benzotropone (1.56 g; 0.01 mole) and ten fold excess of diazomethane in ether (15 ml containing 38% CH<sub>2</sub>N<sub>2</sub>) were reacted in a stoppered 50 ml round bottom flask at 0° for eight days. The reaction mixture was then placed on a steam bath to discharge the unreacted diazomethane and ether. The pale yellow, oily residue was taken up in carbon tetrachloride and the spectral analysis (ir and nmr) indicated the only product present was the original 4,5-benzotropone (110).

Reaction of 4,5-Benzotropone (110) with Phenyl Mercuric Trichloromethane

4,5-Benzotropone (500 mg, 0.003 mole), phenyl mercuric trichloromethane<sup>99</sup> (3.97 g, 0.01 mole) and benzene (20 ml) were placed in a three-neck 50 ml round bottom flask fitted with a condenser and nitrogen inlet. The mixture was heated at 80-85° with stirring for 48 hr. The reaction was cooled and the precipitate of phenyl mercuric chloride filtered off and washed with benzene (5 ml portion). The filtrate and

washings were evaporated to dryness in vacuo and the brown oily residue examined by nmr. The nmr spectrum indicated the presence of 4,5-benzotropone and some unreacted phenyl mercuric trichloromethane. Thin layer chromatography (solvent, 1:1:: ether:petroleum ether) indicated the presence of an unidentified product. Infrared examination of this product showed the absence of a carbonyl function.

Reaction of 4,5-Benzotropone (110) with the Simmons-Smith Reagent

The zinc-copper couple was prepared according to the procedure of Simmons and Smith<sup>91</sup>. British Drug Houses' reagent grade granular zinc (20 mesh) was used in the preparation of the Zn/Cu couple. Methylene iodide (Matheson, Coleman and Bell) was distilled at 70-71°C, 10 Torr pressure just prior to use. Zn/Cu couple (0.13 g) and anhydrous ether (20 ml) were placed into a dried two-neck 50 ml round bottom flask, fitted with a condenser and a calcium chloride drying tube. A serum cap was fitted in the other neck. A small crystal of iodine was added to the reaction mixture and the reaction stirred with a magnetic stir bar until the colour had disappeared. A mixture of methylene iodide (0.53 g) and 4,5-benzotropone (0.30 g) in anhydrous ether (5 ml) was added in one portion using a syringe. The mixture was refluxed for 48 hrs and then cooled to room temperature. The reaction mixture was filtered and the filtrate poured into aqueous ammonium hydroxide (10 ml). The aqueous layer was extracted with ether (three 25 ml portions) and the

combined ether extracts were dried over potassium carbonate and the ether removed in vacuo. The pale yellow oily residue was examined by nmr and the nmr spectrum indicated only the presence of the original 4,5-benzotropone.

#### 7-Hydroxy-3,4-Benzocycloheptatriene

4,5-Benzotropone (0.5 g) and anhydrous ether (25 ml) were placed in a one-neck 50 ml round bottom flask fitted with a reflux condenser having a drying tube. Lithium aluminium hydride (0.20 g) was added to the flask and the reaction mixture stirred with a magnetic stir bar for 2 hr at 0°. The reaction mixture was then poured into an Erlenmeyer flask containing 15 ml of a 10% solution of sodium potassium tartrate. The ether layer was decanted from the aqueous layer and the aqueous layer extracted with ether (three 20 ml lots). The combined ether extracts were dried over potassium carbonate and the ether removed in vacuo<sup>119</sup>: nmr (CS<sub>2</sub>) 3.04-3.26 (m,4, ArH), 3.95 (dd,2,vinyl H, J=10.0 Hz and 1.0 Hz) 4.58 (dd,2, vinyl H, J=10.0 Hz and 2.0 Hz) 6.03 (m,1, α-H) 6.55 (d,1,OH, J=2.5 Hz).

This material was used directly in the next stage without further purification.

#### Reaction of 7-Hydroxy-3,4-Benzocycloheptatriene with the Simmons-Smith Reagent

The procedure used was identical to that used for the reaction of 4,5-benzotropone. Zn/Cu couple (0.13 g), anhydrous ether (20 ml) were placed into a dried two-neck

50 ml round bottom flask, fitted with a condenser and calcium chloride drying tube. A serum cap was fitted in the other neck. A small crystal of iodine was added to the reaction mixture and the reaction stirred with a magnetic stir bar until the colour had disappeared. A mixture of methylene iodide (0.53 g) and 7-hydroxy-3,4-benzocycloheptatriene (0.30 g) in anhydrous ether (5 ml) was added in one portion using a syringe. The mixture was refluxed for 48 hr and then cooled to room temperature. The reaction mixture was poured into aqueous ammonium hydroxide (10 ml) and extracted with ether (three 25 ml portions). The combined ether extracts were dried over potassium carbonate and the ether removed in vacuo. The nmr spectrum of the residue indicated only the presence of the original alcohol.

The procedure was repeated using various methods to prepare the Zn/Cu couple. In all cases only the starting alcohol was found in the reaction mixture.

#### Reaction of 4,5-Benzotropone (110) with Ethylene Glycol

Into a two-neck 250 ml flask fitted with a reflux condenser having a partial take-off head was placed ethylene glycol (50 ml), previously dried over molecular sieve, 4,5-benzotropone (0.5 g) and p-toluenesulfonic acid (50 mg). The reaction mixture was refluxed at 140-145° and 85 torr pressure. The ethylene glycol was removed at the rate of 20 ml per hr until 35 ml of the ethylene glycol had been distilled off. The residue in the flask was cooled to room temperature and poured into a 5% sodium hydroxide in methanol solution (10 ml)

and the aqueous layer extracted with ether (four 25 ml lots). The combined ether layers were dried over potassium carbonate and the ether removed in vacuo. The nmr spectrum of the reaction product showed the presence of 20% of the ethylene ketal of 4,5-benzotropone 125: nmr (CCl<sub>4</sub>)  $\tau$  2.57-2.79 (m,4, ArH), 3.38 (dt,2,vinyl H), 4.15 (dt,2,vinyl H), 6.15 (s,4, ethylene ketal). The remaining 80% of the reaction product was the original 4,5-benzotropone 110

1-Ethoxy-4,5-Benzotropylum Fluoroborate Salt (130 )

4,5-Benzotropone (10.5 g) was dissolved in methylene chloride (10 ml) and the resulting solution added to a solution of triethyloxonium fluoroborate (18.1 g) <sup>120</sup> in methylene chloride (40 ml). The solution was left standing at 5° for 30 hr at which time pale yellow crystals were observed in the bottom of the flask. The solution was filtered and the crystals washed with cold methylene chloride (two 2 ml lots). The pale yellow crystals (18.3g; 95%) were dried under vacuum and used in the next stage without further purification: nmr ((CD<sub>3</sub>)<sub>2</sub>CO)

$\tau$  0.44 (dt,2,vinyl H, J=12.0 Hz and 1.0 Hz), 1.06-1.46 (m,4, ArH), 1.55 (dt,2,vinyl H, J=12.0 Hz and 1.0 Hz), 4.86 (q,2, CH<sub>2</sub>, J=6.5 Hz), 1.78 (t,3,CH<sub>3</sub>, J=6.5 Hz). Anal: Calcd for C<sub>13</sub>H<sub>13</sub>OBF<sub>4</sub>: C, 57.39; H, 4.82. Found: C, 57.15; H, 4.78.

4,5-Benzotropone Ethylene Ketal (125)

1-Ethoxy-4,5-benzotropylum fluoroborate (18.3 g) from the previous stage was added to a solution prepared by dissolving sodium (15.5 g) in ethylene glycol (150 ml) and the mixture

stirred at 65° for 8 hr under nitrogen. The reaction mixture was cooled to room temperature and poured into water (300 ml). The aqueous layer was extracted with ether (four 75 ml portions) and the combined ether extracts washed with water until neutral to litmus (ca five 25 ml washes). The ether layer was dried over potassium carbonate and removed in vacuo. The desired ketal (8.10 g; 91%) was used without further purification in the next stage. A pure sample was obtained by column chromatography using basic alumina (Fisher, activity 2.5), eluting with 10% ether in petroleum ether (bp < 40°): nmr. (CCl<sub>4</sub>)  $\tau$  2.57-2.79 (m, 4, ArH), 3.38 (dt, 2, vinyl H, J= 11.5 Hz and 1.5 Hz), 4.45 (dt, 2, vinyl H, J=11.5 Hz and 1.5 Hz), 6.15 (s, 4, ethylene ketal). Anal: Calcd for C<sub>13</sub>H<sub>12</sub>O<sub>2</sub>: C, 77.98; H, 6.04. Found: C, 77.71; H, 5.98.

Reaction of 4,5-Benzotropone Ethylene Ketal (125) and Phenyl Mercuric Tribromomethane

4,5-Benzotropone ethylene ketal (0.513 g) and phenyl mercuric tribromomethane<sup>99</sup> (6.05 g) were heated in benzene (7.0 ml) under nitrogen to 65-70° with stirring for 14 hr. The reaction was cooled and the precipitate of phenyl mercuric bromide filtered off and washed with cold benzene (two 5 ml portions). The filtrate and washings were evaporated in vacuo and the oily residue was chromatographed on basic alumina (Fisher, activity 2-3). Eluting with 5% chloroform - petroleum ether (bp. < 40°) gave initially some unreacted phenyl mercuric tribromomethane and then the mono-dibromo adduct 131

(267 mg) nmr ( $\text{CDCl}_3$ )  $\tau$  2.40-2.90 (m,4,ArH), 3.70 (d,1,vinyl H  $J=12.5$  Hz), 4.73 (dd,1,vinyl H  $J=12.5$  Hz and 2.0 Hz), 5.77-6.20 (m,4, ethylene ketal), 6.75 (d,1, cyclopropyl H  $J=12.0$  Hz), 7.17 (dd,1, cyclopropyl H  $J=12.0$  Hz and 2.0 Hz) and a mixture of 132 and 133 (120 mg). These could be partially separated by repeated chromatography on basic alumina.

Cis bis dibromo adduct 132 : nmr. ( $\text{CDCl}_3$ )  $\tau$  2.40-2.60 (m,4, ArH), 5.04 (t,2, ethylene ketal  $J=5.0$  Hz), 6.24 (t,2, ethylene ketal  $J=5.0$  Hz), 7.02 (d,2, cyclopropyl H  $J=12.0$  Hz) 7.32 (d,2, cyclopropyl H  $J=12.0$  Hz).

Trans bis dibromo adduct 133 : nmr. ( $\text{CDCl}_3$ )  $\tau$  2.50 (s,4,ArH), 5.70 (s,4, ethylene ketal), 6.78 (d,2, cyclopropyl H  $J=12.0$  Hz), 7.35 (d,2, cyclopropyl H  $J=12.0$  Hz).

Reaction of 4,5-Benzotropone Ethylene Ketal (125) and Phenyl Mercuric Trichloromethane

4,5-Benzotropone ethylene ketal (2.0 g) and phenyl mercuric trichloromethane<sup>99</sup> (7.91 g) were heated in benzene (25 ml) under nitrogen to 90-92° with stirring for 96 hr . The reaction was cooled and additional phenyl mercuric trichloromethane (7.91 g) was added to the reaction mixture. The reaction mixture was heated at 90-92° for a further 76 hr with stirring. The reaction was cooled and the precipitate of phenyl mercuric chloride filtered off and washed with cold benzene (two 10 ml portions). The filtrate and washings were evaporated in vacuo and the oily residue was chromatographed

on basic alumina (Fisher, activity 2-3). Eluting with 5% chloroform in petroleum ether (bp  $< 40^{\circ}$ ) gave initially some unreacted phenyl mercuric trichloromethane and then the cis-bis-dichloro adduct 135 (240 mg). Further elution gave the trans-bis-dichloro adduct 136 (1.25 g) followed by the mono dichloro adduct 134 (450 mg). The chromatographed fractions were recrystallized from methylene chloride to give pure samples.

Mono dichloro adduct 134 : mp  $113.5-114.5^{\circ}$ ; nmr ( $\text{CDCl}_3$ )  
 $\tau$  2.58-2.95 (m, 4, ArH), 3.72 (d, 1, vinyl H  $J=12.5$  Hz), 4.38 (dd, 1, vinyl H  $J=12.5$  Hz and 2.5 Hz), 5.73-6.42 (m, 4, ethylene ketal), 6.90 (d, 1, cyclopropyl H  $J=12.0$  Hz), 7.30 (dd, 1, cyclopropyl H  $J=12.0$  Hz and 2.5 Hz). Anal: Calcd for

$\text{C}_{14}\text{H}_{12}\text{O}_2\text{Cl}_2$  : C, 59.38; H, 4.27. Found: C, 59.16; H, 4.21.

Cis bis dichloro adduct 135 : mp  $184-185^{\circ}$ ; nmr ( $\text{CDCl}_3$ )  
 $\tau$  2.52-2.80 (m, 4, ArH), 6.00 (t, 2, ethylene ketal  $J=6.0$  Hz), 6.39 (t, 2, ethylene ketal  $J=6.0$  Hz), 7.15 (d, 2, cyclopropyl H  $J=12.0$  Hz), 7.41 (d, 2, cyclopropyl H  $J=12.0$  Hz). Anal: Calcd for  $\text{C}_{15}\text{H}_{12}\text{O}_2\text{Cl}_4$  : C, 49.22; H, 3.30. Found: C, 49.28; H, 3.27.

Trans bis dichloro adduct 136 : mp  $136-135^{\circ}$ ; nmr ( $\text{CDCl}_3$ )  
 $\tau$  2.66 (s, 4, ArH), 5.88 (s, 4, ethylene ketal), 7.08 (d, 2, cyclopropyl H  $J=12.5$  Hz), 7.44 (d, 2, cyclopropyl H  $J=12.5$  Hz)  
 Anal: Calcd for  $\text{C}_{15}\text{H}_{12}\text{O}_2\text{Cl}_4$  : C, 49.22; H, 3.30. Found: C, 49.02; H, 3.25.

Trans-4,5-Benzo-2,3:6,7-Bishomotropone EthyleneKetal (138)

In a three neck 50 ml round bottom flask fitted with a condenser having a drying tube, nitrogen inlet and serum cap was placed anhydrous tetrahydrofuran (22 ml), sodium chips (1.8 g) and t-butanol (3.3 ml). To the refluxing mixture was added a solution of trans bis dichloro adduct 136 (0.880 g) in tetrahydrofuran (5 ml) using a syringe. The reaction mixture was refluxed with stirring for 7 hr using a magnetic stir bar and then cooled to room temperature. The cooled reaction mixture was decanted from the sodium chips and poured into ice water (20 ml). The aqueous layer was extracted with ether (four 20 ml portions) and the combined ether extracts washed with water until neutral to litmus (ca five 15 ml portions). The ether extracts were dried over anhydrous potassium carbonate and the ether removed in vacuo to leave a pale yellow oily residue (285 mg, 52%). The product was used without further purification in the next stage. An analytical sample was obtained by column chromatography using basic alumina (Fisher, activity 2-3) eluting with petroleum ether (bp < 40°): nmr (CCl<sub>4</sub>)  $\tau$  2.86-3.12 (m, 4, ArH), 6.13-6.32 (m, 4, ethylene ketal), 8.09-8.34 (m, 2, cyclopropyl H), 8.54-9.14 (m, 6, cyclopropyl H). Anal: Calcd for C<sub>15</sub>H<sub>16</sub>O<sub>2</sub> : C, 78.92; H, 7.07. Found: C, 79.02, H, 7.15.

Cis-4,5-Benzo-2,3:6,7-Bishomotropone EthyleneKetal (137)

The identical procedure was used for the cis bis dichloro adduct 135 as the trans bis dichloro adduct. Thus, cis bis dichloro adduct (540 mg) gave a clear oily product (175 mg, 54%) which was used in the next stage without further purification. An analytical sample was obtained by column chromatography using basic alumina (Fisher, activity 2-3) eluting with petroleum ether (bp < 40°): mp 66-67° nmr (CCl<sub>4</sub>)  $\tau$  2.64-3.00 (m,4,ArH), 6.05-6.37 (m,4, ethylene ketal), 7.91-8.29 (m,4, cyclopropyl H), 8.88-9.10 (m,2, cyclopropyl H, 9.19-9.29 (m,2, cyclopropyl H). Anal: Calcd for C<sub>15</sub>H<sub>16</sub>O<sub>2</sub> : C, 78.92; H, 7.07. Found: C, 78.66; H, 7.06.

Trans-8,8,9,9-Tetradeutero-4,5-Benzo-2,3:6,7-BishomotroponeEthylene Ketal (138-D)

The same procedure as that used for the preparation of trans-4,5-benzo-2,3:6,7-bishomotropone ethylene ketal was used except t-butanol-OD was used instead of t-butanol. Thus, bis dichloro adduct (760 mg) gave a pale yellow oily product (325 mg, 72%). This product was used directly in the next stage without further purification : nmr (CCl<sub>4</sub>)  $\tau$  2.85-3.10 (m,4,ArH), 6.15-6.35 (m,4, ethylene ketal), 8.15 (t,4, cyclopropyl H J=8.0 Hz).

Cis-8,8,9,9-Tetradeutero-4,5-Benzo-2,3:6,7-BishomotroponeEthylene Ketal (137-D)

The same procedure as that used for the preparation of

the cis-4,5-benzo-2,3:6,7-bishomotropone ethylene ketal was used except t-butanol-OD was used instead of t-butanol. Thus, cis bis dichloro adduct (345 mg) gave a pale yellow oily product (125 mg, 57%). This product was directly used in the next stage without further purification : nmr ( $\text{CCl}_4$ )  $\tau$  2.64-3.00 (m,4,ArH), 6.09-6.40 (m,4, ethylene ketal), 8.10 (t,4, cyclopropyl H  $J=8.0$  Hz).

Trans-4,5-Benzo-2,3:6,7-Bishomotropone (112)

Trans-4,5-benzo-2,3:6,7-bishomotropone ethylene ketal (340 mg) was dissolved in 20% aqueous dioxane (7 ml). 0.5% aqueous hydrochloric acid (0.1 ml) was added to the reaction mixture and the solution stirred with a magnetic stir bar at room temperature for 5 hr. The aqueous phase was extracted with ether (three 15 ml portions) and the combined ether extracts washed with water (two 5 ml portions). The ether layer was dried over potassium carbonate and the ether removed in vacuo, to leave a pale yellow oil (245 mg; 90%). Chromatography using neutral alumina (Fisher, activity 2) and ether-petroleum ether (1:1) gave a colourless solid. An analytical sample was obtained by sublimation : mp 90-91<sup>o</sup> nmr ( $\text{CCl}_4$ )  $\tau$  2.71-3.01 (m,4,ArH), 7.80 (m,2, cyclopropyl H), 7.97 (m,2, cyclopropyl H), 8.41 (m,2, cyclopropyl H), 8.73 (m,2, cyclopropyl H). Coupling constants :  $J_{\text{gem}} = 4.92$  Hz;  $J_{\text{cis}} = 3.57$  Hz;  $J_{\text{trans}} = 5.96$  Hz. Mass spectrum (70 eV) m/e 184. Infrared :  $\nu_{\text{C=O}} 1698 \text{ cm}^{-1}$ . Anal: Calcd for :  $\text{C}_{13}\text{H}_{12}\text{O}$  C, 84.75; H, 6.56. Found: C, 85.00; H, 6.65.

Trans-8,8,9,9-Tetradeutero-4,5-Benzo-2,3:6,7-Bishomotropone  
(112-D)

The procedure used was identical to that used for the preparation of trans-4,5-benzo-2,3:6,7-bishomotropone. The sample was purified by chromatography using neutral alumina (Fisher, activity 2) and ether-petroleum ether (1:1). The sample was used for protonation without further purification: nmr ( $\text{CCl}_4$ )  $\tau$  2.71-3.01 (m, 4, ArH), 7.80 (d, 2, cyclopropyl H), 7.97 (d, 2, cyclopropyl H. Coupling constant:  $J_{23} = J_{67} = 9.59$  Hz.

Cis-4,5-Benzo-2,3:6,7-Bishomotropone (111)

Cis-4,5-benzo-2,3:6,7-bishomotropone ethylene ketal (150 mg) was dissolved in 20% aqueous acetone (4 ml). 0.5% aqueous hydrochloric acid (0.1 ml) was added to the reaction mixture and the solution stirred for 5 hr. The aqueous phase was extracted with ether (three 15 ml portions) and the combined ether extracts washed with water (two 5 ml portions). The ether layer was dried over potassium carbonate and the ether removed in vacuo to give a pale yellow oil (70 mg, 60%). The nmr spectrum of this product was identical to that obtained by the reaction of dimethyloxosulfonium methylide and 4,5-benzotropone.

4,5-Benzo-2,3-Homotropone (124)

The dimethyloxosulfonium methylide ylid was prepared using essentially Corey's procedure<sup>94</sup>. Sodium hydride,

50% w/w dispersion in oil (0.616 g) was placed in a dry three neck 50 ml round bottom flask fitted with a nitrogen inlet, 60 ml dropping funnel and stopper. 15 ml of distilled petroleum ether (bp  $< 40^{\circ}$ ) was pipetted into the flask and the mixture rapidly stirred with a magnetic stir bar. The stirring was stopped after ca 5 min and the sodium hydride allowed to settle. The petroleum ether was then pipetted from the flask. This procedure was repeated two more times. After the last wash the remaining petroleum ether was removed in vacuo using a water aspirator. The vacuum was then removed and a steady stream of nitrogen allowed to pass through the flask while trimethyloxosulfonium iodide<sup>121</sup> (2.85 g) was added to the remaining sodium hydride. The two solids were intimately mixed using a magnetic stir bar. The flask was then placed in an ice-bath and dimethylsulfoxide (10 ml) added dropwise to the stirring mixture. After all the dimethylsulfoxide had been added the ice-bath was removed and the mixture allowed to stir at room temperature for 1 hr. Benzotropone (2.0 g) in dimethylsulfoxide (7 ml) was added, with stirring, dropwise to the reaction mixture. After all the benzotropone had been added the reaction was allowed to stir at room temperature for 20 hr and then at  $50^{\circ}$  for 3 hr. The reaction mixture was cooled and poured into water (25 ml). The aqueous phase was extracted with ether (three 25 ml portions) and the combined ether extracts washed with water (ca three 15 ml portions) and dried over potassium carbonate.

The ether was removed in vacuo to give a pale yellow solid (1.94 g: 85%). The crude product was purified by column chromatography using neutral alumina (Fisher, activity 2) eluting with ether. This product had the same spectral properties as previously reported<sup>59</sup> : mp 80-81° nmr (CCl<sub>4</sub>)  $\tau$  2.56-2.84 (m, 4, ArH), 3.27 (d, vinyl H, J=13.3 Hz), 4.13 (dd, 1, vinyl H, J=13.3 Hz and 1.0 Hz), 7.53 (m, 2, cyclopropyl H), 8.20 (m, 2, cyclopropyl H), 8.32 (m, 2, cyclopropyl H). Coupling constants :  $J_{gem} = 4.37$  Hz;  $J_{cis} = 6.95$  Hz;  $J_{trans} = 8.92$  Hz. Infrared :  $\nu_{C=O}$  (KBr) 1640 cm<sup>-1</sup>. Mass spectrum (70 ev) m/e 170.

8,8-Dideutero-4,5-Benzo-2,3-homotropone (124)

Dimethyloxosulfonium methylide-d<sub>6</sub> was prepared in dimethylsulfoxide-d<sub>6</sub> (8 ml) as previously described above from sodium hydride, 50% w/w dispersion in oil (0.616 g) and trimethyloxosulfonium-d<sub>9</sub> iodide (2.90 g). Benzotropone (2.00 g) in dimethylsulfoxide-d<sub>6</sub> (5 ml) was added to the stirring ylid solution and the reaction left at room temperature for 20 hr and then at 50° for 3 hr. The cooled reaction mixture was poured in deuterium oxide (15 ml) and the aqueous layer extracted with ether (three 25 ml portions). The combined ether extracts were washed with deuterium oxide (three 7 ml portions) and the ether dried over potassium carbonate. The ether was removed in vacuo to leave a pale yellow solid (1.75 g: 78%). The crude product was purified by column chromatography using neutral alumina (Fisher, activity 2) :

nmr ( $\text{CCl}_4$ )  $\tau$  2.57-2.84 (m, 4, ArH), 3.27 (d, 1, vinyl H,  $J=13.3$  Hz), 4.13 (dd, 1, vinyl H,  $J=13.3$  Hz and 1.0 Hz), 7.53 (bs, 2, cyclopropyl H).

Cis-4,5-Benzo-2,3:6,7-Bishomotropone (III)

Dimethyloxosulfonium methylide was prepared from sodium hydride, 50% w/w dispersion in oil (2.46 g) and trimethyloxosulfonium iodide (11.6 g) in dimethylsulfoxide (35 ml). To the stirring ylid solution was added a solution of benzotropone (4.00 g) in dimethylsulfoxide (8 ml) and the reaction mixture heated at  $55^\circ$  for 6 hr. The cooled reaction mixture was poured into water (50 ml) and the aqueous phase extracted with ether (four 25 ml portions). The combined ether extracts were washed with water (ca four 20 ml portions) until neutral to litmus and dried over potassium carbonate. The ether was removed in vacuo to leave a brown oily residue. Chromatographic separation on neutral alumina (Fisher, activity 2) eluting with a 10% petroleum ether - ether mixture gave the cis-4,5-benzo-2,3:6,7-bishomotropone (0.615 g; 14%) III. Further elution with ether gave 4,5-benzo-2,3-homotropone 124 (2.53 g; 52%).

Cis-4,5-Benzo-2,3:6,7-Bishomotropone (III) : mp  $63.5-64.5^\circ$   
 nmr ( $\text{CCl}_4$ )  $\tau$  2.71-3.01 (m, 4, ArH), 7.39 (m, 2, cyclopropyl H), 7.83 (m, 2, cyclopropyl H), 8.84 (m, 2, cyclopropyl H), 8.96 (m, 2, cyclopropyl H). Coupling Constants :  $J_{\text{gem}} = 5.01$  Hz;  $J_{\text{cis}} = 7.67$  Hz;  $J_{\text{trans}} = 6.01$  Hz. Infrared :  $\nu_{\text{C=O}}$  (KBr)

1722  $\text{cm}^{-1}$ . Mass spectrum (70 ev) m/e 184. Anal: Calcd for  $\text{C}_{13}\text{H}_{12}\text{O}$  : C, 84.75; H, 6.56. Found: C, 84.77; H, 6.56.

Cis-8,8,9,9-Tetradeutero-4,5-Benzo-2,3:6,7-Bishomotropone  
(111-D)

The same procedure was followed as in the preparation of cis-4,5-benzo-2,3:6,7-bishomotropone except the dimethyl-oxosulfonium methylide- $\text{d}_8$  was prepared from sodium hydride, 50% w/w dispersion in oil (2.46 g) and trimethyloxosulfonium iodide- $\text{d}_9$  (11.7g) in dimethylsulfoxide- $\text{d}_6$  (20 ml). The crude product was purified by column chromatography using neutral alumina (Fisher, activity 2) :

Cis-8,8,9,9-Tetradeutero-4,5-Benzo-2,3:6,7-Bishomotropone (111-D)  
nmr ( $\text{CCl}_4$ )  $\tau$  2.71-3.01 (m,4,ArH), 7.39 (d,2, cyclopropyl H  $J=10.05$  Hz), 7.83 (d,2, cyclopropyl H  $J=10.05$  Hz).

Trans-7-Hydroxy-2,3-Benzotricyclo[6.1.0.0<sup>4,6</sup>] nonane (112-OH)

Trans-4,5-benzo-2,3:6,7-bishomotropone (100 mg) was dissolved in methanol (7 ml) and water (0.35 ml) added to the solution. To the stirring solution was added sodium borohydride (50 mg) over a 1 hr period. The solution was then boiled for 5 min and poured into water (15 ml). The aqueous layer was extracted with ether (two 10 ml portions) and the combined ether extracts washed with ether (two 7 ml portions). The ether layer was dried over potassium carbonate and the ether removed in vacuo to leave a clear oil : nmr ( $\text{CDCl}_3$ )  
 $\tau$ 2.57-2.87 (m,4,ArH), 6.18 (dd,1,  $\alpha$ H  $J=6.5$  Hz and 1.0 Hz),

7.33 (bs, 1, OH), 7.81-9.81 (m, 8, cyclopropyl H).

Trans-5,5,9,9-Tetradeutero-7-Hydroxy-2,3-Benzotricyclo  
[6.1.0.0<sup>4,6</sup>] nonane (112-OH(D))

The same procedure was followed as in the reduction of trans-4,5-benzo-2,3:6,7-bishomotropone : nmr (CDCl<sub>3</sub>)  
 τ 2.57-2.87 (m, 4, ArH), 7.85-8.24 (m, 4, cyclopropyl H), 6.16 (dd, 1, α H), 7.13 (bs, 1, OH).

Trans-7-Deutero-7-Hydroxy-2,3-Benzotricyclo[6.1.0.0<sup>4,6</sup>]  
nonane (112-OH(α D))

Trans-4,5-benzo-2,3:6,7-bishomotropone (75 mg) and lithium aluminum deuteride (35 mg) were refluxed in ether (15 ml) for 1 hr. The reaction mixture was cooled and the excess LiAlD<sub>4</sub> slowly reacted by adding water (ca 10 ml). Ether (15 ml) was added to the aqueous phase and the reaction mixture stirred for ca 15 min, at which time the ether was decanted from the gelatinous precipitate. This was repeated twice more. The combined ether extracts were washed with water (10 ml) and the ether layer dried over potassium carbonate. The ether was removed in vacuo to leave a clear oil : nmr (CDCl<sub>3</sub>)  
 τ 2.57-2.87 (m, 4, ArH), 7.33 (bs, 1, OH), 7.25-9.21 (m, 8, cyclopropyl H).

Cis-7-Hydroxy-2,3-Benzotricyclo[6.1.0.0<sup>4,6</sup>]  
nonane (111-OH)

Cis-4,5-benzo-2,3:6,7-bishomotropone (65 mg) was dissolved in methanol (5.5 ml) and water (0.30 ml) added to the methanolic solution. Sodium borohydride (45 mg) was added to the stirring solution over a period of 1 hr. The solution

was boiled for ca 5 min and poured into water (15 ml). Ether extraction yielded a clear oil : nmr ( $\text{CDCl}_3$ )  $\tau$  2.56-2.86 (m,4,ArH), 5.51 (t,1, $\alpha$  H  $J=4.0$  Hz), 7.98 (m,2, cyclopropyl H), 8.34 (m,2, cyclopropyl H), 8.93 (m,2, cyclopropyl H), 9.27 (m,2, cyclopropyl H), 9.81 (bs,1,OH).

Cis-5,5,9,9-Tetradeutero-7-Hydroxy-2,3-Benzotricyclo

[6.1.0.0<sup>4,6</sup>] nonane

The same procedure was followed as in the reduction of cis-4,5-benzo-2,3:6,7-bishomotropone : nmr ( $\text{CDCl}_3$ )  $\tau$  2.56-2.86 (m,4,ArH), 5.51 (t,1, $\alpha$  H), 7.98 (d,2, cyclopropyl H), 8.34 (bd,2, cyclopropyl H).

Cis-7-Deutero-7-Hydroxy-2,3-Benzotricyclo [6.1.0.0<sup>4,6</sup>] nonane

(111-OH ( $\alpha$ D))

The same procedure was followed as in the reduction of trans-4,5-benzo-2,3:6,7-bishomotropone using lithium aluminum deuteride : nmr ( $\text{CDCl}_3$ )  $\tau$  2.56-2.86 (m,4,ArH), 7.98 (m,2, cyclopropyl H), 8.34 (m,2, cyclopropyl H), 8.93 (m,2, cyclopropyl H), 9.27 (m,2, cyclopropyl H), 9.81 (bs,1,OH).

6-Hydroxy-2,3-Benzobicyclo[5.1.0]oct-4-ene (124-OH)

4,5-Benzo-2,3-homotropone (800 mg) was dissolved in methanol (35 ml) and water (2.0 ml) added to the solution. To the stirring solution was added sodium borohydride (200 mg) over a 2 hr period. The solution was then boiled for 10 min and poured into water (25 ml). The aqueous phase was extracted with ether (three 20 ml portions) and the combined ether extracts washed with water (two 20 ml portions). The ether

layer was dried over potassium carbonate and the ether removed in vacuo to leave a white solid (690 mg: 86%). The spectral properties were identical to those previously reported<sup>59</sup>:

mp 110-111° nmr (CDCl<sub>3</sub>)  $\tau$  2.75-3.06 (m,4,ArH), 3.75 (d,1, vinyl H, J=12.2 Hz), 4.40 (dt,1, vinyl H, J=12.2 Hz, 2.5 Hz and 1.8 Hz), 5.12 (dd,1,  $\alpha$  H, J=2.5 Hz and 2.0 Hz), 7.91 (m,1, cyclopropyl H), 8.04 (m,1, cyclopropyl H), 8.17 (m,1, cyclopropyl H), 9.07 (m,1, cyclopropyl H).

8,8-Dideutero-6-Hydroxy-2,3-Benzobicyclo[5.1.0]oct-4-ene  
(112-OH(D))

The same procedure was followed in the reduction of 8,8-dideutero-4,5-benzo-2,3-homotropone as was used for 4,5-benzo-2,3-homotropone : nmr (CDCl<sub>3</sub>)  $\tau$  2.75-3.06 (m,4,ArH), 3.75 (d,1, vinyl H, J=12.2 Hz), 4.40 (dt,1, vinyl H, J=12.2 Hz, 2.5 Hz and 1.8 Hz), 5.12 (dd,1,  $\alpha$  H, J=2.5 Hz and 2.5 Hz), 7.91 (d,1, cyclopropyl H, J=8.0 Hz), 8.04 (bt,1, cyclopropyl H, J=8.0 Hz, 2.0 Hz and 1.8 Hz).

6-Deutero-6-Hydroxy-2,3-Benzobicyclo[5.1.0]oct-4-ene  
(124-OH( $\alpha$  D))

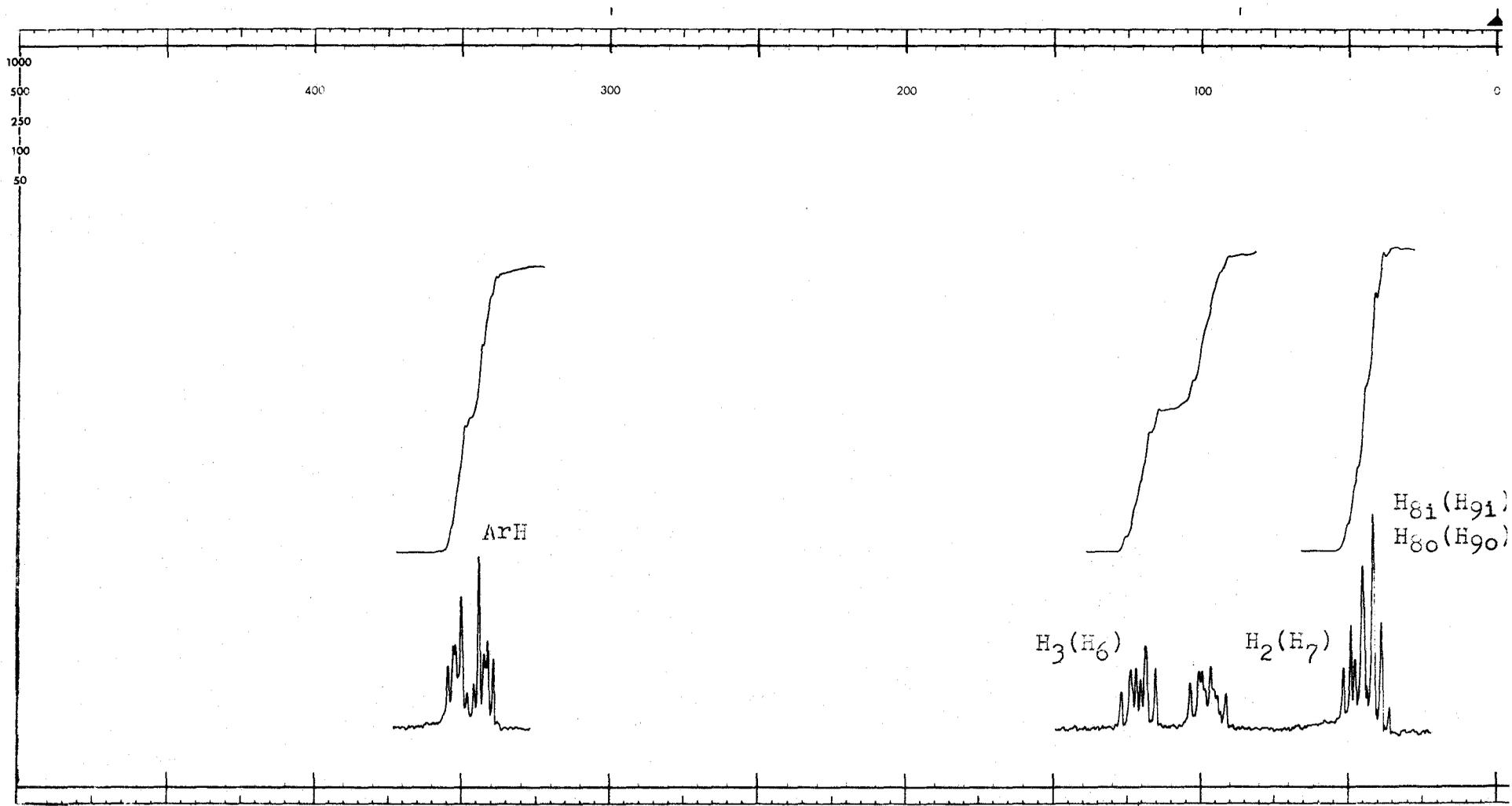
4,5-Benzo-2,3-homotropone (250 mg) and lithium aluminum deuteride (50 mg) were refluxed in ether (25 ml) for 1 hr. The reaction mixture was cooled and the excess LiAlD<sub>4</sub> slowly reacted by adding water (20 ml). Ether (25 ml) was added to the aqueous phase and the reaction mixture stirred for 15 min at which time the ether was decanted from the gelatinous precipitate. This was repeated twice more. The combined ether extracts were washed with water (10 ml) and the ether layer dried over potassium carbonate. The ether

was removed in vacuo to leave a white solid : nmr ( $\text{CDCl}_3$ )  
 $\tau$  2.75-3.06 (m, 4, ArH), 3.75 (d, 1, vinyl H  $J=12.2$  Hz), 4.40  
(dd, 1, vinyl H  $J=12.2$  Hz and 1.8 Hz), 7.91 (m, 1, cyclopropyl H),  
8.04 (m, 1, cyclopropyl H), 8.17 (m, 1, cyclopropyl H), 9.07  
(m, 1, cyclopropyl H).

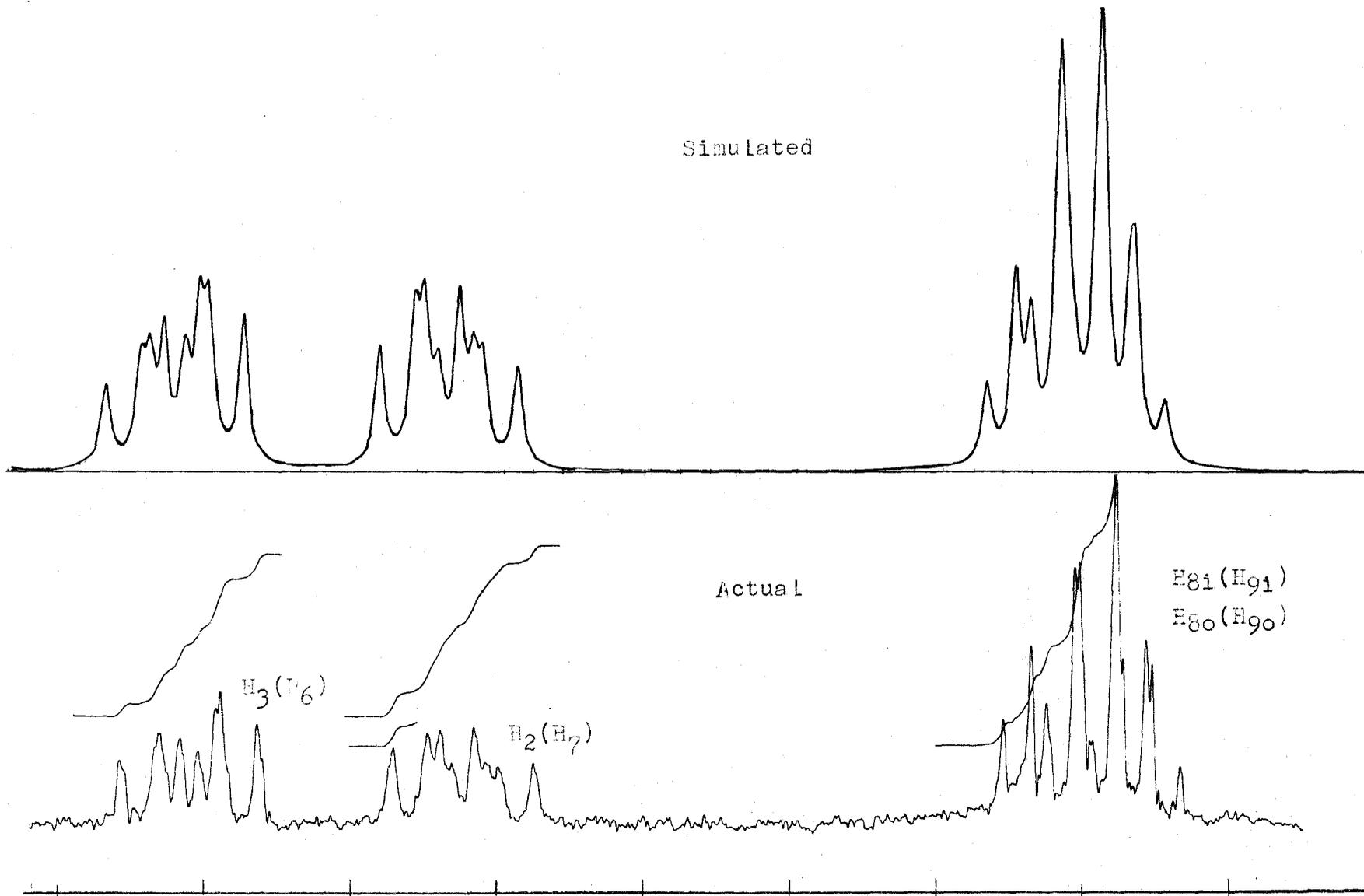
### 2,3-Homotropone (38)

This procedure is essentially the same as that used  
by Houk<sup>110</sup>. Tropone (1.06 g) and diazomethane (from 2.3 g of  
diazald) were allowed to react in ether at 5° for 6 days. The  
ether was removed in vacuo to give a pale yellow oil. Column  
chromatography on neutral alumina (Fisher, activity 2) eluting  
with ether gave pure 2,3-homotropone (135 mg; 11%). The  
spectral properties were identical to those previously reported<sup>59</sup>:  
nmr ( $\text{CCl}_4$ )  $\tau$  3.50 (dd, 1, vinyl H), 3.79 (dd, 1, vinyl H), 4.19  
(d, 1, vinyl H), 4.32 (dd, 1, vinyl H), 7.65 (m, 1, cyclopropyl H),  
8.19 (m, 2, cyclopropyl H), 8.50 (m, 1, cyclopropyl H).

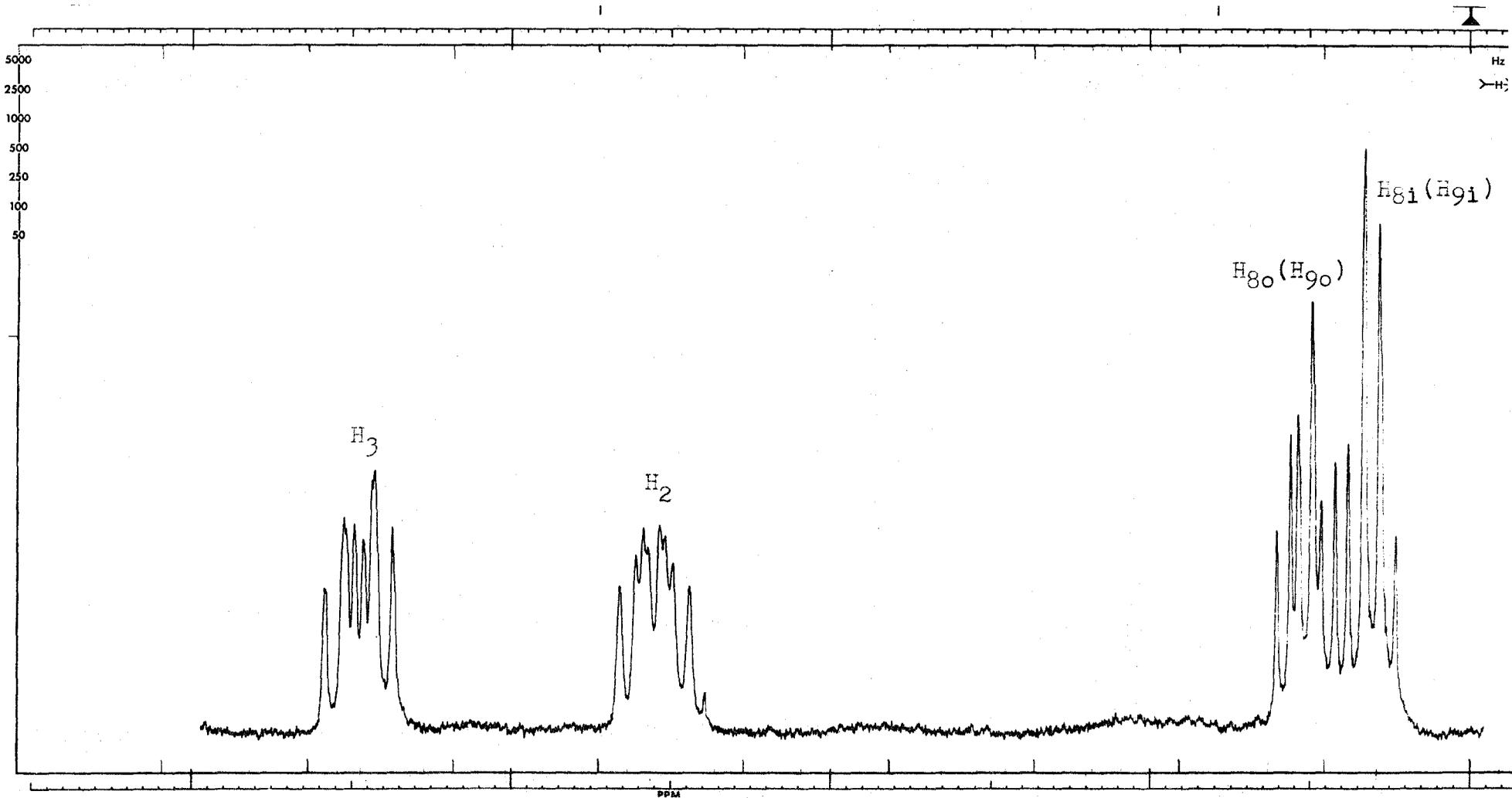
SPECTRA



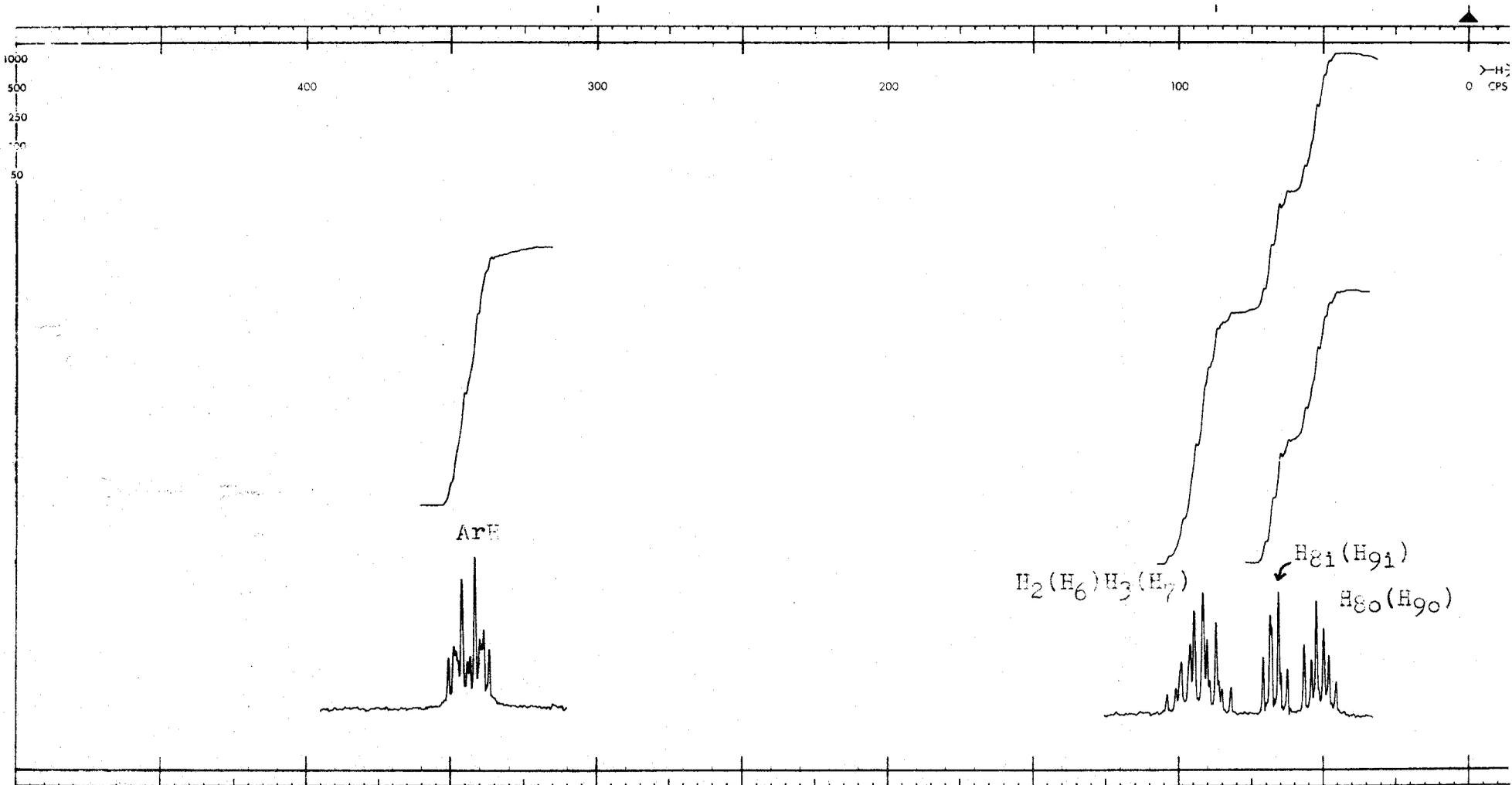
Spectrum I : Cis-4,5-Benzo-2,3:6,7-Bishomotropone III (CCl<sub>4</sub>)



Spectrum 2 : Simulated and Actual Spectrum of the Cyclopropyl Resonances of 4,5-Benzo-2,3:6,7-Bishomotropone 111 (CCl<sub>4</sub>)

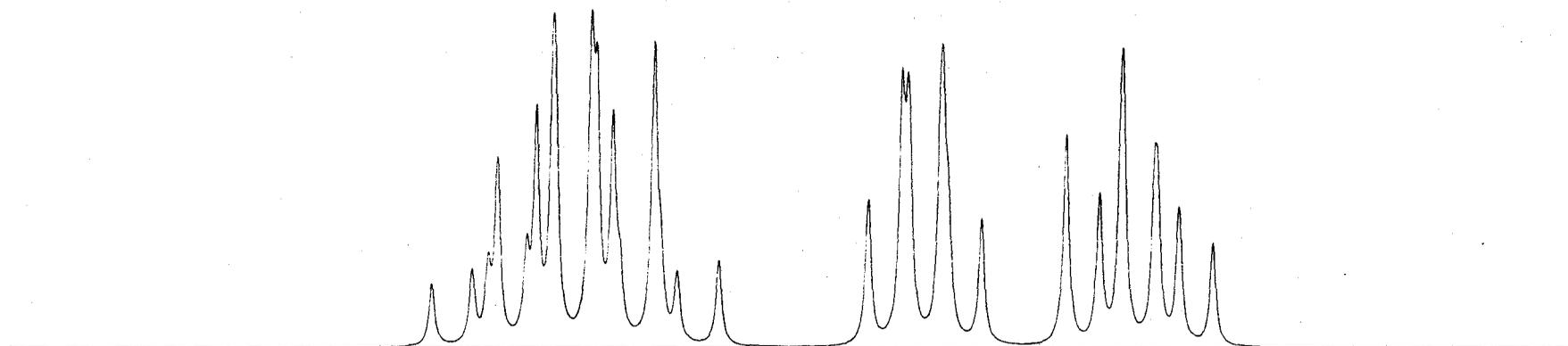


Spectrum 3 : 220 MHz nmr Spectrum of the Cyclopropyl Resonances of  
Cis-4,5-Benzo-2,3:6,7-Bishomotropone 111 (CCl<sub>4</sub>)



Spectrum 4 : Trans-4,5-Benzo-2,3:6,7-Bishomotropone 112 (CCl<sub>4</sub>)

Simulated



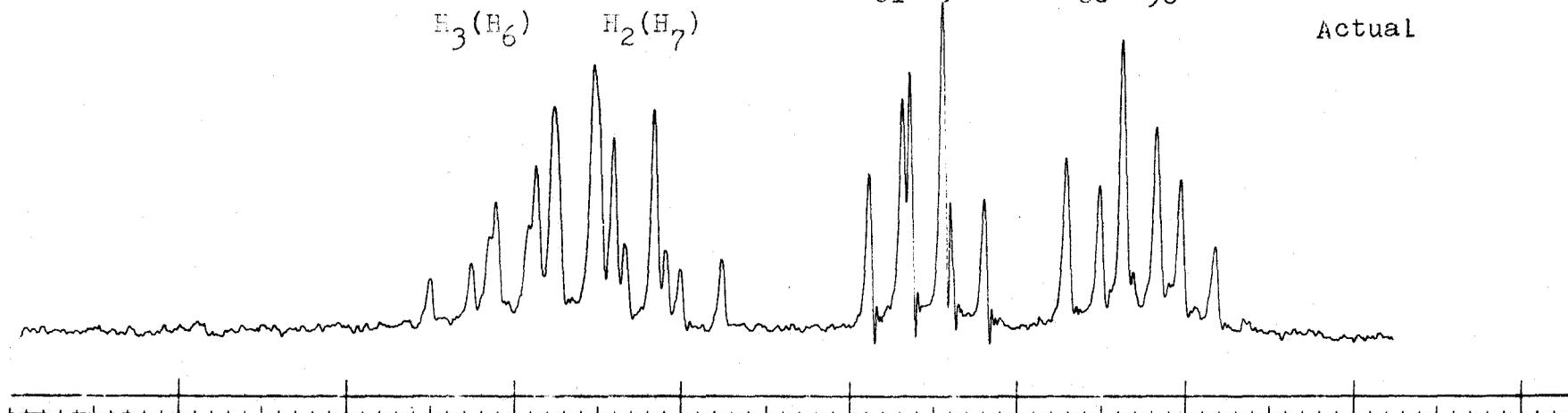
H<sub>3</sub>(H<sub>6</sub>)

H<sub>2</sub>(H<sub>7</sub>)

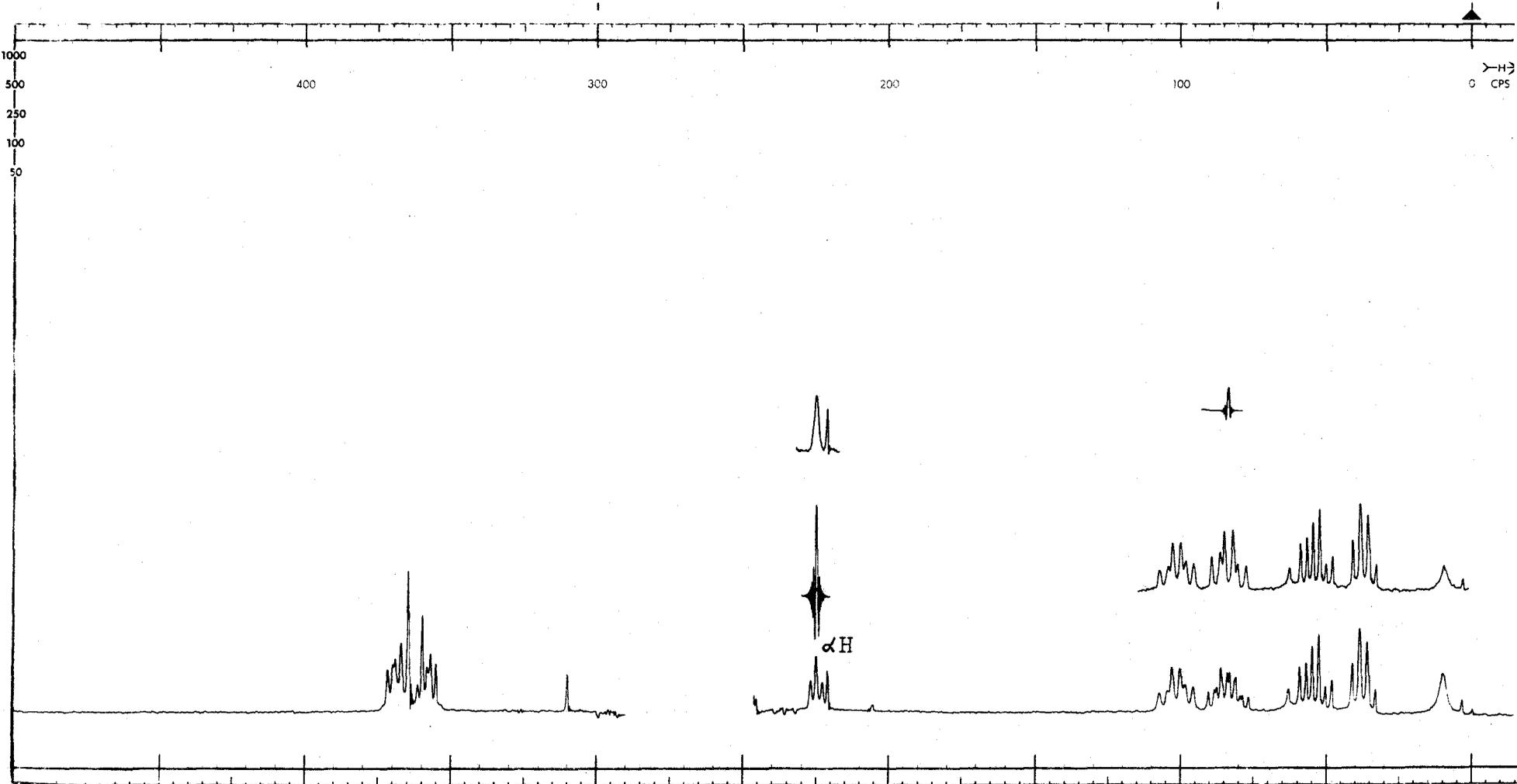
H<sub>81</sub>(H<sub>91</sub>)

H<sub>80</sub>(H<sub>90</sub>)

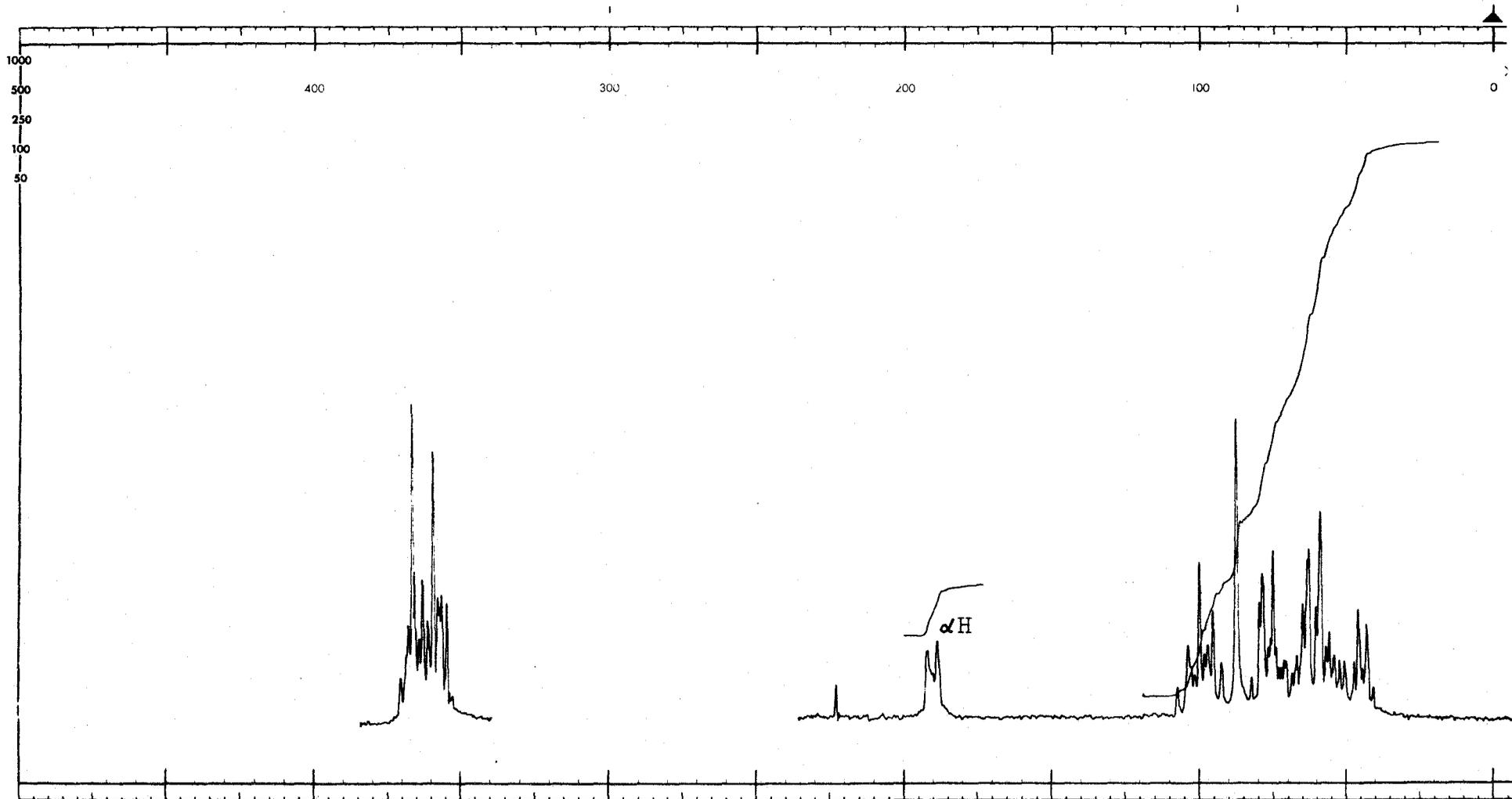
Actual



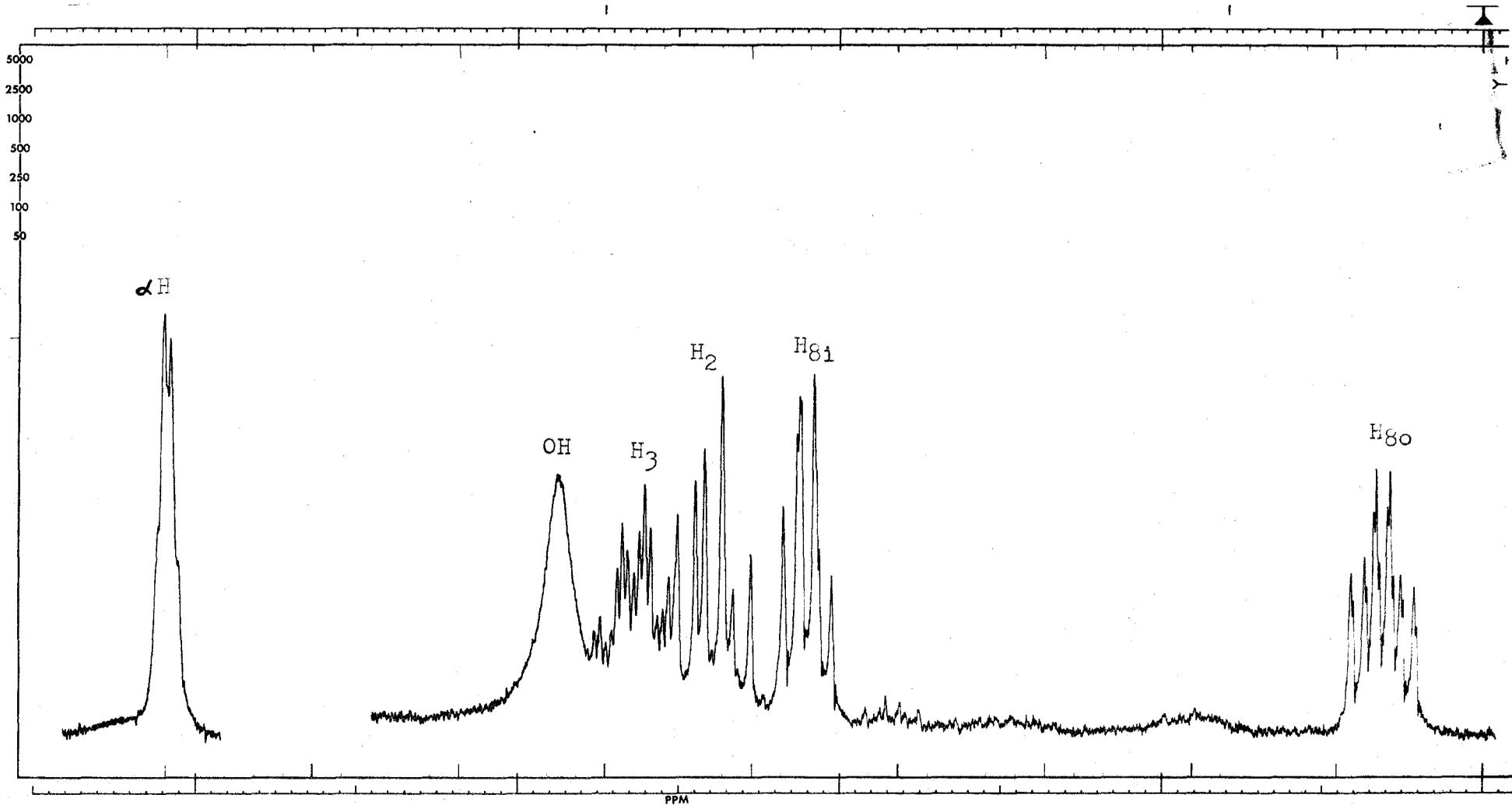
Spectrum 5 : Simulated and Actual nmr Spectrum of the Cyclopropyl Resonances of Trans-4,5-Benzo-2,3:6,7-Bishomotropone 112 (CCl<sub>4</sub>)



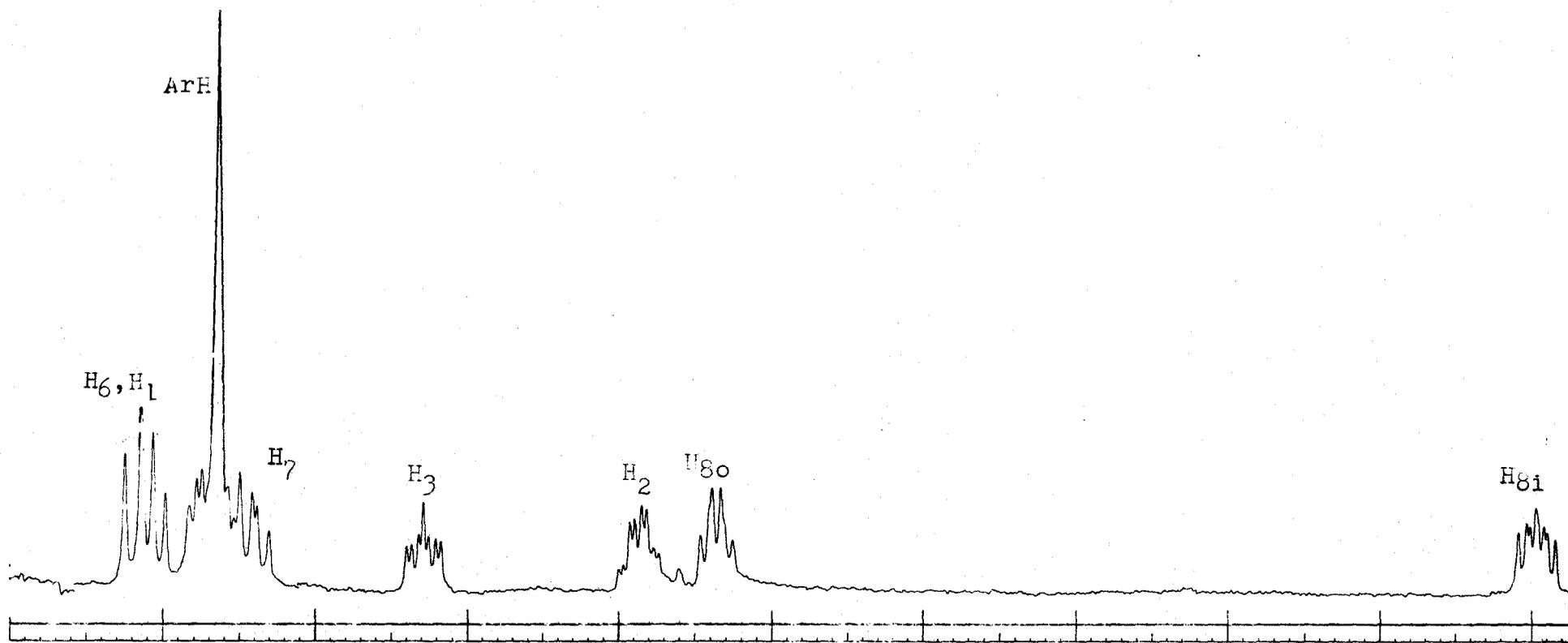
Spectrum 6 : Cis-7-Hydroxy-2,3-Benzotricyclo [6.1.0.0<sup>4,6</sup>] nonane (111-OH) (CDCl<sub>3</sub>)



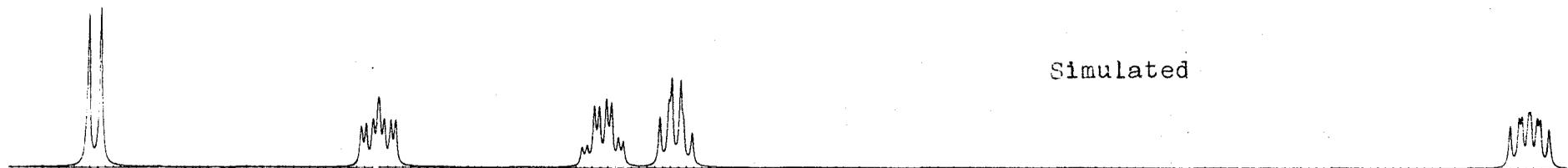
Spectrum 7 : Trans-7-Hydroxy-2,3-Benzotricyclo [6.1.0.0<sup>4,6</sup>] nonane (112-OH) (CDCl<sub>3</sub>) 150



Spectrum 8 : 220 MHz nmr Spectrum of the Cyclopropyl and  $\alpha$  Hydrogen Resonances of 7-Hydroxy-3,4-Benzocycloheptatriene (CDCl<sub>3</sub>)



Spectrum 9 : 4,5-benzo-2,3-fomotroponium Cation [4] FSO<sub>3</sub>H-SO<sub>2</sub>ClF -50°



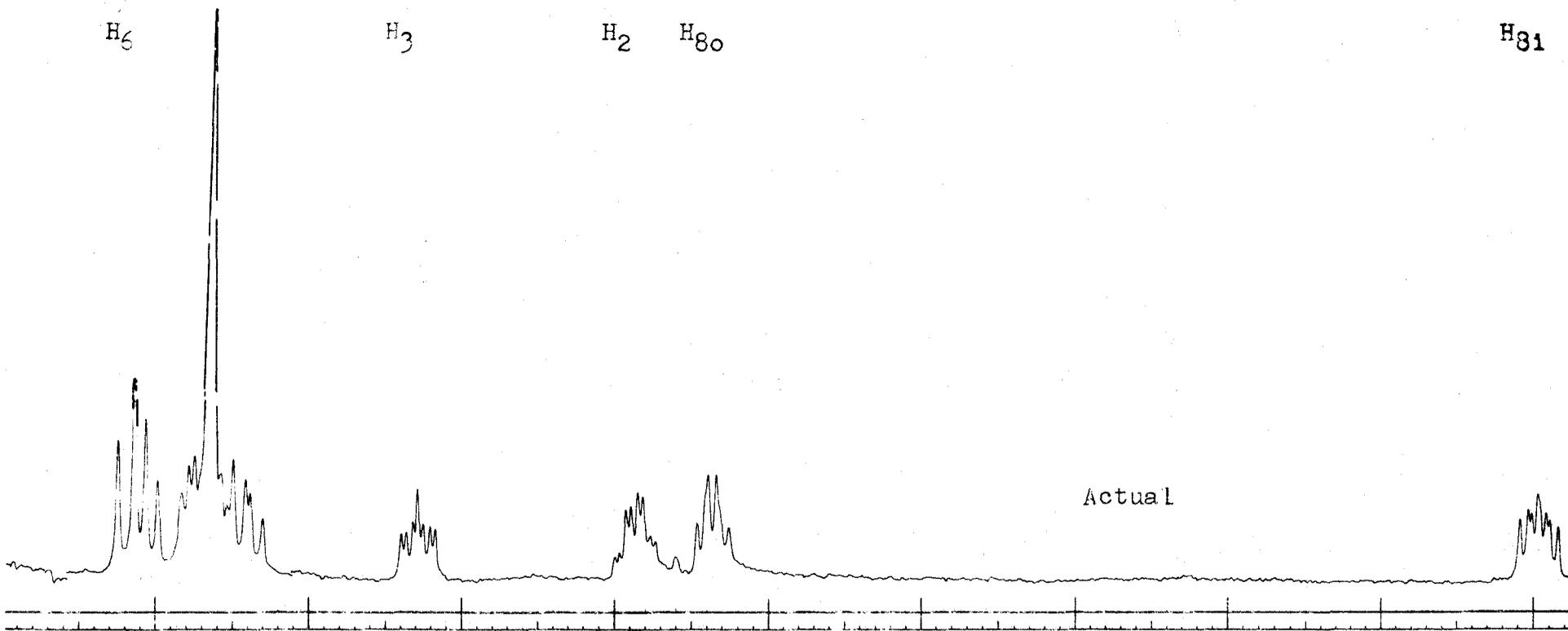
H<sub>6</sub>

H<sub>3</sub>

H<sub>2</sub>

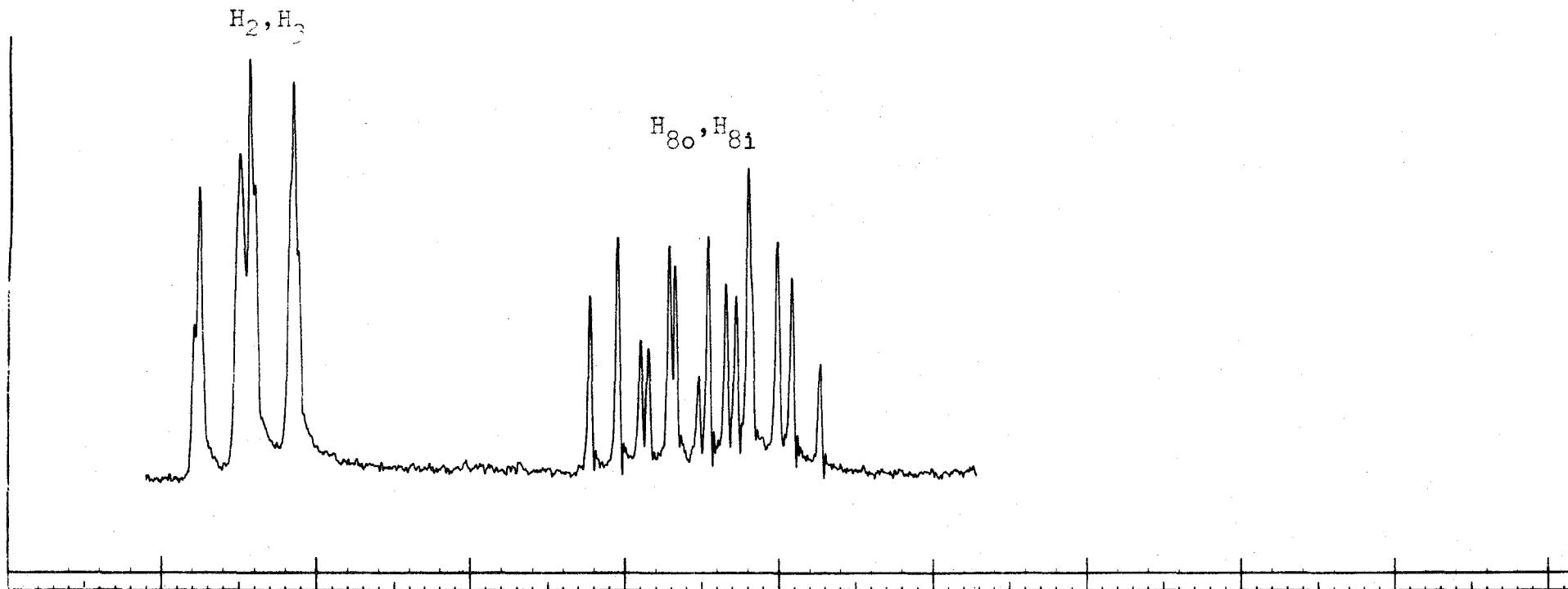
H<sub>80</sub>

H<sub>81</sub>

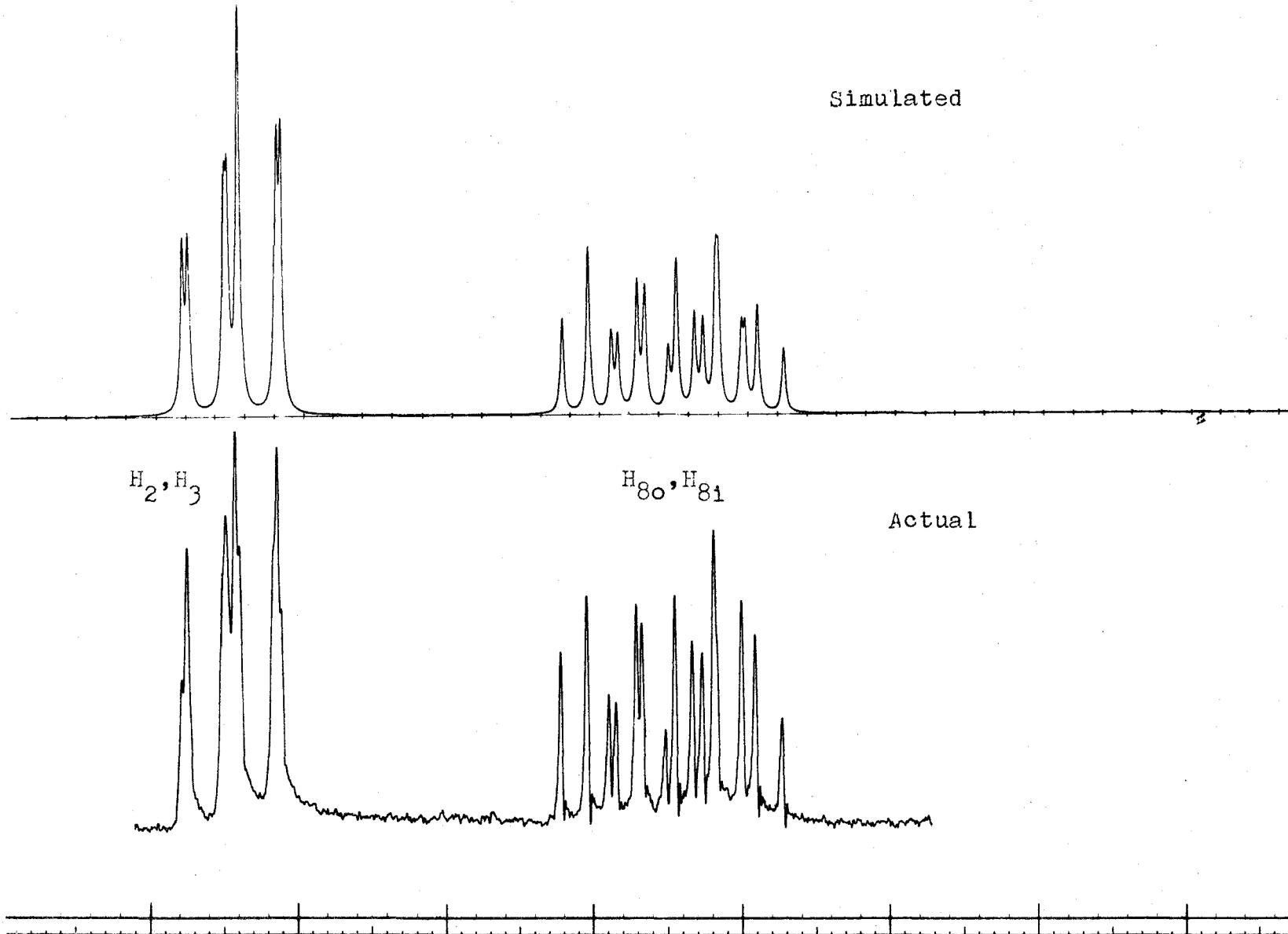


Actual

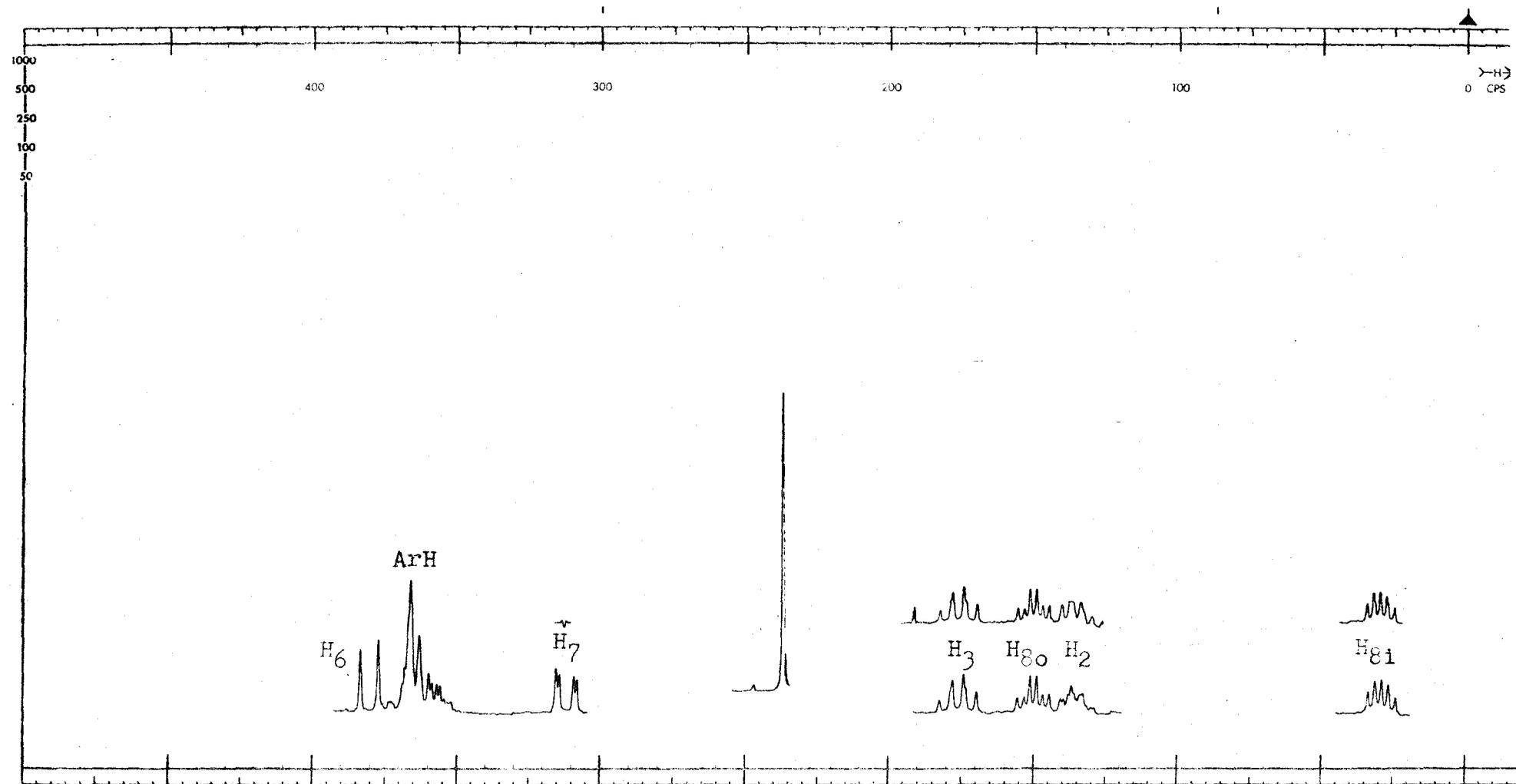
Spectrum 10 : Simulated and Actual nmr Spectrum of 4,5-Benzo-2,3-Homotropylium  
Cation 141. (H<sub>1</sub> and H<sub>7</sub> are not included)



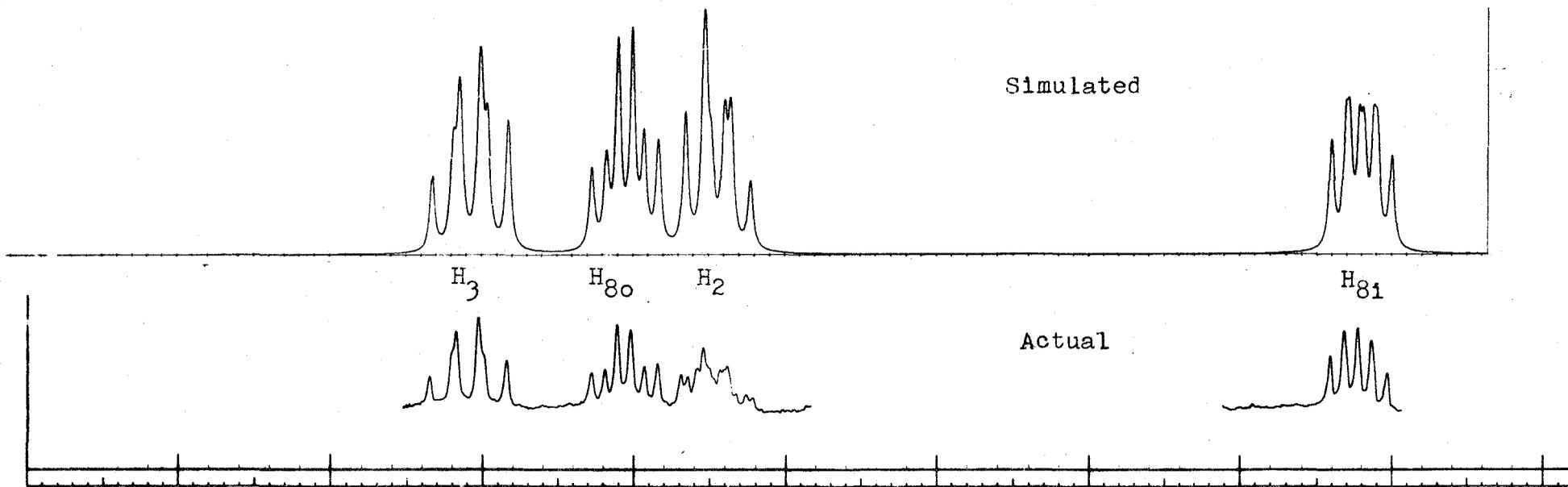
Spectrum 11 : Cyclopropyl Resonances of 4,5-Benzo-2,3-Homotropone 124 (CCl<sub>4</sub>)



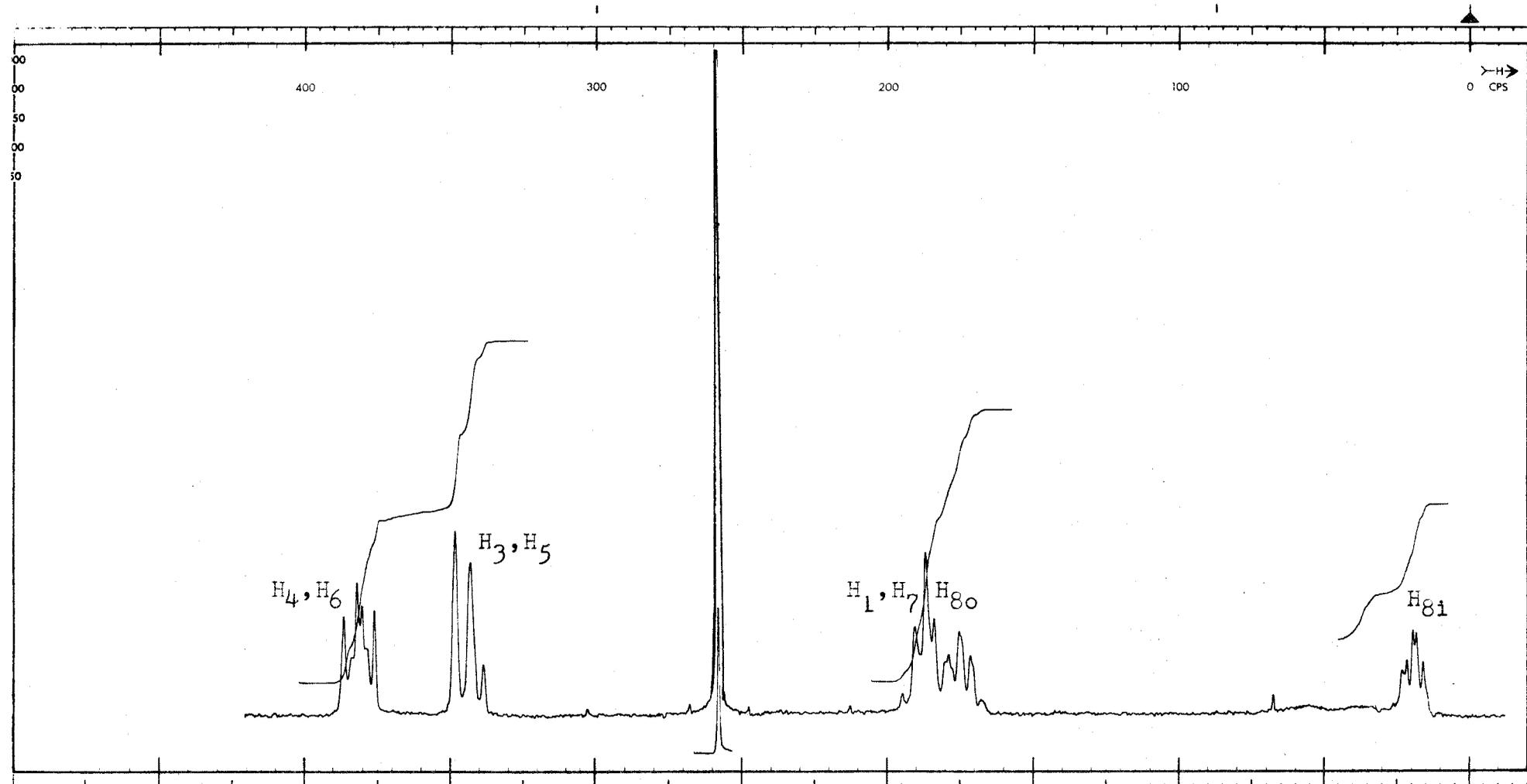
Spectrum 12 : Simulated and Actual nmr Spectrum of 4,5-Benzo-2,3-Homotropone 124



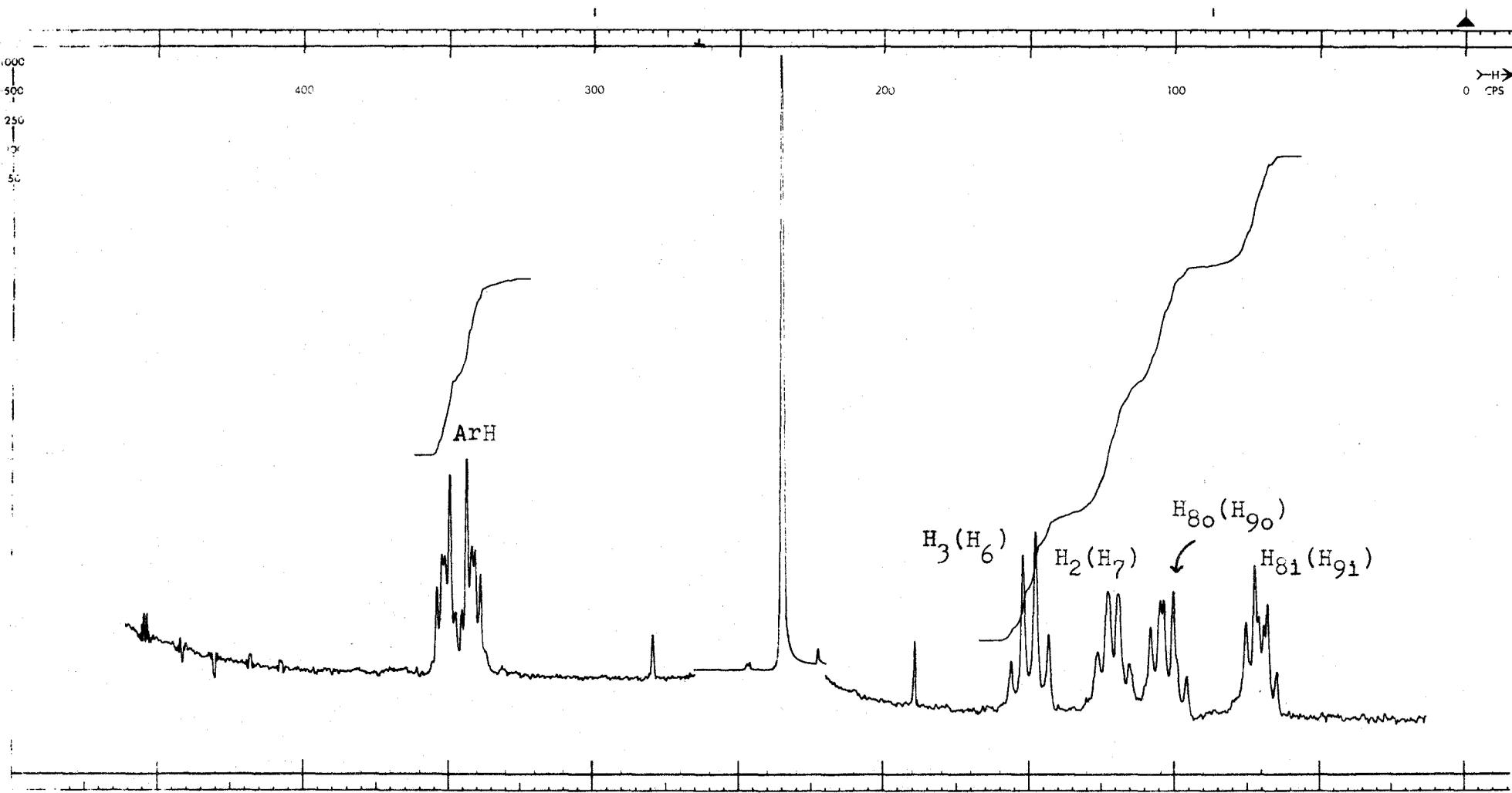
Spectrum 13 : 1-Hydroxy-4,5-Benzo-2,3-Homotropylum Cation 142 FSO<sub>3</sub>H -20°



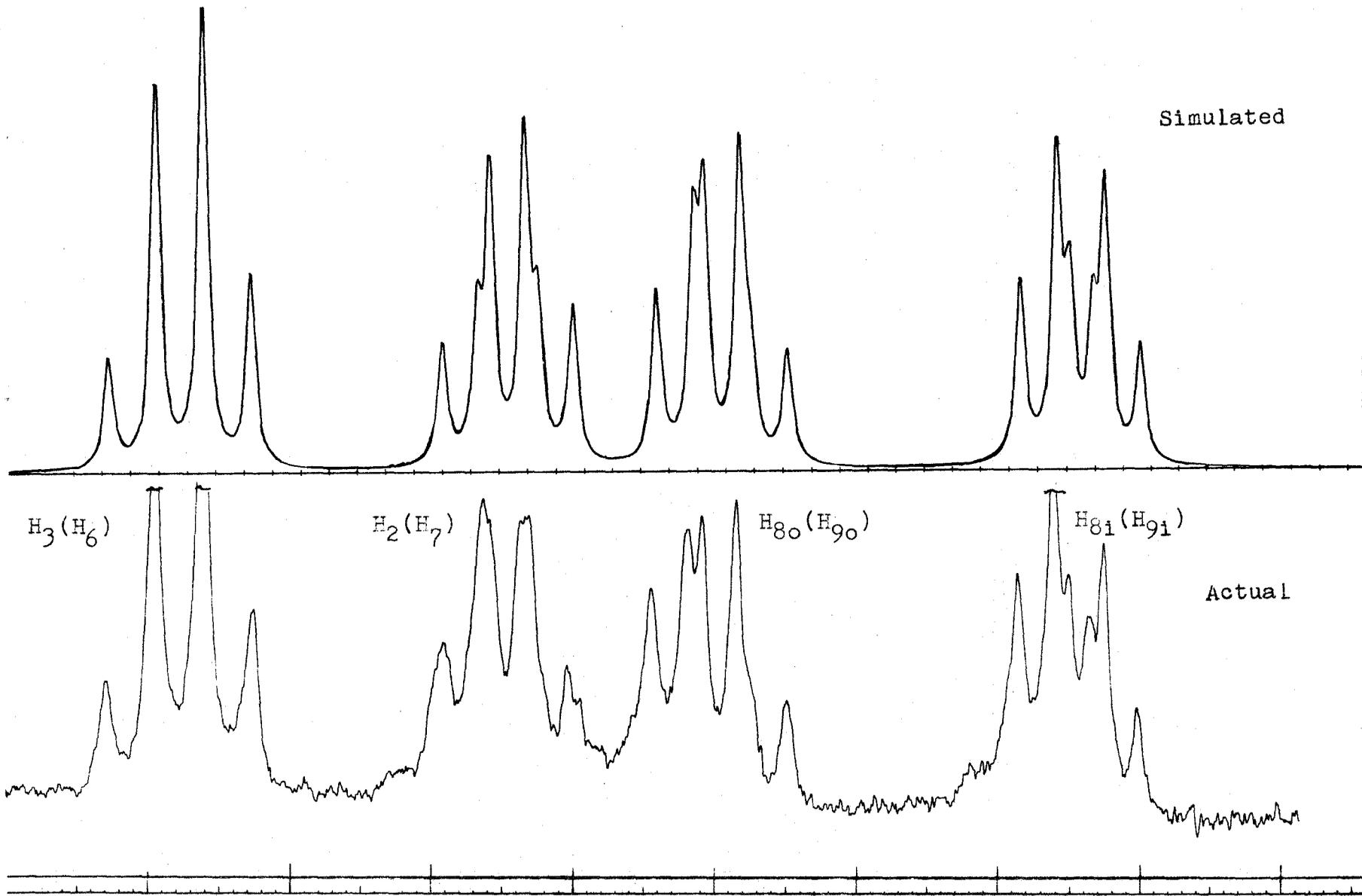
spectrum 14 : Simulated and Actual nmr Spectrum of 1-Hydroxy-4,5-Benzo-2,3-Homotropylium Cation 142 (J<sub>27</sub> is not included)



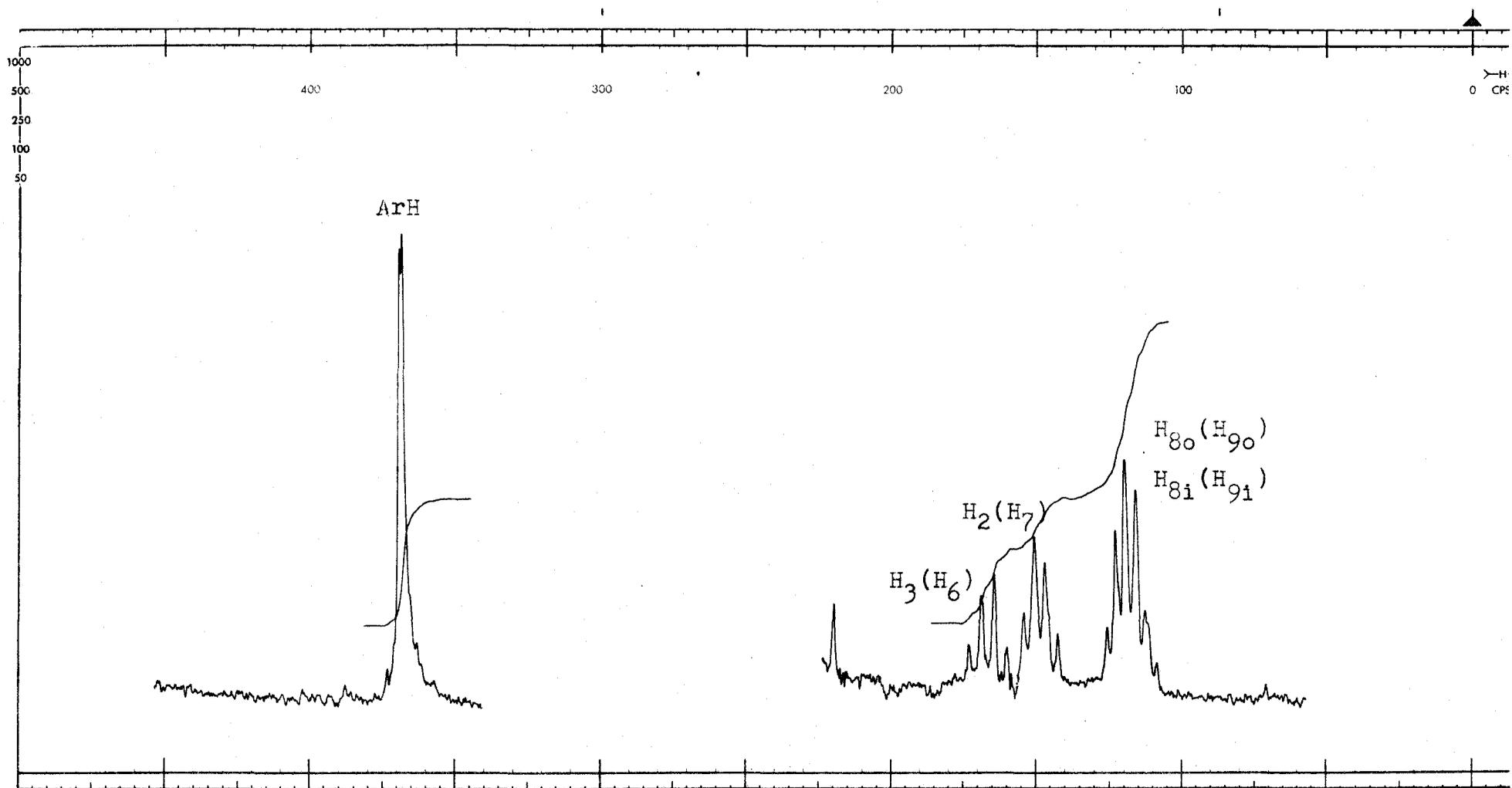
Spectrum 15 : 2-Hydroxy-Homotropylum Cation 39 FSO<sub>3</sub>H +37°



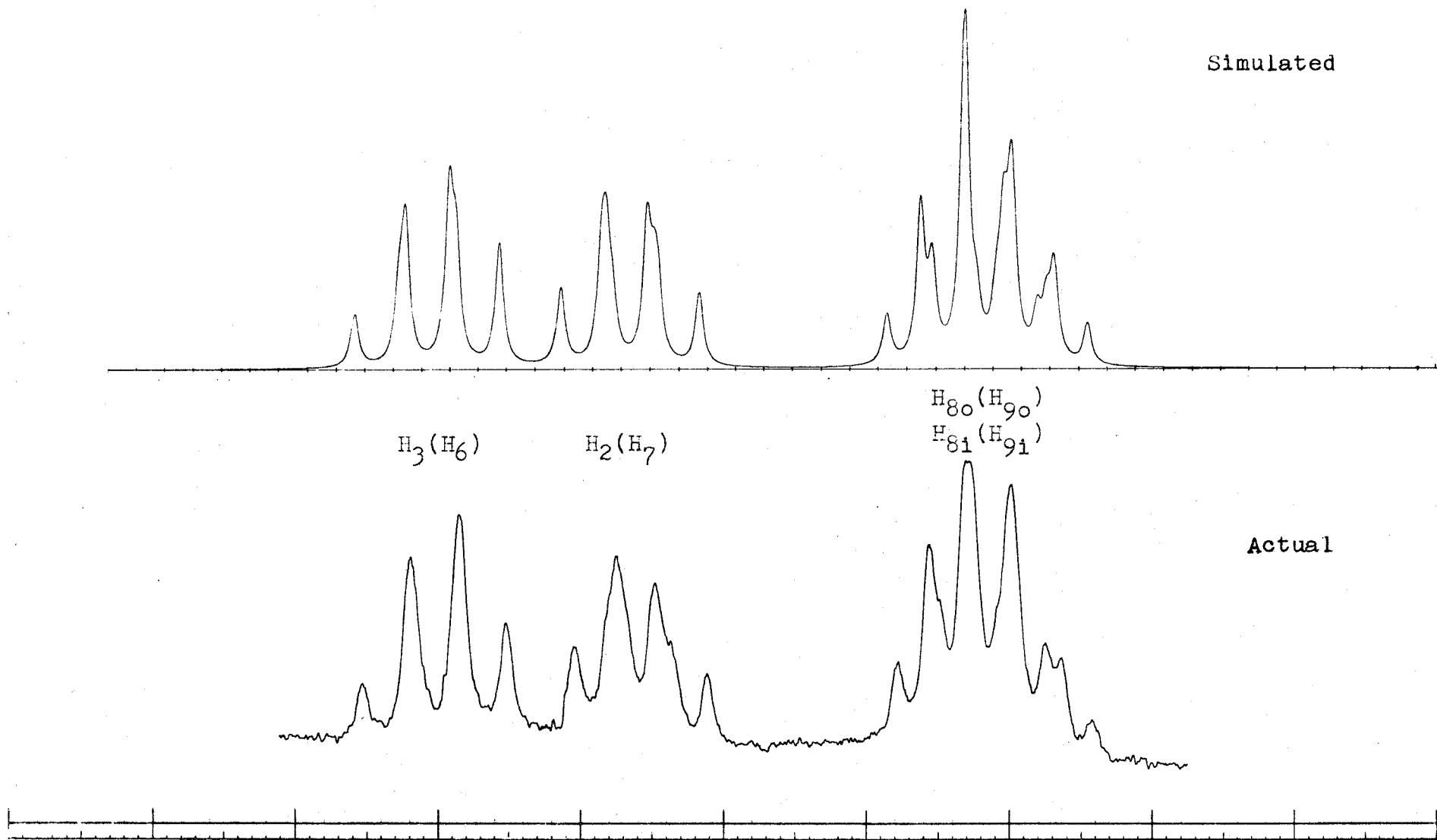
Spectrum 16 : Cis-1-Hydroxy-4,5-Benzo-2,3:6,7-Bishomotropanylium Cation 143  
FSO<sub>3</sub>H -20°



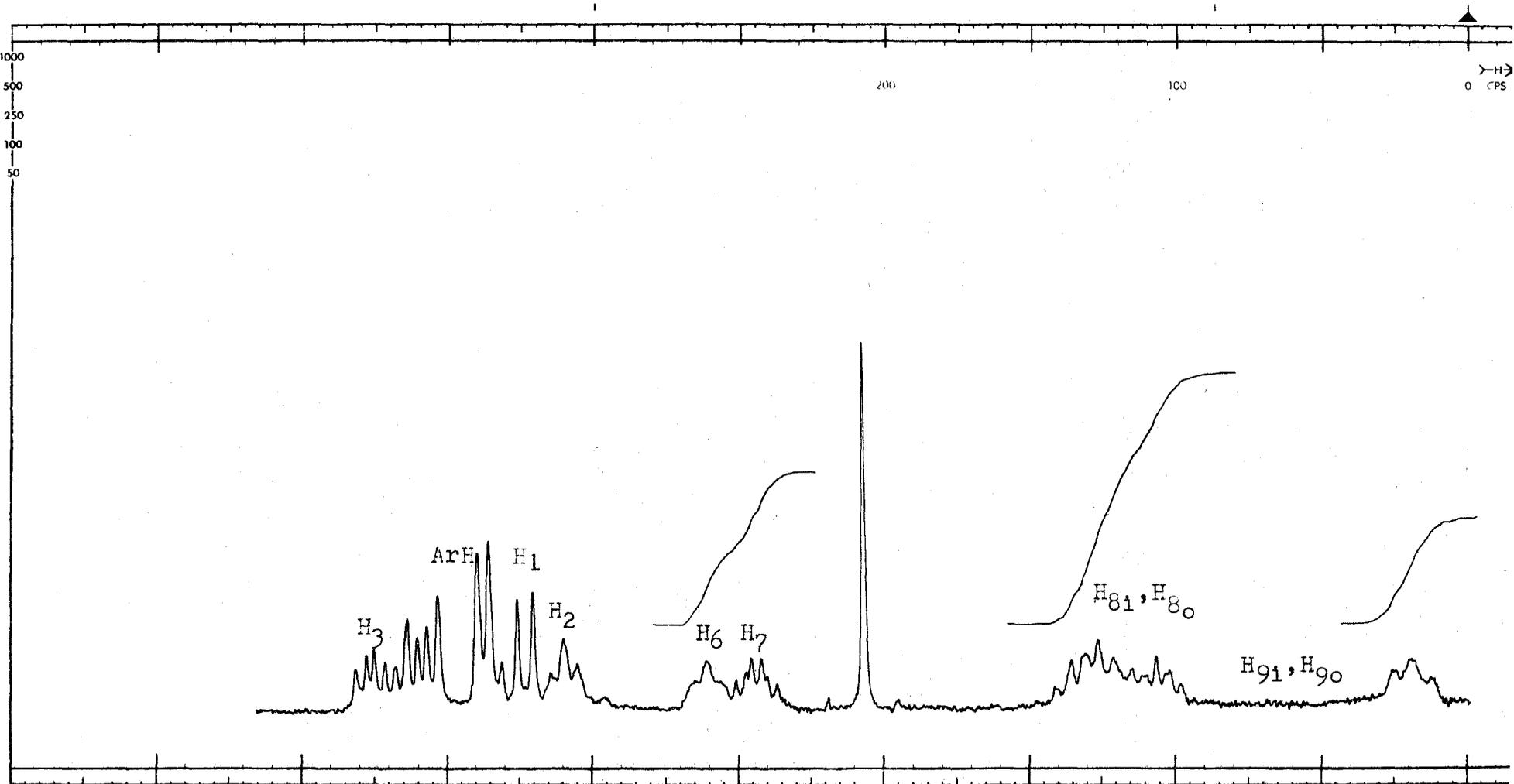
Spectrum 17 : Simulated and Actual nmr Spectrum of the Cyclopropyl Resonances of Cis-1-Hydroxy-4,5-Benzo-2,3:6,7-Bishomotropylium Cation 143



Spectrum 18 : Trans-1-Hydroxy-4,5-Benzo-2,3:6,7-Bishomotropylium Cation 144  
FSO<sub>3</sub>H -20°



Spectrum 19 : Simulated and Actual nmr Spectrum of Cyclopropyl Resonances of Trans-1-Hydroxy-4,5-Benzo-2,3:6,7-Bishomotropylium Cation 144



Spectrum 20 : Trans-4,5-Benzo-2,3:6,7-Bishomotroplium Cation 146 FSO<sub>3</sub>H-SO<sub>2</sub>ClF -75° 163

## BIBLIOGRAPHY

1. S. Winstein, J. Amer. Chem. Soc., 81, 6524 (1959).
2. S. Winstein and R. Adams, ibid., 70, 838 (1948); S. Winstein, H.M. Walborsky and K. Schriber, ibid., 72, 5795 (1950); M. Simonetta and S. Winstein, ibid., 76, 18 (1954).
3. S. Winstein, J. Sonnenberg and L. de Vries, ibid., 81, 6523 (1959).
4. E.J. Corey and R.L. Dawson, ibid., 85, 1782 (1963); E.J. Corey and H. Uda, ibid., 85, 1788 (1963); P.K. Freeman, M.F. Crostic and F.A. Raymond, J. Org. Chem., 30, 771 (1965).
5. S. Winstein, E.C. Friedrich, R. Baker and Yang Lin, Tetrahedron Lett., Suppl. 8, Part 2, 621 (1966); P.G. Gassman and F.V. Zalar, J. Amer. Chem. Soc., 88, 2252 (1966); W.J. Le Noble and B.L. Yates, P.395 of abstracts of the 50th Meeting of A.C.S., Atlanta City, N.J., Sept. 13-17 (1965).
6. S. Winstein, Chem. Soc. Spec. Publ., 21, 5 (1967); S. Winstein, Quart. Rev. Chem. Soc., 23, 141 (1969).
7. (a) G.M. Badger, "Aromatic Character and Aromaticity", Cambridge University Press (1969).  
(b) "Aromaticity, Pseudo-Aromaticity and Anti-Aromaticity", The Jerusalem Symposia on Quantum Chemistry and Biochemistry, Vol. III, Edt. E.D. Bergman and B. Pullman, Academic Press Inc., New York, N.J. (1971).
8. L. Pauling, J. Chem. Phys., 4, 673 (1936).
9. L. Salem, "The Molecular Orbital Theory of Conjugated Systems", Benjamin, New York, N.Y. (1966); J.N. Murrell, S.F.A. Kettle and J.M. Tedder, "Valency Theory", John Wiley and Sons Ltd., New York, N.Y. (1965).
10. G.W. Wheland, "Resonance in Organic Chemistry", John Wiley and Sons Ltd., New York, N.Y. (1955).
11. E. Hückel, Z. Physik., 70, 204 (1931), 76, 628 (1932), Z. Electrochem., 43, 752, 827 (1937).
12. (a) R. Breslow, Chem. Eng. News, 43, 90 (1965).  
(b) E. Heilbronner, Tetrahedron Lett., 1923 (1964).

13. R. Breslow and C. Yuan, J. Amer. Chem. Soc., 80, 599 (1958); R. Breslow and H. Höver, ibid., 82, 2644 (1960).
14. W.E. Doering and L.H. Knox, ibid., 76, 3203 (1954); W.E. Doering and H. Krauch, Angew. Chem., 68, 661 (1956).
15. J.H. Elvidge and L.M. Jackman, J. Amer. Chem. Soc., 83, 859 (1961); G.G. Hall, A. Hardisson and L.M. Jackman, Tetrahedron Lett., Vol. 19, Suppl. 2, 101 (1963).
16. J.I. Musher, J. Chem. Phys., 43, 4081 (1965), 46, 1219 (1967).
17. J.A. Pople, ibid., 41 2559 (1964); A.F. Ferguson and J.A. Pople, ibid., 42, 1560 (1965).
18. R.J. Abraham and W.A. Thomas, J. Chem. Soc., (B), 127 (1966).
19. H.J. Dauben, Jr., J.D. Wilson and J.L. Laity, J. Amer. Chem. Soc., 90, 811 (1968), 91, 1991 (1969).
20. J.D. Roberts, A. Streitweiser and C.M. Regan, ibid., 74, 4579 (1952); S.L. Meatt and J.D. Roberts, J. Org. Chem., 24, 1336 (1959).
21. (a) R.B. Woodward and R. Hoffman, Angew. Chem. Int. Ed. Engl., 8, 781 (1969).  
(b) M.J. Goldstein and R. Hoffmann, J. Amer. Chem. Soc., 93, 6193 (1971).
22. M.J.S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., (1969); K. Fukui, Fortsch. Chem. Forsch., 15, 1 (1970); L. Salem, J. Amer. Chem. Soc., 90, 543, 553 (1968).
23. J.B. Conn, G.B. Kistiakowsky and A. Smith, ibid., 61, 1868 (1939); R.B. Turner, W.R. Meador, W.E. Doering, L.H. Knox, J.R. Mayer and D.W. Wiley, ibid., 79, 4127 (1957).
24. W.E. Doering, G. Laber, R. van Derwahl N.F. Chamberlain and R.B. Williams, ibid., 78, 5448 (1956).
25. W.R. Roth, W.P. Bang, P. Goebel, R.L. Sass, R.B. Turner and A.P. Yu, ibid., 86, 3178 (1964).
26. P. Bischoff, R. Gleiter and E. Heilbronner, Helv. Chim. Acta., 53, 1425 (1970).

27. J.L. Von Rosenberg, J.E. Mahler and R. Pettit, J. Amer. Chem. Soc., 84, 2842 (1962).
28. M. Brookhart, M. Ogliaruso and S. Winstein, ibid., 89, 1965 (1967).
29. N.C. Deno, H.G. Richey, Jr., J.S. Lu, D.N. Lincoln and J.O. Turner, ibid., 87, 4535 (1965).
30. N.C. Deno, Prog. Phys. Org. Chem., 2, 129 (1964).
31. S. Winstein, H.D. Kaesz, C.G. Kreiter and E.C. Friedrich, J. Amer. Chem. Soc., 89, 3267 (1965).
32. G.N. Schrauzer, ibid., 83, 2966 (1961); A. Davidson, W. McFarlane, L. Pratt and G. Wilkinson, ibid., 84, 4821 (1962).
33. P. Warner, D.L. Harris, C.H. Bradley and S. Winstein, Tetrahedron Lett., 4013 (1970).
34. M. Roberts, H. Hamberger and S. Winstein, J. Amer. Chem. Soc., 92, 6346 (1970).
35. P. Warner and S. Winstein, ibid., 94, 2280 (1972).
36. C.U. Pittman, Jr. and G.A. Olah, J. Amer. Chem. Soc., 87, 2998, 5123 (1965); Z. Majerski and P. v. R. Schleyer, ibid., 93, 665 (1961); Y.E. Rhodes and V.G. DiFate, ibid., 94, 7582 (1972); B.A. Hess and A.J. Ashe in "Carbonium Ions", Vol. III, G.A. Olah and P.v.R. Schleyer Edt., Interscience, New York, N.Y. (1973).
37. J.D. Graham and M.T. Rogers, J. Amer. Chem. Soc., 84, 2249 (1962); Aksel A. Bothner-By in "Adv. in Magnetic Resonance", Vol. I, J.S. Waugh Edt., Academic Press, New York, N.Y. (1965).
38. G.A. Olah, D.P. Kelly, C.L. Jeuell and R.D. Porter, J. Amer. Chem. Soc., 92, 2544 (1970).
39. J.M. Bollinger, M.B. Comisarow, C.A. Cupas and G.A. Olah, ibid., 89, 5687 (1967).
40. G.E. Maciel, J.W. McIver, Jr., N.S. Ostlund and J.A. Pople, ibid., 92, 1 (1970); N.H. Werstuik, personal communication.
41. I.S. Isaev, V.I. Mamatyuk, T.G. Egorova, L.I. Kuzubova and V.A. Koptuyug, Izv. Akad. Nauk. SSSR, Ser. Khim., 2089 (1969).

42. S. Winstein, C.G. Krieter and J.I. Brauman, J. Amer. Chem. Soc., 88, 2047 (1966); J.A. Berson and J.A. Jenkins, ibid., 94, 8907 (1972).
43. N.C. Deno, H.G. Richey, Jr., J.D. Hodge and M.J. Wisotsky, ibid., 84, 1498 (1962); N.C. Deno and C.U. Pittman, Jr., ibid., 86, 1871 (1964); N.C. Deno, C.U. Pittman, Jr. and J.O. Turner, ibid., 87, 2153 (1969)
43. N.C. Deno, et. al., ibid., 87, 2153 (1965), 86, 1971 (1964), 84, 1498 (1962).
44. A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", John Wiley and Sons Inc., New York, N.Y., (1961), P.228.
45. H.J. Dauben, Jr., J.D. Wilson and J.L. Laity, J. Amer. Chem. Soc., 91, 1991 (1969).
46. C.E. Keller and R. Pettit, ibid., 88, 604 (1966).
47. M. Brookhart, M. Ogliaruso and S. Winstein, ibid., 89, 1965 (1967).
48. M.S. Brookhart and M. Monroe Atwater, Tetrahedron Lett., 4399 (1972).
49. J.D. Holmes and R. Pettit, J. Amer. Chem. Soc., 85, 2531 (1963).
50. O.L. Chapman and R.A. Fugiel, ibid., 91, 215 (1969).
51. C.E. Johnson, Jr. and F.A. Bovey, J. Chem. Phys., 29, 1012 (1958).
52. C.E. Keller and R. Pettit, J. Amer. Chem. Soc., 88, 606 (1966).
53. G. Boche, W. Hechtl, H. Huber and R. Huisgen, ibid., 89, 3344, 3345 (1967).
54. J. Gasteiger and R. Huisgen, Tetrahedron Lett., 3665 (1972).
55. A.L. Alfred and E.G. Rochow, J. Amer. Chem. Soc., 79, 5361 (1957); J.R. Cavanaugh and B.P. Dailey, J. Chem. Phys., 34, 1099 (1961).
56. C.R. Gawallin, J.E. Mahler and R. Pettit, ibid., 34, 1099 (1961).
57. A.L. Alfred, "Electronegativities of Carbon, Silicon, Germanium, Tin and Lead", Ph.D. Thesis, Harvard University (1956).

58. W. Merk and R. Pettit, J. Amer. Chem. Soc., 90, 814 (1968).
59. Y. Sugimura, N. Soma and Y. Kishida, Tetrahedron Lett., 91 (1971).
60. G.D. Mateescu, C.D. Nenitzescu and G.A. Olah, J. Amer. Chem. Soc., 90, 6235 (1968).
61. R.F. Childs and S. Winstein, ibid., 89, 6348 (1967); R.F. Childs, M.A. Brown, F.A.L. Anet and S. Winstein, ibid., 94, 2175 (1972).
62. M. Brookhart, G.C. Levy and S. Winstein, ibid., 89, 1735 (1967); G. Levy, Ph.D. Thesis, University of California, Los Angeles, Calif. (1968)
63. C.H. DePuy, L.G. Schnack, J.W. Hausser, W. Wiedman, J. Amer. Chem. Soc., 87, 4006 (1965); C.H. DePuy, L.G. Schnack and J.W. Hausser, ibid., 88, 3343 (1966) and references therein.
64. M.A. Battiste, J. Haywood-Farmer, H. Malkus, P. Seidl and S. Winstein, ibid., 92, 2146 (1970) and references cited therein.
65. P. Ahlberg, D.L. Harris and S. Winstein, ibid., 92, 2146 (1970).
66. P. Ahlberg, J.B. Grutzner, D.L. Harris and S. Winstein, ibid., 92, 3478 (1970).
67. P. Ahlberg, D.L. Harris and S. Winstein, ibid., 92, 4454 (1970).
68. G. Schröder, U. Prange, N.S. Bowman and J.F.M. Oth, Tetrahedron Lett., 3251 (1970).
69. G. Schröder, U. Prange, B. Putze, J. Thio and J. Oth, Chem. Ber., 104, 3406 (1971); G. Schröder, U. Prange and J. Oth, ibid., 105, 1854 (1972).
70. J.C. Barborak, J. Daub, D.M. Follweiler and P.v.R. Schleyer, J. Amer. Chem. Soc., 91, 3184 (1969); J.C. Barborak and P.v.R. Schleyer, ibid., 92, 3184 (1970); D. Cook, A. Diaz, J.P. Dirlam, D.L. Harris, M. Sakai, S. Winstein, J.C. Barborak and P.v.R. Schleyer, Tetrahedron Lett., 1405 (1971).
71. P. Seidl, M. Roberts and S. Winstein, J. Amer. Chem. Soc., 93, 4089 (1971).
72. A.F. Diaz, M. Sakai and S. Winstein, ibid., 92, 1405 (1970).

73. P. Warner and S. Winstein, ibid., 93, 1284 (1971)
74. L.A. Paquette, M.J. Broadhurst, Chee-man Lee and J. Clardy, ibid., 94, 630 (1972); L.A. Paquette and M.J. Broadhurst, ibid., 94, 632 (1972).
75. P. Ahlberg, D.L. Harris, M. Roberts, P. Warner, P. Seidl, M. Sakai, D. Cook, A. Diaz, J.P. Dirlam, H. Hamberger and S. Winstein, ibid., 94, 7063 (1972).
76. (a) J.M. Brown and J.L. Occolowitz, Chem. Commun., 376 (1965), J.M. Brown and J.L. Occolowitz, J. Chem. Soc. (B), 411 (1968).
- (b) J.M. Brown, Chem. Commun., 638 (1967), J.B. Grutzner and S. Winstein, J. Amer. Chem. Soc., 90, 6562 (1968)
77. S. Winstein, M. Ogliaraso, M. Sakai and J.M. Nicholson, ibid., 89, 3656 (1967).
78. M.J. Goldstein and R. Hoffmann, ibid., 93, 6193 (1971) and references therein; H.E. Zimmerman, Accounts Chem. Res., 4, 272 (1971).
79. H.J. Dauben, Jr., and H.J. Ringold, J. Amer. Chem. Soc., 73, 876 (1951); Ref. 7(a) P.85
80. R.B. Turner in "Theoretical Organic Chemistry, The Kekule Symposium", Butterworth and Co. Ltd., London (1969) P.69.
81. K. Kimura, S. Sazuki, M. Kimura and M. Kubo, J. Chem. Phys., 27, 320 (1967); Bull. Chem. Soc. Japan, 31, 1051 (1958).
82. D.P. Craig in "Non Benzenoid Aromatic Compounds", D. Ginsburg, Ed., Interscience Publishers, New York, N.Y., (1959) P.29.
83. A. DiGiacomo and C.P. Smyth, J. Amer. Chem. Soc., 74, 4411 (1952); Y. Kurita, S. Seto, T. Nozoe and M. Kubo, Bull. Chem. Soc. Japan, 26, 272 (1953).
84. W. von E. Doering and F.L. Detert, J. Amer. Chem. Soc., 73, 876 (1951).
85. D.J. Bertelli and T.G. Andrews, Jr., ibid., 91 5280 (1969); D.J. Bertelli, T.G. Andrews, Jr. and P.O. Crews, ibid., 91, 5286 (1969).
86. G.L. Buchanan and D.R. Lochart, J. Chem. Soc., 3586 (1959).
87. R.A. Moss, Chem. Eng. News, June 16, 1969; T.L. Gilchrist and C.W. Rees, "Studies in Modern Chemistry Series, Carbenes, Nitrenes and Ayrenes", The Pittman Press, Bath, Great Briton (1969).

88. C.D. Gutsche in Organic Reactions, Vol. 8, P.364 (1968), John Wiley & Sons Inc., New York, N.Y.
89. L.I. Smith and K.L. Howard, J. Amer. Chem. Soc., 65, 165 (1943).
90. W. von E. Doering, E.T. Fossel and R.L. Kaye, Tetrahedron, 25 (1965); W.R. Moser, J. Amer. Chem. Soc., 91, 1135, 1141 (1969); E.J. Corey and C.H. Posner, ibid., 89, 3911 (1967)
91. H.E. Simmons and R.D. Smith, ibid., 80, 5323 (1958); ibid., 81, 4256 (1969).; E.P. Blanchard and H.E. Simmons, ibid., 86, 1337 (1964); H.E. Simmons, E.P. Blanchard and R.D. Smith, ibid., 86, 1347 (1964).
92. E. Le Goff, J. Org. Chem., 29, 2048 (1964); R. Shank and H. Spechter, ibid., 24, 1825 (1959); R.J. Rawson and I.T. Harrison, ibid., 35, 2057 (1970).
93. C.D. Poulter, E.C. Friedrich and S. Winstein, J. Amer. Chem. Soc., 91, 6892 (1969); R. Ginsig and A.D. Cross, ibid., 87, 4629 (1965).
94. E.J. Corey and M. Chaykovsky, ibid., 87, 1353 (1965); E.J. Corey and M. Jautelat, ibid., 89, 3912 (1967); R.S. Bly, C.M. DuBose, Jr., and G.B. Konizer, J. Org. Chem. 33, 2188 (1968).
95. Y. Sugimura and N. Soma, Tetrahedron Lett. 1721 (1970).
96. (a) W. Kirmse, "Carbene Chemistry", 2nd Edition, Academic Press, New York, N.Y. (1971); W. von E. Doering and K. Hoffmann, J. Amer. Chem. Soc., 76, 6162 (1954); F.S. Skell and A.Y. Garner, ibid., 78, 5430 (1956); W.L. Dilling, J. Org. Chem. 29, 960 (1964).
- (b) G.C. Joshi, N. Singh and L.M. Pande, Tetrahedron Lett., 1461 (1972).
97. W.M. Wagner, Proc. Chem. Soc., 229 (1959); W.M. Wagner, H. Kloosterziel and A.F. Bickel, Rec. Trav. Chim., 81, 925, 933 (1962).
98. W.T. Miller, Jr., and D.M. Whalen, J. Amer. Chem. Soc., 86, 2089 (1964).
99. D. Seyferth and J.M. Burlitch, J. Organometal Chem., 4, 127 (1965); D. Seyferth, J.M. Burlitch, R.J. Minasz, J. Yick-Pui Mui, H.D. Simmons, Jr., A.J.H. Treiber and S.R. Dowd, J. Amer. Chem. Soc., 87, 4259 (1965); D. Seyferth and R.L. Lambert, Jr., J. Organometal Chem., 16, 21 (1969).

100. D. Seyferth, H. Yamazake and D.L. Alleston, J. Org. Chem., 28, 703 (1963); H.G. Kuivila and L.W. Menapage, ibid., 28, 2165 (1963).
101. P. Bruck, D. Thompson and S. Winstein, Chem. and Ind., 405 (1960); P.G. Gassman and P.G. Pape, J. Org. Chem., 29, 160 (1964).
102. (a) Q.R. Petersen and E.E. Sowers, ibid., 29, 1627 (1964).  
(b) J.J. Brown, R.H. Lenhard and S. Bernstein, J. Amer. Chem. Soc., 86, 2183 (1964); G.I. Poos, G.E. Arth, R.E. Beyler and L.H. Sarett, ibid., 75, 422 (1953)
103. E.P. Oliveto, T. Clayton and E.B. Hersberg, ibid., 75, 486 (1953).
104. E. Fernholtz, U.S. Patent 2,378,918 (1945); Chem. Abstr., 39, 5052<sup>3</sup> (1945).
105. H. Koster and H. Inhoffen, German Patent 892,450; Chem. Abstr., 52, P18,534g (1958).
106. H.E. Simmons and T. Fukunaga, J. Amer. Chem. Soc., 89, 5208 (1967).
107. F.A.L. Anet, ibid., 86, 458 (1964).
108. S. Castellano and A.A. Bothner-By, J. Chem. Phys., 41, 3863 (1964). A revised program, LAOCN3, is available from the same authors. The major change from LAOCOON II occurs in the error analysis.
109. M. Karplus, ibid., 30, 11 (1959), 33, 316, 914, 1842 (1960); E. Garbisch, J. Amer. Chem. Soc., 86, 5561 (1964).
110. L.J. Luskus and K.N. Houk, Tetrahedron Lett. 1925 (1972)
111. S. Winstein, F.A.L. Anet, P. Carter and A.J. Bourn, J. Amer. Chem. Soc., 87, 5247, 5249 (1965); C.D. Poulter, R.S. Boikess, J.I. Brauman and S. Winstein, ibid., 94, 2291 (1972).
112. R.F. Childs, M. Sakai and S. Winstein, ibid., 90, 7144 (1968); R.F. Childs and S. Winstein, ibid., 90, 7146 (1968); R.F. Childs and B. Parrington, Chem. Commun. 1540 (1970); P. Vogel, M. Sounders, N.M. Hosty and J.A. Berson, J. Amer. Chem. Soc., 93, 1551 (1971).
113. J.B. Grutzner, Ph.D. Thesis, Melbourne, Australia (1967)
114. H.A. Corver and R.F. Childs, J. Amer. Chem. Soc., 94, 6201 (1972).

115. L.A. Paquette, M. J. Broadhurst, Chee-man Lee and J. Clardy, ibid., 95, 4647 (1973).
116. L.A. Paquette, M.J. Broadhurst, P. Warner, G. Olah and G. Liang, ibid., 95, 3386 (1973)
117. Varian Instrument Manual V-6057 for Variable Temperature System, Publication No. 87-100-110.
118. J. Bacon, personal communication.
119. A. Luttringhaus and H. Merz, Arch. Pharm., 293, 881 (1960).
120. Org. Synthesis, 46, 113 (1966)
121. R.T. Manor and H.J. Hess, J. Org. Chem., 23, 1563 (1958); R. Kuhn and H. Trischmann, Ann., 611, 117 (1958).